[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Action of Bromine on Acetomesitylene. Polyhalo Derivatives of 3,5-Dibromoacetylmesitylene[1]

BY C. HAROLD FISHER

Several attempts to prepare α-tribromoacetophenones by direct bromination of the corresponding acetophenones have been reported unsuccessful.[2] However, by working in the absence of solvent, Adams[3] was able to introduce three bromine atoms into the acetyl group of bromopaeonol (2-hydroxy-4-methoxy-5-bromoacetophenone). In view of this fact, and the ease with which the ring of mesitylene derivatives has been brominated,[4] it seemed likely that liquid bromine would convert acetomesitylene into α,α,α,3,5-pentabromoacetylmesitylene (I). It was found that actually a mixture of polybromoacetylmesitylenes melting at 102–108° was formed, which on fractional crystallization yielded the expected pentabromo compound (m. p. 113–114°) and a substance melting at 108–109°. The action of liquid bromine on α,α,α-tribromoacetylmesitylene[5] gave precisely the same results.

Attempts were made to transform the pentabromo compound (I) into 3,5-dibromo-β-isodurylic acid (II) by alkaline cleavage as a method of structure determination. However, this cleavage, which would hardly be expected in view of the difficulty experienced in the cleavage of similarly hindered α-tribromoacetophenones, could not be accomplished. Accordingly, it was planned to synthesize α,α,α,3,5-pentabromoacetylmesitylene (I) by a method[6] which has been shown to be generally applicable to hindered acetophenones. The compound, 3,5-dibromoacetylmesitylene (IV), needed as a starting point in this synthesis was prepared by reducing with zinc and acetic acid[7] the crude product, described above, prepared by brominating acetomesitylene without a solvent. Although the material reduced was a mixture, only one reduction product (IV) was obtained. The bromine content (two atoms) and method of preparation appeared to exclude all structures except that of 3,5-dibromoacetylmesitylene (IV), but confirmation was arrived at by its conversion, in two steps, into 3,5-dibromo-β-isodurylic acid (II).

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(1) A portion of this work was carried out with Professor Reynold C. Fuson (Dissertation, University of Illinois, 1932), to whom the author wishes to express his thanks for the kind permission to continue the work elsewhere.

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

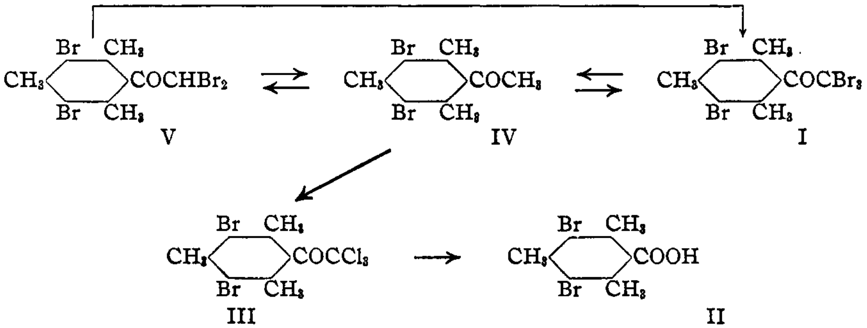
(3) Adams, THIS JOURNAL, **41**, 262 (1919).

(4) Shildneck and Adams, *ibid.*, **53**, 351 (1931).

(5) Fuson and Walker, *ibid.*, **52**, 3269 (1930).

(6) One of the recent papers in this series: Fuson, Bertetti and Ross, *ibid.*, **54**, 4380 (1932).

(7) This reduction method was shown to be applicable to tribromoacetophenones by its use in the case of a previously-described compound, tribromoacetylmesitylene.[5] The product, acetomesitylene, was identified by conversion into its solid nitration product.[5]



The action of sodium hypochlorite caused the formation of α,α,α-trichloro-3,5-dibromoacetylmesitylene (III), which was then cleaved by the action of hot alkali to the dibromo acid (II). This acid was identical with a sample of 3,5-dibromo-β-isodurylic acid prepared according to the directions of Shildneck and Adams.[4]

The preparation of α,α,α,3,5-pentabromoacetylmesitylene (I) was brought about by treating 3,5-dibromoacetylmesitylene (IV) with a solution of sodium hypobromite. The product thus formed was identical with the pentabromo compound (m. p. 113–114°) previously obtained by the bromination of acetomesitylene. The pentabromo ketone (I) was produced also, but in a less pure state, when the mixture obtained by the action of liquid bromine on acetomesitylene was treated with sodium hypobromite.

The other substance (m. p. 108–109°) obtained by the action of liquid bromine on acetomesitylene was prepared by treating an acetic acid solution of 3,5-dibromoacetylmesitylene (IV) with an excess of bromine, and was shown to be composed of the pentabromo ketone (I) and α,α,3,5-tetrabromoacetylmesitylene (V). The evidence supporting this conclusion is as follows: analyses showed the presence of four and one-half bromine atoms, and molecular weight determinations gave a value midway between the molecular weights of tetrabromo- and pentabromoacetylmesitylene. The same product, m. p. 108–109°, was obtained when equimolar quantities of α,α,3,5-tetrabromoacetylmesitylene (V) (prepared by treating an acetic acid solution of 3,5-dibromoacetylmesitylene (IV) with two moles of bromine) and pentabromoacetylmesitylene (I) were crystallized together. Reduction of the product melting at 108–109° with zinc and acetic acid gave the dibromo ketone (IV), and the action of sodium hypobromite caused the formation of the pentabromo ketone (I). The same substance (m. p. 108–109°) was synthesized by the action of bromine on an acetic acid solution of α,α,3,5-tetrabromoacetylmesitylene (V), and in another case by the action of an acetic acid solution of bromine and hydrogen bromide on the pentabromo ketone (I). The substance, m. p. 108–109°, behaved toward cold alkali[8] as would be expected: the dibromo-

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(8) Engler and Wöhrle, *Ber.*, **20**, 2201 (1887).

methyl ketone was converted into an alkali-soluble product, leaving undissolved the pentabromo ketone (I).

The kind and helpful suggestions of Professor Louis F. Fieser are gratefully acknowledged.

Experimental

The Action of Bromine on Acetomesitylene and α,α,α-Tribromoacetylmesitylene.[5]—In each case an excess (5 to 9 parts by weight to one of ketone) of previously-cooled bromine was added slowly to the organic compound contained in a flask surrounded by an ice-bath. After the reaction had become less vigorous the ice-bath was removed, and the reaction mixture allowed to stand four hours with occasional shaking at room temperature. Most of the excess bromine was removed with a stream of air. A cold solution of sodium bisulfite was added and the mixture filtered. Fractional crystallization in alcohol of the residue, a nearly colorless solid, yielded two substances which melted at 108–109° and 113–114°. A larger quantity of the higher melting compound was usually obtained. It was found possible to prepare both products in a high state of purity and more conveniently by other methods described below.

3,5-Dibromoacetylmesitylene (IV).—Reduction with zinc dust and acetic acid caused the replacement of all the bromine atoms of the acetyl group with hydrogen atoms in the case of α,α,α-tribromoacetylmesitylene, pentabromoacetylmesitylene (I), tetrabromoacetylmesitylene (V) and the product (m. p. 108–109°) consisting of the tetra- and pentabromoacetylmesitylenes (V and I). Each ketone (6 g.) was heated for four hours on a steam cone with 12 g. of zinc dust and 60 cc. of acetic acid. The reaction mixture was filtered and the residue washed with hot acetic acid. The combined filtrates were concentrated and added to water. The solid which precipitated crystallized in alcohol as colorless leaflets or cubes, m. p. 147.5–148.5°. The yields were good.

Anal. Calcd. for $C_{11}H_{12}OBr_2$: Br, 50.0. Found: Br, 50.4.

α,α,α-Tribromoacetylmesitylene gave an oil which yielded a nitration product identical with the substance[5] previously prepared by nitrating acetomesitylene.

α,α,α-Trichloro-3,5-dibromoacetylmesitylene (III).—A solution of 2 g. of 3,5-dibromoacetylmesitylene in 100 cc. of pyridine was added to 100 cc. of a sodium hypochlorite solution, which had been prepared[6] from a 10% sodium hydroxide solution. The resulting mixture was agitated for several days. The product was filtered, washed with water, and crystallized from alcohol, giving colorless needles which melted at 102–103°.

Anal. Calcd. for $C_{11}H_9OCl_3Br_2$: C, 31.2; H, 2.1. Found: C, 31.1; H, 2.1.

3,5-Dibromo-β-isodurylic Acid (II).—A small amount of the dibromo acid was obtained by heating 1.9 g. of α,α,α-trichloro-3,5-dibromoacetylmesitylene with 10 g. of sodium hydroxide, 10 cc. of water and 20 cc. of dioxane on a steam cone for twelve hours, and then two hours (refluxing) over a flame. Most of the starting material was recovered unchanged.

A good yield of the acid was obtained by refluxing for five hours a mixture of 1.5 g. of the trichloro ketone, 10 g. of sodium hydroxide, 15 cc. of water and 5 cc. of methyl alcohol. The sodium salt of the acid was washed with ether, dissolved in hot water (the sodium salt is comparatively insoluble in cold water) and filtered. The precipitate obtained by acidification with hydrochloric acid was crystallized from a methanol–water solution, and found to be identical (mixed melting point) with an authentic sample of 3,5-dibromo-β-isodurylic acid.[4]

Brominations with Sodium Hypobromite.—3,5-Dibromoacetylmesitylene (IV), α,α,3,5-tetrabromoacetylmesitylene (V) and the sharply-melting (108–109°) mixture (VI) of the tetra- and pentabromoacetylmesitylenes (V and I) were converted into the pentabromo ketone (I). The data are given below.

Ketone, g.	Pyridine, cc.	Water, cc.	Sodium hydroxide, g.	Bromine, cc.	Time of stirring, hrs.	M. p., °C.	Yield, g.
IV, 1	25	275	30	9.5	48	112–113.5	1
V, 1.5	25	300	30	9.5	67	112.5–113.5	1.3
VI, 1.5	50	250	30	9.5	48	112.5–113.5	1.3

The proportions of pyridine and water used in the last-mentioned preparation caused the formation of two layers. After several crystallizations from alcohol the product was obtained as large, colorless needles melting at 113–114°.

Anal. Calcd. for $C_{11}H_9OBr_5$: C, 23.7; H, 1.6; mol. wt., 557. Found: C, 23.8; H, 1.7; mol. wt. (cryoscopic in benzene), 539.

The Action of an Excess of Bromine on 3,5-Dibromoacetylmesitylene in Acetic Acid.—A solution of 8 g. (0.025 mole) of the dibromo ketone in 100 cc. of glacial acetic acid was stirred mechanically, and heated in a boiling water-bath, and 12 g. (0.075 mole) of bromine was added from a dropping funnel in the course of ten minutes. After stirring and heating had continued for one and one-half hours, the dropping funnel was replaced by a glass tube extending below the surface of the solution, and for one and three-quarters hours air was drawn through this tube by means of a water pump connected to the top of the condenser (heating and stirring). The solution on cooling deposited 9.8 g. of needles melting at 107.5–109°. After repeated crystallization from alcohol the product melted at 108–109°, and was found to be identical with the substance (m. p. 108–109°) obtained by the action of bromine, without solvent, on acetomesitylene. The bromination of α,α,3,5-tetrabromoacetylmesitylene under these conditions gave the same result.

Anal. Calcd. for $C_{11}H_{10}OBr_4 \cdot C_{11}H_9OBr_5$: C, 25.5; H, 1.9; mol. wt., 518. Found: C, 25.8, 25.5; H, 2.0, 2.0; mol. wt. (cryoscopic in benzene), 516, 513.

A preparation carried out later with different quantities (11 g. (0.034 mole) of dibromo ketone, 22.4 g. (0.14 mole) of bromine, 110 cc. of acetic acid) was found to yield a mixture (separated by fractional crystallization) of the usual product (m. p. 108–109°) and α,α,α,3,5-pentabromoacetylmesitylene.

The Crystallization of a Mixture of Tetrabromoacetylmesitylene (V) and Pentabromoacetylmesitylene (I).—A mixture of the pentabromo (0.56 g.) and tetrabromo (0.48 g.) ketones was crystallized from alcohol. The product (0.9 g.) melted at 108–109°, and was identical with the product, m. p. 108–109°, obtained by the action of an excess of bromine on 3,5-dibromoacetylmesitylene in acetic acid. The melting point was not altered by six additional crystallizations from alcohol.

α,α,3,5-Tetrabromoacetylmesitylene (V).—This compound was prepared in good yield by adding 2 moles of bromine to an acetic acid solution of 3,5-dibromoacetylmesitylene, which was mechanically stirred and heated by a water-bath. The product crystallized from alcohol as colorless needles melting at 143–144°.

Anal. Calcd. for $C_{11}H_{10}OBr_4$: Br, 66.9. Found: Br, 66.8.

The Action of Bromine and Hydrogen Bromide on α,α,α,3,5-Pentabromoacetylmesitylene.—A solution of 0.56 g. of pentabromoacetylmesitylene, 10 cc. of acetic acid, 10 drops of 48% hydrobromic acid and 5 drops of bromine was heated with mechanical stirring in a three-necked flask on a water-bath for half an hour. Five drops of bromine was then added, and the stirring continued one hour. The needles (0.30 g.) which formed when the reaction solution cooled melted at 108–109°, and was identical with the sharply-melting (108–109°) substance previously obtained by treating an acetic acid solution of 3,5-dibromoacetylmesitylene with an excess of bromine. More of the same product (m. p. 107.5–109°) was precipitated by adding water to the mother liquor.

α,α,α,3,5-Pentabromoacetylmesitylene (I). (By Use of Potassium Hydroxide.)—

One gram of the sharply-melting (108–109°) product obtained by treating an acetic acid solution of 3,5-dibromoacetylmesitylene with an excess of bromine was pulverized in an agate mortar and shaken mechanically with 50 cc. of a 10% potassium hydroxide solution for twenty-four hours. Acidification of the reaction mixture (after washing with ether) gave a precipitate in insufficient amount for identification. Evaporation of the ether left a residue, from which the pentabromo ketone, melting at 112–113°, was isolated by extraction with hot alcohol. A small amount of a substance sparingly soluble in hot alcohol, and very soluble in benzene, was isolated but not identified.

Summary

It has been shown that bromine reacts in the absence of solvent with acetomesitylene to give a tribromomethyl ketone and a sharply-melting substance consisting of the same tribromomethyl ketone and the corresponding dibromomethyl ketone. Bromine in acetic acid was less efficient in halogenating the acetyl group since the chief product was the sharply-melting mixture of the dibromo- and tribromo-methyl ketones.

CAMBRIDGE, MASSACHUSETTS

RECEIVED JUNE 16, 1933
PUBLISHED OCTOBER 6, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY]

The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. IV. The Dehydrogenation of Paraffin Hydrocarbons and the Strength of the C–C Bond

BY F. O. RICE AND M. DENISE DOOLEY

The thermal decomposition of ethane has been studied recently in two papers,[1] and it has been concluded that the only reaction occurring to an appreciable extent is the simple dehydrogenation to C_2H_4; the reaction is homogeneous and unimolecular, with an activation energy of about 73 cal. It would seem from this that the decomposition of ethane can best be represented as the separation of molecular hydrogen from the ethane molecule with the formation of a double bond between the two carbon atoms to give ethylene. This view has received further support from the work of Pease,[2] who has shown that the formation of ethane from ethylene and hydrogen is a second order reaction with an energy of activation of 43,150 cal. The heat of the reaction $C_2H_4 + H_2 \longrightarrow C_2H_6$ at room temperature and constant pressure is 30,600 cal.[3] and at 600–700° and constant volume is 31,244 cal.[4] The activation energy of the reaction $C_2H_6 \longrightarrow C_2H_4 + H_2$ is therefore $43{,}150 + 31{,}244 = 74{,}394$ cal., a figure which is in excellent agreement with the experimental value of 73,170 cal. obtained by Marek and McCluer.[1]

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(1) Frey and Smith, *Ind. Eng. Chem.*, **20**, 948 (1928); Marek and McCluer, *ibid.*, **23**, 878 (1931).

(2) Pease, THIS JOURNAL, **54**, 1878 (1932).

(3) Von Wartenberg and Krause, *Z. physik. Chem.*, **151**, 105 (1930).

(4) Pease and Durgan, THIS JOURNAL, **50**, 2715 (1928).