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## Carbanions. V. Rearrangement in the Reaction of 1-Chloro-2,2,3-triphenylpropane with Lithium

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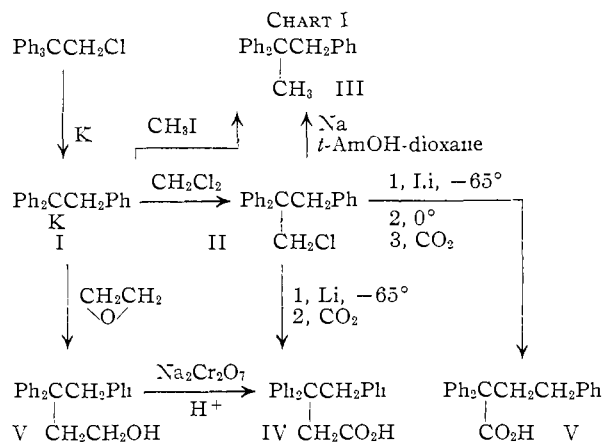
Lithium reacts with 1-chloro-2,2,3-triphenylpropane in tetrahydrofuran at  $-65^\circ$  to give 2,2,3-triphenylpropyllithium. When the latter is allowed to warm to  $0^\circ$ , rearrangement to 1,1,3-triphenylpropyllithium occurs. The more ready rearrangement of 2,2,3-triphenylpropyllithium than of 2,2,2-triphenylethyllithium and the preferred migration of benzyl over phenyl in the former are interpreted as supporting a carbanion mechanism of rearrangement. The composition of the organolithium compounds reported here is based upon characterization of the carboxylic acids resulting from carbonation.

Rearrangements of a phenyl group have been discovered in the reaction of sodium<sup>1,2</sup> and potassium<sup>3</sup> with 2-chloro-1,1,1-triphenylethane to give 1,1,2-triphenylethyl-sodium or -potassium under all conditions so far investigated. On the other hand, lithium<sup>3</sup> reacts with the same halide at temperatures of  $-65^\circ$  to  $-30^\circ$  to give 2,2,2-triphenylethyllithium, which is comparatively stable at these temperatures but rearranges at  $0^\circ$  or higher to give 1,1,2-triphenylethyllithium. The rearrangements have been interpreted<sup>1,3</sup> as rearrangements of the 2,2,2-triphenylethyl carbanion. The reaction of 1-chloro-2,2,3-triphenylpropane (II) with lithium has now been studied in order to broaden the scope of the rearrangement and to learn more of the mechanism of the process.

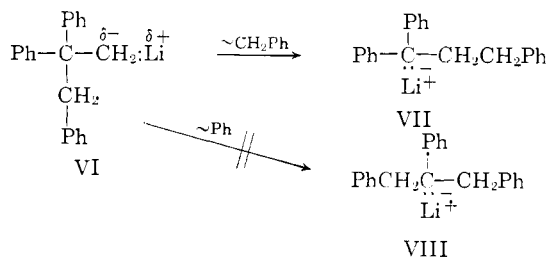
The required 1-chloro-2,2,3-triphenylpropane (II) was synthesized by reaction of 1,1,2-triphenylethylpotassium (I) with excess methylene chloride. The 1,1,2-triphenylethylpotassium was prepared by reaction<sup>3</sup> of potassium with 2-chloro-1,1,1-triphenylethane. The proof of structure of the 1-chloro-2,2,3-triphenylpropane (II) is based upon its method of synthesis,<sup>4</sup> elementary analysis and reduction to 1,2,2-triphenylpropane (III) by sodium in dioxane-*t*-amyl alcohol. The 1,2,2-triphenylpropane from this reduction was identical with a sample prepared<sup>5</sup> from 1,1,2-triphenylethylpotassium and methyl iodide. These reactions are summarized in Chart I.

Further confirmation of the structure of chloride II is provided by reaction of this halide with lithium metal in tetrahydrofuran at  $-65^\circ$ . Carbonation of the reaction mixture gave carboxylic acid IV of m.p.  $174.5$ – $175.1^\circ$  and of elementary analysis which agreed with  $C_{22}H_{20}O_2$ . The identity of this acid was established by synthesis. Reaction of 1,1,2-triphenylethylpotassium (I) with ethylene oxide gave an alcohol, m.p.  $107.2$ – $108.5^\circ$ , of elementary analysis which agreed with  $C_{22}H_{22}O$ ; this alcohol is doubtlessly 3,3,4-triphenylbutanol-1 (V). Oxidation of the alcohol with acidified sodium dichromate solution gave a carboxylic acid which was found to be identical with carboxylic acid IV. Carboxylic acid IV therefore is 3,3,4-triphenylbutanoic acid which must have come from carbonation of 2,2,3-triphenylpropyllithium. These reactions are summarized in Chart I.

(1) E. Grovenstein, Jr., *J. Am. Chem. Soc.*, **79**, 4985 (1957).  
 (2) H. E. Zimmerman and F. J. Smentowski, *ibid.*, **79**, 5455 (1957).  
 (3) Paper IV of this series, E. Grovenstein, Jr., and L. P. Williams, Jr., *ibid.*, **83**, 412 (1961).  
 (4) Cf. the analogous synthesis of 2-chloro-1,1,1-triphenylethane given in ref. 1.  
 (5) Cf. K. Ziegler and B. Schnell, *Ann.*, **437**, 244 (1924).



Since at  $-65^\circ$  lithium metal reacted with 1-chloro-2,2,3-triphenylpropane in tetrahydrofuran to give 2,2,3-triphenylpropyllithium without rearrangement of carbon skeleton, a sample of 2,2,3-triphenylpropyllithium prepared as before at  $-65^\circ$  was allowed to warm to  $0^\circ$  and was kept at  $0^\circ$  for one hour before carbonation. The carboxylic acid which resulted was nearly pure 2,2,4-triphenylbutanoic acid (V), m.p.  $186.1$ – $187.1^\circ$ , as shown by comparison with an authentic sample of this acid prepared after the procedure of Ziegler and co-workers.<sup>6</sup> Thus at  $0^\circ$ , 2,2,3-triphenylpropyllithium (VI) was converted essentially completely in one hour to 1,1,3-triphenylpropyllithium (VII). This reaction evidently involves a 1,2-shift of a benzyl group as shown in the formulation

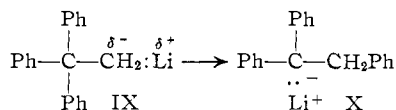


Two aspects of the rearrangement of VI are striking. In the first place, VI rearranged to VII rather than to VIII. Carbonation of VIII would have given the known<sup>7</sup> 2,3-diphenyl-2-benzylpropanoic acid (m.p.  $125$ – $126^\circ$ ) of which no evidence was found in the present work. Thus a benzyl group of VI migrates more readily than a phenyl

(6) K. Ziegler, F. Crössmann, H. Kleiner and O. Schäfer, *ibid.*, **473**, 27 (1929).

(7) K. Ziegler and B. Schnell, *ibid.*, **437**, 253 (1924).

group. We will refer to this as an "internal comparison" of migratory aptitudes of the two groups. In the second place, VI rearranges to VII more readily than 2,2,2-triphenylethyllithium (IX) rearranges to 1,1,2-triphenylethyllithium (X) since



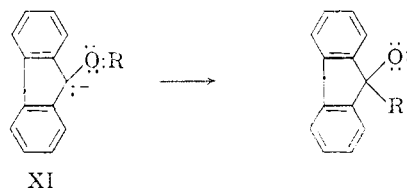
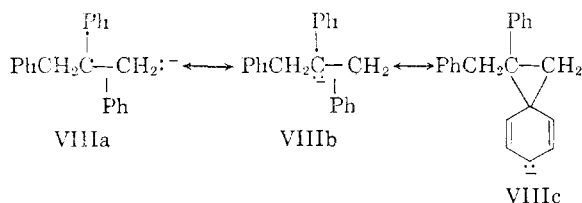
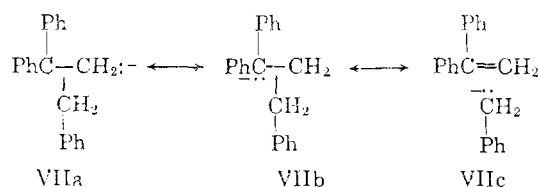
under comparable conditions only about 64% of IX was rearranged to X.<sup>3,8</sup> A comparison of the rates of rearrangement of VI and IX seems appropriate because of their close similarity in structure and the similarity of their products of rearrangement. This comparison permits what we will refer to as an "external comparison" of migratory aptitudes of phenyl and benzyl groups. On the basis of this comparison also, a benzyl group migrates more readily than a phenyl group.

The importance of an external comparison of migratory aptitudes is that, if the comparison is well chosen, it permits comparison of migratory aptitudes under more similar conditions than does an internal comparison in cases such as the present. For example, if we assume that the rearrangement of VI to VII or VIII goes by way of rearrangement of a carbanion, then the rearrangement of VI to VII gives a carbanion which is stabilized by two  $\alpha$ -phenyl groups while rearrangement to VIII gives a carbanion which is stabilized by only one  $\alpha$ -phenyl group. In absence of more detailed information we will assume that the transition states for these rearrangements have atomic and electronic configurations somewhere near midway between products and reactants, thus somewhat as implied by the hybrids of structures VIIa-VIIc and VIIIa-VIIIc (and related structures). Structure VIIb resembles the product VII and VIIIb the product VIII. To the extent that structures VIIb and VIIIb make important contributions to the transition state, then the factors which contribute toward stabilization of the product will stabilize the transition state. If this is the dominant factor, then we would predict migration of benzyl over phenyl regardless of the "intrinsic migratory aptitudes"<sup>9</sup> of these groups. Such is the limitation of the internal comparison of migratory aptitudes in the present case. On the other hand, a comparison based on the rates of rearrangement of VI and VII is made under more similar conditions in that both rearrangements give carbanions of about equal stability. The chief error in the present comparison may

(8) To obtain a better numerical comparison of the relative rate of rearrangement of IX and VI, VI was prepared as previously at  $-65^\circ$  and then kept at  $0^\circ$  for 15 minutes before carbonation. The acid which was obtained was again at least 98% V (see Experimental Details). From this and previous data<sup>3</sup> it can be estimated, on the assumption that the rearrangement is first order in organolithium compound, that VI undergoes rearrangement at least 12 times more readily than IX. Since rearrangement of phenyl in IX is favored over benzyl in VI by a statistical factor of three because of difference in the number of groups available for migration, the intrinsic migratory aptitude of benzyl is at least 36 times that of phenyl in these rearrangements.

(9) By the "intrinsic migratory aptitude" of a group we mean the migratory aptitude of a group as measured relative to some standard group under conditions such that all factors governing the rearrangement are the same save the groups which are migrating. Unfortunately, such migratory aptitudes are frequently not subject to direct experimental measurement.

lie in a difference in steric compression in VI and IX, although this difference is not expected to be large.



From the above discussion it appears quite likely that benzyl has a larger intrinsic migratory aptitude than phenyl in the present rearrangement. The question arises as to whether this difference has any mechanistic significance. In the rearrangement of ethers, which appears to involve rearrangement of carbanions of the type of XI, Wittig<sup>10</sup> and co-workers observed the following order of decreasing ease of migration of groups as the group (R) was varied:  $\text{CH}_2=\text{CHCH}_2$ ,  $\text{PhCH}_2 > \text{CH}_3$ ,  $\text{CH}_3\text{CH}_2$ , Ph. These workers considered that phenyl migrated less readily than methyl or ethyl; however, considerable uncertainty must be attached to this interpretation since the lithium derivative of the phenyl ether underwent a side reaction under conditions whereby rearrangement of the methyl and ethyl ethers occurred. There appears, however, no uncertainty in the conclusion that the benzyl ether underwent rearrangement more readily than the phenyl ether and, since this is an external comparison of migratory aptitudes, that the intrinsic migratory aptitude of benzyl exceeds that of phenyl in such ether rearrangements. If rearrangement of a carbanion can be regarded as an intramolecular nucleophilic displacement, then the greater migratory aptitude of benzyl over phenyl was to be anticipated because ordinary nucleophilic substitutions occur much more readily on benzyl than on phenyl derivatives.

For the rearrangement of free radicals the superior migratory aptitude of phenyl over methyl has been demonstrated,<sup>11</sup> but the migratory aptitude of benzyl has apparently not been determined. We would anticipate that the migratory aptitude

(10) G. Wittig, H. Döser and I. Lorenz, *Ann.*, **562**, 192 (1949); see also D. Y. Curtin and W. R. Proops, *J. Am. Chem. Soc.*, **76**, 494 (1954).

(11) See the discussion by J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, pp. 446-450.

of benzyl was less than that of phenyl for rearrangement of free radicals because radical displacements at a saturated carbon atom are very rare<sup>12</sup> while radical additions to aromatic rings are common.

For the rearrangement of carbonium ions the following order of decreasing ease of migration of groups has been observed<sup>13</sup>:  $\text{Ph} > \text{CH}_3 > \text{H} > \text{PhCH}_2$ . Moreover it has been pointed out<sup>13</sup> that this order corresponds with that established by the direction of cleavage of unsymmetrical organomercury compounds with hydrogen chloride (*i.e.*, with the ease of electrophilic substitution).

In conclusion, our demonstration that benzyl has a higher migratory aptitude than phenyl in the rearrangement of 2,2,3-triphenylpropyllithium rules out the possibility of rearrangement occurring in the 2,2,3-triphenylpropyl carbonium ion, is unlikely explained as rearrangement of the corresponding radical, but is satisfactorily explained as rearrangement of the 2,2,3-triphenylpropyl carbonium ion. The present state of knowledge of migratory aptitudes in rearrangements of free radicals makes this conclusion less certain than would be desired. The preferred migration of phenyl over *p*-tolyl in the related rearrangement<sup>14</sup> of 2-phenyl-2-(*p*-tolyl)-propyllithium has been interpreted, along with other evidence, as support for rearrangement by a carbanion rather than a free-radical mechanism.

In summary, the following factors appear to be important in determining whether or not an organometallic compound will undergo rearrangement: (1) the nature of the metal<sup>3,14</sup>; (2) the extent of stabilization of the anion before, during and after rearrangement by resonance or other electrical effects; and (3) steric strain in reactant, transition state and product. The last factor has not been adequately stressed. All of the hydrocarbon carbonium ions which have so far been found to undergo rearrangement<sup>1-3,14</sup> have had a quaternary carbon, bearing two or three large substituents, which was converted by rearrangement into a trigonal carbon bearing one less large substituent. It is therefore reasonable to suppose that the product in each case has less steric compression than the reactant.

### Experimental Details<sup>15</sup>

**1-Chloro-2,2,3-triphenylpropane (II).**—A solution of 1,1,2-triphenylethylpotassium, prepared<sup>3</sup> from 4.5 g. (0.11 g. atom) of potassium and 10.0 g. (34.3 mmoles) of 2-chloro-1,1,1-triphenylethane in 200 ml. of tetrahydrofuran, was forced under nitrogen through a tube containing a glass-wool plug (to remove particles of unreacted potassium) into 100 ml. of methylene chloride at room temperature. During the initial part of the addition the red color of 1,1,2-triphenylethylpotassium disappeared almost immediately upon contact with the methylene chloride, but during the latter stages of the addition the red color disappeared only upon swirling the now somewhat viscous solution. The reaction mixture was filtered twice through sintered glass filters to remove the last traces of potassium, was concentrated on a steam-bath to about 100 ml., and was treated with 300 ml. of

water. The mixture was extracted with three 100-ml. portions of ether and the ether extracts dried over anhydrous magnesium sulfate. The ether extracts after removal of magnesium sulfate and evaporation of ether on a steam-bath gave an orange oil which crystallized upon standing. This product after two recrystallizations from aqueous ethanol (with aid of Nuchar C to decolorize) gave 3.1 g. (30% yield) of pale yellow crystals, m.p. 124–127°. After two recrystallizations from aqueous acetone and two more recrystallizations from *n*-hexane, the colorless product (II) had m.p. 127.5–128.5°.

*Anal.* Found: C, 81.78, 82.18; H, 6.39, 6.28; Cl, 11.20, 11.34. Calcd. for  $\text{C}_{21}\text{H}_{19}\text{Cl}$ : C, 82.20; H, 6.24, Cl, 11.56.

A higher yield of product was obtained from a large-scale reaction with 1,1,2-triphenylethylpotassium prepared in a 3-liter Morton flask from 50.0 g. (171 mmoles) of 1,1,1-triphenyl-2-chloroethane dissolved in 85 ml. of tetrahydrofuran which was added to 15.1 g. (0.386 g. atom) of potassium in 1400 ml. of tetrahydrofuran under otherwise usual conditions.<sup>3</sup> The solution of 1,1,2-triphenylethylpotassium was filtered as above and stored under nitrogen in a 2-liter glass-stoppered bottle for 3 days before use. Finally it was forced by nitrogen through a tube containing a glass-wool filter into 500 ml. of methylene chloride (which had been freshly distilled and stored over anhydrous calcium sulfate) contained in a 3-liter Morton flask equipped with a high-speed stirrer.<sup>16</sup> The addition of 1,1,2-triphenylethylpotassium to the methylene chloride was made over a 35-minute period with vigorous stirring at a temperature which was maintained at  $15 \pm 5^\circ$ . The solution was filtered through a sintered-glass filter and was concentrated on a steam-bath, finally *in vacuo*, to give a semi-crystalline mass. Addition of 30 ml. of acetone gave crystals which were removed by filtration and washed with 30 ml. of additional acetone to give 28.5 g. of essentially white crystals, m.p. 126–128.7°. Slow evaporation of the combined acetone solutions gave 4.7 g. of crystals, m.p. 123–126°. The total yield of product was therefore 33.2 g. or 63%. Recrystallization from acetone gave 27 g. of white crystals, m.p. 127.7–128.7°.

Compound II dissolved in 95% ethanol showed the following absorption maxima for which wave length is expressed in  $\mu$  and molar extinction coefficient is given in parentheses: 270.5 ( $4.5 \times 10^3$ ), 265.5 ( $6.7 \times 10^3$ ), 259.5 ( $7.6 \times 10^3$ ), 253.5 ( $6.6 \times 10^3$ ), 250 (shoulder) ( $5.5 \times 10^3$ ), 211.5 ( $2.5 \times 10^4$ ). This absorption is as expected for isolated phenyl chromophores.<sup>1</sup>

**Reaction of II with Sodium in Dioxane-*t*-Amyl Alcohol.**—In a 500-ml. Morton flask equipped with high-speed stirrer,<sup>16</sup> reflux condenser and provisions for maintaining an atmosphere of nitrogen was placed 1.61 g. (5.25 mmoles) of 1-chloro-2,2,3-triphenylpropane (m.p. 127.0–128.5°), 6.0 g. of sodium, 110 ml. of dioxane and 140 ml. of *t*-amyl alcohol. The reaction mixture was heated to reflux and stirring was commenced and continued for 1 hour. To decompose all traces of sodium, 50 ml. of 95% ethyl alcohol was added and the mixture was allowed to stand for 3 days. The reaction mixture was acidified with a small excess of concentrated hydrochloric acid and was concentrated on a steam-bath *in vacuo* almost to dryness. Water (100 ml.) was added and the mixture was extracted with three 100-ml. portions of ether. The ethereal extract, after drying over anhydrous magnesium sulfate, was heated on a steam-bath to remove all ether. The product was sublimed twice at 0.03 mm. and a bath temperature of 104–127° to give 1.52 g. of pale yellow crystals, m.p. 105–114°. A portion of these crystals (0.80 g.) upon crystallization from 95% ethanol gave 0.65 g. (86% yield based on starting halide and the fraction of product recrystallized) of white crystals, m.p. 116.0–117.3°, or after a second crystallization 0.59 g., m.p. 116.3–117.2°. This compound was identical with a sample of 1,2,2-triphenylpropane (prepared from I as indicated below) according to mixed m.p. and infrared spectral comparisons.

**1,2,2-Triphenylpropane (III) from I.**—To 1,1,2-triphenylethylpotassium, prepared<sup>3</sup> from 10.0 g. (34.3 mmoles) of 2-chloro-1,1,1-triphenylethane and 3.4 g. of potassium in tetrahydrofuran, was added excess methyl iodide (5.2 ml., 83 mmoles) over a period of 15 minutes with stirring at about 15°. The reaction mixture was heated at reflux for 15

(12) For a possible example see R. A. Herrmann and R. M. Noyes, *J. Am. Chem. Soc.*, **78**, 5764 (1956).

(13) A. W. Fort and J. D. Roberts, *ibid.*, **78**, 584 (1956), and references therein cited.

(14) (a) H. E. Zimmerman and A. Zweig, *Am. Chem. Soc., Abstr.*, Cleveland, Ohio, A.C.S. Meeting, 1960, p. 170; (b) *Chem. Eng. News*, **38**, No. 16, 65 (1960).

(15) Melting points are corrected. Analyses are by Geller and by Galbraith Microanalytical Laboratories.

(16) A. A. Morton and L. M. Redman, *Ind. Eng. Chem.*, **40**, 1190 (1948).

minutes. On the next day 25 ml. of 95% ethanol was added to decompose any residual potassium and the reaction mixture was worked up as in the previous preparation from II. The crude product consisted of 9.5 g. of a brown-black oily solid which evidently was contaminated with iodine and a rather nonvolatile alkyl iodide. A 2.96-g. portion of this product was sublimed twice at 0.03 mm. and a bath temperature up to 130°; a preliminary red-brown oil which collected at a bath temperature up to 80° was discarded. The product consisted of 2.45 g. of light brown crystals, m.p. 96–108°. After two recrystallizations from 95% ethanol, 1.67 g. of white crystals, m.p. 116.0–117.0°, were obtained (m.p. recorded<sup>5</sup> 116–117°). The yield of purified product based on starting chloride is hence calculated to be 57%.

**Reaction of II with Lithium at -65°.**—Purified<sup>3</sup> tetrahydrofuran (250 ml.) was distilled from lithium aluminum hydride into the usual apparatus for alkali-metal reactions. To this solvent was added 0.70 g. of lithium ribbon which had been cut into small pieces. The lithium ribbon was of a low-sodium grade (0.005% Na max.) obtained from the Lithium Corp. of America. A small portion of a solution of 8.0 g. (26.1 mmoles) of 1-chloro-2,2,3-triphenylpropane in 25 ml. of tetrahydrofuran was added. When after 5 hours of vigorous stirring at -10° no evidence of reaction was observed, 0.6 ml. of methyl iodide was added and a red color appeared in about 20 minutes. The reaction temperature was lowered to -65 ± 5° and the remainder (~95% of the chloride II) was added over a period of 20 minutes. Stirring was continued for 3 more hours at -65° and then the reaction mixture was forced onto pulverized solid carbon dioxide. The next day the reaction mixture was acidified with 10% hydrochloric acid, which reacted with the remainder of the lithium, and then the solvents were removed *in vacuo* at steam-bath temperature. The residue was treated with excess of aqueous sodium hydroxide and 4.18 g. of neutral material was extracted with ether. Acidification and extraction with ether gave, in the ether extract, 3.36 g. of acidic material, m.p. 157–165°. The acidic material was sublimed at 0.05 mm. at a bath temperature of 180–190° to give 2.63 g. (31% yield) of acid, m.p. 170–174°. A 1.00-g. sample of this acid after two recrystallizations from benzene gave 0.73 g. of acid IV, m.p. 174.5–175.1°. This acid was identical with a sample of 3,3,4-triphenylbutanoic acid (synthesized by the procedure which follows) according to mixed melting point and infrared spectral comparisons.

*Anal.* Found: C, 83.86; H, 6.14. Calcd. for C<sub>22</sub>H<sub>20</sub>O<sub>2</sub>: C, 83.51; H, 6.37.

The neutral material from this run was distilled at 0.03 mm. at a bath temperature of 175° to give 3.0 g. of material, m.p. 80–110°. A 1.0-g. sample of this material was recrystallized twice from ethanol to give 0.44 g. of material, m.p. 104–116°. The infrared spectrum of this product indicated that it was 1,2,2-triphenylpropane containing a small amount of 1-chloro-2,2,3-triphenylpropane.

**3,3,4-Triphenylbutanol (V).**—To a solution of 1,1,2-triphenylethyl-potassium, prepared<sup>3</sup> from 10.0 g. of 2-chloro-1,1,1-triphenylethane and 4.0 g. of potassium in 250 ml. of tetrahydrofuran, was added 3.0 g. of ethylene oxide dissolved in 25 ml. of tetrahydrofuran. The addition was made at room temperature over a period of 30 minutes with stirring at room temperature continued for an additional 30 minutes. The unreacted potassium was decomposed by slow addition of ordinary *t*-butyl alcohol and then *t*-butyl alcohol to which water was added. The reaction mixture was neutralized with hydrochloric acid and evaporated on the steam-bath *in vacuo* to dryness. The residue after addition of water was extracted with ether and the ether extract gave 9.8 g. of amorphous product. Some 4 g. of this product was distilled at 0.05 mm. and a bath temperature of 190° to give a pale yellow glass which after two recrystallizations from *n*-hexane gave 1.16 g. of white crystals, m.p. 105–108°. This product was redistilled *in vacuo* as before to give 1.01 g. of crystals, m.p. 107.2–108.2°. For analysis this compound was distilled, recrystallized from *n*-hexane, and redistilled to give 3,3,4-triphenylbutanol-1 (V), m.p. 107.2–108.5°.

*Anal.* Found: C, 87.17; H, 7.05. Calcd. for C<sub>22</sub>H<sub>22</sub>O: C, 87.37; H, 7.34.

The remainder of the crude product was chromatographed<sup>3</sup> on silicic acid with chloroform used as solvent and for elution. The main fractions (3.3 g.) after recrystallization

from *n*-hexane and distillation *in vacuo* gave 2.35 g. of alcohol V, m.p. 104–107°.

**3,3,4-Triphenylbutanoic Acid.**—3,3,4-Triphenylbutanol (1.0 g., m.p. 104–107°) was dissolved in 22 ml. of benzene and the solution added slowly with stirring to a solution of 1.26 g. of Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>·2H<sub>2</sub>O in 7.5 ml. of water, 1.0 ml. of acetic acid and 2.0 ml. of sulfuric acid.<sup>17</sup> During this addition the reaction mixture was cooled in an ice-bath; after completion of the addition the reaction mixture was allowed to warm to room temperature and was stirred for 5 hours. The benzene layer was separated, washed twice with water, and extracted with five 20-ml. portions of 5% sodium hydroxide. The sodium hydroxide extracts and a solid which appeared during the extraction were combined and acidified with sulfuric acid. Extraction of the acidified solution with ether gave 0.74 g. of acidic material, m.p. 145–165°. From the benzene layer 0.36 g. of neutral material was recovered. The acidic material was sublimed (or distilled) twice at 0.04 mm. at a bath temperature of 190°. The sublimate amounted to 0.32 g. of acid, m.p. 160–170°, and a considerable amount of non-distillable black residue remained. The acid after two recrystallizations from benzene yielded 0.18 g. of white crystals, m.p. 171–174°. Another sublimation gave 0.15 g. of acid, m.p. 173–175°.

An attempt to prepare 3,3,4-triphenylbutanoic acid by Arndt-Eistert synthesis from 2,2,3-triphenylpropanoic acid was unsuccessful, apparently because of steric hindrance in the reaction of the corresponding acid chloride with diazomethane.<sup>18</sup>

**Reaction of II with Lithium at -65° and then at 0°.**—1-Chloro-2,2,3-triphenylpropane was treated with lithium at -65° in exactly the same manner and with the same quantities of reactants as specified previously for the reaction at -65°. After the 3-hour stirring period at -65°, the reaction mixture was allowed to warm to 0° (about 5 minutes was required to obtain this temperature) and was then stirred at 0° for exactly 1 hour. After carbonation of the reaction mixture and isolation of products in the manner described for the previous reaction with lithium, there was obtained 2.95 g. of neutral material and 5.05 g. of acidic material. The acidic material after sublimation at 0.05 mm. at a bath temperature of 200–210° amounted to 4.56 g. (55% yield) of acid, m.p. 183–186°. A second sublimation gave 4.36 g. of acid of the same m.p. A portion of this acid (2.00 g.) after recrystallization from benzene gave 1.85 g. of crystals, m.p. 186.1–187.1°.

*Anal.* Found: C, 83.28, 83.37; H, 6.15, 6.26. Calcd. for C<sub>22</sub>H<sub>20</sub>O<sub>2</sub>: C, 83.51; H, 6.37.

This acid (V) gave no depression of m.p. when mixed with an authentic sample of 2,2,4-triphenylbutanoic acid, while a 50/50 mixture with 3,3,4-triphenylbutanoic acid melted at 148–162°. The infrared spectrum of V (whether after the first sublimation or after recrystallization) was identical with that of the authentic sample of 2,2,4-triphenylbutanoic acid.

In another run a small portion of a solution of 10.0 g. (32.6 mmoles) of 1-chloro-2,2,3-triphenylpropane in 25 ml. of tetrahydrofuran was added to 0.70 g. of lithium in 250 ml. of tetrahydrofuran. When after 30 minutes of vigorous stirring at -10° no evidence of reaction was observed, 0.6 ml. of methyl iodide was added and a red color appeared after 20 minutes of additional stirring. The reaction temperature was lowered to -65 ± 5° and the remainder (~95%) of the chloride was added over a period of 30 minutes. Stirring was continued for an additional 3 hours at -65°. The reaction mixture was then allowed to warm with stirring to 0° (5 minutes was required to attain this temperature) and stirred at 0° for 15 minutes before carbonation. After the usual isolation procedure, there was obtained 4.29 g. of neutral material and 4.58 g. of acidic material. The acidic material after sublimation *in vacuo* amounted to 4.20 g. (41% yield) of acid, m.p. 177–185°. After two additional sublimations 3.98 g. of acid, m.p. 182–187°, was obtained. The infrared spectrum of this acid was essentially identical with that of an authentic sample of 2,2,4-triphenylbutanoic acid. A finely ground mixture of 5% 3,3,4-triphenylbutanoic acid and 95% 2,2,4-triphenylbutanoic acid melted at 165–184° and after resolidification melted at about 172–

(17) We are indebted to Dr. John W. Huffman for suggesting this procedure for oxidation.

(18) Cf. W. E. Bachmann and W. S. Struve, "Organic Reactions," Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 45.

184°; therefore, it appears likely that the acid of m.p. 182–187° consisted of 2,2,4-triphenylbutanoic acid with less than 2 mole % impurity. A portion (2.00 g.) of the acid of m.p. 182–187° was recrystallized from benzene and then sublimed *in vacuo* to give 1.80 g. of acid, m.p. 186.1–187.1°. This acid gave no depression of m.p. when mixed with an authentic sample of 2,2,4-triphenylbutanoic acid.

The authentic sample of 2,2,4-triphenylbutanoic acid was prepared from 1,1,3-triphenylpropanol-1 which was made from 2-phenylethylmagnesium bromide and benzophenone after the method of Kharasch and Burt.<sup>19</sup> This alcohol was converted to its methyl ether and the ether was cleaved by Na–K alloy by the procedure of Ziegler and co-workers<sup>6</sup> ex-

(19) M. S. Kharasch and J. G. Burt, *J. Org. Chem.*, **16**, 150 (1951).

cept that instead of shaking with the alloy, stirring for 6 hours on a high-speed stirrer<sup>16</sup> was employed. Carbonation of the reaction mixture gave after the usual isolation and purification procedure 2,2,4-triphenylbutanoic acid, m.p. 186.1–186.9° (recorded<sup>6</sup> m.p. 181°).

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## Amine Boranes. VIII. The Hydroboration of Terminal Olefins, Dienes and Terminal Acetylenes with Trimethylamine *t*-Butylborane<sup>1</sup>

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Trimethylamine *t*-butylborane reacted with terminal olefins to afford a convenient synthesis of *t*-butyldialkylboranes. Similarly, 1,4-pentadiene, 1,3-butadiene and 2-methyl-1,3-butadiene formed 1-*t*-butyl-1-boracycloalkanes when treated with trimethylamine *t*-butylborane. Divinyl ether and dimethyldivinylsilane afforded similar cyclic derivatives which contained an additional heteroatom. Terminal acetylenes and trimethylamine *t*-butylborane provide a route to *t*-butyl di-(1-alkenyl)-boranes of unknown stereochemistry.

The recent application of pyridine borane<sup>3</sup> and trimethylamine borane<sup>4,5</sup> to the hydroboration<sup>6</sup> of olefins suggested the possibility of similar reactions with the recently described trimethylamine alkylboranes.<sup>7</sup> As previously reported,<sup>7</sup> the latter materials were prepared by the lithium aluminum hydride reduction of alkylboronic anhydrides in the presence of trimethylamine.

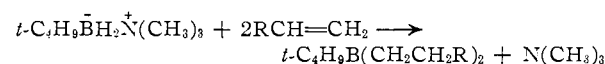
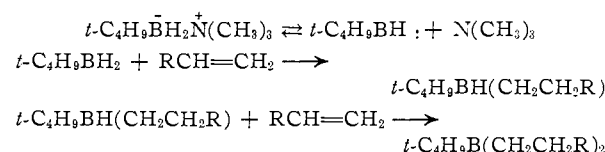
Hennion, McCusker and Rutowski<sup>8</sup> have convincingly demonstrated that the mixed trialkylborane, *t*-butyldiisobutylborane, is relatively stable toward disproportionation. This enhanced stability presumably arises from the large steric requirement of the *t*-butyl group in the transition state which leads to disproportionation.

Brown and Zweifel<sup>9</sup> have employed a sterically encumbered dialkylborane in their study of terminal acetylene hydroboration. This reagent was di-(3-methyl-2-butyl)-borane prepared from diborane and 2-methyl-2-butene. This same reagent was also employed to provide steric control of olefin hydroboration.<sup>10</sup> Thus the stabilization of mixed trialkylboranes and the moderation of the facile hydroboration reaction have been accomplished by the use of bulky alkyl substituents on boron. In view of these results and our own past experiences

with trialkylamine alkylboranes, it appeared to be possible to utilize a sterically moderated member of that series of reagents in selective hydroboration reactions. Such reactions could conceivably lead to the preparation of novel boranes. Trimethylamine *t*-butylborane was chosen as the hydroboration reagent and employed with such model substrates as terminal olefins, dienes and terminal acetylenes.

### Results and Discussion

The reversible thermal dissociation of trimethylamine-*t*-butylborane<sup>1</sup> would produce *t*-butylborane. If this process were carried out in the presence of an unsaturated substrate the free *t*-butylborane might be easily captured to produce a hydroboration product. Since *t*-butylborane contains two boron—hydrogen bonds, this process could be repeated once again with the release of trimethylamine.<sup>11</sup>



***t*-Butyldialkylboranes from Terminal Olefins.**—In contrast to the reactions of pyridine borane<sup>3</sup> and trimethylamine borane<sup>4,5</sup> with olefins, trimethylamine *t*-butylborane reacted readily with such simple olefins as ethylene and propylene at temperatures as low as fifty degrees. The amine

(11) Since the higher molecular weight trialkylboranes have low vapor pressures and form weak complexes with trimethylamine, this result was anticipated.

(1) Previously presented in part as a Communication to the Editor, *J. Am. Chem. Soc.*, **82**, 748 (1960).

(2) Visiting Lecturer, Harvard University, Fall, 1960.

(3) M. F. Hawthorne, *J. Org. Chem.*, **23**, 1788 (1958).

(4) R. Köster, *Angew. Chem.*, **69**, 684 (1957).

(5) E. C. Ashby, *J. Am. Chem. Soc.*, **81**, 4791 (1959).

(6) H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957).

(7) M. F. Hawthorne, *J. Am. Chem. Soc.*, **81**, 5836 (1959).

(8) G. F. Hennion, P. A. McCusker and A. J. Rutowski, *ibid.*, **80**, 617 (1958).

(9) H. C. Brown and G. Zweifel, *ibid.*, **81**, 1512 (1959).

(10) H. C. Brown and G. Zweifel, *ibid.*, **82**, 3222 (1960); **82**, 3227 (1960).