[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 157]

Condensations by Sodium. IX. Preparation and Properties of Trixenyl- and Trimethyltrixenylcarbinols and Some of Their Derivatives

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One of the important syntheses developed in the course of this work has been that of symmetrical triarylcarbinols from sodium, diethylcarbonate and an aryl chloride. Trixenylcarbinol in particular has been prepared by this simple one-step process. We have been engaged in extending this synthesis to other trixenylcarbinols such as the trimethyl-, trimethoxy-, and hexamethyl-triamino- substituted compounds, which because of their similarity to the important triphenylcarbinols should eventually give added light on such problems as the basicity of carbinols and the relation of color to chemical constitution. We are reporting in this paper the synthesis of trimethyltrixenylcarbinol. Both it and the parent trixenylcarbinol were reduced to the corresponding methanes, then converted to perbromides by reaction with bromine, and hydrolyzed back to the carbinols by way of proving that the synthesis of trimethyltrixenylcarbinol had produced a material with characteristic reactions and that the processes of reduction had indeed been as expected. In the hope of obtaining a simple trinitro derivative, trixenylmethane was nitrated also but the product was a nonanitro compound whose exact structure is still to be determined.

Colors in the trixenylmethyl series are in general of greater depth than those of corresponding compounds in the triphenylmethyl series. Thus trimethyltrixenylcarbinol is blue changing to red and trixenylcarbinol is red in concentrated sulfuric acid. Triphenylcarbinol on the other hand is yellow in this solvent. In hot acetic acid both trixenylcarbinols give their characteristic colors, changing to colorless when cold. Triphenylcarbinol gives no color under the same conditions. A novel occurrence of these colors was observed when trimethyltrixenyl- and trixenylchloromethane were deposited as films on glass surfaces by heating colorless ethereal solutions contained in test-tubes in a steam jet. The violet and red films so formed disappeared on cooling. All of these facts are in agreement with the general opinion of greater basicity of high molecular weight carbinols.

The perbromides too are more strongly colored, those of the trixenylmethane series being olive-green and that of triphenylmethane being red. Far more thermal stability was exhibited by the larger compounds trixenylmethyl tetrabromide $(C_6H_5C_6H_4)_3CBr_4$ having a definite melting point at 170–171°, and its trimethyl analog, $(CH_3C_6H_4C_6H_4)_3CBr_4$, fusing at 99–103°. Both compounds are stable for indefinitely long periods at room temperature in a dry atmosphere. It will be recalled[1] that the perbromide (hexabromide) of triphenylbromomethane, or of tritolylbromomethane, loses bromine readily when stored in a desiccator in a laboratory. We make no attempt to trace a relationship between greater basicity of these large tertiary carbinols and thermal stability of the perbromides but it is interesting to note that perhalides in general[2] are formed with organic nitrogen bases, diazonium salts, iodonium salts, sulfonium salts, and salts of inorganic bases and that the melting points of many are very high. Formation of these perhalides, therefore, is not out of character with what might be expected of carbonium salts.

Our real object in preparing the perhalides was to circumvent a peculiar inertness of trixenylmethane to oxidation by chromic anhydride in acetic acid. Long refluxing in this solution, which Hemilian[3] has shown to be effective in converting triphenylmethane to carbinol, proved of no avail with trixenylmethane. Bromination in carbon disulfide solution in presence of sunlight, however, caused a convenient substitution with a halogen atom which was hydrolyzed easily. This series of changes showed the absence of a fluorene compound as a dehydration product accompanying reduction.

By contrast to the great inactivity toward chromic anhydride exhibited by the hydrogen on the central carbon atom, nitration of trixenylmethane occurred more readily than did that of triphenylmethane. Using conditions known to

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(1) Gomberg, *Ber.*, **35**, 1831 (1902); THIS JOURNAL, **20**, 776 (1898); Tousley and Gomberg, *ibid.*, **26**, 1519 (1904).

(2) See, for example, Hantzsch. *Ber.*, **28**, 2754 (1895); Gomberg, THIS JOURNAL, **20**, 790 (1898); Tinkler, *J. Chem. Soc.*, **93**, 1611 (1908); Chattaway and Hoyle, *ibid.*, **123**, 654 (1923).

(3) Hemilian, *Ber.*, **7**, 1206 (1874).

be effective in preparing tris-(*p*-nitrophenyl)-methane, we obtained, after some difficulty in purification, a nonanitrotrixenylmethane. This product, in keeping with the previous experience of greater color in the trixenylmethane series, gave a black precipitate with a pyridine solution of sodium ethylate. Trinitrotriphenylmethane gives a Prussian blue color. Alcoholic sodium hydroxide, however, gave no color with the nonanitro compound. Trinitrotriphenylmethane[4] under the same conditions gave a violet color. Color with this reagent is indeed a common occurrence with aromatic compounds[5] heavily laden with nitro groups and in this respect the behavior of the trixenyl compound appears to be unusual. At this writing we are not disposed to speculate on the significance, if any, of this fact.

Experiments

Trixenylcarbinol.—In this modification of the original[6] procedure, 113 g. of *p*-chlorobiphenyl, 29.7 g. of diethyl carbonate, and 600 ml. of anhydrous thiophene-free benzene were heated to boiling in a 3-liter, 3-necked flask provided with mercury-sealed stirrer and condenser. The burner was then removed and fine sodium sand, 30.4 g., added through the third neck as fast as the condenser could handle the reflux. The mixture was refluxed for two hours after addition of sodium was completed. It was then cooled, decomposed with alcohol followed by water, freed from benzene by heating on a water-bath, and filtered to recover the crude carbinol. It was decolorized in xylene solution from which solvent it crystallized in 39% yield (38 g.), m. p. 206–207°.

Tris-(4′-methylxenyl)-carbinol.—*p*-Methylbiphenyl was prepared by the method of Sherwood, Short and Stansfield[7] and brominated[8] to form 4-bromo-4′-methylbiphenyl. A solution of 34 g. of this compound and 6.5 g. of diethyl carbonate in 150 ml. of anhydrous thiophene-free benzene was treated in the same manner described for the previous preparation with 7 g. of sodium sand. The time of addition was eighty-five minutes; that for refluxing was one hour. It was decomposed as before and volatile impurities removed first by steam distillation and then by extraction with six portions of boiling alcohol. The residue was dissolved in benzene, precipitated by petroleum ether, recrystallized from glacial acetic acid, filtered, washed with ether, and dried: yield 23%, 5.5 g.; m. p. 221.0–221.5°. *Anal.* Calcd. for $C_{40}H_{34}O$: C, 90.5; H, 6.42. Found: C, 90.9, 89.9; H, 6.37, 6.50. In concentrated sulfuric acid trimethyltrixenylcarbinol dissolves with a deep red-violet color which changes to scarlet on standing. In boiling glacial acetic acid it gives a violet color which disappears on cooling.

Trixenylmethane.—A mixture of 15 g. of trixenylcarbinol, 30 g. of stannous chloride, 60 ml. of concentrated hydrochloric acid, 600 ml. of glacial acetic acid and a few crystals of iodine[9] was heated in a liter flask until no pink color remained. After addition of 50 ml. of concentrated hydrochloric acid the precipitate was filtered and washed first with 50 ml. more of hydrochloric acid and then with several portions of water. By extraction with 100 ml. of boiling benzene, followed by recrystallization from chloroform, 12 g. (83%) of trixenylmethane was obtained; m. p. 235–237°; recorded value 236–237°.[10] Reduction of the carbinol with zinc and hydrochloric acid gave only a 15% yield.

Tris-(4′-methylxenyl)-methane.—Reduction of 1 g. of trimethyltrixenylcarbinol was effected with alcohol and sulfuric acid according to the method of Schmidlin and Garcia-Banús.[10] The product was recrystallized from benzene and methanol, m. p. 174.0–174.5°. *Anal.* Calcd. for $C_{40}H_{34}$: C, 93.4; H, 6.62. Found: C, 93.2, 93.8; H, 6.69, 6.71.

Trixenylmethyl Tetrabromide.—A solution of 2 g. of trixenylmethane and 0.4 ml. of bromine, in 50 ml. of carbon disulfide in a 100-ml. Erlenmeyer flask was exposed to sunlight for four hours. Hydrogen bromide was evolved and olive-green needles separated from the solution. These crystals were filtered and washed with a very little carbon disulfide: yield 1 g. (30%); m. p. 170–171°. *Anal.* Calcd. for $C_{37}H_{27}Br_4$: Br, 40.3. Found: Br, 40.1, 40.1. Calcd. for bromine hydrolyzed as $-OBr$: 15.12. Found: 14.95.

This compound is stable for a few minutes in cold water but is hydrolyzed rapidly to trixenylcarbinol (m. p. 206.0–206.5°) by boiling aqueous alkali; mixed melting point with an authentic sample 204–206°. When placed in contact with cinnamic acid in carbon disulfide solution the green color changes to violet; when dissolved in an olefin solvent it is promptly decolorized.

Tris-(4′-methylxenyl)-methyl Tetrabromide.—This compound, m. p. 99–103°, was prepared from 0.2 g. of the corresponding carbinol by the foregoing method. *Anal.* Calcd. for $C_{40}H_{33}Br_4$: Br, 38.3. Found: Br, 36.8, 37.4.

Attempted Oxidation of Trixenylmethane by Chromic Oxide.—After boiling a mixture of 0.5 g. of trixenylmethane, 1 g. of chromic anhydride, and 25 ml. of glacial acetic acid for fifty minutes, it was poured into water and the white precipitate crystallized from xylene. Recovery of trixenylmethane, m. p. 220–226°, was quantitative.

Nonanitrotrixenylmethane.—A mixture of 50 ml. of fuming nitric acid, sp. gr. 1.6, 10 ml. of concd. sulfuric acid, and 10 ml. of 30% fuming sulfuric acid was cooled to a paste with a carbon dioxide freezing mixture. During an eighty-minute period, 10 g. of trixenylmethane was added with stirring to this mixture. Stirring was con-

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[4] Von Richter, *Ber.*, **21**, 2475 (1888); Ziegler and Boye, *Ann.*, **458**, 248 (1927).

[5] See Desvergnes, *Ann. chim. anal. chim. appl.*, **13**, 321 (1931), for a summary of this phenomenon.

[6] Morton and Stevens, THIS JOURNAL, **53**, 4028 (1931). We are indebted to Dr. J. R. Miles (unpublished research) for improvements which have resulted in higher yields. Our attention has also been called to the results of Bachmann and Wiselogle, *J. Org. Chemistry*, **1**, 371 (1936). In spite of the use of a stirrer our yields are somewhat less than those obtained by either of these investigators.

[7] Sherwood, Short and Stansfield, *J. Chem. Soc.*, 1832 (1932).

[8] Gomberg and Pernert, THIS JOURNAL, **48**, 1372 (1926).

[9] Method of Wanscheidt and Moldawski, *Chim. Shur.*, **1** [63] 304 (1931); *Chem. Zentr.*, 102, II, 3208 (1931).

[10] Schmidlin and Garcia-Banús, *Ber.*, **45**, 3188 (1912).

tinued for three and a quarter hours longer during which time 40 ml. of fuming nitric acid, 10 ml. of fuming sulfuric acid and 13 ml. of concd. sulfuric acid were added in small portions keeping the ratio of the two acids constant. After pouring the mixture into 600 ml. of cold water, the precipitated crude product was purified by extraction first with ether in a Soxhlet apparatus, then with boiling glacial acetic acid in several portions, and finally with boiling chloroform in a continuous extractor. The residue at this point amounted to about 8 g., which after seven recrystallizations from nitrobenzene and glacial acetic acid was dried over concentrated sulfuric acid in a vacuum desiccator; m. p. 278–279° with decomposition. The compound is a pale yellowish powder which darkens on exposure to light and ignites with a flash when heated on a spatula in a flame. It gives no color with alcoholic potassium hydroxide but does give a black precipitate with sodium ethylate in pyridine. It is unaffected by bromine in carbon disulfide. *Anal.* Calcd. for $C_{37}H_{19}O_{18}N_9$: N, 14.39. Found: N, 14.31, 14.52, 14.40. The conditions described above for nitrating the triarylmethane are somewhat more severe than those used by Montagne[11] in nitrating triphenylmethane. They have been checked against the latter compound and found to give better yields of trinitrotriphenylmethane than were obtained by him.

Trimethyltrixenylchloromethane.—The procedure of Schlenk and Weickel[12] for preparing trixenylchloromethane was followed. After excess acetyl chloride was distilled from the reaction mixture the residue was shaken with anhydrous ether, filtered, and washed with more ether, m. p. 204–205°. *Anal.* Calcd. for $C_{40}H_{33}Cl$: Cl, 6.92. Found: Cl, 6.97, 7.00. Just as solid trixenylchloromethane turns pink on standing in a closed container, so does trimethyltrixenylchloromethane turn blue. Likewise if the anhydrous ether solution of either compound is heated in a test-tube under a steam jet, a red or blue band, as the case may be, appears on the side of the tube above the liquid. When the tube is held under the cold water tap, the color disappears. This phenomenon can be repeated as long as any anhydrous ether is left in the tube.

Summary

Trimethyltrixenylcarbinol has been prepared by the sodium condensation method for synthesis of tertiary carbinols.

Reduction to the methane, conversion of the latter to the perbromide, and hydrolysis to the original carbinol has been accomplished on both trixenyl- and trimethyltrixenylcarbinol.

Nitration of trixenylmethane produced a nonanitro compound.

The colors of compounds in the trixenylmethyl class are in general more intense than those of corresponding ones in the triphenylmethyl series.

CAMBRIDGE, MASS. RECEIVED JUNE 16, 1937

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[11] Montagne, *Rec. trav. chim.*, **24**, 125 (1905).

[12] Schlenk and Weickel, *Ann.*, **368**, 295 (1909).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Preparation and Pyrolysis of Some Triphenylmethyl Ethers of Complex Function

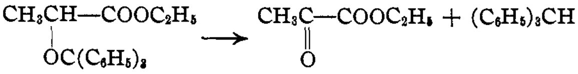
BY CHARLES D. HURD AND EDWARD M. FILACHIONE

The pyrolysis of several triphenylmethyl alkyl ethers into triphenylmethane and an aldehyde or ketone was established by Norris and Young[1]

$$Ph_3C{-}O{-}CH_2R \longrightarrow Ph_3CH + RCHO$$

This interesting work made it seem reasonable to infer that more complex aldehydes or ketones might be synthesized similarly, such, for example, as ethyl pyruvate from ethyl lactate, glycolaldehyde from ethanediol (ethylene glycol), ethoxyacetaldehyde from ethanediol ethyl ether ("cellosolve"), or glyceraldehyde from glycerol.

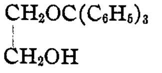
To test this idea, the triphenylmethyl ethers of the above compounds were synthesized. One of the ethers, namely, ethyl α-triphenylmethoxypropionate (I), underwent pyrolysis in the anticipated manner. At 300°, ethyl pyruvate was formed in about 70% yield:



$$\underset{\displaystyle OC(C_6H_5)_3}{CH_3CH}{-}COOC_2H_5 \longrightarrow \underset{\displaystyle \overset{\|}{O}}{CH_3C}{-}COOC_2H_5 + (C_6H_5)_3CH$$

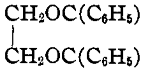
I

This type of reaction, however, was not observed with the other ethers. Instead, ethanediol triphenylmethyl ether (II) underwent disproportionation at 140° into ethanediol and ethanediol triphenylmethyl diether (III).



$$\begin{array}{l} CH_2OC(C_6H_5)_3 \\ | \\ CH_2OH \end{array}$$

II



$$\begin{array}{l} CH_2OC(C_6H_5)_3 \\ | \\ CH_2OC(C_6H_5)_3 \end{array}$$

III

This seemed to be an equilibrium reaction because the yield of III was made practically quantitative if the ethanediol was removed as formed by performing the reaction at 140° under diminished pressure. At atmospheric pressure the yield of III was only 33%. The reverse reaction was achieved by refluxing the diether (III) with ethanediol.

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[1] Norris and Young, THIS JOURNAL, **46**, 2580 (1924); **52**, 753 (1930).