that we become familiar with the properties of the oxygenated derivatives of BHT.

Registry No.—**2**, 38895-88-4; **3**, 66483-19-0; 3,3-dimethyl-1,2-butanediol bis(*p*-nitrobenzoate), 66483-13-4.

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(1) Research sponsored by the Division of Basic Energy Sciences of the Department of Energy under contract with the Union Carbide Corporation.

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Carbon Monoxide–Hydrogen–Water: Reduction of Anthracene, Dihydroanthracene, and Quinoline

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Anthracene is reduced by CO–H_2O, CO–H_2O–H_2, or H_2 at 425 °C and an initial pressure of 1500 psi to dihydroanthracene, 1,2,3,4-tetrahydroanthracene, and methylbenzohydrindene. Hydrocracked products and dimers are formed to a minor extent. The hydrogen donor solvent, tetralin, promotes rearrangement and cracking. Tetralin also increases the formation of methylbenzohydrindene, but does not influence the overall conversion. Ferrous sulfide promotes rearrangement and cracking while lowering the overall conversion. Sodium carbonate retards the reaction. Dihydroanthracene disproportionates to anthracene and tetrahydroanthracene under the reaction conditions. The principal reduction product of quinoline under similar conditions is 1,2,3,4-tetrahydroquinoline. Fragmented aniline derivatives, dimeric quinoline species, and methylated compounds are also found in the reaction mixture. Hydrogen is most effective as a reducing gas, and carbon monoxide must have water present to accomplish the reduction. Iron sulfide and sodium carbonate promote the carbon monoxide reductions.

Carbon monoxide is a versatile feedstock in that it can be used to synthesize a variety of chemicals such as sodium formate, methanol, ketones, adipic acid, aldehydes, ethylene glycol, glycidic acids, and hydrocarbons. This is in spite of the fact that it contains the strongest covalent bond known which exceeds that of nitrogen gas by 30 kcal/mol[1,2] and acetylene by 27 kcal/mol.[3,4] Carbon monoxide is now recognized as a superior reducing agent for the liquefaction of lignite[4–7] and other materials.[8,9] With benzophenone, there is evidence that it reacts via the formate ion in basic solutions.[8]

Anthracene reduction has been studied using hydrogen and hydrocracking catalysts.[10–14] Blom et al.[13] have reported dihydroanthracene and tetrahydroanthracene are formed under more mild hydrogenation conditions. As the conditions become more severe, isomerization to substituted indane and hydrocracking to naphthalene and benzene derivatives occur.

Since pyridine is more readily reduced than benzene,[15] it is not surprising that the pyridine portion of quinoline is selectively saturated. However, in acid media, the benzo group of quinoline can be selectively reduced.[16] Hydrogenation to decahydroquinoline is difficult.[17] Ring rupture to give 3-methylindole, *N*-methyl-*o*-toluidine, and *o*-toluidine occurred when quinoline was reduced over nickel in the vapor phase at 260–380 °C.[16] Catalytic hydrogenation of quinoline can also give alkylated anilines.[18]

Carbon monoxide can alkylate molecules also. Under Fischer-Tropsch-like conditions, a synthesis gas mixture of carbon monoxide, nitrogen, and hydrogen containing piperidine gave C_{1-8}-alkylpiperidines.[19]

The study herein described utilizes three sets of reducing gases with and without potential catalysts to reduce quinoline and anthracene, models for portions of the lignite structure. Quinoline assumes additional importance in model compound studies in relation to denitrification processes so important to coal conversion studies.

Experimental Section

Batch Autoclave Reductions. All the reductions were done in two 250-mL Hastelloy alloy C batch autoclaves (Autoclave Engineers, Inc.) using a heater designed to accommodate both autoclaves simultaneously and mixing achieved by rocking. Each autoclave contained, when specified, a catalyst, solvent, water, and reducing gases. The time of each run was 2 h at 425 °C not including heat-up and cool-down times. The initial charging pressure at room temperature was 1500 psi.

After the autoclaves were cooled and decompressed, the organic

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Table I. Mass Spectral Data for 1,2,3,4-Tetrahydronaphthalene Compared With the Mass Spectrum of the Compound Thought to be 1,2,3,4-Tetrahydroanthracene

1,2,3,4-tetrahydronaphthalene			1,2,3,4-tetrahydroanthracene		
m/e	*a*	rel intensity	*m/e*	*a*	rel intensity
132	0	62	182	0	100
131	1	12	181	1	20
117	15	12	167	15	18
116	16	4	166	16	11
115	17	9	165	17	18
104	28	100	154	28	32
103	29	8	153	29	11
91	41	43	141	41	34

[a] Mass of fragment(s) lost.

and water layers were separated. The organic layers were filtered through sintered glass funnels and analyzed by gas chromatography. The autoclaves were cleaned by washing with acetone, scrubbing with steel wool, washing with a soap solution, and rinsing with distilled water.

The gas chromatograph used in this study was a Varian Aerograph 90-P. The column was 0.25 in. × 10 ft 5% Carbowax with Chromosorb W as a column support, and the column temperatures were 50 to 220 °C. The internal standard was methyl benzoate. The conversion percentage was obtained by subtracting the amount of unconverted starting material from 100. The averages of the duplicated results were normalized to the conversion percentage and entered in the tables. The precision variation in the yields is ±6%.

Mass spectral (MS) and GC/MS analysis of reaction mixtures were performed using methods developed for coal-derived liquids. The column used was 3% OV 17 on Chromosorb W-HP packed in a 1/8 in. o.d. by 10 ft. stainless steel column. The chromatograph was a Varian Model 2740 with a splitter which directed 1/3 of the column effluent to the flame ionization detector and 2/3 to a duPont Model 21-491B low resolution mass spectrometer. Mass spectra were recorded for each peak which appeared in the chromatograms. Compounds were identified by their mass spectra or retention times. Authentic samples were used for comparison where possible. The GC temperature was programmed from 70–275 °C at 8 °C/min, and the helium flow rate was 30 mL/min. The amount of sample solution injected was 0.5 μL.

Low voltage MS was performed using an AEI MS 30 mass spectrometer equipped with a 325 °C heated glass inlet. A 2-3-mg sample was introduced into the mass spectrometer and vaporized. After the intensities had attained stable values, at least six spectra were recorded and the intensities were averaged. The source pressure was approximately 2×10^{-6} Torr, and an ionizing voltage of 10.0 V was used for obtaining low voltage spectra at a resolution of 1000. High resolution spectra were obtained at a resolving power of approximately 7000 and an ionizing voltage of 70 V. An AEI DS 50 data system was used for collecting and manipulating low voltage and high resolution data. The high resolution mass spectra confirmed the presence of the dimeric and methylated compounds indicated by GC/MS analysis.

Sodium carbonate was supplied by Mallinckrodt, Inc., St. Louis, Mo. Ferrous sulfide (99.999%) was purchased from Research Organic/Inorganic Chemical Corporation, Sun Valley, Calif. Dihydroanthracene was supplied by Pfaltz and Bauer, Inc., Stanford, Conn. The structure of 1,2,3,4-tetrahydroanthracene is postulated on the basis of its relative retention time and mass spectrum fragmentation pattern comparison to that of 1,2,3,4-tetrahydronaphthalene, cf. Table I. Dihydroanthracene proved identical to an authentic sample of 9,10-dihydroanthracene by GLC retention time and mass spectrum fragmentation pattern.

Results and Discussion

The reduction results of anthracene under 11 conditions and 9,10-dihydroanthracene under 2 conditions are given in Table II. Table III presents data from GLC–mass spectrometry analysis of the anthracene reaction products (run 3 in Table II). The mass spectrometrically determined "tetrahydroanthracene" of Table III is a mixture of 1,2,3,4-tetrahydroanthracene and methylbenzohydrindene as shown by GLC analysis.

Anthracene is pyrolytically stable under the conditions of these reductions, cf. run 1, Table II. With reducing gases, the principal products of the anthracene are tetrahydroanthracene (42–59%), 9,10-dihydroanthracene (14–23%), and an isomer of tetrahydroanthracene, methylbenzohydrindene (7–17%). Cracking occurs to give 3–8% of naphthalenes, biphenyl, and benzenes (Table III) along with ca. 1% dimerization. Methylation occurs to a minor extent forming methylanthracene.

In regard to reducing gases for anthracene in the absence of added potential catalysts, hydrogen alone is the superior performer giving a 97% conversion and 59% yield of tetrahydroanthracene (run 2 of Table II). Water (run 4) reduces the conversion and product yields for all but dihydroanthracene. This implies the reduction sequence: anthracene → dihydroanthracene → tetrahydroanthracene and cracked products. Carbon monoxide and water (run 5) give comparable conversions to that of hydrogen and water, lower yields of dihydro- and tetrahydroanthracene and higher yields of rearranged and cracked products. The blend of carbon monoxide, water, and hydrogen (run 6) offers merely an averaged response.

Table II. Reduction of Anthracene (A)[a] and Dihydroanthracene (D)[a,b] at 425 °C

run/ (compd)	gas[c]	catalyst	dihydro-anthracene, %, or anthracene, %	tetrahydro-anthracene, %	methylbenzo-hydrindene, %	cracked, %	conversion, %
1/(A)	Ar, H_2O	Na_2CO_3	3.6 (D)	0.0	0.0	0.0	3.6
2/(A)	H_2	none	13.6 (D)	59.0	16.2	7.9	96.7
3/(A)	CO, H_2	none	16.3 (D)	41.5	14.8	4.3	76.9
4/(A)	H_2, H_2O	none	17.2 (D)	56.2	11.9	6.0	91.3
5/(A)	CO, H_2O	none	13.3 (D)	53.2	16.9	7.4	90.8
6/(A)	CO, H_2O, H_2	none	15.3 (D)	55.0	13.1	6.3	89.7
7/(A)	H_2, H_2O	Na_2CO_3	23.1 (D)	52.3	6.8	3.4	85.6
8/(A)	CO, H_2O	Na_2CO_3	20.3 (D)	52.7	8.5	3.9	84.6
9/(A)	CO, H_2O,H_2	Na_2CO_3	21.8 (D)	51.9	8.7	4.5	86.9
10/(A)	CO, H_2O, H_2	Na_2CO_3 (with tetralin)[e]	13.7 (D)	38.9	20.0	16.2	88.8
11/(A)	CO, H_2O, H_2	FeS	14.8 (D)	33.4	16.2	8.6	73.0
12/(D)	H_2, H_2O	none	8.7 (A)	53.3	8.3	5.4	75.7
13/(D)	H_2, H_2O	Na_2CO_3	9.3 (A)	56.9	9.6	5.0	80.0

[a] 0.15 mol. [b] 9,10-Dihydroanthracene supplied by Pfaltz and Bauer, Inc., Stanford, Conn., containing 7% anthracene. [c] Each gas at 750 psi, except when hydrogen and carbon monoxide are used simultaneously, then each are at 375 psi. [d] Weight percent. [e] 0.15 mol of which 73% was converted principally into naphthalene (47%) plus ca. 26% fragmented products.

Table III. GLC–Mass Spectral Analysis of the Anthracene Reaction Solution (Run 3, Table II)[a]

probable compd	wt, %	probable compd	wt, %
dimer of anthracene	0.5	anthracene	39.5
methylanthracene	0.2	methylbiphenyl	1.0
octahydroanthracene	0.5	dimethylnaphthalenes	0.2
hexahydroanthracene	1.7	biphenyl	0.1
tetrahydroanthracene	44.1	methylnaphthalenes	0.6
dihydroanthracene	11.6		

[a] These results were based on one specific reaction solution.

The presence of the base sodium carbonate reduced the overall conversion, reduced the yields of rearrangement and cracking products, maintained the yield of tetrahydroanthracene, and increased the yield of dihydroanthracene, cf. runs 7–9 with 4–6, Table II. This infers the reduction sequence: anthracene → dihydroanthracene → tetrahydroanthracene → rearranged and cracked products by further retarding the reduction from that caused by water.

Again, as in the absence of sodium carbonate (runs 5 and 6 with 4, Table II), the presence of carbon monoxide and water (runs 8 and 9 with run 7) gives comparable conversions to that of hydrogen and slightly higher yields of rearranged and cracked products. The yields of dihydro- and tetrahydroanthracene remain about the same on changing reducing gases (runs 4, 5, 6 and 7, 8, 9). Thus carbon monoxide and water probably reacts through several reaction pathways, one of which is via the shift reaction.

The presence of the hydrogen donor solvent tetralin maintained the anthracene conversion yields (run 10 vs. 9, Table II) and promoted fragmentation and rearrangement at the expense of dihydro- and tetrahydroanthracene yields. Ferrous sulfide reduced the conversion more than did sodium carbonate and, in contrast to sodium carbonate, it further enhanced rearrangement and cracking (run 11 vs. 9 and 6).

To check the reaction sequence order, 9,10-dihydroanthracene was exposed to the conditions of the anthracene reaction, and it did form the expected products (runs 12 and 13, Table II). In addition, anthracene was formed which implied that dihydroanthracene disproportionates during the reduction. With the exception of anthracene, the distribution of products in the dihydroanthracene reaction mixture approximate that of the anthracene reaction solutions. Hence the reduction sequence now becomes: anthracene $\rightleftharpoons$ dihydroanthracene → tetrahydroanthracene → rearranged and cracked products. These conclusions are in accord of the postulated pathways for anthracene reduction of Blom et al.[13] and Quader et al.[14]

The results of quinoline reduction under 14 conditions are illustrated in Table IV. The complex mixture of reaction products from run 8, Table IV, are illustrated in Table V. 1,2,3,4-Tetrahydroquinoline is the major reaction product. As with anthracene, dimerization and methylation occurs. Products of lower molecular weights than quinoline and those with higher molecular weights than quinoline have been gathered together in the table with the exception of 1,2,3,4-tetrahydroquinoline. Quinoline, itself, is thermally stable (runs 1 and 7, Table IV).

In the absence of added possible catalysts and water, hydrogen gas is superior to carbon monoxide for converting quinoline into products, i.e., H_2 (run 3) > H_2–CO (run 2) ≫ CO (run 1), Table IV. Carbon monoxide does not reduce quinoline to any appreciable extent. The presence of water aids the carbon monoxide reductions of quinoline (runs 4 and 5 with runs 1 and 2) but has no effect on the hydrogen one. These results are consistent with the carbon monoxide reduction proceeding through the shift reaction, and that hydrogen is the principal reducing agent.

The base, sodium carbonate, does promote the carbon monoxide reduction conversion, cf. run 4 vs. 8, Table IV, but did not influence the product distribution. Sodium carbonate has little effect on the carbon monoxide–water–hydrogen reduction, cf. run 5 vs. 9, and has a negative effect on the hydrogen reduction, cf. run 6 vs. 10.

The neutral catalyst, iron sulfide, is slightly superior to sodium carbonate for catalyzing the carbon monoxide reduction conversion and promotes fragmentation and dimerization to a greater extent, cf. runs 8 with 11 and 9 with 12, Table IV. Therefore, base strength is not the only factor for the quinoline reduction catalysis. The hydrogen donor solvent, tetralin, has little effect on the reduction conversions of quinoline, cf. runs 12 with 13 and 9 with 14.

Since the quinoline product distribution for the hydrogen reduction differs little from that of the carbon monoxide reduction, the methylation carbons most probably originate from the fragmentation process of the heterocyclic ring of quinoline. However, carbon monoxide must be considered as an alternate source.[18]

The dimer products of quinoline and anthracene presumably originate from radical processes and represent a possible mechanism for the "repolymerization" thought to occur during the liquefaction of coals.

Table IV. Reduction of Quinoline[a]

run	reducing agent[b]	solvent[a]	catalysts[c]	1,2,3,4-tetrahydroquinoline, %[d]	fragmentation, %[d]	higher mol[d] wt products, %	conversion, %[e]
1	CO	none	none	0	0	0	1
2	CO–H_2	none	none	21	3	12	36
3	H_2	none	none	42	6	15	63
4	CO–H_2O	none	none	9	1	2	12
5	CO–H_2O–H_2	none	none	28	4	11	43
6	H_2–H_2O	none	none	44	6	13	63
7	none	none	Na_2CO_3	0	0	0	1
8	CO–H_2O	none	Na_2CO_3	31	3	7	41
9	CO–H_2O–H_2	none	Na_2CO_3	31	3	7	41
10	H_2–H_2O	none	Na_2CO_3	20	2	7	29
11	CO–H_2O	none	FeS	28	6	11	45
12	CO–H_2O–H_2	none	FeS	39	6	14	59
13	CO–H_2O–H_2	tetralin	FeS	41	2	15	58
14	CO–H_2O–H_2	tetralin	Na_2CO_3	24	3	9	36

[a] 0.15 mol. [b] Each gas at 750 psi, except when hydrogen and carbon monoxide are used simultaneously, then each are at 375 psi. [c] 0.015 mol. [d] Normalized to converted quinoline. [e] Based on converted quinoline.

Table V. GLC–Mass Spectral Analysis of the Quinoline Reaction Solution (Run 8, Table IV)

probable compd	wt, %	probable compd	wt, %
tetrahydroquinoline dimer	0.01	hexahydroquinoline	0.7
dihydroquinoline dimer	0.04	tetrahydroquinoline	26.4
quinoline dimer	0.6	dihydroquinoline	1.7
tetrahydromethylquinoline	0.02	quinoline	63.2
dimethylquinoline	0.3	dimethylaniline	0.5
tetrahydromethylquinoline	1.1	indan	0.6
dihydromethylquinoline	0.3	methylaniline	3.3
methylquinoline	0.4	aniline	0.6
methylnaphthalene	0.2		

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Registry No.—1,2,3,4-Tetrahydronaphthalene, 119-64-2; 1,2,3,4-tetrahydroanthracene, 2141-42-6; anthracene, 120-12-7; 9,10-dihydroanthracene, 613-31-0; methylbenzohydrindene, 37977-37-0; quinoline, 91-22-5; 1,2,3,4-tetrahydroquinoline, 635-46-1; CO-H_2O, 40217-37-6; CO-H_2O-H_2, 66402-63-9; H_2, 1333-74-0.

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Chemistry of Allene Oxides[1,2]

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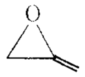
A general and facile method to the highly reactive allene oxides has been developed. 1-*tert*-Butylallene oxide is isolated and characterized. 1-Alkyl-, 3-alkyl-, and 3-aryl-substituted allene oxides, when similarly generated, suffer regiospecific nucleophilic epoxide opening to give substituted ketones. On the other hand, 1-aryl- and 1,1-dialkyl-substituted allene oxides give products characteristic of cyclopropanones. These allene oxides, once generated, are believed to have undergone facile isomerization to cyclopropanones. The mechanism of the isomerization process is discussed.

Allene oxide (1) is an extremely unusual molecule. Within its simple framework, it has encompassed the structural features of epoxide, double bond, and enol ether. Allene oxide is also highly strained. Several quantum mechanical calculations[3–8] have concluded that it has a higher energy content than cyclopropanone (2), a molecule already notorious for its instability and reactivity.[9] It is not surprising, therefore, to find that allene oxide is very reactive and has eluded isolation. Prior to our work, only two substituted allene oxides, 1,1-di-*tert*-butyl[10] and 1,1,3-tri-*tert*-butyl,[11,12] both sterically encumbered, have been properly characterized. There are reasons, however, other than its intrinsic interest, to investigate the chemistry of allene oxide. Reactions at carbon-1 and carbon-3 of the allene oxide molecule should render it a useful synthon (eq 1). Furthermore, allene oxide is linked structurally to its valence tautomers, cyclopropanone (2)[8,9] and oxyallyl (3),[13] interesting species in their own right. The relationships between these isomers have not been entirely clear and are a problem of much current interest.[14] There are two aspects to the problem; one is the relative stability of these structures and the other is the mechanism of the isomerization process. An understanding of this problem would inevitably lead to a better understanding of the fundamental nature of bonding in small-ring compounds and may cast light on the validity of some of the theoretical calculations.



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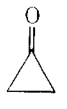

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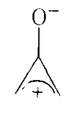

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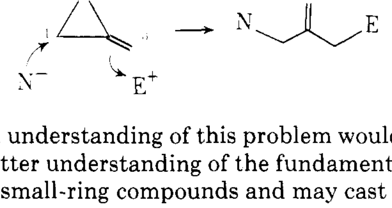

(1)

One difficulty associated with the study of the chemistry of allene oxides is the lack of an adequate method of synthesis. A generally employed approach is by way of epoxidation of allenes, which, for all practical purposes, means the reaction of allenes with peracids (eq 2).[15] This approach suffers the

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