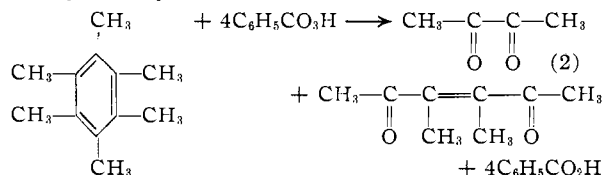


benzoic acid reaction. Such a methyl group steric effect may account for the relatively low observed ratios for the rate constants for the two hexaalkylbenzenes.

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 $315\text{ m}\mu$ 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 diacetyl-ethylene.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



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 Miller⁶ 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 $300\text{--}400\text{ m}\mu$ 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 $315\text{ m}\mu$. After several days this peak reached a maximum value of $d_{315\text{m}\mu} = 0.985$ and had the characteristic shape and wave length of maximum absorption of an α,β -unsaturated carbonyl compound in a non-polar solvent.⁹

(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 Auflage, Julius Springer, Berlin, 1927, pp. 446, 453.

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. $160\text{--}161^\circ$. 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*-dimethyldiacetyl-ethylene. 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 $\text{C}_{16}\text{H}_{14}\text{N}_8\text{O}_8$: 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.

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

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

BY NELSON R. EASTON¹ AND VELMER B. FISH

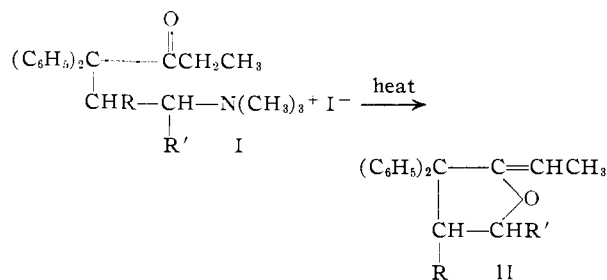
RECEIVED SEPTEMBER 20, 1954

In the first papers of this series^{2,3} the pyrolytic decomposition of dimethylamino ketones of the methadol 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

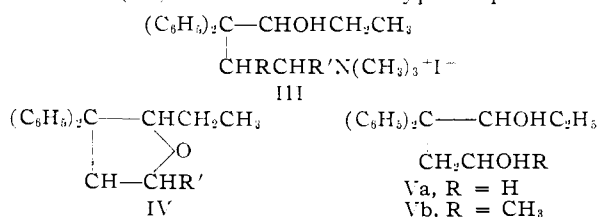
(1) Lilly Research Laboratories, Eli Lilly and Company, Indianapolis, Ind.

(2) N. R. Easton, S. J. Nelson, V. B. Fish and P. N. Craig, *THIS JOURNAL*, **76**, 3751 (1953).

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



by the reduction of these ketones should give an analogous reaction to produce substituted tetrahydrofurans (IV). Carbinols of this type are produced



readily by the reduction of the ketones with lithium aluminum hydride.⁴⁻⁸ In the case of methadone and isomethadone, two *dl*-pairs are possible but only one (α) is isolated when the reduction is carried out with lithium aluminum hydride, whereas both are produced when the reduction is effected by sodium and isopropyl alcohol; in this case the β -form is the predominant one.⁷ In this study we have used only the α -forms of these carbinols and have included α -*dl*-methadol, α -*d*-, α -*l*- and α -*dl*-isomethadol and 6-dimethylamino-4,4-diphenyl-3-hexanol. In each case the reaction proceeded smoothly to give the expected products.

The preparation of 2-ethyl-3,3-diphenyltetrahydrofuran and its 5-methyl derivative by the cyclization of the diols has been reported.⁹ The syntheses of the diols were by the action of ethylmagnesium bromide on the 2,2-diphenylbutano- and pentanolactones. Although the presence of two optically active centers in the diol Vb would necessitate the existence of 2 *dl*-pairs, only one was isolated from the above reaction.⁹ This indicates the highly stereospecific attack of the Grignard reagent upon the lactone or, more probably, upon some intermediate product. It is of interest to note that the identical form of the tetrahydrofuran IV was produced from the cyclization of Vb as that obtained by the decomposition of the methiodide of α -*dl*-methadol. This methadol isomer is the one obtained by the lithium aluminum hydride reduction of methadone,⁷ and also this reaction was stereospecific. Since it is quite probable¹⁰ that the formation of the tetrahydrofuran by means of the decomposition of the quaternary salt is the rearward attack of the oxygen atom on the carbon atom attached to the nitrogen moiety, this would cause an inversion

(4) M. E. Speeter, W. M. Byrd, L. C. Cheney and S. B. Binkley, *THIS JOURNAL*, **71**, 57 (1949).

(5) A. Pohland, F. J. Marshall and T. P. Carney, *ibid.*, **71**, 460 (1949).

(6) E. L. May and E. Mosettig, *J. Org. Chem.*, **13**, 459, 663 (1948).

(7) N. B. Eddy, E. L. May and E. Mosettig, *ibid.*, **17**, 321 (1952).

(8) E. L. May and N. B. Eddy, *ibid.*, **17**, 1210 (1952).

(9) N. R. Easton, C. A. Lukach, V. B. Fish and P. N. Craig, *THIS JOURNAL*, **75**, 4731 (1953).

(10) N. R. Easton and V. B. Fish (to be published).

of this atom. Therefore, the conversion of the amino alcohol to the tetrahydrofuran also involves a stereochemical change. Whether a similar change takes place during the formation of the tetrahydrofuran from the diol has not been determined.

It has been reported,² that the pyrolysis of the quaternary hydroxide of methadone causes a cleavage of the propionyl group to give 1,1-diphenyl-3-dimethylaminopropane but no neutral material is produced. However, the ethylenetetrahydrofurans are produced from both isomethadone and 6-dimethylamino-4,4-diphenyl-3-hexanone under these conditions. Therefore, it was decided to investigate the pyrolysis of the quaternary hydroxide of α -*dl*-methadol under the same conditions. It was found that the pyrolysis of the quaternary hydroxide of α -*dl*-methadol gave the same tetrahydrofuran as did the methiodide but only in a very small yield. Another neutral product was formed and the structure of this compound is now under investigation. The quaternary hydroxide of α -*d*-isomethadol, however, gave the expected tetrahydrofuran in slightly better yield than that obtained from the methiodide.

Acknowledgment.—The authors wish to thank Dr. E. L. May for the sample of α -*dl*-methadol and the Mallinckrodt Chemical Works for the samples of isomethadone used in these experiments.

Experimental

PHYSICAL CONSTANTS OF METHIODIDES

Compound	Derivative	M.p., °C. (dec.)	Analyses, %		α^{20D} (2.5% in EtOH)
			Found	Calcd.	
α - <i>dl</i> -Methadol	Me I	193-194	C	58.30	58.27
			H	7.19	7.11
α - <i>dl</i> -Isomethadol	Me I	225-226	I	28.20	27.99
α - <i>d</i> -Isomethadol	Me I	224-225	I	27.80	27.99 +24.2°
α - <i>l</i> -Isomethadol	Me I	224-225	I	27.85	27.99 -24.4°
6-Dimethylamino-4,4-diphenyl-3-hexanol	Me I	187-189	C	57.05	57.40
			H	7.03	6.88

PHYSICAL CONSTANTS OF 2-ETHYL-3,3-DIPHENYLTETRAHYDROFURANS

Substituents	M.p., °C.	Yield g. (from 5 g. methiodide)	Analyses, %		Empirical formula	
			Found	Calcd.		
None	70-71 ^a	1.2	C	85.45	85.67	C ₁₈ H ₂₀ O
			H	7.76	7.99	
α - <i>dl</i> -5-Me	89-90 ^b		C	85.80	85.67	C ₁₉ H ₂₂ O
			H	8.45	8.33	
α - <i>dl</i> -4-Me	73.5-75	1.4	C	85.60	85.67	C ₁₉ H ₂₂ O
			H	8.21	8.33	
α - <i>d</i> -4-Me ^c	62.5-64	1.1	C	85.90	85.67	C ₁₉ H ₂₂ O
			H	8.53	8.33	
α - <i>l</i> -4-Me ^d	62-63.5	1.3	C	85.50	85.67	C ₁₉ H ₂₂ O
			H	8.53	8.33	

^a Reported⁹ 70-71°. ^b Reported⁹ 89.5-90.5°. ^c α^{20D} +43.6° (2.5% in ethanol). ^d α^{20D} -43.8° (2.5% in ethanol).

The carbinols were prepared by the reduction of the ketones with lithium aluminum hydride.

The methiodides were prepared in the usual manner and recrystallized from methanol or ethanol with the exception of the methiodide of α -*dl*-methadol which was recrystallized from acetone.

Decomposition of Quaternary Salts.—The methiodide (usually 5 g.) was placed in a Claisen flask and heated with a free flame under 15-20 mm. pressure. The product distilled and was taken up in ether, washed with dilute acid, dried and concentrated under reduced pressure. The residue was taken up in ethanol and crystals formed. The product was recrystallized from ethanol.

Decomposition of Quaternary Hydroxides. (a) α -*dl*-Methadol.—To a solution of 5 g. of α -*dl*-methadol methiodide in aqueous ethanol was added 3 g. of silver oxide. The mixture was stirred vigorously until the presence of iodide ion could no longer be detected. The mixture was filtered and the precipitate was washed with ethanol and water. The filtrate and washings were combined and concentrated at reduced pressure. The residue was transferred to a Claisen flask (using a minimum amount of ethanol) and the material was pyrolyzed under 15–20 mm. pressure. The distillate was dissolved in ethanol and cooled. The crystals which separated were recrystallized from ethanol; m.p. 88–89°.

(b) α -*d*-Isomethadol.—This was run as above using 10 g. of α -*d*-isomethadol methiodide. The yield was 3.9 g. of material melting at 63–64.5°.

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Bromohydrins from Olefins and N-Bromosuccinimide in Water

BY CYRUS O. GUSS¹ AND RUDOLPH ROSENTHAL

RECEIVED DECEMBER 21, 1954

The reaction of olefins with N-bromoacetamide in water to form bromohydrins has been known and used for many years.^{2,3} It might be assumed that N-bromosuccinimide would behave similarly. Results have verified this assumption; for several years we have employed the latter reagent for the preparation of bromohydrins, and thence, olefin oxides. The availability and stability of this reagent, the ease of reaction and the yields obtained make this method superior, in many instances, to alternative methods. Some of the results that illustrate the scope of this method are summarized in Table I to supplement those already reported.⁴

Experimental

The general procedure used can be illustrated by the reaction of styrene (26.0 g., 0.25 mole), NBS (47 g., 95% purity, 0.25 mole) and water (100 ml.). These were stirred together vigorously at room temperature until the solid NBS disappeared (35 minutes). In all experiments, the disappearance of the NBS was a good criterion of the progress of the reaction. The styrene bromohydrin layer was separated and the aqueous layer extracted with benzene. Distillation of the combined product gave 41.0 g. (81.6%) of styrene bromohydrin, b.p. 120–123° (5 mm.), n_D^{18} 1.5785; lit.⁵ b.p. 109–110° (2 mm.), n_D^{18} 1.5800.

In a similar run the styrene bromohydrin was taken up in ether and, after removal of the ether, was converted to styrene oxide by stirring for one-half hour with sodium hydroxide (15 g.) in water (75 ml.) at 60°. Extraction with ether and distillation gave 25.6 g. (85.3%) of styrene oxide, b.p. 65° (5 mm.), n_D^{20} 1.5340; lit.⁶ b.p. 87–88° (23 mm.), n_D^{20} 1.5331. α -Methylstyrene gave equally good results.

The aqueous solution of succinimide from the separation of the bromohydrin was treated with sodium hydroxide (10 g.), cooled to 0°, and then bromine (13.6 ml.) was added. The mixture was shaken for two minutes, and the NBS filtered off, washed with cold water and dried to give 23.5 g. (50% recovery by reversion) of NBS of 95% purity.

It was found that the bromohydrin could often be converted to the oxide by adding sufficient aqueous sodium hydroxide without separating the bromohydrin from the NBS-olefin mixture.

Tetrachloroethylene, crotonaldehyde, cinnamaldehyde

(1) Department of Chemistry, Colorado A. and M. College, Fort Collins, Colorado.

(2) E. Schmidt, W. Knilling and A. Ascherl, *Ber.*, **59**, 1279 (1926).

(3) (a) S. Winstein and H. J. Lucas, *THIS JOURNAL*, **61**, 1576 (1939); (b) S. Winstein, *ibid.*, **64**, 2780 (1942).

(4) S. Winstein and L. L. Ingraham, *ibid.*, **74**, 1160 (1952).

(5) J. Read and W. Reid, *J. Chem. Soc.*, **133**, 1487 (1928).

(6) C. Golombic and D. L. Cottle, *THIS JOURNAL*, **61**, 996 (1939).

and benzalacetophenone were used in this reaction without success.

TABLE I
BROMOHYDRINS FROM OLEFINS AND NBS IN WATER

Olefin	Time	Yield, ^a %	
		Bromo-hydrin	Oxide
Cyclohexene ^b	10 min.	79.3 ^c	81.2 ^d
Trimethylethylene ^b	25 min.	76.5 ^e	78.2 ^f
Allylbenzene ^g	48 hr. ^h		56.3 ⁱ
1,4-Dihydronaphthalene ^g	12 hr.	30.0 ^j	
Indene ^k	3 hr.	59.1 ^l	
Mesityl oxide ^g	15 min.		56.1 ^m
Fumaric acid ^g (Na salt)	48 hr.		60.6 ⁿ
Cinnamic acid ^{g,o} (K salt)	2 hr.	35.0 ^p	

^a The oxides usually were obtained by taking the bromohydrins up in ether and then converting the crude material directly to the oxide. ^b 0.25 mole of olefin, 0.25 mole of NBS and 100 ml. of water. ^c B.p. 73–75° (5 mm.), n_D^{20} 1.5180; lit.^{3b} b.p. 86.6–88.4° (10 mm.), n_D^{20} 1.5184. ^d B.p. 129–130°, n_D^{20} 1.4528; "Organic Syntheses," Coll. Vol. 1, 2nd Edition, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 185, gives b.p. 129–134°. ^e B.p. 49–51° (10 mm.), n_D^{20} 1.4723; lit.⁴ b.p. 48–51° (10 mm.), n_D^{20} 1.4712. Comparable results were obtained by Winstein and Ingraham⁴ in this same reaction. ^f B.p. 72–74°, n_D^{18} 1.3885; lit.⁴ b.p. 73–73.3°, n_D^{20} 1.3822. ^g 0.125 mole of olefin in 100 ml. of ether stirred with 0.125 mole of NBS in 100 ml. of water. ^h A 50% yield of the oxide was obtained when the ether was omitted and a 4-hour reaction time used. ⁱ B.p. 72–75° (3 mm.); E. Fourneau and M. Tiffeneau, *Compt. rend.*, **140**, 1596 (1905), report b.p. 94–98° (15 mm.). ^j M.p. 106–106.5°; E. Bamberger and W. Lodter, *Ber.*, **26**, 1833 (1893), report the same value. ^k 0.063 mole of olefin, 0.063 mole of NBS and 50 ml. of water. ^l M.p. 130–131°, lit.² m.p. 131–132°. ^m B.p. 61–63° (20 mm.), n_D^{18} 1.4290; E. Weitz and A. Scheffer, *ibid.*, **54**, 2327 (1921), report b.p. 44–48° (15 mm.). ⁿ M.p. 212–213°; W. Lossen, *Ann.*, **348**, 299 (1906), reported m.p. 203° and R. Kempf, *J. prakt. Chem.*, **83**, 388 (1911), reported m.p. 215°. These references describe the isolation method used. ^o 200 ml. of water used and reaction flask cooled in ice-bath during reaction. ^p M.p. 124–125°; E. Erlenmeyer, *Ber.*, **39**, 788 (1906), reported m.p. 125°.

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The Oxygenation of the Tri-(*p*-nitrophenyl)-methide Ion. A Novel Oxidation-Reduction Reaction¹

BY M. F. HAWTHORNE² AND GEORGE S. HAMMOND

RECEIVED NOVEMBER 26, 1954

Tri-(*p*-nitrophenyl)-methane (I) is a pseudo-acid probably having a pK_a near 13³ and its solution in alcoholic alkali exhibits the deep purple color of the high resonance stabilized anion II.

Previously, it was reported that the air oxidation of the anion II in alcoholic alkali gave high yields of tri-(*p*-nitrophenyl)-carbinol (III) as well as traces of *p*-nitrophenol and 4,4'-dinitrobenzophenone.⁴ This nearly exclusive production of carbinol III seemed anomalous to us in view of the ease of

(1) Presented at the 125th National Meeting of the American Chemical Society, Kansas City, Missouri, 1954.

(2) Rohm and Haas Company, Redstone Arsenal Research Division, Huntsville, Ala.

(3) G. W. Wheland and A. A. Danish, *THIS JOURNAL*, **62**, 1125 (1940).

(4) O. Fischer and G. Schmidt, *Chem. Zentr.*, **75**, I, 460 (1904).