

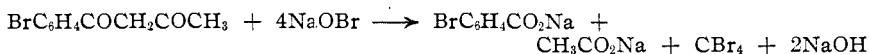
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

## The Cleavage of Carbonyl Compounds by Alkalies. XI. The Action of Hypobromite Solutions on Beta-Diketones

BY C. F. WOODWARD AND REYNOLD C. FUSON

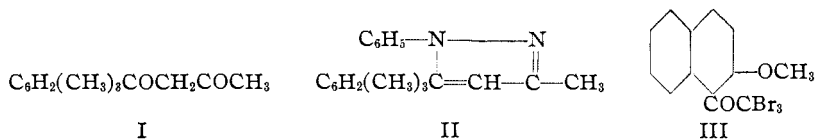
In view of the fact that certain compounds containing active methylene groups are rapidly halogenated by alkali hypohalites,<sup>1</sup> it became a matter of interest to determine what course the reaction would take in the case of  $\beta$ -diketones of the type  $\text{RCOCH}_2\text{COCH}_3$  which contain both an active methylene group and an active methyl group. It was to be expected that if R is an aryl group carrying suitable ortho substituents, the chain scission at the adjacent carbonyl group would be arrested and this might permit the isolation of an intermediate which would offer a clue to the mechanism. That this expectation has been realized will appear from the experiments described in this paper.

Exploratory work with *p*-bromobenzoylacetone showed that in the presence of an excess of sodium hypobromite solution the products are sodium *p*-bromobenzoate, sodium acetate and carbon tetrabromide. The reaction evidently proceeds according to the equation



It might be expected that since this is a methyl ketone the methyl group would be eliminated as bromoform which would then be converted into carbon tetrabromide. The alternative possibility is that bromination might take place at the methylene group, producing a dibromo diketone which would then be cleaved into an acid and a dibromomethyl ketone. Finally, the latter would undergo the normal haloform reaction.

As indicated above it was possible to test these suggestions by the use of steric hindrance in such a way as to permit the isolation of intermediate products. The case of  $\beta$ -isoduryloylacetone will serve to illustrate the plan. The synthesis of this diketone (I) was effected by condensing acetomesitylene with ethyl acetate. The structure of the compound was



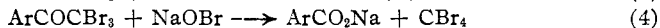
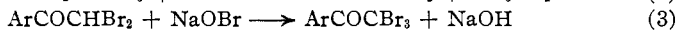
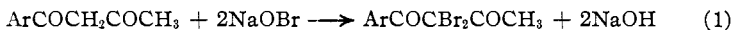
checked by the preparation of the phenylhydrazone and the pyrazole (II). Treatment of this diketone with hypobromite gave neither bromoform nor carbon tetrabromide. Instead, the compound was converted into sodium acetate and  $\alpha, \alpha, \alpha$ -tribromoacetomesitylene according to the equation

$$\text{C}_6\text{H}_2(\text{CH}_3)_3\text{COCH}_2\text{COCH}_3 + 3\text{NaOBr} = \text{C}_6\text{H}_2(\text{CH}_3)_3\text{COBr}_3 + \text{CH}_3\text{CO}_2\text{Na} + 2\text{NaOH}$$
(1) Fuson and Beveridge, *THIS JOURNAL*, **53**, 1985 (1931).

The tribromo ketone was identified by comparison with an authentic specimen and the sodium acetate was isolated in the form of *p*-bromophenacyl acetate.

Very similar results were obtained with  $\beta$ -methoxy- $\alpha$ -naphthoylacetone; in this case the principal product was the 1-tribromoacetyl-2-methoxynaphthalene (III) previously reported.<sup>2</sup>

From the foregoing results it is clear that the first step in the reaction is the replacement of the two hydrogen atoms of the methylene group by bromine atoms. Then follows cleavage of the dibromo diketone. In the case of the hindered diketones this takes place according to equation 2.



In the mesitylene series the resulting dibromo compound is known to react with hypobromite to form the corresponding tribromo compound according to equation 3.<sup>3</sup>

In view of the fact that the aroylacetones themselves undergo cleavage with alkali to give acetic acid and aryl methyl ketones rather than aromatic acids and acetone,<sup>4</sup> it seems certain that, with the exception of those which contain ortho substituents, the reaction with hypobromite proceeds according to the scheme represented by equations 1, 2, 3 and 4.<sup>5</sup> The reaction represented by equation 4 undoubtedly involves the intermediate formation of bromoform. The latter is converted quantitatively into carbon tetrabromide in the presence of an excess of hypobromite.<sup>6</sup>

An example of a  $\beta$ -diketone in which both carbonyl groups are hindered was reported in an earlier paper.<sup>3</sup> It was found that di- $\beta$ -isoduryloylmethane reacted with hypohalite solutions to yield the corresponding dihalogen derivatives in which the two hydrogen atoms of the methylene group were replaced by halogen atoms. This represents a case in which the action of the hypohalite is arrested at the second step. Thus, by progressive introduction of hindrance we have been able to interrupt the overall reaction at two different stages. For, whereas the unhindered diketone, *p*-bromobenzoylacetone, undergoes halogenation and two successive chain fissions, the  $\beta$ -isoduryloylacetone is cleaved in only one place while the di- $\beta$ -isoduryloylmethane is only halogenated, and resists cleavage altogether.

### Experimental

#### The Reaction of *p*-Bromobenzoylacetone with Sodium Hypobromite.—Nine

(2) Fuson, Farlow and Stehman, *THIS JOURNAL*, **53**, 4097 (1931).

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

(4) Fischer and Bülow, *Ber.*, **18**, 2132 (1885). For a recent reference see Kutz and Adkins, *THIS JOURNAL*, **52**, 4036 (1930).

(5) A similar result has been reported by Hurd and Thomas [*THIS JOURNAL*, **55**, 1646 (1933)] who obtained dichloroacetic acid by treating ethyl acetoacetate with bleaching powder.

(6) Dehn, *ibid.*, **31**, 1220 (1909).

grams of *p*-bromobenzoylacetone prepared by the method of Auwers and Heimke,<sup>7</sup> was dissolved in 500 cc. of cold 10% sodium hydroxide solution. A solution of 11.2 cc. of bromine in 175 cc. of cold 10% sodium hydroxide was added; a cloudy solution resulted. An oil which separated within three minutes was slowly converted to a solid over a period of six hours. The yield of crude solid material was 8 g. Recrystallization from ethyl alcohol yielded a colorless solid melting at 92–93° which was shown by the method of mixed melting points to be carbon tetrabromide.

Six grams of solid material was obtained by acidification of the filtrate. This substance, after one recrystallization from ethyl alcohol, melted at 248–249.5° and was shown by the method of mixed melting points to be *p*-bromobenzoic acid.

**Acetylacetomesitylene.**<sup>8</sup>—A mixture of 240 g. of ethyl acetate and 240 cc. of absolute ether was allowed to drop gradually into a flask which contained 32 g. of powdered sodium. The addition was complete in half an hour and the solution turned reddish-brown. A solution of 149 g. of acetomesitylene dissolved in 160 cc. of absolute ether was then dropped into the mixture, with continuous stirring and gentle heating. The stirring and heating were continued for twelve hours after the completion of the addition. After the mixture had stood for twelve hours more it was poured into 800 cc. of cold water. The aqueous layer was separated and washed twice with 100-cc. portions of ether to recover any unchanged acetomesitylene. The water solution containing the sodium salt of the diketone was cooled in an ice-bath and 112 cc. of glacial acetic acid was added, with continuous stirring. The yellow oil which separated was extracted with ether and the ether extract was dried over calcium chloride. The residue which remained after removal of the ether on the water-bath was distilled under diminished pressure. The yield of the diketone, boiling at 143–146° at 8 mm., was 69.1% of the theoretical amount. Several recrystallizations from methyl alcohol yielded a colorless crystalline solid melting at 45–46°.

*Anal.* Calcd. for C<sub>13</sub>H<sub>16</sub>O<sub>2</sub>: C, 76.5; H, 7.8. Found: C, 76.6; H, 7.6.

**Phenylhydrazone and Phenylpyrazole of Acetylacetomesitylene.**—Five grams of acetylacetomesitylene was treated with 7 cc. of phenylhydrazine in 15 cc. of 10% acetic acid at room temperature. After three days standing 13 g. of crude solid material was obtained. Several recrystallizations from petroleum ether (b. p. 65–110°) yielded the pyrazole in the form of orange-colored crystals; m. p. 86–87°.

*Anal.* (Micro) Calcd. for C<sub>19</sub>H<sub>20</sub>N<sub>2</sub>: N, 10.1. Found: N, 10.1.

The mother liquor from the petroleum ether recrystallization was evaporated to dryness and the solid residue was recrystallized from methanol. The colorless crystalline phenylhydrazone melted at 128.5–129.5°.

*Anal.* (Micro) Calcd. for C<sub>19</sub>H<sub>22</sub>ON<sub>2</sub>: N, 9.5. Found: N, 9.8.

**Reaction of Acetylacetomesitylene with Sodium Hypobromite.**—Ten and twentieths grams of acetylacetomesitylene in 50 cc. of cold 10% sodium hydroxide was added to a solution of hypobromite containing 15 cc. of bromine in 480 cc. of cold 10% alkali. The solution, which immediately became cloudy, was stirred for one day at room temperature. The colorless solid which separated was filtered and dried in a vacuum desiccator. The yield of crude product was 90.2% of the theoretical amount. Several recrystallizations from methanol yielded a colorless, crystalline solid melting at 69–70°. A mixed melting point determination showed this compound to be  $\alpha,\alpha,\alpha$ -tribromo-2,4,6-trimethylacetophenone.<sup>9</sup> No bromoform or carbon tetrabromide could be isolated.

(7) Auwers and Heimke, *Ann.*, **458**, 219 (1927).

(8) This compound was first prepared by Mr. E. P. Czerwin.

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

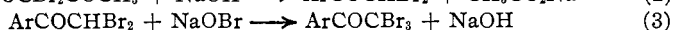
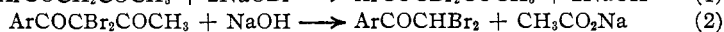
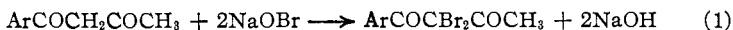
The distillate obtained by acidification and distillation of the filtrate was neutralized with 10% sodium hydroxide solution and evaporated to dryness. The sodium salt obtained was converted into the *p*-bromophenacyl ester which melted at 84.5–85°. The melting point of *p*-bromophenacylacetate recorded in the literature is 84.5–85°.

**$\beta$ -Methoxy- $\alpha$ -naphthoylacetone.**—2-Methoxy-1-acetonaphthone was converted into  $\beta$ -methoxy- $\alpha$ -naphthoylacetone by the method of Wittig and Blumenthal.<sup>10</sup> The yield of the colorless solid melting at 71–72.5° was 41.3% of the theoretical amount.

**The Reaction of  $\beta$ -Methoxy- $\alpha$ -naphthoylacetone with Sodium Hypobromite.**—Five grams of the diketone in 300 cc. of cold 10% alkali was added to a hypobromite solution containing 7.2 cc. of bromine in 150 cc. of cold 10% alkali. Eight grams of solid was obtained after twenty-four hours stirring. The compound after recrystallization from methanol melted at 136–137°, and was shown by the mixed melting point method to be 1-tribromoacetyl-2-methoxynaphthalene.<sup>2</sup> No bromoform or carbon tetrabromide was obtained.

### Summary

The action of hypobromite solutions on  $\beta$ -diketones of the type  $\text{ArCO-CH}_2\text{COCH}_3$  has been shown to take the course represented by the equations



(10) Wittig and Blumenthal, *Ber.*, **60B**, 1085 (1927).

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

## The Addition of Free Radicals to Certain Dienes, Pyrrole and Maleic Anhydride

By J. B. CONANT AND BACON F. CHOW

In a preliminary paper,<sup>1</sup> it was shown that the free radical, triphenylmethyl, combines with isoprene and 2,3-dimethylbutadiene-1,3, addition taking place in the 1 and 4 positions. We have now extended the study of this reaction to include a number of unsaturated compounds and two other free radicals, namely, phenylxanthyl and benzylxanthyl. Both of these radicals combined with isoprene, although in the case of the slightly dissociated benzyl compound,<sup>2</sup> no reaction was evident at room temperature after seven days; in both cases the best yield was obtained by heating the two compounds at 100° for twenty-four hours. Since phenylxanthyl is much less associated than triphenylmethyl and benzylxanthyl much more so, it is evident that the reaction between a butadiene and a dissociable ethane does not depend on the degree of dissociation.

Triphenylmethyl was allowed to interact with butadiene-1,3 and penta-1,3 (piperylene). The addition reaction proceeded in both cases at

(1) *THIS JOURNAL*, **53**, 1941 (1931).

(2) *Ibid.*, **47**, 572 (1925).