[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, GEORGIA INSTITUTE OF TECHNOLOGY]

Preparation of 2-Chloro-1,1,1-triphenylethane and Rearrangement in its Reaction with Sodium[1]

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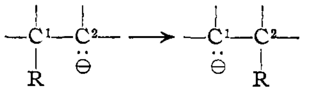
The reported rearrangement during the reaction of "2-chloro-1,1,1-triphenylethane" (prepared from reaction of phosphorus pentachloride on 1,1,1-triphenylethane) with sodium in liquid ammonia is shown to be in error. Rearrangement, instead, occurred during the preparation of the chloride which is in fact 1-chloro-1,2,2-triphenylethene. Authentic 2-chloro-1,1,1-triphenylethane (from triphenylmethylsodium and methylene chloride) is converted by sodium in refluxing dioxane–*t*-amyl alcohol predominantly to 1,1,1-triphenylethane, but with sodium in refluxing dioxane alone, a red-colored carbanion is formed which upon carbonation affords 2,2,3-triphenylpropanoic acid and a hydrocarbon, largely 1,1,2-triphenylethane. The rearrangement cannot proceed by way of triphenylethylene since this substance affords a different carbanion upon reaction with sodium in refluxing dioxane. The rearrangement apparently proceeds *via* rearrangement of the 2,2,2-triphenylethyl carbanion, but rearrangement of the corresponding free radical is not excluded.

While molecular rearrangements of carbon skeleton involving 1,2-shifts are exceedingly common for carbonium ions (Wagner rearrangement) and are becoming fairly common for free radicals, corresponding rearrangements of carbanions in which the migrating group shifts from one carbon to another (as opposed to the Stevens and Wittig rearrangements[2]) have seldom, if ever, been realized. This type of carbanion rearrangement may be summarized as



$$-\overset{|}{\underset{\substack{|\\ R}}{C^1}}-\overset{|}{\underset{\ddot{\ominus}}{C^2}}- \longrightarrow -\overset{|}{\underset{\ddot{\ominus}}{C^1}}-\overset{|}{\underset{\substack{|\\ R}}{C^2}}- \qquad (1)$$

As a possible example, Wooster and Mitchell[3] have reported that when the compound I to which Cone and Robinson[4] provisionally assigned the structure of 2-chloro-1,1,1-triphenylethane was treated with sodium in liquid ammonia, a red organosodium compound was obtained which upon treatment with ammonium chloride gave 1,1,2-triphenylethane. Wooster and Mitchell considered the possibility that their starting chloride might have a rearranged structure, but since it could not likely have been 1-chloro-1,1,2-triphenylethane they concluded that "the structure of the original chloride seems to be in little doubt." Wooster and Ryan[5] later confirmed the structure of the red organosodium compound by its interaction with ethyl bromide to give 1,2,2-triphenylbutane. Wooster and Mitchell concluded that the reaction of the chloride I with sodium gave rise to the expected 2,2,2-triphenylethylsodium which then rearranged with migration of a phenyl group to give the observed red organosodium compound.

Synthesis of 2-Chloro-1,1,1-triphenylethane.—Since rearrangements of organosodium compounds according to equation 1 are so rare,[6] we deemed it of interest to confirm the work of Wooster and Mitchell by synthesis of 2-chloro-1,1,1-triphenylethane by an independent path. A reasonable process appeared to be the reaction of triphenylmethylsodium with methylene chloride according to the process

$$(C_6H_5)_3CNa + CH_2Cl_2 \longrightarrow (C_6H_5)_3CCH_2Cl + NaCl \qquad (2)$$

Dropwise addition of triphenylmethylsodium to excess methylene chloride gave rise to an essentially instantaneous loss of the red color of triphenylmethylsodium and a halide II of m.p. 101–102° was obtained in good yield. The halide I of Cone and Robinson,[4] on the other hand, has m.p. of 118°. A mixed melting point of I and II showed depression. Halide II gave a satisfactory elementary analysis for 2-chloro-1,1,1-triphenylethane ($C_{20}H_{17}Cl$) while the compound I prepared according to the procedure of Cone and Robinson gave a C,H-analysis which agreed somewhat more closely with $C_{20}H_{15}Cl$. Elementary analyses alone do not provide a clear distinction since in any event the analyses are similar.

The Wurtz synthesis of II would be expected to occur without rearrangement. On the other hand, halide I was synthesized by reaction of phosphorus pentachloride with 1,1,1-triphenylethane at 190–200°; under similar conditions Cone and Robinson[4] found that 1,1,1,2-tetraphenylethane gave tetraphenylethylene with migration of a phenyl group. If a similar rearrangement occurred during the reaction of 1,1,1-triphenylethane with phosphorus pentachloride, triphenylethylene would be expected as an intermediate. The reaction of phosphorus pentachloride in benzene upon triphenylethylene at room temperature for five days has been reported[7] to give a 49% yield of 1,2-dichloro-1,1,2-triphenylethane, which when heated above its melting point (111.5°) is quantitatively converted to 1-chloro-1,2,2-triphenylethene (m.p. 117.5–118°). We have found that at bath temperatures of 190–200° for two hours, phosphorus pentachloride converts triphenylethylene in 67% yield into a halide III, doubtlessly 1-chloro-1,2,2-triphenylethene. Halide III has essentially the same melting point and gives no melting point depression with the halide I of Cone and Robinson.

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[1] Our conclusions concerning the structure of the compound of Cone and Robinson and the preparation of 2-chloro-1,1,1-triphenylethane were presented at the Southwide Chemical Conference, Atlanta, Ga., Oct. 16, 1950. For abstract see *The Filter Press* (Ga. Section of the Am. Chem. Soc.), V, No. 8, 12 (1950).

[2] For a survey of the related Stevens rearrangement of quaternary ammonium salts and Wittig rearrangement of ethers see C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, pp. 523–528.

[3] C. B. Wooster and N. W. Mitchell, THIS JOURNAL, **52**, 1042 (1930).

[4] L. H. Cone and C. S. Robinson, *Ber.*, **40**, 2160 (1907).

[5] C. B. Wooster and J. F. Ryan, THIS JOURNAL, **54**, 2419 (1932).

[6] Rearrangements observed during the reaction of certain highly arylated olefins with sodium may provide additional examples; see K. Ziegler and F. Crossman, *Ber.*, **62**, 1768 (1929); C. F. Koelsch, THIS JOURNAL, **55**, 3394 (1933), and **56**, 480 (1934).

[7] J. van de Kamp and M. Sletzinger, *ibid.*, **63**, 1879 (1941).

We conclude that halides I and III are 1-chloro-1,2,2-triphenylethene while II is 2-chloro-1,1,1-triphenylethane.

To confirm these structural assignments the ultraviolet absorption spectra were run and are recorded in Fig. 1. Compounds I and III have identical ultraviolet absorption spectra and the spectra are similar to that of triphenylethylene (V). The effect of the chlorine atom upon the spectrum of triphenylethylene appears to be analogous to that of an α-methyl group upon the spectrum of *trans*-stilbene.[8] The ultraviolet absorption spectrum of chloride II is very different from that of I and is instead similar to that of 1,1,1-triphenylethane (IV).

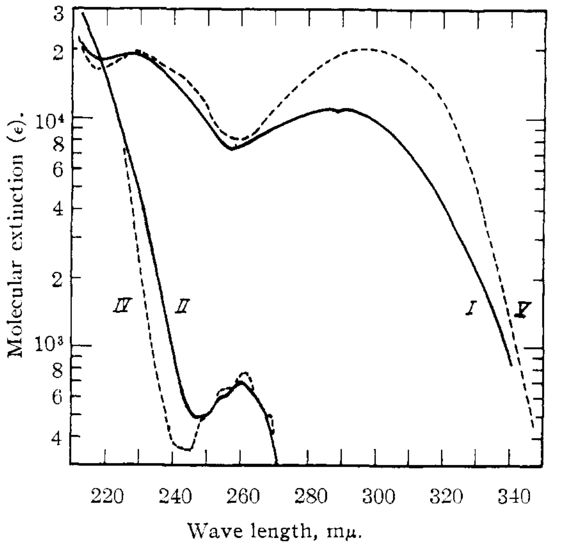

Fig. 1.—Ultraviolet absorption spectra in 95% ethanol for $Ph_2C{=}CClPh$ (I), Ph_3CCH_2Cl (II), Ph_3CCH_3 (IV) and $Ph_2C{=}CHPh$ (V).

When compound II, 2-chloro-1,1,1-triphenylethane, is heated with phosphorus pentachloride or a mixture of phosphorus pentachloride and phosphorus trichloride, 1-chloro-1,2,2-triphenylethene is formed in good part. Thus the synthesis of the chloride[9] of Cone and Robinson may be formulated[10] in broad scope as

$$Ph_3CCH_3 \xrightarrow{PCl_5} [Ph_3CCH_2Cl] \longrightarrow Ph_2C{=}CHPh \xrightarrow{PCl_5} Ph_2C{=}CClPh \quad (3)$$

Here we regard 2-chloro-1,1,1-triphenylethane as a possible but by no means necessary intermediate, since the chlorination of 1,1,1-triphenylethane by phosphorus pentachloride probably proceeds by way of the 2,2,2-triphenylethyl free radical and this radical is known[11] to rearrange readily with migration of a phenyl group.

The synthesis of 2-chloro-1,1,1-triphenylethane and the structural determinations given here were, unknown to us at the time, carried out also by Charlton, Dostrovsky and Hughes.[12]

Reaction of 2-Chloro-1,1,1-triphenylethane with Sodium.—It is evident from the above discussion that the rearrangement which Wooster and Mitchell thought they observed in the reaction of the chloride of Cone and Robinson with sodium in liquid ammonia actually took place during the synthesis of Cone and Robinson. We may now interpret Wooster and Mitchell's work according to the scheme

$$Ph_2C{=}CClPh \xrightarrow[NH_3]{Na} Ph_2C{=}CHPh \xrightarrow[NH_3]{Na} \underset{Na}{Ph_2CCH_2Ph} \xrightarrow{NH_4Cl} Ph_2CHCH_2Ph \quad (4)$$

The reduction of triphenylethylene in liquid ammonia as shown here has in fact been demonstrated by Wooster and co-workers.[3,5]

Charlton, Dostrovsky and Hughes[12] have found that authentic 2-chloro-1,1,1-triphenylethane upon reaction with sodium in liquid ammonia followed by treatment with ammonium chloride gave 1,1,1-triphenylethane. Moreover the Grignard reagent prepared from this halide gave[12] the same hydrocarbon upon treatment with water. Thus no valid evidence exists in the literature for the rearrangement of the 2,2,2-triphenylethyl carbanion.[13]

From the inception of this problem it has seemed to us that the 2,2,2-triphenylethyl carbanion was a favorable case to look for rearrangement since rearrangement would convert a reactive primary carbanion into a more stable benzhydryl type carbanion

$$\underset{VI}{Ph_3CCH_2\overset{\ominus}{:}} \longrightarrow \underset{VII}{Ph_2\overset{..\ominus}{C}{-}CH_2Ph} \quad (5)$$

A carbanion such as VI, unlike VII, would not be expected to be stable[5] in a solvent of as good proton-donating ability as liquid ammonia. Accordingly we have studied the reaction of 2-chloro-1,1,1-triphenylethane in less reactive solvents. Charlton, Dostrovsky and Hughes[12] have reported that the reaction of this chloride with sodium is tardy and complicated by the thermal decomposition of the chloride; at 120° in petroleum solution, triphenylethylene was isolated from the reaction products. Similarly we[14] have recovered 70% of unreacted chloride from attempted reaction with sodium sand in *n*-pentane on the Morton high-

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[8] R. N. Jones, This Journal, **65**, 1818 (1943).

[9] E. P. Kohler and H. Potter, *ibid.*, **57**, 1316 (1935), have reported that when a sulfone apparently $p\text{-}CH_3C_6H_4SO_2CH_2C(C_6H_5)_3$, is heated at 200° with phosphorus pentachloride a chloride identical with an "authentic sample" of 2-chloro-1,1,1-triphenylethane is obtained. Since the only such chloride known at the time was that of Cone and Robinson, Kohler and Potter's product would likewise appear to be 1-chloro-1,2,2-triphenylethene and their proof of structure of their sulfone by its reaction with phosphorus pentachloride is insecure.

[10] *Cf.* E. D. Hughes, *Bull. soc. chim. (France)*, [5] **18**, C. 41 (1951), and also ref. 12.

[11] D. Y. Curtin and M. J. Hurwitz, This Journal, **74**, 5381 (1952).

[12] J. C. Charlton, I. Dostrovsky and E. D. Hughes, *Nature*, **167**, 986 (1951). The author is indebted to Professor Hughes for kindly communicating his results before publication.

[13] A referee has pointed out that 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 the expected 3,3,3-triphenylpropanoic acid.

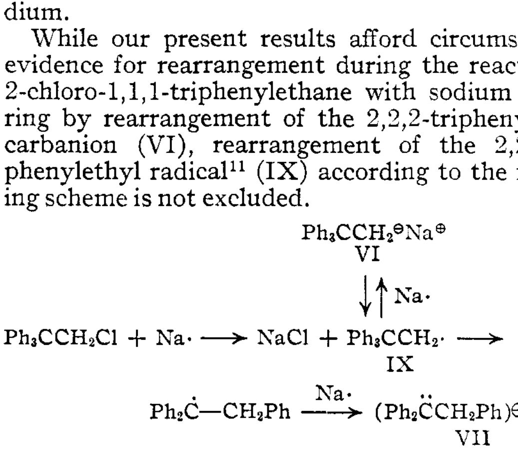
[14] Experiment performed by Dr. Wendell P. Long to whom the author is indebted.

speed stirring apparatus and obtained no significant amount of carboxylic acid upon carbonation of the reaction mixture. With finely divided molten sodium in refluxing dioxane, however, 2-chloro-1,1,1-triphenylethane reacted rapidly to give a red-colored solution which upon carbonation afforded a 43% yield of carboxylic acid, identified as 2,2,3-triphenylpropanoic acid, and a neutral hydrocarbon fraction consisting of 70 ± 2% 1,1,2-triphenylethane and the remainder 1,1,1-triphenylethane as deduced from infrared analysis.

Decomposition with *t*-amyl alcohol of the red-colored solution of organosodium compound from the reaction of 2-chloro-1,1,1-triphenylethane with sodium in dioxane gave a hydrocarbon consisting of 81 ± 3% 1,1,2-triphenylethane with the remainder 1,1,1-triphenylethane. On the other hand reaction of this chloride with sodium in a refluxing mixture of dioxane and *t*-amyl alcohol gave a product which consisted of 93.7 ± 0.5% 1,1,1-triphenylethane and only 6.3 ± 0.5% of 1,1,2-triphenylethane as deduced by infrared analysis. This latter reaction confirms the structure assigned to chloride II. The mechanism of the reduction of alkyl halides by sodium and alcohols is not well established. If such reductions proceed by way of carbanions, then these reactions may be interpreted on the basis that in the presence of *t*-amyl alcohol, carbanion VI receives a proton to form hydrocarbon before appreciable rearrangement has occurred while in absence of alcohol carbanion VI rearranges to carbanion VII.

Wooster and Mitchell[3] considered an alternative mechanism for their alleged rearrangement, namely that 2-chloro-1,1,1-triphenylethane loses the elements of hydrogen chloride with rearrangement to give triphenylethylene which is then reduced to carbanion VII. Moreover Charlton, Dostrovsky and Hughes[12] report that 2-chloro-1,1,1-triphenylethane undergoes a slow decomposition into hydrogen chloride and triphenylethylene at temperatures in the neighborhood of its melting point. In the present work this alkyl chloride II could be recovered substantially unchanged after refluxing for one hour in dioxane in absence of sodium under otherwise the same conditions as used for the reaction of II with sodium. Even if triphenylethylene were formed by thermal or other processes during the reaction of II with sodium, experiments have shown that it would not be converted by sodium in refluxing dioxane into carbanion VII, unlike the case (see equation 4) in which liquid ammonia is used as solvent. Instead addition of triphenylethylene to an excess of finely divided molten sodium in refluxing dioxane gives a dark green solution which upon carbonation affords an incompletely identified mixture of carboxylic acids whose neutralization equivalent shows approximately two carboxyl groups per triphenylethylene and which in part undergoes dehydration to give triphenylacetic anhydride (VIII). Reaction of the dark green organosodium solution from triphenylethylene with *t*-amyl alcohol gives 1,1,2-triphenylethane in substantially quantitative yield. From the corresponding reactions of the product from triphenylethylene and sodium in diethyl ether at room temperature, Schlenk and Bergman[15] have, somewhat similarly, reported only triphenylsuccinic acid (as anhydride) and triphenylethane. These experiments, of course, do not exclude the intervention of small amounts of triphenylethylene as some sort of catalyst or sodium carrier for the reaction of 1,1,1-triphenyl-2-chloroethane with sodium.

While our present results afford circumstantial evidence for rearrangement during the reaction of 2-chloro-1,1,1-triphenylethane with sodium occurring by rearrangement of the 2,2,2-triphenylethyl carbanion (VI), rearrangement of the 2,2,2-triphenylethyl radical[11] (IX) according to the following scheme is not excluded.



$$\begin{array}{c}\underset{\text{VI}}{Ph_3CCH_2^{\ominus}Na^{\oplus}}\\ \downarrow\uparrow Na\cdot\\ Ph_3CCH_2Cl + Na\cdot \longrightarrow NaCl + \underset{\text{IX}}{Ph_3CCH_2\cdot} \longrightarrow\end{array}$$

$$Ph_2\dot{C}\text{—}CH_2Ph \xrightarrow{Na\cdot} \underset{\text{VII}}{(Ph_2\ddot{C}CH_2Ph)^{\ominus}Na^{\oplus}}$$

Here carbanion VI is depicted as being in reversible equilibrium with IX. The mechanism of the rearrangement obviously resolves in part to the mechanism of the first step of the Wurtz reaction. Just as direct formation of carbanions (as opposed to free radicals) most simply[16] explains the first phase of the Wurtz reaction with primary alkyl halides, a carbanion intermediate VI most simply explains the rearrangement, since it can account (see above) for the absence of appreciable products of rearrangement when *t*-amyl alcohol is present in the reaction medium.

Experimental Details[17,18]

1-Chloro-1,2,2-triphenylethene (I) from 1,1,1-Triphenylethane.—Phosphorus pentachloride was allowed to react with 1,1,1-triphenylethane[19] according to the procedure of Cone and Robinson.[4] The product after several recrystallizations from ethanol and from *n*-hexane had m.p. 117.3–118.9°. Since the original workers analyzed the compound only for chlorine, the halide was submitted for C, H analysis. Found: C, 82.56, 82.35; H, 5.41, 5.47 (Calcd. for $C_{20}H_{15}Cl$: C, 82.61; H, 5.20. Calcd. for $C_{20}H_{17}Cl$: C, 82.04; H, 5.85).

In a repetition of the synthesis of Cone and Robinson with 5.0 g. (19.4 mmoles) of 1,1,1-triphenylethane and 8.75 g. (41.9 mmoles) of phosphorus pentachloride heated under conditions for reflux in a bath at 190–197° for 2.0 hours, there was obtained, after one recrystallization from ethanol, 3.9 g. of white crystals of m.p. 63–103° whose ultraviolet absorption spectrum indicated the presence of 51% by weight of I (or 36% yield of I from starting hydrocarbon). The higher yield of I reported by Cone and Robinson evidently is due either to conducting the reaction with phosphorus pentachloride in a sealed tube or permitting the phosphorus trichloride produced to distil from the reaction vessel in order to maintain an effective reaction temperature of 190–200°.

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[15] W. Schlenk and E. Bergman, *Ann.*, **463**, 45 (1928).

[16] A. A. Morton, J. B. Davidson and H. A. Newey, THIS JOURNAL, **64**, 2240 (1942); D. Bryce-Smith, *J. Chem. Soc.*, 1603 (1956).

[17] Melting points are uncorrected and were determined in capillary tubes.

[18] Analyses by Clark Microanalytical Laboratory.

[19] M. Gomberg and L. H. Cone, *Ber.*, **39**, 1466 (1906). The present author is indebted to Mr. Charles W. Glankler for conducting this preparation and also for carrying out a portion of the literature survey upon the present problem.

2-Chloro-1,1,1-triphenylethane (II).—Freshly prepared triphenylchloromethane[20] (5.0 g., 17.9 mmoles) and 2.2 g. (0.097 g. atom) of sodium (poppy-seed size particles) in 50 ml. each of anhydrous ether and benzene were converted into triphenylmethylsodium by shaking with sharp particles of glass by the procedure of Bachmann and Wiselogle.[21,22] The resulting dark red solution was filtered through a glass wool plug to remove unreacted sodium and then added in a slow stream to 50 ml. (0.79 mole) of methylene chloride. All of these operations were conducted under a nitrogen atmosphere. The red color of the triphenylmethylsodium disappeared essentially instantly upon contact of this reagent with methylene chloride and the reaction mixture became warm. The resulting solution was washed with water, dried over anhydrous magnesium sulfate, and concentrated (finally *in vacuo*) to about seven milliliters. The remaining oil was dissolved in hot ethyl alcohol and chilled to give 3.3 g. of light yellow crystals of m.p. 86–96°. Recrystallization from alcohol gave 0.08 g. of substance, m.p. *ca.* 165–170°, which was insoluble in the hot alcohol used, and after treatment with Nuchar C, 2.1 g. (40% yield) of nearly pure 2-chloro-1,1,1-triphenylethane, m.p. 98–100.5°, was obtained. Final recrystallization from *n*-hexane and then alcohol gave a product of m.p. 101.0–101.8°.

Anal. Found: C, 82.26; H, 5.79; Cl, 12.24. Calcd. for $C_{20}H_{17}Cl$: C, 82.04; H, 5.85; Cl, 12.11.

In another preparation similar to the above but with four times the quantity of reactants and with use of a mechanical stirrer during the addition of triphenylmethylsodium to methylene chloride, 12.5 g. (59% yield) of product, m.p. 96–99.5°, was obtained.

In preparations on a larger scale, triphenylmethylsodium was prepared after the procedure of Renfrow and Hauser[23] from powdered sodium amalgam (51 g. of sodium and 2100 g. of mercury) and triphenylchloromethane (278.8 g., 1.00 mole) in 1.25 l. of anhyd. ether. The triphenylmethylsodium was siphoned under a nitrogen atmosphere from the mercury and added over a 35-minute period to 1000 ml. of well-stirred methylene chloride at 18 ± 5°. The mixture was worked up somewhat as described above, but the oil after removal of solvent was dissolved in 600 ml. of thiophene-free benzene and the benzene solution was extracted 24 times with 100-cc. portions of concentrated sulfuric acid. The first sulfuric acid extract was black and the last sulfuric acid extract was light red in color. The benzene layer was washed with water, sodium hydroxide, then water, dried over anhyd. magnesium sulfate, filtered, concentrated somewhat, and allowed to evaporate slowly upon standing. A nearly completely crystalline residue was obtained from which some oil was separated by decantation and the crystalline product washed with four 25-ml. portions of *n*-pentane. The resulting light yellow crystals of crude 2-chloro-1,1,1-triphenylethane had m.p. 89–96° and totaled 195.5 g. (66.7% yield). Several recrystallizations from acetone and, sometimes, cyclohexane gave a pure product. During these preparations and purifications small amounts of high melting material, m.p. 178–190°, and a considerable amount of low melting to semi-crystalline oil was obtained and not investigated further.[24]

1-Chloro-1,2,2-triphenylethene (III).—1,1,2-Triphenylethylene[25] (5.0 g., 19.5 mmoles) was heated in a bath at 190–200° under conditions for reflux with 7.0 g. (33 mmoles) of phosphorus pentachloride for two hours. The product was disssolved in 35 ml. of benzene and the solution washed (caution) with two 10-ml. portions of water, then sodium carbonate followed by water again. The benzene was removed by distillation (eventually *in vacuo*) and the residue crystallized from ethyl alcohol to give 3.8 g. (67% yield) of 1-chloro-1,2,2-triphenylethene, m.p. 115.5–118°, which upon recrystallization from ethyl alcohol with aid of Nuchar C gave colorless crystals of m.p. 117.8–119.3°. A melting point upon a well ground mixture of equal portions of halide I and halide III showed no depression. The ultraviolet absorption spectrum of III was identical with that of I shown in Fig. 1.

Conversion of II to I.—2-Chloro-1,1,1-triphenylethane (5.66 g., 9.35 mmoles) with 4.4 g. (21 mmoles) of phosphorus pentachloride was heated under conditions for reflux at a bath temperature of 190–197° for 2.0 hours. Some of the PCl_5 solidified in the condenser and three times was scraped back into the reaction vessel. The product was separated as described for III above and recrystallized once from ethyl alcohol to give 4.1 g. of crystals of m.p. about 80–113° whose ultraviolet absorption spectrum indicated a composition of 60% by weight of 1-chloro-1,2,2-triphenylethene I (43% yield based upon compound II). That halide II is unreactive toward phosphorus trichloride was shown by refluxing halide II (2.00 g., 6.8 mmoles) with 0.90 ml. (10 mmoles) of phosphorus trichloride for three hours and working up the reaction mixture as described for III above to give a 71% recovery of unreacted starting halide. Moreover when halide II (4.00 g.) was heated at reflux (bath temp. 200 ± 10°) with 3.02 g. (14.5 mmoles) of phosphorus pentachloride and 0.90 ml. of phosphorus trichloride for four hours and the reaction mixture worked up similarly, 2.35 g. of crystalline product, m.p. 78–107°, whose ultraviolet absorption spectrum indicated a composition of 65 ± 5% of I, was obtained.

Reaction of II with Sodium in Dioxane.—The apparatus consisted of a 500-ml. Morton flask (2 creases, inverted cone) and a Morton high-speed stirrer.[26] To one neck of the flask a Vigreux type column was attached to act as an air-cooled condenser and to the other neck was attached, by large diameter rubber tubing, a flask containing the 2-chloro-1,1,1-triphenylethane (10.0 g., 34.3 mmoles). To the flask was added 200 ml. of purified[27] anhydrous 1,4-dioxane and 2.62 g. (0.114 g. atoms) of freshly cut sodium metal. The apparatus was swept with nitrogen and kept under an atmosphere of nitrogen. The solvent was heated to the boiling point, stirring was commenced, and the chloride added portion-wise over a period of one-half hour with stirring and refluxing continued for a second half-hour period. An orange-red color developed immediately upon addition of the first portion of chloride and the final color was a dark red (bromine color). After cooling, the contents of the flask were forced onto solid carbon dioxide. After volatilization of unreacted carbon dioxide upon standing, 50 ml. of ethyl alcohol was added to decompose unreacted sodium. The mixture was then made slightly acidic by addition of gaseous hydrogen chloride and the solvents removed at steam-bath temperature under partial vacuum. The residue was treated with excess sodium hydroxide and 4.60 g. of a neutral material was extracted with ether. Acidification and extraction with ether gave, in the ether extract, 4.51 g. (43% yield) of crude carboxylic acid of m.p. 120–126°. One crystallization from ethyl alcohol and treatment with Nuchar C gave 3.3 g. of white crystals of m.p. 130–132°. Recrystallization from alcohol gave an acid of m.p. 131.0–132.0° and of neutralization equivalent of 302.2 (acid. for $C_{21}H_{18}O_2$, 302.35). This acid is identified as 2,2,3-triphenylpropanoic acid, containing perhaps a trace of an isomeric acid as an impurity, on the following basis. Authentic 2,2,3-triphenylpropanoic acid, m.p. 132.0–133.0°, was prepared by the procedure of Ramart[28] and gave no mixed melting point depression with our acid of m.p. 131.0–132.0°. Moreover these acids showed identical infrared absorption spectra with one another and with a 50/50 mixture of the two acids in carbon disulfide solution. The benzyl ester of our acid was prepared *via* the acid chloride and had m.p. 81–83°; this melting point was not sharpened by two recrystallizations from ethyl alcohol and one distillation *in vacuo*. A

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(20) E. C. Horning, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 841.

(21) W. E. Bachmann and F. Y. Wiselogle, THIS JOURNAL, **58**, 1943 (1936).

(22) We wish to thank Dr. C. J. Collins for pointing out to us and instructing us in this convenient technique for small scale preparations of triphenylmethylsodium.

(23) A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 607.

(24) The by-products might reasonably result from interaction of triphenylmethylsodium with 2-chloro-1,1,1-triphenylethane. Prof. E. D. Hughes (private communication) has kindly informed us that he is investigating this and related reactions.

(25) The author is indebted to Mr. Robert C. Bryan, Jr., for the preparation of triphenylethylene (A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., 1943, p. 606) and also for aid in conducting the literature survey upon the present problem.

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

(27) L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., Inc., New York, N. Y., 1941, p. 369.

(28) P. Ramart, *Bull. Soc. Chim. (France)*, [4] **35**, 196 (1924); *cf.* C. R. Hauser and W. J. Chambers, THIS JOURNAL, **78**, 4942 (1956).

mixed m.p. of 81.5–84.1° was obtained with an equal portion of authentic benzyl 2,2,3-triphenylpropionate, m.p. 83.6–85.0°, prepared in 68% yield by the procedure of Ramart.[28] The amide of our acid had m.p. 109–110° (recorded[28] 111–112°). Finally the ultraviolet absorption spectrum of the acid had maxima at 209, 253, 260, 265 and 270 mμ with molar extinction coefficients, respectively, of 26,000, 610, 680, 550 and 330, which is similar to the spectrum of 1,1,1-triphenylethane (Fig. 1) or 1,1,2-triphenylethane (Fig. 2) as expected for isolated phenyl chromophores and confirms the absence of a double bond or a carboxyl group conjugated with a benzene ring.

In another reaction of 20.0 g. of 2-chloro-1,1,1-triphenylethane with 5.23 g. of sodium according to the procedure described above except that the chloride was dissolved in dioxane and added dropwise to the molten sodium, the yield of crude carboxylic acid was 8.4 g. (40.5%) and the neutral fraction amounted to 10.8 g. of light yellow oil which partially crystallized upon standing. The acidic fraction is a little smaller and the neutral fraction somewhat larger percentagewise than in the previous run, possibly because of a trace of water in the dioxane used to dissolve the chloride. The color was removed from a 9.65-g. portion of the neutral fraction by passage of a *n*-pentane–benzene solution through a column packed with activated alumina; this gave 8.5 g. of colorless product whose ultraviolet absorption spectrum was similar to that of 1,1,1-triphenylethane or 1,1,2-triphenylethane and excluded the presence of more than 0.3% of triphenylethylene. The infrared spectrum of the sample indicated that 70 ± 2% by weight was 1,1,2-triphenylethane and the remainder 1,1,1-triphenylethane; two distillations of the sample *in vacuo* at 0.06 mm. did not alter the infrared analysis. A 1.1-g. portion of the original yellow neutral fraction after passage over alumina and two recrystallizations from ethyl alcohol gave 0.32 g. of white crystals of m.p. 50.5–53.6° (*cf.* m.p. 56° recorded[15] for pure 1,1,2-triphenylethane).

In a third reaction 2-chloro-1,1,1-triphenylethane (10.0 g.) was added with stirring over a half-hour period to 3.12 g. of sodium in 260 ml. of refluxing dioxane and then the mixture refluxed for a half-hour in the apparatus described above. To the reaction mixture was added slowly 50 ml. of *t*-amyl alcohol with stirring and refluxing for a half-hour and then 50 ml. of 95% ethyl alcohol with stirring for 15 minutes. The reaction mixture was concentrated to 150 ml., 100 ml. of water was added, and the mixture extracted well with ether. The ether extract yielded 9.0 g. of light brown somewhat oily crystalline material. Distillation at 0.1 mm. of an 8.8-g. portion of the product gave 8.1 g. of waxy crystals whose infrared analysis indicated 81 ± 3% 1,1,2-triphenylethane with the remainder 1,1,1-triphenylethane. Redistillation *in vacuo* gave a product of the same infrared analysis. The 1,1,1-triphenylethane evidently results from proton donation by the solvent to the carbanion before rearrangement has occurred even though the solvent was purified[27] anhydrous 1,4-dioxane which was refluxed for 15 minutes with molten sodium on the high-speed stirring apparatus before addition of 2-chloro-1,1,1-triphenylethane was commenced.

To determine the stability of 2-chloro-1,1,1-triphenylethane in refluxing dioxane under the reaction conditions 10.0 g. of the chloride (m.p. 100–102°) was added to 250 ml. of dioxane in the apparatus described above for the sodium reaction and the mixture was refluxed with stirring for 1.0 hour. The solution was transferred to an apparatus for distillation and concentrated to 80 ml. by distillation of solvent at atmospheric pressure over a 45-minute period. Addition of 350 ml. of water to the cooled residue and chilling gave pale yellow crystals which after drying *in vacuo* at 50–70° for 2.5 hours weighed 10.4 g. and had m.p. 94.5–99° (contamination by stopcock grease and/or lubricant from bearings of Morton stirrer?). One recrystallization from *n*-hexane gave 8.5 g. of white crystals of m.p. 100–102° which gave no m.p. depression with pure 2-chloro-1,1,1-triphenylethane.

Reaction of II with Sodium in Dioxane–*t*-Amyl Alcohol.—2-Chloro-1,1,1-triphenylethane (10.0 g., m.p. 99.3–101.5°), 5.29 g. of sodium, 110 ml. of dioxane and 140 ml. of *t*-amyl alcohol were stirred together at reflux for one hour in the apparatus described above. The solution immediately developed a pale pink-brown coloration which faded to a pale cream color within 20 minutes; 50 ml. of 95% ethyl alcohol was added slowly with stirring to the refluxing reaction mixture to destroy any remaining sodium. The resulting solution was acidified with hydrochloric acid, concentrated to about 100 ml., an equal volume of water added, and extracted with ether. The ether extract contained 8.84 g. (100% yield if $C_{20}H_{18}$) of a yellow colored solid of m.p. about 85–90°. A 1.00-g. sample of this substance was sublimed twice *in vacuo* to give 0.97 g. of white crystals whose infrared analysis at four wave lengths indicated a binary mixture of 1,1,1-triphenylethane and 1,1,2-triphenylethane, containing 93.7 ± 0.5% of the former hydrocarbon. Recrystallization of 0.52 g. of this material once from ethyl alcohol gave 0.38 g. of white needles of m.p. 94.3–95.2°; an authentic sample[19] of 1,1,1-triphenylethane had the same melting point and gave no melting point depression with this substance.

Reaction of Triphenylethylene with Sodium in Dioxane.—Crystalline 1,1,2-triphenylethylene[25] (17.6 g., 0.0686 mole) was added to 5.24 g. (0.228 g. atom) of sodium metal in 250 cc. of refluxing dioxane according to the general procedure described for chloride II. A yellow-red coloration first developed which within one minute of vigorous stirring turned dark green and eventually green-black in color. The reaction mixture was carbonated and worked up approximately as for II to give 2.5 g. of brown colored neutral material and 24 g. of crude yellow-orange viscous carboxylic acid, probably containing some solvent. The neutral material was treated in ethyl alcohol with Nuchar C and twice recrystallized from this solvent to give 1.4 g. of crystals of m.p. 51–53°; this material is doubtlessly essentially 1,1,2-triphenylethane. The carboxylic acid fraction was dissolved in 65% acetic acid for crystallization since Schlenk and Bergmann[15] obtained from this solvent (after drying their product *in vacuo* at 78° for two hours) triphenylsuccinic anhydride, m.p. 115°, from carbonation of the reaction product of triphenylethylene and sodium in ethyl ether. Slow evaporation of our acetic acid solution gave, after drying the product *in vacuo* at 78° for five or more hours, a first batch of 8.9 g. of yellow crystals, m.p. *ca.* 115–216° (more 65% acetic acid was added to the mother liquor as required to keep it mobile), a second batch of 2.75 g. of cream colored compound, m.p. *ca.* 111–114°, and finally a brown residue of 7.4 g. (an additional *ca.* 1 g. of this residue was lost during evaporation of all solvent) which was soft at 78° but hard at room temperature. For purification these products were taken up in sodium hydroxide, the solutions filtered to remove a small amount of undissolved material, and the acids precipitated by acidification. Bulky white precipitates were so produced; while being dried *in vacuo* at 78° these lost water and sometimes melted and resolidified to give cream to brown colored solids. Extraction of the first two batches of acid with hot *n*-hexane gave 4.1 g. of hexane-insoluble acid of m.p. 155–234° dec. and neutralization equivalent about 176. From the material soluble in hexane was obtained 5.6 g. of crystals of m.p. 109–115°. Recrystallization of these from hexane–benzene gave definite rectangular tablets but did not sharpen the melting point; recrystallization from 65% acetic acid gave white crystals, which even after drying *in vacuo* at 100° for three hours, had m.p. *ca.* 168–174° (evolution of gas to give colorless melt). Recrystallization from acetic anhydride gave 2.7 g. of crystals of m.p. 113–116°. The compound upon solution in excess of standardized hot sodium hydroxide and back titration with hydrochloric acid gave a neutralization equivalent of about 167; the titration curve showed a second break as expected for a dibasic acid but the end-point here was rather indeterminate. The melting point of the compound was sharpened to 112–114° (largely 113–114°) by distillation *in vacuo*. We conclude that this compound (VIII) is probably triphenylsuccinic anhydride as described by Schlenk and Bergmann.[15] The ultraviolet absorption spectrum of VIII (Fig. 2) is rather similar to that of 1,1,2-triphenylethane and confirms this structural assignment. On the other hand, the ultraviolet absorption spectrum of the residue from the acetic acid crystallization (neutralization equivalent of about 175) has rather strong absorption (maxima or shoulder) at 238 and 305 mμ as does also the hexane-insoluble acid (above) of m.p. 155–234°. Such absorption maxima suggest the presence of carboxyl group directly attached to a benzene ring (238 mμ) and of an olefinic double bond as in triphenylethylene (305 mμ) for at least a portion of the acidic material.

In a second reaction, triphenylethylene was allowed to react with sodium in dioxane with the same amount of each reagent and under the same conditions as described above

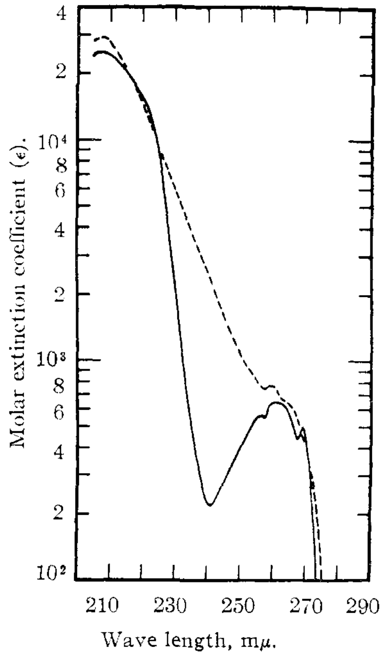

Fig. 2.—Ultraviolet absorption spectra of Ph_2CHCH_2Ph (———) and triphenylsuccinic anhydride (VIII) (--------) in 95% ethyl alcohol.

except that at the end of the one hour reaction period 50 ml. of *t*-amyl alcohol was added cautiously to the refluxing reaction mixture and stirring continued for 15 minutes. Finally 50 ml. of 95% ethyl alcohol was added to decompose a little remaining sodium. Neutralization with hydrochloric acid, concentration, and extraction with ether gave 17.3 g. of light brown product of m.p. 53.8–56.0°. Decolorization with Nuchar C and crystallization from ethyl alcohol gave 14.0 g. of white crystals of m.p. 55.0–56.2° as expected for 1,1,2-triphenylethane.[15,29] Two sublimations *in vacuo* at 0.07 mm. gave crystals of m.p. 55.5–56.7° which were used as standard for 1,1,2-triphenylethane in the infrared analyses.

Absorption Spectra.—Ultraviolet absorption spectra were determined by means of a Beckman quartz spectrophotometer, model DU. Quantitative analyses for 1-chloro-1,2,2-triphenylethene (I) were made at 290 or 300 mμ and probably were accurate within 5% composition by weight. It was assumed that all of the absorption at this wave length was due to I since triphenylethylene, which has a similar absorption band, reacts much more rapidly with phosphorus pentachloride than does 1,1,1-triphenylethane or 2-chloro-1,1,1-triphenylethane (II).

Infrared spectra were determined with a Perkin–Elmer double beam model 21 infrared spectrophotometer. Quantitative analyses for mixtures of 1,1,1-triphenylethane were made in 0.5-mm. rock salt cells upon solutions containing 0.450 g. of triphenylethane in 5.00 ml. of carbon disulfide. Analyses were conducted at wave lengths of 8.238, 9.359, 9.449 and 12.719 μ which correspond to maxima of 1,1,1-triphenylethane at the first and third wave lengths and of 1,1,2-triphenylethane at the remaining wave lengths. Analyses at 9.449 μ were made only for samples which were predominantly 1,1,1-triphenylethane because of the rather steep slope of the absorption curve of 1,1,2-triphenylethane in this region. Compositions were read from nearly linear empirical calibration curves prepared from synthetic mixtures of the triphenylethanes. Analyses are reported as the average of the three or four values so obtained along with the mean deviation from the average.

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(29) A. Klages and S. Heilmann, *Ber.*, **37**, 1455 (1904).

Atlanta, Ga.

[Contribution from the Noyes Chemical Laboratory, University of Illinois]

The Synthesis of a Polyampholyte of Regular Structure[1,2]

By C. S. Marvel and Wendell W. Moyer, Jr.

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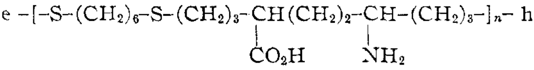
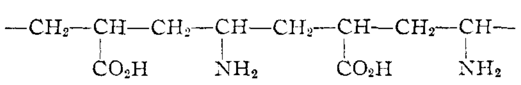
A polyampholyte of the structure  $-[-S-(CH_2)_6-S-(CH_2)_3-\underset{CO_2H}{CH}(CH_2)_2-\underset{NH_2}{CH}-(CH_2)_3-]_n-$ has been synthesized.

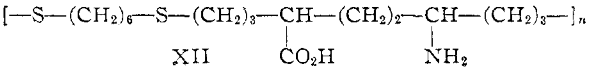
With but one exception all previously reported synthetic polyampholytes have been obtained by copolymerization techniques using acidic and basic monomers such as vinylpyridine and acrylic acid, or 2-dimethylaminoethyl methacrylate and vinylsulfonic acid. The composition of these copolymers may be determined, but the composition gives no real indication of the internal structure of the copolymer.

The only known synthetic polyampholyte not prepared by copolymerization techniques is the one reported by Vrancken and Smets.[3] They described the synthesis of a fairly regular polyampholyte from polyacrylyl chloride by the Curtius and Lossen type rearrangement) whose acidic and basic functions largely alternate along the backbone of the polymer as



$$-CH_2-\underset{CO_2H}{CH}-CH_2-\underset{NH_2}{CH}-CH_2-\underset{CO_2H}{CH}-CH_2-\underset{NH_2}{CH}-$$

While this polyampholyte undoubtedly has for the most part a regular alternation of the acidic and basic functions, the amphoteric units are close together and thus the electrical interactions are greatly complicated. This paper describes the synthesis of a polyampholyte having unequivocally regular, isolated amphoteric units.



$$[-S-(CH_2)_6-S-(CH_2)_3-\underset{CO_2H}{CH}-(CH_2)_2-\underset{NH_2}{CH}-(CH_2)_3-]_n$$

XII

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(1) The work discussed herein was performed as a part of the polymer research project sponsored by the National Science Foundation.

(2) Abstracted from a portion of a thesis submitted in partial fulfillment of requirements for the Ph.D. degree by Wendell William Moyer, Jr., to the Graduate College of the University of Illinois in 1957.

(3) M. Vrancken and G. Smets, *J. Polymer Sci.*, **14**, 521 (1954).