nished hard white prisms: m.p. 122–124°; λ_{max}^{EtOH} 222 mμ (ε 276,000), 265 sh (10,600), 275 (13,350), 278 (13,200), 283 (12,300) 291 sh (9320), 307 (2320), 313 (1700), and 321 (2660).

Anal. Calcd. for $C_{26}H_{24}$: C, 92.81; H, 7.19; mol. wt., 336. Found: C, 92.92; H, 7.32; mol. wt. (ebullioscopic in $CHCl_3$), 332.

Elution of the chromatographic column with ether afforded a small amount of a sulfur-containing (not a sulfone) compound which was not further identified.

B. **Acid-Catalyzed Dimerization of 2-Isopropenylnaphthalene.**—A mixture of 5.0 g. (0.03 mole) of 2-isopropenylnaphthalene[19] and 25 ml. of polyphosphoric acid was allowed to stand overnight at room temperature. The reaction was completed by heating on a steam bath for 0.5 hr. accompanied by occasional swirling with a glass rod. The mixture was poured into water, and the product was extracted twice with chloroform. The combined organic phases were washed with water, dried, filtered, and evaporated. The resulting viscous oil was purified by chromatography on neutral alumina (elution with hexane) and recrystallization from hexane. There was obtained 1.35 g. (27.0%) of white solid, m.p. 121–122°, identical by the usual criteria with the above sample.

2a,3,8,8a-Tetrahydro-3,8-epoxy-2H-naphtho[2,3-*b*]thiete 1,1-Dioxide (XIII and XIV).—A solution of 26.4 g. (0.05 mole) of XI[14] and 5.0 g. (0.048 mole) of thiete sulfone[20] in 125 ml. of diglyme was heated under reflux with stirring for 16 hr. The major portion of the diglyme was distilled under reduced pressure, and the residual material was chromatographed on neutral alumina. Elution with hexane–benzene (3:1) afforded, after recrystallization from benzene–hexane, 17.85 g. (97.4%) of 1,2,3,4-tetraphenylbenzene, m.p. 190–191.5°. Elution with benzene–methanol (19:1) gave 9.6 g. (90.7%) of white solid, m.p. 150–210°. Recrystallization of this material from a large volume of ethyl acetate furnished 7.2 g. of the *exo* isomer XIII, m.p. 218–219°. The analytical sample was obtained as white needles from ethyl acetate, m.p. 219° dec.

Anal. Calcd. for $C_{11}H_{10}O_3S$: C, 59.44; H, 4.54; S, 14.43. Found: C, 59.29; H, 4.58; S, 14.41.

From the mother liquor of the above purification, there was isolated 1.6 g. of solid, m.p. 150–170°. Three recrystallizations of this material from ethyl acetate–hexane gave pure *endo* isomer XIV, m.p. 165–167°.

Anal. Found: C, 59.37; H, 4.48; S, 14.34.

2H-Naphtho[2,3-*b*]thiete 1,1-Dioxide (XV).—A mixture of 11.2 g. (0.05 mole) of the *exo* isomer XIII and 100 ml. of polyphosphoric acid was heated on a steam bath for 3 hr. with stirring and allowed to stand at room temperature overnight. The mixture was poured into 900 ml. of water, and the product was extracted with chloroform. The combined organic layers were washed with water, dried, filtered, and evaporated to give 5.70 g. (52.8%) of a grayish white solid, m.p. 184–200°. Pure XV could be obtained by recrystallization from benzene–hexane, or preferably from dimethyl sulfoxide: m.p. 226°; λ_{max}^{EtOH} 214 mμ sh (ε 30,600), 233 (69,000), 272.5 sh (5470), 284 (4630), 289 (4440), 294 (4240), 313 (1640), 319 sh (1110), and 327 (1550).

Anal. Calcd. for $C_{11}H_{18}O_2S$: C, 64.68; H, 3.95; S, 15.70. Found: C, 65.00; H, 3.99; S, 15.39.

Acknowledgment.—We gratefully thank the National Science Foundation for partial support of this work. The authors are also indebted to Mr. Robert Davisson for his assistance in preparing the sample of compound XI.

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[19] Prepared by the action of triphenylphosphinemethylene on 2-acetonaphthone, m.p. 52–54° [see L. H. Klemm, W. C. Solomon, and A. J. Kohlik, *J. Org. Chem.*, **27**, 2777 (1962)].

[20] D. C. Dittmer and M. E. Christy, *ibid.*, **26**, 1324 (1961).

Reaction Paths in the Kolbe Synthesis

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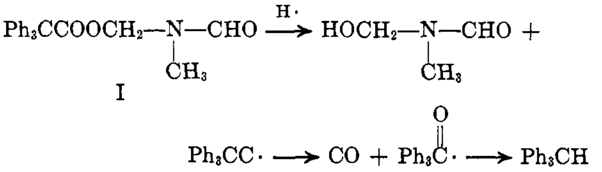
The products from the electrolysis of phenylacetic, diphenylacetic, mesitylacetic, and 2,4,6-triisopropylphenylacetic acids provide evidence for the formation of the Kolbe hydrocarbon at both electrodes. The formation of an ester and then a reductive cleavage at the cathode is suggested as the route for the unexpected hydrocarbon synthesis at the cathode.

One of the main products expected from the electrolysis of a carboxylic acid is a hydrocarbon.[1] It has been established that this reaction, the Kolbe synthesis, proceeds through a one-electron transfer at the anode, decarboxylation of the acyloxy radical, and coupling of the resulting alkyl radicals.

$$R{-}COO^- \xrightarrow{-e} R{-}COO\cdot \longrightarrow CO_2 + R\cdot \xrightarrow{R\cdot} R{-}R \quad (1)$$

More recently, attention has been directed toward those acids which yield substances other than the usual hydrocarbons. Most of these products, ethers, alcohols, and esters, depend on the solvent and can be reconciled with radical intermediates. There is convincing evidence[2] that in certain cases, however, carbonium ions resulting from a two-electron transfer at the anode account for some of the compounds produced. Some of the probable reaction paths are summarized in Chart I.

In an earlier article,[3] we reported that the electrolysis of triphenylacetic acid in dimethylformamide afforded a good yield of N-methyl-N-(triphenylacetoxymethyl)-formamide (I). This ester, after prolonged electrolysis, underwent reductive cleavage at the cathode as shown in eq. 2.



$$Ph_3CCOOCH_2{-}\underset{\underset{CH_3}{|}}{N}{-}CHO \xrightarrow{H\cdot} HOCH_2{-}\underset{\underset{CH_3}{|}}{N}{-}CHO + Ph_3CC\cdot \longrightarrow CO + Ph_3\overset{\overset{O}{\|}}{C}\cdot \longrightarrow Ph_3CH \quad (2)$$

I

Since the half-esters of dicarboxylic acids often are successfully utilized in the Kolbe synthesis, it was of interest to determine if the cleavage illustrated in eq. 2 was a general reaction. Under conditions similar to those employed for the electrolysis of triphenylacetic

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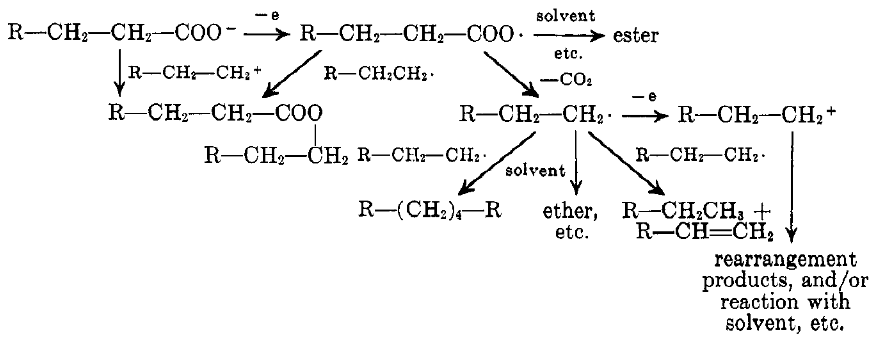
[1] Several reviews of this reaction are (a) B. C. L. Weedon, *Quart. Rev.* (London), **6**, 380 (1952); (b) B. C. L. Weedon, *Advan. Org. Chem.*, **1**, 1 (1960); (c) M. J. Allen, "Organic Electrode Processes," Reinhold Publishing Corp., New York, 1958, pp. 95–115; (d) A. P. Tomilov and M. Ya. Fioshin, *Russ. Chem. Rev.*, **32**, 30 (1963).

[2] (a) W. J. Koehl, Jr., *J. Am. Chem. Soc.*, **86**, 4686 (1964); (b) W. A. Bonner and F. D. Mango, *J. Org. Chem.*, **29**, 430, 1367 (1964); (c) E. J. Corey, N. L. Bauld, R. T. LaLonde, and J. Casanova, Jr., *J. Am. Chem. Soc.*, **82**, 2645 (1960); (d) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 581; (e) L. Eberson, *Acta Chem. Scand.*, **17**, 1196, 2004 (1963).

[3] L. Rand and A. F. Mohar, *J. Org. Chem.*, **30**, 3156 (1965).

CHART I

SOME PROBABLE REACTION PATHS IN THE KOLBE ELECTROLYSIS

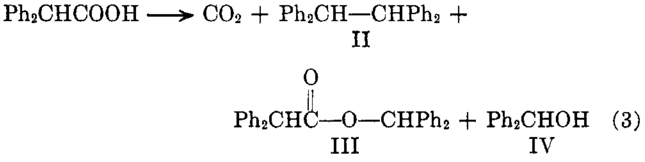


acid, the series comprised of phenylacetic, diphenylacetic, mesitylacetic, and 2,4,6-triisopropylphenylacetic acids was studied. For each acid, the total carbon dioxide evolved was measured, and the isolable products were characterized. In addition, qualitative tests for carbon monoxide[4] were made.

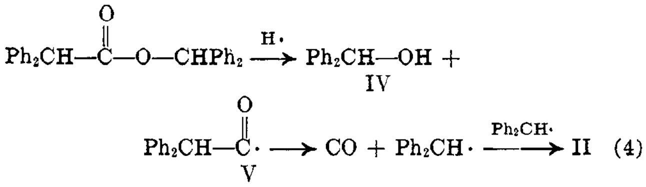
The solvent used for each acid was dimethylformamide. Electrolyses carried out in this medium have been shown[5] to produce fewer side reactions and furthermore, dimethylformamide is less likely to undergo primary anodic oxidation. Methanol, which is commonly used as the solvent, may produce secondary radicals by hydrogen abstraction after initial oxidation to the methoxyl radical.[6]

The electrolysis of phenylacetic acid afforded a 67% yield of carbon dioxide and an 88% yield, based on the carbon dioxide, of 1,2-diphenylethane. Thin layer chromatography of the residue showed the presence of six components which could not be separated. The R_f value of one of the fractions corresponded to that of benzyl alcohol.

Anodic oxidation of diphenylacetic acid gave 52% of the theoretical amount of carbon dioxide and 51%, based on the carbon dioxide, of 1,1,2,2-tetraphenylethane (II). In addition, 3% of diphenylmethyl diphenylacetate (III) and 31% of diphenylcarbinol (IV) were obtained. The residue consisted of a mixture which could not be eluted from the chromatography column. The amount of carbon dioxide measured is approximately 73% of the quantity that would correspond to the products, since each mole of II requires 2 moles of carbon dioxide and each mole of III and IV, respectively, requires that 1 mole of carbon dioxide be evolved. The discrepancy between the amount of carbon dioxide calculated and that found may be explained by considering the products from the reductive cleavage of the ester (eq. 4). An acyl–oxygen cleavage[7] by a hydrogen atom would give rise to diphenylcarbinol and the diphenylacyl radical V. The radical would be expected to eliminate carbon monoxide,[9] and the resulting diphenylmethyl radical could couple with a second radical to yield II. Carbon monoxide qualitatively was shown to be present,[10] and by later experiments using divided electrode compartments the carbon monoxide was demonstrated to be generated exclusively in the cathode section. The net result of this sequence is the *cathodic* formation of the Kolbe product without a concomitant discharge of carbon dioxide. Correcting the expected amount of carbon dioxide on the basis of the carbinol gives closer agreement to the amount found.



$$\mathrm{Ph_2CHCOOH \longrightarrow CO_2 + \underset{II}{Ph_2CH{-}CHPh_2} + \underset{III}{Ph_2CH\overset{O}{\overset{\|}{C}}{-}O{-}CHPh_2} + \underset{IV}{Ph_2CHOH}} \qquad (3)$$



$$\mathrm{Ph_2CH{-}\overset{O}{\overset{\|}{C}}{-}O{-}CHPh_2 \xrightarrow{H\cdot} \underset{IV}{Ph_2CH{-}OH} + \underset{V}{Ph_2CH{-}\overset{O}{\overset{\|}{C}}\cdot} \longrightarrow CO + Ph_2CH\cdot \xrightarrow{Ph_2CH\cdot} II} \qquad (4)$$

Under the conditions of the electrolyses, it appears from the products that the rate of decarboxylation decreases in the order phenylacetic > diphenylacetic > triphenylacetic acids, and that the ester or its reductive-cleavage products increases in that order. The formation of ester can be explained by two routes as indicated in Chart I.

The trend toward higher yields of ester may be explained by increased steric requirements operating at the anode where the Kolbe product is most likely to form. This conclusion is qualitatively supported by the results of the electrolysis of substituted phenylacetic acids. Mesitylacetic acid afforded 59% of 1,2-dimesitylethane based on a 75% yield of carbon dioxide. In addition, 2,4,6-trimethylbenzyl mesitylacetate (18%) and 2,4,6-trimethylbenzyl alcohol (26%) were obtained. Although the amount of carbon dioxide found corresponds to only 80% of that calculated on the basis of the products (eq. 5, $R = CH_3$), a correction for Kolbe product formed at the cathode provides closer agreement. Similarly, 2,4,6-triisopropylphenylacetic acid (eq. 5, $R = i\text{-}C_3H_7$) provided 67%

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[4] R. Nowicki, *Chem. Zentr.*, **35**, 1120 (1911); H. Gilman and C. W. Gerow, *J. Am. Chem. Soc.*, **77**, 4675 (1955).

[5] M. Finkelstein and R. C. Petersen, *J. Org. Chem.*, **25**, 136 (1960).

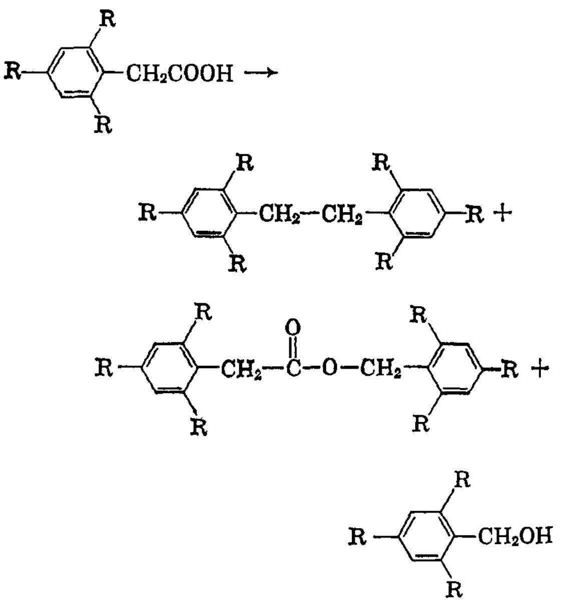
[6] T. Inoue, K. Koyama, and S. Tsutsumi, *Bull. Chem. Soc. Japan*, **37**, No. 11, 1597 (1964).

[7] Some examples of the reductive cleavage of an ester may be inferred from some of the products obtained by the electrolysis of sodium acetate–acetic acid in the presence of 1,1-diphenylethane[2b] and from the electrolysis of potassium diphenylacetate.[8]

[8] H. Katagashi, Y. Ginbayashi, and M. Matsui, *Mem. Coll. Sci., Univ. Kyoto*, **A12**, 57 (1929); *Chem. Zentr.*, **100** (I), 2980 (1929).

[9] Reference 2d, p. 279.

[10] Carbon monoxide, in small amounts, has been reported from the electrolysis of carboxylic acids. See, for example, S. Goldschmidt, W. Leicher, and H. Haas, *Ann.*, 153 (1952).



(5)

of 1,2-bis(2,4,6-triisopropylphenyl)ethane based on 47% of the theoretical amount of carbon dioxide. As in the other cases, the carbon dioxide found accounted for only 68% of the products, but correction for the cathodic reaction provides closer agreement. Carbon monoxide evolution was qualitatively established in the last two electrolyses and shown to be restricted to the cathode.

Experimental Section

The electrolyses were carried out in the apparatus and with the d.c. power supply described in the preceding paper[3] and were conducted under a nitrogen atmosphere. All melting and boiling points are uncorrected. The infrared analyses were performed on a Beckman IR-5. Elemental analyses were performed by Weiler and Strauss, Oxford, England.

Electrolysis of Phenylacetic Acid.—A solution of 5.44 g. (0.04 mole) of phenylacetic acid, 0.6 ml. of triethylamine, and 30 ml. of dimethylformamide (DMF) was electrolyzed at 35–50° for 3.7 hr. at a current density of 16.7–10.4 ma./cm.^{2} (52–150 v.). A total of 1.17 g. (67%) of CO_2 was evolved. The solvent was removed by distillation under reduced pressure. The brown, oily residue was dissolved in ether and extracted with aqueous Na_2CO_3 solution. Acidification of the aqueous layer resulted in the recovery of 1.3 g. of the starting acid. The ether layer was evaporated and the remaining material was chromatographed over alumina. Elution with *n*-hexane afforded 2.14 g. (59%) of 1,2-diphenylethane, m.p. 52° (lit.[11] m.p. 53°). Elution with benzene–hexane followed by ether gave 0.62 g. of a viscous yellow oil which showed six spots upon thin layer chromatography. This material was not separated.

Electrolysis of Diphenylacetic Acid.—A solution of 4.25 g. (0.02 mole) of diphenylacetic acid, 0.6 ml. of triethylamine, and 30 ml. of DMF was electrolyzed for 5.5 hr. at a current density of 8.3–2.5 ma./cm.^{2} (80–150 v.) during which time the temperature was maintained between 35 and 50° by means of a refrigerated circulating bath. A total of 0.450 g. (52.3%) of CO_2 was collected. The solvent was removed under reduced pressure. No acid was recovered by extraction with Na_2CO_3, and the residue was chromatographed over alumina. Elution with *n*-hexane and *n*-hexane–benzene gave 1.150 g. (35.7%) of 1,1,2,2-tetraphenylethane, m.p. 214° (lit.[11] m.p. 209°). Elution with benzene gave 0.110 g. (3.0%) of diphenylmethyl diphenylacetate, m.p. 100–102° (lit.[8] m.p. 106°). Elution with ether and CCl_4 gave 1.130 g. (31.3%) of diphenylcarbinol, m.p. 68–69° (lit.[12] m.p. 68°).

Preparation of Mesitylacetic Acid.—To a stirred solution of 30.0 g. (0.61 mole) of NaCN in dimethyl sulfoxide, heated to 90°, was added 84.0 g. (0.5 mole) of 2,4,6-trimethylbenzyl chloride.[13] The temperature rose to 125° and was allowed to drop to 50°. The mixture was then warmed to 100° for 2 hr., allowed to cool, and poured into water. The light brown solid which precipitated was recrystallized from ethanol to yield 75.8 g. (95%) of mesitylacetonitrile, m.p. 74–78°. A second recrystallization from *n*-hexane afforded colorless needles, m.p. 80–81° (lit.[14] m.p. 79.8°).

A mixture of 27.0 g. (0.17 mole) and 27 g. (0.48 mole) of KOH in 300 ml. of ethylene glycol was heated for 6 hr. at 155°. The resulting solution was acidified with HCl to give 27.8 g. of light yellow needles. Two recrystallizations from acetone and benzene, respectively, gave 22.5 g. (74.5%) of acid, m.p. 172–174° (lit.[14] m.p. 167–168°).

Electrolysis of Mesitylacetic Acid.—A solution of 3.56 g. (0.02 mole) of mesitylacetic acid, 0.6 ml. of triethylamine, and 30 ml. of DMF was electrolyzed at 35–50° at a current density of 16.7–2.5 ma./cm.^{2} (140–150 v.) for 6 hr. A total of 0.670 g. (76%) of CO_2 was collected. The solvent was removed under reduced pressure. No acid was recovered by extraction with Na_2CO_3. The reaction mixture was placed on an alumina column and eluted with *n*-hexane to yield 1.17 g. (44.0%) of 1,2-dimesitylethane, m.p. 117–119° (lit.[15] m.p. 117–118°). Elution with hexane–benzene (3:2) gave 0.56 g. (18%) of 2,4,6-trimethylbenzyl mesitylacetate, m.p. 103–105° (alcohol), λ_{ester} 5.8 and 8.7 μ.

Anal. Calcd. for $C_{21}H_{26}O_2$: C, 81.25; H, 8.44. Found: C, 81.64; H, 8.36.

An authentic sample of the ester was prepared by warming a solution of mesitylacetyl chloride, 2,4,6-trimethylbenzyl alcohol, and pyridine in dry ether.

Further elution with benzene followed by ether gave 0.770 g. (25.7%) of 2,4,6-trimethylbenzyl alcohol as needles, m.p. 89–90° (lit.[16] m.p. 88–89°). The phenylurethan of the alcohol was prepared, m.p. 151–152°.

Anal. Calcd. for $C_{17}H_{19}NO_2$: C, 76.81; H, 7.11; N, 5.21. Found: C, 76.82; H, 7.01; N, 5.08.

Preparation of 2,4,6-Triisopropylyhenylacetic Acid.—To a solution of 19.2 g. (0.4 mole) of NaCN in 85 ml. of dimethyl sulfoxide heated to 90° was added, with stirring, 60.5 g. (0.24 mole) of 2,4,6-triisopropylbenzyl chloride.[17] The temperature rose to 115° and was then maintained at 100° for 2 hr. The reaction mixture was allowed to cool and poured into water. The precipitate was recrystallized from ethanol to give a light brown solid, 48.0 g., m.p. 82–87°. Recrystallization from *n*-hexane gave the crystalline colorless nitrile, 39.2 g. (68%), m.p. 89–90°.

Anal. Calcd. for $C_{17}H_{25}N$: C, 83.89; H, 10.35; N, 5.76. Found: C, 83.95; H, 10.29; N, 5.64.

A solution of 20.7 g. (0.085 mole) of 2,4,6-triisopropylbenzonitrile and 13.5 g. (0.24 mole) of KOH in 250 ml. of ethylene glycol was heated at gentle reflux for 4 days until ammonia could be detected no longer. The solution was cooled and poured into dilute HCl. The impure acid which resulted was recrystallized from *n*-hexane after treatment with decolorizing charcoal to give 19.6 g. (88%) of colorless needles, m.p. 148–149°.

Anal. Calcd. for $C_{17}H_{26}O$: C, 77.82; H, 9.99. Found: C, 77.83; H, 9.87.

Electrolysis of 2,4,6-Triisopropylphenylacetic Acid.—A solution of 5.32 g. (0.02 mole) of 2,4,6-triisopropylphenylacetic acid, 0.6 ml. of triethylamine, and 40 ml. of DMF was electrolyzed for 6.5 hr. at a current density of 8.33 ma./cm.^{2} (90–150 v.). The temperature was maintained at 35–50° by means of a refrigerated circulating bath. A total of 0.409 g. (46.5%) of CO_2 was collected. The solvent was removed under reduced pressure and the residue was taken up in ether. The ether solution was washed with a solution of Na_2CO_3. The aqueous extract, upon acidification, provided a recovery of 0.76 g. of the acid. The residue, after evaporation of the ether, was chromatographed over alumina. Elution with *n*-hexane afforded 1.35 g. (31%) of 1,2-bis(2,4,6-triisopropylphenyl)ethane, m.p. 164–165° (ethanol–benzene).

Anal. Calcd. for $C_{32}H_{50}$: C, 88.41; H, 11.59. Found: C, 88.42; H, 11.69.

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[11] W. H. Zartman and H. Adkins, *J. Am. Chem. Soc.*, **54**, 1668 (1932).

[12] F. Y. Wiselogle and H. Sonneborn, III, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 90.

[13] G. Vavon and J. Bolle, *Compt. rend.*, **204**, 1826 (1937).

[14] R. C. Fuson and N. Rabjohn, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 557.

[15] F. Wezel, *Monatsh.*, **35**, 945 (1904).

[16] P. Carre, *Compt. rend.*, **151**, 149 (1910).

[17] R. C. Fuson and C. H. McKeever, *Org. Reactions*, **1**, 68 (1942).

The second fraction (hexane–benzene, 3:2), after evaporation of the solvent, gave 0.50 g. (10.4%) of a colorless oil which crystallized after standing for 2 months. The solid, m.p. 65–68°, gave a spectrum similar to the ester from the electrolysis of mesitylacetic acid (λ_{ester} 5.8 and 8.7 μ.) and corresponded to 2,4,6-triisopropylbenzyl 2,4,6-triisopropylphenylacetate.

Anal. Calcd. for $C_{33}H_{50}O_2$: C, 82.79; H, 10.53. Found: C, 82.29; H, 10.85.

A third fraction was eluted with benzene which afforded 1.5 g. (32%) of a crystalline solid, m.p. 94–96° (hexane). The infrared spectrum showed bonded and nonbonded OH (in $CHCl_3$), a split band at 7.2–7.3 μ (isopropyl), and a strong band at 10.2 μ. This spectrum was similar to that of 2,4,6-trimethylbenzyl alcohol and corresponded to 2,4,6-triisopropylbenzyl alcohol.

Anal. Calcd. for $C_{16}H_{26}O$: C, 81.98; H, 11.18. Found: C, 81.80; H, 11.20.

The phenylurethan was prepared, m.p. 148–149°.

Anal. Calcd. for $C_{23}H_{31}NO_2$: C, 78.14; H, 8.84; N, 3.96. Found: C, 78.17; H, 8.76; N, 4.08.

Electrolyses in a Divided Cell.—Each of the acids above was electrolyzed in a cell with separated electrode compartments. An electroosmotic effect resulted in migration of solution through the dividing glass frit from the anode compartment to the cathode compartment. This migration prevented a quantitative determination of the products produced at each electrode. Carbon monoxide was determined qualitatively by observing the darkening of absorbent paper soaked in a 1% aqueous solution of $PdCl_2$. The paper was placed in a flask which was preceded by a water-cooled condenser, a Dry Ice cold trap, and two Ascarite-filled absorption bulbs. Darkening of the paper was observed from the cathode only.

Acknowledgment.—The authors gratefully acknowledge support by the University Research Council. They also thank Miss A. F. Bresak for some technical assistance.

Quaternary Benzylammonium Ion Rearrangements with Organolithium Compounds. II.[1a] Influence of Halide Anion, Solvent, and Base on the Benzyltrimethylammonium Ion Reaction

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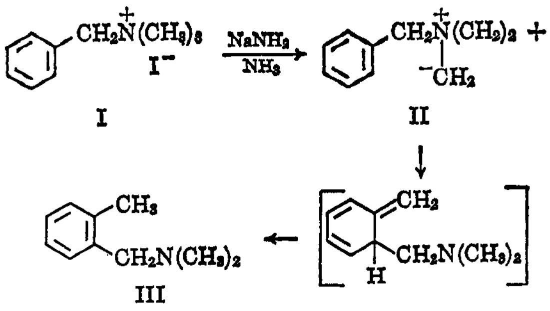
Received July 26, 1965

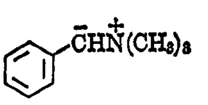
The reaction of organolithium compounds with benzyltrimethylammonium halides gives two monomeric rearrangement products, α,N,N-trimethylbenzylamine and *o*,N,N-trimethylbenzylamine. The relative and over-all yields depend on the halide anion, the medium, and the organolithium compound. Alkyllithium compounds give predominantly *ortho* rearrangement, but with phenyllithium, mainly the α rearrangement occurs. The over-all rates increase with base strength but the *ortho*/α ratios do not correlate with ylide equilibria or proton acidities in benzyltrimethylammonium salts. An ylide intermediate in the formation of the α product and a concerted mechanism leading to the *ortho* product give better agreement with previous and present studies.

Kantor and Hauser[2] assumed that the Sommelet rearrangement of benzyltrimethylammonium iodide (I) proceeds through the methyl ylide (II), Chart I. Carbon-14 experiments[3] prove that the *o*-methyl carbon atom in the product, *o*,N,N-trimethylbenzylamine (III), was the methylene carbon atom of I.

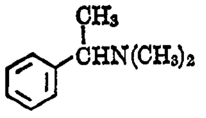
CHART I



Later, however, Puterbaugh and Hauser[4] isolated the benzyl ylide (IV) in the reaction when run at −80°, as shown by the addition of IV to benzophenone. Since the benzyl ylide was shown to rearrange to III on warming to −33°, an inter- or intramolecular ylide equilibrium was suggested. No evidence for II or the rearrangement product V was found. On the other hand, IV was proposed[5] as the intermediate in the Stevens rearrangement to α,N,N-trimethylbenzylamine (V), Chart II.



IV



V

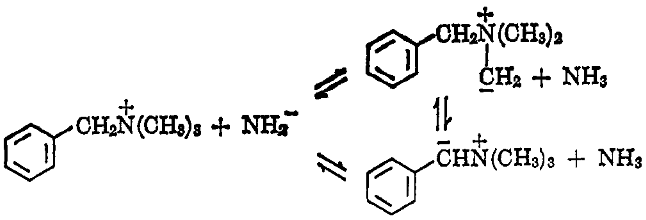
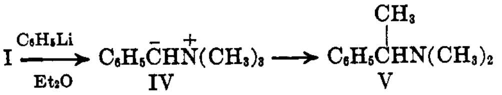


CHART II



$$\mathrm{I} \xrightarrow[\mathrm{Et_2O}]{\mathrm{C_6H_5Li}} \underset{\mathrm{IV}}{\mathrm{C_6H_5\bar{C}H\overset{+}{N}(CH_3)_3}} \longrightarrow \underset{\mathrm{V}}{\mathrm{C_6H_5\overset{CH_3}{\overset{|}{C}}HN(CH_3)_2}}$$

We have recently observed[1a] that both III and V are formed at room temperature when I reacts with *n*-butyllithium in ether; the rearrangement of I to β-phenethyl-

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[1] (a) Part I: A. R. Lepley and R. H. Becker, *Tetrahedron*, **21**, 2365 (1965). (b) Reprint requests should be sent to A. R. L., Department of Chemistry, Marshall University, Huntington, W. Va.

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

[3] N. J. Jones and C. R. Hauser, *J. Org. Chem.*, **26**, 2979 (1961).

[4] W. H. Puterbaugh and C. R. Hauser, *J. Am. Chem. Soc.*, **86**, 1105 (1964).

[5] G. Wittig, R. Mangold, and G. Felletschin, *Ann.*, **560**, 116 (1948).