[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE STATE UNIVERSITY OF IOWA]

THE NITRATION OF TRIPHENYLCARBONIUM SULFATE

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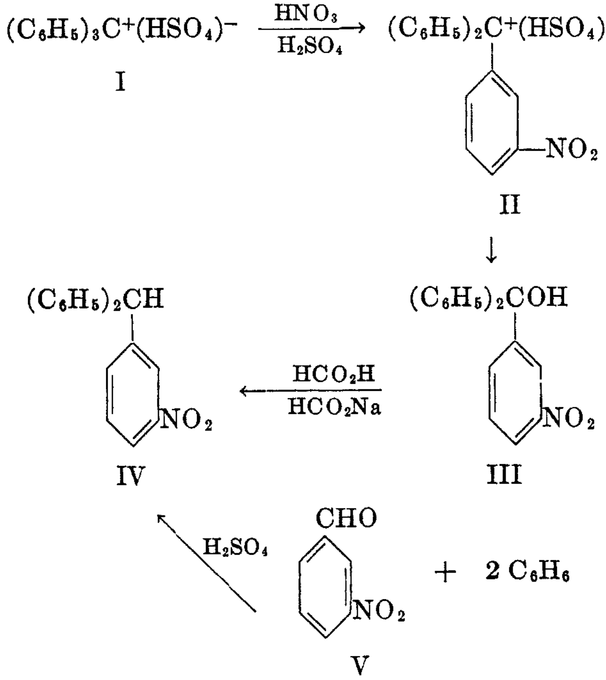
Vorländer (1) studied the stepwise nitration of triphenylcarbonium salts and after hydrolysis obtained carbinols whose analyses indicated them to be approximately mononitro-, dinitro-, and trinitro- derivatives. However, these compounds could not be isolated in the pure crystalline state and attempts to establish their structure by oxidation to nitrobenzoic acids were unsuccessful. Since acid reduction of the trinitrotriphenyl carbinol to the triamino compound did not give a fuchsin dye, it was concluded that the nitro groups were not in the *para*-position. No other data are available on orientation.

The mononitration of triphenylcarbonium sulfate (I) has been reinvestigated. Nitration studies at different temperatures and concentrations of sulfuric and nitric acids showed that mixtures of mono-, di- and tri-nitrated products were always formed in varying ratios. The best conditions for obtaining some of the mononitro derivative consisted in nitration of I in concentrated sulfuric acid at 25° with fuming nitric acid. Dilution with water and neutralization gave a mixture of carbinols containing the *m*-nitroderivative (III) as one component. It was found impossible to separate III in the pure state. However, by reduction



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to the nitrotriphenylmethanes by the formic acid-sodium formate method of Kovache (2) followed by fractional distillation under low pressure there was isolated a 15.4% yield of the *m*-nitrotriphenylmethane (IV); m.p. 91–92°. No other mononitro derivative could be detected.

Since triphenylmethane, and the isomeric *ortho-*, *meta-*, and *para*-nitrotriphenylmethanes all melt within the temperature range of 90 to 94° it was necessary to synthesize these compounds for comparison with the above product. The isomeric nitro compounds were made by condensing *o*-, *m*-, and *p*-nitrobenzaldehyde with benzene with concentrated sulfuric acid (3). It was found that the product from *m*-nitrobenzaldehyde (V) did not depress the melting point of the compound (IV) whereas all the others did cause marked lowering of the melting point of IV.

It was not possible to find experimental conditions which would give exclusively a high yield of the mononitrated compound. Although the yield of the *meta*-nitro derivative (IV) was only 15.4%, the present work taken in conjunction with Vorländer's (1) data on the trinitrotriphenylcarbinol (which must be the *tri-m*-nitrophenylcarbinol) shows that the triphenylmethyl cation (I) is a *meta*-directing structure and hence should be added to the list of compounds (4) containing a positively charged atom attached to the ring which orients the entering nitro group to the *meta* position.

EXPERIMENTAL PART

Nitration of triphenylcarbonium sulfate (I). A solution of 10 g. of triphenylcarbinol in 8 ml. of conc'd sulfuric acid was treated with 100 ml. of fuming nitric acid (*d.* 1.50), allowed to stand at 25° for 24 hours, poured into 1 l. of cold water, and neutralized by the addition of conc'd ammonium hydroxide. The precipitate was washed and dried. The tan powder weighed 12.2 g., m.p. 70–85°. It was a mixture of triphenylcarbinol and nitrated triphenylcarbinols which could not be separated by fractional crystallization although numerous solvents and conditions were studied.

Formic acid reduction of carbinols. The crude nitration product described above was refluxed for eight hours with 150 ml. of 98% formic acid containing 5 g. of sodium formate and then allowed to stand at 25° for two hours. The liquid was decanted from the dark viscous oil which had separated from the solution, and the oil was dissolved in 50 ml. of benzene. The benzene solution was washed with 100-ml. portions of water, 5% sodium bicarbonate, and water. After removal of the benzene by distillation, the residual oil weighed 9.7 g. Distillation of this oil under reduced pressure gave 1.8 g. (15.4%) of pale yellow crystals, b.p. 170–180° (0.35 mm.), m.p. 87–89°. The remainder of the material decomposed with a vigorous evolution of gas. Recrystallization of the crude distillate from 10 ml. of Skellysolve B gave 1.4 g. (12%) of *m*-nitrotriphenylmethane (III), m.p. 90–91°. Mixed melting points with a sample of *m*-nitrotriphenylmethane whose synthesis is described below showed no depression. However, the melting point was depressed upon admixture with samples of *p*-nitrotriphenylmethane (5) (m.p. 91°) and *o*-nitrotriphenylmethane (6) (m.p. 91°).

m-Nitrotriphenylmethane (III). A mixture of 10 g. of *m*-nitrobenzaldehyde, 25 ml. of conc'd sulfuric acid, and 150 ml. of benzene was placed in a bottle with a wired-on glass stopper and shaken at 25° for 24 hours. The benzene layer was separated and washed with 100 ml. each of water, 5% sodium carbonate, 5% sodium bisulfite, and water. The benzene was removed by distillation, and the residual yellow oil was crystallized from 20 ml. of Skellysolve B. The yield of white crystals was 14.5 g. (76%); m.p. 91–92° which checked the value given by Tschacher (3) who made the compound by the above method but gave no description of the procedure. This compound has recently been prepared by Ungnade and Crandall (7) from the same reactants but using aluminum chloride as the condensing agent; they reported m.p. 91.5–93°.

p-Nitrotriphenylmethane. A sample of this compound was prepared by the same procedure as described for the *meta*-isomer. A 75% yield of white crystals melting at 90–91° was obtained. Lit. value, 90° [Baeyer and Lohr (5)]; 90–91° [Ungnade and Crandall (7)]. The latter authors mention that purification by chromatographic adsorption raised the m.p. to 93–94°.

o-Nitrotriphenylmethane. The above sulfuric acid condensation gave only a 10% yield of the *ortho* compound; m.p. 90–91°. Lit. values 88–89° [Ungnade and Crandall (7)]; 93–94° [Kliegl (6)].

SUMMARY

The nitration of triphenylcarbonium sulfate produced a mixture of nitration products which yielded a mixture of nitrated triphenylcarbinols. By reduction to the nitrotriphenylmethanes, there was isolated a 15.4% yield of *m*-nitrotriphenylmethane. This compound was identical with that obtained by the condensation of *m*-nitrobenzaldehyde with benzene, thus establishing the *meta* orientation of the nitro group.

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