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STUDIES OF COAL STRUCTURE USING CARBENE CHEMISTRY

Final Report September 15, 1986—June 14, 1990

Prof. Martin Pomerantz
Project Director

DOE Grant Number DE-FG22-86PC90532

For
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Pittsburgh, Pennsylvania

By
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FINAL REPORT

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Original Objective

The object of this grant was to react coal, derivatized forms of coal, and solvent swelled coal with carbenes (divalent carbon species) under mild conditions. These carbenes were to be prepared by treating the coal with several diazo compounds and then thermally decomposing them at relatively low temperatures (80-130 °C). The carbenes were to be chosen to show varying selectivity toward aromatic rings containing heteroatom functionalities and toward polynuclear aromatic systems. In some instances, where selectivities toward aromatic and heteroaromatic ring systems were not known, model studies were to be carried out. Because of the generally mild conditions employed and the good selectivity anticipated, and actually observed with one particular system, it was expected that this methodology would provide structural information about the coal, along with data on the extent of occurrence and type of aromatic systems. After carbene reactions, treatment of the coal samples was to include extractions and thermolysis. Physical studies included thermogravimetric analysis, diffuse reflectance FT-IR spectroscopy, NMR (^{1}H and ^{13}C) spectroscopy, gas chromatography, GC/MS and GC/FT-IR. Finally, it was suggested that, where necessary, model systems and reactions would be studied.

Publications and Presentations

1. Martin Pomerantz and Peter Rooney, "Studies on the Reaction of Illinois No. 6 Coal with (Ethoxycarbonyl)carbene", *Energy and Fuels*, **1**, 401 (1987).

2. Martin Pomerantz, Peter Rooney and Raúl Cardona, "The Effect of Various Minerals on the Catalyzed Decomposition of Ethyl Diazoacetate: Implications for the Reaction of Ethyl Diazoacetate with Coal", *Fuel*, **67**, 1096 (1988); *Fuel*, **68**, 135 (1989).

3. Martin Pomerantz and Peter Rooney, "The Relative Rates of the Reaction of (Ethoxycarbonyl)-carbene with Several Aromatic and Heteroaromatic Compounds. Selectivity and Mechanism", *J. Org. Chem.*, **53**, 4374 (1988).

4. Martin Pomerantz and Peter Rooney, "Studies on the Decomposition of Ethyl Diazoacetate and its Reaction With Coal. Formation of a New Tetrameric Product and Reagent Access Within the Coal", *Energy and Fuels*, **3**, 357 (1989).

5. Martin Pomerantz and Moshe Levanon, "Bis(dimethyl Malonato)ketazine. Formation and Inversion/Rotation Barrier", *Tetrahedron Lett.*, **31**, 4265 (1990).

6. Martin Pomerantz and Peter Rooney, "Studies on the Reaction of Coal with (Ethoxycarbonyl)-carbene", Paper presented at the 193rd National Meeting of the American Chemical Society, Denver CO, April, 1987. *Am. Chem. Soc. Div. Fuel Chem. Preprints*, **32** (Part 1), 583 (1987).

7. Martin Pomerantz and Peter Rooney, "Studies on the Reaction of Coal with (Ethoxycarbonyl)-carbene", Paper presented at the 20th Annual Meeting-in-Miniature of the Dallas-Fort Worth Section of the American Chemical Society, Fort Worth, TX, April, 1987.

8. Martin Pomerantz and Peter Rooney, "The Relative Rates of the Reaction of (Ethoxycarbonyl)-carbene with Several Aromatic and Heteroaromatic Compounds. Selectivity and Mechanism", Paper presented at the 21st Annual Meeting-in-Miniature of the Dallas-Fort Worth Section of the American Chemical Society, Arlington, TX, April, 1988.

9. Martin Pomerantz and Peter Rooney, "The Relative Rates of Reaction of (Ethoxycarbonyl)-carbene with Several Aromatic and Heteroaromatic Compounds. Selectivity and Mechanism", Paper presented at the 22nd Reaction Mechanisms Conference, Pittsburgh, Pennsylvania, June, 1988.

10. Martin Pomerantz and Peter Rooney,"Studies on the Decomposition of Ethyl Diazoacetate and its Reaction With Coal. Formation of a New Tetrameric Product and Reagent Access Within the Coal", Paper presented at the 197th National Meeting of The American Chemical Society, Dallas, Texas, April, 1989.

11. Martin Pomerantz and Moshe Levanon, "Reactions of Dimethyl Diazomalonate and Bis(methoxycarbonyl)carbene", Paper presented at the 10th International Union of Pure and Applied Chemistry (IUPAC) Conference on Physical Organic Chemistry (ICPOC 10), Haifa, Israel, August, 1990.

Results Obtained and Discussion

The first of the carbenes to be studied was (ethoxycarbonyl)carbene (**1**) which can be produced thermally and catalytically (also photochemically) from ethyl diazoacetate (**2**; eqn. 1). A sample of Illinois No. 6 HVCB bituminous coal obtained from the Pennsylvania State University Coal Research Section (PSOC-1351) was crushed to <100 mesh under argon, dried at 120-125 °C, and then treated with ethyl diazoacetate (**2**) in pentane. The mixture was stirred overnight at room temperature, under N_2, the pentane was removed in vacuum and the coal/**2** mixture was slowly heated to 100 °C until nitrogen evolution ceased. The temperature was then raised to 120 °C for an additional 30 minutes to insure complete decomposition of **2**. After weighing, a portion of the samples was extracted (Soxhlet) for 24 hours with toluene/methanol (9:1), and the extract was concentrated by distillation. The above procedure was run using 1, 2 and 3 grams of **2** to 1 g of coal and, in addition, a control experiment, using the coal but omitting **2**, was also conducted. (The runs were called Coal 1, 2, 3 and 0 respectively.) Further, a control experiment without the coal (monitored by ^{1}H NMR spectroscopy) showed that **2** was stable to the overnight stirring procedure. Table 1 shows the results. It should be noted that the decomposition of **2** apparently begins below 80 °C and N_2 evolution is fairly vigorous at 80 °C. This suggests that, since ethyl diazoacetate

$$\underset{\mathbf{2}}{N_2CHCO_2Et} \xrightarrow[\Delta]{} N_2 + \underset{\mathbf{1}}{:CHCO_2Et} \qquad (1)$$

normally requires higher temperatures for decomposition, the reaction is being catalyzed, presumably by the mineral matter in the coal. It is also well known that catalyzed decomposition of **2** gives rise to carbene products.

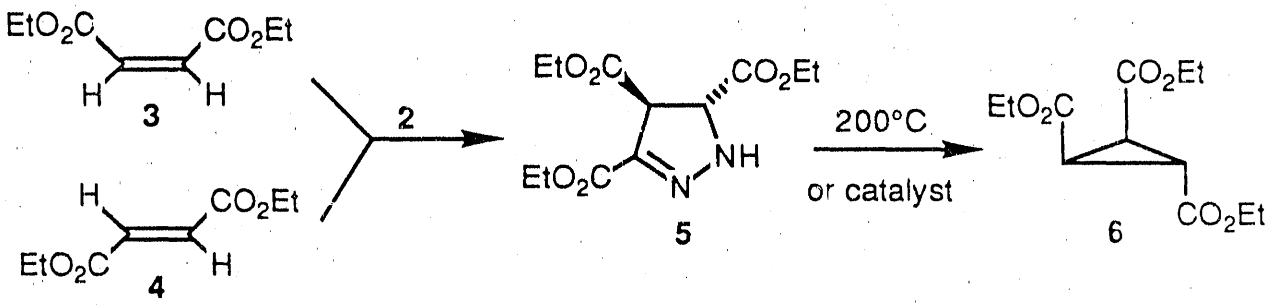
Table 1. Results of the Reaction of N_2CHCO_2Et (2) with Illinois No. 6 Coal

	Coal 0	Coal 1	Coal 2	Coal 3
2 (g)	0	1.016	2.028	3.000
coal (g)	1.004	1.002	1.010	1.015
Amt. recovered (g)[a]	1.015	1.563	2.264	2.654
% yield[b]	101	88	89	81
% extracted	31	45	63	71

a) Weight after heating and loss of N_2.
b) Calculated based on weight of coal and carbene **1**.

In order to be sure that the major reactions of the carbene, **1**, were with the coal, we independently prepared the known products formed when **2** decomposes by itself and when **2** reacts with the dimers of **1**. The dimers, namely diethyl maleate (**3**) and diethyl fumarate (**4**), are known to give the pyrazoline, **5**, on reaction with **2**, and this, in turn, thermally (above 180 °C), or catalytically, is known to decompose to the cyclopropane, **6** (equation 2). Analysis of the extracts showed small amounts of **3-6** in coal 1 (about 8 area percent total of the non-solvent peaks eluting from the CC column), a little more of these in coal 2 (*ca.* 10%) and a bit more in coal 3 (*ca.* 13%). Also, since **5** does not produce **6** below 180-200 °C except by catalysis with metal ions, we must conclude that the reaction **5** → **6** was catalyzed in the coal. It was thus clear that the major reaction of the species **1** and **2** was with the coal.

Figure 1 shows the results of thermogravimetric analyses (TGA) giving weight loss between 80° and 1050 °C for the coal samples before extraction. It should be noted that carbene treatment increased the amount of material which was volatile below 600 °C by a factor of 2 to 3 (from 21% in coal 0 to 45%, 57% and 63% in coal 1, 2 and 3 respectively), a rather significant increase. Also, the



(2)

largest effect was shown on going from coal 0 to coal 1 and 2 while a smaller effect was shown on going from coal 2 to 3. The derivative plots (DTGA, Figure 2) show the maximum rate of weight loss for coal 0 (2.0%/min) at 470 °C, for coal 1 (6.2%/min) at 260 °C, and for coal 2 (9.1%/min) at about 260 °C. Coal 3 is essentially the same as coal 2. It is thus clear that in addition to increasing the amount of material which can be volatilized below 600 °C, carbene treatment also lowered very substantially the temperature of maximum decomposition. In addition, since the TGA and DTGA curves changed substantially in the carbene treated coals compared with the control, coal 0, the diazo compound (2) and hence the carbenes must have gotten into the interior pores of the coal and gave rise to reaction. Thus it is clear we were not looking simply at a surface reaction.

Diffuse reflectance FT-IR (DRIFT) spectra were also obtained for the various coal samples before extraction (Figure 3). There were several differences observed after carbene treatment. First, and most trivial, was that an ester carbonyl appeared at 1736 cm^{-1} (peak C, Figure 3) in all samples. More significantly, the small peak at about 3050 cm^{-1} (peak A), which is presumably due to aromatic C-H, disappeared with increasing amount of 2. A new aliphatic CH peak appeared at 2962 cm^{-1} (peak B) while a substantial aromatic peak at 1610 (peak D) in coal 0 got much smaller in coal 1 and disappeared in coals 2 and 3. A peak at 856 cm^{-1} (peak E) appeared with carbene treatment and a smaller one at 771 cm^{-1} (peak F) also grew in. One or both of these could be due to alkene C-H out of plane deformations which occur in this region.

One area that also merits notice is the 400-550 cm^{-1} region. This region is due to metal-sulfur and metal-oxygen bonds in the minerals of the coal. In the present study the 546 cm^{-1} peak (peak G) progressively disappeared on going from coal 0 to coal 3 and the 475 cm^{-1} peak (peak H)

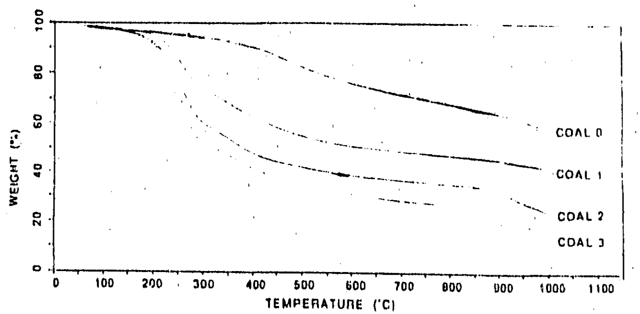


Figure 1. Thermogravimetric analysis (TGA) of coal samples before extraction.

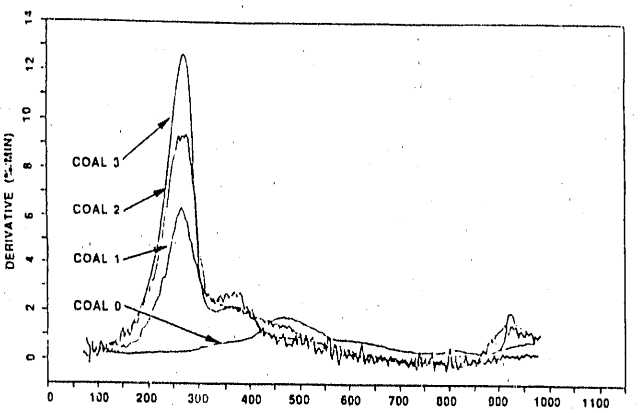


Figure 2. Derivative thermogravimetric analysis plots (DTGA) of coal samples before extraction.

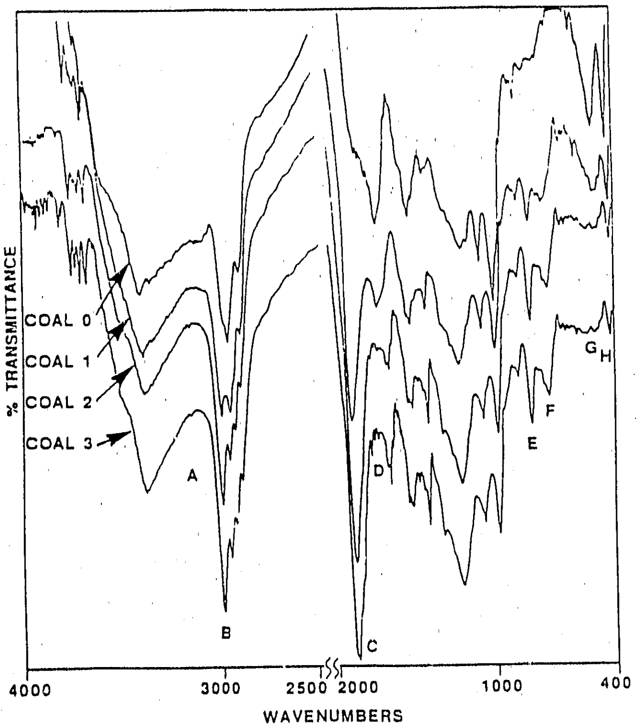


Figure 3. Diffuse reflectance FT-IR (DRIFT) spectra of coal samples before extraction.

also got smaller. This is consistent with the suggestion that the diazo compound decomposition was catalyzed and the reaction of the minerals with the ethyl diazoacetate (2) caused these absorptions to decrease.

In order to examine the catalytic effect of minerals on the thermal decomposition of ethyl diazoacetate (2), 2 was decomposed in the presence of a series of minerals, most of which can be found in coal. The minerals used in this study, called M1-M22, are described in Table 2. Three coal samples, called C1, C2, and C3 (Table 3), obtained from the Pennsylvania State University Coal Research Section, were crushed to < 100 mesh under argon, dried at 120-125 °C. Table 4 shows the quantities of 2, coal or glass (control) used for each run and Figure 4 shows the plot of the evolution of nitrogen vs. temperature for each.

We monitored the reactions by plotting the evolution of nitrogen versus temperature. Copper sulfate (M12), though admittedly to be expected in small amounts in coal, was too reactive, even at room temperature to be monitored kinetically. Three other minerals, cuprite (M21), chalcopyrite

(M15) and hematite (M13) proved to be especially active (Figure 5). Cuprite decomposed **2** completely at 40 °C while chalcopyrite and hematite decomposed **2** 50% below 90 °C and 100% below 130 °C. The reason for the apparent decomposition of **2** in two steps, is quite interesting and is discussed below. Several other minerals M4, M5, M7 and M9 showed up to 50% decomposition

Table 2. Minerals Used in this Study and Structure

Number	Name	Structure
M1	G-15 (Regan) Glauconite	$(K,Na)(Fe,Al,Mg)_2(Si,Al)_4O_{10}(OH)_2$
M2	Kaolinite H-4	$Al_4Si_4O_{10}(OH)_8$
M3	Gypsum	$CaSO_4{\cdot}2H_2O$
M4	Halloysite H-13	$Al_4Si_4(OH)_8O_{10}{\cdot}8H_2O$
M5	Illite H-35	$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2, H_2O]$
M6	Oil Creek Sand	SiO_2
M7	Montmorillonite H-25 Bentonite	$(Na,Ca)_{0.33}\ (Al,Mg)_2Si_4O_{10}(OH)_2{\cdot}\ nH_2O$
M8	Dickite H-16	$Al_2Si_2O_5(OH)_4$
M9	Nontronite H-33b	$(Na,Ca)_{0.33}(Fe,Mg)_2Si_4O_{10}(OH){\cdot}\ nH_2O$
M10	Pyrite	FeS_2
M11	Marcasite	FeS_2
M12	Copper(II) Sulfate (Hydrocyanite)	$CuSO_4$
M13	Iron(III) Oxide (Hematite)	Fe_2O_3
M14	Magnetite	Fe_3O_4
M15	Chalcopyrite	$CuFeS_2$
M16	Siderite	$FeCO_3$
M17	Sphalerite	$(Zn,Fe)\ S$
M18	Rutile	TiO_2
M19	Barium Sulfate (Barite)	$BaSO_4$
M20	Potassium Feldspar	$K(Si,Al)_4O_8$
M21	Copper(I) Oxide (Cuprite)	Cu_2O
M22	Zircon	$ZrSiO_4$

Table 3. Description of Coal Samples Used in This Study

Number	Description	Elemental Analysis % (dry)
C1	PSOC-1351 Illinois No. 6 HVCB	67.3C, 4.1H, 1.2N, 2.9 organic sulfur 10.7 oxygen (diff.), 13.7 mineral matter (includes 2.9 FeS_2)
C2	PSOC-1403P Wyodak SUBB	64.3C, 4.0H, 1.1N, 0.8 organic sulfur 18.0 oxygen (diff.), 11.9 mineral matter (includes 0.5 FeS_2)
C3	PSOC-628 Penn. No. 2 Anthracite	82.2C, 2.9H, 0.9N, 0.5 organic sulfur 0.1 oxygen (diff.), 13.3 mineral matter (includes 0.2 FeS_2)

Table 4. Amount of Glass, Mineral (or Coal) and 2 Used for Each Run

Run Number	Glass (g)	Coal (g) and type	Mineral (mg)	2 (ml)
g0	1.0	0	0	1.0
m1-m22[a]	1.0	0	100	1.0
c1(0)[b]	0	1.0 C1	0	0
c2(0)[b]	0	1.0 C2	0	0
c3(0)[b]	0	1.0 C3	0	0
c1	0	1.0 C1	0	1.0
c2	0	1.0 C2	0	1.0
c3	0	1.0 C3	0	1.0

a) Corresponds to minerals M1-M22 (Table 2)
b) Controls

of **2** at 120 °C (Figure 6). All of the other minerals showed nearly complete decomposition of **2** between 120 and 150 °C.

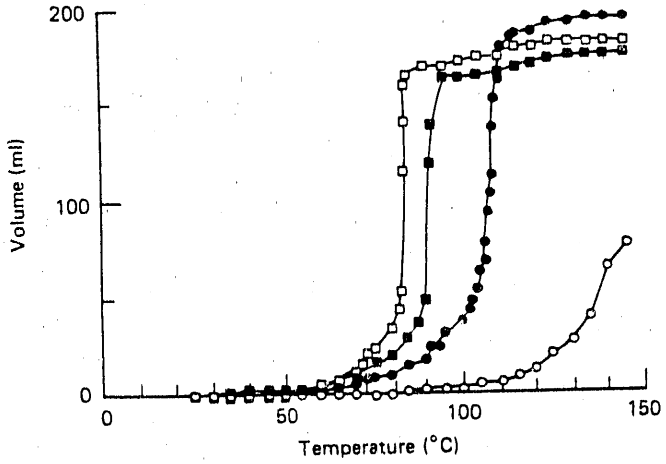


Figure 4 Evolution of nitrogen *versus* temperature for runs: □, c1; ●, c2; ■, c3; ○, g0

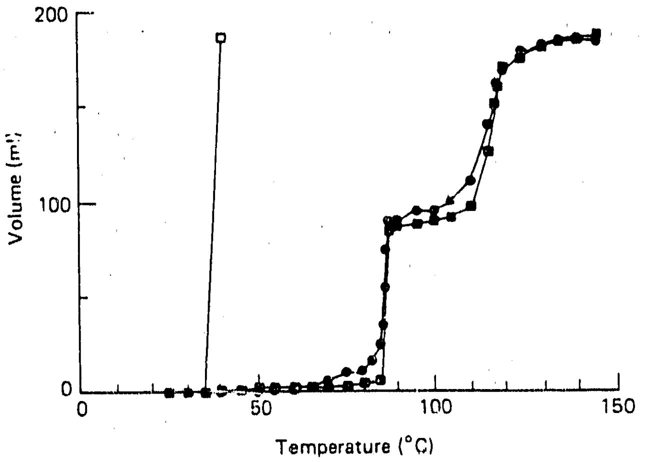


Figure 5 Evolution of nitrogen *versus* temperature for runs: □, m21; ●, m15; ■, m13

Our results also confirm what has been suggested in the literature, namely that Cu(II) is an active catalyst in the decomposition of **2**. The behavior of chalcopyrite (M15; $CuFeS_2$) was also consistent with the fact that Cu(II) was an active catalyst since the oxidation states of Cu and Fe are +1 and +3 respectively. Since chalcopyrite and hematite (M13; Fe_2O_3) behaved similarly, and Fe is in the +3 valence state in both, it must have been Fe(III) which was the catalyst or the rate of Fe(III) and Cu(I) [via Cu(II)] catalysis were fortuitously the same.

Another interesting characteristic of the iron minerals M13 and M15 was that their catalytic effect on the decomposition of **2** (Figure 5) occured in two steps. That is, an initial high rate of decomposition of **2** between 85-100 °C [that we have attributed (*vide infra*) to the presence of Fe(III)] and a later one between 110-130 °C. When we looked at the rate of decomposition of minerals M10, M11 and M17, all of which have iron in the +2 oxidation state, we found that they reactied at about 110-130 °C (M16, although not included in Figure 7, behaves similarly). This observation suggested that for M13 and M15 the decomposition of **2** occurred at 110-130 °C through an Fe(II) intermediate which meant that the initial fast decomposition was occuring by Fe(III) catalysis and at the same time the Fe(III) was being reduced to Fe(II).

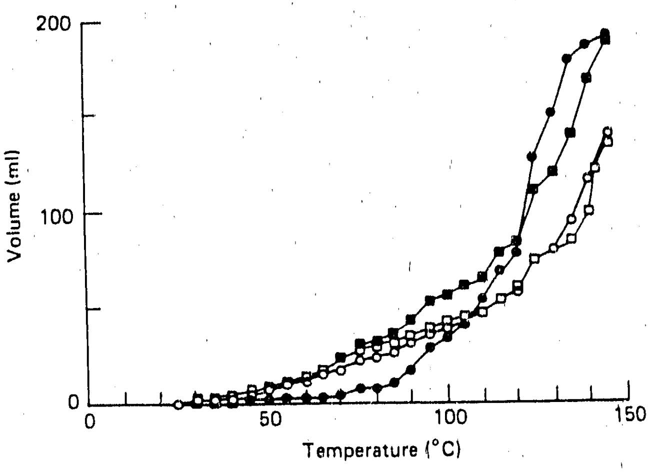


Figure 6 Evolution of nitrogen *versus* temperature for runs: □, m4; ●, m5; ■, m7; ○, m9

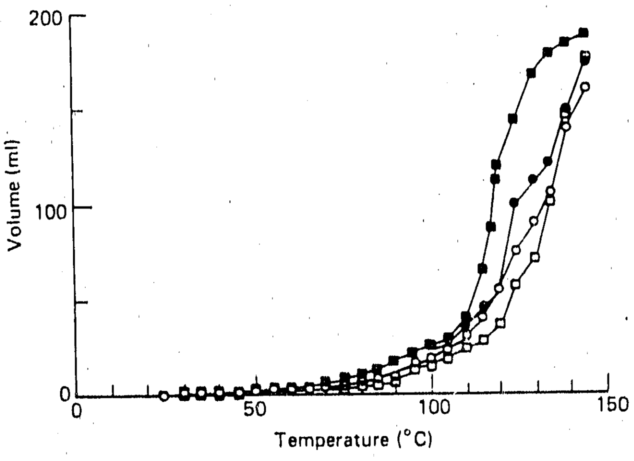


Figure 7 Evolution of nitrogen *versus* temperature for runs: □, m10; ●, m11; ■, m17; ○, m14

The lower oxidation state of Fe [Fe(II)], therefore, only modestly catalyzed the decomposition of **2**. Magnetite (M14), which contains both Fe(III) and Fe(II) appeared to be the exception. The reason for this was not determined.

The effect of the minerals in Figure 6 also merits attention. Two possibilities exist as to how these clays catalyzed the decomposition of **2**. It may have been that impurities such as Fe or Cu were present. For example, M9 is known to be iron rich with an appreciable amount of Fe^{3+}. The other possibility is that acidic water (H_3O^+) may have had an effect on the decomposition of **2**. Natural clays are known to contain acidic water and have Brønsted acidities as low as −3 and, further, the acid catalyzed decomposition of **2** is known. The question as to which of these possibilities was the most important could not answered.

Finally, a control experiment [c1(0)] was run using **2** and C1 to determine if the ethyl diazoacetate was extracting the active mineral catalysts and then decomposing **2**. In these experiments, 1 ml of **2** and 1 g of C1 were allowed to stir overnight. The sample was then vacuum filtered with 50 ml of distilled pentane, and the pentane was flash distilled at room temperature. The amount of **2** recovered was about 10-20% less than that used and agreed with the weight increase of the coal after filtration. DRIFT spectra of this filtered coal showed the prominent N_2 stretch of **2** at 2110 cm^{-1}, suggesting that **2** was trapped in the pores of the coal and not easily extracted. Decomposition of the recovered **2** was essentially identical to g0, the control of **2** and glass, which meant that **2** did not solubilize the active mineral catalysts. We could not, however, rule out the possibility that at the reaction temperatures, the active catalyst was being extracted.

A search of the literature revealed no study of the selectivity of carbene **1** toward fused aromatics, heteroaromatics and benzo-fused aromatics. We studied the relative reactivity of **1**, produced by the thermal decomposition of **2**, with toluene, anisole, phenanthrene, pyridine, quinoline, acridine, furan, benzofuran, dibenzofuran, thiophene, benzothiophene, dibenzothiophene, pyrrole, indole, carbazole, fluorene and several methoxy-substituted aromatics all versus naphthalene. This work not only has provided much needed data on the selectivity of thermally produced carbene **1**, but also provided required information which is necessary for studies of the reaction of carbene **1** with coal. Since each of these compounds has been identified in various coal extracts, the knowledge of which type of molecules reacts fastest should prove useful in determining the mechanism(s) of the formation of increased volatiles and solvent extractables from coals treated with **2**.

Generation of carbene **1** from ethyl diazoacetate (**2**) in the presence of two aromatic substrates x and y in an inert solvent creates a competitive system from which the relative rates may be obtained by standard treatment of first-order rate equations. In principle, these data may be determined by measuring the extent of disappearance of x and y at time t or by measuring the appearance of products at time t due to the reaction of x and y with **1**. For reactions in which several isomeric products may be formed, the former is preferred and was adopted in this work. Product analysis was by capillary gas chromatography. The solvent chosen for these competitive experiments was hexafluorobenzene. Solutions were 0.05 M in each of the two competing aromatics and 0.063 M in the carbene precursor. In each case the carbene precursor, **2**, was decomposed at 150 °C in the presence of the competing aromatics in a sealed tube for approximately 12 hours. Control experiments using a 10 fold excess of **2** in hexafluorobenzene showed no detectable diazo absorption by FT-IR when the solution was heated in a sealed tube at 150 °C for 30 minutes. Each experiment was done in triplicate, and each of the three reaction tubes was analyzed by gc with a minimum of three injections. For each of the nine (or more) injections, a separate k_{rel} was determined. The average of each of these values was then used in reporting k_{rel} (Table 5).

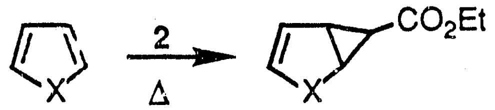
Table 5. Relative Rate Ratios for the Reaction of 2 Versus Naphthalene at 150 °C

Substrate	k_{rel}
toluene	0.24
anisole	0.25[a]
naphthalene	1.0
phenanthrene	1.8
pyridine	21[b]
quinoline	27
acridine	37
thiophene	1.5
benzothiophene	1.0
dibenzothiophene	0
furan	14
benzofuran	2.9
dibenzofuran	0.79
pyrrole	23
indole	12
carbazole	7.5
fluorene	0.17
1,2-dimethoxybenzene	0.48
1,4-dimethoxybenzene	0.63
1,2,4-trimethoxybenzene	2.4
1-methoxynaphthalene	1.5
2-methoxynaphthalene	1.3
2,6-dimethoxynaphthalene	1.5
2,7-dimethoxynaphthalene	1.5

a) Calculated using $k_{anisole}/k_{toluene} = 1.03$
b) Corrected for ca. 8% decomposition

For the aromatic series toluene, naphthalene and phenanthrene it was seen that the order of reactivity increased modestly with increasing ring fusion. This is consistent with the fact that the delocalization energy of the 1,2-bond in each is decreased with additional fused aromatic rings and that there is less aromatic stabilization energy per electron as more fused rings are added. Attempts to experimentally determine k_{rel} of anthracene versus naphthalene failed due to the extremely low solubility of anthracene in hexafluorobenzene.

The thermal decomposition of **2** in the presence of thiophene, benzothiophene, furan and benzofuran to give the cyclopropanated products (eqns 3, 4; X = S, O) has been well established. In addition, benzothiophene has been reported to also react by cyclopropanation of the benzene ring (eqn 5).



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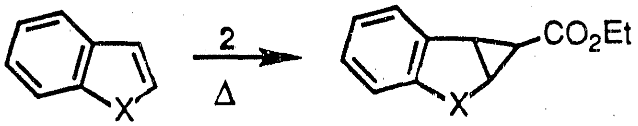

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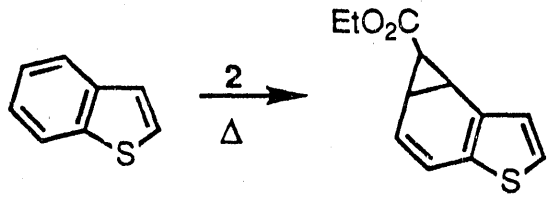
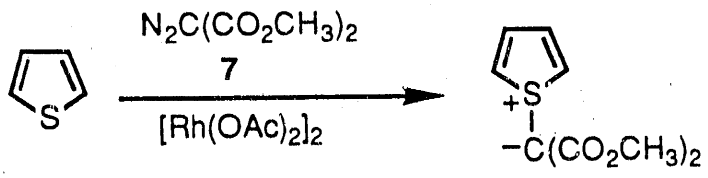


(5)

For the thermal reaction of **2** with benzofuran, the mechanism suggested involved the direct addition of carbene **1** to the enol-ether type double bond. Our relative rate data (Table 5) was consistent with this mechanism. Comparison of furan, benzofuran and dibenzofuran indicated that reactivity was related to the number of reactive enol-ether type double bonds. Also, since fluorene was very slightly less reactive than toluene, and anisole was slightly more reactive than toluene (Table 5), one would have expected dibenzofuran to be somewhat less reactive than it actually was. The origin of this enhanced reactivity was not apparent.

Although the mechanism of the reaction of **2** with thiophene has not been definitely established, the observations that cyclopropanes form (equations 3 and 4) and that a cyclopropane far removed from the sulfur forms in one case (eqn 5), suggest that the mechanism is a direct carbene addition to a double bond. No ylides have been observed in reactions of **2** with thiophene molecules. When dimethyl diazomalonate [**7**, $N_2C(COOCH_3)_2$] reacted with thiophene in the presence of Rh(II) acetate, however, an ylide was isolated (eqn 6). The ylide negative charge here was stabilized by two ester groups. When the ylide was less stabilized than that shown in equation 6 it could not be observed. Thus when electron donating substituents were put on the thiophene ring the ylides were formed in high yields but when electron withdrawing substituents were used there was no reaction with **7**. Further, as mentioned above, when only one ester was present to stabilize the ylide (use of **2** rather than **7**), no ylide was observed. Thus a mechanism of direct cyclopropanation of thiophenes by carbene **1** seemed most reasonable. If this was indeed the case, then as expected, the relative rates of thiophene, benzothiophene and dibenzothiophene were seen to parallel the furan series.



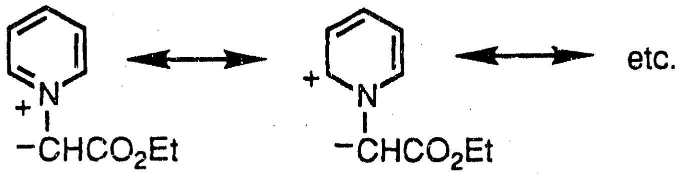
(6)

In the pyrrole, indole, carbazole series, once again, the order was the same, also suggesting a similar mechanism. However, here one of the most significant observations was that the selectivity of (ethoxycarbonyl)carbene (**1**) was about one hundred fold relative to toluene, a simple benzene derivative. Pyrroles and indoles are known to undergo α- and β- substitution to produce ethoxycarbonylmethyl derivatives (C-H insertion type products) while in a few cases cyclopropanes were formed. Indeed, a number of pyrrole-carbene reactions were postulated to go through cyclopropanes which rearrange or ring expand while others were suggested to go through direct electrophilic substitution. In no case, however, has an ylide been shown to be an intermediate.

The order from one heteroatom series to the other (pyrroles, furans and thiophenes) was exactly the sequence observed in various reactions where electron donation is important from the heteroatom. Thus, for example, electrophilic aromatic substitution rates are in the order $Ph-NR_2 >$

Ph-OR > Ph-SR. This points out the electrophilic nature of the carbene and underscores the fact that (ethoxycarbonyl)carbene (**1**) was quite selective with the right system. While our data clearly showed that the more nucleophilic the ring system the greater was the selectivity, there was no compelling reason at this time to choose either the direct, one step, polar cyclopropanation mechanism or the two step electrophilic substitution mechanism over the other.

There was one series which appeared anomalous, however, and that was pyridine, quinoline and acridine. Since the nitrogen in these systems renders them less reactive in reactions such as electrophilic aromatic substitution, it was expected that these compounds would react more slowly than their carbocyclic counterparts with carbene **1**. However, they reacted from 20 to about 100 times faster! This strongly suggested an alternative mechanism for reaction. Although the reaction of **2** with pyridine and quinoline in the presence of $CuSO_4$ gave the 3-ethoxycarbonyl derivatives, the thermolysis of **2** with isoquinoline provided the stable ylide. This suggested that the alternative mechanism likely involved ylides. If one assumes that steric problems were not important, then a comparison of ylides **8**, **9** and **10** (equations 7, 8 and 9) reveals that the stability was **10**>**9**>**8** since more resonance forms involving delocalization of the positive charge onto the aromatic ring carbons



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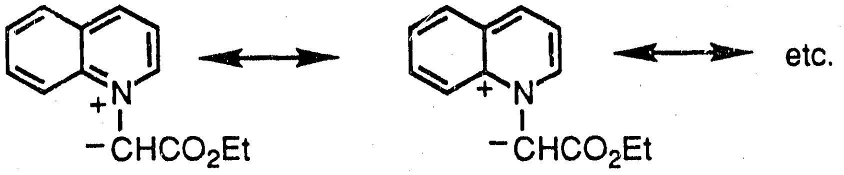

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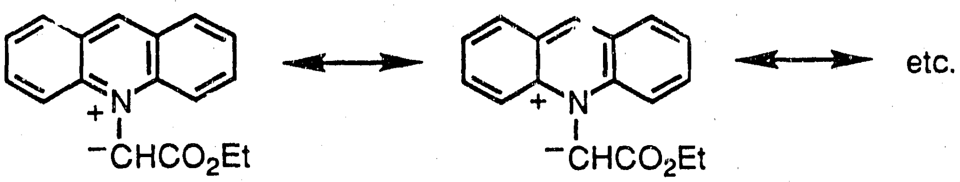

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(9)

could be drawn for **10** than **9** and more for **9** than for **8**. Thus, acridine would react faster than quinoline and pyridine. It should also be mentioned that very recent flash photolytic work by Platz has demonstrated that pyridine gave transient ylides with several different carbenes.

Finally, several methoxy-substituted benzenes and naphthalenes were analyzed to determine how the simple electron donating substituents would affect k_{rel} versus naphthalene (Table 5). The addition of a second methoxy group in anisole resulted in an approximately two-fold increase in rate for 1,2-dimethoxybenzene and a slightly greater than two-fold rate increase for 1,4-dimethoxybenzene. Interestingly, the addition of a third methoxy group in 1,2,4-trimethoxybenzene resulted in a ten-fold increase in rate relative to anisole. Clearly, the electron donating effect of three methoxy group was much greater than any steric hindrance present in the 1,2,4-trimethoxybenzene. For the case where methoxy group(s) were substituted in naphthalene, we saw that a simple methoxy group enhanced the rate by a factor of 1.3-1.5 while putting one methoxy group in each ring did not increase the rate very much over a single methoxy. Thus, carbene **1** was significantly selective only when there were several oxygens attached to a single ring.

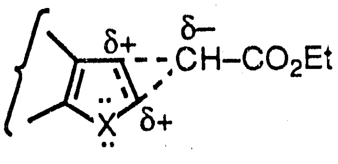
Recently Gaspar and Jones suggested that the carbene fluorenylidene forms a complex with hexafluorobenzene when the latter was used as a solvent, and so the fluorenylidene reacted as a carbenoid rather than a free carbene. To probe whether (ethoxycarbonyl)carbene (**1**) formed a complex with C_6F_6 and thus enhanceed its selectivity, we examined the reaction of **1** with several acceptors over a fairly large range of relative reactivities in isooctane as the solvent. Isooctane was chosen since it was not likely to form any type of complex and has only C–H bonds available for reaction with the carbene and the slightly more reactive secondary and tertiary hydrogens are sterically hindered. We found it necessary to use somewhat greater concentrations of ethyl diazoacetate (**2**; 0.375 M), and the acceptor and naphthalene (0.094 M in each) in order to readily quantify the relative reactivity in the presence of solvent which was also reacting. The results shown in Table 6, indicated that the carbene **1** most likely did not form a complex with C_6F_6 and that the small observed effect wa a simple solvent effect. Not only were the concentrations of the reactants somewhat higher in the isooctane, but if there was polar character in the transition state, such as

Table 6. Relative Rate Ratios for the Reaction of 2 with Three Aromatics Versus Naphthalene at 150 °C in Two Solvents

	k_{rel}	
Solvent Compound	C_6F_6	isooctane
phenanthrene	1.8	1.4
furan	14	6.8
pyrrole	23	15

shown in **11**, and there was a spectrum of polarity depending on the heteroatom X, then the reaction would have been expected to go faster in C_6F_6 and there should have been a compression in the overall range in selectivities.

Finally, in order to demonstrate that the rate determining step in these reactions was formation of the carbene **1**, and not the reaction of the aromatic substrate with either **1** or **2**, we measured the kinetics for three of the systems and a control of **2** without an aromatic acceptor. The



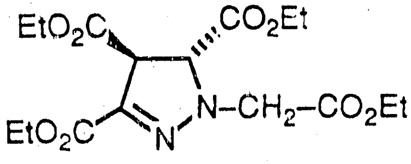
11

rate constants, at 150 °C, for acridine, carbazole, benzofuran and the control were 0.08, 0.07, 0.08 and 0.09 min^{-1} respectively. Thus, since all were the same within experimental error, the rate determining step must have been carbene formation in all cases.

In further studies we reacted a Wyoming Wyodak with ethyl diazoacetate (**2**) and observed that the amount of material extractable in toluene/methanol went from 10% for untreated coal to 47% for coal reacted with **2** in pentane to 51% for coal which had first been swelled with dioxane and then reacted with **2** in pentane. We have also determined by titration, that our Illinois No. 6 coal contained 1.69 mmol of titratable hydrogen per gram of coal (2.4%) and the Wyoming Wyodak contained 2.74 mmole of titratable hydrogen per gram of coal (3.8%). This was the hydrogen which readily reacted with base. We methylated both coals using tetrabutylammonium hydroxide and methyl iodide and each of the methylated coals then provided 13% of toluene/methanol extractables. However, after treatment with ethyl diazoacetate, the methylated coals gave 63% and 51% extractables for the Illinois No. 6 and Wyoming Wyodak respectively.

We examined the very mild, 250°C, pyrolysis of ethyl diazoacetate (2) treated Illinois No. 6 coal. The treated sample produced 17% gas as opposed to the untreated sample which gave only 5% gas. The residue after pyrolysis provided an additional 13% of extractable (toluene/methanol) material whereas the unreacted coal provided 11% of extractable material.

Further studies of the thermal decomposition of ethyl diazoacetate (2) showed that a new tetramer 12 was formed. It was shown to be both a product from 2 itself (by reaction with pyrazoline 5) and in the reaction of 2 with coal.



12

Pyrazoline 12 was independently prepared by the reaction of 2 with 5 in the presence of CuCl. Isolation of this new compound by radial chromatography gave a light green colored oil, which capillary gas chromatography showed to be >99% pure. Elemental analysis, FT-IR, ^{13}C and ^{1}H NMR spectroscopy and GC-MS were all consistent with structure 12. Analysis of the appropriate blocks of a 2-D ^{1}H NMR COSY spectrum gave a three bond coupling constant, $^{3}J_{HH}$, of the hydrogens attached to C-4 and C-5 (H_4 and H_5) of 10.6 Hz. This value, at first sight, appeared rather large when compared with the value of 5.4 Hz which we observed in 5 for the corresponding trans C-4 and C-5 hydrogens. (This compares with the literature value of 6.5 Hz.) Although the three bond coupling constants of the trans hydrogens on these positions of 2-pyrazolines are typically in the range of 3-10 Hz, it is known that that substituents on nitrogen can have a rather significant effect on these coupling constants. Also, since the starting pyrazoline 5 was well known to have the trans configuration at C-4 and C-5 as mentioned above, it was expected that **12** would maintain this stereochemistry and thus the large value of $^3J_{HH}$ must have been the result of a simple substituent effect.

Next, the amount of **3-6** and **12** formed when an Illinois No. 6 HVCB coal was treated with an equal weight of **2**, under various conditions, was determined (Table 7). For one sample, called Coal A, the coal, **2** and pentane were stirred overnight and the pentane was removed under reduced pressure. For a second sample, called Coal B, the coal was first swelled with dioxane, and dried. It was then mixed with **2** and pentane, stirred overnight and the pentane was removed under reduced pressure. Finally, for a third sample, called Coal C, the dioxane swollen coal and **2** were stirred overnight, without solvent. In each of these cases the ethyl diazoacetate (2) was then decomposed by heating the coal/**2** samples slowly to 130 °C. With all three samples, the evolution of nitrogen was vigorous at approximately 70 °C. The treated coal samples were then extracted in a Soxhlet extractor using toluene:methanol (9:1). The amount of **3-6** and **12** was determined quantitatively by GC using authentic samples. The results are presented in Table 7.

Table 7. Percent of 3-6 and 12 Observed in Various Coal Extracts[a]

Compound	Coal A[b,c]	Coal B[b]	Coal C[b]
3	0 (trace)	trace	trace
4	0 (0.43)	trace	trace
5	1.1 (2.3)	2.1	5.5
6	11.3 (8.2)	12.8	9.4
12	4.0 (3.8)	4.4	3.9
Total % extracted[d]	26 (37)	37	35

a) % of total extractable material.
b) For a description of the different coal samples, see text.
c) The numbers in parentheses are the result of further extraction with dioxane, see text.
d) Based on the weight of coal before and after Soxhlet extraction.

When the dioxane preswelled samples, Coals B and C, were Soxhlet extracted, more extractable material was obtained than when dioxane was not used (Coal A). One explanation was that this difference was due to swelling of the coal by dioxane, which would allow for better penetration of **2** into the coal matrix. However, if this were true, much more of the products **3-6** and **12** should have been observed in Coal A than were actually detected, since simple surface reaction of small droplets of **2** on the coal would result in very extensive reaction of **1** and **2** with themselves and each other. When Coal A, which had been extracted with the toluene-methanol mixture, was subjected to an additional extraction with dioxane (12 h) the total extractable material of Coal A increased to 37%, with the total (from both extractions) percent of **3-6** and **12** observed as 0.43, trace, 2.3, 8.2 and 3.8%, respectively, comparable with the results obtained for preswelled Coals B and C. From these results, it is clear that dioxane did little to facilitate access of **2** into the coal. Instead, the dioxane acted to distort the structure of Coals B and C and, after reaction with ethyl diazoacetate (**2**), this more open structure was maintained and allowed for more of the reaction products to be extracted. In Coal A, which was not dioxane swelled, considerably less material was extracted. However, the remaining products were extracted with an additional extraction using dioxane. Control experiments showed that with Coals B and C after toluene-methanol extraction nothing more could be extracted with an additional dioxane extraction.

Several points concerning the amounts of products **3-6** and **12** should be discussed. First, and most important, the total amounts of compounds **3-6** and **12** in the extracts of Coals A-C were only 16-19% of the total coal extracts (15% of total extracts when Coal A was further extracted with dioxane). The treated coal samples showed a 50% increase of extractable material (about 30-35% when the amounts of **3-6** and **12** were taken into account) relative to untreated coal, which showed 24% Soxhlet extractable material. In addition, GC-MS analysis of the extracts of the treated coal indicated that much of the treated coal extracts are able to elute through a gas chromatograph and that the vast majority of these elutable products contained ester groups attributable to the incorporation of **1** into the coal fragments. While the reason for the enhanced extractability of the ethyl diazoacetate treated coal, and whether this involved depolymerization of the coal or greater extractability of trapped species due to the attachment of ester groups, could not be established with certainty until the extracts could be identified more fully, it was clear that the major reaction of **2** was with the coal. It is also interesting to note that since cyclopropane **6** did not form from pyrazoline **5** at the low temperatures used here, its formation must have been the result of a catalyzed reaction (vide infra). Further, products **6** and **12** were the result of two competing reactions of pyrazoline **5**, both of which were most likely catalyzed, but only one of which (**5** → **12**) required additional diazo compound **2** or carbene **1**. The observations of trimers and particularly tetramer **12** suggested there are regions of relatively high concentrations of **2** (and **1**) which seemed to pose a paradox since we have also concluded that the majority of **1** and **2** reacted with the coal. The observations described below, however, involving the catalytic decomposition of **2**, indicated that these trimers and tetramers could form under relatively dilute conditions.

To further explore this idea of possible regions of high and low concentration of **2** and what effect a catalyst such as Fe_2O_3 (which may well be the active mineral catalyst in the coal) might have on these product distributions, the ethyl diazoacetate (**2**) was decomposed thermally both neat and diluted to 10% w/v in *p*-xylene. In addition, **2** was decomposed using Fe_2O_3 as the heterogeneous catalyst both neat and as a 10% w/v solution in *p*-xylene. Table 8 shows the results of these studies and gives the amounts of **3-6** relative to tetramer **12**, which was set equal to 1.0.

Table 8. Relative Amounts of 3-6 and 12 Produced from the Decomposition of 2 Thermally and Catalytically[a]

Compound	**2** neat	**2** dilute[b]	**2**+Fe_2O_3 neat	**2**+Fe_2O_3 dilute[b]
3	–	1.1	–	1.1
4	–	2.7	–	2.5
5	3.0	8.7	0.69	2.6
6	–	–	–	13.6
12	1.0	1.0	1.0	1.0

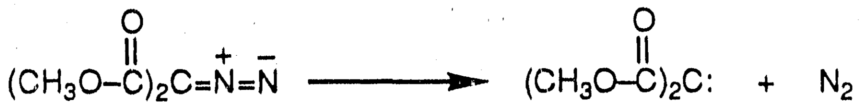
a) In each case, **2** was decomposed by slowly heating to 130–135 °C.
b) 10% w/v of **2** in *p*-xylene.

The data in Table 8 showed that the dimers **3** and **4** were not detected when **2** was reacted neat both with and without catalyst. This, of course, was because they were quite reactive in the presence of high concentrations of ethyl diazoacetate (**2**) and resulted in the formation of pyrazoline **5**. This, in turn, reacted with more **2** to provide tetramer **12**. No cyclopropane **6** was observed when only neat **2** was heated since the temperature was not high enough to get tautomerism and nitrogen extrusion. Since there was also no cyclopropane **6** formed from **2** and Fe_2O_3 neat, we concluded that in the competing reactions of **5** to form **6** by nitrogen extrusion and **12** by reaction with **2**, the reaction to give tetramer **12** won out as a result of the high concentration of **2** (neat).

When the ethyl diazoacetate (**2**) was thermally decomposed in a much more dilute solution (10% w/v in *p*-xylene) there were significant quantities of the dimers **3** and **4** produced and at the same time there was less of tetramer **12** relative to trimer pyrazoline **5**. This was reasonable since each step in the sequence **3**/**4** → **5** → **12** required more **2** and each depended on the concentration of **2**. Again, as expected, no cyclopropane **6** was formed. Further, the Fe_2O_3 catalyzed decomposition of **2** in more dilute solution (10% w/v in *p*-xylene) also provided significant amounts of **3** and **4** but now when **5** reacted, the catalyzed reaction **5** → **6** occurred at the expense of the **5** → **12** reaction, which was dependent on the **2** concentration. Once more this was reasonable since with the lower concentration of **2** the reaction **5** → **12** was much slower while the reaction **5** → **6** was not significantly affected. Finally the attempted reduced pressure distillation of dioxane (60 - 62 °C) from a dioxane/**2**/coal mixture, which resulted in decomposition of **2**, gave a product distribution which was very similar to that obtained from **2**+Fe_2O_3 dilute.

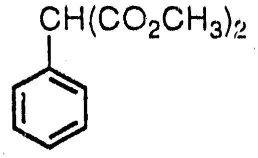
Now, comparing these results with the coal results, we can first see that since cyclopropane **6** was always formed with the coal in largest amounts, these coal reactions were most similar to the dilute **2**+Fe_2O_3 reaction. The most reasonable explanation for the similarity of these two systems was that within the coal the ethyl diazoacetate (**2**) was fairly well dispersed throughout the coal matrix. It was also clear that the formation of trimers and tetramers, particularly cyclopropane trimer **6**, did not require very high concentrations of **2**, particularly when the catalyst was present. Thus one can now conclude, as indicated above, that in the coal the ethyl diazoacetate (**2**) was probably distributed in regions of relatively low concentrations which was consistent with our observations that the majority of the ethyl diazoacetate (**2**) appeared to be reacting with the coal.

We have also studied the reactions of bis(methoxycarbonyl)carbene (**13**), formed by the thermal decomposition of dimethyl diazomalonate (**7**) with several model compounds. In the presence of benzene the major product was dimethyl phenylmalonate (**14**) with small amounts of the dimer **15** and a number of other minor products also formed. With *p*-xylene the major products were **16** and **17**. With naphthalene the products were **18-21** along with small amounts of dimer **15**, azine **22** (see below) and two other dimers discussed below. The formation of the benzotropilidene **21**, in yields of 5-15%, is unique and this is the first time the addition of a carbene to the 2,3-bond of naphthalene has ever been observed.



$$(CH_3O\overset{\overset{O}{\|}}{C})_2C{=}\overset{+}{N}{=}\overset{-}{N} \longrightarrow (CH_3O\overset{\overset{O}{\|}}{C})_2C: \;+\; N_2$$

7 **13**



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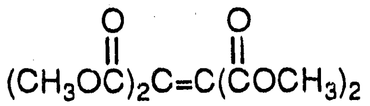

$$(CH_3O\overset{\overset{O}{\|}}{C})_2C{=}C(\overset{\overset{O}{\|}}{C}OCH_3)_2$$

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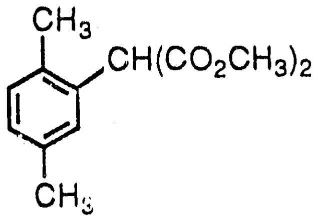

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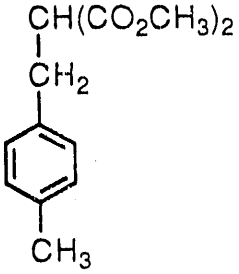

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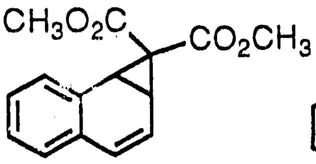

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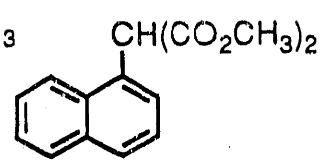

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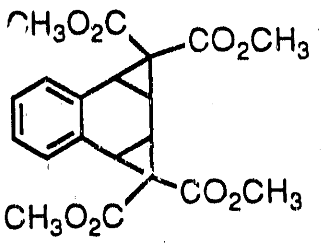

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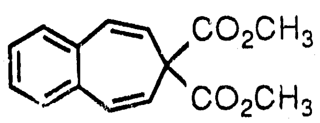

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The use of $[Rh(OAc)_2]_2$ as a catalyst for the naphthalene and benzene reactions with **7**, gave major amounts of the bis-carbene adducts **20** and **23** respectively. This was not surprising since it was expected that the carbenoid formed in the presence of the rhodium catalyst would be quite selective and react with the most reactive double bond. The X-ray crystal structure of **20** was kindly obtained by Dr. Felix Frolov, Department of Structural Chemistry, Weizmann Institute of Science, Israel, and, among other features, showed the non-bonded distance between the

$(CH_3O_2C)_2C{=}N{-}N{=}C(CO_2CH_3)_2$

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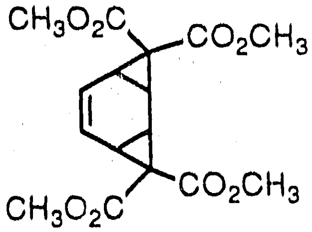

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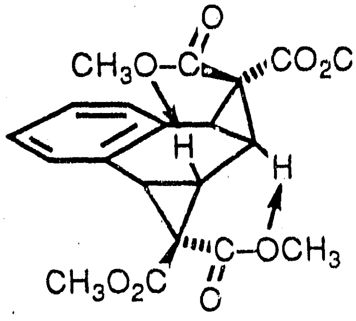
cyclopropyl hydrogen and the methoxyl oxygen (see structure below) to be about the sum of the van-der Waals radii, 2.7 Å. This would explain why the base peak in the mass spectrum of **20**



was the parent minus 2 molecules of CH_3OH and why M–CH_3OH was also a large peak.

It should also be mentioned that when a mixture of benzene and naphthalene was reacted thermally with **7**, the ratio of **14**:**18**+**19** formed indicated that naphthalene was roughly 10 times more reactive than benzene, showing that carbene **13** was more selective than (ethoxycarbonyl)carbene (**1**).

The formation of the azine **20** is also interesting and noteworthy. Azines are generally not observed in reactions of bis(carbonyl)diazo compounds. Not only is **20** observed in minor amounts in rhodium catalyzed reactions with several aromatics but it can be made the major product under the right conditions.

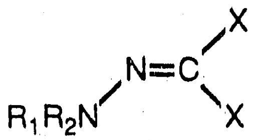
When the decomposition of **7** was catalyzed by $CuSO_4$ or CuCl at about 40-50 °C the major product (>90%) was the "regular" dimer **15**. However, when dimethyl diazomalonate (**7**) was reacted neat, at room temperature, with 0.2% rhodium(II) acetate dimer as the catalyst, nitrogen was evolved slowly. Even after 200 h traces of unreacted **7** could still be detected. The mixture became viscous and solidified, and GC and GC-MS showed only 10-15% of the dimer **15**, along with 50-

60% of the azine **22** and a small amount of an as yet unidentified higher boiling material. Azine **22** was purified by crystallization from absolute EtOH. Although the crystalline solid (mp 75-76 °C) appeared white, solutions of **22** were yellow. The ^1H NMR spectrum ($CDCl_3$) showed a singlet at δ 3.90 while the ^{13}C NMR spectrum ($CDCl_3$) showed three bands at δ 53.4, 135.1 and 159.6. The band at 159.6 was quite broad. The mass spectrum (EI) showed the parent at $^m/_z$ 288 and other significant peaks at 229 ($M-CO_2CH_3$), 173, 100 and 59. The IR spectrum showed bands at 3057, 3008, 2956, 2850, 1745, 1730, 1606, 1455, 1436, 1324, 1241, 1187, 1088, 1047, 977, 936, 829, 802, 750 and 605 cm^{-1}.

The observation of the unusually broad ^{13}C NMR carbonyl signal at δ 159.6 suggested that an exchange process was taking place. At low temperatures (–30 °C; $CDCl_3$) the ^{13}C NMR spectrum showed two carbonyl bands at δ 160.2 and 158.7 and two methoxy bands at δ 54.1 and 53.8. Coalescence for these bands occurred at about 273-283 K and 263 K respectively at 75.47 MHz. The band at δ 135.1 remained virtually unchanged.

The activation parameters for this process were obtained by examining the ^1H spectra at 8 temperatures between 232 K and 294 K, at 200 MHz, and then fitting the bands at each temperature to a calculated spectrum obtained using the Nicolet-GE program NMCXCH-Two Site Exchange Simulation Routine, to obtain the rate constants. These in turn provided activation parameters as follows: $\Delta H^{\ddagger} = 8.2 \pm 0.5\ ^{kcal}/_{mol}$, $\Delta S^{\ddagger} = -19.8 \pm 0.3$ eu, $E_{act} = 8.7 \pm 0.5\ ^{kcal}/_{mol}$ and log A = 8.86. The correlation coefficients for the plots to obtain $\Delta H^{\ddagger}$ and E_{act} were 0.991. At 200 MHz the coalescence temperature was 261 K.

Definitive determination from the data whether the observed dynamic process was inversion or rotation could not be done. Inversion, however, seemed more likely for the following reasons. First, the entropy of activation was fairly negative indicating a constrained transition state (vide infra). Second, it has been shown by Shvo that in the hydrazones **24** changing the groups on the carbon atoms from CH_3 to CO_2CH_3 had little effect on the barrier ($\Delta G^{\ddagger}$) which indicated that these systems interconverted by nitrogen inversion. In these cases the activation free energies ($\Delta G^{\ddagger}$) were

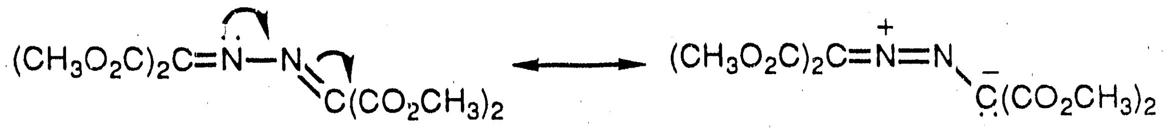


24

$X = CH_3$ or CO_2CH_3

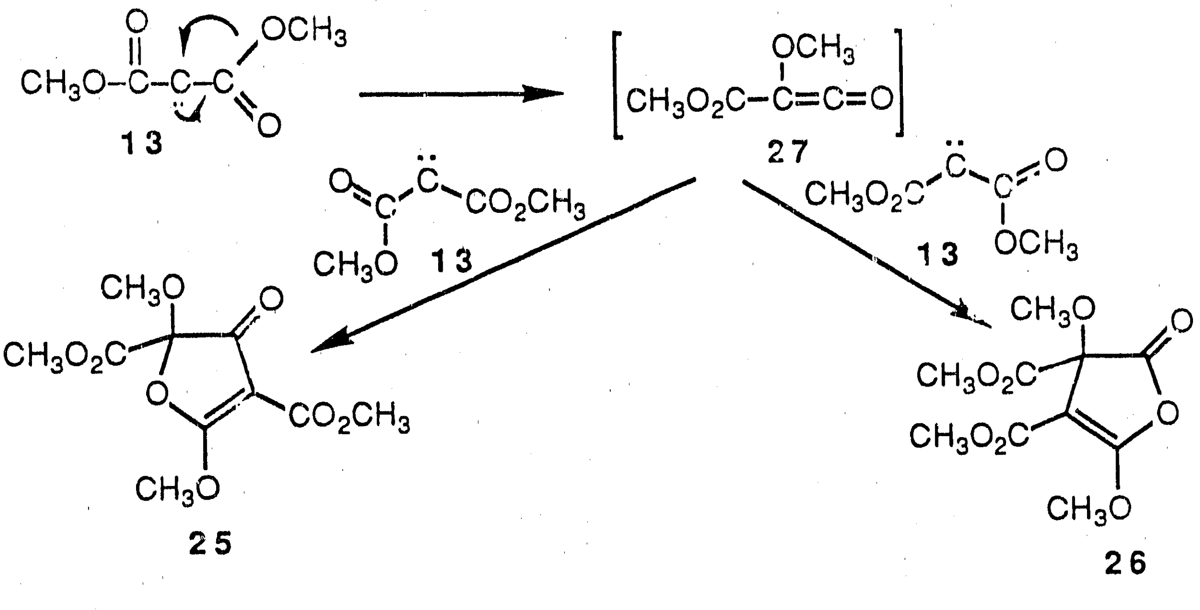
$R_1, R_2 = CH_3$, Ph, $PhCH_2$

over 21 $^{\text{kcal}}/_{\text{mole}}$. In the case of **22**, the lower barrier (compared to **24**) was explained by a stabilization of the transition state with the linear nitrogen as shown below. This would have the effect of lowering the barrier.



In addition to the products discussed above, in some rections, we observed the known dimer **25** and and also observed a heretofore unknown dimer, lactone **26**, as significant products. Indeed, when **7** was decomposed thermally neat, **26** was formed to the exclusion of **25**. Both **25** and **26** were formed by a 1,3-dipolar cycloaddition of carbene **13** to the ketene **27** which was formed by Wolff rearrangement of another carbene. This is illustrated in Scheme 1. With various substrates

Scheme 1



the ratio of **25**:**26** varied considerably. Thus, for example, with naphthalene as the substrate there was an approximately 30% yield of the two dimers and the ratio of **25**:**26** was 5:1. With *p*-dichlorobenzene the ratio was 7:1, with chlorobenzene it was 6.5:1 while with 1-chloronaphthalene the ratio inverted to 1:1.8. Table 9 presents the observed **25:26** ratio and the yields of the two dimers. The reasons for the ratios and the change in the ratios with solvent/reactant was not clear. This was, however, a complicated series of reactions providing two different, but related, products where various intermediates and/or complexes of intermediates with the solvent could be written.

Table 9. Dimers 25 and 26 Formed in the Thermal Decomposition of Dimethyl Diazomalonate (7) in Several Solvents

Solvent/ Reactant	Ratio of Dimers **25**	**26**	Total Yield(%)
Naphthalene	5 (3)*	1 (1)[a]	ca. 30
Anthracene	none	only dimer	ca. 20
Phenanthrene	none	only dimer	ca. 10
2,3-Dimethylnaphthalene	only dimer	none	<3
Benzene	none	none	
p-Xylene	none	none	
p-Dichlorobenzene	7	1	ca. 50
Chlorobenzene	6.5	1	ca. 30
1-Chloronaphthalene	1	1.8	ca. 30
Bromobenzene	1	1	ca. 50
p-Dimethoxybenzene	none	none	
Neat	none	only dimer	20

a) When 7 was added slowly.

We also studied the reaction of dimethyl diazomalonate (7) and the carbene **13** with an Illinois No. 6 coal, which proceeded rather differently from the reaction of ethyl diazoacetate (2) with the same Illinois No. 6 coal. Since the diazo compound **7** was less reactive than **2**, the decomposition was much slower which meant higher temperatures and longer reaction times were required. One gram portions of the Illinois No. 6 coal were mixed with 10 ml of pentane and dimethyl diazomalonate (7). Three samples using 0, 1 and 2 grams of **7** were prepared and called coal 0, coal 1 and coal 2 respectively. The mixture was stirred under N_2, the pentane was removed under vacuum and the samples were heated slowly to 130-135 °C for 2 days until the N_2 evolution ceased. The samples were weighed and extracted with 9:1 toluene:methanol for 2 days. Evaporation of the solvent gave a viscous brown liquid along with the extracted brown solid. Results of the reaction of dimethyl diazomalonate (7) with the Illinois No. 6 coal are given in Table 10.

Table 10. Results of the Reaction of Dimethyl Diazomalonate 7 with an Illinois No. 6 Coal[a]

	coal 0	coal 1	coal 2
7, g	0	1.001	2.003
coal, g	1.004	1.003	1.001
amt. recovered, g[b]	0.98	1.69	2.50
% recovery[c]	98	93	94
% extracted[d]	10	38	58

a) Average of three runs
b) Weight after heating and loss of N_2
c) Calculated based on the weight of coal plus carbene
d) Using 9:1 toluene:methanol.

The results of thermogravimetric analyses (under nitrogen, at 10 °/min temperature increase) were that while the maximum rate of weight loss for Coal 0 occured at about 450 °C, the maxima for Coals 1 and 2 were at about 200 °C, a lowering of around 250 °C. Further, there was a considerable amount of the coal which, after treatment with **7**, was volatile. Thus, with Coal 0 at 600 °C there was 75 % remaining (25 % volatile) while with Coals 1 and 2 there was 43 % and 32 % (57 % and 68 % volatile) respectively. Before extraction with toluene/methanol there was 60 %, 26 % and 22 % residue for Coals 0, 1 and 2 respectively at 850 °C, while the coal remaining after extraction showed 55 %, 45 % and 44 % residue for Coals 0, 1 and 2 respectively at 850 °C. Thus it was clear that not only did the dimethyl diazomalonate (**7**) treated coal give rise to more extractables and more volatiles but there was incorporation of the carbene **13** into the coal itself as shown by the increase in the residue left by the coal residue after extraction.

Diffuse reflectance Fourier transform infrared (DRIFT) spectroscopy has confirmed that the dimethyl diazomalonate (**7**) and carbene **13** reacted with the coal and that there were ester groups present in both the extracts and the residues after extraction. These esters are, of course, not observed in the control experiments on Coal 0.

Conclusions

We have shown that carbenes react with coal to produce a significant increase in the amount of extractable and volatile (below 250 °C) material. Carbene treatment lowers the major decomposition temperature by 200-250 °C. (Ethoxycarbonyl)carbene has been shown to be quite selective and reacts more readily with more nucleophilic aromatic rings. Ethyl diazoacetate has been shown to get into the coal pores and the corresponding carbene has been shown to react with the coal. Ethyl diazoacetate and (ethoxycarbonyl)carbene react with themselves also to produce dimers, trimers and a new tetramer. The minerals in the coal were shown to catalyze the decomposition of ethyl diazoacetate. Dimethyl diazomalonate also reacts with the coal although more slowly. Thermal and catalyzed reactions, neat and with naphthalene, benzene and many other aromatic substrates have provided the first example of the reaction of a carbene with the 2,3-bond in naphthalene, and the azine (azines are seldom formed in these reactions). Activation parameters for what appears to be inversion in the azine have been obtained. The 1,3-dipolar cycloaddition products of bis(methoxycarbonyl)carbene to the ketene formed by Wolff rearrangement of this carbene have been observed. Both regioisomers have been observed and their ratio as a function of substrate was studied.

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