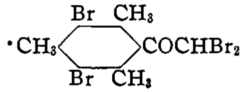
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

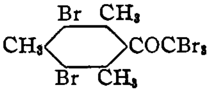
Polyhalo Derivatives of Acetomesitylene. II. The Bromination of 3,5-Dichloroacetylmesitylene

BY C. HAROLD FISHER

In a former paper[1] it was reported that an excess of bromine reacted with 3,5-dibromoacetylmesitylene in acetic acid to give a sharply melting product which consists of equimolar quantities of α,α,3,5-tetrabromoacetylmesitylene (I) and α,α,α,3,5-pentabromoacetylmesitylene (II). Compound formation between di- and tribromomethyl phenyl ketones had not been described previously, and the introduction of three bromine atoms into the acetyl group is of interest in the light of the difficulty experienced[2] earlier in attempts to prepare tribromomethyl ketones[3] from acetophenones. To see if similar results could be obtained with other and simpler acetophenones, the bromination of 4-chloroacetophenone has been studied under similar conditions. It was found that only α,α-dibromo-4-chloroacetophenone was formed when an excess of bromine was used, either in acetic acid or in the absence of solvent. In view of the known ease of reduction of α-bromo ketones it seemed likely that the failure to obtain the tribromo ketone in this and other cases is due to the reducing action of the hydrogen bromide simultaneously formed. In this connection the action of hydrobromic acid on a hot acetic acid solution of pentabromoacetylmesitylene (II) was studied, and it was found that reduction to the tetrabromo ketone (I) occurred with ease.



I



II

Attention was directed next to the bromination of an acetophenone, 3,5-dichloroacetylmesitylene (IV), more closely related to 3,5-dibromoacetylmesitylene.[1] The desired dichloro ketone (IV) was synthesized by the reduction with zinc and acetic acid of α,α,3,5-tetrachloroacetylmesitylene (III), which had been prepared by the chlorination of an acetic acid solution of acetomesitylene. That the tetrachloro ketone possesses the structure (III) assigned to it seems probable in view of the fact that sodium hypochlorite converted it, as well as 3,5-dichloroacetylmesitylene (IV), into α,α,α,3,5-pentachloroacetylmesitylene (V).

The bromination of 3,5-dichloroacetylmesitylene (IV) in acetic acid was found to be similar to the bromination of the corresponding dibromo

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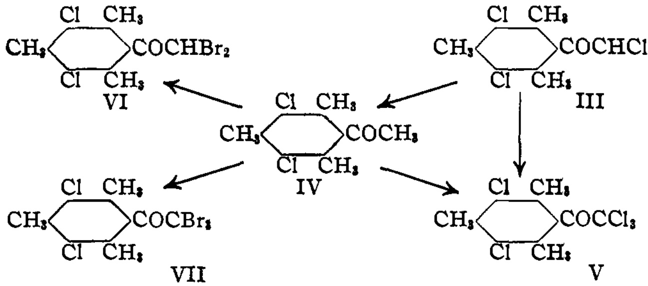
[1] Fisher, THIS JOURNAL, **55**, 4241 (1933).

[2] Hunnius, *Ber.*, **10**, 2010 (1877); Engler and Zielke, *ibid.*, **22**, 204 (1889); Gabriel and Michael, *ibid.*, **11**, 1007 (1878).

[3] It has been shown [Fuson and students, THIS JOURNAL, **54**, 1114, 4380 (1932); other references may be obtained from these two papers] that hindered acetophenones may be converted into tribromomethyl ketones in good yield by treatment with sodium hypobromite.



ketone.[1] A sharply melting (103.5–104.5°) product was formed which was subsequently shown to be composed of α,α,α-tribromo-3,5-dichloroacetylmesitylene (VII) and α,α-dibromo-3,5-dichloroacetylmesitylene (VI). This product (m. p. 103.5–104.5°) was prepared also by crystallizing together equimolar quantities of its components (VI and VII); the separation of these components, however, could not be effected by repeated crystallization. As was expected, the action of sodium hypobromite caused conversion of the acetic acid bromination product (m. p. 103.5–104.5°) into the tribromo ketone (VII). The tribromo ketone (VII) was prepared also by the action of the same brominating agent on dichloroacetylmesitylene (IV). The dichlorodibromo ketone (VI) mentioned above was obtained by treating an acetic acid solution of 3,5-dichloroacetylmesitylene (IV) with two moles of bromine.

Experimental

α,α-Dibromo-4-chloroacetophenone.[4]—Attempts to prepare the tribromomethyl ketone were made unsuccessfully following the procedure (excess bromine, acetic acid solvent at 90–95°, stream of air to remove hydrogen bromide) outlined previously.[1] The tribromo compound was not isolated where the bromination was carried out without solvent, or in a carbon tetrachloride suspension of calcium carbonate. In each case the product obtained was the dibromomethyl ketone, m. p. 93.5–94.5° (previously given, 92.5°).[4]

Anal. Calcd. for $C_8H_5OClBr_2$: C, 30.7; H, 1.6. Found: C, 30.5; H, 1.8.

α,α,3,5-Tetrabromoacetylmesitylene (I).—A mixture of 1 g. of α,α,α,3,5-pentabromoacetylmesitylene, 10 cc. of 48% hydrobromic acid and 30 cc. of acetic acid was boiled for a few minutes and allowed to cool. The solid which appeared was collected, crystallized several times from alcohol and found to be tetrabromoacetylmesitylene.

α,α,3,5-Tetrachloroacetylmesitylene (III).—A stream of chlorine was bubbled, with mechanical stirring, into 8.1 g. of acetomesitylene and 10 cc. of acetic acid in a three-necked flask (to which a small amount of iodine and iron filings had been added) for one and one-half hours (8 g. of the gas was absorbed). Heat was generated and the product precipitated as a light-yellow paste. Crystallization from alcohol gave, in good yield, colorless needles melting at 106.5–107.5°.

Anal. Calcd. for $C_{11}H_{10}OCl_4$: C, 44.0; H, 3.4. Found: C, 44.1; H, 3.7.

3,5-Dichloroacetylmesitylene (IV).—A mixture of 6.7 g. of crude (the reaction product described above after removal of solvent) tetrachloroacetylmesitylene, 15 g.

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(4) Collet, *Bull. soc. chim.*, [3] **21**, 70 (1899).

of zinc dust and 75 cc. of acetic acid was heated for three hours under a return condenser with a boiling water-bath. The mixture was filtered hot, and the residue washed with hot acetic acid. The combined filtrates were concentrated, and added to water. The solid which was precipitated crystallized from alcohol as large, colorless leaflets melting at 107.5–109°.

Anal. Calcd. for $C_{11}H_{12}OCl_2$: C, 57.1; H, 5.2. Found: C, 56.7; H, 5.4.

α,α,α,3,5-Pentachloroacetylmesitylene (V).—A solution of 0.5 g. of α,α,3,5-tetrachloroacetylmesitylene in 10 cc. of pyridine was added to 100 cc. of sodium hypochlorite (4 g. of sodium hydroxide in 40 cc. of water added to a chlorine-saturated solution of 6 g. of sodium hydroxide in 60 cc. of water), and the resulting mixture was mechanically agitated for forty-eight hours. The reaction product was filtered, washed with water and crystallized from alcohol. The colorless leaflets obtained melted at 90–91°, and was identical with the pentachloroacetylmesitylene prepared from 3,5-dichloroacetylmesitylene by treatment with sodium hypochlorite.

α,α,α,3,5-Pentachloroacetylmesitylene (V). (Second Method).—A solution of 2.3 g. of 3,5-dichloroacetylmesitylene in 20 cc. of pyridine was added to 280 cc. of sodium hypochlorite (80 cc. of 10% sodium hydroxide added to 200 cc. of chlorine-saturated 10% sodium hydroxide), and the resulting mixture agitated for sixty-nine hours. The residue obtained by filtering was washed with water and extracted with hot alcohol. The product was crystallized from alcohol, appearing as small leaflets (sometimes as needles) and melting at 90–91°.

Anal. Calcd. for $C_{11}H_9OCl_5$: C, 39.5; H, 2.7. Found: C, 39.4; H, 2.9.

Action of Bromine in Acetic Acid on 3,5-Dichloroacetylmesitylene.—Bromine (5 g.) was added from a dropping funnel, with mechanical stirring, to a solution of 1 g. of 3,5-dichloroacetylmesitylene in 15 cc. of glacial acetic acid contained in a three-necked flask surrounded by a water-bath. The dropping funnel was replaced by a tube extending beneath the surface of the solution and air was drawn through the solution (with heating and stirring) by a water-pump attached to condenser for one hour. Most of the excess bromine was then removed by an air-stream after stopping the flow of water in the condenser. The needles which appeared on cooling were crystallized from alcohol; m. p. 103.5–104.5°.

Anal. Calcd. for $C_{11}H_{10}OCl_2Br_2 \cdot C_{11}H_9OCl_2Br_3$: C, 30.8; H, 2.2. Found: C, 30.9; H, 2.4.

Crystallization of a Mixture of α,α-Dibromo-3,5-dichloroacetylmesitylene (VI) and α,α,α-Tribromo-3,5-dichloroacetylmesitylene (VII).—Crystallization of 0.39 g. of the dibromo ketone and 0.47 g. of the tribromo ketone gave 0.62 g. of colorless needles melting at 103–104°. The melting point was the same after six more crystallizations from alcohol, and it was not lowered by being mixed with the product obtained by the action of bromine (excess) in acetic acid on 3,5-dichloroacetylmesitylene.

α,α,α-Tribromo-3,5-dichloroacetylmesitylene (VII).—A solution of 3.5 g. of 3,5-dichloroacetylmesitylene in 20 cc. of pyridine was added to sodium hypobromite (9.5 cc. of bromine, 30 g. of sodium hydroxide and 280 cc. of water), and the resulting mixture agitated for forty-five hours. The solid obtained by filtration was washed with water and crystallized from alcohol. Stout needles (3.8 g.) melting at 84–85° were obtained.

Anal. Calcd. for $C_{11}H_9OCl_2Br_3$: C, 28.2; H, 1.9. Found: C, 28.3; H, 2.2.

The same tribromo ketone (VII) was obtained when 0.2 g. (in 2 cc. of pyridine) of the product (m. p. 103.5–104.5°) formed by the action of an excess of bromine in acetic acid on 3,5-dichloroacetylmesitylene was treated in a similar manner with sodium hypobromite (2 cc. of bromine, 6 g. of sodium hydroxide and 55 cc. of water).

α,α-Dibromo-3,5-dichloroacetylmesitylene (VI).—Bromine (6.4 g., 0.04 mole) was added, with stirring, from a dropping funnel during five minutes to 4.6 g. (0.02 mole) of 3,5-dibromoacetylmesitylene and 60 cc. of acetic acid in a three-necked flask surrounded by a water-bath. After one hour of stirring and heating, the solution was allowed to cool.

The crystalline material which appeared melted (after several crystallizations from alcohol) at 121–122°, and amounted to 5.7 g.

Anal. Calcd. for $C_{11}H_{10}OCl_2Br_2$: C, 33.9; H, 2.6. Found: C, 33.9; H, 2.7.

Summary

A satisfactory synthesis of 3,5-dichloroacetylmesitylene has been developed. It was found that the bromination of this acetophenone in acetic acid proceeded as in the case of 3,5-dibromoacetylmesitylene, giving a sharply melting product composed of the corresponding di- and tribromomethyl ketones. When 4-chloroacetophenone was brominated under the same conditions only α,α-dibromo-4-chloroacetophenone was isolated.

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The Michael Condensation. I. The Behavior of Diethyl Phenylmalonate in the Michael Condensation

BY RALPH CONNOR

The investigation of the reaction of diethyl phenylmalonate in the Michael condensation was undertaken for the purpose of studying the rearrangement which has been reported[1] in the reaction of diethyl methylmalonate, ethyl α-cyanopropionate and ethyl α-cyanobutyrate with α,β-unsaturated esters and ketones. This compound was selected because the tendency of an aryl group to migrate (according to the mechanism of Michael and Ross[1a,d]) or its influence upon the change in position of a carboethoxyl group (by the mechanism of Holden and Lapworth[1b]) might differ considerably from that of an alkyl group.

The first reaction carried out was that of diethyl phenylmalonate with ethyl crotonate in absolute alcohol containing a molecular equivalent of sodium ethoxide. Instead of the expected tribasic ester the products were diethyl carbonate and diethyl α-phenyl-β-methylglutarate (I). Similar results were obtained with ethyl tiglate, ethyl cinnamate and benzalacetophenone. It was also found that diethyl phenylmalonate in absolute alcohol with sodium ethoxide underwent alcoholysis to give diethyl carbonate and ethyl phenylacetate. This is analogous to the results obtained by Cope and McElvain[2] working with disubstituted malonic esters. Thus it

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(1) (a) Michael and Ross, THIS JOURNAL, **52**, 4598 (1930); **53**, 1150 (1931). (b) Holden and Lapworth, *J. Chem. Soc.*, 2368 (1931). (c) Michael and Ross, THIS JOURNAL, **54**, 407 (1932). (d) Michael and Ross, *ibid.*, **55**, 1632 (1933).

(2) Cope and McElvain, *ibid.*, **54**, 4319 (1932).