

being tested by the use of various shaped reaction vessels. These experiments should have some bearing on the mechanism, since the present mechanisms for the ammonia photodecomposition assume the reaction to be homogeneous and independent of pressure.

The results with the single line 2100 Å. throw some doubt on one widely quoted result of Kuhn's measurements. His yield of 0.45 was obtained using all four zinc lines at 2026, 2062, 2100 and 2138 Å. On using pure, monochromatic light of λ 2062 Å. Kuhn found a yield of only 0.10. The photolysis was carried out in a vessel which had its quartz windows held onto the walls by a cement and the reaction was followed by measuring the increase in the total pressure by means of a differential manometer. Ammonia was taken up by the cement so that Kuhn had to apply a correction for the decrease in pressure due to this absorption of ammonia. In the experiments with the single line 2062 Å. no increase in pressure was obtained but on applying the correction for the absorption of ammonia by the cement a yield of 0.10 resulted. In a footnote Kuhn called attention to the fact that this result should be checked in an all-sealed quartz vessel. In the present work a few experiments with the single line 2062 Å., Table III, gave the same yields at corresponding ammonia pressures as similar experiments with the single line 2100 Å. These same yields were also

obtained when two lines were used. Furthermore, these yields, instead of being much smaller, are all about the same as those obtained in previous investigations with all four zinc lines. These results would seem to indicate that the yield is the same whether the light absorbed contains a single line, two lines or all four zinc lines and that Kuhn's low result was in error due to the correction he had to apply. Further experiments will shortly settle this question.

In conclusion, the data reported here show a distinct effect of ammonia pressure on the quantum yield for the photodecomposition of ammonia. The reaction might still be used as an actinometer provided that the yield, especially at higher pressures where absorption is complete, is independent of the size and shape of the reaction cell.

Summary

The quantum yield for the decomposition of ammonia by light of λ 2100 Å. is found to be dependent upon the ammonia pressure, the yield rising from *ca.* 0.10 at 1–10 mm. to *ca.* 0.30 at 65–120 mm. and then falling to 0.18 at one atmosphere of ammonia. The yield appears to be independent of the "purity" of the light, contrary to earlier work; the amount of decomposition is the same whether one, or two or more of the four zinc lines of $\lambda\lambda$ 2026, 2062, 2100 and 2138 Å. is used.

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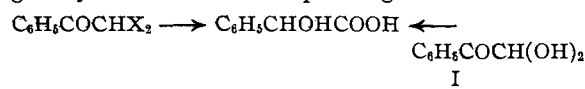
RECEIVED JUNE 18, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Reaction of Alpha-Dihaloacetophenones with Alkali

BY C. HAROLD FISHER AND CHEVES T. WALLING

In most of the cases¹ thus far studied, α -dihaloacetophenones have been found to react readily at room temperature with dilute alkali to give good yields of the corresponding mandelic acids.



Indeed, in several instances substituted mandelic acids may be prepared most expeditiously by this method.

Although no extensive study has been made, it seems that this interesting transformation has

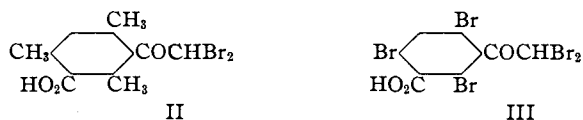
(1) Engler and Wöhrle, *Ber.*, **20**, 2201 (1887); Engler and Zielke, *ibid.*, **22**, 204 (1889); Schweitzer, *ibid.*, **24**, 547, 997 (1891); Houben and Fischer, *ibid.*, **64B**, 2636 (1931); Collet, *Bull. soc. chim.*, [3] **21**, 70 (1899).

been regarded as a benzylic acid rearrangement of the glyoxal, or its hydrate (I), which had been produced previously by a metathetical reaction between alkali and the dihalo ketone. According to this view of the reaction a dihaloacetophenone with substituents in the ortho positions should react in the same way with alkali to give the glyoxal hydrate, which then would undergo the benzylic acid rearrangement² in the normal manner. Evidence to the contrary was obtained in a preliminary examination³ which shows that α , α -dibromo-4-chloroacetophenone dissolves in dilute potas-

(2) It has been shown that steric hindrance does not prevent this rearrangement of phenylglyoxal [Gray and Fuson, *THIS JOURNAL*, **56**, 739 (1934)].

(3) Fisher, *ibid.*, **55**, 5005 (1933)

sium hydroxide solution several hundred times more rapidly than does α, α -dibromoacetylmesitylene (IV), and it was suggested that steric hindrance would retard the conversion of dihaloacetophenones into mandelic acids. It has been demonstrated⁴ since, in connection with other work, that this is true in the case of two hindered α -dihaloacetophenones (II and III).



The ketones, II and III, were recovered unchanged, and their unreactivity toward alkali is all the more striking in view of the presence of the solubilizing carboxyl groups. This evidence, as well as the results described below, indicates with certainty that, in the first step of mandelic acid formation, alkali attacks the carbonyl group of dihaloacetophenones instead of the halogen atoms.⁵

A study of the action of alkali at room temperature on α -dihaloacetophenones having ortho methyl groups has now shown that dihalo ketones thus hindered with two methyl groups dissolve slowly in alkali and reappear unchanged on acidification, a phenomenon which might escape detection in dihalo ketones possessing the usual solubilizing groups. Two of the dihalo ketones observed to have this type of acidity are α -dichloro- and α -dibromoacetylmesitylene (IV). The dichloro ketone dissolved much more rapidly than did the corresponding dibromo ketone. Whether or not the hindered dihalo ketones dissolve as enols, a phenomenon which might compete to a small degree with addition to the carbonyl group in unhindered ketones, is not now known. In this connection it should be noted that certain α -bromo ketones have been found to be acidic; however, in these cases⁶ the acidity was not ascribed to enolization.

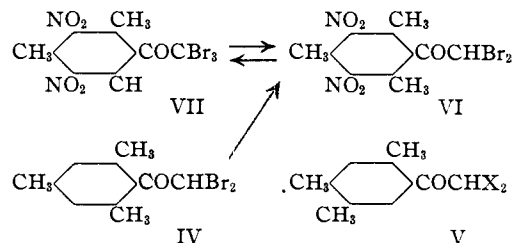
As might be expected, it was found that one methyl group in the ortho position offers only a negligible hindering effect, and the usual reaction, formation of a mandelic acid, was the only one observed. The compounds studied in this connection are α -dihalo derivatives of 2,4-dimethyl-

(4) Johnson and Fuson, *THIS JOURNAL*, **56**, 1418 (1934); Bull. Ross and Fuson, *ibid.*, **57**, 765 (1935).

(5) It has been suggested that alkali adds to the carbonyl group of certain aliphatic α, α -dihalo ketones, and that subsequently an ethylene oxide ring is formed which rearranges to give various products [Faworsky, *J. prakt. Chem.*, **88**, 661 (1913)].

(6) Watson, Nathan and Laurie, *J. Chem. Phys.*, **3**, 170 (1935).

and 2,4,5-trimethylacetophenone. The derivatives (V) of the latter ketone are especially interesting because any difference of behavior toward alkali, as compared with derivatives of acetomesitylene, may be ascribed almost entirely to the location of the third methyl group in the ortho or meta position. The two appropriate polymethyl mandelic acids were obtained conveniently by this method, and both forms of 2,4-dimethylmandelic acid previously reported were isolated.



Effect of Meta Nitro Groups.—The introduction of a nitro group into the meta position of benzoylcamphor⁷ appeared to enhance its acidity, and a similar influence seems to be exerted by the presence of two nitro groups in the meta positions of α, α -dibromoacetylmesitylene. This is indicated by the readiness with which α, α -dibromo-3,5-dinitroacetylmesitylene (VI) dissolves in aqueous alkali, and the fact that this dinitro derivative (VI) may be titrated with alkali.

The two meta nitro groups exert a marked influence also on the tribromo ketone (VII). When treated with alkali at room temperature this tribromo derivative (VII) dissolved with evolution of heat, and the dibromo compound (VI) was precipitated on acidification. The preparation of VI was achieved also, and in excellent yield, by the nitration of α, α -dibromoacetylmesitylene (IV). By treatment with hypobromite VI was converted into the tribromo compound (VII).

Experimental

α, α -Dichloro- and α, α -Dibromoacetylmesitylene.—The ketones were pulverized in an agate mortar, and agitated with 10% potassium hydroxide (50 cc. for 0.008 mole of ketone). The mixture was filtered, and acidification of the filtrate caused the original dihalo ketone to appear. About 45% of the dichloro ketone⁸ (m. p. 72–73°) dissolved during one-half hour of agitation.

Anal. Calcd. for $C_{11}H_{12}OCl_2$: C, 57.14; H, 5.24. Found: C, 57.38; H, 5.44.

The dibromo ketone^{3,8} (m. p. 73–74°) dissolved much more slowly (about 15% during 100 hours).

(7) Forster and Micklethwait, *J. Chem. Soc.*, **81**, 406 (1902).

(8) Fisher, Snyder and Fuson, *THIS JOURNAL*, **54**, 3665 (1932).

Dihalo Derivatives of 2,4-Dimethylacetophenone.—

(a) Bromine (6.5 g.) in 25 cc. of acetic acid was added gradually and, with agitation to a warm solution of 7.3 g. of α -chloro-2,4-dimethylacetophenone in 25 cc. of acetic acid. The solution was then warmed for a few minutes on a steam cone and added to water. The oil which separated was washed with water, and shaken with 150 cc. of 10% potassium hydroxide solution for three hours (no oil was visible after one hour). After acidification there was obtained 6.4 g. of acid melting at 99–101°. Numerous crystallizations from different solvents did not raise the melting point of this substance, *2,4-dimethylmandelic acid*, at first above 101–103°. Later, however, the melting point changed abruptly to 118.5–119.5°, and was not raised by further crystallization. From this it would seem that the lower melting polymorph was described by Söderbaum⁹ (who gave 103° as the melting point after crystallization from toluene), while two other investigators¹⁰ encountered the higher melting form (in both cases¹⁰ the melting point observed after crystallization from benzene and from water was 119°).

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.6; H, 6.6. Found: C, 66.3; H, 6.4.

(b) In a similar manner 2,4-dimethylacetophenone was brominated with two moles of bromine, and then treated with alkali to get the mandelic acid. The product melted in the beginning at 101–103°, and then at 118.5–119.5° without seeding or further crystallization as soon as 2,4-dimethylmandelic acid from the preceding experiment had been obtained in the higher melting form.

Dihalo Derivatives of 2,4,5-Trimethylacetophenone.—

To obtain a pure derivative of 2,4,5-trimethylacetophenone from technical (Eastman Kodak Company) pseudocumene, advantage was taken of the fact that the α -chloro derivative is a solid melting at 76°.¹¹ As obtained in the present work this ketone (m. p. 76.5–77.5° after crystallization from ligroin and from alcohol) was accompanied by a small amount of another substance (m. p. 55–56°, not further examined) which boiled about 20° at 6 mm. higher than did the main product. Chloroacetyl pseudocumene¹¹ and acetyl pseudocumene (the latter ketone was prepared from technical pseudocumene and hence was impure) were brominated and then treated with 10% potassium hydroxide, using essentially the procedures described above for α -chloro-2,4-dimethylacetophenone and for 2,4-dimethylacetophenone, respectively. The product, *2,4,5-trimethylmandelic acid*, melted at 137.5–138.5° (previously reported^{10a} to melt at 138°) after crystallization from benzene.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.04; H, 7.27. Found: C, 68.39; H, 7.53.

2,4,5-Trimethylbenzoic Acid.—Oxidation of the acetyl pseudocumene and 2,4,5-trimethylmandelic acid, mentioned above, with hypobromite and potassium permanganate, respectively, gave the same acid melting at 149–150°. The melting point previously given for 2,4,5-trimethylbenzoic acid¹² is 148–149°.

(9) Söderbaum, *Ber.*, **25**, 3464 (1892).

(10) (a) Gattermann, *Ann.*, **347**, 373 (1906); (b) Claus, *J. prakt. Chem.*, [2] **41**, 486 (1890).

(11) Kunckell, *Ber.*, **30**, 1713 (1897).

(12) Mills, *J. Chem. Soc.*, **101**, 2192 (1912).

α,α -Dibromo-3,5-dinitroacetylmesitylene (VI).¹³—(a) **By Nitration.**—One gram of pulverized α,α -dibromoacetylmesitylene was added to an ice-cold mixture of 40 cc. of nitric acid (sp. gr. 1.5) and 10 cc. of concd. sulfuric acid. The mixture was then allowed to stand for a quarter-hour out of the ice bath, and poured into cold water. The product, obtained in almost quantitative yield, was crystallized from alcohol; the melting point was 168–169.5°.

(b) **By Dehalogenation of α,α,α -Tribromo-3,5-dinitroacetylmesitylene (VII) with Alkali.**—A mixture of 4.3 g. of the tribromo ketone¹⁴ and an alkaline solution (5 g. of sodium hydroxide, 10 cc. of water and 20 cc. of methanol) was allowed to stand for three hours with occasional shaking. During this time the ketone dissolved and the solution became brown and warm. After addition of water and extraction with ether the aqueous solution was acidified. The product thus precipitated, after crystallization from alcohol, was found to melt at 167.5–170°. A mixed melting point with the nitration product of α,α -dibromoacetylmesitylene was not lowered. In contrast with α,α -dichloro- and dibromoacetylmesitylene, this dinitro compound (VI), if well pulverized, dissolves almost instantly in dilute potassium hydroxide. However, it is not soluble in sodium bicarbonate or sodium carbonate, and it does not give a ferric chloride test.

Anal. Calcd. for $C_{11}H_{10}O_6Br_2N_2$: Br, 39.0. Found: Br, 39.2.

Using alcohol (100 cc.) as solvent and phenolphthalein as indicator, about 0.4-g. samples of the dibromo compound (VI) were titrated with approximately 0.1 *N* sodium hydroxide. It was difficult to determine the endpoint because of an amber color which developed during the addition of alkali. In three determinations the values 389, 352 and 387 were obtained (calculated, 410).

To transform the dibromo dinitro compound (VI) into the tribromo dinitro ketone (VII) an alkaline solution of VI was added to sodium hypobromite. The tribromo ketone (VII), which precipitated at once, was crystallized from alcohol and identified by a mixed melting point.

Summary

It has been demonstrated further that the usual reaction, which leads to the appropriate mandelic acid, between α,α -dihaloacetophenones and alkali does not occur if two ortho substituents are present. One ortho substituent offers negligible hindrance and the substituted mandelic acid is formed.

Alpha dihaloacetophenones with two ortho methyl groups are acidic, dissolving in alkali and reappearing unchanged on acidification. This acidity appears to be augmented by the presence of nitro groups in the meta positions.

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RECEIVED JUNE 24, 1935

(13) Most of the work on the derivatives of 3,5-dinitroacetylmesitylene has been described in a thesis of one of the authors (C. H. F., University of Illinois, 1932). We are very grateful to Professor Reynold C. Fuson for his kind permission to use this material.

(14) Fuson and Walker, *This Journal*, **52**, 3273 (1930).