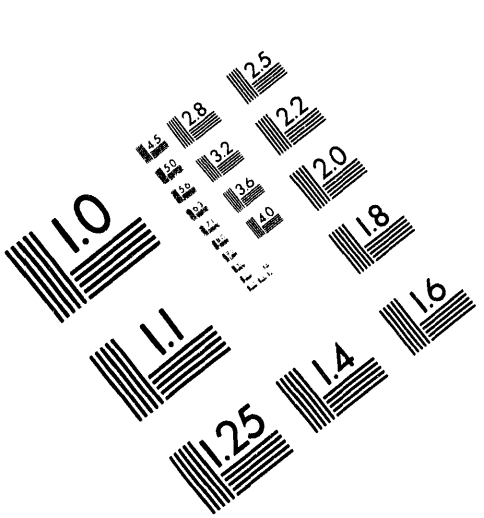

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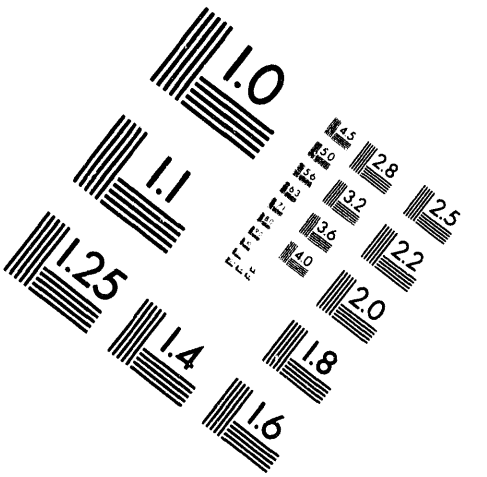

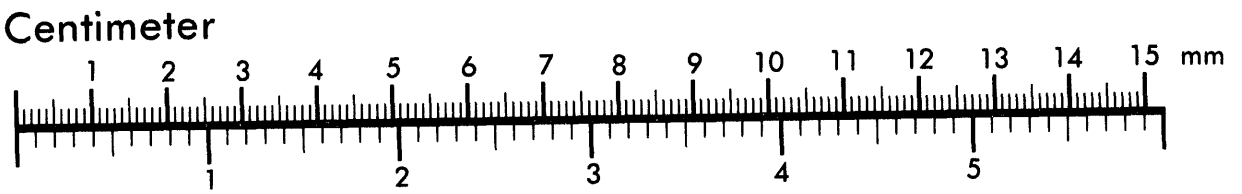

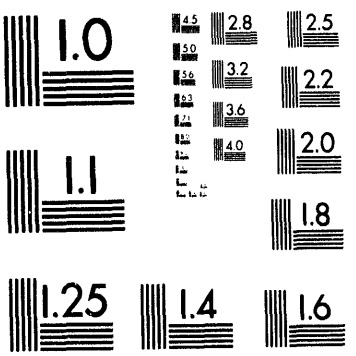

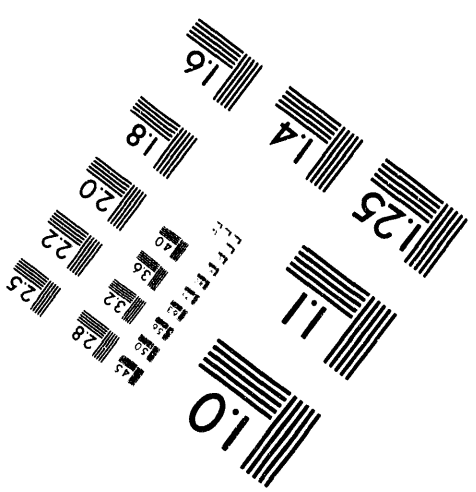

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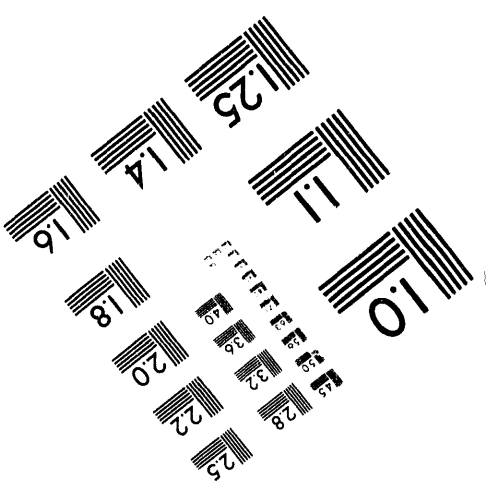

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FINAL REPORT

CATALYSIS AND CO-CATALYSIS OF BOND CLEAVAGES IN COAL AND COAL ANALOGS

DOE GRANT #90PC90298

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FINAL REPORT
CATALYSIS AND CO–CATALYSIS OF BOND CLEAVAGES IN COAL AND COAL ANALOGS

Introduction

In work prior to the inception of this project, we observed that mixtures of phenolic materials and polyalkoxyaromatic molecules were appreciably more effective in catalyzing the decompositions of di–2–naphthyl ether and of di–1–naphthyl sulfide in tetralin solutions at 450°C than were the phenols by themselves, even though the polyalkoxyaromatic molecules, in the absence of phenolic co–catalysts, show essentially no catalytic activity. This was of appreciable interest in coal research because dinapthyl ether and dinapthyl sulfide have been employed as model compounds for coals in studies aimed at cleaving ether and sulfide bonds similar to those in coals.

We proposed (R. K. Sharma, K. P. Raman, and B. Miller, *Fuel*, 1986, *65*, 738) that the mixed catalysts used in our studies catalyze cleavages of ether and sulfide bonds by means of a mechanism involving electron transfer from the polyalkoxyaromatics to the substrates, which are activated as electron acceptors by hydrogen bonding to phenols. Since phenols themselves are electron donors, we also proposed that the well known effects of phenols in catalyzing the conversion of coals are due to similar electron transfer mechanisms.

Tests of the Electron Transfer Mechanism

9–Phenylthioanthracene (9–PTA) was chosen as an appropriate substrate to test the hypothesis that reductive cleavage of bonds to aromatic rings caused by heating in hydrogen donor solvents, such as tetralin, may be catalyzed by electron donating agents in the absence of hydrogen bonding or acidic reagents.

9–PTA was prepared according to literature procedures in two ways: by reaction of sodium thiophenoxide with 9–bromoanthracene and by acid catalyzed exchange of thiophenol with 9–

methoxyanthracene. Both procedures required use of multiple crystallizations to yield pure 9–PTA, and gave low yields of the purified product.

In order to carry out analyses of product mixtures, several potential internal standards for vpc analysis were examined. Eicosane was chosen as the most useful standard, since vpc retention time did not coincide with that of the starting material or any of the reaction products. VPC analyses were carried out on a 0.5 meter, 1% OV101 on chromosorb W column. During analyses the temperature was kept at 170° for 3 min, then raised to 180° for an additional 3 min, and then rapidly raised to 250° for the remainder of the analysis. Under these conditions, anthracene had a retention time of ca. 2.4 min, eicosane of ca. 4.8 min, and 9–PTA of 8.0 min

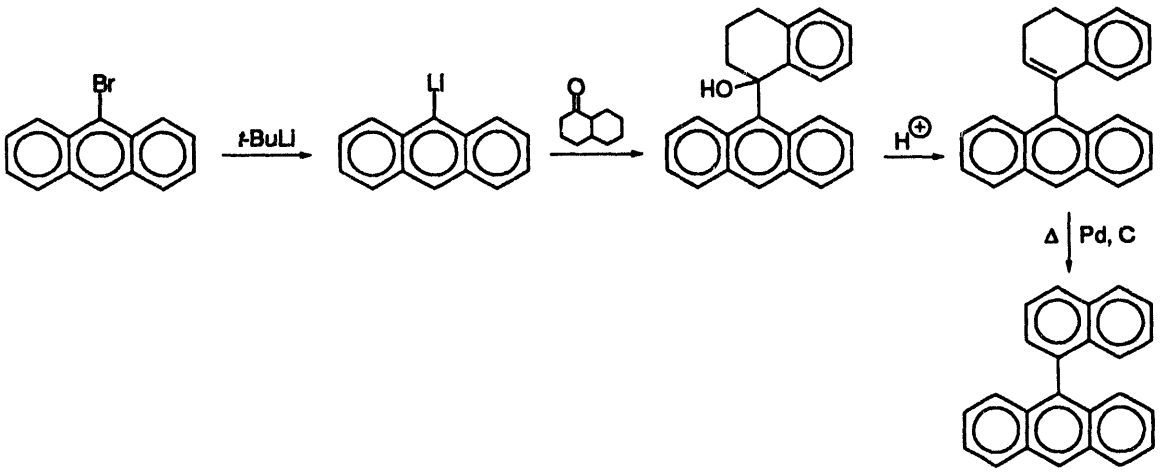
Ca. 0.02 M solutions of 9–PTA in tetralin (purified by chromatography on neutral alumina) were heated in glass ampoules.

It was observed that decomposition of 9–PTA occurs on heating at temperatures as low as 250°C, even in the absence of additives or catalysts. Reductive cleavage (measured by yields of anthracene), however, was invariably a minor process. Two major products, obtained at retention times of ca. 6.5 and 9.0 min, respectively, were observed in all runs. (These products were obtained in rather variable yields, with an increase in the yield of one product often being accompanied by a decrease in the yield of the other.)

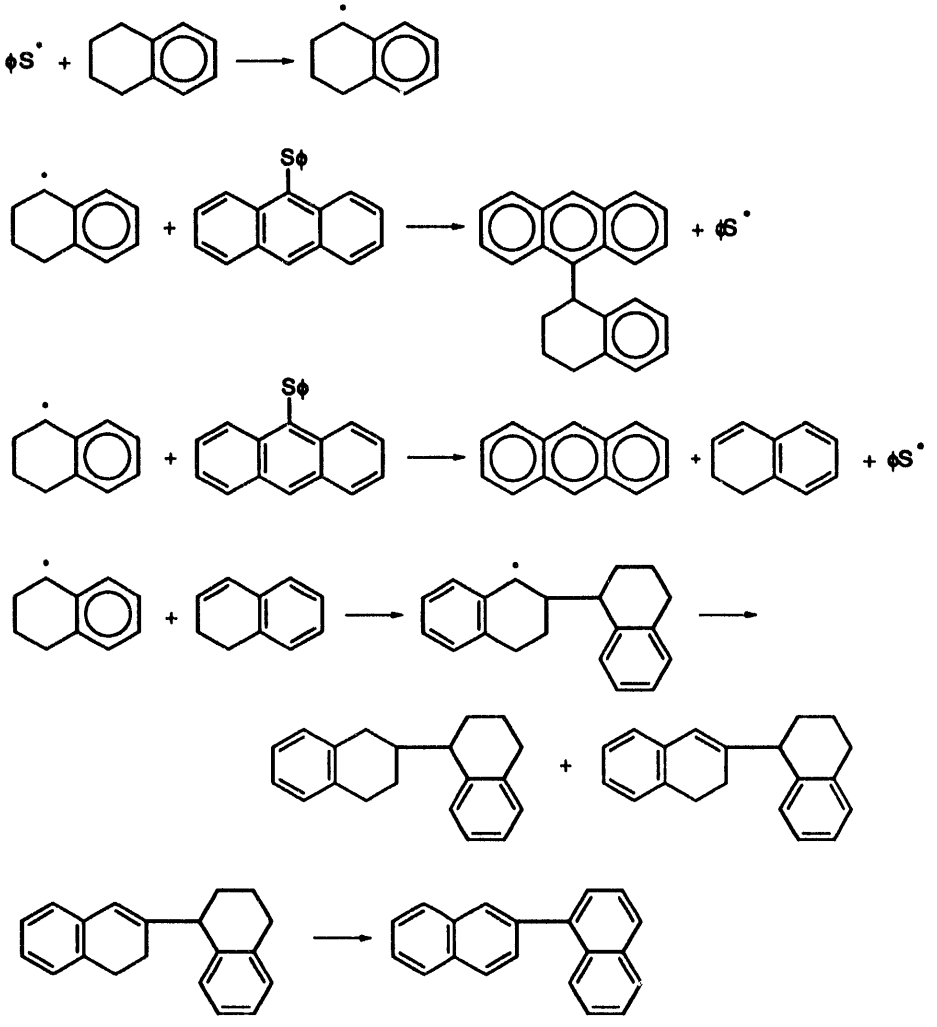
The products from reaction of 9–phenylthioanthracene with tetralin were identified by GC–MS analysis. The "product" with retention time = 6.5 min was separated by glass capillary chromatography into four components, with relative abundances of 4.3 : 1.9 : 2.3 : 1.5. The first two components showed principal peaks at m/e 131, with no molecular ions. They were therefore assigned the structure 1–(1–1,2,3,4–tetrahydronaphthalenyl)naphthalene (with the *R,S* form presumably the major isomer and the *meso* form the minor isomer). The next two components were identifed by comparison with published spectra as 1–(2–1,2,3,4–tetrahydronaphthalenyl)naphthalene and 1–(2–naphthalenyl)naphthalene, respectively.

The product with retention time = 9.0 min ("product B") was found to have a molecular ion at m/e 308, corresponding to a molecular formula of $C_{24}H_{22}$. It was therefore assigned the structure 9–(1 or

2-tetrahydronaphthalenyl)anthracene. Independent synthesis as shown below demonstrated that it was 9-(1-tetrahydronaphthalenyl)anthracene.



Formation of the products from the reaction can be rationalized by the mechanism shown below. However, the nature of the initiation process is still not clear.



Addition of 2,6–xylenol, 1,3,5–trimethoxybenzene, or 1,4–dimethoxynaphthalene to the thermolysis mixtures appeared to offer, at best, only slight increases in reaction rates, and little change in product compositions. The results are summarized in Table I.

Table I

Reaction of 0.02 M 9–Phenylthioanthracene in Tetralin

Temp. (°C)	Reaction Time (hrs)	Additive (Molarity)	% Unreacted 9–PTA	% Yield anthracene [3]	Unidentified Products (ratio + peak areas to initial area of 9–PTA) Product A [1]	Product B [2]
250	18	---	0.67	6.7	0.17	0.18
300	5	---	0.57	9.4	0.59	0.09
300	5	---	0.61	6.9	0.31	0.21
300	5	---	0.58	10.1	0.21	0.23
300	5	2,6-xylenol (0.15)	0.53	10.7	0.19	0.25
300	5	2,6-xylenol (0.15)	0.54	9.4	0.34	0.19
300	5	1,3,5-trimethoxy-benzene (0.18)	0.55	8.9	0.21	0.29
300	5	1,3,5-trimethoxy-benzene (0.18)	0.47	11.3	0.34	0.21
300	5	2,4-dimethoxyna-phthalene (0.15)	0.49	9.4	0.48	0.17
300	5	2,4-dimethoxyna-phthalene (0.15)	0.55	10.7	0.27	0.28
350	5	---	0.12	22.4	0.57	0.48
350	5	---	0.17	20.9	0.71	0.31
350	2	---	0.43	14.7	0.43	0.24
350	2	---	0.46	15.3	0.17	0.49
350	2	2,6-xylenol (0.16)	0.39	15.1	0.49	0.29
350	2	2,6-xylenol (0.16)	0.44	12.2	0.31	0.34
350	2	1,3,5-trimethoxy-benzene (0.15)	0.42	14.7	0.50	0.27
350	2	1,3,5-trimethoxy-benzene (0.15)	0.49	13.3	0.30	0.41
400	0.5	---	0.29	18.4	0.40	0.31

[1] Retention time = 6.5 min; [2] Retention time = 9.0; [3] Based on starting quantity of 9-PTA.

As indicated above, 9–phenylthioanthracene derivatives decompose on heating in tetralin solution even in the absence of catalytic additives and exhibited little, if any, response to addition of polyalkoxyarenes or phenols. Therefore, in continuation of our attempts to demonstrate catalytic activity of polyalkoxyarenes in the absence of hydrogen bonding co–catalysts, we examined the thermolytic reactions of 9–bromoanthracene (9–BA) and 9,10–dibromoanthracene (9,10–DBA) in tetralin solutions.

9–BA was found to decompose spontaneously on heating at 300°C in tetralin solutions in glass ampoules (Table II, runs 1, 2). The products obtained were identical with those obtained from 9–phenylthioanthracene, consisting of anthracene, a mixture of C_{20} hydrocarbons (binaphthyls and bitetralyl derivatives) and a product of molecular weight 308, whose mass spectrum corresponded to that of 9–(1–tetrahydronaphthalenyl) anthracene.

Addition of 1,3,5–trimethoxybenzene (Table II, runs 3–16) or 1,4–dimethoxynaphthalene (runs 17, 18) to thermolysis reactions of 9–BA resulted in appreciable acceleration of the rate of loss of 9–BA. The products were not significantly changed by the presence of the catalysts. The catalytic effect was approximately linearly related to the concentrations of 1,3,5–trimethoxybenzene (Chart I). The possibility was considered that the catalytic effect of the polyalkoxyarenes was initiated or enhanced by formation of hydrogen bromide during decomposition reactions of 9–BA. However, examination of Chart II shows that no evidence for any induction period or for enhanced rates of reaction after liberation of hydrogen bromide.

9,10–DBA showed little reaction on heating in tetralin at 250°C in the absence of catalysts. Addition of 1,3,5–trimethoxybenzene resulted in enhancement of the rate of disappearance of 9,10–DBA. The products of the reaction differed from those of 9–BA in that little MW 308 product was obtained. (It is believed that high molecular weight products consisting of dimeric or polymeric anthracenyl derivatives are indeed formed, but are not detectable by glpc analysis.) Some hydrogenolysis to form anthracene occurred, but no more than trace amounts of 9–BA were detected. This is surprising, since studies on reaction of 9–BA indicate that appreciable amounts would remain if it were formed as an intermediate in the reaction.

Thus, we have for the first time demonstrated that polyalkoxyarenes capable of acting as electron donating agents can catalyze loss of hetero atoms bonded to aromatic rings even in the absence of hydrogen bonding co-catalysts.

Table II

Thermolysis of 9-Bromoanthracene in Tetralin [1]

Run	Temp. (°C)	Reaction Time (hrs)	Additive (Molarity)	% Recovered 9-BA	% Yield anthracene [2]	Ratio of Peak Areas to Initial Area of 9-BA	
						Product A [3]	Product B [4]
1	300	5	---	66	12	0.59	0.23
2	300	5	---	71	12	0.63	0.26
3	250	5	---	93	1.3	0.08	0.04
4	250	5	---	98	2.9	0.09	0.075
5	250	5	---	92	5.1	0.21	0.13
6	250	5	1,3,5-TMB [5] (0.13)	67	11	0.33	0.22
7	250	5	1,3,5-TMB (0.13)	62	7.1	0.38	0.18
8	250	3	1,3,5-TMB (0.13)	85	7.2	0.33	0.23
9	250	5	1,3,5-TMB (0.034)	86	5.3	0.29	0.14
10	250	5	1,3,5-TMB (0.062)	78	5.6	0.38	0.15
11	250	5	1,3,5-TMB (0.062)	81	8.0	0.49	0.15
12	250	5	1,3,5-TMB (0.11)	75	10	0.39	0.14
13	250	5	1,3,5-TMB (0.18)	65	9.4	0.48	0.21
14	250	2	1,3,5-TMB (0.14)	84	5.0	0.20	0.21
15	250	4	1,3,5-TMB (0.14)	71	7.4	0.31	0.24

Table II. Continued

Run	Temp. (°C)	Reaction Time (hrs)	Additive (Molarity)	% Recovered 9-BA	% Yield anthracene [2]	Ratio of Peak Areas to Initial Area of 9-BA: Product A [3]	Product B [4]
16	250	6	1,3,5-TMB (0.14)	61	11	0.47	0.23
17	250	5	1,4-DMF [f] (0.17)	71	8.0	0.44	0.19
18	250	5	1,4-DMF [f] (0.17)	68	11.2	0.57	0.17

[1] 0.16–0.18 M; [2] Based on starting quantity of 9-BA; [3] C_{20} products; [4] MW 308 products; [5] 1,3,5-Trimethoxybenzene; [6] 1,4-Dimethoxynaphthalene.

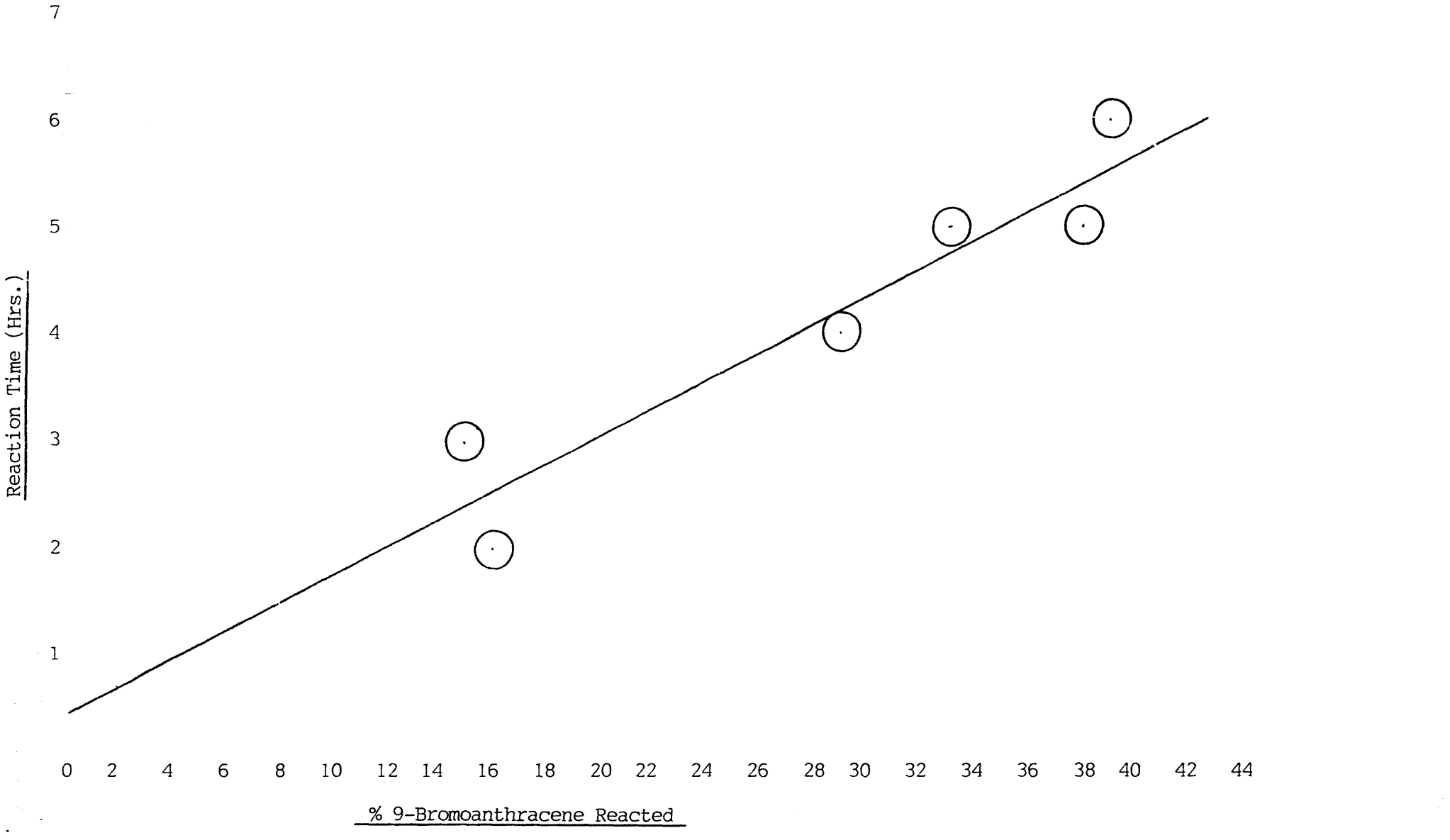
Table III

Thermolysis of 9,10-Dibromoanthracene in Tetralin

Run	Temp. (°C)	Reaction Time (hrs)	Additive (Molarity)	% Recovered 9,10-DBA	% Yield anthracene	% Yield 9-BA	Ratio of Peak Areas to Initial Area of 9,10-DBA: Product A	Product B
1	250	5	---	97	0.4	---	0.18	---
2	250	5	---	96	0.2	---	0.29	0.01
3	250	5	1,3,5-TMB (0.11)	74	4.5	0.1	0.67	0.06
4	250	5	1,3,5-TMB (0.11)	70	6.1	---	0.72	0.04
5	250	5	1,3,5-TMB (0.064)	71	6.1	0.1	0.63	---

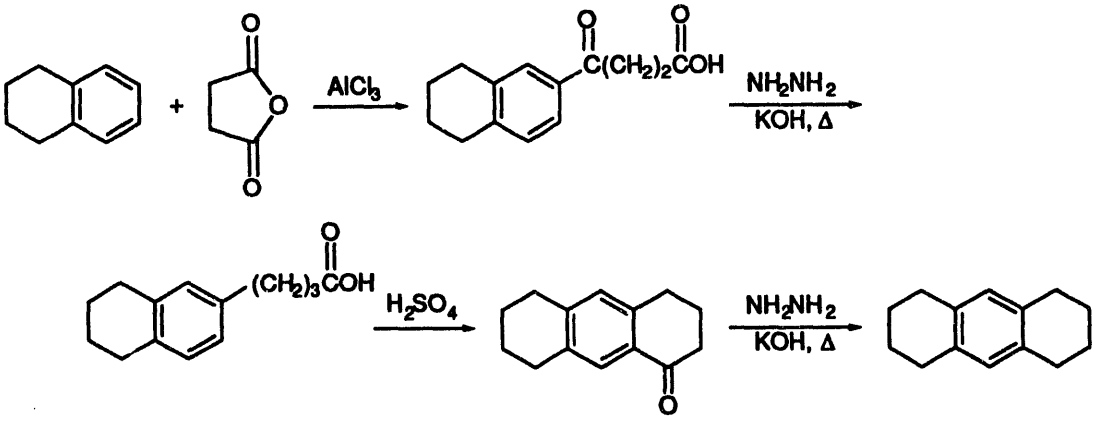
CHART 1. EFFECT OF CATALYST CONCENTRATION ON THE RATE OF 9-BROMOANTHRACENE

CHART II. EFFECT OF REACTION TIME ON THERMOLYSIS OF 9-BROMOANTHRACENE (0.13-0.14 M 1,3,5-TMB CATALYST)



Products from Catalyzed Hydrogenolyses

The absence of appreciable yields of anthracene from thermolyses of 9–bromoanthracene and 9–phenylthioanthracene in tetralin solutions made it desirable to re-examine the thermolyses in tetralin of di–2–naphthyl ether and di–1–naphthyl sulfide, to assure that the disappearance of these compounds does indeed result from transfer hydrogenolyses to form naphthalene. Thermolysis reactions of these compounds, with and without added catalysts, were therefore carried out employing ca. 20/1 molar excesses of 1,2,3,4,5,6,7,8–octahydroanthracene as the hydrogen donor solvent. The procedure shown below for preparation of that compound is a variant on literature procedures for the synthesis.



In these reactions, analyses for residual di–2–naphthyl ether or di–1–naphthyl sulfide were carried out employing a 0.5 meter, 3% OV 101 column, using triphenylmethane added after completion of the reactions as an internal standard. Analyses for naphthalene and tetralin were carried out on a 2 meter, 3% OV 101 column, employing 1–methylnaphthalene (also added after completion of the reaction) as the internal standard.

The results of these reactions are summarized in Table IV.

Both naphthalene and tetralin are formed during the thermolysis reactions. However, as can be seen from entry 10, naphthalene is not converted to tetralin under the reaction conditions, so formation of tetralin must involve reaction paths other than hydrogenation of naphthalene. The combined yields of naphthalene and tetralin are approximately equivalent to the amount of dinaphthyl ether which reacts in each run. However, in agreement with previous results, no 2–

naphthol was detected in the reaction products. The fate of the naphthol has not been determined, but naphthol probably disappears via radical coupling processes.

In contrast to the ether, each mole of di-1-naphthyl sulfide is converted to ca. 1.5 moles of naphthalene and tetralin. The fate of the remaining sulfide has not been established.

Table IV

Thermolysis Reactions in Octahydroanthracene at 450°C

Substrate [1]	Catalyst (mole/mole) [2]	Reaction Time (hrs)	No. of Runs	Reactor Type [3]	Products: % Disappearance of Substrate	Products: Mole % Naphthalene	Products: Mole % Tetralin
1) —	---	5	2	SS	---	0	0
2) E	---	5	2	SS	1.7 ± 0.5	2.1 ± 0.2	~ 0.1
3) E	Phenol (12.6)	5	2	SS	10.0 ± 0.8	9.0 ± 3.3	3.1 ± 1.0
4) E	Phenol (12.6)	5	1 [4]	Glass	6.2 ± 0.3	5.2 ± 0.1	1.2 ± 0.2
5) E	1,3,5-Trimethoxybenzene (14.0)	5	1	SS	2.7 ± 0.1	2.4 ± 0.1	0.4 ± 0.2
6) E	Phenol (6.3) + Trimethoxybenzene (7.0)	5	1	SS	17.9 ± 0.4	16.1 ± 0.3	2.8 ± 0.1
7) E	Phenol (6.3) + 1,4-Dimethoxynaphthalene (6.81)	5	1	SS	22.4 ± 0.3	15.1 ± 0.1	3.9 ± 0.4
8) S	---	2	2	SS	13.0 ± 1.4	18.1 ± 2.0	2.2 ± 1.4
9) S	Phenol (12.8)	2	1	SS	21.2	30.4 ± 0.4	1.5 ± 0.4
10) Naphthalene	---	5	1	SS	(–1.5)	---	~ 0

Amines as Catalysts

Our attempts to confirm the report by Yao and Kamiya (*Bull. Chem. Soc. Japan*, 1979, 52, 492) that quinoline catalyzes the transfer hydrogenolysis of di-2-naphthyl ether (DNE) in tetralin at 450°C were unsuccessful. As is shown in Table V, neither quinoline nor pyridine, even when present in large excess, exhibited any catalytic effects in increasing the rate of disappearance of DNE. Furthermore, addition of either quinoline or pyridine actually *decreased* the effect of added phenol on the rates of disappearance of DNE. Studies employing di-1-naphthyl sulfide (DNS) as substrate similarly showed no evidence that either quinoline or pyridine had catalytic properties by themselves, and resulted in almost total disappearance of rate acceleration by phenol.

Table V

Amines as Catalysts for Transfer Hydrogenolysis in Tetralin at 450°C in Stainless Steel Reactors

	Substrate [1]	No. of Runs	Catalyst (mole/mole) [2]	Reaction Time (hrs)	% Disappearance of Substrate
1)	E	2	Quinoline (14.7)	5	4.0 ± 2.1
2)	E	2	Pyridine (12.9)	5	3.2 ± 1.6
3)	E	2	Quinoline (7.4) Phenol (7.1)	5	8.6 ± 2.7
4)	E	1	Quinoline (8.2) Phenol (15.2)	5	10.1
5)	E	1	Pyridine (6.5) Phenol (7.1)	5	7.7 ± 0.9
6)	E	2	N,N-Dimethylaniline (14.0)	5	2.7 ± 0.9
7)	E	1	Aniline (16.1)	5	4.1
8)	S	2	Quinoline (15.4)	2	12.0 ± 4.0
9)	S	2	Quinoline (7.7) Phenol (7.1)	2	12.7 ± 1.2
10)	S	2	Pyridine (9.4) Phenol (7.1)	2	10.0 ± 2.1

[1] E = di-2-naphthyl ether, S = di-1-naphthyl sulfide; [2] mols catalyst / mols substrate.

It seems probable that the basicities of the amines reduced the effects of hydrogen bonding of phenol to DNE or DNS in the transition states for transfer hydrogenolysis, and thereby vitiated any possible effects of electron transfer from the amines to the substrates.

Bifunctional Catalysts

Although mixtures of phenols and aromatic amines are not effective catalysts for thermolytic cleavage of aromatic ethers and sulfides, presumably due to reduction of the protonating abilities of the phenols by the basic amines, when the amino group is directly substituted on to the phenolic ring, the resulting molecules can be effective catalysts, as is shown in Table VI.

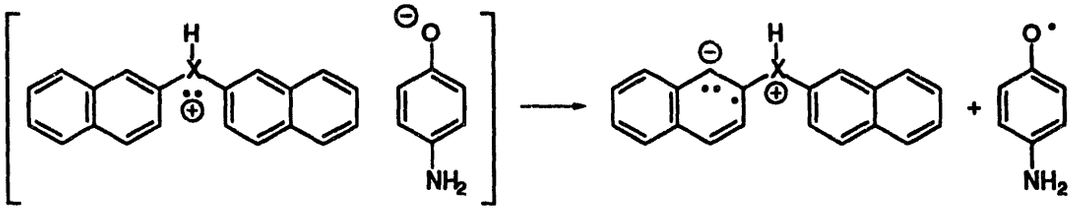
Table VI

Aminophenols as Catalysts for Transfer Hydrogenolysis in Tetralin at 450°C in Stainless Steel Reactors

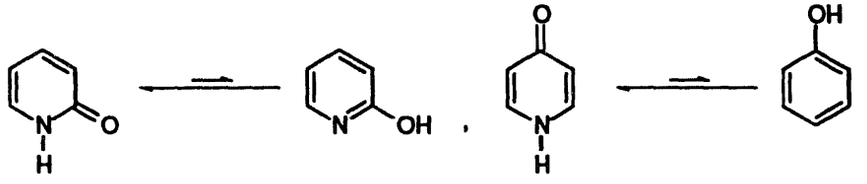
	Substrate [1]	No. of Runs	Catalyst (mole/mole) [2]	Reaction Time (hrs)	% Disappearance of Substrate
1)	E	2	2–Aminophenol (6.7)	5.0	14.6 ± 1.9
2)	E	2	2–Aminophenol (13.1)	5.0	26.4 ± 2.9
3)	E	2	4–Aminophenol (15.1)	5.5	21.6 ± 3.7
4)	S	1	2–Aminophenol (7.1)	2.0	24.1
5)	E	1	2–Aminophenol (13.6)	3.0	14.2
6)	E	1	2–Aminophenol (13.6)	1.1	6.1
7)	E	1	2–Aminophenol (13.6)	8.4	32.0
8)	E	1	2–Aminophenol (13.6)	22.5	40.5

[1] E = di–2–naphthyl ether, S = di–1–naphthyl sulfide; [2] mols catalyst / mols substrate.

The effectiveness of aminophenols as catalysts is presumably due to their interaction with aromatic sulfides and ethers to form tight ion pairs, resulting in exceptionally facile electron transfer:



Since 2–aminophenol and 4–aminophenol are exceptionally effective catalysts for transfer hydrogenolyses of dinaphthyl ether and dinaphthyl sulfide, we investigated the catalytic efficiency of 2–pyridone and 4–pyridone, the tautomers of 2–hydroxy and 4–hydroxypyridine.



As can be seen in Table VII (entries 1 and 2), neither compound appeared to be a particularly effective catalyst for hydrogenolysis of di–2–naphthyl ether under the conditions usually employed (5 hrs at 450°C). However, a comparison of the effectiveness of 2–pyridone and 2–aminophenol at shorter reaction times showed that 2–pyridone was as effective as 2–aminophenol if the reaction time were reduced to one hour. At longer reaction times, the effectiveness of 2–pyridone dropped sharply, suggesting that the catalyst is destroyed under the reaction conditions.

Table VII

Pyridones as Catalysts for Transfer Hydrogenolysis of Di–2–Naphthyl Ether in Tetralin at 450°C in Stainless Steel Reactors

	No. of Runs	Catalyst (mole/mole) [1]	Reaction Time (hrs)	% Disappearance of DNE
1	2	2–Pyridone (14.6)	5.0	12.2 ± 1.1
2	2	4–Pyridone (13.9)	5.0	10.9 ± 1.6
3	1	2–Pyridone (14.6)	3.0	10.4
4	1	2–Pyridone (14.6)	1.1	7.2
5	1	2–Pyridone (14.2)	8.4	14.5
6	1	2–Pyridone (14.2)	22.5	19.1

[1] Moles catalyst / moles DNE.

In a continuation of our studies on the efficacy of aromatic amines as catalysts for transfer hydrogenolysis reactions, we studied 2–anilinoethanol as a possible catalyst. As can be seen from Table VIII, this molecule proved to be almost as effective as 2–aminophenol for hydrogenolysis of di–2–naphthyl ether in a five hour reaction period, despite the fact that it should be a less effective electron transfer agent and a poorer hydrogen bonder. It did prove to be a significantly less effective catalyst than 2–aminophenol when the reaction time was reduced to two hours. Paradoxically, this was considered to be an encouraging sign, since it suggested that 2–anilinophenol was more stable under the reaction conditions than 2–aminophenol, and should be a more effective catalyst at even longer reaction times or higher temperatures. However, this proved not to be so (see Table VIII, entries 10 and 11). Rather surprisingly, 2–anilinophenol was a comparatively poor catalyst for hydrogenolysis of di–1–naphthyl sulfide. This is the first instance in which catalytic activity in reduction of the sulfide did not correlate reasonably well with reduction of the dinaphthyl ether.

CHART III. CATALYTIC EFFECTIVENESS OF 2-PYRIDONE AND 2-AMINOPHENOL

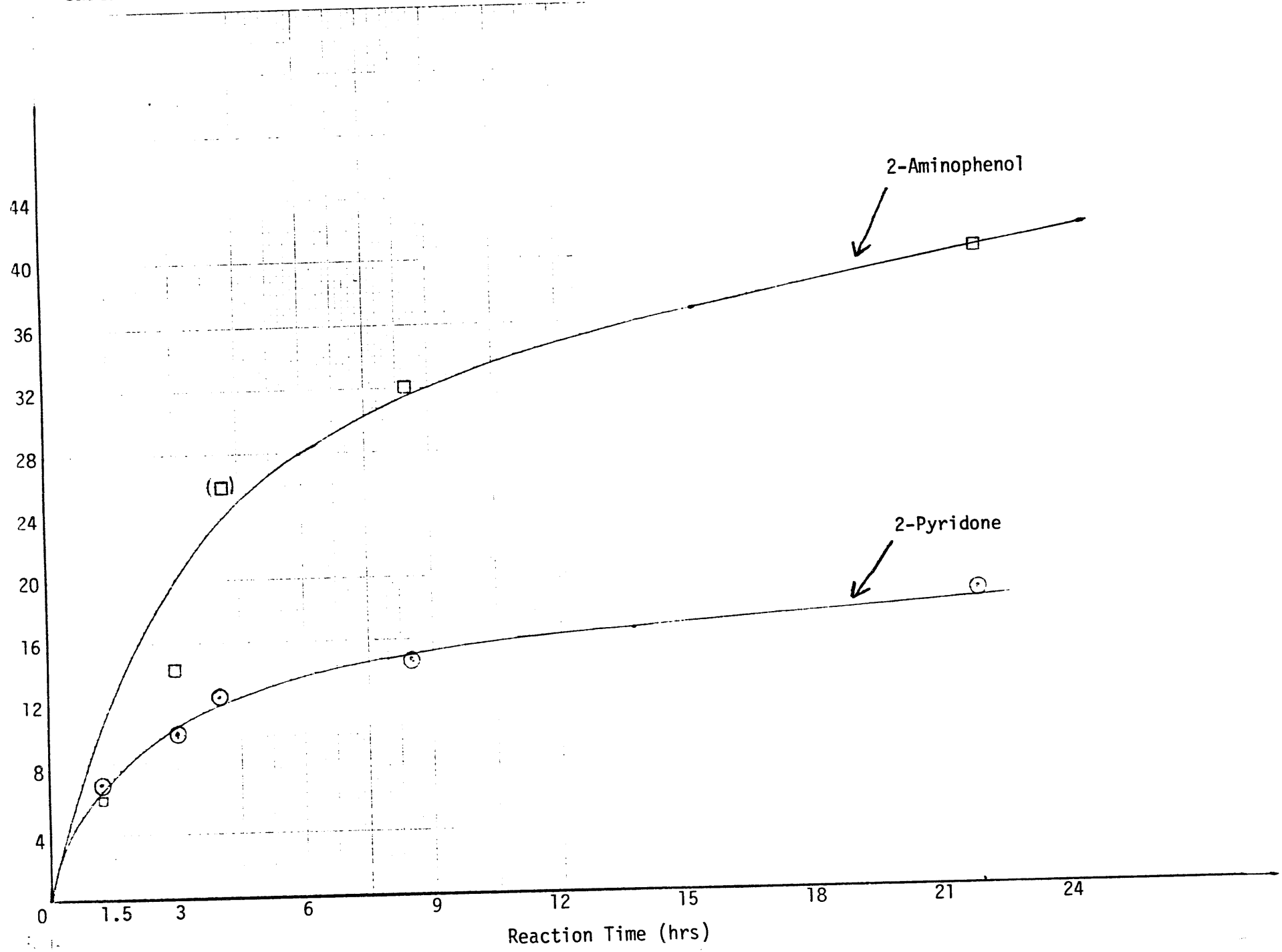


Table VIII

Anilinoethanols as Catalysts for Transfer Hydrogenolysis of Di–2–Naphthyl Ether in Tetralin at 450°C in Stainless Steel Reactors

Substrate [1]	No. of Runs	Catalyst (mole/mole) [2]	Reaction Time (hrs)	% Disappearance of Substrate
1) E	2	2–anilinoethanol (7.1)	5	12.7 ± 1.0
2) E	2	2–anilinoethanol (14.2)	5	20.8 ± 0.9
3) E	3	2–anilinoethanol (14.2)	2	14.0 ± 0.7
4) S	2	2–anilinoethanol (14.2)	2	15.2 ± 1.4
5) E [3]	2	2–anilinoethanol (7.1)	5	12.7 ± 1.0
6) E [3]	2	2–anilinoethanol (14.2)	5	20.8 ± 0.9
7) E [3]	3	2–anilinoethanol (14.2)	2	14.0 ± 0.7
8) S [3]	2	2–anilinoethanol (14.2)	2	15.2 ± 1.4
9) E	2	2–anilinoethanol (14.0)	3	10.7 ± 0.8
10) E	2	2–anilinoethanol (14.0)	8.5	30.1 ± 1.4
11) E	2	2–anilinoethanol (14.0)	26	41.1 ± 1.0
12) E	2	N,N–di(2–hydroxy-ethyl)aniline (13.9)	3	9.7 ± 0.2
13) E	2	N,N–di(2–hydroxy-ethyl)aniline (13.9)	5	14.2 ± 0.8
14) E	1	N,N–di(2–hydroxy-ethyl)aniline (13.9)	8	18.1
15) E	2	N,N–di(2–hydroxy-ethyl)aniline (13.9)	24.5	25.2 ± 2.4
16) S	2	N,N–di(2–hydroxy-ethyl)aniline	2	19 ± 0.9

[1] E = di–2–naphthyl ether; S = di–1–naphthyl sulfide. [2] Mols catalyst / mols substrates. [3] Repeated from previous report.

N,N–di(2–hydroxyethyl)aniline was synthesized by the base catalyzed reaction of aniline with 2–chloroethanol, and tested for catalytic efficacy (entries 12–16). The presence of a second 2–hydroxyethyl group resulted in lowered effectiveness of this molecule compared to 2–anilinoethanol, particularly at long reaction times. It is not clear whether the relatively poor performance of the di(2–hydroxyethyl)aniline was due to lowered electron transfer ability or to decreased stability at high temperatures. It did, however, appear to be slightly more effective than 2–anilinoethanol in catalyzing conversion of dinaphthyl sulfide (entry 16), possibly due to the shorter reaction times involved in that process.

(2–N-Methylanilino)ethanol was prepared and tested as a catalyst for conversion of dinaphthyl ether (Table IX). It appears to be the most effective catalyst studied thus far of both long and short reaction times and at relatively low concentration. However, it showed only moderate effectiveness against di–1–naphthyl sulfide. We believe that the relatively low hydrogen bonding ability of the catalyst is responsible for its poor performance against the sulfide.

Table IX

Transfer Hydrogenolysis in Tetralin at 450°C in Stainless Steel Reactors Using 2–(N–Methylanilinoethanol) as Catalyst

Substrate [1]	No. of Runs	Catalyst (mole/mole) [2]	Reaction Time (hrs)	% Disappearance of Substrate
1) E	2	13.9	10	35.8 ± 2.9
2) E	2	13.9	3	18.7 ± 1.4
3) E	2	13.9	1.5	11.1 ± 3.1
4) E	2	6.3	5	16.5 ± 2.4
5) E	2	3.2	5	10.9 ± 1.7
6) S	2	12.8	2	18.4 ± 1.7
7) S	2	12.8	1	10.9 ± 0.1
8) E	2	13.9	5	26.0 ± 2.1

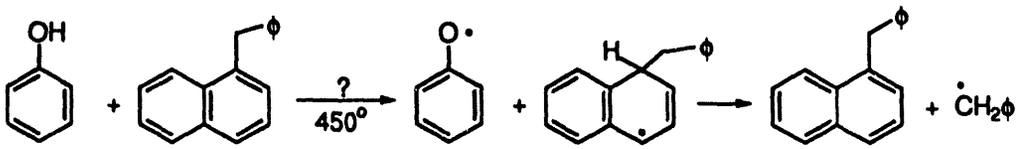
[1] E = di–2–naphthyl ether; S = di–1–naphthyl sulfide. [2] Moles catalyst / moles substrate.

Rupture of Aryl–Carbon Bonds

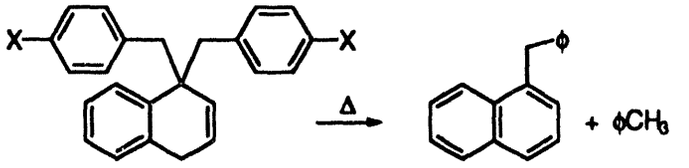
1–Benzylnaphthalene (1–BN) was chosen as the substrate to determine whether our catalysts are useful in cleaving aryl carbon bonds. Thermolysis studies were again carried out at 450°C in stainless steel reactors in tetralin solutions.

As can be seen in Table X, little reaction occurs after 5 hours at 450°C either in the absence or presence of phenol. However, a relatively small but significant amount of reaction occurred after 18 hours (entry 4) and a still larger amount after 41 hours (entry 5). No increased catalytic activity was observed when either 1,3,5–trimethoxynaphthalene (entries 6 and 7) or 1,4–dimethoxynaphthalene (entry 8) was added as a potential co–catalyst.

The absence of co–catalytic effects of aromatic polyethers, as well as the absence of electronegative groups in 1–BN, suggest that the catalytic effects of phenol on the thermolysis of 1–BN are not due to the occurrence of an electron transfer mechanism. It seemed possible that phenol initiates radical chains by a hydrogen atom transfer process:



We had previously observed that carbon–carbon bonds could be ruptured at temperatures as low as 120°C in the thermolysis of 1,1–dibenzyl–1,4–dihydronaphthalenes (**1a–c**). It seemed probable that



1a, X = H
1b, X = CH_3
1c, X = Cl

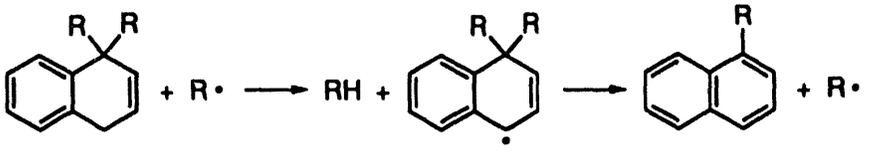
these reactions proceed via intermediates similar to that proposed above for reductive cleavage of 1–benzylnaphthalene.

Table X

Effects of Catalysts on Thermolysis of 1–Benzylnaphthalene in Tetralin (450°C, SS Reactor)

	Mols Catalyst/Mols 1–BN	Reaction Time (hrs)	No. of Runs	% Reaction
1	---	5	2	(–0.2 ± 1.0)
2	Phenol (8.4)	5	2	1.1 ± 0.6
3	---	18	2	1.4 ± 0.7
4	Phenol (8.4)	18	2	8.8 ± 3.4
5	Phenol (8.4)	41	1	13.4
6	Phenol (4.2) + 1,3,5–Trimethoxybenzene (6.1)	18.5	2	5.8 ± 2.6
8	Phenol (8.4) + 1,4–Dimethoxynaphthalene (7.5)	19.5	2	8.4 ± 1.7
10	Phenol (8.4) + 1,3,5–Trimethoxybenzene (6.1)	18	2	6.7 ± 0.6

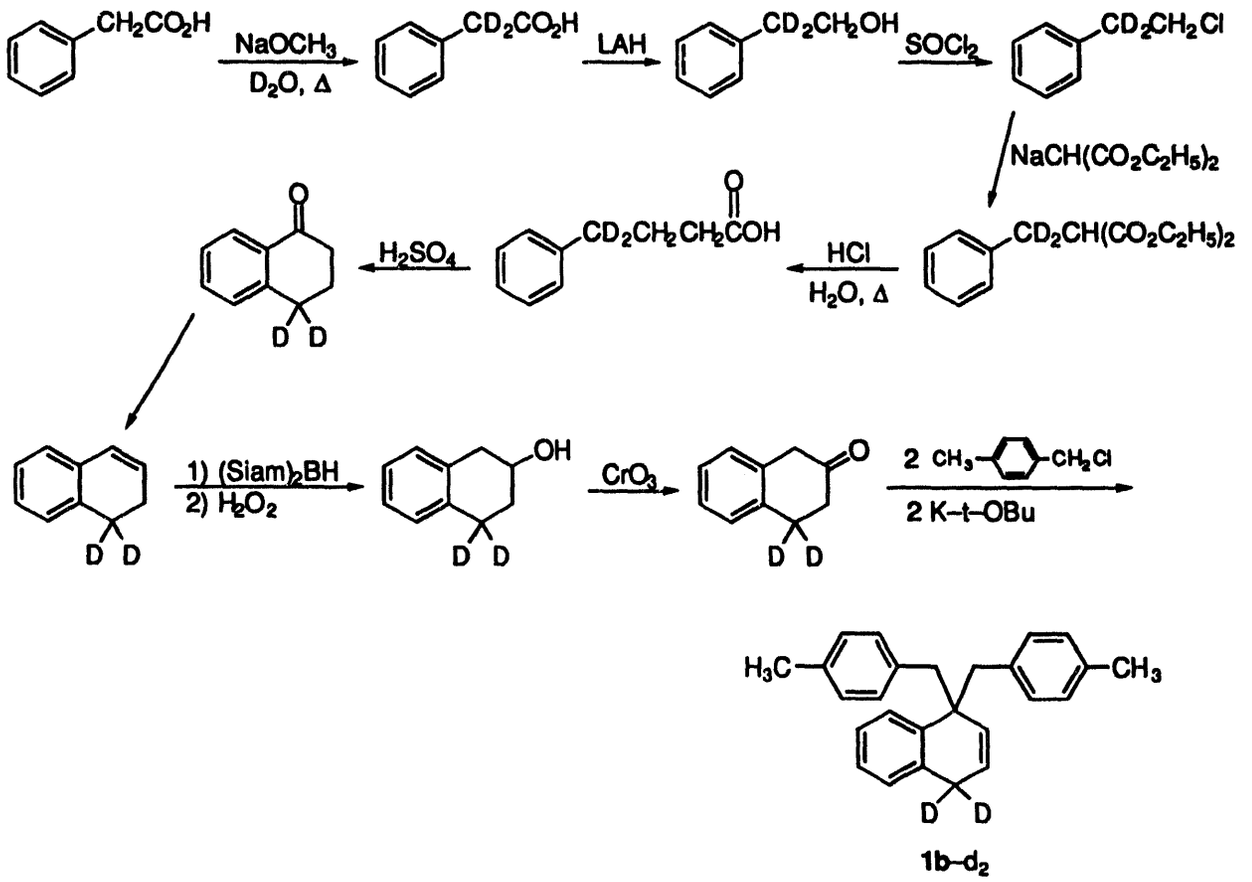
Kinetic studies of the decompositions of **1a** and **1b**, followed by ^{1}H NMR analysis, showed that rates were variable. Addition of free radical chain inhibitors, including 2,6–di–*t*–butylphenol, galvinoxyl, and (most effective) diphenylamine resulted in decreases in the rates of fragmentation of the alkenes, indicating that radical chain processes accounted for at least part of the fragmentation processes. However, even addition of very large amounts of diphenylamine did not completely suppress

(2) 

the decompositions. Residual fragmentation processes occurred in each case, and the rates of those processes were independent of inhibitor concentration (see Charts IV–VI). The half lives for disappearance of **1a**, **1b**, and **1c**, respectively, in the presence of ca. 30–50 mol % of diphenylamine at 150°C, were approximately 3 hours, 2 hours, and 6 hours, respectively. Thus, the rates of fragmentation

follow an order paralleling the relative bond energies of the carbon–carbon bonds being cleaved in each reaction.

To determine whether the residual fragmentation reactions are due to free radical processes continuing even in the presence of large amounts of inhibitor, or whether a concerted fragmentation process remains after all free radical chains are inhibited, the deuterated olefin **1b–d** was synthesized as shown below.



Mass spectroscopic analyses were obtained on products from thermolytic decomposition of a mixture of **1a** and **1b**–d_2 in the presence of *ca.* 50 mole % of diphenylamine. Mass spectra of the volatile fraction showed it to consist of a *p*–xylene fraction containing *ca.* 23% *p*–xylene-d_1 and a *p*–chlorotoluene fraction containing *ca.* 28% *p*–chlorotoluene–d_1.

CHART IV. Effects of Diphenylamine on Fragmentation of 1,1-Dibenzyl-1,4-dihydronaphthalene at 150 C.

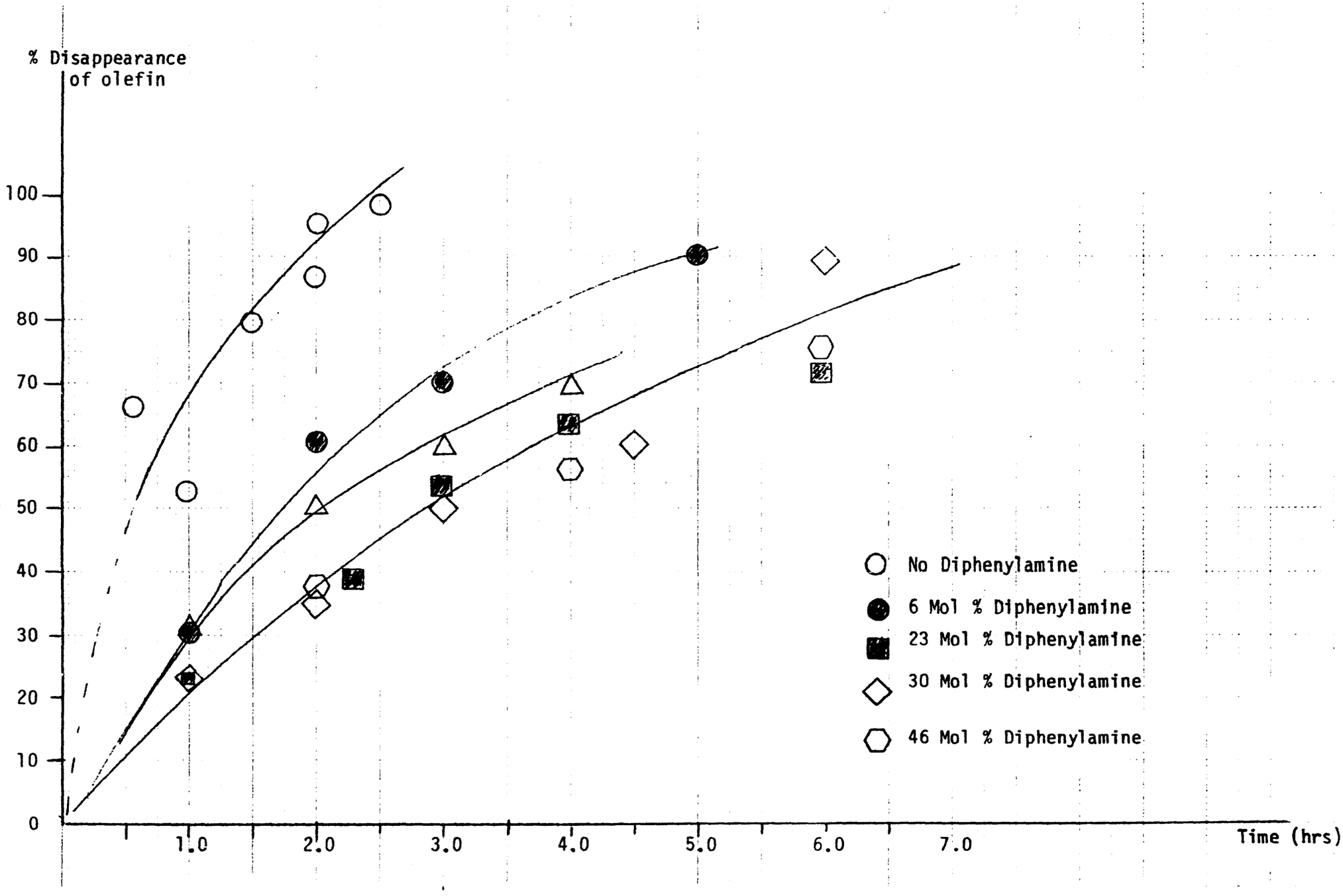


CHART V. Effect of Diphenylamine on Rate of Fragmentation of 1,1-Di-p-tolyl-1,4-dihydronaphthalene at 150°C.

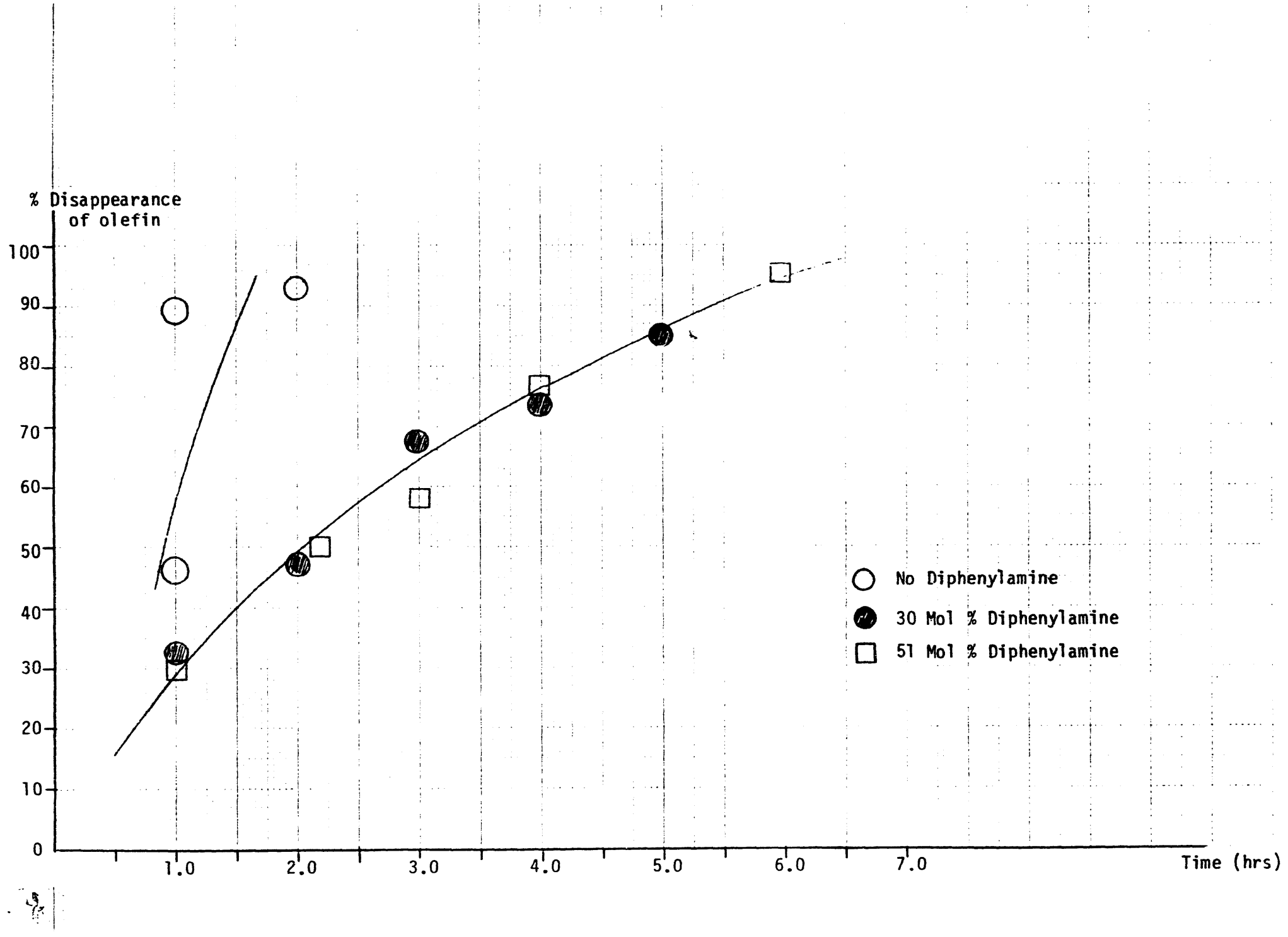
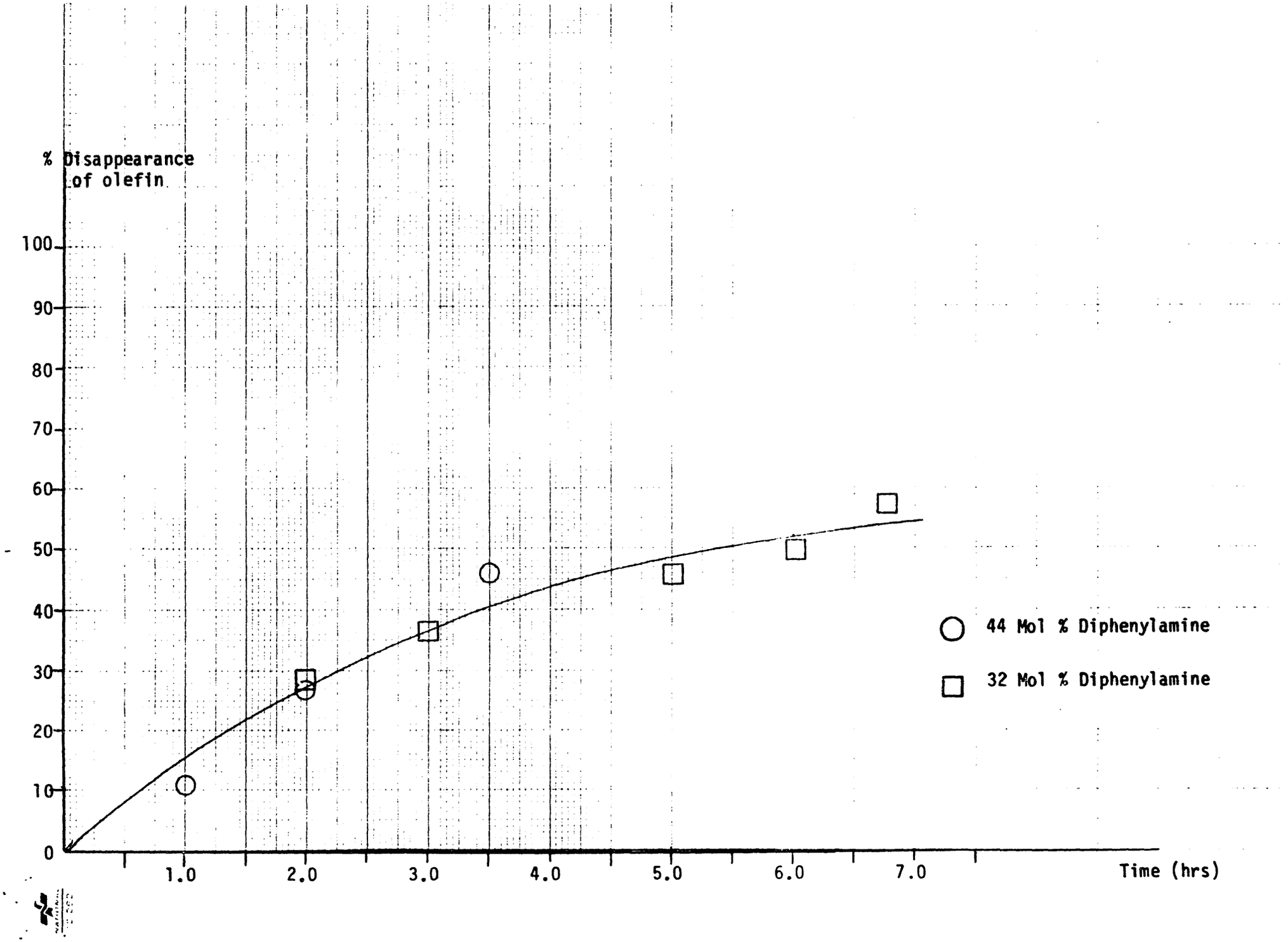
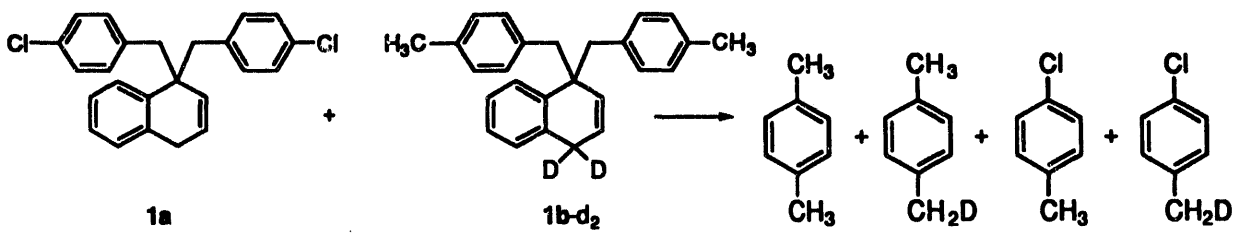


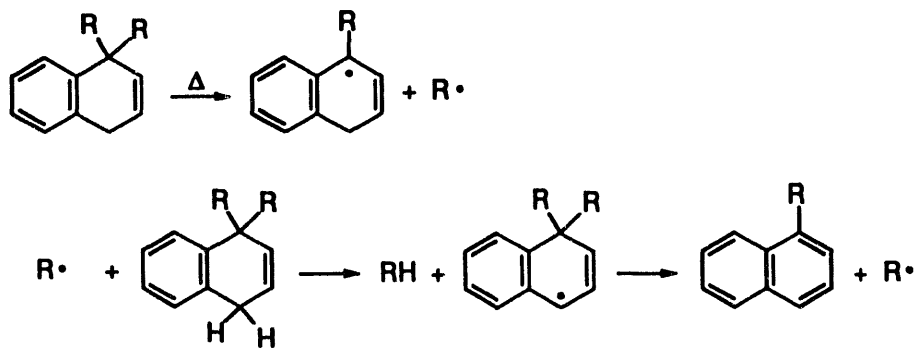
CHART VI. Fragmentation of 1,1-Di-(4-chlorobenzyl)-1,4-dihydronaphthalene at 150°C.





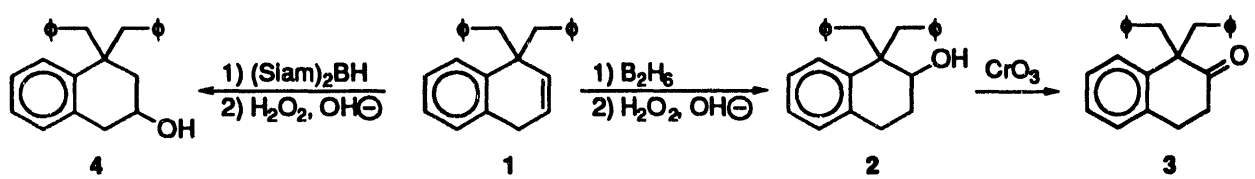
1a 1b-d_2

This result is inconsistent with a concerted mechanism for the fragmentation processes, and demonstrates that the reactions proceed essentially entirely via radical chain mechanisms:



Hydroboration of Dibenzylcycloalkenes

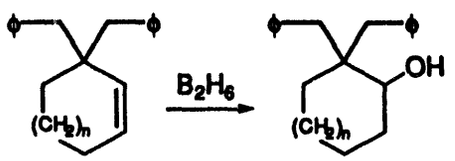
In the course of studying the properties of hydrocarbon **1**, it was discovered that reaction of **1a** with diborane results in hydroboration at the most hindered position to yield alcohol **2** (identified by conversion to ketone **3**).



4 **1** **2** **3**

In contrast reaction of **1** with diisoamylborane yields, as was previously observed, the expected alcohol **4**.

Reaction of other 3,3–dibenzylcycloalkenes, such as **5** and **6**, with diborane similarly results

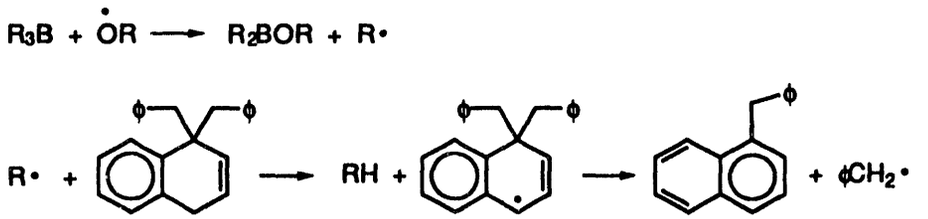


5, n = 1
6, n = 2

principally in formation of the more hindered alcohol, although the less hindered alcohols are formed, as expected, if substituents other than benzyl groups are located at C–3.

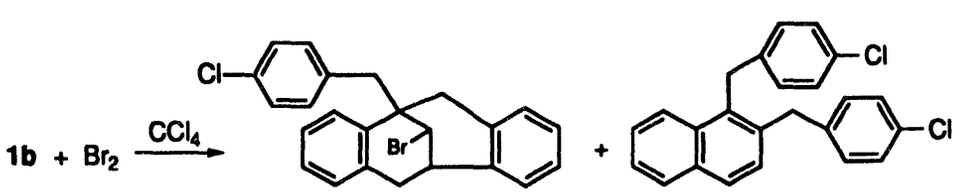
At present, we have no satisfactory explanation for this phenomenon.

If oxygen is not rigorously excluded from hydroboration with diisoamylborane, 1–benzylnaphthalene is formed along with the C–3 alcohol. A radical chain mechanism such as that shown below is suggested for this novel reaction.



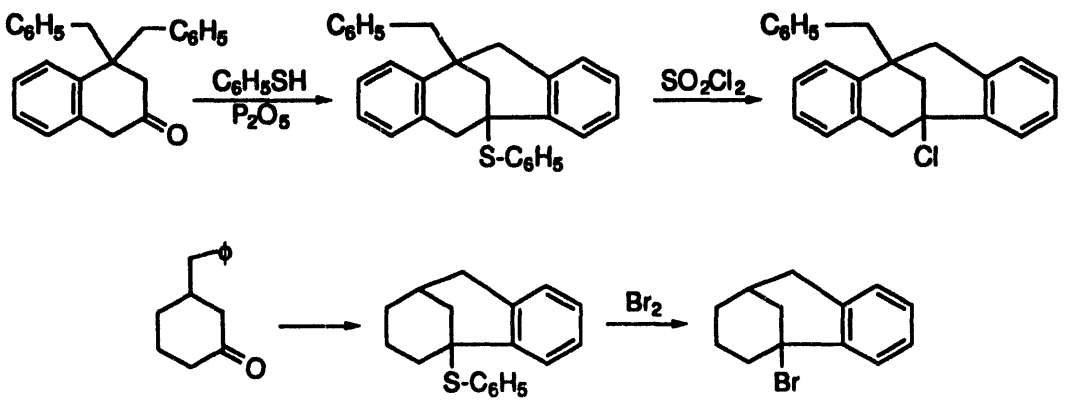
Cyclization Reactions of 3–Benzylcycloalkanones and Cycloalkenes

In the course of studying thermal decomposition of compound **1b** we investigated the reaction **1b** with bromine. In carbon tetrachloride solution this reaction yielded the interesting bromine–free rearrangement product **5**, along with the cyclization product **6**. Surprisingly, in acetonitrile solution only **6** was formed.



6 5

We have observed that 3–benzylcyclohexanones undergo phosphorus pentaoxide catalyzed reactions with thiophenol or 1–butanethiol to form molecules containing bicyclo[3.3.1]nonene skeletons. These products can be converted to bridgehead halides by reaction with sulfuryl chloride or bromine.



PUBLICATIONS RESULTING FROM THIS PROJECT

1) "Thermal Fragmentation Reactions of Dihydroaromatic Molecules," B. Miller, X. Shi, G. Grosu, and R. Zhou, *J. Org. Chem.* **1993**, *58*, 2320.

2) "Cyclization and Rearrangement Processes Resulting from Bromination of 3–Benzylcycloalkenes," X. Shi and B. Miller, *J. Org. Chem.* **1993**, *58*, 2907.

3) "Unusual Regiochemistry in the Hydroboration of 3,3–Dibenzylcycloalkenes," X. Shi and B. Miller, *Tetrahedron Letters*, **1994**, *35*, 223.

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