zoic acid (6.0 g.) and nitrobenzene (60 ml.) were mixed and anhydrous aluminum chloride (9.0 g.) was added portionwise. After the aluminum chloride had been added, the reaction mixture was heated slowly to 150°. It was maintained at this temperature for about 3.5 hr. Ice water was added slowly to the cooled reaction mixture, and the nitrobenzene was then removed by steam distillation. The hot solution was then filtered and strongly acidified with concentrated hydrochloric acid. Cooling (overnight) yielded the ketone, which was collected and crystallized from ethanol-water (1.52 g., 25.2%, m.p. 225–227°).

Anal. Calcd. for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19. Found: C, 62.13; H, 5.37.

3. *2-Methoxy-5-carbomethoxypropiophenone.* 2-Hydroxy-5-carboxypropiophenone (2.30 g.), acetone (30 ml.), and anhydrous potassium carbonate (4.6 g.) were heated under reflux for 15 min. Methyl iodide (6.44 g.) was then added through the top of the condenser, and the mixture heated under reflux for 20 hr. The acetone was then removed by a stream of air, and water (150 ml.) was added to the solid residue. Ether extraction (4 × 60 ml.), followed by drying (magnesium sulfate) and distillation, yielded a solid which was crystallized from ethanol-water (1.78 g., 67.2%, m.p. 74–75°).

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 65.07; H, 6.44.

4. *2-Methoxy-5-carboxypropiophenone.* 2-Methoxy-5-carbomethoxypropiophenone (1.52 g.) and methanolic potassium hydroxide (15 ml., 20%) were mixed and heated for 30 min. The methanol was removed by distillation, and the solid residue was dissolved in water (100 ml.). The basic solution was extracted with ether and then acidified with sulfuric acid (6*N*). The solid precipitate was collected and crystallized from ethanol-water (1.20 g., 84%, m.p. 209–211°).

Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.17; H, 5.75.

The 2,4-dinitrophenylhydrazone of this ketone was prepared, m.p. 237–238°.

Anal. Calcd. for $C_{17}H_{16}O_7N_4$: C, 52.58; H, 4.15; N, 14.43. Found: C, 52.44; H, 4.42; N, 14.42.

The 2,4-dinitrophenylhydrazone of the isomeric 2-(1-methoxy-5-carboxyphenyl)propionaldehyde, obtained as a result of the ozonolysis of the methyl ether derived from the rearrangement product, melted at 231–232°. A mixture of these two dinitrophenylhydrazones melted at 218–226°. The ultraviolet spectra (Beckman Model DU) showed the following:

(a) The 2,4-dinitrophenylhydrazone of 2-methoxy-5-carboxypropiophenone: λ_{max} (chloroform) 371 mμ, log ε 4.36.

(b) The 2,4-dinitrophenylhydrazone of 2-(1-methoxy-5-carboxyphenyl)propionaldehydes: λ_{max} (chloroform) 361 mμ, log ε 4.36.

The semicarbazone of 2-methoxy-5-carboxypropiophenone was prepared in the usual manner and crystallization from *N,N*dimethylformamide–water, m.p. 210–212°.

Anal. Calcd. for $C_{12}H_{15}O_4N_3$: C, 54.33; H, 5.70; N, 15.84. Found: C, 54.10; H, 5.64; N, 15.79.

Ultraviolet spectra (Cary).

(a). Semicarbazone of 2-methoxy-5-carboxypropiophenone: λ_{max} (95% ethanol) 246 mμ, log ε 4.29.

(b). Semicarbazone of 2-methoxy-5-carboxypropionaldehyde, m.p. 226–228°: λ_{max} (95% ethanol) 235 mμ, log ε 4.32.

F. *Radioactivity measurements.* The Van Slyke-Folch wet oxidation method[14] was used for all the oxidations herein described. The counting was done with a Nuclear-Chicago Model 186 Decade Scaler with an automatic timer and with a Nuclear-Chicago Model D-47 Gas-flow (Q-gas) Counter with a Model M-5 semiautomatic sample changer. Table I gives the results which were obtained.

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(14) D. D. Van Slyke and J. Folch, *J. Biol. Chem.*, **136**, 509 (1940); R. M. McCready and W. Z. Hassid, *Ind. Eng Chem., Anal. Ed.*, 14, 525 (1942); A. Lindebaum, J. Schubert and W. D. Armstrong, *Anal. Chem.*, 20, 1120 (1948).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Ortho Substitution Rearrangement *vs.* Elimination Reaction of 2-, 3-, and 4-Benzylbenzyltrimethylammonium Ions with Sodium Amide[1]

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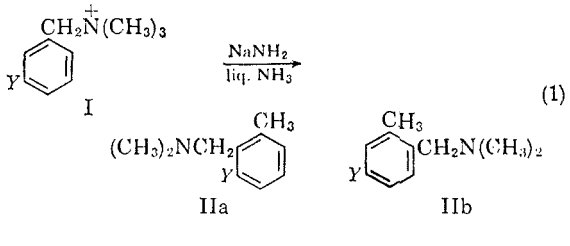
The 3-benzylbenzyltrimethylammonium ion reacted with sodium amide in liquid ammonia to form rearranged amine, whereas the 2- and 4-benzylbenzyltrimethylammonium ions underwent an elimination reaction to give amorphous hydrocarbon material. Evidently α-phenyl-*o*- and -*p*-xylylenes were intermediates in the latter type of reaction.

It has previously been shown that the 2-, 3-, and 4-alkyl-,[3–6] methoxy-,[3,5] and chloro[5]-benzyltrimethylammonium ions undergo the *ortho* substitution rearrangement with sodium amide in liquid ammonia, not the possible Stevens 1,2-shift. The reaction may be illustrated with the 3-methyl- and 3-methoxy- quaternary ammonium ions (I. $Y = CH_3$ and OCH_3), which afford mixtures of the corresponding isomeric rearranged amines IIa and IIb (Equation 1).



(1)

(1) Supported by the National Science Foundation.

(2) Present address: Ethyl Corp., Baton Rouge, La.

(3) S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **73**, 4122 (1951).

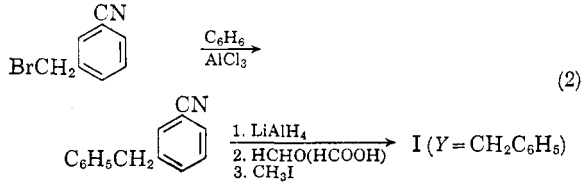
(4) C. R. Hauser and A. J. Weinheimer, *J. Am. Chem. Soc.*, **76**, 1264 (1954).

(5) W. Q. Beard, Jr., and C. R. Hauser, *J. Org. Chem.*, **25**, 334 (1960).

(6) W. Q. Beard, Jr., D. N. Van Eenam, and C. R. Hauser, *J. Org. Chem.*, **26**, 2310 (1961).

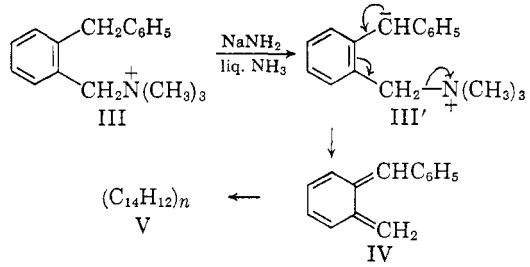
It has now been found that the 3-benzylbenzyltrimethylammonium ion (I. $Y = CH_2C_6H_5$) likewise undergoes rearrangement to give presumably a mixture of the corresponding amines IIa and IIb. This mixture of isomeric amines was obtained in yields of 11% and 22% in two and four hours respectively. No other product was isolated; much of the starting quaternary ion was recovered. That the product consisted of the two isomers was supported by its infrared spectrum, which showed peaks characteristic of the benzyldimethylamino group[5] at 11.73 μ and of the 1,2,3- and 1,2,4-trisubstituted benzene rings[7] of IIa and IIb at 12.90 and 13.12 μ and at 11.33, 11.91, and 14.10 μ respectively.

Incidentally, the starting quaternary ion as well as several of the intermediates in its synthesis appeared to be new compounds (Equation 2).



(2)

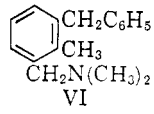
However, the 2- and 4-benzylbenzyltrimethylammonium ions underwent an elimination type of reaction with sodium amide in liquid ammonia. Thus, the 2-benzyl quaternary ion III afforded hydrocarbon material in almost quantitative yield. The analysis of this material corresponded to formula V. Its molecular weight was that of a dimer, but no pure substance was isolated. No rearranged amine was obtained. Apparently trimethylamine was eliminated from intermediate carbanion III′ to form α-phenyl-*o*-xylylene (IV), which dimerized (Equation 3).



(3)

The infrared spectrum of the product showed strong bands at 6.25, 13.38, 13.69, and 14.32 μ, suggesting aromatic and olefinic unsaturation. The product was highly reactive toward electrophilic reagents (see Experimental).

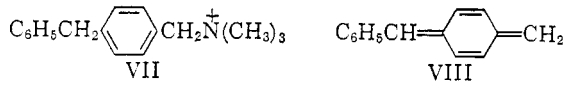
Reaction of quaternary ion III with lithium amide in liquid ammonia gave rearranged amine, presumably VI, in 3% yield. The predominant product was hydrocarbon material identical with that produced by sodium amide.



VI

When III was added to two molecular equivalents of succinimide dianion in liquid ammonia,[8] there was obtained polymeric material that contained some units of the succinimide molecule, as evidenced by the nitrogen content and infrared spectrum. Apparently the elimination reaction occurred to form IV, part of which reacted with the succinimide dianion.

Similarly, the 4-benzylbenzyltrimethylammonium ion (VII) reacted with sodium amide in liquid ammonia to give a product similar to that obtained from III, though the sum of the analytical values for carbon and hydrogen was only 98.5% and the molecular weight was nearly that of a trimer of VIII. Presumably, α-phenyl-*p*-xylylene (VIII) was an intermediate.



VII

VIII

Xylylenes IV and VIII have previously been proposed as intermediates in the reactions of quaternary ions III and VII with refluxing aqueous potassium hydroxide to form two diastereoisomers of 5,6-diphenyl-*sym*-dibenzocyclooctane (20% each) and 1,2-diphenyl[2.2]paracyclophane (7%), respectively.[9-11] Polymeric material was also obtained. Our eliminations with sodium amide in liquid ammonia (see Equation 3) are of interest because they were realized at a much lower temperature (−33°).

Even the 2- and 4-methylbenzyltrimethylammonium ions have been observed[3,5] to yield, besides rearranged amines, some hydrocarbon material with sodium amide in liquid ammonia,[12] whereas the 2-ethyl- and 4-isopropylbenzyltrimethylammonium ions have afforded only the corresponding rearranged amines.[4,5] These earlier results as well as the present related ones are summarized in Table I.

(7) See L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, 2nd ed., J. Wiley and Sons, Inc., New York, 1958, p. 78.

(8) D. R. Bryant and C. R. Hauser, *J. Am. Chem. Soc.*, **83**, 3468 (1961).

(9) H.-W. Bersch and R. Meyer, *Arch. Pharm.*, **287**, 613 (1954).

(10) H.-W. Bersch, A. v. Mletzko, K. H. Fisher, and H. Vogel, *Angew Chem.*, **68**, 617 (1956).

(11) H.-W. Bersch, *Angew Chem.*, **69**, 237 (1957).

(12) Pyrolysis of the 2- and 4-methylbenzyltrimethylammonium hydroxides at 200–250° has recently been observed to produce hydrocarbon material, spirodi-*o*-xylylene being obtained from the former and cyclodi-*p*-xylylene from the later. L. A. Errede, *J. Am. Chem. Soc.*, **83**, 949 (1961). Also see H. E. Winberg, F. S. Fawcett, W. E. Mochel, and C. W. Theobald, *J. Am. Chem. Soc.*, **82**, 1428 (1960).

TABLE I

HYDROCARBON *vs.* REARRANGED AMINES FROM 2- AND 4-SUBSTITUTED BENZYLTRIMETHYLAMMONIUM IONS WITH SODIUM AMIDE

Substituent	Hydrocarbon Material, Yield, %	Rearranged Amine, Yield, %
2- or 4-Benzyl	90–100	0
2-[a] or 4-Methyl[b]	12–40[c]	30–64
2-Ethyl[d] or 4-isopropyl[b]	—	90–92

[a] Ref. 3. [b] Ref. 5. [c] Dimeric and trimeric amines also obtained; ref. 3. [d] Ref. 4.

Table I shows that the relative amount of hydrocarbon material formed has decreased and that of rearranged amine has increased as the activity (acidity) of the α-hydrogen of the 2- or 4-substituent decreased: this α-hydrogen is initially ionized in the elimination reaction (see Equation 3). This suggests that not only the hydrocarbons from the 2- and 4-benzyl quaternary ions III and VII but also those from the 2- and 4- methylbenzyltrimethylammonium ions arose from the elimination type of reaction. A self-alkylation β-elimination mechanism has been previously proposed[3] to account for the formations of 2,2′- and 4,4′-dimethylstilbenes, which have been isolated from the hydrocarbon materials afforded by the 2- and 4-methyl quaternary ions, respectively. Indirect evidence against this earlier mechanism appears to be the failure of the 3-methyl- and the 2-, 3-, and 4-methoxybenzyltrimethylammonium ions to produce similar hydrocarbon material, as about as much self-alkylation might be expected to occur with these compounds as with the 2- and 4-methyl quaternary ions. However, only the latter type of compounds could exhibit the present elimination mechanism.

EXPERIMENTAL[13]

3-Benzylbenzyltrimethylammonium iodide (I. $Y = CH_2C_6H_5$). A mixture of 117 g. (1.0 mole) of 3-tolunitrile, 178 g. (1.0 mole) of *N*-bromosuccinimide, and 4.0 g. of benzoyl peroxide was stirred at reflux in 800 ml. of carbon tetrachloride for 8 hr. The succinimide was removed by filtration and the resulting solution was concentrated. The residue was recrystallized three times from absolute ethanol, giving 100 g. (52%) of 3-cyanobenzyl bromide, m.p. 92–93°; reported[14] m.p. 93°.

To a stirred, cooled solution of 69.4 g. (0.35 mole) of 3-cyanobenzyl bromide in 273 g. (3.5 mole) of benzene was added 40 g. (0.30 mole) of anhydrous aluminum chloride. When the initial reaction subsided, 16 g. (0.12 mole) more of aluminum chloride was added. After standing overnight at room temperature, the reaction mixture was worked up to give 47.7 g. (71%) of 3-benzylbenzonitrile, b.p. 140–143° at 0.9 mm.

Anal. Calcd. for $C_{14}H_{11}N$: C, 87.01; H, 5.74; N, 7.25. Found: C, 86.95; H, 5.98; N, 7.32.

To a stirred suspension of 14.0 g. (0.35 mole) of 95% lithium aluminum hydride in 500 ml. of ether was added 33.8 g. (0.175 mole) of 3-benzylbenzonitrile in 100 ml. of ether. After refluxing for 3 hr., the reaction mixture was worked up to give 29.2 g. (85%) of 3-benzylbenzylamine, b.p. 142–146° at 1.5 mm.

Anal. Calcd. for $C_{14}H_{15}N$: C, 85.23; H, 7.66; N, 7.10. Found: C, 85.05; H, 7.54; N, 7.35.

To a mixture of 28.6 g. (0.145 mole) of 3-benzylbenzylamine and 39.2 g. (0.72 mole) of 85% formic acid warmed on a steam bath was added during 30 min. 27.3 g. (0.319 mole) of 35% formaldehyde solution. After refluxing for 11 hr., 10 ml. of concd. hydrochloric acid was added and the solvents were evaporated under reduced pressure on the steam bath. The residue was dissolved in water and the resulting solution was made basic with sodium hydroxide. The amine which separated was extracted with ether and fractionated, giving 26.2 g. (80%) of 3-benzylbenzyldimethylamine, b.p. 134–138° at 1.5 mm.

Anal. Calcd. for $C_{16}H_{19}N$: C, 85.28; H, 8.50; N, 6.22. Found: C, 85.48; H, 8.26; N, 6.02.

To 25.8 g. (0.115 mole) of 3-benzylbenzyldimethylamine in 100 ml. of acetonitrile was added 23.4 g. (0.165 mole) of methyl iodide, the resulting rapid reaction being controlled by cooling on ice. After 15 min., slow addition of 400 ml. of dry ether precipitated 37.2 g. (88%) of 3-benzylbenzyltrimethylammonium iodide (I. $Y = CH_2C_6H_5$), m.p. 172.5–173°.

Anal. Calcd. for $C_{17}H_{22}IN$: C, 55.63; H, 6.04; N, 3.82. Found: C, 55.76; H, 5.89; N, 3.68.

Rearrangement of I($Y = CH_2C_6H_5$). To a stirred suspension of 0.11 mole of sodium amide in 300 ml. of liquid ammonia[15] was added 18.2 g. (0.049 mole) of 3-benzylbenzyltrimethylammonium iodide. An intense red color developed immediately. After 4 hr., excess ammonium chloride was added, and the ammonia was evaporated as an equal volume of ether was added. The resulting ether suspension was filtered. Extraction of the solid with acetonitrile in a Soxhlet extractor afforded 58% recovery of quaternary iodide I($Y = CH_2C_6H_5$), m.p. 171.5–173°. The ether filtrate was extracted three times with 2*N* hydrochloric acid, and the combined extracts were made basic with sodium hydroxide solution. The liberated amine was extracted with ether. Fractionation of the resulting ether solution gave 2.56 g. (22%) of presumably a mixture of amines IIa and IIb ($Y = CH_2C_6H_5$), b.p. 136–140° at 1.4 mm.

Anal. Calcd. for $C_{17}H_{21}N$: C, 85.30; H, 8.84; N, 5.85. Found: C, 85.55; H, 9.03; N, 6.02.

2-Benzylbenzyltrimethylammonium iodide (III). 2-Benzylbenzyldimethylamine, b.p. 133–135° at 2.1 mm., was prepared by the *ortho* substitution rearrangement of benzhydryltrimethylammonium chloride as described previously.[3] The methiodide (III) of this amine was prepared as described for methiodide I ($Y = CH_2C_6H_5$), and was recrystallized from ethanol-acetonitrile; it melted at 217.5–218°, reported[3] m.p. 214.5–215°.

Reaction of III *with sodium amide.* To a stirred suspension of 0.39 mole of sodium amide in 400 ml. of liquid ammonia[15] was added 66.5 g. (0.18 mole) of 2-benzylbenzyltrimethylammonium iodide. A dark green color developed. After 3 hr., the reaction mixture was neutralized with ammonium chloride and the ammonia was replaced with ether. The resulting ether suspension was filtered and the solvent was removed from the filtrate. The residue was pulverized and dried at 1 mm. pressure to give 35 g. (95)% of colorless, noncrystalline hydrocarbon material (V), softening point about 120°. Attempts to isolate a crystalline compound from this material by chromatography failed.

Anal. Calcd. for $(C_{14}H_{12})_2$: C, 93.30; H, 6.70; mol. wt. 360. Found: C, 93.07; H, 6.87; mol. wt. (ebullioscopic) 378, 366.

Similar material was obtained when the reaction was

(13) Melting points and boiling points are uncorrected. Analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Infrared spectra were recorded by a Perkin-Elmer Infracord.

(14) J. von Braun and H. Reich, *Ann.*, **445**, 237 (1925).

(15) See C. R. Hauser, F. W. Swamer, and J. T. Adams, *Org. Reactions*, **VIII**, 122 (1954).

repeated using equimolar quantities of the reactants and without neutralizing with ammonium chloride. In another experiment the ether solution of the reaction product was extracted with 2*N* hydrochloric acid; no trace of amine was obtained on filtering the resulting mixture and neutralizing the acid extract.

The hydrocarbon material V was soluble in ether but insoluble in ethanol. It readily decolorized bromine in carbon tetrachloride to produce dark gum, reacted slowly with maleic anhydride in ether to yield tarry material, but failed to take up hydrogen in ethyl acetate solution over Adams catalyst at 5 atm. during 24 hr., V being recovered. Treatment of ether solutions of V with 6*N* hydrochloric acid and with anhydrous aluminum chloride at room temperature produced polymeric material which precipitated immediately. This polymeric material had an average molecular weight of about 1100 (ebullioscopic). The infrared spectrum of this material was similar to that of V, with small differences. Hydrocarbon V did not react with butyllithium in ether.

Reaction of III *with lithium amide.* This reaction was carried out as described above for sodium amide employing 18.5 g. (0.05 mole) of salt III and 0.09 mole of lithium amide in 300 ml. of liquid ammonia. After replacing the ammonia with ether and filtering the resulting suspension, the ether filtrate was extracted with 2*N* hydrochloric acid, causing separation of much polymeric material. The mixture was filtered and the two layers of the filtrate were separated. The aqueous layer was made basic with sodium hydroxide and the liberated amine was extracted with ether. The ether was removed from this extract, leaving 0.35 g. (3%) of oil, presumably 3-benzyl-2-methylbenzyldimethylamine (VI). The infrared spectrum of this oil had strong peaks at 11.73 μ, characteristic of the benzyldimethylamino group,[5] at 12.85 μ, suggesting aromatic 1,2,3-trisubstitution,[7] and at 13.71 and 14.30 μ, suggesting aromatic monosubstitution.[16] The methiodide of this amine, prepared in dry acetone and recrystallized twice from this solvent, melted at 199–200.5°.

Anal. Calcd. for $C_{18}H_{24}IN$: C, 56.70; H, 6.30. Found: C, 56.33; H, 6.15.

Reaction of III *with disodiosuccinimide.* To a stirred suspension of 0.115 mole of disodiosuccinimide in 1200 ml. of liquid ammonia[8] was added 21.0 g. (0.057 mole) of salt III over a 5-hr. period. After 1 more hr., excess ammonium chloride was added, and the ammonia was replaced with ether. The resulting ether suspension was stirred with 3*N* sodium hydroxide to precipitate a gum insoluble in ether and water. On prolonged stirring with 2*N* hydrochloric acid this gum was changed to an ether soluble form. The resulting ether solution was concentrated to leave 4.7 g. of polymer (dried *in vacuo*).

Anal. Found: C, 88.02; H, 6.96; N, 1.50; mol. wt. (Rast) 763, 765.

This analysis suggests the xylylene IV and succinimide were involved in the molar ratio 4.4:1.

The infrared spectrum of this material was similar to that of V, but had additional strong peaks at 5.92 and 3.01 μ.

4-Benzylbenzyltrimethylammonium iodide (VII). Trimethylamine was bubbled through a solution of 32.3 g. (0.15 mole) of 4-benzylbenzyl chloride[17] for 30 min. After cooling, ether was added to precipitate 32.3 g. (79%) of 4-benzylbenzyltrimethylammonium chloride, which was highly hygroscopic.

A mixture of 31.8 g. (0.115 mole) of this chloride, 17.3 g. (0.115 mole) of sodium iodide, and 200 ml. each of ethanol and acetonitrile was rapidly stirred for a few minutes. The resulting mixture was filtered through a mat of Hyflow Supercel, and the filtrate was concentrated to about 200 ml. After another filtration to remove an additional small quantity of sodium chloride, 1500 ml. of ether was added to precipitate the iodide of VII. After recrystallization from acetonitrile, 31.0 g. (73%) of this salt was obtained, melting at 170–171°, and at 178–179° after another recrystallization.

Anal. Calcd. for $C_{17}H_{22}IN$: C, 55.63; H, 6.04; N, 3.82. Found: C, 55.80; H, 6.11; N, 3.88.

Reaction of VII *with sodium amide.* Essentially the same procedure was used as described above for VII. A dark green color developed. The product was an amorphous hydrocarbon almost identical in appearance to V.

Anal. Calcd. for $(C_{14}H_{12})_3$: C, 93.30; H, 6.70; mol. wt. 540. Found: C, 91.19; H, 7.32.

A sample of this material was dissolved in ether and precipitated with ethanol.

Anal. Found: C, 91.08; H, 6.60; mol. wt. (ebullioscopic) 558, 550, 481.

The reactions of this material with acid and with bromine were similar to those of V.

DURHAM, N. C.

(16) Ref. 7, p. 76.

(17) C. Maquin and H. Gault, *Chem. Abstr.*, **49**, 13181i (1955); *Compt. rend.*, **234**, 629 (1952); *Bull. soc. chim. France*, C48 (1953).

[CONTRIBUTION FROM THE SHELL DEVELOPMENT CO.]

Reactions of Hydrogen Peroxide. X. Oxidative Rearrangements with Certain β-Diketones

GEORGE B. PAYNE

Received June 27, 1961

The oxidation of several β-diketones by hydrogen peroxide in *tert*-butyl alcohol has been studied. In general, 2-acylcyclohexanones gave cyclopentanecarboxylic acids in 80–87% yields. 2-Acetylcyclopentanone, on the other hand, showed no comparable ring contraction to cyclobutanecarboxylic acid. Instead, α-methyladipic acid was secured in 93% yield. Other diketones investigated were 2-formylcyclohexanone, acetylacetone, and mono- and dimethylacetylacetone.

The reaction of β-diketones with peroxy acids has recently been studied.[1] As a general rule, hydroxy diketones (I) were obtained. Epoxidation of the enol form of the diketone was believed to be a reasonable path to account for the products observed.

Mannich[2] described the oxidation of a dispiro

(1) H. O. House and W. F. Gannon, *J. Org. Chem.*, **23**, 879 (1958); see reference therein to earlier work on the peroxy acid oxidation of β-diketones.

(2) C. Mannich, *Ber.*, **74**, 1007 (1941).