[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

Carbanion Rearrangements. I

BY HOWARD E. ZIMMERMAN AND FRANK J. SMENTOWSKI

RECEIVED APRIL 25, 1957

The reaction of amylsodium with 1,1,1-triphenyl-2-chloroethane (I) has been found to yield triphenylethylene. To determine the likelihood of a carbanion mechanism, the reaction of I with sodium was investigated; this was found to lead to the stable carbanion $(C_6H_5)_2\underset{..}{C}CH_2C_6H_5$.

Although many examples of electrophilic rearrangements are known in which the migration is from nitrogen or oxygen to carbon, no case exactly paralleling the well known carbon-to-carbon rearrangement of carbonium ions has been established.[1] Such a rearrangement was reported by Wooster and Mitchell[2] who stated that treatment of 1,1,1-triphenyl-2-chloroethane (I) with sodium in liquid ammonia yielded the rearranged carbanion III which on acidification led to 1,1,2-triphenylethane (V).

$$\underset{\text{I}}{(C_6H_5)_3CCH_2Cl} \xrightarrow[NH_3]{Na} \underset{\text{II}}{(C_6H_5)_3C\text{—}\underset{..}{C}H_2\ Na^+} \longrightarrow$$

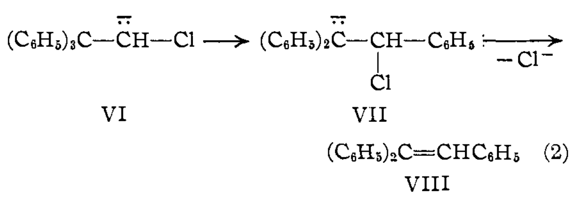
$$\underset{\text{III}}{(C_6H_5)_2\underset{..}{C}CH_2C_6H_5\ Na^+} \longrightarrow \underset{\text{V}}{(C_6H_5)_2CHCH_2C_6H_5}$$

However, as recently shown by Hughes, *et al.*,[3] the halide employed by Wooster was not I but was chlorotriphenylethylene, thus vitiating the evidence for rearrangement.[4] Furthermore, Hughes demonstrated that authentic 1,1,1-triphenyl-2-chloroethane (I) did not rearrange with sodium in liquid ammonia but rather gave 1,1,1-triphenylethane (IV). Compound I did rearrange to yield triphenylethylene when treated with sodium in a petroleum solvent at 120°, but no conclusion could be drawn since compound I rearranged at its melting point (101°) in the absence of sodium to yield the same product.

In the present study of carbanion rearrangements it was of interest to ascertain whether the formation of triphenylethylene from I was merely a thermal rearrangement or was catalyzed by 2,2,2-triphenylethylsodium (II) formed from I; this required the treatment of I with strong bases under conditions where this compound would otherwise be stable. Indeed it was found that while compound I was unaffected by sodamide in refluxing ether, it did rearrange when treated with the stronger base amylsodium in isoöctane or isooctane–ether at 35°, yielding triphenylethylene.[5,6]

Two reasonable ways in which this α-elimination might occur are[7]

$$(C_6H_5)_3C\text{—}CH_2\text{—}Cl \xrightarrow[\text{AmNa}]{} \underset{\text{VI}}{(C_6H_5)_3C\text{—}\overset{..}{C}H\text{—}Cl} \quad (1)$$



$$\underset{\text{VI}}{(C_6H_5)_3C\text{—}\overset{..}{C}H\text{—}Cl} \longrightarrow \underset{\text{VII}}{(C_6H_5)_2\overset{..}{C}\text{—}\underset{\substack{|\\ Cl}}{CH}\text{—}C_6H_5} \xrightarrow[-Cl^-]{} \underset{\text{VIII}}{(C_6H_5)_2C{=}CHC_6H_5} \quad (2)$$

$$\text{VI} \xrightarrow[-Cl^-]{} \underset{\text{IX}}{(C_6H_5)_3C\text{—}\overset{\cdot\cdot}{C}H} \longrightarrow \text{VIII} \quad (2')$$

If the first mechanistic possibility were correct, then a comparable rearrangement should be observable in a situation where no chloride ion might be expelled and hence where a carbene intermediate may be excluded. Therefore efforts were directed at a study of the 2,2,2-triphenylethyl carbanion (*i.e.*, II). It was felt that the failure of II to rearrange in liquid ammonia, suggested by the results of Hughes,[3] was not unexpected; proton abstraction from ammonia by II would almost certainly be rapid.

It was found that by use of high speed stirring techniques 1,1,1-triphenyl-2-chloroethane (I) reacted smoothly with sodium in ether–isoöctane at room temperature to yield the deep red, ether-soluble carbanion III. Protonation with ethanol gave 1,1,2-triphenylethane (V) together with 1,1,1-triphenylethane (IV). When carbonation replaced ethanol protonation, the carboxylic acid fraction contained only 2,2,3-triphenylpropanoic acid, and this appeared to correspond in quantity to the 1,1,2-triphenylethane isolated from a run of similar duration followed by protonation. Thus it seems that 2,2,2-triphenylethylsodium (II) is not a stable intermediate under the reaction conditions and the formation of IV occurs prior to protonation with ethanol.

While the rearrangement postulated by Wooster

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(1) (a) An exact analogy would require the carbon atoms to be singly bonded. (b) A similar comment has been made recently by G. Wittig and R. Clausinzer, *Ann.*, **588**, 145 (1955).

(2) C. Wooster and N. Mitchell, THIS JOURNAL, **52**, 1042 (1930).

(3) J. Charlton, I. Dostrovsky and E. Hughes, *Nature*, **167**, 987 (1951).

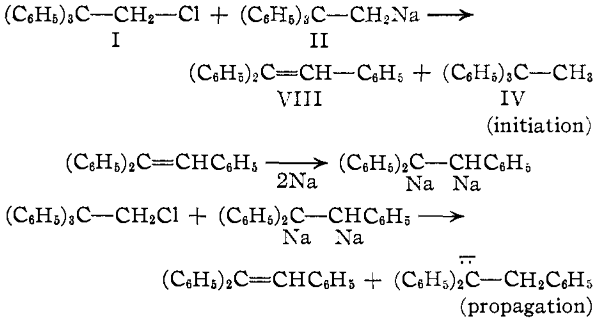
(4) It was reported by Hughes (ref. 3) that tbe same conclusion regarding the structure of Wooster's compound had been reached by E. Grovenstein. These results bave been reported recently by Dr. Grovenstein: Abstracts of the 131st A.C.S. Meeting, Miami, Florida, April, 1957.

(5) A similar rearrangement reported without experimental details is the reaction of 1,1,1-trichloro-2,2-dianisylethane with sodium in refluxing benzene to yield the corresponding stilbene, E. Harris and G. Frankforter, THIS JOURNAL, **48**, 3144 (1926); 1,1-dianisyl-2,2-dichloroethylene was not an intermediate, since this compound yielded the tolan under the reaction conditions; also *cf.* F. Whitmore, *et al.*, *ibid.*, **65**, 1469 (1943).

(6) Thus it is seen that β-elimination of the diethyl ether solvent by amylsodium under the reaction conditions is not a serious complication.

(7) In equation 2 loss of chloride might be concerted with the last stage of migration so that VII would not be an intermediate; likewise in 2′, phenyl participation might facilitate loss of chloride.

under the proper conditions is a reality,[8,9] a second mechanistic possibility remains. This is suggested both by the facile α-elimination of I effected by strong bases and also by the formation of IV by processes prior to ethanol addition.[10]



$$\underset{\text{I}}{(C_6H_5)_3C{-}CH_2{-}Cl} + \underset{\text{II}}{(C_6H_5)_3C{-}CH_2Na} \longrightarrow \underset{\text{VIII}}{(C_6H_5)_2C{=}CH{-}C_6H_5} + \underset{\text{IV}}{(C_6H_5)_3C{-}CH_3} \quad \text{(initiation)}$$

$$(C_6H_5)_2C{=}CHC_6H_5 \xrightarrow[2Na]{} (C_6H_5)_2\underset{Na}{C}{-}\underset{Na}{CHC_6H_5}$$

$$(C_6H_5)_3C{-}CH_2Cl + (C_6H_5)_2\underset{Na}{C}{-}\underset{Na}{CHC_6H_5} \longrightarrow (C_6H_5)_2C{=}CHC_6H_5 + (C_6H_5)_2\overset{\overline{\cdot\cdot}}{C}{-}CH_2C_6H_5 \quad \text{(propagation)}$$

Further research is being pursued both to ascertain the generality of these reactions and to clarify the mechanism.

Experimental[11]

1,1,1-Triphenyl-2-chloroethane.—The following is a convenient modification of the method of Hughes.[3] To a 500-ml. Morton flask fitted with a high speed stirrer, nitrogen inlet, drying tube and dropping funnel was added 2.00 g. of sodium followed by 18 ml. of mercury added slowly from the dropping funnel. To the resulting liquid amalgam was added 80 ml. of anhydrous ether, and stirring was then begun under the oxygen-free nitrogen (Fieser soln., lead acetate, $CaCl_2$ train used). Shortly thereafter a solution of 10.0 g. of triphenylchloromethane in 70 ml. of anhydrous ether was added. At the end of a 10-minute induction period, the mixture became warm and suddenly became deep red. Stirring was continued for 2 hr. at room temperature. Then the reaction mixture was cooled in a methanol–Dry Ice-bath maintained at −40°. To the flask was added 10 ml. of methylene chloride as rapidly as possible. The bath temperature was raised until at −10° the red-brown reaction mixture decolorized leaving a gray suspension. Stirring was then continued at room temperature for 0.5 hr. The mixture was poured onto 500 ml. of ice and was ether extracted, the extracts dried over sodium sulfate and concentrated. Five crystallizations of the residue from hexane gave 3.30 g., m.p. 97.5–98.0°. The filtrates on recrystallization gave an additional 2.51 g., m.p. 97.0–98.5° (reported[3] m.p. 101.5°). In a second run five crystallizations gave 4.39 g., m.p. 96.0–97.5°, with additional product isolable from the combined filtrates. Use of a more concentrated amalgam led to poor results; useful infrared maxima: 7.80, 9.20, 9.30sh, 9.65, 13.15, 13.30 and 13.70 μ.

Reaction of Amylsodium with 1,1,1-Triphenyl-2-chloroethane.—A suspension of amylsodium (0.0097 mole) in 15 ml. of isoöctane was prepared from amyl chloride and sodium essentially as described by Morton[12] using a 100-ml. indented flask equipped with a high speed (12,000 r.p.m.) stirrer. To this was added 2.00 g. of 1,1,1-triphenyl-2-chloroethane in 30 ml. of anhydrous ether. The mixture was then stirred under nitrogen at 35° for 30 minutes, after which time 1 ml. of ethanol was added and the mixture was poured onto ice and then benzene was extracted, the extracts dried over sodium sulfate and concentrated *in vacuo*. The residue was chromatographed on a silica gel column (31 × 730 mm.) slurry packed with 10% ether in hexane and rinsed with hexane. Four 250-ml. fractions were eluted using hexane followed by four using 10% ether in hexane. This was followed by elution with 20% ether and finally by 40% ether in hexane. Fractions 3 through 5 contained a total of 624 mg. of oily solid whose infrared spectrum was that of triphenylethylene except for minor contamination. This conclusion was supported by the ultraviolet spectrum (λ_{max}^{EtOH} 231.0 mμ (log ε 4.3); 299.5 mμ (4.3)); an authentic sample of triphenylethylene exhibited maxima at 231.0 mμ (4.1) and 299.0 mμ (4.2). Also, crystallization brought the melting point to 63–65°, a mixed m.p. with an authentic sample not being depressed (reported m.p. 62°,[13] 68–69°[14]).

Essentially the same results were obtained in a run in which the same quantities were used except that no ether was employed; instead finely powdered 1,1,1-triphenyl-2-chloroethane was rinsed into the amylsodium with 20 ml. of isoöctane followed by stirring for 1 hr. at 38°. The crude product was seen to be only slightly impure triphenylethylene by infrared analysis. Chromatography as above yielded 1.34 g. of the triphenylethylene fraction followed by 0.31 g. of starting material; useful infrared maxima of VIII: 9.30, 9.65, 10.57, 12.85, 13.10 and 13.86 μ.

Reaction of 1,1,1-Triphenyl-2-chloroethane with Sodamide.—Two grams of 1,1,1-triphenyl-2-chloroethane was added to a suspension of sodamide (prepared from 0.18 g. of sodium) in 50 ml. of ether followed by refluxing for 30 minutes. The reaction mixture was poured onto ice and benzene extracted. From the extracts only starting material could be isolated and this in 90% yield.

Preparation of Authentic 1,1,2-Triphenylethane.—The following is the method of Wooster and Ryan[15] which was described without experimental detail. To 25 ml. of liquid ammonia was added 0.135 g. of sodium. The resulting blue solution was treated with a soln. of 0.50 g. of triphenylethylene in 7 ml. of anhydrous ether. After 10 minutes 0.5 g. of ammonium chloride was added to the red solution. The reaction mixture was diluted with water, ether extracted, the extracts dried and concentrated to leave 0.48 g. of crude product. Several crystallizations from hexane yielded 207 mg., m.p. 50–52° (reported m.p. 54°,[13] 56°[16]). The infrared spectrum of the crystallized product was identical with that of the crude material; useful maxima: 9.20 sh, 9.30, 9.65, 12.57, 12.70, 13.30 and 13.60 μ.

Preparation of Authentic 1,1,1-Triphenylethane.—This was prepared essentially by the method of Schlenk and Marcus[17] except that the triphenylmethylsodium was obtained as described above in the preparation of 1,1,1-triphenyl-2-chloroethane. The product melted at 92–93° (reported[17] m.p. 95°); useful infrared maxima: 9.70 and 13.15 μ.

Reaction of 1,1,1-Triphenyl-2-chloroethane with Sodium.—To a 50-ml. indented flask fitted with a reflux condenser, nitrogen inlet, drying tube and high speed (12,000 r.p.m.) stirrer was added 8 ml. of isoöctane and 0.262 g. of sodium. Refluxing and stirring for 30 minutes achieved a sodium dispersion which was then cooled. To the flask was then added 1.68 g. of 1,1,1-triphenyl-2-chloroethane dissolved in 35 ml. of anhydrous ether. Stirring at room temperature was continued for 12 hr. The mixture first turned brown and then deep red; 5 ml. of ethanol was added and the mixture was then poured onto ice and water and ether extracted. The extracts were dried and concentrated to yield 1.31 g. of oil which crystallized. The infrared spectrum indicated that the major component was 1,1,2-triphenylethane. This material was chromatographed on silica gel (22 × 1500 mm.) with increasing amounts of benzene in hexane. Five 100-ml. fractions were collected by elution with 40%

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[8] Recently C. Shoppee, *Chemistry & Industry*, 759 (1954), has quoted a private communication from Hughes to the effect that carbonation of the Grignard reagent derived from I yields both rearranged and unrearranged acids; it was suggested that the rearrangement was carbanionic. However, in view of the presence of magnesium chloride during Grignard formation and the known facile carbonium ion rearrangement of I in the presence of Lewis acids (ref. 3), a carbanionic rearrangement is not a mandatory explanation.

[9] After this study was well under way, it was reported (ref. cited in footnote 4) that carbanion V results on treatment of I with sodium in refluxing dioxane.

[10] That IV is not formed by reduction with sodium and ethanol at the end of the run is suggested both by the recovery of starting material from reactions worked up in the same manner but run for short times, and also by the lack of correlation between the amounts of I and IV isolated in runs made for different times.

[11] All melting points were taken on a Fisher–Johns block checked with known compounds.

[12] A. Morton, J. Davidson and B. Hakan, THIS JOURNAL, **64**, 2246 (1942).

[13] A. Klages and S. Heilmann, *Ber.*, **37**, 1455 (1904).

[14] *Org. Syntheses*, **17**, 90 (1937).

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

[16] W. Schlenk and E. Bergmann, *Ann.*, **463**, 45 (1928).

[17] W. Schlenk and E. Marcus, *Ber.*, **47**, 1667 (1914).

benzene in hexane. The first fraction contained 101 mg. of solid, m.p. 53–67°; recrystallization yielded 65 mg. of essentially pure 1,1,1-triphenylethane, m.p. 88–92°. Fraction 2 weighed 148 mg., m.p. 48–50°, and was essentially pure 1,1,2-triphenylethane. Fraction 3 contained 330 mg., m.p. 47–50°; recrystallization from hexane gave 300 mg. of 1,1,2-triphenylethane, m.p. 51–53°. Fraction 4 weighed 95 mg. and melted at 45–48°. Crystallization brought the m.p. to 50–52°, wt. 85 mg. Fraction 5 yielded 44 mg., m.p. 35–42; the infrared spectrum indicated this to be only slightly impure 1,1,2-triphenylethane. The identity and purity of the crystallized products obtained from fractions 1, 3 and 4 were checked by infrared analysis. Thus 617 mg. of the 1,1,2-triphenylethane chromatographic fraction was obtained while only 101 mg. of the 1,1,1-triphenylethane fraction was isolated; the crystallized yields totaled 533 mg. of 1,1,2-triphenylethane and 65 mg. of 1,1,1-triphenylethane.

In a second run the reaction time was reduced to 5 hr.; 1.34 g. of crude product was isolated. Chromatography was effected on silica gel (31 × 730 mm.) slurry packed with 10% ether in hexane and washed with hexane. Seven 200-ml. fractions were collected by elution with hexane followed by an eighth and ninth using 10% ether in hexane. Fraction 4 contained 110 mg. of material seen from the infrared to be impure 1,1,1-triphenylethane. Fraction 5 yielded 412 mg. of similar material. Fraction 6 gave 349 mg. of a mixture of 1,1,1-triphenylethane and 1,1,1-triphenyl-2-chloroethane. Fraction 7 afforded 195 mg. of essentially pure 1,1,1-triphenyl-2-chloroethane and 8 gave 120 mg. of similar material. Crystallization of the material from fractions 4 and 5 brought the m.p. to 92–94°. The final filtrates indicated small amounts of 1,1,2-triphenylethane. Crystallization of the material from fractions 7 and 8 brought the m.p. to 97–99° with a little loss to the filtrate.

In a third run the reaction time was only 2.5 hr. The crude product, isolated as before, was chromatographed on silica gel (1100 × 23 mm.) packed with hexane; 24 50-ml. fractions were collected by elution with 25% benzene in hexane. Fractions 10 through 13 crystallized and were found to be essentially pure 1,1,1-triphenylethane, total wt. 276 mg. Fraction 14 weighed 26 mg. and was found to be a mixture of triphenylethylene, 1,1,1-triphenylethane and 1,1,2-triphenylethane. Fractions 15 and 16 totaled 126 mg. and were found to contain both triphenylethylene and 1,1,2-triphenylethane by infrared analysis. Fractions 17 through 24 were solid and melted at 90–94°, wt. 549 mg.; this was shown to be virtually pure 1,1,1-triphenyl-2-chloroethane by infrared analysis.

In a fourth run made for 5 hr. the reaction mixture was poured onto 150 g. of chopped Dry Ice. The acidic fraction weighed 101 mg. and melted at 128–131°; one crystallization brought the melting point to 131–132°. Thus only 2,2,3-triphenylpropanoic acid was formed.

In the reactions of sodium with 1,1,1-triphenyl-2-chloroethane with sodium it was found that for smooth reaction, stirring at 12,000 r.p.m. was necessary; a non-settling sodium dispersion was obtained readily by use of 10 mg. of detergent.

Acknowledgment.—The authors gratefully acknowledge support of this research by the Petroleum Research Fund of the American Chemical Society.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

Studies of Some Nitro-substituted Benzhydrylcarbonium Ions

BY BURCH B. STEWART AND HILTON A. SMITH

RECEIVED MAY 6, 1957

The behavior of the following nitro compounds in 100% sulfuric acid has been studied: 4-nitrobenzhydrol, bis-(3-nitrobenzhydryl) ether, and 3,3′-dinitrobenzhydrol. The first two gave carbonium ions which were rather unstable and readily polymerized. The last gave no visible carbonium ion but did yield a soluble polymer. The properties were investigated utilizing *i*-factors, ultraviolet and near-visible spectra, titration studies, and chemical studies, all using sulfuric acid. Some discussion of the structure and composition of the polymers is presented.

Introduction

The ionization of benzhydrols[1–5] in 100% sulfuric acid to give stable carbonium ions has been shown to be promoted by electron releasing groups. Electron withdrawing groups should have an effect of decreasing the thermodynamic stability as well as promoting the tendency for polymerization. Since benzhydrol[1] and 3-methylbenzhydrol[3] readily polymerize in 100% sulfuric acid, it was desired to determine the effect of nitro-substitutions on the formation and stabilization of benzhydrylcarbonium ions. It would be predicted that nitrobenzhydrols and bis-nitrobenzhydryl ethers would give unstable carbonium ions in sulfuric acid.

Results

***i*-Factors.**—Table I gives the *i*-factors as extrapolated to zero time for the compounds studied. Since 4-nitrobenzhydrol and bis-(3-nitrobenzhydryl) ether polymerized rapidly and went into solution slowly, the *i*-factors were not determined until solution was essentially complete. These solutions required about five or six hours of mechanical shaking at constant temperature. 3,3′-Dinitrobenzhydrol dissolved to give a very pale yellow solution and constant *i*-factors could be determined 40 minutes after addition of the compound to sulfuric acid.

TABLE I

CHARACTERISTICS OF NITRO COMPOUNDS IN SULFURIC ACID

Compound	Color in H_2SO_4	Min. % acid[a] for color	Initial *i*-factors (extrapd.)	M.p., °C. of polymer[d]
4-Nitrobenzhydrol	Red-brown	84.3	2.9–3.0[b]	136–250[e]
Bis-(3-nitrobenzhydryl) ether	Red-brown	82.8	3.9–4.1[b]	130–250[e]
3,3′-Dinitrobenzhydrol	Very faint yellow	89.8	3.03[c]	170–210[f]

[a] Titration to form visible color with sulfuric acid. [b] Obtained by extrapolation of the straight line portion which began after complete solution was achieved. [c] Value of 3.03 was obtained after 40 minutes and did not change for 17 hours. [d] Melting points were taken on an aluminum melting point block. [e] Darkening occurred at the lower temperature; at the final temperature the polymer had turned black. [f] Darkened at 170° and melted at 210°.

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(1) C. M. Welch and H. A. Smith, THIS JOURNAL, **72**, 4748 (1950).

(2) M. S. Newman and N. C. Deno, *ibid.*, **73**, 3644 (1951).

(3) H. A. Smith and B. B. Stewart, *ibid.*, **79**, 3693 (1957).

(4) V. Gold and F. L. Tye, *J. Chem. Soc.*, 2172 (1952).

(5) H. A. Smith and R. G. Thompson, THIS JOURNAL, **77**, 1778 (1955).