

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## The Replacement of Groups by Hydrogen in Certain Substituted Methanes. $\alpha$ -Tribromoacetophenones

BY C. HAROLD FISHER

It has been long known that methanes highly substituted with certain groups and/or atoms (nitro, acyl, aroyl, halogen, cyano, etc.) undergo replacement of a group or atom by hydrogen, when treated with reagents such as alkali,<sup>1</sup> hydrazine hydrate<sup>2</sup> and sodium iodide,<sup>3</sup> and sufficient data are at hand already to predict in some cases which group will be replaced. For instance, it has been shown that a bromine atom will undergo replacement<sup>4</sup> before a chlorine atom, and that generally an acyl or aroyl group is even more easily replaced.<sup>5</sup> A methane substituted with three bromine atoms and a benzoyl group (tribromoacetophenone) has not been studied from this standpoint, although some work<sup>6</sup> has been done which indicates that a bromine atom instead of the benzoyl group (excepting when alkali is used) is replaced by hydrogen in certain  $\alpha$ -tribromoacetophenones. The present paper is a report of work which shows conclusively that in most of the cases studied a bromine atom of tribromomethyl aryl ketones has a predominating tendency to be replaced by hydrogen. A hindered tribromomethyl ketone,  $\alpha, \alpha, \alpha, 3, 5$ -pentabromoacetylmesitylene<sup>7</sup> (I), was selected for this study to eliminate complicating reactions of the carbonyl group, and because of its availability. The products (3,5-dibromo- $\beta$ -isodurylic acid<sup>8</sup> and tetrabromoacetylmesitylene (IV)<sup>7</sup>) formed by replacement of either the benzoyl group or a bromine atom of this ketone are solids which may be easily identified.

When potassium iodide and  $\alpha, \alpha, \alpha, 3, 5$ -pentabromoacetylmesitylene (I) were allowed to react in acetone at room temperature two bromine atoms were replaced by hydrogen, the product being  $\alpha, 3, 5$ -tribromoacetylmesitylene (II). The structure of this tribromo ketone (II) was established by its reactions and synthesis. Reduction with zinc and acetic acid gave 3,5-dibromoacetylmesitylene (III),<sup>7</sup> and treatment with sodium hypobromite

(1) Norris and Thorpe, *J. Chem. Soc.*, **119**, 1203 (1921); Macbeth *et al.*, *ibid.*, **117**, 880 (1920); **119**, 355 (1921); Baker, *ibid.*, **2419** (1931); Woodward and Fuson, *THIS JOURNAL*, **55**, 3472 (1933); Neff, *Ann.*, **308**, 329 (1899); Hantzsch and Rinckenberger, *Ber.*, **32**, 628 (1899); see also Cope, *THIS JOURNAL*, **54**, 1250 (1932); this and other lists of references in this paper are not necessarily complete.

(2) (a) Macbeth and students, *J. Chem. Soc.*, 1870 (1931); 1248 (1926); **121**, 2173 (1922); (b) Howk and McElvain, *THIS JOURNAL*, **55**, 3372 (1933).

(3) (a) Backes, West and Whiteley, *J. Chem. Soc.*, **119**, 377 (1921); (b) Willstätter and Hottenroth, *Ber.*, **37**, 1775 (1904); (c) Birkenbach, Kelleman and Stein, *ibid.*, **65**, 1071 (1932); (d) Goldschmidt and Nagel, *ibid.*, **63**, 1212 (1930); (e) Löwenbein and Schuster, *Ann.*, **481**, 106 (1930); see Ref. 2b.

(4) Gott and Hunter, *J. Chem. Soc.*, **125**, 442 (1924); Zincke and Gerland, *Ber.*, **21**, 2388 (1888).

(5) (a) Myddleton, Barrett and Seager, *THIS JOURNAL*, **52**, 4405 (1930); (b) Bull and Fuson, *ibid.*, **55**, 3424 (1933).

(6) Fisher, Snyder and Fuson, *ibid.*, **54**, 3665 (1932).

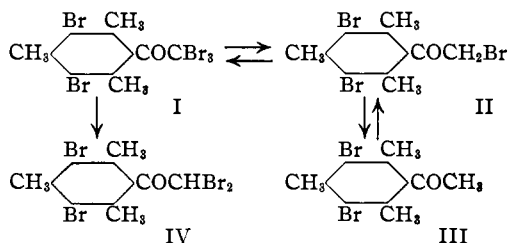
(7) Fisher, *ibid.*, **55**, 4241 (1933).

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

caused the formation of the pentabromo ketone (I). The synthesis of II was carried out by treating an acetic acid solution of 3,5-dibromoacetylmesitylene (III) with one mole of bromine. It seems probable that  $\alpha,\alpha,3,5$ -tetrabromoacetylmesitylene (IV) is an intermediate in the reduction of the pentabromo ketone (I) to the tribromo ketone (II), since the action of potassium iodide on the sharply-melting substance<sup>7</sup> composed of equimolar quantities of the penta- and tetra-bromo ketones (I and IV) yielded the same tribromo ketone (II).

Ethylmagnesium bromide in excess reacted with the pentabromo ketone (I) to yield the partially dehalogenated ketone (IV). Presumably, this reaction proceeded according to the equation recently proposed for the dehalogenation of  $\alpha$ -halo ketones by Grignard reagents.<sup>9</sup>

The reaction of hydrazine hydrate with pentabromoacetylmesitylene (I) in alcohol proceeded very slowly, and was not complete, as judged by the volume of nitrogen liberated, even after fifty-six hours. The product isolated was tetrabromoacetylmesitylene (IV). The same transformation (I to IV) was brought about also by the action of phenol. The dehalogena-



tion of  $\alpha$ -bromo ketones by phenols has been shown to proceed, in the cases<sup>8,10</sup> previously studied, with the formation of *p*-bromophenol. That pentabromoacetylmesitylene (I) reacts more readily with phenol than does the tetrabromo ketone (IV) is shown by the fact that the sharply-melting addition product<sup>7</sup> of these two ketones (I and IV) reacted under the same conditions with phenol to give a good yield of tetrabromoacetylmesitylene (IV).

Conditions (refluxing for one hour) similar to those used for the dehalogenation with acetone of  $\alpha$ -bromo- $\alpha,\alpha$ -diphenylacetophenone<sup>3c,11</sup> caused no appreciable reaction in the case of pentabromoacetylmesitylene (I). Dehalogenation to the tetrabromo ketone (IV) proceeded smoothly, however, when the pentabromo ketone (I) was heated for six hours on a steam cone with acetophenone.

It is already well known that  $\alpha$ -tribromoacetophenone<sup>5a</sup> and tribromo-methyl ketones in general suffer replacement of the benzoyl group (or acyl group) by hydrogen under the influence of alkali. Since this replacement

(9) Kohler and Tishler, *THIS JOURNAL*, **54**, 1594 (1932); see also Ref. 6.

(10) Koelsch, *ibid.*, **53**, 1147 (1931).

(11) See also Jackson and Adams, *ibid.*, **37**, 3522 (1915).

of the benzoyl group takes place with difficulty and in poor yield when ortho substituents<sup>5b</sup> are present, it seemed possible that dehalogenation might be detected in the case of tribromomethyl aryl ketones thus hindered. The product formed in case of dehalogenation by alkali probably would be the corresponding mandelic acid instead of a dibromomethyl ketone, since alkali converts dibromomethyl aryl ketones<sup>12</sup> into substituted mandelic acids ( $\text{RCOCHBr}_2 \longrightarrow \text{RCHOHCOOH}$ ). As yet, however, neither the corresponding mandelic acid (indicating dehalogenation) nor the benzoic acid (indicating cleavage) has been isolated after treatment of pentabromoacetylmesitylene (I) with alkali. The starting material was recovered unchanged when cold alkali was used, and the action of hot alkali yielded a mixture from which no pure substance was isolated. Before making a thorough study of the action of alkali on pentabromoacetylmesitylene (I), it seemed advisable to examine the behavior of similarly hindered  $\alpha$ -dibromoacetophenones toward alkali.<sup>13</sup> For a preliminary study of this reaction two dibromomethyl ketones were selected which do not have widely different molecular weights and melting points. It was found that under similar conditions  $\alpha, \alpha$ -dibromo-4-chloroacetophenone (V,



m. p.  $94^\circ$ ) dissolves in an aqueous solution of potassium hydroxide several hundred times as rapidly as does  $\alpha, \alpha$ -dibromoacetylmesitylene (VI, m. p.  $74^\circ$ ).

### Experimental

**$\alpha, \alpha, 3, 5$ -Tribromoacetylmesitylene (II).**—Iodine was liberated immediately when 0.278 g. of  $\alpha, \alpha, \alpha, 3, 5$ -pentabromoacetylmesitylene in 10 cc. of acetone was treated with 5.1 cc. of a potassium iodide solution (0.539 g. of potassium iodide in 70 cc. of acetone). After standing for forty-two hours the mixture was filtered to remove a finely divided precipitate, and a dilute solution of sodium thiosulfate was added dropwise to the filtrate until the disappearance of color. The solid which appeared when water was added was crystallized several times from alcohol, coming out as colorless needles melting at  $123.5$ – $125^\circ$  (the amount was insufficient for further purification). When mixed with an authentic sample of  $\alpha, \alpha, 3, 5$ -tribromoacetylmesitylene (m. p.  $126$ – $127^\circ$ ) the m. p. was  $125$ – $127^\circ$ .

The sharply-melting substance<sup>7</sup> (0.278 g.) composed of equimolar quantities of  $\alpha, \alpha, 3, 5$ -tetrabromoacetylmesitylene and  $\alpha, \alpha, \alpha, 3, 5$ -pentabromoacetylmesitylene was treated in the same way with the same quantity of potassium iodide solution used before, and allowed to stand for forty-two hours. The product, isolated and purified as in the above-described experiment, melted at  $126$ – $127^\circ$ . The mixed melting point with  $\alpha, \alpha, 3, 5$ -tribromoacetylmesitylene was not depressed.

(12) Engler and Wöhrlé, *Ber.*, **20**, 2201 (1887).

(13) The action of alkali on hindered  $\alpha$ -dibromoacetophenones is of interest also in connection with the mechanism of the conversion of dibromomethyl aryl ketones into substituted mandelic acids, since retardation of this reaction by steric hindrance might indicate that addition of alkali to the carbonyl group is the first step of the reaction.

**$\alpha,3,5$ -Tribromoacetylmesitylene (Second Method).**—To 3.2 g. of 3,5-dibromoacetylmesitylene dissolved in 50 cc. of acetic acid was added 24.2 cc. of a bromine solution (16.5 g. of bromine in 250 cc. of acetic acid) during eight minutes, with vigorous stirring. The stirring and heating (water-bath at 55°) were continued twelve minutes. The solvent was then boiled until the solution was concentrated. On cooling 3.3 g. of colorless needles melting at 117–122° appeared. After several crystallizations from alcohol the m. p. was 126–127°.

*Anal.* Calcd. for  $C_{11}H_{11}OBr_3$ : C, 33.1; H, 2.8. Found: C, 33.2; H, 2.8.

**3,5-Dibromoacetylmesitylene (III).**—A mixture of 0.3 g. of  $\alpha,3,5$ -tribromoacetylmesitylene, 1.5 g. of zinc dust and 5 cc. of acetic acid was heated under a return condenser on a steam cone for four hours. The reaction mixture was filtered while hot, and after cooling and adding water, washed with ether. The solid which remained after evaporation of the ether was crystallized from alcohol, and found to melt at 146.5–147.5°. It was shown to be 3,5-dibromoacetylmesitylene<sup>7</sup> by the mixed melting point method.

**$\alpha,\alpha,3,5$ -Pentabromoacetylmesitylene (I).**—A solution of 0.2 g. of  $\alpha,3,5$ -tribromoacetylmesitylene in 5 cc. of pyridine was added to sodium hypobromite solution (2 cc. of bromine, 6 g. of sodium hydroxide and 55 cc. of water), and the resulting mixture was agitated forty-eight hours. The solid was collected, washed with water and crystallized from alcohol. The melting point, 111.5–113°, was not depressed when mixed with pentabromoacetylmesitylene.<sup>7</sup>

**$\alpha,\alpha,3,5$ -Tetrabromoacetylmesitylene (IV).** (a) **By Action of Grignard Reagent.**—An ether solution (5.6 g. of ketone in 75 cc. of ether) of pentabromoacetylmesitylene was added from a dropping funnel with stirring during eight minutes to ethylmagnesium bromide prepared from 1.21 g. of magnesium, 7.4 g. of ethyl bromide and 60 cc. of ether. During the eight-minute period of addition a gray, finely divided precipitate appeared, and the reaction mixture refluxed gently. After being stirred for one-half hour longer the reaction mixture was shaken with dilute hydrochloric acid and ether. Evaporation of the ether layer left needle-like crystals which melted at 142–143.5° after several crystallizations from alcohol.

(b) **By Action of Hydrazine.**—The reaction was carried out in a modification of the usual Zerewitinoff machine.<sup>14</sup> Pentabromoacetylmesitylene (0.525 g., pulverized) and 10 cc. of alcohol were placed in the reaction flask and treated with 5 cc. of an alcohol solution of hydrazine hydrate (0.0373 g. of hydrazine hydrate per cc. of solution). After 56.5 hours (no increase in quantity of nitrogen occurred during the last thirty hours) the amount of nitrogen liberated was 6.55 cc. (corr.). Based on the equation<sup>2a</sup> which has been written for the hydrazine reaction, the replacement of one atom of bromine should cause the liberation of 10.6 cc. of nitrogen. The product was isolated by adding a large amount of alcohol, and crystallizing from alcohol the precipitate thus formed. The melting point was 142.5–143.5°.

(c) **By Action of Phenol.**—Pentabromoacetylmesitylene (1.12 g., 0.002 mole) and 0.19 g. (0.002 mole) of phenol were heated on a steam cone for 3.5 hours. After cooling the reaction mixture was triturated with 10% sodium hydroxide solution, filtered and washed with water. Crystallization from alcohol yielded colorless needles melting at 142–143°.

When the same quantities of pentabromo ketone and phenol were heated for two hours on a steam cone the product obtained was the substance<sup>7</sup> (m. p. 108–109°) previously described, composed of penta- and tetra-bromoacetylmesitylene. Phenol (0.19 g.) reacted with 1.12 g. of this substance (m. p. 108–109°), when heated for three and one-half hours on a steam cone, to give tetrabromoacetylmesitylene, m. p. 142–143°.

(14) The author wishes to acknowledge his indebtedness to Mr. Max Tishler, who supplied this apparatus.

(d) **By Action of Acetophenone.**—A mixture of 0.56 g. of pentabromoacetylmesitylene and 0.2 g. of acetophenone was heated for six hours on a steam cone. The product solidified on standing several hours; the resulting solid was crystallized several times from alcohol, and was found to be  $\alpha,\alpha,3,5$ -tetrabromoacetylmesitylene, melting at 142–143.5°. A lachrymator, probably  $\alpha$ -bromoacetophenone, was also formed in the reaction.

**The Action of Acetone on Pentabromoacetylmesitylene (I).**—The starting material was recovered unchanged after an acetone solution (0.56 g. of ketone in 5 cc. of acetone) of pentabromoacetylmesitylene had been refluxed for one hour. To isolate the product, the reaction mixture was poured into water, and the product which precipitated was crystallized (m. p. 113–114°) from alcohol.

**The Action of Alkali on Pentabromoacetylmesitylene (I).**—The pentabromo ketone (0.56 g., pulverized) and 50 cc. of a 10% potassium hydroxide solution were shaken for twenty-four hours. The solid was collected by filtration, washed with water and dried. The amount thus obtained was 0.55 g.; the m. p. was 113–114°. A mixed melting point determination indicated that this substance was unchanged starting material.

The action of potassium hydroxide at higher temperatures on 1–5 g. portions of pentabromoacetylmesitylene caused the formation of alkali-soluble products from which no pure substance was obtained.

**$\alpha,\alpha$ -Dibromoacetylmesitylene.**<sup>8</sup>—A solution of bromine (16 g., 0.1 mole) in acetic acid (20 cc.) was added with mechanical stirring during one-half hour to 8.1 g. (0.05 mole) of acetomesitylene in 40 cc. of acetic acid, which was contained in a three-necked flask equipped with a return condenser, and surrounded by a boiling water-bath. After stirring and heating had been continued for another one-half hour, the reaction mixture was allowed to cool. Scratching caused crystals to appear; the amount of solid was increased by adding water. After several crystallizations from alcohol this solid was obtained as crystals melting at 73–74°; the amount was 6.7 g.

To establish the identity of this product it was converted into  $\alpha,\alpha,\alpha$ -tribromoacetylmesitylene by the action of sodium hypobromite according to previously-reported directions.<sup>6</sup> The melting point (68.5–69.5°) of the tribromo ketone thus prepared was not depressed when mixed with  $\alpha$ -tribromoacetylmesitylene prepared by the method of Fuson and Walker.<sup>15</sup>

***p*-Chloromandelic Acid.**—After being pulverized in an agate mortar, 2.50 g. (0.008 mole) of  $\alpha,\alpha$ -dibromo-4-chloroacetophenone<sup>16</sup> was added to 50 cc. of 10% aqueous potassium hydroxide, and the resulting mixture was mechanically shaken for one-half hour. The undissolved solid was collected, washed with water and dried. This solid (0.1 g. melting at 93.5–94.5°) was starting material.

The filtrate was boiled a few minutes, acidified with hydrochloric acid, and extracted three times with ether. Evaporation of the ether left 1.3 g. of a solid melting at 119–120.5°. After crystallization from ligroin–benzene the m. p. was 119.5–120.5°. The m. p. of *p*-chloromandelic acid<sup>17</sup> has been given as 120.5–121°.

**The Action of Alkali on  $\alpha,\alpha$ -Dibromoacetylmesitylene (VI).**—The same conditions used in the case of  $\alpha,\alpha$ -dibromo-4-chloroacetophenone were employed in this experiment. Pulverized  $\alpha,\alpha$ -dibromoacetylmesitylene (2.56 g., 0.008 mole) was agitated with 50 cc. of a 10% potassium hydroxide solution for eighteen hours; 2.25 g. of starting material remained undissolved.

This experiment was repeated, using identical conditions and quantities of reagents. After 194 hours of agitation there remained undissolved 1.80 g. of starting material

(15) Fuson and Walker, *THIS JOURNAL*, **52**, 3269 (1930).

(16) Fisher, *ibid.*, **55**, 4594 (1933).

(17) Jenkins, *ibid.*, **53**, 2341 (1931).

(mixed melting point). The filtrate was boiled for a few minutes, acidified with hydrochloric acid (a precipitate appeared) and extracted with ether. Evaporation of the ether left a brown oil which changed into a viscous semi-solid on standing. This substance was not identified.

### Summary

The behavior of a tribromomethyl aryl ketone toward potassium iodide, ethylmagnesium bromide, hydrazine hydrate, phenol, acetone, acetophenone and alkali has been studied. All these reagents except alkali cause partial dehalogenation of the tribromomethyl ketone.

A preliminary study of the action of alkali on dibromomethyl aryl ketones is described which indicates that the conversion of these dibromo ketones into substituted mandelic acids may be retarded by steric hindrance.

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## Triphenylsilicly Ethylamine ( $C_6H_5$ )<sub>3</sub>Si·C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>

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### I. Introduction

The elements of the fourth group form compounds of the type (R<sub>3</sub>A)<sub>2</sub> where R is commonly an organic radical or, less frequently, hydrogen. The bond A-A has a varying stability depending on the nature of the central element and of the substituents R. In some instances, the compounds dissociate into the free groups R<sub>3</sub>A in solution, while in others the dimers are relatively stable. Stability usually increases with decreasing atomic number. These groups are amphoteric, forming compounds R<sub>3</sub>AX with negative elements or groups and salts R<sub>3</sub>AM with electropositive elements such as the alkali metals. Various of the free groups and their reduction products have been investigated in this Laboratory, particularly those of tin, germanium, and carbon.<sup>2</sup> The free groups are ordinarily formed by reducing the halogen derivatives with the alkali metals in liquid ammonia and the salts are formed by further reduction of the resulting free groups. In the case of silicon, it has not been possible, heretofore, to obtain either the free groups (or their dimers (R<sub>3</sub>Si)<sub>2</sub>) or the alkali metal salts MSiR<sub>3</sub> by reduction of the halogen derivatives R<sub>3</sub>SiX in liquid ammonia. The reason for this is that the tertiary organic halogen derivatives are ammonolyzed in liquid ammonia.

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(2) Kraus and Kawamura, *THIS JOURNAL*, **45**, 2756 (1923); Kraus and Sessions, *ibid.*, **47**, 2361 (1925); Kraus and Foster, *ibid.*, **49**, 457 (1927). For the conductivity of these compounds see Kraus and Callis, *ibid.*, **45**, 2624 (1923); Kraus and Johnson, *ibid.*, **55**, 3542 (1933); Kraus and Kahler, *ibid.*, **55**, 3537 (1933).