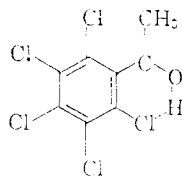


slow ionic hydrogen bromide addition to pentachlorostyrene to give the 1-pentachloro-1-bromoethane in contrast to the facile radical addition which gives 1-pentachlorophenyl-2-bromoethane¹²; (6) the difficulty of oxidizing pentachlorophenylethane.

The polar effect of the pentachlorophenyl group shows up in another manner. While phenylmethylcarbinol is largely intermolecularly hydrogen-bonded, pentachlorophenylmethylcarbinol is appreciably intramolecularly hydrogen-bonded.²¹ Both have sharp free O-H bands at 2.80 μ similar in intensity at comparable molar concentrations in carbon tetrachloride. The former exhibits a broad intermolecular O-H band at 3.0 μ while the pentachloro compound has a weak band at 2.91 μ . It appears that this is an intramolecular O-H band and may be attributed to the structure (see also Fig. 1)



The carbonyl frequency of the aldehyde IX is somewhat above normal at 1730 cm^{-1} .²² The pentachlorophenyl methyl ketone band at 1727 cm^{-1} appears to be extremely high for ketone

(21) A. W. Baker and A. T. Shulgin, *THIS JOURNAL*, **80**, 5358 (1958); G. M. Badger, *Rev. Pure Appl. Chem.*, **7**, 55 (1957).

(22) L. J. Bellamy, "Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, Ch. 9.

carbonyl²²; yet it is about what one would predict from a σ (or σ^+) versus $\nu_{\text{C=O}}$ plot.²³ Both steric and electrostatic (field) effects would tend to shift $\nu_{\text{C=O}}$ upward; however, scale models indicate no pronounced interference between the *o*-chloro atoms and the carbonyl oxygen. Thus, strong polar effects of the pentachlorophenyl group are indicated here also.

Previous workers have largely emphasized the steric influence¹⁴ of the pentachlorophenyl group while we have stressed the polar effect. Models indicate that in pentachlorophenylethane rotation is possible between carbon 1 and the ring and carbon 2 and carbon 1 providing there is cog-wheeling between the terminal hydrogens and the *o*-chlorine atoms. Once a 1-substituent is present, rotation between the carbon 1 and the ring is hindered. Thus, in the di- and tribromoethanes, the most stable conformations are also most suitable for *trans* eliminations with base or zinc, to lead almost exclusively to the *trans*- ω -bromostyrene (Va). But these are expected conformational results—the reported inertness of pentachlorophenylmethyl ketone to the usual carbonyl reagents is more striking.^{14,24} Only in the sense that these fairly exaggerated polar and steric effects can be rationalized may they be considered "normal."

Acknowledgment.—We wish to thank Mr. L. Clemens for some technical assistance and the Dow Chemical Co. for samples of pentachlorophenylethane.

(23) R. Stewart and K. Yates, *THIS JOURNAL*, **80**, 6355 (1958).

(24) G. Lock and E. Bock, *Ber.*, **70**, 916 (1937).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, GEORGIA INSTITUTE OF TECHNOLOGY, ATLANTA 3, GA.]

Carbanions. IV. Rearrangements in the Reaction of 2-Chloro-1,1,1-triphenylethane with Lithium and Potassium

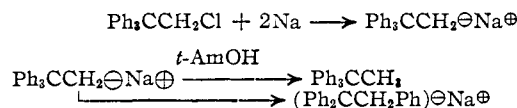
BY ERLING GROVENSTEIN, JR., AND LANEY P. WILLIAMS, JR.

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Potassium reacts with 2-chloro-1,1,1-triphenylethane at temperatures of -50 to 66° to give 1,1,2-triphenylethylpotassium as the only detectable monopotassium derivative. On the other hand, lithium reacts with 2-chloro-1,1,1-triphenylethane at temperatures of -65 to -30° to give 2,2,2-triphenylethyllithium which is comparatively stable at these temperatures but rearranges rather readily at temperatures of 0° or higher to give 1,1,2-triphenylethyllithium. These reactions are considered to strengthen the previous interpretation¹ that such rearrangements are rearrangements of the 2,2,2-triphenylethyl carbanion. The ease of rearrangement of 2,2,2-triphenylethylalkali compounds parallels the degree of ionic character of the carbon-metal bond. The structures of the organometallic compounds described here are inferred from the structures of the carboxylic acids obtained after reaction with carbon dioxide.

The reaction of 2-chloro-1,1,1-triphenylethane with sodium has been found to proceed with rearrangement of carbon skeleton *via* 1,2-shift of a phenyl group when the reaction is conducted in refluxing dioxane¹ or in ethyl ether-isoöctane at room temperature.² When the reaction was run in a mixture of dioxane and *t*-amyl alcohol, however, 94% of the triphenylethane obtained had the same carbon skeleton as the starting material, while 6% had undergone rearrangement of a phenyl group to give 1,1,2-triphenylethane.¹ These results were most simply explained on the basis that the reaction

of 2-chloro-1,1,1-triphenylethane with sodium gives 2,2,2-triphenylethyl carbanion, which in the presence of *t*-amyl alcohol undergoes fast protonation before appreciable rearrangement of phenyl has occurred but which in absence of a proton donor rearranges to give the more stable 1,1,2-triphenylethyl carbanion.¹ If, as seems likely, the reaction



of alkyl halides and of tetraalkylammonium halides with sodium proceeds by a similar mechanism,

(1) E. Grovenstein, Jr., *THIS JOURNAL*, **79**, 4985 (1957).

(2) H. E. Zimmerman and F. J. Smentowski, *ibid.*, **79**, 5455 (1957).

then the demonstration that primary alkyl groups are cleaved from nitrogen by sodium in dioxane or liquid ammonia as carbanions rather than free radicals^{3,4} strengthens the previous arguments concerning the nature of the above rearrangement. In the present work additional confirmation of mechanism was sought by study of the reaction of 2-chloro-1,1,1-triphenylethane with potassium and lithium.

Reaction of 2-Chloro-1,1,1-triphenylethane with Potassium.—The reaction of molten potassium with 2-chloro-1,1,1-triphenylethane in refluxing tetrahydrofuran (b.p. 65–66°) produced a dark red-colored solution which upon carbonation gave, under optimum conditions, some 72% yield of 2,2,3-triphenylpropanoic acid and 4.7% of diphenylacetic acid. The major acidic product was therefore identical with that obtained previously with sodium though the yield was appreciably improved (43% yield of 2,2,3-triphenylpropanoic acid reported with sodium in dioxane¹).

Diphenylacetic acid must come from diphenylmethylpotassium which evidently results from cleavage of a carbon-carbon bond of some intermediate product by potassium. 1,1,2,2-Tetraphenylethane is known to be cleaved by sodium-potassium alloy to diphenylmethylpotassium,^{5,6} 1,1,1,2-tetraphenylethane is similarly cleaved to triphenylmethylpotassium,⁶ while 1,2-diphenylethane is not cleaved.⁶ Although the compound undergoing cleavage by potassium under the present conditions is not known with certainty, 1,1,2-triphenylethane (which has been identified in the corresponding reaction with sodium¹) appears to be an attractive possibility.

It was of interest to see if reaction of potassium with 2-chloro-1,1,1-triphenylethane proceeded with rearrangement at lower temperature. Toward this end the reaction was studied with liquid sodium-potassium alloy in tetrahydrofuran at 20 and at 0° and gave, respectively, 53 and 32% yields of 2,2,3-triphenylpropanoic acid and 1 and 0% yields of diphenylacetic acid. Attempts to study the reaction of 2-chloro-1,1,1-triphenylethane with finely divided potassium at -78° were unsuccessful because of agglomeration of the potassium metal under all conditions studied wherein the surface of the metal was clean enough to permit reaction. We could detect no visible blue color due to solubility of potassium in tetrahydrofuran either at the boiling point of the solvent or at the temperature of a Dry Ice-acetone-bath although such blue solutions have been claimed⁷ for this solvent. On the other hand, we confirm that a blue solution is formed by potassium in 1,2-dimethoxyethane⁷ at temperatures near the freezing point of the solvent. At about -50° this blue color was discharged and replaced by a red-brown color upon addition of a small portion of 2-chloro-1,1,1-triphenylethane. The blue color returned upon

(3) E. Grovenstein, Jr., E. P. Blanchard, Jr., D. A. Gordon and R. W. Stevenson, *THIS JOURNAL*, **81**, 4842 (1959).

(4) Paper III, E. Grovenstein, Jr., and R. W. Stevenson, *ibid.*, **81**, 4850 (1959).

(5) K. Ziegler and F. Thielmann, *Ber.*, **56B**, 1743 (1923).

(6) J. B. Conant and B. S. Garvey, *THIS JOURNAL*, **49**, 2599 (1927).

(7) J. L. Down, J. Lewis, B. Moore and G. Wilkinson, *Proc. Chem. Soc.*, **209** (1957).

stirring the finely divided suspension of potassium. In this manner a small quantity of 2-chloro-1,1,1-triphenylethane was allowed to react with potassium at -50° until the reaction had to be terminated because of agglomeration of the potassium. Carbonation of the reaction product gave a mixture in which only 2,2,3-triphenylpropanoic acid and triphenylsuccinic anhydride were identified. The triphenylsuccinic anhydride probably resulted from carbonation of the addition product of potassium and triphenylethylene (*cf.* the corresponding reaction of sodium¹). Triphenylethylene could be formed by α -elimination upon the starting chloride by an organopotassium compound.²

The most significant result of all of the present reactions is that potassium reacts with 2-chloro-1,1,1-triphenylethane at temperatures of from -50 to 66° to give 1,1,2-triphenylethylpotassium but no detectable 2,2,2-triphenylethylpotassium. Moreover the yields of 1,1,2-triphenylethyl carbanion are generally higher with potassium than with sodium. These results lend no support to the supposition that rearrangement in the reaction of 2-chloro-1,1,1-triphenylethane with alkali metals occurs in an intermediate 2,2,2-triphenylethyl free radical since this radical would be expected to be reduced more rapidly and completely by potassium than by sodium. The results are, however, what might be expected if rearrangement takes place in the 2,2,2-triphenylethyl carbanion since 2,2,2-triphenylethylpotassium would be expected to be more ionic in character⁸ and, therefore, to undergo rearrangement more readily than 2,2,2-triphenylethylsodium.

Reaction of 2-Chloro-1,1,1-triphenylethane with Lithium.—2-Chloro-1,1,1-triphenylethane reacted with lithium metal in tetrahydrofuran at -10° to give a deep red-colored solution. This solution after stirring for one hour at 28° was carbonated and gave after separation of the acids by chromatography 18% yield of 2,2,3-triphenylpropanoic acid and 10% yield of triphenylsuccinic anhydride. The triphenylsuccinic anhydride probably arose (in a manner analogous to that described above with potassium) from carbonation of the addition product of lithium to triphenylethylene. Indeed some 5% yield of triphenylethylene was found in the neutral products from this reaction.

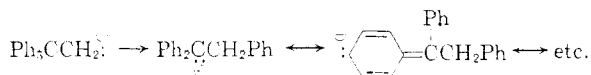
In sharp contrast with these results was a reaction run at a temperature of -60° until carbonation. This reaction gave 62% yield of acids which consisted of 94% 3,3,3-triphenylpropanoic acid and some 3% each of 2,2,3-triphenylpropanoic acid and triphenylsuccinic anhydride. Thus at -60° lithium reacts with 2-chloro-1,1,1-triphenylethane to give 2,2,2-triphenylethyllithium which undergoes no appreciable rearrangement in 3.5 hours at this low temperature. It seems reasonable to suppose that in the first experiment with lithium 2,2,2-triphenylethyllithium was formed initially but underwent rearrangement to 1,1,2-triphenylethyllithium at the higher temperature employed. That such a rearrangement can take place was shown more convincingly by conducting

(8) *Cf.* E. G. Rochow, D. T. Hurd and R. N. Lewis, "The Chemistry of Organometallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 65.

a reaction with lithium at -60° as previously and then warming to 0° and keeping the reaction mixture at 0° for one hour before carbonation. In two such runs the ratio of 2,2,3-triphenylpropanoic acid to 3,3,3-triphenylpropanoic acid was about 1.7–1.9. Thus almost two-thirds of the 2,2,2-triphenylethyllithium underwent rearrangement to 1,1,2-triphenylethyllithium under these conditions.

Attempts were made to accelerate the rearrangement of 2,2,2-triphenylethyllithium by increasing the solvating power of the medium for cations. To this end a solution of 2,2,2-triphenylethyllithium prepared at -65° in 225 ml. of tetrahydrofuran was stirred for one hour at -65° with 100 ml. of triethylamine. The carboxylic acid from the reaction, however, proved to be essentially pure 3,3,3-triphenylpropanoic acid.

In conclusion 2-chloro-1,1,1-triphenylethane has been found to react with lithium at temperatures of from -65 to -30° to give 2,2,2-triphenylethyllithium which is comparatively stable at these temperatures but undergoes rearrangement fairly readily at temperatures of 0° or higher to give 1,1,2-triphenylethyllithium. These results are therefore in sharp contrast to those obtained with sodium and potassium. If the initial reaction of 2-chloro-1,1,1-triphenylethane with alkali metals were the formation of 2,2,2-triphenylethyl free radical, then rearrangement might have been expected to occur more extensively with lithium than with potassium since potassium should reduce the radical more rapidly and completely than lithium.⁹ Since rearrangement was not more facile with lithium than with potassium, but less, the present results lend no support to the supposition that rearrangement occurs by way of the 2,2,2-triphenylethyl radical. All of the present results, however, can be readily interpreted on the basis that rearrangement occurs in an organoalkali compound. Thus the sequence for ease of rearrangement of 2,2,2-triphenylethylalkali compounds $R\text{Li} < R\text{Na} \leq R\text{K}$, parallels the degree of ionic character of the carbon-metal bond. The more ionic the carbon-metal bonds, the more facile the rearrangement. This result is to be expected since the more ionic the carbon-metal bond, the more charge is localized on carbon. Presumably the driving force for the present carbanion rearrangements¹⁰ is the delocalization of charge which rearrangement permits



(9) The superior reducing power of potassium over lithium in ethereal solvents is indicated in the present work by the visible tendency of potassium to dissolve in 1,2-dimethoxyethane with formation of a blue solution⁷ while lithium gave no visible color in this medium. Moreover the physical state of the potassium (finely divided solid or liquid) should tend to make reductions by this metal more facile than those by lithium (a ribbon cut into small chips).

(10) It would seem appropriate to define what we mean by the term "carbanion rearrangement." The somewhat analogous Wagner-Meerwein rearrangement is classified as a carbonium ion rearrangement since the carbon atom to which the migrating group becomes attached has developed some fraction of positive charge in the transition state of the rearrangement. Similarly we will classify a carbanion rearrangement as one in which the migrating group becomes attached to an atom with an excess of negative charge. The role of the alkali metal cation in the present carbanion rearrangement is, therefore, not specified in our mechanistic designation. Either free carbanions,

The rather covalent magnesium derivative of 2,2,2-triphenylethyl might be expected to be similar to the lithium derivative and incomplete reports¹¹ indicate that this is true. A preliminary report has been made upon what appears to be a 1,2-shift of a vinyl group in the Grignard reagent from 3-butenyl chloride.¹² After completion of the present work Zimmerman and Zweig¹³ announced the rearrangement of 2,2-diphenylpropyllithium and of 2-phenyl-2-(*p*-tolyl)-propyllithium and concluded that these are rearrangements of carbanions on the basis of the greater extent of migration of phenyl than *p*-tolyl. These workers further observed that only rearranged potassium analogs could be obtained while magnesium analogs were immune to rearrangement.

Experimental Details¹⁴

2-Chloro-1,1,1-triphenylethane was prepared by the procedure previously published.¹ Anhydrous tetrahydrofuran was prepared by heating at reflux a commercial grade of tetrahydrofuran containing finely divided molten potassium which was vigorously stirred in a Morton high-speed stirring apparatus¹⁵ for one hour with final distillation of the tetrahydrofuran from the potassium through a Vigreux column, 35 cm. in length. In some of the earlier experiments tetrahydrofuran was purified by distillation from the sodium addition product of anthracene. In the experiments with lithium, tetrahydrofuran purified as above was heated at reflux with lithium aluminum hydride, and then distilled directly into the apparatus for conducting the reaction with lithium metal. 1,2-Dimethoxyethane (Eastman Kodak Co. white label grade) was purified over potassium in the same manner as for tetrahydrofuran.

Triethylamine (Eastman Kodak Co. white label grade) was purified by treatment of a 500-ml. portion with 30 ml. of benzoyl chloride and removal of the resulting white precipitate by filtration. The remaining liquid was heated at reflux for one hour with 30 ml. of additional benzoyl chloride and after cooling was filtered again. The product was distilled and the distillate allowed to stand for several hours over potassium hydroxide pellets. The resulting clear solution was then treated with potassium in the same manner as described for tetrahydrofuran.

Reaction of 2-Chloro-1,1,1-triphenylethane with Potassium.—The apparatus consisted of a high-speed Morton stirrer¹⁵ and a 500-ml. Morton flask; general reaction conditions were as previously described¹ for reaction with sodium. Freshly cut potassium metal (4.7 g., 0.12 g. atom) was heated in 200 ml. of tetrahydrofuran until reflux was attained. Vigorous stirring and reflux were maintained while 10.0 g. (34.3 mmoles) of 2-chloro-1,1,1-triphenylethane was dusted into the reaction mixture over a period of 30 minutes and stirring and heating were maintained for another 30 minutes. The first portion of the halide added caused a deep red color to appear in the solution and the final color was like that of bromine. After cooling to room temperature, the contents of the flask were forced onto a large excess of crushed solid carbon dioxide. The next day 50 ml. of absolute ethanol was added to decompose any unreacted potassium. The following day the reaction mixture was made slightly acidic by addition of gaseous hydro-

ion pairs or covalent organoalkali compounds may be the species which undergo rearrangement under the present conditions.

(11) C. W. Shoppee, [*Chemistry & Industry*, 759 (1954)] has quoted a personal communication from E. D. Hughes to the effect that carbonation of the Grignard reagent from 2-chloro-1,1,1-triphenylethane gave 2,2,3-triphenylpropanoic acid as well as 3,3,3-triphenylpropanoic acid. Earlier reports on this Grignard reagent [J. C. Charlton, I. Dostrovsky and E. D. Hughes, *Nature*, **167**, 986 (1951)] mentioned only products of normal structure.

(12) J. D. Roberts, *et al.*, *THIS JOURNAL*, **82**, 2646 (1960).

(13) H. E. Zimmerman and A. Zweig, *Am. Chem. Soc. Abst.*, Cleveland, April, 1960, p. 17-O; *Chem. Eng. News*, **38**, No. 16, 65 (1960).

(14) Melting points are uncorrected. Analyses are by Galbraith Microanalytical Laboratories.

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

gen chloride and the solvents were removed on the steam-bath under partial vacuum. The residue was treated with excess of aqueous sodium hydroxide and 3.4 g. of neutral material was extracted with ether. Acidification and extraction with ether gave, in the ether extract, 4.91 g. of crude acids, m.p. 99–134°. A 3.62-g. sample of the crude acids in chloroform was subjected to chromatography on a column, 3.4 cm. in diameter, packed to a height of 14 cm. with silicic acid (Mallinckrodt, 100 mesh, analytical reagent grade) wetted with chloroform. The column was eluted with chloroform containing increasing amounts of methanol.¹⁶ The first acid eluted from the column weighed 3.25 g. and had m.p. 100–120°. One recrystallization of 3.0 g. of this acid from ethyl alcohol gave 1.7 g. of acid, m.p. 129–131°. This acid was found to be identical with authentic 2,2,3-triphenylpropanoic acid (m.p. 130–131.5°, prepared by the procedure of Ramart¹⁷) as shown by mixed melting point and infrared spectral determinations. The second acid eluted from the column weighed 0.33 g. and had m.p. 129–140°. A 0.193-g. sample of this acid upon recrystallization from ethyl alcohol gave 0.136 g. of acid, m.p. 140–142°. A recrystallization gave 0.100 g., m.p. 143–145°. This acid had a neutralization equivalent of 219, which is close to the theoretical value of 212 for diphenylacetic acid and much smaller than the value of 302 for a triphenylpropanoic acid. A sample of this acid obtained from the following run by the same procedure could be sublimed at 50 μ at a bath temperature of about 115° and upon recrystallization from cyclohexane had m.p. 145–146°. This acid was found to be identical,¹⁸ according to mixed melting point and infrared spectral comparison, with a sample of diphenylacetic acid, m.p. 145–147°, obtained from Matheson, Coleman and Bell and purified by vacuum sublimation.

A second reaction between 2-chloro-1,1,1-triphenylethane and potassium metal was carried out exactly as in the first run except that the tetrahydrofuran and potassium were heated under reflux with vigorous stirring for 30 minutes before addition of the alkyl chloride. The yield of acids was 7.79 g. and this material upon chromatography gave 6.7 g. of crude 2,2,3-triphenylpropanoic acid and 0.31 g. of crude diphenylacetic acid, with most of the remainder of the product being an intermediate fraction.

Liquid sodium-potassium alloy was prepared in the usual apparatus from 4.7 g. of potassium and 0.53 g. of sodium in 200 ml. of tetrahydrofuran heated at reflux with stirring. The mixture was cooled to room temperature and 11.0 g. of 2-chloro-1,1,1-triphenylethane was added over a period of 25 minutes with stirring continued for an additional 30 minutes while the temperature was maintained at 20 \pm 3° with a cooling bath. The mixture was carbonated and worked up in the usual manner to give 6.22 g. of acids and 3.6 g. of neutral product. Chromatography on silicic acid indicated that the product was predominantly 2,2,3-triphenylpropanoic acid with about 0.1 g. of diphenylacetic acid.

Liquid sodium-potassium alloy prepared as above from 6.4 g. of potassium and 1.6 g. of sodium was treated in 250 ml. of tetrahydrofuran at 0 \pm 3° with 10.0 g. of 2-chloro-1,1,1-triphenylethane by slow addition of the latter over a period of 30 minutes. The mixture was then stirred for 60 additional minutes at this temperature before carbonation. At the first addition of halide to the alloy a red color developed immediately and this rapidly deepened to the color of bromine. From the reaction mixture was isolated 3.36 g. of acid whose infrared spectrum indicated that it was essentially all 2,2,3-triphenylpropanoic acid. The neutral material from this run gave a strong positive test for chloride upon sodium fusion; therefore, evidently considerable unreacted starting material was recovered.

Potassium metal (4.72 g.) in 250 ml. of 1,2-dimethoxyethane was heated at reflux with stirring for 10 minutes and then, with stirring stopped, the mixture was cooled to the freezing point of the solvent (–58°). After stirring for some 30 minutes at this temperature the solution acquired a pale blue color which rapidly developed a rather deep blue-black color. This color was observed to persist in the tem-

perature range of –58 to –35°. With the reaction mixture kept at –50 \pm 5°, a small portion of 2-chloro-1,1,1-triphenylethane was added. An immediate red-brown color was produced and on stirring some 10 minutes the blue-black color reappeared. After about a gram of the alkyl chloride had been added in this manner, the potassium sand suddenly agglomerated and stirring had to be stopped to prevent breaking the reaction vessel. The mixture was carbonated and gave 0.70 g. of acids and 0.34 g. of neutral material. The acidic fraction was sublimed twice at 50 μ and at a bath temperature of about 200° to give 0.34 g. of pale yellow crystals, m.p. 68–110°. The infrared spectrum of this material showed that it contained triphenylsuccinic anhydride and 2,2,3-triphenylpropanoic acid. This mixture was treated with hydrazine (see the details below under lithium) to give 0.12 g. of crude cyclic triphenylsuccinic hydrazide and 0.26 g. of acidic material. The acidic fraction upon chromatography gave 0.11 g. of essentially pure 2,2,3-triphenylpropanoic acid with the remainder of the acidic fraction also being chiefly this acid according to its infrared absorption spectrum.

Reaction of 2-Chloro-1,1,1-triphenylethane with Lithium.—The apparatus and general procedure for conducting reactions with lithium was the same as that for potassium except that the 2-chloro-1,1,1-triphenylethane (10.0 g., 34.3 mmoles) was dissolved in 25 ml. of tetrahydrofuran and added from a dropping funnel through a side-arm of the reaction flask. In 250 ml. of freshly distilled tetrahydrofuran was placed 0.62 g. (0.0883 g. atom) of lithium ribbon chopped into small pieces. The lithium ribbon was a low-sodium grade (0.005% Na max.) obtained from the Lithium Corp. of America. A small portion of the halide was added to the reaction mixture at –30°, but when after 40 minutes at this temperature no reaction was apparent, the temperature was raised to –10° and a red color was observed in 10 minutes. The reaction mixture was again lowered to –30 \pm 5° and the remainder of the halide was added over a period of 30 minutes. The reaction was stirred for an additional 30 minutes at this temperature before carbonation. The final color of the solution was a black-purple, almost like that of KMnO₄. During carbonation about half of the reaction mixture was lost due to excessive frothing. Water (25 ml.) was added to decompose any unreacted lithium and the product was worked up as with potassium. The yield was 2.35 g. of neutral material and 2.82 g. of acidic material, m.p. 165–174°. A 1.9-g. sample of the acidic fraction upon chromatography on silicic acid gave 1.8 g. of acid of m.p. 165–179°; this acid upon recrystallization from ethyl alcohol gave 1.1 g. of acid, m.p. 179–180°. This acid was shown to be identical with 3,3,3-triphenylpropanoic acid, m.p. 179.2–180.3°, prepared by the method of Fosse as elaborated by Hellerman,¹⁹ by a mixed melting point determination and by intercomparison of infrared spectra. The remaining 0.1 g. of acid from the chromatography, which was the initial acid to come off the column, was non-crystalline; its infrared spectrum indicated that it was a mixture of 3,3,3-triphenylpropanoic acid and 2,2,3-triphenylpropanoic acid.

A reaction at 28 \pm 3° was carried out on the same scale and by the general technique as for the first reaction. An attempt to initiate this reaction at 66° was unsuccessful as judged by the appearance of the solution. At –10° 2 hours of vigorous stirring were required to initiate the formation of a red color; this color serves as a useful indicator for reaction. The halide was then added dropwise over a period of 30 minutes at –10°. The solution was allowed to warm to 28° and was stirred at this temperature for 1 hour. After carbonation and the usual work-up there was isolated 5.3 g. of neutral material and 3.49 g. of acidic material. The ultraviolet absorption of the neutral material at 300 m μ indicated the presence of about 8% by weight of triphenylethylene. Chromatography of a 2.7-g. sample of the acids on silicic acid gave as first fraction 0.86 g. of compound, m.p. 109–113°, which was identified as triphenylsuccinic anhydride (m.p. 112.5–114°) by comparison of its infrared spectrum with that of a known sample.¹ A second fraction of 1.28 g., m.p. \sim 119–129°, was essentially 2,2,3-triphenylpropanoic acid according to comparison of its infrared spectrum with that of an authentic sample.¹⁷ Recrystallization of a 0.12-g. sample of the second fraction from

(16) We are greatly indebted to Dr. John Dyer for instruction in the technique of this chromatography.

(17) P. Ramart, *Bull. soc. chim. (France)*, [4] **35**, 196 (1924).

(18) We are indebted to Dr. Jack Hine for first suggesting diphenylacetic acid for the possible identity of this acid.

(19) L. Hellerman, *THIS JOURNAL*, **49**, 1735 (1927); R. Fosse, *Compt. rend.*, **145**, 197 (1907).

ethyl alcohol gave 0.066 g. of acid, m.p. 130.5–131°, as expected for pure 2,2,3-triphenylpropanoic acid. A third fraction of 0.45 g. was a glassy material of which only 40% could be distilled at 20 μ and a bath temperature up to 190°; the infrared spectrum of the distillate was identical with the spectrum of 2,2,3-triphenylpropanoic acid.

Another reaction, which was initiated in 80 minutes after addition of a small amount of halide at -10° , was cooled to $-55 \pm 5^\circ$ and the remainder of halide was added over a period of 30 minutes with stirring for an additional 30 minutes at -55° before carbonation. There resulted 4.88 g. of neutral material and 4.46 g. of acidic material. The acidic material had m.p. 173–179°, which is close to that of pure 3,3,3-triphenylpropanoic acid (m.p. 179–180°). Infrared spectra on a sample distilled at 20 μ confirmed this composition and showed the presence of a trace (about 3%) of 2,2,3-triphenylpropanoic acid and some 0.7% of triphenylsuccinic anhydride. Presumably the 2,2,3-triphenylpropanoic acid resulted from 1,1,2-triphenylethyl carbanion which was formed during initiation at -10° and must have been responsible for the deep red-purple color of the solution. A sodium fusion test upon the neutral material gave a strong test for chloride ion; therefore subsequent reactions at low temperatures were run for longer times.

Another reaction between 10.0 g. of 2-chloro-1,1,1-triphenylethane and 0.70 g. of lithium was initiated at -10° after 3.5 hours of vigorous stirring. The major portion (~96%) of the halide was added at $-60 \pm 5^\circ$ over a period of 30 minutes and the reaction mixture was stirred at this temperature for three hours before carbonation. There was isolated 6.42 g. of acid, m.p. 174–176°. Infrared spectral analysis of a sample of this acid which had been sublimed at 20 μ pressure showed that the acid was 94% pure 3,3,3-triphenylpropanoic acid containing about 3% of 2,2,3-triphenylpropanoic acid and about 3% triphenylsuccinic anhydride. The neutral material from this run amounted to 3.43 g. and this gave only a weak test for chloride ion upon sodium fusion.

Another run was made exactly like the previous one except that after stirring for 3 hours at -60° it was allowed to warm to 0° and was maintained at this temperature with stirring for 60 minutes before carbonation. There was isolated 5.35 g. of acids and 4.21 g. of neutral material. Chromatographic separation of the acids on a column of silicic acid was not very successful, possibly because triphenylsuccinic acid tended to come off the column both in the form of the free acid and as the anhydride. The following method of separation was devised based on reaction of the acids with hydrazine.

Triphenylsuccinic anhydride (0.50 g.) and 5.0 ml. of hydrazine hydrate were placed in a flask fitted with a condenser and the mixture was heated on the steam-bath for 1 hour. The mixture was cooled to room temperature and the crystals which precipitated were removed by filtration and washed with water. After drying *in vacuo* at 78° the crystals had m.p. 180–181.5° and weighed 0.50 g. (96% yield). The product was sublimed at a bath temperature of 190–196° and a pressure of 15 μ without change in melting point and were analyzed.

Anal. Found: C, 77.46; H, 5.42; N, 7.94. Calcd. for $C_{22}H_{18}N_2O_2$: C, 77.17; H, 5.30; N, 8.18.

This compound therefore appears to be a cyclic hydrazide of triphenylsuccinic acid. 3,3,3-Triphenylpropanoic acid when subjected to similar treatment with hydrazine gave a water-soluble salt of hydrazine from which the starting acid could be recovered in 94% yield upon acidification. Similar treatment of 2,2,3-triphenylpropanoic acid gave a 90% recovery of an impure acid. Most of the impurities in the acid could be removed by extraction of the aqueous hydrazine solution of the acid with chloroform before acidification and then vacuum sublimation of the product. The over-all recovery of 2,2,3-triphenylpropanoic acid was at least 70%.

The acids from the last run above with lithium were distilled (or sublimed) *in vacuo* at 20 μ at a bath temperature

up to 189° with some 90% recovery of acids and removal of some tarry material (test experiments showed that 3,3,3- and 2,2,3-triphenylpropanoic acids could be similarly distilled with 90% or better recovery of acids of unchanged m.p.). A 1.00-g. sample of the distilled acids after heating for 1 hour on a steam-bath with 5.0 ml. of hydrazine hydrate and steam distillation of most of the excess hydrazine gave 0.35 g. of crude hydrazide upon extraction of the aqueous solution with chloroform. Acidification and extraction with ether gave 0.69 g. of acids. Distillation of the acids at 20 μ gave 0.59 g. of volatile acids. Analysis of these acids by infrared absorption by the technique summarized below gave $38 \pm 8\%$ of 3,3,3-triphenylpropanoic acid, $62 \pm 8\%$ of 2,2,3-triphenylpropanoic acid and some 0.5% of triphenylsuccinic anhydride. In a similar reaction of 2-chloro-1,1,1-triphenylethane with lithium at -60° for 3.5 hours and then at 0° for 1 hour, the acids which resulted upon carbonation were partially reacted with hydrazine as described. The unreacted acids after distillation at 20 μ were separated by chromatography on silicic acid; 2,2,3-triphenylpropanoic acid and 3,3,3-triphenylpropanoic acid were found in a ratio of about two to one.

A run to test the effect of triethylamine was made with the usual quantities of reactants in 200 ml. of tetrahydrofuran. Reaction between lithium and 2-chloro-1,1,1-triphenylethane was initiated at -10° and then the remainder of the halide was added over a period of 30 minutes at a temperature of $-65 \pm 5^\circ$. The reaction mixture was stirred for 2 hours at this temperature and then 100 ml. of cold triethylamine was added with the low temperature being maintained. There was an immediate color change from dark red to light orange. The reaction mixture was stirred at -65° for 1 hour and then carbonated. At the end of the period of stirring the reaction mixture was again dark red; however, at no time in this entire run was the red color as deep as in any of the previous runs with lithium. This reaction yielded 3.10 g. of acid which melted at 175.5–178.0°. The infrared spectrum confirmed that this was essentially pure 3,3,3-triphenylpropanoic acid.

Three attempts to effect reaction between 2-chloro-1,1,1-triphenylethane and lithium at -50° in 1,2-dimethoxyethane as solvent were unsuccessful. These reactions were initiated in the usual manner at -10° and even though the usual red color was observed at this stage little or no further reaction took place upon cooling to -50° for reaction times up to 3 hours in an atmosphere of helium or the usual atmosphere of nitrogen. From these runs some 80% of unreacted starting chloride was recovered. In a run which was at -50° for 3 hours and at 0° for 1 hour, 10 g. of 2-chloro-1,1,1-triphenylethane with lithium in 1,2-dimethoxyethane gave after carbonation 1.8 g. of acids which after two distillations at 30–50 μ yielded 1.1 g. of product, m.p. 95–105°. Recrystallization from ethanol gave 0.8 g. of crystals, m.p. 105–108°, whose infrared spectrum indicated the substance to be predominately triphenylsuccinic anhydride.

Infrared spectra were determined with a Perkin-Elmer double beam model 21 infrared spectrometer. 2,2,3-Triphenylpropanoic acid has absorption maxima near 7.90 and 13.86 μ which distinguish it from 3,3,3-triphenylpropanoic acid which has characteristic maxima near 8.14 and 13.23 μ . Triphenylsuccinic anhydride has characteristic absorption at 5.58 μ which is of sixfold or greater intensity than the four previous absorption bands. For quantitative analysis solutions containing 0.0480 g. of acid in 10.0 ml. of carbon disulfide were placed in 3-mm. rock salt cells and measured at the five wave lengths.

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