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The Department of Energy

Progress Report

ELECTRON PHOTOEJECTION IN CARBANIONS

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Electron Photoejection in Carbanions

ABSTRACT

We have completed a systematic study of the mechanism of photomethylation of triphenylmethyl anion in dimethyl sulfoxide. The salient features of the mechanism include the intervention of an electron transfer as the primary process, followed by a radical + carbanion reaction to lead to a radical anion which ultimately restores its odd electron to the original triphenylmethyl radical formed. The photochemistry is extremely well behaved; the quantum yield for the process is concentration independent, no chain processes are initiated, and the photoproducts are concentration invariant. Thus the stage is set for our goal of using the photo-disappearance of resonance-stabilized carbanions as a model for photochemical electron transfer reactions.

We are nearing completion of our automated quantum yield apparatus, which will allow precise determination of wavelength dependence in quantum yield determinations. Initial results indicate the quantum yield of disappearance of triphenylmethyl anion, which is constant from _ca_. 400-600 nm, shows a remarkable increase at shorter wavelengths, which may represent the onset of photoelectrons.

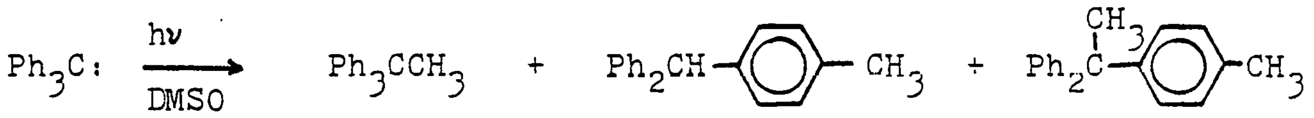
INTRODUCTION

In order to firmly establish the photomethylation of resonance-stabilized anions in dimethyl sulfoxide as sufficiently "well-behaved" to serve as a model for phtotchemical electron transfer reactions at strongly negative potentials, we undertook a rigorous investigation of the mechanism of the reaction. Our study is now complete, and we summarize our findings below. Particularly important to us was the lack of a chain mechanism and, consequently, the concentration independence of the quantum yield. Thus our original concept remains sound and we have begun studies on the factors controlling the reaction. Especially pleasing to us, although not included in the original proposal, was the discovery that we could use this reaction to investigate relative rates for the reactions of radicals with carbanions. Such studies are otherwise difficult to carry out.

Other aspects of the work completed during this review period are the synthesis of a variety of anionic triphenylmethane dyes, a preliminary finding of a wavelength dependence for the triphenylmethyl anion reaction, and the construction of the major part of our quantum yield apparatus.

1. The Mechanism of Triphenylmethyl Anion Photomethylation.

Our effort in determining the mechanism of light-induced methylation of triphenylmethyl anion in dimethyl sulfoxide (DMSO) was enhanced by the isolation of the product of para alkylation, p-tolyldiphenylmethane (2), in addition to the major product 1:



1 2

(See Fig. 1). Thus the ratio of para to alpha alkylated products provided a fingerprint for the transition state, proving that the reaction of methyl radical with triphenylmethyl anion provided the only significant pathway in product formation, and excluding radical-radical reactions. Additionally, we were able to show that the quantum yield was concentration independent, eliminating the intervention of a chain mechanism, and that triphenylmethyl anion was alkylated even when another anion was irradiated. Finally, the mass balance of the reaction (90%) clearly indicated that the final step involved electron transfer from the product radical anion to triphenylmethyl radical. Thus the signigicant steps of the reaction are as follows:

$$1)\quad Ph_3C\!:^- + CH_3SOCH_3 \xrightarrow{h\nu} Ph_3C\cdot + CH_3 + CH_3SO^-$$

$$2)\quad Ph_3C\!:^- + CH_3\cdot \longrightarrow Ph_3CCH_3^{\dot{-}}$$

$$3)\quad Ph_3CCH_3^{\dot{-}} + Ph_3C\cdot \longrightarrow Ph_3CCH_3 + Ph_3C\!:^-$$

Our experimental data and mechanistic arguments are more extensively delineated in the attached manuscript, "Carbanion Photochemistry. 3."

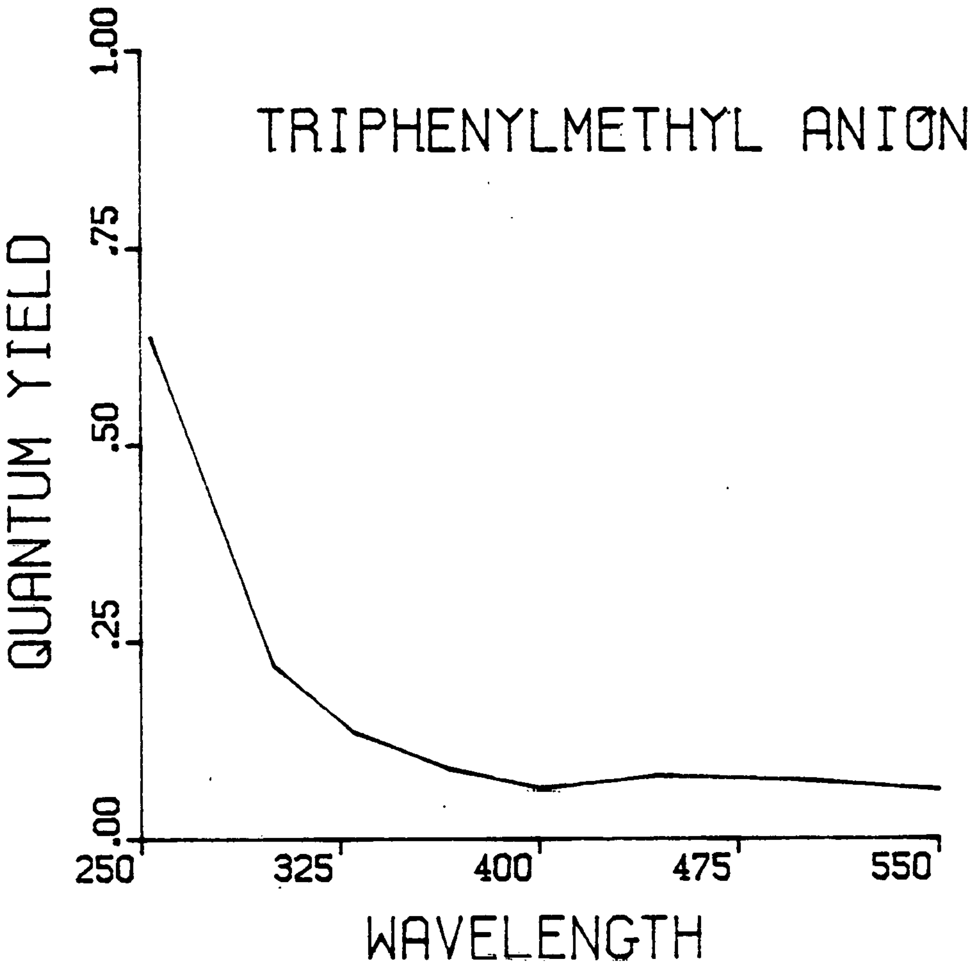
2. The Reactions of Methyl Radical with Carbanions.

The uncoupling of steps 1 and 2 in the reaction allow us to investigate the combination of methyl radical with various anions. For instance, the irradiation of mixtures of carbanions allowed the relative rates to be ascertained. Surprisingly, these rates were not controlled by the stability of the radical anion formed, as we initially had projected, but rather, by the pK_a of the conjugate acid, i.e., the strength of the carbanion base. Thus triphenylmethyl anion alkylated much more readily than either diphenylyldiphenylmethyl anion or tetraphenylallyl anion. Conversely, we had already noted the more ready alkylation of p-tolyldiphenylmethyl anion, a stronger base, than the triphenylmethyl anion. This rather surprising result is explained on the basis of molecular orbital control. The experimental data and rationale are presented extensively in "Carbanion Photochemistry 2."

3. Initial Quantum Yield Results.

The disappearance quantum yield of triphenylmethyl anion is .06, consistent with the lack of a chain mechanism. Experiments are in progress to determine the importance of back electron transfer in the energy wasting mechanism. Additionally, we were able to get some preliminary results on the wavelength dependence of the quantum yield. We observed that the quantum yield was constant from 400 to 600 nm, but that an appreciable increase in the quantum yield occurred at shorter wavelengths. These results are depicted in Figure 1. Unfortunately, the lack of ultraviolet bands shorter than 254 nm on our light source prevented us from investigating this trend in the 200 nm region. At this time we have no information as to the origin of this wavelength dependence, and part of our proposed work is to examine this phenomenon. We suspect, but have no evidence, that this change is quantum yield corresponds to the onset of photoelectrons.

Figure 1. Photodisappearance Quantum Yield of Triphenylmethyl Anion



4. Substituted Triphenylmethanes.

We modified our original proposal on substitution effects (Experiments I-7 and II-1 of our original proposal) by dividing our anions into two classes: strongly perturbed and weakly perturbed. Our choices for the latter class were the mono-, di-, and tri-methylated triphenylmethyl anions. This choice was based upon (1) the realization that even modest perturbations would have a significant effect, and (2) the publication of extremely good numbers for the oxidation potentials and pK_b's for the methylated anions. This will facilitate the correlation of reactivities with oxidation potentials. For the strongly perturbed class we have triphenylmethanes substituted on one ring by methoxy, chloro, carboxy, and nitro groups, in addition to the already available parent compounds. We have synthesized all of these compounds and are engaged in an analysis of their relative photochemical reactivity.

5. Electron Acceptors.

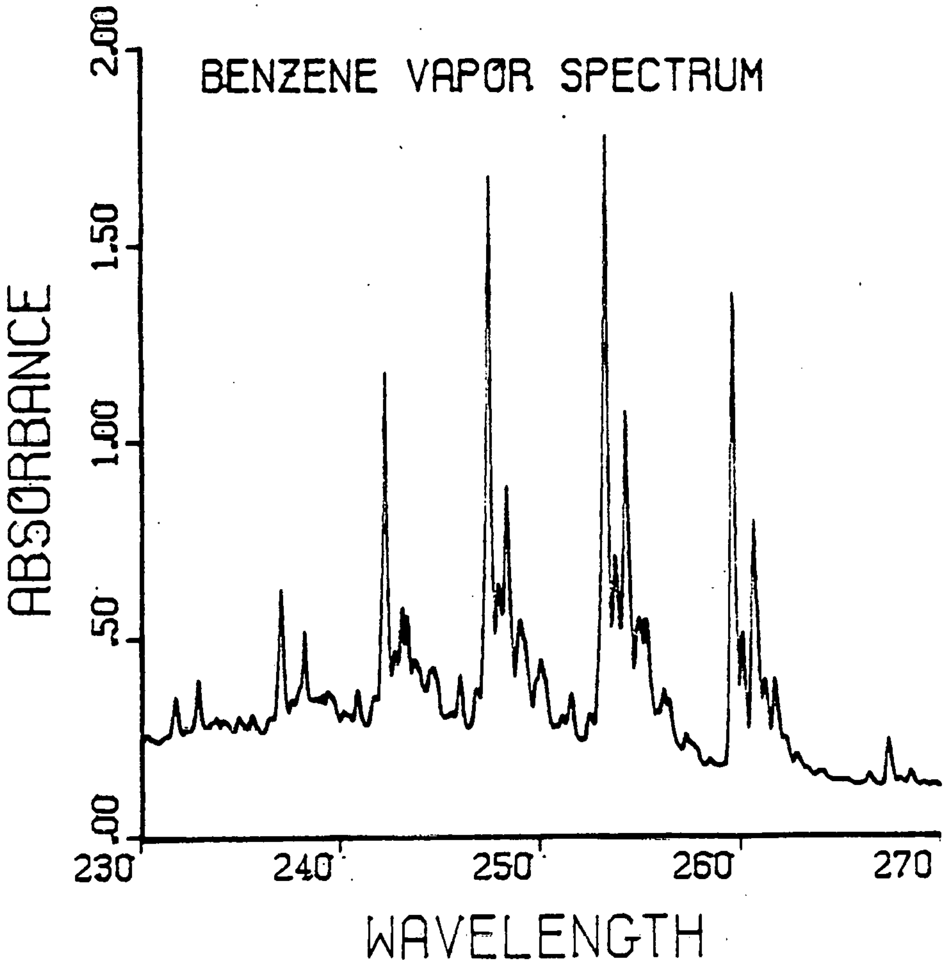
At low concentrations of di-t-butyl nitroxide, a diversion of the photochemical reaction path is noted for triphenylmethyl anion, presumably by trapping of the methyl radical. At high concentrations, the photochemistry is completely quenched. We believe that electron transfer quenching is occurring under these conditions, which is consistent with the reduction potentials of the species involved. We have not yet studied hydrocarbon acceptors.

6. Quantum Yield Instrumentation.

Our automated quantum yield apparatus is close to completion. The observation spectrophotometer (a Gilford 250) is now completely interfaced to a DEC LSI-11 based minicomputer equipped with an incremental plotter. We can now obtain reproducible absorption spectra of extremely high precision (±.01 A). The quality of the spectra obtainable are shown using the standard benzene vapor spectrum shown in Figure 2. We are currently using just this part of the instrumentation to develop a standard series of filter solutions for use in photochemistry.

The only remaining component to be interfaced is the integrating photometer. In collaboration with Professor Floyd J. Holler of our department, we are developing a highly linear photometer which can be calibrated automatically under computer control. Our best results to date appear to favor the use of a Scientech disc calorimeter as a calibration device. When completed, the degree of flexibility allowed by experiment design through FORTRAN programming will allow a virtually limitless variety of experimental parameters to be investigated.

Figure 2.



PERSONNEL

Dr. L. M. Tolbert, Assistant Professor, Principal Investigator

Dr. F. J. Holler, Assistant Professor, Senior Collaborator

Mr. S. Siddiqui, Graduate Student

Mr. M. Z. Ali, Graduate Student

Mr. Gary Williams, Graduate Student

Mr. Claudio Feler, Undergraduate Assistant

Mr. Barry Hardison, Undergraduate Assistant

During the grant period the principal investigator has dedicated 100% of his time during the summer months and 30% of his time during the academic year on to this contract.

TALKS AND PUBLICATIONS

On Department of Energy supported research:

"Photochemical Mechanisms in Carbanions," L. M. Tolbert 178th National Meeting, American Chemical Society, Washington, D. C., September 1979.

"Carbanion Photochemistry. 2. Kinetic Control of Product Formation in Reactions of Radicals with Anions," L. M. Tolbert, J. Amer. Chem. Soc., **102** (1980) in press.

"Carbanion Photochemistry. 3. Electron Transfer and Radical Anion Control in the Photochemistry of Triphenylmethyl Anion," L. M. Tolbert, J. Amer. Chem. Soc., submitted.

Others by the principal investigator:

"Cationic Cyclizations. Cation Generation through Magnesium Alkoxide Thermolysis. Regioselective Indene Formation," L. M. Tolbert, J. Org. Chem., 44, 4584 (1979).

"Serendipitous Two-Step Synthesis of a Naph[3,2,1-cd]-indole," M. J. Kornet, A. P. Thio, and L. M. Tolbert, J. Org. Chem., **45**, 30 (1980).

EXPENDITURE STATEMENT

Contract No. DE-AS05-79ER10424

Detail	Budgeted	Expenditures 7-1-79 to 2-28-80	Est. Expenditures 3-1-80 to 6-30-80	Balance
S and W	$ 19,835	10,765	9,093	(13)
Fringe Benefits	533	281	252	0
Travel	700	246	625	(171)
Publication Costs	1000	0	250	750
General Operations[a]	3200	1873	900	427
Computer Services	500	-	50	450
Capital Equipment	6460	-	7475	(1015)[b]
Total direct	$ 32,228	13,165	18,645	418
Indirect	11,901	6,459	5,456	11,915
Total	$ 44,129	19,624	24,101	404

Notes:

a. This item includes supplies and equipment plus technical services.

b. Approval for this expenditure from other categories has been received.

Carbanion Photochemistry. 2. Kinetic Control of Product Formation in Reactions of Radicals with Carbanions.

by

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Abstract. The interaction of resonance-stabilized carbanions with methyl radicals produced by the irradiation of the carbanions in dimethyl sulfoxide is governed by the pK_a of the carbanion conjugate acid to a greater extent than by the stability of the resulting radical anion. This kinetic effect is explained using energetic considerations based on the Hammond postulate and is further rationalized by a molecular orbital correlation diagram.

Our studies in carbanion photochemical mechanisms[1] have drawn us inexorably to an investigation of the interaction of radicals with anions, not only because of the significance of this process in carbanion photochemistry,[2] but also because of its involvement in the $S_{RN}1$ and related reactions.[3] The factors controlling the rate of reaction between radical and anion and the distribution of the resulting products have not been well studied. We have shown that the stability of the radical anion can have a decisive effect in determining product distribution. For instance, the $S_{RN}1$ photoarylation of trityl anion leads to predominant *para* arylation in contrast to the *alpha* arylation obtained through a radical-radical pathway.[4] We now report that radical anion stability is not the only factor affecting the rate of the reaction and, in fact, is a relatively minor contributor compared to the pK_a of the conjugate acid of the anion.

Results. Competitive Irradiation of Anions. The subjects of our work were triphenylmethyl anion (**1**), diphenylyldiphenylmethyl anion, (**2**) and 1,1,3,3-tetraphenylpropenyl anion (**3**), all of which undergo photomethylation in dimethyl sulfoxide by a mechanism which we now know to be a modified $S_{RN}1$ process,[5] with the key step being the reaction of a methyl radical with the ground state anion (see Fig. 1). We were interested in the rate of reaction of the methyl radical with the anion.

Figure 1.

1) $\mathrm{Ar\ddot{C}Ph_2^{\ominus}} \xrightarrow[\text{DMSO}]{h\nu} \mathrm{Ar_3\dot{C}Ph_2} + \cdot\mathrm{CH_3} + \mathrm{CH_3SO^-}$

1, Ar = Ph

2, Ar = $-\mathrm{C_6H_4{-}Ph}$

3, Ar = $-\mathrm{CH{=}CPh_2}$

2) $\cdot\mathrm{CH_3} + \mathrm{Ar\ddot{C}Ph_2^{\ominus}} \longrightarrow \mathrm{Ph_2(Ar)CCH_3^{\dot{-}}}$

3) $\mathrm{Ph_2(Ar)CCH_3^{\dot{-}}} + \mathrm{Ar\dot{C}Ph_2} \longrightarrow \mathrm{Ph_2(Ar)CCH_3} + \mathrm{Ar\ddot{C}Ph_2^{\ominus}}$

4, Ar = Ph

5, Ar = $-\mathrm{C_6H_4{-}Ph}$

6, Ar = $-\mathrm{CH{=}CPh_2}$

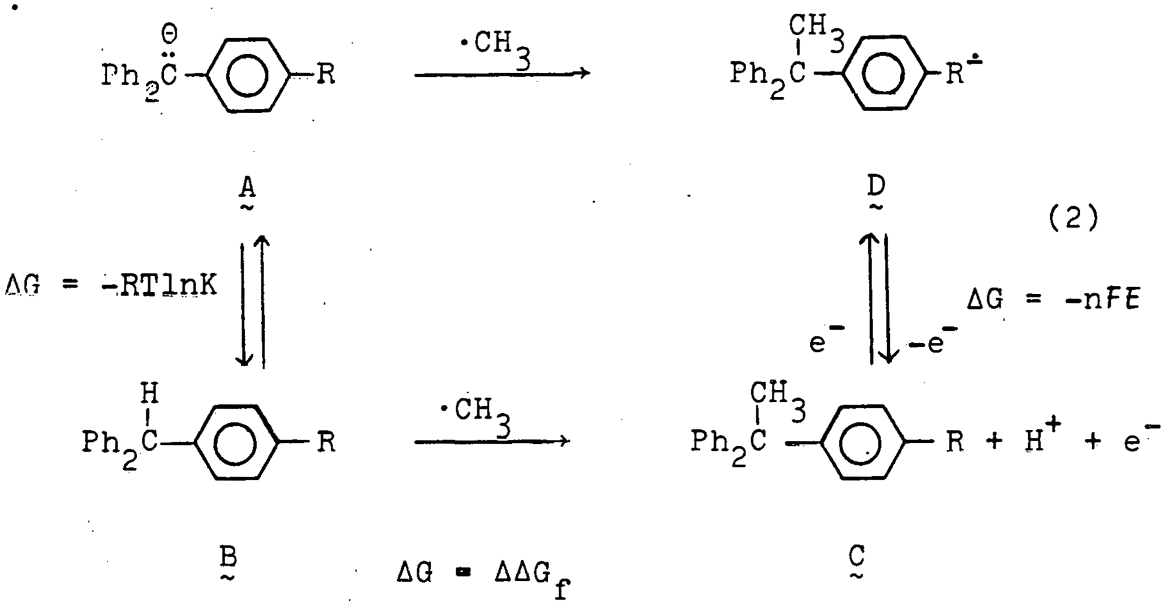
However, such rates are difficult to obtain directly and we chose instead to obtain the relative rates from a competition experiment. We were aided by the fact that anions **1** and **2** have distinctively different chromophores, the bright red trityl anion having a λ_{max} in DMSO of 496 nm and the purple diphenylyldiphenylmethyl anion a λ_{max} of 600 nm (see Fig. 2). Thus it was possible in principle to irradiate each anion independently in the presence of the other. If radical anion stability were the controlling factor in product formation, alkylation of the diphenylyl anion leading to the radical anion with the electron localized in the biphenyl moeity would predominate.

Two identical 50 ml solutions of 0.01 M total equimolar mixtures of anions **1** and **2** were prepared by treatment of the appropriate hydrocarbons with a two-fold excess of potassium methylsulfinyl methide ("dimsyl"). At these concentrations, ion association and ion pairing effects are known to be negligible.[6] One solution was irradiated at 546 nm, the other at 578 nm, using the appropriate solution filters and a Hanovia 450 W medium pressure mercury lamp. Irradiation for 12 hr and analysis of the products by gas chromatography using independently prepared products for standarization proved that the anion alkylated most readily was not the diphenylyl anion but rather the trityl anion (see Table I).

To determine if this result was unique to the two anions used, we investigated the competition between triphenylmethyl anion and the tetraphenylallyl anion 3. In the latter case radical anion intermediates would place the extra electron in a diphenylvinyl moiety, which should be even more favorable than a biphenylyl moiety. Unfortunately the similarity between the absorption spectra of the two anions precluded unequivocal irradiation of one species in the presence of the other. Our approach to decoupling the photochemical electron transfer step from the radical-anion forming step was to irradiate the pure anion simultaneously with a mixture. Using an optical arrangement similar to the Merry-go-round, and a solution filter to pass both 546 and 578 nm wavelengths, we irradiated 5 ml solutions of .01 M tetraphenylallyl anion 3 prepared as above and .01 M tetraphenylallyl anion in the presence of .01 M triphenylmethyl anion. Again, both anions were methylated, and the results are listed in Table II. Significantly, more tetraphenylbutene 6 was produced in the presence of triphenylmethyl anion than in its absence despite the fact that the triphenylmethyl anion was competing for light absorption! We attribute this unexpected result to the fact that allyl anion 3 captures methyl radical more efficiently than it undergoes photochemical electron transfer, although energy transfer from tritylanion may account for part of this phenomenon. In any event, we see that despite the greater light capture by tetraphenylallyl anion and the greater stability of the product radical anion, the major product is still triphenylethane **4**. Thus some energetic constraint other than radical anion stability must be operative, which we may determine by examining the thermodynamics of the reaction.

Discussion. **Thermodynamics of Radical Anion Formation.** The thermodynamics for the process radical + anion → radical anion cannot be obtained directly. Instead we must obtain the relative energies for the process by using a thermochemical cycle (see Fig. 3). This technique has been used to estimate pK_a's of various hydrocarbons,[7] and we employ it here to estimate the energetics of the triphenylmethyl/diphenylyldiphenylmethyl system.

Figure 3.



We wish to estimate the free energy ΔG for the process A → D, which we cannot obtain directly. The energy for the process A → B is given by -RT·lnK i.e., -2.3 RT·pK_a, while that for C → D is given by the reduction potential (vs $H+/H_2$)[8] of the neutral C. Finally, the free energy of the process B → C is given by the free energy of the hydrogen ion (0)[8], plus the increment in free energy of formation for the homologation $R-H \rightarrow R-CH_3$ (2 kcal)[9] less the free energy of formation of methyl radical (34.6 kcal)[10]. Using the values 30.6 and 29.4 for the pK_a's of triphenylmethane and diphenylyldiphenylmethane,[6] respectively, and the values 2.89 V and 1.99 V as the half-wave reduction potentials of benzene and biphenyl,[11] respectively, we obtained the estimated free energies for the overall process listed in Table III. We see that the overall reaction is exothermic, as we might predict, but that the reaction of the biphenyl system is more exothermic by 19 kcal. How then do we account for the formation of the less stable product? Although the $\Delta G_{C \rightarrow D}$ term favors the biphenyl product, the $\Delta G_{A \rightarrow B}$ term favors reaction of the more basic anion. That is, the energy gain upon methylation is analogous to the energy gain upon protonation of structurally similar anions. The exoergocity of the reaction implies that the transition state is more accurately represented by the reactants, according to Hammond's postulate. Although a smaller overall contributor to the free energy of the reaction, the pK_a effect plays a dominant role in the activation energy of the reaction.[12]

Discussion. Molecular Orbital Considerations. The analysis of the kinetic effect in controlling reactivity can be illustrated more dramatically by using a correlation diagram for a model system, the interaction of a methyl radical with an allyl anion. Using the technique of "MO following"[13] we construct the orbitals of the half reacted product analogously to those for butadiene and add the Hückel orbitals for the starting allyl anion and methyl radical as well as the final σ and π orbitals (see Fig. 4). The one modification to this one electron treatment is placement of the methyl orbital at slightly higher energy than the allyl nonbonding MO, reflecting the greater electron affinity of allyl radical.[14] The significant feature of the correlation diagram is that it is the half-occupied methyl orbital which eventually becomes the π^* orbital of the product. Thus any pertubation of the orbital system to lower the energy of the π^* orbital, i.e., to make the radical anion more stable relative to the neutral, cannot be perceived until the reaction is very close to product. For an early transition state this effect will be minimal. It is instructive to consider the correlation diagram with the odd electron removed, i.e., an empty orbital reacting with an anion. This diagram corresponds to the protonation of an anion, and the maximum on this energy surface corresponds to the kinetic pK_a (or pK_b), which for hydrocarbons closely approximates the true pK_a. Thus for reaction of a radical with resonance stabilized carbanions, the kinetics of the reaction are controlled not by the half-occupied orbital but by the subjacent orbitals!

Conclusions. The relative role of pK_a and radical anion stability in determining the outcome of radical-anion combination reactions has important consequences for understanding reactivities in $S_{RN}1$ and related reactions. In general, where regioselectivity in $S_{RN}1$ reactions is attributed to radical-anion stability, consideration of the pK_a of the conjugate acid would lead to the same prediction. To our knowledge this work is the first in which the two effects act in opposite direction and allow clear distinction between the two. The relative purity of products, absence of dimers, and lack of other products associated with radical-radical reactions provide a further contrast. The high exothermicity of radical-radical reactions generally results in no activation energy and diffusion controlled reactions. Reactions of radicals with anions, although sufficiently exothermic to be kinetically controlled, are accompanied by activation energies and are more discriminate in reactivity. In the limit, if the anionic reactant is sufficiently non-basic, other reactions may compete. We believe this explains the failure of certain stabilized carbanions such as enolates of 1,3-dicarbonyl compounds to undergo the $S_{RN}1$ arylation.[3e]

Acknowledgment. We acknowledge the Research Corporation and the Division of Chemical Sciences of the Department of Energy for support of this work.

EXPERIMENTAL SECTION

Melting points were taken on a hot-stage apparatus and are uncorrected. Nuclear magnetic resonance spectra were obtained on a Varian T-60 spectrometer.

Manipulations. Apparatus and nonvolatile materials were degassed repeatedly by evacuating to less than .1 torr and purging with argon dried and deoxygenated with an Ace-Burlitch inert atmosphere system. Liquids were transferred by reaching through the bore of a 4 mm three-way stopcock with the needle of a degassed syringe or with a double-tipped stainless steel needle. A stream of argon through the side opening of the stopcock protected the liquid from air.

Photochemical Equipment. Irradiations were carried out with a Hanovia 450 W lamp in a Pyrex immersion well equipped with an ellipsoidal reflector which focused the light on a cylindrical 3 cm x 20 cm reaction vessel. Light filtration was provided by a cylindrical container surrounding the immersion well and containing .1 M K_2CrO_4 in a pH 10 buffered medium. This filter solution effectively excluded all light below 450 nm. Additional filtration, if necessary (see below), was provided by an additional cylindrical container surrounding the reaction flask.

Analyses. Gas chromatographic analysis was performed on a Varian 3700 Gas Chromatograph using a 3 m column of 2% OV-101 on Chromosorb G. Elemental analyses were performed by Galbraith Laboratories of Knoxville, Tennessee.

Materials. Dimethyl sulfoxide was purified as described by Bordwell[6] and stored over molecular sieves. Solutions of potassium methylsulfinylmethide ("dimsyl") were prepared by syringing 20 ml of 20-25% potassium hydride in an argon-filled serum-capped 50 ml centrifuge tube, adding 20 ml of dry pentane, and successively shaking, centrifuging, removing and readding pentane onto the potassium hydride. After the third centrifugation, the pentane and dissolved oil were removed by syringe, the entire apparatus pumped dry, and the weight of potassium hydride remaining measured by difference. A 25 ml portion of dimethyl sulfoxide was added through a Teflon tube under a positive pressure of nitrogen, and after the frothing had subsided, the remaining hydrogen was removed under vacuum. The concentrated solution was transferred under argon to a Schlenk tube equipped with an automatic buret and diluted to 200 ml with additional dimethyl sulfoxide. The solution was titrated with potassium hydrogen phthlate using phenolphthalein as indicator. A typical solution had a total base concentration of .2 M. Solutions prepared in this manner were stored without noticeable decomposition for two weeks, provided light was excluded.

Triphenylmethane was obtained from Aldrich Chemical Company and was either used as received or recrystallized from methanol. 1,1,3,3-Tetraphenylpropene was prepared by the method of Garbisch[15] and had mp 125-126° (lit[15] mp 125-126°). Diphenylyldiphenylmethane was obtained by the method of Bordwell.[6]

1-(4-Tolyl)-1,1-diphenylethane. To .674 g (2.61 mmol) of (4-tolyl)-diphenylmethane in 10 ml of DMSO were added 15 ml (5.52 mmol) of .368 M potassium dimsyl. The red solution was allowed to equilibrate for 30 min, then .40 ml (6.42 mmol) of methyl iodide was added. Thirty ml of water was added, and the solution extracted three times with ether. The extracts were dried and concentrated, leaving a slowly crystallizing oil. The crystals were recrystallized from hexane to yield .464 g (1.71 mmol, 65%) of colorless prisms, mp 66-68°. The spectral data were: nmr ($CDCl_3$): δ 2.15 (s, 3H, Ar_3CCH_3), 2.29 (s, 3H, $ArCH_3$), 7.00 (s, 4H, $-C_6H_4-$), 6.89-7.32 (m, 10H, arom). Anal. ($C_{21}H_{20}$) C, H.

1,1,1-Triphenylethane. To 1.04 g (4.28 mmol) of triphenylmethane in 10 ml of DMSO was added 13 ml (4.78 mmol) of potassium dimsyl. The red solution was allowed to equilibrate for 30 min, then .311 ml (5.0 mmol) of methyl iodide was added dropwise. The red color disappeared after <u>ca</u>. 90% of the methyl iodide was added. A few drops of water were added, and the solution allowed to stand. After 7 days, long needles had formed. These were removed by filtration to yield 0.747 g (2.90 mmol, 68%) of crystals, mp 90-92° (lit[16] mp 90-92.5). Additional less pure product was obtained by adding 10 ml of water to the filtrate and allowing the coludy mixture to stand for several days more. The spectral data were: nmr ($CDCl_3$); δ 2.17 (s, 3H, CH_3), 7.00-7.38 (m, 15H, arom).

1,1,3,3-Tetraphenyl-1-butene. Evan's procedure[17] was used with slight modification. To 15 ml of freshly distilled benzene were added 2.00 g 1,1-diphenylethylene (Aldrich Chemical Co.) and .25 ml stannic chloride. The blue-green mixture was stirred for four days, decomposed with 10 ml water, and ether extracted. Recrystallizations of the organic residue in methanol yielded 1.56 g (78%) of 1,1,3,3-tetraphenyl-1-butene as colorless prisms, mp 112-115° (lit[17] mp 111-113°). The spectral data were: nmr ($CDCl_3$) δ 1.44 (s, 3H), 6.85 (s, 1H), 7.25 (br s, 20 H); ms 360 (100), 345 (16), 283 (14), 282 (29); ir ($CHCl_3$) 2980, 1590, 1485, 1440, 1020, 685, 590 cm^{-1}.

Preparative Photolysis of Triphenylmethylpotassium. To 1.601 g (6.50 mmol) of triphenylmethane in 15 ml of dimethylsulfoxide contained in the reaction vessel was added 35 ml (7.0 mmol) of 0.20 M potassium dimsyl. The degassed solution was irradiated without a solution filter until the red color disappeared (ca. 3 hr). The solution was added to 200 ml of water and ether extracted. Silica gel chromatography of the residue after concentration yielded 0.954 g of a white solid. Recrystallization from methanol yielded .852 g (3.30 mmol), 50%) of colorless prisms. The mp (90.0-92.5°) and spectral data were identical to 1,1,1-triphenylethane[16]. The mother liquor and remaining hydrocarbon fractions from the chromatography column were combined. Preparative high pressure liquid chromatography and preparative gas chromatography failed to separate the residue, which proved by analytical gas chromatography, analytical high pressure liquid chromatography, and nmr comparison to be a mixture of 1,1,1-triphenylethane and 1-(4-tolyl)-1,1-diphenylethane.

Preparative Photolysis of 1,1,3,3-Tetraphenyl-1-propene-3-ylpotassium.

A solution of .875 g (2.52 mmol) of 1,1,3,3-tetraphenylpropene in 35 ml of dimethyl sulfoxide was placed in the phtolysis vessel, thoroughly degassed under vacuum, and purged with dry argon. A 15 ml portion (3.0 mmol) of 0.20 M potassium dimsyl was added by syringe, the resulting deep red solution vacuum degassed for several minutes, and argon reintroduced. The solution was irradiated for 12 hr, excess base was decomposed by adding 10 ml of water, the solvent removed *in vacuo*, and the residue taken up in an ether-water mixture. Separation of the organic fraction followed by dyring and concentrating *in vacuo* gave a brown residue. Silica gel chromatography (2% ether-hexane) yielded, .7212 g (2.01 mmol, 80%) of 1,1,3,3-tetraphenyl-1-butene, mp 105-109°. Recrystallization from methanol yielded colorless prisms, mp 111.5-113.5 (lit[17] mp 111-113°). The spectral data were identical to those of authentic 1,1,3,3-tetraphenyl-1-butene.

Preparative Photolysis of (4-Diphenylyl)diphenylmethyl Potassium.

A solution of 1.23 g (3.84 mmol) of diphenylyldiphenylmethane in 30 ml of dimethyl sulfoxide was treated with 20 ml (4.00 mmol) of .20 M dimsyl potassium and the solution degassed in the manner previously described. The solution was irradiated for 96 hr, *i.e.*, until the purple color had been replaced by a light brown, the reaction quenched with 2 ml water, and the solvent removed *in vacuo*. The extracted from ether washing of the residue was washed 3 times with water, dried, and concentrated. Recrystallization from methanol yielded light yellow crystals (1.02 g, 3.12 g, 82%). Recrystallization from hexane yielded .88 g of colorless prisms, mp 92-93°. The spectral data were: nmr ($CDCl_3$) δ 2.21 (s, 3H, CH_3), 6.9-7.6 (m, 19H, arom); ir ($CDCl_3$) 3060, 3052, 2990, 1601, 1500, 1491, 1450, 1030, 1012, 762, 733, 698 cm^{-1}. Anal. ($C_{26}H_{22}$)C,H.

Competitive Irradiation Experiments. Solutions of mixtures of the anions were prepared analogously to those for preparative photolysis of individual anions, using a 50% excess of base over the amount required to quantitatively deprotonate the hydrocarbons. For the diphenylyldiphenylmethyl/triphenylmethyl experiments, additional filter solutions were used as described under Table I, and irradiations were carried out in 50 ml vessels for 12 hr. For the tetraphenylallyl/triphenylmethyl experiments, the irradiations were carried out in 5 ml irradiation tubes, irradiations were carried out for 2 hr, and identical tubes were arranged so as to ensure virtually identical light absorption throughout the irradiation. Analyses of the mixtures were performed by gas chromatography using independently prepared products to calibrate the chromatograph. The amounts of starting materials used and products formed are listed in the appropriate tables.

Table I. Results of Competition Experiment between 1 and 2.

	Experiment 1	Experiment 2
Irradiation Wavelength	546[a]	578[a]
Starting Materials:		
Mmol Trityl anion (1)	0.257	0.275
Mmol Biphenylyl anion (2)	0.175	0.196
Products:		
Mmol Triphenylethane (4)	0.157	0.174
Mmol p-Tolyldiphenylethane[b]	0.046	0.060
Mmol 4-Diphenylyldiphenylethane (5)	0.035	0.034
Ratio 1 Products/2 Products	85:15	87:13

(a) Serial filter solutions were used. The first cell contained 0.2 M $K\ CrO_4\cdot 6H_2O$ in a pH 10 solution. The second cell contained either 0.50 M $NiSO_4$ in water (500 nm) or 0.43 M $CoSO_4\cdot 6H_2O$ in water (600 nm); absorption spectra of the filter solutions were taken before and after the irradiations to ensure that no degradation in the solutions had occurred. (b) This is the "unidentified product" of ref. 1.

Table II. Results of Competion Experiment between 1 and 3.[a]

Starting Materials:	Experiment 1	Experiment 2
Mmol Trityl anion (1)	--	.0593
Mmol Allyl anion (3)	0.0451	0.0417
Products:		
Mmol Triphenylmethane	--	0.0128
Mmol Tetraphenylpropene	0.0349	0.0220
Mmol Triphenylethane (4)	--	0.0302
Mmol p-Tolyldiphenylethane	--	0.0061
Mmol Tetraphenylbutene (6)	0.0025	0.0064
Ratio 1 Products/3 Products		85:15

(a) A pH 10 buffered solution of 0.2 M $K_2CrO_4 \cdot 6H_2O$ was used to filter out all light below 450 nm.

Table III.

Anion	$\Delta G_{A\rightarrow B}$	$\Delta G_{B\rightarrow C}$	$\Delta G_{C\rightarrow D}$	$\Delta G_{A\rightarrow D}$
Triphenylmethyl	-41.7	-32.6	66.7	-7.6 kcal
Biphenylyldiphenylmethyl	-40.1	-32.6	45.9	-26.8 kcal

1. Tolbert, L.M., *J. Am. Chem. Soc.*, **1978**, *100*, 3952.

2. (a) van Tamelen, E.E., Schwartz, J. and Brauman, J.I., *J. Am. Chem. Soc.*, **1970**, *92* 5798; (b) Schwartz, J., *Chem. Commun.*, **1969**, 833 (c) Brauman, J.I., Schwartz, J., and van Tamelen, E.E., *J. Am. Chem. Soc.*, **1968**, *90*, 5328; (d) van Tamelen, E.E., Brauman, J.I., and Ellis, L.E., *ibid.*, **1967**, *89*, 5073.

3. (a) Komin, A.P. and Wolfe, J.F., *J. Org. Chem.* **1977**, *42*, 2481; (b) Scamehorn, R.G. and Bunnett, J.F., *ibid.*, **1977**, *42*, 1457; (c) Kornblum, N., *Angew Chem., Int. Ed., Eng.*, **1975**, *14*, 734; (d) Russell, G.A. and Danen, W.C., *J. Am. Chem. Soc.*, **1966**, *88*, 5663; (e) Bunnett, J.F. and Sundberg, J.E., *J. Org. Chem.*, **1976**, *41*, 1702; (f) Wolfe, J.F., Moon, M.P., Sleevi, M.C., Bunnett, J.F., Bard, R.R., *ibid*, **1978**, *43*, 1019.

4. Tolbert, L.M. and Martone, D.P., *Abstracts*, 176th National Meeting, American Chemical Society, Miami, September 1978, Paper ORGN-37.

5. Tolbert, L.M., *J. Am. Chem. Soc.*, submitted.

6. Matthews, W.S., Bares, J.E., Bartmess, J.E., Bordwell, F.G., Cornforth, F.J., Drucker, G.E., Margolin, Z., McCallum, R.J., McCollum, G.J., and Vanier, N.R., *J. Am. Chem. Soc.*, **1975**, *97*, 7006.

7. Breslow, R., and Chu, W., *J. Am. Chem. Soc.*, **1970**, *92* 2165.

8. For the ease of calculation, we use the standard potential of the hydrogen electrode, which is, of course, taken in water. Since this term drops out of the calculation, its exact value in dimethyl sulfoxide is irrelevant.

9. (a) This increment was estimated by using the free energy for the homologation $PhCH_3 \rightarrow PhCH_2CH_3$.[9b] Although this is not an exact approximation, errors will be small and, in any event, constant for the structurally similar triaryl methanes[7] and thus may safely be neglected; (b) Rossini, F.D., Pitzer, K.S., Arnett, R.L., Braun, R.M., and Primental, G.C., *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, Carnegie Press*, Pittsburg, **1953**.

10. Golden, D.M. and Benson, S.W., *Chem. Rev.*, **1969**, 125; corrected for entropy using data from ref. 7.

11. These were corrected to the H^+/H_2 standard electrode: Sternberg, H.W., Markby, R.E., Wender, I., Mohilner, D.M., *J. Electrochem. Soc.*, **1966**, *113*, 1060.

12. A referee has suggested an alternative explanation based upon the equilibrium

$$Ph_3C:^- + Ph_2(Ar)CCH_3^{\dot{-}} \rightleftarrows Ph_3CCH_3^{\dot{-}} + Ph_2\ddot{C}Ar^-$$

followed by rate limiting electron transfer from the less stable $Ph_3CCH_3^{\dot{-}}$ anion. However, the same unfavorable potentials which make the $Ph_3CCH_3^{\dot{-}}$ anion less stable reduce its concentration and, hence, the rate of reaction by a compensating amount.

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14. Zimmerman, A.H. and Brauman, J.I., *J. Am. Chem. Soc.*, **1977**, *99*, 3565.

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17. Evans, A.G. and Price, D. *J. Chem. Soc.*, **1959**, 2982.

(This figure is redundant and is included only for typesetting)

Figure 1.

1) $\mathrm{Ar\ddot{C}Ph_2}^{\ominus} \xrightarrow[\mathrm{DMSO}]{h\nu} \mathrm{Ar_3\dot{C}Ph_2} + \cdot\mathrm{CH_3} + \mathrm{CH_3SO}^{-}$

1, Ar = Ph

2, Ar = $-\mathrm{C_6H_4{-}Ph}$

3, Ar = $-\mathrm{CH{=}CPh_2}$

2) $\cdot\mathrm{CH_3} + \mathrm{Ar\ddot{C}Ph_2}^{\ominus} \longrightarrow \mathrm{Ph_2(Ar)CCH_3}^{\dot{-}}$

3) $\mathrm{Ph_2(Ar)CCH_3}^{\dot{-}} + \mathrm{Ar\dot{C}Ph_2} \longrightarrow \mathrm{Ph_2(Ar)CCH_3} + \mathrm{Ar\ddot{C}Ph_2}^{\ominus}$

4, Ar = Ph

5, Ar = $-\mathrm{C_6H_4{-}Ph}$

6, Ar = $-\mathrm{CH{=}CPh_2}$

Figure 2. Relative Absorbances

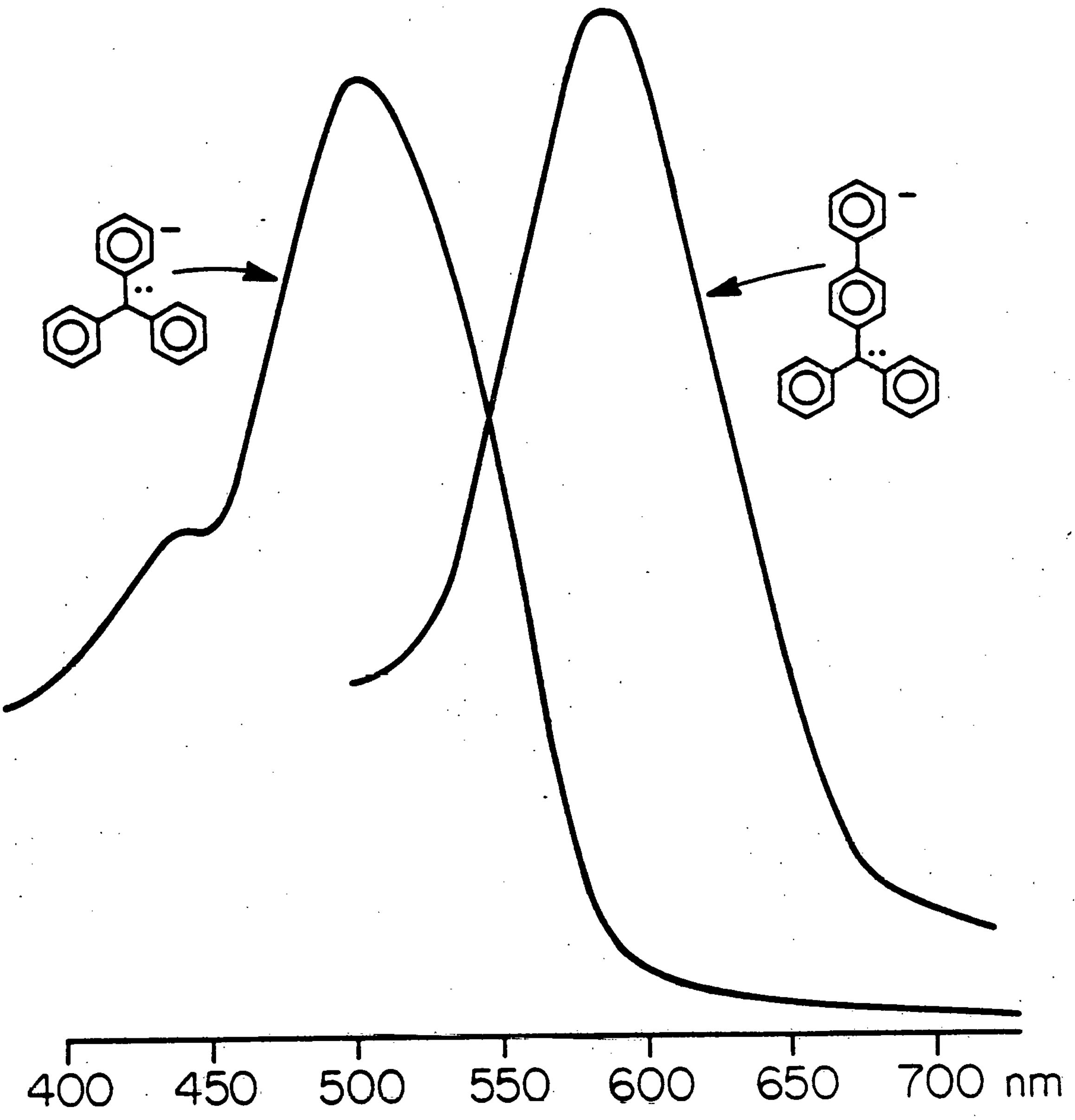

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Figure 3.

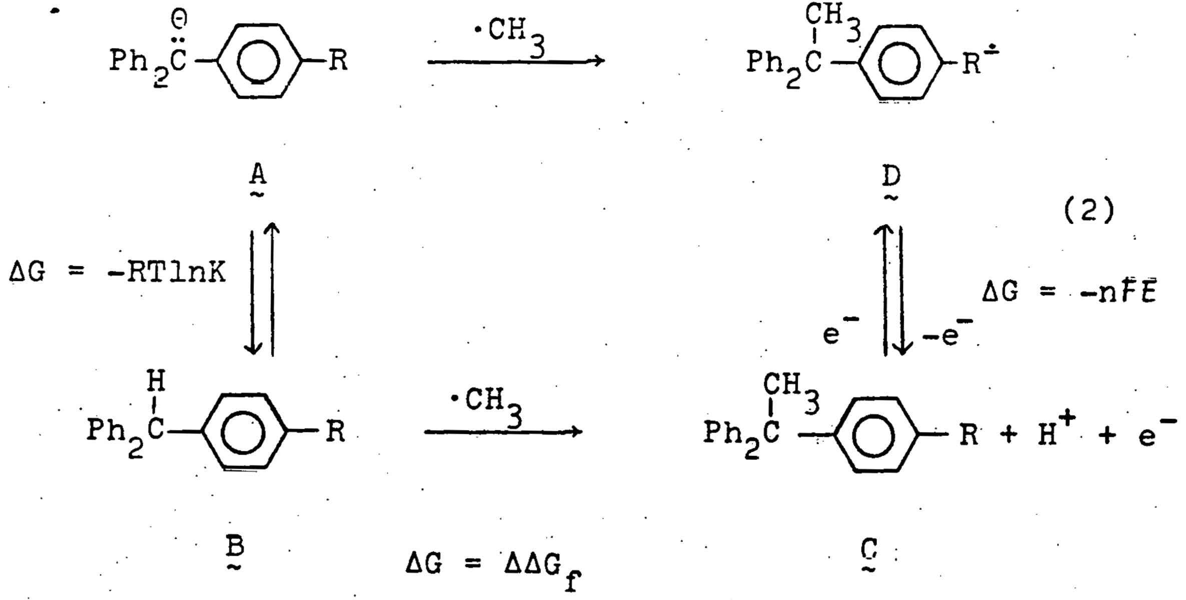
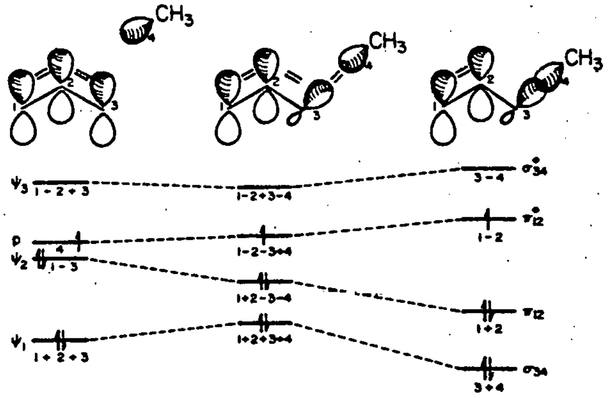


Figure 4. Correlation Diagram



Carbanion Photochemistry 3. Electron Transfer and Radical Anion Control in the Photochemistry of Triphenylmethyl Anion[1]

by

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Abstract: On the basis of concentration and competition studies, the photomethylation of triphenylmethyl anion in dimethyl sulfoxide is shown to involve the reaction of methyl radical with triphenylmethyl anion to yield the radical anions of 1,1,1-triphenylethane and 3-diphenylmethylene-6-methyl-1,4-cyclohexadiene. However, there are no chain carrying steps as there are for typical $S_{RN}1$ reactions. The intervention of radical anions produces the unconventional product of para alkylation, but the reaction is dominated by the bond strength of the newly formed bond as indexed by pK_a.

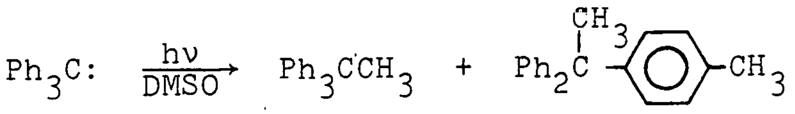
Recently we observed the facile photomethylation of resonance stabilized carbanions in dimethyl sulfoxide.[2] Our subsequent work in this area has led us to the conviction that the overwhelming reaction pathway is electron transfer, despite some rather formidable energy constraints. The relatively low energy light employed and the obvious applications to fundamental studies in solar energy conversion via electron photoejection have prompted us to narrow our scope to the photochemistry of triphenylmethyl anion itself, the results of which we now present.

Background. The early forays by Brauman, van Tamelen, and coworkers into the area of carbanion photochemistry have demonstrated that the major pathway involves electron transfer.[3,4] The reasons for this predominance are clear, if not always stated: Associated with a negatively charged species is an excess of electron-electron repulsion terms over nuclear attraction terms; that is, the valence electrons are shielded from the nucleus. Thus photoexcitation easily places a carbanion in a state of excess energy relative to the state corresponding to neutral plus a free electron, and the species autodetaches. The crucial parameter determining whether a species will autodetach, then, is the relative magnitude of the excitation energy E_λ and the electron affinity (E.A.) of the neutral (see Fig. 1.).

Substitution by phenyl increases the electron affinity of a radical center at the expense of the excitation energy. Thus the electron affinity of benzyl is at least 7 kcal greater than methyl,[5] while λ_{max} for triphenylmethyl anion is red shifted by 45 nm relative to diphenylmethyl anion,[6] corresponding to a decrease in E_λ of 6 kcal. Figure 1 illustrates these opposing effects.

By irradiating triphenylmethyl anion in dimethyl sulfoxide, we anticipated that electron transfer would be circumvented. DMSO is resistant to reduction at potentials less negative than -3.1 v vs SCE,[7] while the reduction potential of triphenylmethyl radical is reported as -1.20 v vs SCE.[8] Thus the energy required for the reduction of DMSO by trityl anion corresponding to a potential of 1.9 volts is 44 kcal. As a minimum this requires that all the available excited state energy (the onset of absorption of some carbanions is 650 nm) is incorporated in the electron transfer.

Results. Preliminary Photolyses. Triphenylmethyl anion underwent smooth photomethylation under the influence of .1M K_2CrO_4 filtered 450 W Hanovia light to produce two products, 1,1,1-triphenylethane, (1) and 1,1-diphenyl-1-p-tolylethane (2) (see Eq. (1)).



(1)

1 (50%) 2 (8%)

The 60% yield is based upon material isolated by extraction and recrystallization. Actual yields approached 90%.

The presence of para-methylated product 2 suggested the intervention of diphenyl-p-tolylmethane (3) which was confirmed by irradiation to lower conversions, chromatographic detection, and comparison with independently prepared material. The dimethylated product 2 was also prepared independently.

Mechanistic Investigations. Electron Transfer vs. Exciplex Formation. Mechanisms for the photomethylation can be grouped into two types, those involving electron transfer and those involving two-electron processes (nucleophilic attack or exciplex formation). The former is exemplified by the $S_{RN}1$ mechanism,[9] given here as Mechanism I:

Mechanism I:

(a) $\mathrm{Ph_3C:^-} \underset{\longleftarrow}{\xrightarrow[\mathrm{DMSO}]{h\nu}} \mathrm{Ph_3C\cdot} + \mathrm{CH_3SOCH_3^{\dot{-}}}$

(b) $\mathrm{CH_3SOCH_3^{\dot{-}}} \longrightarrow \mathrm{CH_3\cdot} + \mathrm{CH_3SO^-}$

(c) $\mathrm{CH_3\cdot} + \mathrm{Ph_3C:^-} \longrightarrow \mathrm{Ph_3CCH_3^{\dot{-}}}$

(d) $\mathrm{Ph_3CCH_3^{\dot{-}}} + \mathrm{CH_3SOCH_3} \longrightarrow \mathrm{Ph_3CCH_3} + \mathrm{CH_3SOCH_3^{\dot{-}}}$

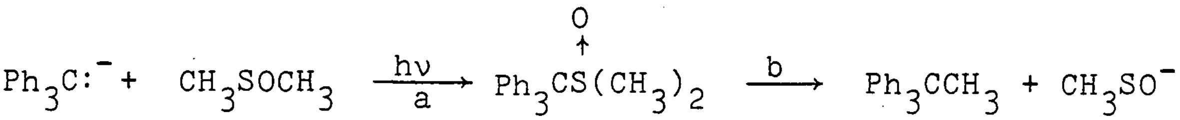
(e) $\mathrm{CH_3\cdot} + \mathrm{Ph_3C\cdot} \longrightarrow \mathrm{Ph_3CCH_3}$

(f) $\mathrm{Ph_3CCH_3^{\dot{-}}} \xrightarrow{\mathrm{Ph_3C\cdot}} \mathrm{Ph_3CCH_3} + \mathrm{Ph_3C^{\theta}}$

(g) $\mathrm{CH_3SOCH_3^{\dot{-}}} \xrightarrow{\mathrm{Ph_3C\cdot}} \mathrm{Ph_3C:^-} + \mathrm{CH_3SOCH_3}$

The latter process is represented by the exciplex mechanism, Mechanism II:

Mechanism II:

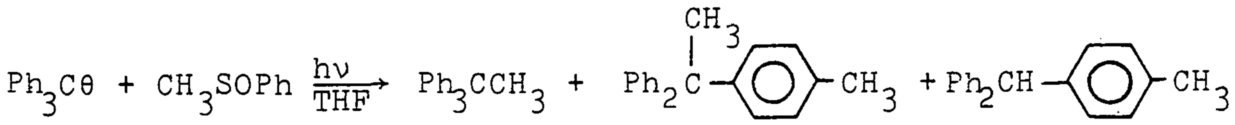


$$\mathrm{Ph_3C:^-} + \mathrm{CH_3SOCH_3} \xrightarrow[a]{h\nu} \mathrm{Ph_3C\overset{\overset{O}{\uparrow}}{S}(CH_3)_2} \xrightarrow{b} \mathrm{Ph_3CCH_3} + \mathrm{CH_3SO^-}$$

One of the most clearly distinguishing features of these two mechanisms is the concertedness of the carbon-sulfur bond breaking and carbon-carbon bond making in step b of Mechanism II. In contrast, Mechanism I requires carbon-sulfur bond breaking as a first step.

Thus irradiation in the presence of an unsymmetrical sulfoxide should lead to different products for each mechanism, since mechanism I would transfer the group having the weakest carbon-sulfur bond while Mechanism II would transfer the group with more favorable migratory aptitute. Such a requirement is satisfied with methyl phenyl sulfoxide.

The irradiation of triphenylmethyl anion in tetrahydrofuran containing methyl phenyl sulfoxide led to a hydrocarbon product mixture essentially indistinguishable from that in dimethyl sulfoxide:



1(58.6%) **2**(8.4%) **3**(4.3%)

No traces of tetraphenylmethane or diphenylyldiphenylmethane were detected. This result strongly implicates carbon-sulfur bond breaking as the critical step in determining product formation.

The Role of Radical-Anion vs. Radical-Radical Recombination. The previous experiment established dimethyl sulfoxide decomposition, either via its radical anion or via dissociative electron transfer, as the key initial step upon photoexcitation. Our next goal was determining the fate of methyl radicals so generated and the mechanistic pathway leading to products. As outlined in Mechanism I, two product forming pathways are possible. One involves methyl adding electrophilically to trityl anion to generate product radical anion (step c); the other involves methyl radical adding to trityl radical generated in the initial electron transfer step to form final product directly (step e). In this regard we were fortunate to have additional products of <u>para</u> alkylation (diphenyltolymethane 3 and diphenyltolylethane 2) which were reminiscent of products obtained from photoarylation of trityl anion in the presence of bromobenzene.[10] We had speculated that the radical-anion pathway should exhibit a greater preference for the <u>para</u> product than in the neutral pathway because of the greater delocalization in the diphenylmethylenecyclohexadiene system, which is the required intermediate in formation of 2 and 3 (see Fig. 2).

Insert Fig. 2

Conversely, the radical-radical pathway should lead to the single product 1,1,1-triphenylethane (1). Bentrude and Fu reported that methyl radical generated from trimethylphosphite during the decomposition of phenylazodiazomethane combines with trityl radical

$$\mathrm{Ph_3CN{=}NPh} \xrightarrow{(\mathrm{CH_3O})_3\mathrm{P}} \mathrm{Ph_3C\cdot} + \mathrm{CH_3\cdot} \longrightarrow \underset{1}{\mathrm{Ph_3CCH_3}} \qquad (2)$$

to yield exclusively the α product 1,[11] (see Eq. 2) and we confirmed this result, excluding the presence of diphenyl-p-tolylmethane. Thus, radical-radical recombination cannot account for all of the product formed, and we attribute the presence of para-alkylated products to the radical anion pathway.

Although radical-radical recombination cannot account for all of the products, it is still possible for this pathway to be responsible for the major reaction product 1. Our next goal, then, was to determine the relative importance of the two pathways. We note that the radical-radical pathway is unimolecular in triphenylmethyl anion. That is, the triphenylmethyl moiety undergoing irradiation is also the one incorporated into product. The radical-anion pathway, however, involves methyl radical combining with trityl anion, and the rate for this pathway will have a linear dependence upon anion concentration. To the extent step c or step e are involved simultaneously, the ratio of *para* alkylated products 2 and 3 to *alpha* alkylated product 1 should be dependent upon the concentration of trityl anion.

We irradiated trityl anion in DMSO at different initial concentrations and observed the ratios of *alpha* to *para* products formed. We included dimethylated product **2** with monomethylated product **3** because **2** is the direct product of **3**. The results are listed in Table I. Within experimental error, the ratio of *para* to *alpha* products is constant. Thus we conclude that both products are formed at the same step, and since we have concluded that the radical-anion pathway must be involved in part of the mechanism, it must represent the dominant reaction pathway.

Results and Discussion. **Competitive Trapping of Methyl Radical by the Radical Anion Pathway.** The independence of methyl radical generation and product formation requiresthat the same products be formed regardless of the source of methyl radical. Competitive trapping experiments confirmed this hypothesis.

The visible absorption spectra of triphenylmethyl anion and 4-biphenyldiphenylmethyl anion (**4**) exhibit markedly different absorption spectra, with the first having a λ_{max} of 496 nm and the second 592 nm. We prepared separate but identical mixtures of the two anions such that 70% of the light at 500 nm was absorbed by trityl anion and 90% of the light at 600 nm was absorbed by biphenyldiphenylmethyl anion. We irradiated one solution with a filter solution transmitting at 600 nm.[12] These results are reported in Table II, while the relative absorption spectra of the anions for the samples used are depicted in Figure 3. *The product mixtures from the separate experiments were nearly identical*. Thus product formation is bimolecular in anion, and since triphenylethane is the major product even when anion **4** is irradiated, the formation of triphenylethane under these conditions is the result of photocatalysis by diphenylyldiphenylmethyl anion.

Results and Discussion. The Role of Chain Processes. Than quantum yield of disappearance of trityl anion upon irradiation was measured[13] and found to be .06, strongly suggesting that a chain process is not involved. However, quantum yields below unity are not necessarily compelling evidence for such a conclusion. More conclusive are anion concentration dependent quantum yields. For a chain process, the limiting quantum yield is given by Equation 3.[14]

$$\phi_r = \left(\frac{k_r k_{et}}{k_c (k_{et} + k_d) I k_t} [T^-] \right)^{1/2}, \qquad (3)$$

where

k_r	is the rate constant for radical-anion combination (step c);
k_{et}	is the rate constant for electron transfer (step a);
k_c	is the rate constant for the chain carrying step (step d);
k_d	is the rate constant for excited state decay in the absence of electron transfer;
I	is the rate of light absorption;
k_t	is the rate of back electron transfer (step g); and
$[T^-]$	is the concentration of the trityl anion.

The limiting quantum yield for the non-chain process ($k_c \simeq 0$) is given by more standard kinetics (see Eq. 4).

$$\Phi_r = \frac{k_{et}}{k_{et} + k_d} \qquad (4)$$

By simultaneously monitoring light output and triphenylethane produce formation, we obtained the plot shown in Figure 4. Within experimental error, the slope over one half-life of trityl anion is linear, giving a correlation coefficient of .999. The linearity of this plot and the constancy of the quantum yield clearly exclude the appreciable intervention of a chain mechanism.

Discussion. Unexpected Product Selectivities in Photomethylation. The preference for triphenylmethyl anion alkylation despite the greater stability, by 19 kcal, of the biphenyl radical anion over benzene radical anion is an unexpected result. We have analyzed the relative energetics for methyl radical plus triaryl anion combination for the two systems, and we attribute the anomalous product to a kinetic effect arising from quenching the less stable anion. That is, the transition state for the reaction incorporates the bond strength of the newly formed bond, for which one index of reactivity is the pK_a. Furthermore, we were intrigued by the observation that diphenyltolylmethyl anion apparently aklylates much more readily than the parent trityl anion, since even at low conversions substantial amounts of the bisalkylated produce **2** were observed and at higher conversions **2** predominated over **3**, despite relatively higher pK_a for **3** over **1**. We attribute this to the same effect, but further work is currently underway to test this hypothesis.

Discussion. Effect of Substrate Modification on $S_{RN}1$ Processes. The $S_{RN}1$ pathway is clearly a ubiquitous mechanism in carbanion ground state chemistry and photochemistry. Modification of the substrates can alter or completely eliminate certain steps in the reaction scheme, however. As a result of our work, we have concluded three mechanistic consequences of this substrate modification: 1) *Using an acceptor of low electron affinity stops the chain process*. Conventionally, chain processes are facilitated by the use of acceptors (bromobenzene or nitroaliphatics, among others) of high electron affinity. 2) *Use of an acceptor of low electron affinity requires photoassistance*. 3. In contrast with enolates, *resonance - stabilized carbanions are ambident with respect to radical attack*. As a result, products are formed which differ from those obtained by S_N2 mechanisms.

The use of dimethyl sulfoxide as the electron acceptor provides an interesting simplification of alkylation by $S_{RN}1$ pathways, for it is the first such example for which *the leaving group is also the electrophore*, and thus the necessity for incorporating a nitro group into the product, for instance, is circumvented. Additionally, dimethyl sulfoxide provides a convenient method for generating methyl radicals in the presence of highly basic carbanions which circumvents the base instability of other methyl radical sources such as di-t-butyl peroxide.

Finally, the unconventional regiochemistry observed in alkylation of triphenylmethyl anion under these conditions suggests the exploitation of this reaction synthetically to obtain different sites of alkylation from those obtainable by ordinary ground state methods.

Conclusions. The photochemistry of triphenylmethyl anion provides a unique vehicle for investigating step by step the consequences of interaction of light with a negatively charged species. We have discovered that electron ejection is still the dominant pathway, but we are astounded by the relatively high potential of the electron so ejected. Electron transfer to DMSO leads to the formation of methyl radicals, which combine with other anions at a rate at least partially dependent on the pK_a of the corresponding carbon acid. The resulting radical anion does not carry on a chain process, but ultimately restores an electron to triphenylmethyl radical. We have the important result that excited triphenylmethyl anion can reversibly promote a chemical reaction in another substrate.

The photochemistry of triphenylmethyl anions also provides an interesting contrast to ground state chemistry promoted by dissolving metals. The radicals and radical anions produced under the latter conditions are formed quantitatively and in high concentrations, since back transfer is energetically forbidden. Thus radical-radical reactions readily occur, leading to complex mixtures of products. Under photopromoted conditions however, without the presence of highly reducing species, no more than a low steady state of methyl radical is produced, so that radical-radical reactions do not occur and the resulting products are remarkably clean and free from side products.

Clearly important questions remain to be answered, e.g., whether electron transfer is inner-sphere or outer-sphere, or whether electron transfer to DMSO is reversible or not. However, we now understand the crucial steps in product formation. Understanding how structural changes affect these steps in our next goal.

EXPERIMENTAL SECTION

Melting points were taken on a hot-stage apparatus and are uncorrected. Nuclear magnetic resonance spectra were obtained on a Varian T-60 spectrometer.

Manipulations. Apparatus and nonvolatile materials were degassed repeatedly by evacuating to less than .1 torr and purging with argon dried and deoxygenated with an Ace-Burlitch inert atmosphere system. Liquids were transferred by reaching through the bore of a 4 mm three-way stopcock with the needle of a degassed syringe or with a double-tipped stainless steel needle. A stream of argon through the side opening of the stopcock protected the liquid from air.

Photochemical Equipment. Irradiations were carried out with a Hanovia 450 W lamp in a Pyrex immersion well equipped with an ellipsoidal reflector which focused the light on a cylindrical 3 cm x 20 cm reaction vessel. Light filtration was provided by a cylindrical container surrounding the immersion well and containing .1 M K_2CrO_4 in a pH 10 buffered medium. This filter solution effectively excluded all light below 450 nm. Additional filtration, if necessary (see below), was provided by an additional cylindrical container surrounding the reaction flask.

Materials. Dimethyl sulfoxide was purified as described by Bordwell[15] and stored over molecular sieves. Solutions of potassium methylsulfinylmethide ("dimsyl") were prepared by syringing 20 ml of 20-25% potassium hydride in an argon-filled serum-capped 50 ml centrifuge tube, adding 20 ml of dry pentane, and successively shaking, centrifuging, removing and readding pentane onto the potassium hydride. After the third centrifugation, the pentane and dissolved oil were removed by syringe, the entire apparatus pumped dry, and the weight of potassium hydride remaining measured by difference. A 25 ml portion of dimethyl sulfoxide was added through a Teflon tube under a positive pressure of nitrogen, and after the frothing had subsided, the remaining hydrogen was removed under vacuum. The concentrated solution was transferred under argon to a Schlenk tube equipped with an automatic buret and diluted to 200 ml with additional dimethyl sulfoxide. The solution was titrated with potassium hydrogen phthlate using phenolphthalein as indicator. A typical solution had a total base concentration of .2 M. Solutions prepared in this manner were stored without noticeable decomposition for two weeks, provided light was excluded.

Triphenylmethane was obtained from Aldrich Chemical Company and was either used as received or recrystallized from methanol. 4-Tolydiphenylmethane[8] was obtained by boiling formic acid treatment of 4-tolyldiphenylcarbinol, which in turn was obtained from 4-tolylmagnesium bromide treatment of benzophenone. Diphenylyldiphenylmethane was obtained by the method of Bordwell.[15]

Chromatography. Gas chromatographic analysis was performed on a Varian 3700 Gas Chrmatograph using a 3 m column of 2% OV-101 on Chromosorb G. High pressure liquid chromatography was performed on a 25 cm x 2 mm column of Porasil - ODS on a Laboratory Data Control modular system incorporating a variable wavelength detector set at 238 nm and using 60% acetonitrile-water as eluent.

Preparative Photolysis of Triphenylmethylpotassium. To 1.601 g (6.50 mmol) of triphenylmethane in 15 ml of dimethylsulfoxide contained in the reaction vessel was added 35 ml (7.0 mmol) of 0.20 M potassium dimsyl. The degassed solution was irradiated without a solution filter until the red color disappeared (ca. 3 hr). The solution was added to 200 ml of water and ether extracted. Silica gel chromatography of the residue after concentration yielded 0.954 g of a white solid. Recrystallization from methanol yielded .852 g (3.30 mmol, 50%) of colorless prisms. The mp (90.0-92.5) and spectral data were identical to 1,1,1-triphenylethane[16]: nmr ($CDCl_3$) 2.17 (s, 3H), 7.10 (br s, 15 H); ms 258, 243. The mother liquor and remaining hydrocarbon fractions from the chromatography column were combined. Preparative high pressure liquid chromatography and preparative gas chromatography failed to separate the residue, which proved by analytical gas chromatography, analytical high pressure liquid chromatography, and nmr comparison with authentic material, to consist of 1,1,1-triphenylethane and 1-(4-tolyl)-1,1-diphenylethane(.141 g, 8% yield).

Quantum Yields. Quantum yields were determined on a chemists optical bench essentially identical to that described by Zimmerman. Irradiations of triphenylmethyl anion were carried out at 550 nm using a Bausch and Lomb super high pressure mercury arc lamp equipped with a high intensity grating monochromator. Light output was monitored by an integrating photometer using an EG and G HUV-1000B operational amplifier-photodiode combination as a detector. The detector was mounted at right angles to the light beam so as to capture the light reflected by a quartz plate beam splitter placed at 45° in the light beam. For maximum sensitivity and linearity, the photodiode was run in the reversed bias mode. Calibration was carried out with a Scientech Model 36-0001 Disc Calorimeter. Analysis of product formation was by gas chromatography.

In the run represented by Figure 4, 49.2 mg of triphenylmethane in 48 ml of dimethylsulfoxide were reacted with 2 ml of .368 M potassium dimsyl. The solution was irradiated at 550 nm, and aliquots were removed at 1, 2, 4, 7, 17, and 24 hr. Calibrated volumes were injected on the gas chromatograph, and the detector response was standardized using authentic samples. The detector counts were converted to light output in Einsteins, and the product vs. light output gave the plot in Figure 4. Least squares treatment of the points gave a quantum yield of triphenylethane appearance of .0406 ± .0003. Similar treatment of starting material gave a quantum yield of disappearance of .0658 ± .0043.

Concentration Dependent Runs. To 2 g of triphenylmethane in DMSO was added .138 M potassium dimsyl in the amount indicated. The initial amount of DMSO added was precalculated to bring the total volume of solution to 50 ml. The solution was irradiated until the red color disappeared (4-20 hr). Triphenylethylene (*ca*. .5 g) was added as an internal standard, and the solutions were analyzed by gas chromatography. Calibration of the detector response was performed using a standard solution of authentic materials. The amounts of materials introduced and products produced were as follows, with percentages based upon initial base concentration:

Run 1: Triphenylmethane, 1.96 g; potassium dimsyl, 50 ml; triphenylethylene, .453 g. Products: triphenylethane, 1.07 g, 50.8% 4-tolyldiphenylmethane, .125 g, 7.0%; 4-tolyldiphenylethane, .184 g, 9.8%.

Run 2: Triphenylmethane, 2.12 g; potassium dimsyl, 18 ml; triphenylethylene, .196 g. Products: triphenylethane, .412 g, 64.2% 4-tolyldiphenylmethane .103 g, 16.0%; 4-tolyldiphenylethane, 0.259 g, 3.8%.

Run 3: Triphenylmethane, 1.82 g; potassium dimsyl, 12.1 ml; triphenylethylene .107 g. Products: triphenylethane, .283 g, 65.2%; 4-tolyldiphenylmethane, .0766 g, 17.7%, 4-tolyldiphenylmethane, 11.6 g, 2.5%.

Irradiation of Triphenylmethylpotassium in Methyl Phenyl Sulfoxide.
A solution of potassium phenylsulfinylmethide was prepared as follows: A sample of dry potassium hydride in argon was prepared by washing 3.0 ml of 20% potassium hydride with pentane using the procedure outlined for potassium dimsyl. This amount of potassium hydride was calculated on the basis of previous experiments to yield 8.3 mmol of active potassium hydride. A solution of 25 ml of dry tetrahydrofuran containing 3.0 g (21.0 mmol) of methyl phenyl sulfoxide was added slowly so as to control frothing. The resulting solution was degassed by cooling to below 0° and evacuating the vessel to < .1 torr. Argon was reintroduced, and the solution added to the previously degassed photolysis chamber containing 2.73 g (11.2 mmol) of triphenylmethane. The red solution was irradiated for 12 hr. The solution was diluted with water and extracted with ether. Analysis of the extract by gas chromatography

and nuclear magnetic resonance spectroscopy showed the presence of triphenylmethane (.406 g, 1.66 mmol), 1,1,1-triphenylethane (1.69 g, 6.55 mmol), 1-tolyl-1,1-diphenylmethane (.124 g, .48 mmol), and 1-(4-tolyl)-1,1-diphenylethane (.255 g, .94 mmol).

1-(4-Tolyl)-1,1-diphenylethane. To .674 g (2.61 mmol) of (4-tolyl)-diphenylmethane in 10 ml of DMSO were added 15 ml (5.52 mmol) of .368 M potassium dimsyl. The red solution was allowed to equilibrate for 30 min, then .40 ml (6.42 mmol) of methyl iodide was added. Thirty ml of water was added, and the solution extracted three times with ether. The extracts were dried and concentrated, leaving a slowly crystallizing oil. The crystals were recrystallized from hexane to yield .464 g (1.71 mmol, 65%) of colorless prisms, mp 66-68°. The spectral data were: nmr ($CDCl_3$): δ 2.15 (s, 3H, Ar_3CCH_3), 2.29 (s, 3H, $ArCH_3$), 7.00 (s, 4H, $-C_6H_4-$), 6.89-7.32 (m, 10H, arom). Anal. ($C_{21}H_{20}$) C, H.

1,1,1-Triphenylethane. To 1.04 g (4.28 mmol) of triphenylmethane in 10 ml of DMSO was added 13 ml (4.78 mmol) of potassium dimsyl. The red solution was allowed to equilibrate for 30 min, then .311 ml (5.0 mmol) of methyl iodide was added dropwise. The red color disappeared after *ca*. 90% of the methyl iodide was added. A few drops of water were added, and the solution allowed to stand. After 7 days, long needles had formed. These were removed by filtration to yield 0.747 g (2.90 mmol, 68%) of crystals, mp 90-92° (lit[16] mp 90-92.5). Additional less pure product was obtained by adding 10 ml of water to the filtrate and allowing the coludy mixture to stand for several days more. The spectral data were: nmr ($CDCl_3$); δ 2.17 (s, 3H, CH_3), 7.00-7.38 (m, 15H, arom).

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References and Footnotes

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12. There is an inherent danger in relying exclusively on the transmittance spectrum of a filter solution as a guide to the spectrum of light put out by the filtered lamp. This is particularly true when using a medium or high pressure mercury arc lamp whose output spectrum consists of a series of unevenly distributed lines. In this particular case, the "500 nm" filter solution is not truly effective, since the nearest mercury line is at 546 nm, and the two anions absorb equally in this region. This would throw the analysis of the experiment into jeopardy were it not for the fact that triphenylethane products are produced even when the "600 nm" filter is used and light capture by the diphenylyl anion exceeds 94%.

13. Actually this is the quantum yield of disappearance of triphenylmethane. To the extent that triphenylmethane is a photochemical product of triphenylmethyl anion,- for instance, by hydrogen abstraction,- the true quantum yield for triphenylmethyl anion disappearance will be increased by a compensating amount.

14. A steady state treatment of transient intermediates was employed similar to that of Benson, S.W., *The Foundations of Chemical Kinetics*, McGraw-Hill Company, New York, **1960**.

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Table I. Effect of Carbanion Concentration

$Ph_3C:^-$ conc.	Yields of Methylated Products			p/α
	1	3	2	
0.138 M	59.8	7.0	9.8	28.1%
0.050 M	64.2	16.0	3.8	30.9%
0.033 M	65.2	17.7	2.5	31.1%

Table II. Results of Competition Experiment

	Experiment 1	Experiment 2
Irradiation Wavelength	500[a]	600[a]
Mmol Trityl anion[b]	0.257	0.275
Mmol Biphenylyl anion[b]	0.175	0.196
Mmol Triphenylethane	0.157	0.174
Mmol p-Tolydiphenylethane	0.046	0.060
Mmol 4-Diphenylyldiphenylethane	0.035	0.034

(a) Serial filter solutions were used. The first cell contained 0.2 M $K_2CrO_4 \cdot 6H_2O$ in a pH 10 solution. The second cell contained either 0.50 M $NiSO_4$ in water (500 nm) or 0.43 M $CoSO_4 \cdot 6H_2O$ in water (600 nm); (b) This was produced by reacting the hydrocarbon with excess base.

FIGURE 1. EFFECT OF PHENYL SUBSTITUTION.

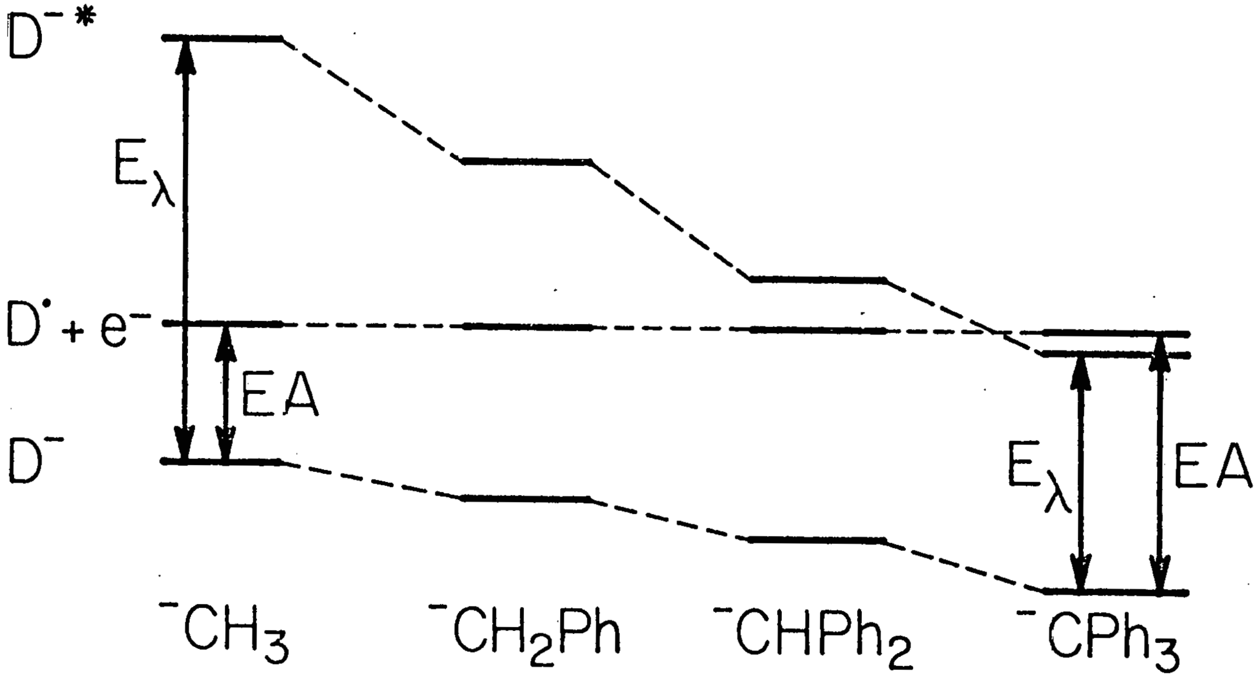

FIGURE 2.

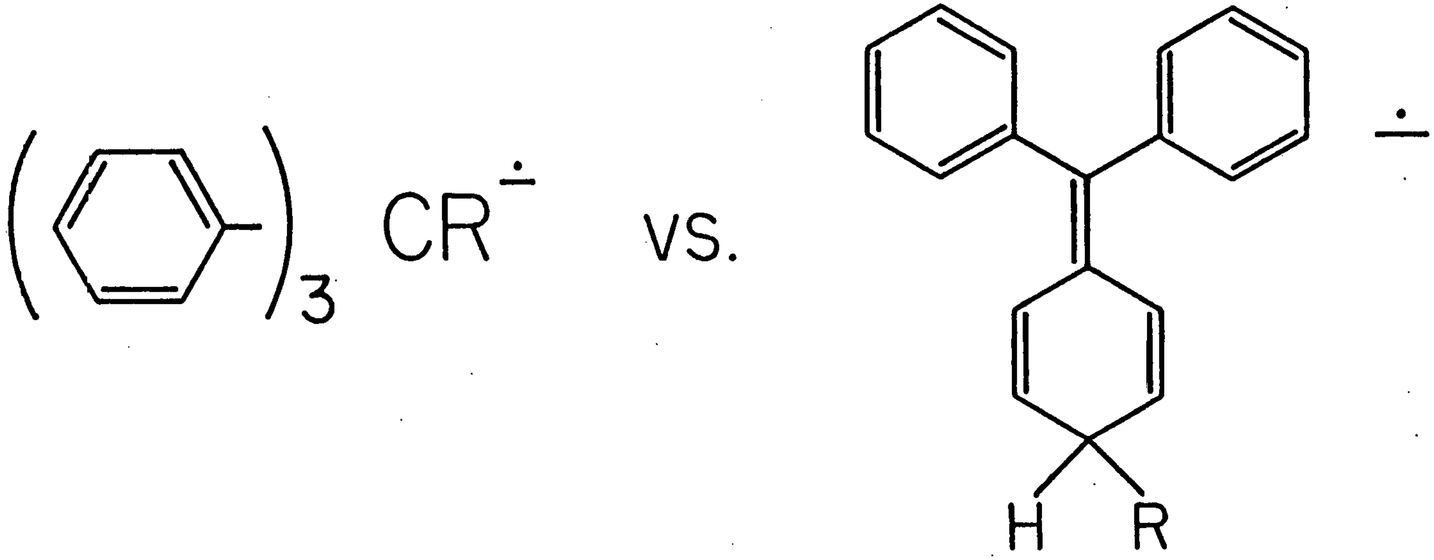

FIGURE 3. RELATIVE ABSORBANCIES.

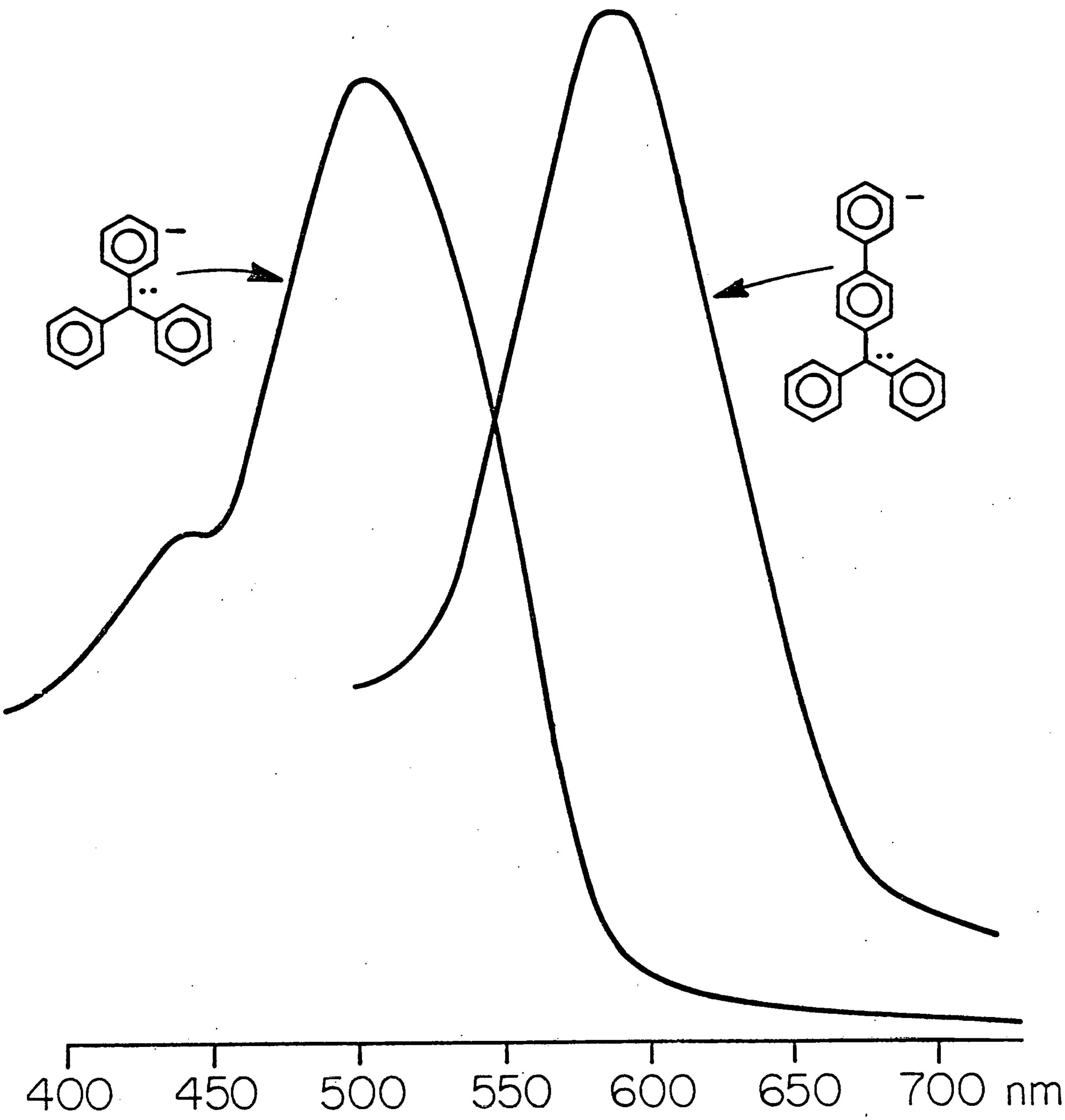

FIGURE 4. CONCENTRATION-DEPENDENT PRODUCT FORMATION.