tached to the system. After the reaction is complete, water is added dropwise to decompose the excess hydride, and the volume of hydrogen is measured.

Filtered solutions of lithium aluminum hydride in diethyl ether are prepared in bulk, following the procedure of Finholt, Bond and Schlesinger.[1] These stock solutions are assayed by the method given by these authors and stored in closed containers until needed. The solid hydride obtained from Metal Hydrides assayed 84% lithium aluminum hydride. However, after dissolving the material in ether and filtering through a sintered glass funnel using helium pressure the product assayed 94% lithium aluminum hydride.

Following procedures similar to those outlined below, modified only to the extent necessitated by the individual problems of isolating and purifying the products, a number of nitriles were reduced using the same concentration of organic material and hydride.

Reduction of Diphenylacetonitrile to 2,2-Diphenylethylamine by LiAlH$_4$.—A one-liter, three-necked flask was equipped with a reflux condenser, a mechanical mercury-sealed stirrer and a dropping funnel. The gas outlet tube on the condenser was attached to two traps cooled at −80° and then to a wet-test meter. A solution of 0.1 mole of lithium aluminum hydride in 250 ml. of ether was placed in the flask. Through the dropping funnel, a solution of 19.3 g. (0.1 mole) of diphenylacetonitrile in 200 ml. of ether was added dropwise to the well-stirred mixture. During the addition of nitrile, hydrogen was liberated and by calculation the standard volume was 1.03 liters. One hour after the last addition of organic compound, water was added dropwise to decompose the excess hydride and the volume of gas evolved was measured. By calculation the standard volume was found to be 5.13 liters. Then 140 ml. of 6 *N* sulfuric acid and 100 ml. of water were added. The clear mixture was transferred to a separatory funnel and, after separating the ether layer, the aqueous layer was extracted with four 100-ml. portions of ether. Next the aqueous layer was cooled by ice-water and potassium hydroxide pellets were cautiously added until the *p*H of the solution was 11. The basic mixture was diluted with 600 ml. of water and then extracted with four 100-ml. portions of ether. From the combined ether extracts there was obtained, after drying over drierite and removal of ether, 6.5 g. of crude material in the acid extract and 14 g. of crude material in the basic extract. The latter was purified by fractional distillation through a 12-inch column under reduced pressure and there was obtained a 61% yield of 2,2-diphenylethylamine, b.p. 182° (14 mm.), m.p. 44–44.5°. The acetyl derivative melted at 88–89°.

Reduction of Diphenylacetonitrile to 2,2-Diphenylethylamine by LiAlH$_4$–AlCl$_3$.—The apparatus described above was employed. A solution of 0.1 mole of lithium aluminum hydride in 100 ml. of ether was placed in the three-necked flask. Through the dropping funnel, a solution of 13.3 g. (0.1 mole) of aluminum chloride in 150 ml. of ether was added rapidly to the hydride solution. Five minutes after the last addition of halide, a solution of 19.3 g. (0.1 mole) of diphenylacetonitrile in 200 ml. of ether was added dropwise to the well-stirred mixture. An evolution of 0.075 liter of hydrogen was noted during the addition of nitrile. One hour after the last addition of organic compound, water was added dropwise to decompose the excess hydride and the volume of gas evolved was measured. By calculation the standard volume of hydrogen was found to be 4.14 liters. The reaction mixture was treated as described in the previous example. From the combined ether extracts there was obtained, after drying over drierite and removal of ether, 0.5 g. of crude material from the acid extract and 21 g. of crude material from the basic extract. The latter was purified by fractional distillation through a 12-inch column under reduced pressure and there was obtained a 91% yield of 2,2-diphenylethylamine, b.p. 184° (17 mm.), m.p. 44–45°. The acetyl derivative melted at 88.5–89°.

Attempted Reduction of *p*-Nitrotoluene by LiAlH$_4$–AlCl$_3$.—The apparatus and techniques described above were employed. During the addition of *p*-nitrotoluene to the hydride solution, no evolution of hydrogen was noted. Five minutes after the last addition of nitro compound, 50 ml. of water was added dropwise to decompose the excess hydride. The organic material was isolated in the usual manner and the starting material was recovered.

By employing longer reaction times before hydrolysis in other experiments, a liberation of hydrogen and production of basic material was noted. The results of these experiments will be reported in a forthcoming paper.

URBANA, ILLINOIS

NOTES

The Relative Rates of Reaction of Hexamethylbenzene and Hexaethylbenzene with Perbenzoic Acid

BY L. J. ANDREWS AND R. M. KEEFER

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The equilibrium constant for the interaction of hexaethylbenzene with iodine to form a 1:1 complex in carbon tetrachloride solution is much less than that for hexamethylbenzene.[1,2] Presumably the alkyl groups of hexaethylbenzene are collectively sufficiently bulky to prevent the close approach of the iodine acceptor to the π-electrons of the aromatic nucleus.[3]

In the absence of such steric problems the equilibrium to form aromatic donor–acceptor complexes is electronically favored by an increase in the number of alkyl substituents in the donor molecule; similarly an increase in the number of alkyl substituents in general enhances the rate at which the aromatic nucleus is attacked by electrophilic reagents.[4] Therefore the possibility has been considered that the steric barrier which leads to repression of formation of the hexaethylbenzene complex might also have an unfavorable effect on the kinetic course of the reaction of hexaethylbenzene with an electrophilic reagent. This point has been tested in the present study by determining the relative rates of reaction of hexamethylbenzene and hexaethylbenzene with perbenzoic acid in chloroform solution at 25°.[5] To evaluate the relative contributions of electronic influences of methyl and ethyl ring substituents to the over-all kinetic picture, the rates of reaction of mesitylene and *sym*-

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(1) L. J. Andrews and R. M. Keefer, THIS JOURNAL, **74**, 4500 (1952).

(2) M. Tamres, D. R. Virzi and S. Searles, *ibid.*, **75**, 4358 (1953).

(3) R. M. Keefer and L. J. Andrews, *ibid.*, **77**, 2164 (1955).

(4) L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954).

(5) It has been established previously that perbenzoic acid functions as an electrophilic reagent in initiating the oxidation of aromatic substances to form ring cleavage products or quinoid derivatives: *cf.* I. M. Roitt and W. A. Waters, *J. Chem. Soc.*, 3060 (1949); S. L. Friess and A. Miller, THIS JOURNAL, **72**, 2611 (1950); S. L. Friess, A. H. Soloway, B. K. Morse and W. C. Ingersoll, *ibid.*, **74**, 1305 (1952).

triethylbenzene (in which unfavorable steric situations are presumed to be absent) with perbenzoic acid also have been investigated. It should be noted that the equilibrium constant for formation of the iodine complex of *sym*-triethylbenzene is only slightly less than that of mesitylene.[3]

Because perbenzoic acid decomposes slowly even at room temperature it has not been possible to establish with certainty the number of moles of perbenzoic acid which are consumed per mole of aromatic hydrocarbon which is oxidized. Experiments similar to those made by Friess and Miller[5] on the reaction of mesitylene with a large excess of perbenzoic acid suggest that in the reaction of hexamethylbenzene, the most reactive of the hydrocarbons considered in this investigation, four moles of perbenzoic acid are used per mole of aromatic substance. All of the rate data taken for the several hydrocarbons at 25° have been interpreted successfully by the bimolecular rate law

$$k = \frac{2.303}{t(\text{PBA}-4\text{Ar})} \log \frac{(\text{Ar})(\text{PBA}-4x)}{(\text{PBA})(\text{Ar}-x)} \qquad (1)$$

in which (PBA) and (Ar) are the initial concentrations of perbenzoic acid and aromatic material and $(\text{PBA}-4x)$ is the measured concentration of perbenzoic acid at time t. It appears that the rate-determining step in these reactions involves one molecule each of hydrocarbon and perbenzoic acid and that all following reactions are rapid. The rate constants reported in Table I have been calculated from the slopes of straight lines obtained by plotting log $(\text{PBA}-4x)/(\text{Ar}-x)$ *vs.* t. In general, data recorded to at least two-thirds of completion of reaction conform to these plots.[6]

The observed rate constants vary somewhat with changes in the method of preparation of the reaction mixtures. The initial perbenzoic acid concentrations which are reported in Table I were attained by mixing varying amounts of chloroform and a stock solution of perbenzoic acid in chloroform.[7] The stock perbenzoic acid solution, because of the manner in which it was prepared, undoubtedly contained small amounts of solvents other than chloroform which influenced the reaction rate in a manner determined by the amounts in which they were present in the reaction mixture. The last column of Table I lists the percentage by volume to which the stock perbenzoic acid contributed to the total solvent mixture in each run. In spite of these solvent effects it would appear that for hexamethylbenzene and hexaethylbenzene, which were investigated in some detail, k values are independent of changes in concentration of perbenzoic acid and of hydrocarbon.

Table II shows the ratio of rate constants for the reactions of hexamethylbenzene and hexaethylbenzene in the various solvent mixtures. The rate ratios vary from about 7 to 12 depending on the solvent mixture. The rate ratio for mesitylene and *sym*-triethylbenzene in a solvent composed entirely of stock perbenzoic acid solution is 1.48, while that for hexamethylbenzene and hexaethylbenzene in the same solvent is 7.37.

TABLE I

RATE CONSTANTS FOR THE REACTION OF PERBENZOIC ACID AND POLYALKYLBENZENES (25°)

(Ar), mole/l.	(PBA), mole/l.	k, hr.$^{-1}$ mole^{-1} l.	Volume % stock PBA in solution
	Ar = hexamethylbenzene		
0.0198	0.1160	0.70	100
.0133	.1370	0.81	100
.0571	.0688	1.17	50
.0272	.0700	1.22	50
.0129	.0676	1.23	50
.0130	.0411	1.52	30
.0555	.0268	1.57	20
.0276	.0270	1.55	20
.0545	.0137	1.77	10
	Ar = hexaethylbenzene		
0.1148	0.0505	0.103	100
.0505	.0697	.183	50
.0263	.0703	.202	50
.1505	.0267	.165	20
.0756	.0268	.176	20
.0771	.0135	.147	10
	Ar = mesitylene		
0.500	0.217	0.0191	100
.254	.231	.0222	100
	Ar = *sym*-triethylbenzene		
0.477	0.213	0.0124	100
.244	.226	.0155	100

TABLE II

RATE CONSTANT RATIOS FOR THE POLYMETHYLBENZENES AND POLYETHYLBENZENES (25°)[a]

Volume % stock PBA in soln.	100	50	20	10
$k_{\text{HMB}}/k_{\text{HEtB}}$	7.37	6.27	9.1	12.0
$k_{\text{Mes}}/k_{s\text{-TEB}}$	1.48	...	..	..

[a] HMB, HEtB, Mes and *s*-TEB refer to hexamethylbenzene, hexaethylbenzene, mesitylene and *sym*-triethylbenzene, respectively. The rate ratios are based on averages of k values for a given solvent mixture.

Hexaethylbenzene is therefore considerably less reactive compared to hexamethylbenzene than it should be if the rate behavior of the trialkylbenzenes is a safe criterion of the relative electronic effects of methyl and ethyl groups in controlling these reaction rates. However the differences in the ratios of rate constants for the hexaalkyl- and trialkylbenzenes is not sufficiently great so that these results may be regarded as dramatic proof that the ethyl groups in hexaethylbenzene hinder sterically the formation of the transition state intermediate in the oxidation reaction. Since the association of the aromatic hydrocarbon and the electrophilic reagent in the transition state must be considerably more intimate than that of a donor and acceptor in a π-complex, it is entirely conceivable that even the methyl groups of hexamethylbenzene may offer some steric inhibition in the per-

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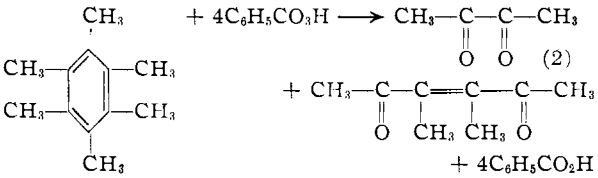
(6) The kinetic data may be explained equally well in terms of a bimolecular rate law based on the assumption that six moles of perbenzoic acid are consumed per mole of hydrocarbon. The k values thus obtained do not conflict with the conclusions made on the basis of the data summarized in Tables I and II. When the data are treated in terms of integers less than four for the ratio of moles of perbenzoic acid consumed per mole of hydrocarbon, individual runs cannot be analyzed successfully according to a bimolecular rate law.

(7) Prepared in chloroform solution according to the directions of M. Tiffeneau "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 422.

benzoic acid reaction. Such a methyl group steric effect may account for the relatively low observed ratios for the rate constants for the two hexaalkylbenzenes.

Since no broad interpretation of the present results seems justified, no extensive investigation of the products or mechanisms of these oxidation reactions has been undertaken. Some attention has been given to the nature of the reaction products of hexamethylbenzene. The spectrum of a dilute solution of this hydrocarbon and perbenzoic acid was found to develop an absorption peak in the vicinity of 315 mμ which resembled that of an α,β-unsaturated carbonyl compound. The composition of the reaction products was rather complex, and attempts to isolate a pure unsaturated carbonyl compound were unsuccessful. However, samples of crude products showed general chemical properties which were similar to those reported for diacetylethylene.[8] Biacetyl was identified in the reaction product by its odor and by its isolation as its bis-2,4-dinitrophenylhydrazone. In view of these facts and the observed stoichiometry, it is suggested that the oxidation of hexamethylbenzene by perbenzoic acid may, in large part, be accounted for by the equation



(2)

Experimental

The Rate Runs.—All chloroform used in these experiments had been washed successively with concentrated sulfuric acid, dilute sodium hydroxide and water and dried over calcium chloride. This material and the stock solution of perbenzoic acid, which was dried over sodium sulfate, were stored in the refrigerator. Solutions for rate work were prepared by adding known volumes of chloroform and perbenzoic acid solutions, which previously had been warmed to 25°, to weighed amounts of the aromatic hydrocarbons. The resultant solutions were stored in a 25° bath, and samples which were removed from time to time were analyzed for unreacted perbenzoic acid by addition to acidified potassium iodide solution followed by titration with standard sodium thiosulfate solution. The comments of Friess and Miller[5] concerning the necessity for corrections, based on blank runs, for spontaneous decreases in perbenzoic acid concentrations during the rate runs were found to be generally applicable in this work. The concentrations of perbenzoic acid at zero times were assigned on the basis of analyses made immediately after preparation of the reaction mixtures.

The Products of Reaction of Hexamethylbenzene and Perbenzoic acid.—One ml. of a solution of 0.50 *M* hexamethylbenzene in carbon tetrachloride was treated with 1 ml. of a 0.15 *M* solution of perbenzoic acid in chloroform and 8 ml. of carbon tetrachloride. The optical densities of this solution over a wave length range of 300–400 mμ were determined from time to time using a 0.050 *M* carbon tetrachloride solution of hexamethylbenzene as a blank. At the outset the solution showed relatively low absorption in this region, but rather rapidly developed an absorption peak at 315 mμ. After several days this peak reached a maximum value of $d_{315 m\mu}$ = 0.985 and had the characteristic shape and wave length of maximum absorption of an α,β-unsaturated carbonyl compound in a non-polar solvent.[9]

For product isolation work 3.33 g. (0.0205 mole) of hexamethylbenzene was dissolved in 500 ml. of a cold chloroform solution of 0.165 *M* perbenzoic acid. After four days at room temperature this solution was light yellow, and analysis showed that the perbenzoic acid concentration had fallen to 0.0158 *M*. The solution was extracted repeatedly with 10% sodium carbonate solution until the extracts no longer yielded a precipitate of benzoic acid on acidification. The chloroform phase was dried over sodium sulfate, and the solvent was removed by distillation first at atmospheric pressure and finally at 200 mm. The viscous oily yellow-orange residue was distilled at 8 mm. pressure. Considerable difficulty was experienced during the distillation owing to partial solidification of distillate in the condenser, and accurate recordings of distillation temperature (in the region of 100°) could not be made. The odor of biacetyl was detectable in the exodus stream of the vacuum pump.

The crystalline material in the distillate was identified as unreacted hexamethylbenzene through two recrystallizations from aqueous methanol, m.p. 160–161°. Small samples of the distillate gave positive Fehling and Tollens tests, reduced neutral permanganate solutions and absorbed bromine from its solution in carbon tetrachloride.

Samples of the oily distillate were treated with ethanolic or methanolic solutions of 2,4-dinitrophenylhydrazine in an attempt to separate a derivative of what was presumed to be *sym*-dimethyldiacetylethylene. In all cases a brick-red precipitate formed slowly. When this material was recrystallized from ethanol, it melted over a wide range terminating at about 170°. Attempts were made to fractionate this material, which was obviously a mixture, by chromatographic techniques. However the dinitrophenylhydrazone mixture could not be induced to move on the column; this behavior is characteristic of dicarbonyl derivative of this type.[10]

Samples of the crude derivative were recrystallized from nitrobenzene and also from pyridine. In both cases the recovery was poor. From nitrobenzene fine brick-red needles were obtained which melted at about 315° dec., on an electrically heated block. An authentic sample of biacetyl bis-2,4-dinitrophenylhydrazone melted at about 320° dec., and mixtures of the two samples melted at 320°. Combustion analysis of the isolated material also suggested that it was the biacetyl derivative. *Anal.* Calcd. for $C_{16}H_{14}N_8O_8$: C, 43.05; H, 3.16. Found: C, 43.64; H, 3.25. Apparently small amounts of biacetyl survived the reduced pressure distillation.

From pyridine fine dark brownish-red needles were obtained. These darkened and sintered at 304°, but no true melting occurred even at higher temperatures. The material was probably a mixture of dicarbonyl derivatives. Combustion analysis gave inconclusive results. *Anal.* Found: C, 44.31; H, 3.9.

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(8) K. F. Armstrong and R. Robinson, *J. Chem. Soc.*, 1650 (1934).

(9) *Cf.* data for spectra of crotonaldehyde and mesityl oxide in hexane, Landolt-Börnstein, "Physikalisch-Chemisch Tabellen," Erster Ergänzungsband, Fünfte Anflage, Julius Springer, Berlin, 1927, pp. 446, 453.

(10) R. E. Kepner, private communication.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
DAVIS, CALIFORNIA

Decomposition of Quaternary Salts. III. Carbinols of the Methadol Type

BY NELSON R. EASTON[1] AND VELMER B. FISH

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In the first papers of this series[2,3] the pyrolytic decomposition of dimethylamino ketones of the methadone type were reported to give ethylidene tetrahydrofurans of the general formula II. Since this reaction involves the formation of a carbon-to-oxygen bond between the ketonic oxygen and the carbon atom attached to the amino group, it would seem quite logical that the carbinols III produced

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(1) Lilly Research Laboratories, Eli Lilly and Company, Indianapolis, Ind.

(2) N. R. Easton, S. J. Nelson, V. B. Fish and P. N. Craig, THIS JOURNAL, 75, 3751 (1953).

(3) N. R. Easton and V. B. Fish, *ibid.*, 76, 2836 (1954).