ing agents. Alcohol–ether or acetone–ether mixtures are the best solvents for crystallizing the salts, as they are sparingly soluble in ether.

No.	Hydrochloride	Appearance	FeCl₃	Ammon. AgNO₃	Excess NaOH
1	2-Hydroxy	Thin, pearly plates	Dull violet	No redn.	Colorless, stable
2	3-Hydroxy	Glittering plates	Pale violet	No redn.	Colorless, stable
3	2,3-Dihydroxy	Stars of prisms	Dull green	Reduced in cold	Rapidly blackens
4	2,5-Dihydroxy	Felted tiny plates	Transient pale green	Reduced in cold	Rapidly blackens

No.	Hydrochloride	M. p., °C.	Formula	Calcd. C	Calcd. H	Found C	Found H
1	2-Hydroxy	148	$C_9H_{14}ONCl$	57.63	7.53	57.98	7.49
2	3-Hydroxy	89	$C_9H_{14}ONCl$	57.63	7.53	57.43	7.60
3	2,3-Dihydroxy	149	$C_9H_{14}O_2NCl$	53.05	6.93	53.30	6.72
4	2,5-Dihydroxy	128	$C_9H_{14}O_2NCl$	53.05	6.93	53.23	7.01

The analyses given in this paper are all micro-analyses (Pregl). The author is indebted to Mr. W. S. Ide for these.

Summary

The paper describes the synthesis of four of the seven previously unknown hydroxy- and dihydroxyphenylethylmethylamines. The synthesis of one of the remaining three broke down at the last stage. It has not been possible to obtain starting material to attempt the syntheses of the other two.

TUCKAHOE, NEW YORK

THE HALOFORM REACTION. VI. ALPHA-HALOGEN DERIVATIVES OF HINDERED KETONES

BY C. HAROLD FISHER, HAROLD R. SNYDER AND REYNOLD C. FUSON

The study of the halogenation phase of the haloform reaction has now been extended to types other than methyl ketones, and it has been found that the replacement of α-hydrogen by halogen is a fairly general reaction between hindered ketones and hypohalite solutions. This investigation has also included a study of certain unusual reactions which are apparently general for this type of compound. These reactions are (1) cleavage by alkali, (2) the dehalogenation by phenol and (3) dehalogenation by the Grignard reagent. These several phases of the work will be discussed under separate headings.

The Halogenation.—From the previous work[1] in this series it appears that the hindered methyl ketones are generally converted directly into the corresponding trihalomethyl compounds. In no case has the mono- or the di-halomethyl derivative been isolated as an intermediate.

[1] (a) Fuson and Walker, THIS JOURNAL, 52, 3269 (1930); (b) Gray, Walker and Fuson, ibid., 53, 3494 (1931); (c) Fuson, Farlow and Stehman, ibid., 53, 4097 (1931); (d) Fuson, Lewis and Du Puis, ibid., 54, 1114 (1932).

On the other hand, α-bromoacetylmesitylene, α-chloroacetylmesitylene and di-(α-chloroacetyl)-mesitylene have been converted into the corresponding trihalomethyl ketone. It remained to try the dihalomethyl ketones to see if they likewise would yield the fully halogenated derivatives.
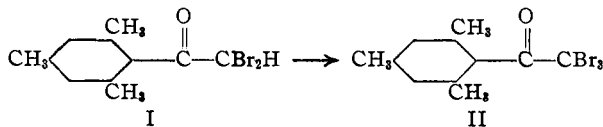

When α,α-dibromoacetylmesitylene (I) was treated with a solution of sodium hypobromite it was, in fact, converted into the corresponding tribromo derivative, tribromoacetylmesitylene (II).

The halogenation of propionylmesitylene (III) was next studied.
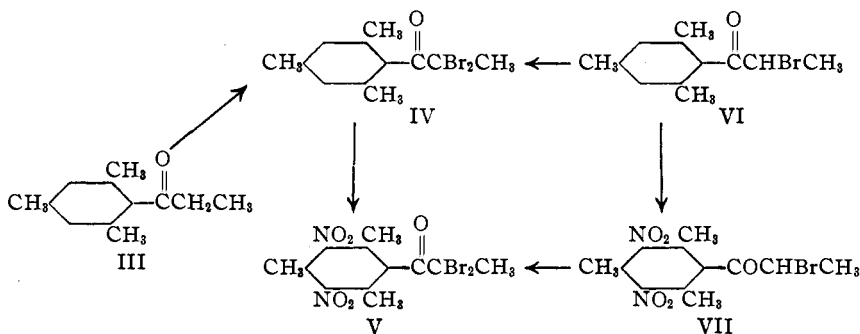
The product in this case was α,α-dibromopropionylmesitylene (IV) isolated in the form of its dinitro derivative, α,α-dibromo-3,5-dinitropropionylmesitylene (V). As might be expected from the foregoing work, α-bromopropionylmesitylene (VI) when treated with a solution of sodium hypobromite gave α,α-dibromopropionylmesitylene, which was also identified by means of the dinitro derivative (V). Also α-bromo-3,5-dinitropropionylmesitylene (VII) was converted directly into α,α-dibromo-3,5-dinitropropionylmesitylene (V) by treatment with a hypobromite solution.
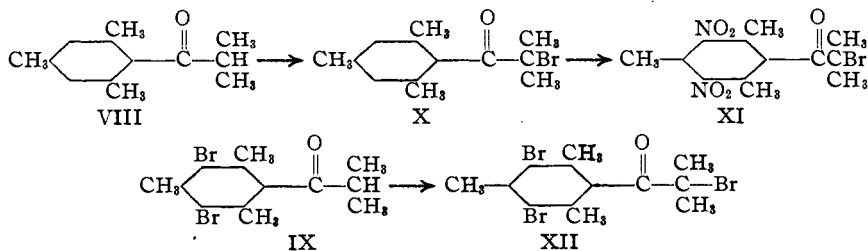
In a similar fashion isobutyrylmesitylene (VIII) and 3,5-dibromoisobutyrylmesitylene (IX) gave α-bromoisobutyrylmesitylene (X) (which was identified by its solid dinitro derivative (XI)) and α,3,5-tribromoiso-

butyrylmesitylene (XII), respectively. The α-bromo-3,5-dinitroisobutyryl-mesitylene (XI) was also prepared by direct bromination of the corresponding dinitro compound.[2] When a very pure sample of the dinitro compound was treated with a solution of sodium hypobromite, the bromo derivative obtained melted at 125–126°. The melting point (117.8–118.5°) reported earlier for this compound is, therefore, to be corrected.[3]

Of unusual interest is the case of the 1,3-diketones. In this work di-(β-isoduryloyl)-methane (XIII) was used. Although direct halogenation by use of chlorine and bromine gave only the corresponding monohalogen derivatives, (XIV) and (XV), the original diketone was converted into the dihalogen derivatives (XVI) and (XVII) by the action of solutions of alkali hypohalites.
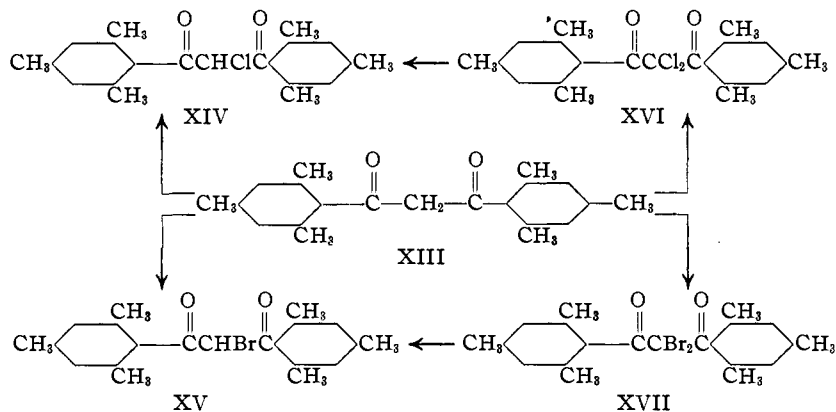
The Action of Alkali.—The cleavage of trichloroacetylmesitylene by hot, concentrated solutions of alkali has been carried out by Houben and Fischer.[4] Tribromoacetylmesitylene was found to undergo cleavage only with great difficulty and in small yields. When di-(β-isoduryloyl)-di-chloromethane (XVI) and di-(β-isoduryloyl)-dibromomethane (XVII) were treated with strong solutions of alkali, they did not undergo cleavage but dehalogenation, giving the corresponding monohalogen derivatives (XIV) and (XV).

Dehalogenation by the Action of Phenol.—The dehalogenating action of phenol on certain α-halo ketones has been reported by Löwenbein and Schuster,[5] and by Koelsch.[6] A similar study was made of the halogenating action of two of the polyhalogen ketones which have been obtained in this

[2] Maxwell and Adams, THIS JOURNAL, **52,** 2959 (1930).

[3] Fisher, Oakwood and Fuson, *ibid.,* **52,** 5039 (1930).

[4] Houben and Fischer, *Ber.,* **63B,** 2459 (1930).

[5] Löwenbein and Schuster, *Ann.,* **481,** 106 (1930); also Schuster, *Ber.,* **63,** 2397 (1930).

[6] Koelsch, THIS JOURNAL, **53,** 1147 (1931).

investigation. It was found that tribromoacetylmesitylene reacted with phenol to give dibromoacetylmesitylene and p-bromophenol: C_9H_{11}-$COCBr_3 + C_6H_5OH \longrightarrow C_9H_{11}COCHBr_2 + p\text{-}BrC_6H_4OH$. In a similar manner di-(β-isoduryloyl)-dibromomethane reacted with phenol to yield the corresponding monobromo diketone.

Dehalogenation by the Action of the Grignard Reagent.—The reaction of the Grignard reagent on α-halo ketones, which has been studied by Kohler and others,[7] also represents a process apparently peculiar to halogen derivatives of this type. The trihalomethyl ketones are transformed into the corresponding dihalomethyl compounds under the influence of this reagent. Tribromoacetylmesitylene and trichloroacetylmesitylene were converted in this way into dibromoacetylmesitylene and dichloroacetylmesitylene, respectively.

In a similar manner, di-(β-isoduryloyl)-dichloromethane and di-(β-isoduryloyl)-dibromomethane were converted, respectively, into di-(β-isoduryloyl)-chloromethane and di-(β-isoduryloyl)-bromomethane.

The Grignard reagent caused dehalogenation also in the case of α,α-dibromoacetylmesitylene; α-bromoacetylmesitylene was the product formed in the reaction.

The action of the Grignard reagent on α-chloroacetylmesitylene was tried but the original compound was recovered unchanged. On the other hand, α-bromoacetylmesitylene was converted into acetomesitylene by this treatment. The acetomesitylene was identified by converting it into its dinitro derivative, a solid melting at 138–139°.

The case most carefully studied was that of $\alpha,3,5$-tribromoisobutyrylmesitylene. This ketone was treated with n-butylmagnesium bromide, n-amylmagnesium chloride, phenylmagnesium bromide and p-tolylmagnesium bromide. In all cases the products were 3,5-dibromoisobutyrylmesitylene and the alkyl or aryl bromide corresponding to the Grignard reagent used. The equation is
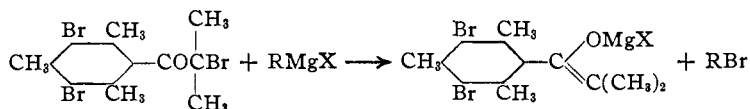
Analyses of the Grignard solutions used showed alkyl or aryl bromides to be absent, thus indicating that the bromide obtained in each case was a product of the reaction.[8]

[7] Malmgren, *Ber.*, **36**, 2626 (1903); Kohler and Johnstin, *Am. Chem. J.*, **33**, 39 (1905); Kohler, Richtmyer and Hester, THIS JOURNAL, **53**, 207 (1931); Kohler and Erickson, *ibid.*, **53**, 2301 (1931); see also Umnova, *J. Russ., Phys.-Chem. Soc.*, **45**, 881 (1913); Löwenbein and Schuster, *Ann.*, **481**, 106 (1930); and Fisher, Oakwood and Fuson, THIS JOURNAL, **52**, 5036 (1930).

[8] Since this work was finished a similar result has been reported by Kohler and Tishler [THIS JOURNAL, **54**, 1594 (1932)].

Experimental

α,α,α-Tribromoacetylmesitylene (II).—The method of Fuson and Walker[1a] was used to convert the dibromomethyl to the tribromomethyl ketone. One gram of α,α-dibromoacetylmesitylene was mechanically shaken with a dilute solution of sodium hypobromite (15 g. of bromine and 15 g. of sodium hydroxide in 150 cc. of water) for fifty-two hours. The product was filtered, dissolved in hot alcohol, and the insoluble material was separated by filtration. The crystals obtained when the solution was cooled were recrystallized from alcohol. The product (amounting to 0.8 g.) melted at 66–68° and was shown to be the known tribromomethyl ketone by the fact that a mixture of the two showed no lowering of the melting point. A mixture of the product and the starting material melted at 50–60°.

α-Bromopropionylmesitylene (VI).[9]—To 85 g. (0.5 mole) of α-bromopropionyl chloride, 60 g. (0.5 mole) of mesitylene, and 340 g. of carbon disulfide contained in a three-necked flask equipped with a reflux condenser and an air-propelled stirrer, and surrounded by an ice–salt mixture, was added 80 g. of aluminum chloride in 10-g. portions at intervals of ten minutes. The stirring was continued for one and one-half hours and the carbon disulfide was then distilled. After the addition of ice and hydrochloric acid, the product was extracted with ether, the ether washed with sodium hydroxide solution, then with water and dried over magnesium sulfate. After removal of the ether the residue was distilled. The fraction which distilled at 169–178° at 31 mm. was redistilled, 70 g. (55.5% of the theoretical) being obtained at 174–176° under the same pressure.

Anal. Calcd. for $C_{12}H_{15}OBr$: Br, 31.4. Found: Br, 31.6.

α-Bromo-3,5-dinitropropionylmesitylene (VII).—A mixture of 20 g. each of concentrated sulfuric acid and nitric acid was added to 5 g. of α-bromopropionylmesitylene. The mixture was kept cold and allowed to stand for fifteen minutes, during which time a solid formed. Water was added, the product filtered, washed with water and dissolved in 100 cc. of hot alcohol. When the solution was allowed to cool, cotton-like needles were formed which, after several recrystallizations from alcohol, melted at 148.5–149°.

Anal. Calcd. for $C_{12}H_{13}O_5N_2Br$: N, 8.1. Found: N, 8.1.

α,α-Dibromo-3,5-dinitropropionylmesitylene (V).—Three grams of propionylmesitylene was brominated with a solution of sodium hypobromite consisting of 300 g. of water, 30 g. of sodium hydroxide and 30 g. of bromine. The viscous oil remaining at the bottom of the flask was extracted with ether. The oil remaining after the removal of the ether was poured slowly into ice-cold, fuming nitric acid, and the nitric acid mixture was then poured into cold water. The solid product was filtered and recrystallized from alcohol. The melting point was 99–99.5°.

Anal. Calcd. for $C_{12}H_{12}O_5N_2Br_2$: N, 6.6. Found: N, 6.6.

α,α-Dibromo-3,5-dinitropropionylmesitylene (V).—(Second Method). Three grams of α-bromopropionylmesitylene was stirred for three days with a solution (300 g. of water, 30 g. of sodium hydroxide and 30 g. of bromine) of sodium hypobromite. The dense, viscous oil which formed was extracted with ether, and the ether solution was dried over magnesium sulfate. The oil remaining after removal of the ether was nitrated with a solution of equal parts of concentrated nitric and sulfuric acids. The solid which precipitated when the nitration mixture was added to water was filtered, washed with water and recrystallized several times from alcohol. The needle-like crystalline material melted at 98–99.5° and was shown by the mixed melting point method to be α,α-dibromo-3,5-dinitropropionylmesitylene.

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[9] The preparation and nitration of this compound were carried out by Mr. R. C. Waymire.

α,α-Dibromo-3,5-dinitropropionylmesitylene (V).—(Third Method). α-Bromo-3,5-dinitropropionylmesitylene (0.6 g.) was brominated with a sodium hypobromite solution (150 cc. of water, 15 g. of sodium hydroxide and 15 g. of bromine). After the reaction mixture had been stirred vigorously for thirty-six hours, the melting point of the crude product was 84–104°. The reaction mixture was stirred for four days. After being filtered, washed and recrystallized twice from aqueous alcohol, the product melted at 97–100°. The amount obtained was 0.4 g. After one more recrystallization the melting point was 97–98°. The mixed melting point with α,α-dibromo-3,5-dinitropropionylmesitylene was 98–99°.

α-Bromo-3,5-dinitroisobutyrylmesitylene (XI). (By Bromination with Sodium Hypobromite.)—Three grams of isobutyrylmesitylene was brominated with a solution of sodium hypobromite consisting of 300 g. of water, 30 g. of sodium hydroxide and 30 g. of bromine. The viscous oil remaining at the bottom of the flask was extracted with ether. The oil remaining after the removal of the ether was poured slowly into a mixture of equal parts of concentrated sulfuric and nitric acids. The reaction mixture was then poured into cold water. The solid which precipitated was crystallized once from alcohol. In this way was obtained 3.1 g. of crystals melting at 117–120°. The melting point, 124.5–125.5°, finally obtained after several recrystallizations, was not lowered when the product was mixed with a known sample of α-bromo-3,5-dinitroisobutyrylmesitylene, melting at 125–126°.

α-Bromo-3,5-dinitroisobutyrylmesitylene (XI). (By Bromination of 3,5-Dinitroisobutyrylmesitylene.)—A pyridine solution (1.6 g. of ketone, 20 cc. of pyridine) of the dinitro ketone was added to a hypobromite solution made from 9.5 cc. of bromine, 30 g. of sodium hydroxide and 280 cc. of water, and stirred for thirty-six hours. The solid which was in the bottom of the reaction mixture was filtered and, after several recrystallizations from alcohol, found to melt at 125–126°. The melting point was not lowered when mixed with the product obtained on nitrating the hypobromite bromination product of isobutyrylmesitylene, which melted at 124.5–125.5°.

α,3,5-Tribromoisobutyrylmesitylene (XII).—Thirty grams of bromine was added slowly and with shaking to a cold solution of 30 g. of sodium hydroxide in 250 cc. of water. To this solution was then added 3 g. of 3,5-dibromoisobutyrylmesitylene dissolved in 50 cc. of pyridine. The reaction mixture was stirred vigorously for three hours, after which a small sample of the finely divided solid was removed from the flask and found to melt, without recrystallization, at 96–103°. This indicated that most of the starting material (m. p. 70–71°) had been converted to the desired product (m. p. 106–107°). After being stirred for twenty-four hours longer, the reaction mixture was filtered, and the solid extracted with hot alcohol. The alcohol on cooling deposited 3.5 g. of colorless crystals melting at 104–106°. A mixed melting point with α,3,5-tribromoisobutyrylmesitylene showed no depression.

Di-(β-isoduryloyl)-methane (XIII).—The compound was prepared from mesitylene and malonyl chloride by the method of Béhal and Auger.[10] The yields were variable, amounting in some cases to as much as 70% of the theoretical.

Di-(β-isoduryloyl)-bromomethane (XV). (a) By the Use of Bromine.—A dilute solution of bromine was prepared by adding carbon disulfide to 10 g. of bromine until a volume of 250 cc. was reached. Five grams of di-(β-isoduryloyl)-methane was dissolved in 50 cc. of carbon disulfide and to this solution through a buret 130 cc. of the bromine solution was added slowly and with shaking. The solution remained colorless until about one-third of the bromine solution had been added, after which it developed the reddish color of bromine. After the addition was complete, the solution was warmed and stirred for four hours, the color, however, persisting. The solvent was removed

10 Béhal and Auger, *Bull. soc. chim.*, [3] 9, 702 (1893).

by distillation under reduced pressure and the residue was crystallized from alcohol. It formed colorless needles which melted at 163.5–164°.

Anal. Calcd. for $C_{21}H_{23}O_2Br$: Br, 20.6. Found: Br, 20.5.

(b) **By the Use** of Sodium Hypobromite.—Fifteen grams of bromine was dissolved in an ice-cold solution of 15 g. of sodium hydroxide in 150 cc. of water. One gram of finely ground di-(β-isoduryloyl)-methane was placed with this solution in a 250-cc. round-bottomed flask and the mixture was left on a mechanical shaker for ten days. The solid material was filtered and dissolved in alcohol. From this solution there separated on standing a few needle-like, colorless crystals which melted at 161.5–162.5° and which were shown by the mixed melting point method to be identical with the monobromo derivative obtained above.

Di-(β-isoduryloyl)-chloromethane (XIV).—Ten cc. of carbon tetrachloride in a 250-cc. Erlenmeyer flask was cooled to 0° in an ice-bath and saturated with chlorine by passing a slow stream of the gas into the liquid, the temperature being kept at 0°. Twenty cc. of carbon tetrachloride containing 7.7 g. of di-(β-isoduryloyl)-methane was then added to this solution and the flask was kept in the ice-bath for an hour longer. Hydrogen chloride was slowly evolved. The solution was allowed to stand at room temperature for an hour and was boiled for ten minutes. After the solvent was evaporated, the residue was recrystallized several times from alcohol. The monochloro compound melted at 157.5–158°; the yield was 45% of the theoretical.

Anal. Calcd. for $C_{21}H_{23}O_2Cl$: Cl, 10.4. Found: Cl, 10.7.

Di-(β-isoduryloyl)-dibromomethane (XVII).—A sodium hypobromite solution was prepared by using 112.5 g. of sodium hydroxide, 112.5 g. of bromine and 1125 cc. of water. To this solution in a 2-liter flask was added 7.5 g. of finely ground di-(β-isoduryloyl)-methane. After the mixture had been shaken for sixty hours, the solid material was filtered and recrystallized from alcohol. In this way was obtained 7.5 g. of the dibromo compound in the form of thick colorless needles melting at 136–136.5°.

Anal. Calcd. for $C_{21}H_{22}O_2Br_2$: Br, 34.3. Found: Br, 34.0.

Di-(β-isoduryloyl)-dichloromethane (XVI).—A solution of sodium hypochlorite was prepared by passing chlorine into a cold solution of 12.5 g. of sodium hydroxide in 150 cc. of water until the greenish color of free chlorine appeared. Then another 2.5 g. of sodium hydroxide was added. To this solution in a 250-cc. flask was added 2 g. of finely ground di-(β-isoduryolyl)-methane and the mixture was shaken for five days. The solid material was filtered and purified by recrystallization from alcohol. It melted at 104.104.5°; the yield was 83% of the theoretical.

Anal. Calcd. for $C_{21}H_{22}O_2Cl_2$: Cl, 18.8. Found: Cl, 18.6.

The Action of Alkali on α,α,α-**Tribromoacetylmesitylene.**—Five grams of the tribromo ketone was boiled for a few hours with a large excess of 40% aqueous sodium hydroxide. The reaction mixture was decanted from resinous material and acidified. The acid-insoluble portion yielded 0.2 g. of crystals which were shown by the method of mixed melting points to be β-isodurylic acid.

The Action of Alcoholic Sodium Hydroxide on Di-(β-isoduryloyl)-dibromomethane.—Two grams of finely powdered di-(β-isoduryloyl)-dibromomethane was added to a solution of 25 g. of sodium hydroxide in 20 cc. of water and 30 cc. of methyl alcohol. The resulting solution was heated on a steam cone overnight. Addition of dilute hydrochloric acid precipitated a solid which, after three recrystallizations from alcohol, melted at 160–162°. A mixed melting point showed it to be the monobromo derivative of di-(β-isoduryloyl)-methane. The yield was 41% of the theoretical.

The Action of Alcoholic Sodium Hydroxide on Di-(β-isoduryloyl)-dichloromethane.—Using the above procedure with 2 g. of the dichloro diketone, 1 g. of di-(β-iso-

duryloyl)-chloromethane was obtained. It was identified by a mixed melting point determination with an authentic specimen. The yield was 54% of the theoretical.

The Action of Phenol on α,α,α-Tribromoacetylmesitylene.—Ten grams of α,α,α-tribromoacetylmesitylene and 2.35 g. of phenol were heated together at 100° for three hours. The heavy brown oil which resulted was shaken with 100 cc. of 5% sodium hydroxide solution until a solid formed. This solid when recrystallized from alcohol melted at 69–71° and by means of a mixed melting point determination was identified as α,α-dibromoacetylmesitylene. The yield was 60% of the theoretical.

In a second run a 60% yield of p-bromophenol was obtained and identified by the mixed melting point method. However, in this run only a small amount of α,α-dibromoacetylmesitylene was isolated.

The Action of Phenol on Di-(β-isoduryloyl)-dibromomethane.—A mixture of 2.3 g. of the dibromo diketone and 0.5 g. of phenol was heated at 100° for three hours. Extraction with a 10% sodium hydroxide solution left an amorphous residue. This solid after recrystallization from alcohol melted at 160–162° and was identified by a mixed melting point as di-(β-isoduryloyl)-bromomethane. The yield was 47% of the theoretical.

The Action of Grignard Reagents on α-Haloalkyl Mesityl Ketones.—In each case an ether solution of the α-halo ketone was added dropwise from a separatory funnel to the Grignard reagent (1.5 moles) contained in a three-necked flask equipped with a mercury-sealed stirrer and a reflux condenser. Gentle refluxing occurred during the addition, and a colorless, finely-divided solid precipitated. The stirring was continued for an hour after the addition. The Grignard complex was decomposed with dilute hydrochloric acid. The ether layer was washed with a sodium bicarbonate solution and water, and then was dried over magnesium sulfate. The ether was removed either by distillation from a steam cone or by evaporation in a current of air. The isolation of the products is described below.

(a) Ethylmagnesium Bromide with α,α,α-Tribromoacetylmesitylene.—Removal of the ether left large, square, crystalline plates. After one crystallization from 85% methyl alcohol there was obtained 5.5 g. (68.7% of the theoretical) of the colorless, crystalline dibromomethyl ketone. A mixture of the product and the starting material melted at 43–55°. The pure product melted at 73–74°.

Anal. Calcd. for $C_{11}H_{12}OBr_2$: Br, 50.0. Found: Br, 49.8.

(b) Ethylmagnesium Bromide with α,α-Dibromoacetylmesitylene.—The residue was crystallized from petroleum ether. The crystals which resulted melted at 56–57.5°, and amounted to 2.7 g., or 56.2% of the theoretical. The substance was shown to be α-bromoacetylmesitylene by the mixed melting point method.

(c) Ethylmagnesium Bromide with α-Bromoacetylmesitylene.—Nearly all of the residue, a light brown oil, distilled at 79–83° at 2 mm. The yield was 5.3 g., or 65.4% of the theoretical. Part of the product was nitrated with equal parts of cold, concentrated sulfuric and nitric acids. After several recrystallizations from alcohol, the resulting product melted at 137–138.5°. A mixture of an authentic sample of 3,5-dinitroacetylmesitylene (m. p. 138–139°) and the product melted at 138–139°.

(d) Phenylmagnesium Bromide with α,α,α-Trichloroacetylmesitylene.—The residue was high-boiling and crystallized in the receiver. After recrystallization from petroleum ether, it melted at 71–72°. An analysis showed it to be α,α-dichloroacetylmesitylene. The yield was 46% of the theoretical.

Anal. Calcd. for $C_{11}H_{12}Cl_2O$: Cl, 30.7. Found: Cl, 30.6.

(e) Ethylmagnesium Bromide with α-Chloroacetylmesitylene.—The residue was a colorless, crystalline solid melting at 66–67°. This was found to be α-chloroacetyl-mesitylene by the mixed melting point method. The compound was almost quantitatively recovered.

(f) *n*-Butylmagnesium Bromide with α,3,5-Tribromoisobutyrylmesitylene.—By distillation at atmospheric pressure the residue was separated into two fractions. Redistillation of the low boiling portion yielded 7.9 g. of *n*-butyl bromide (57.6% of the theoretical) boiling at 100–105°. The mercuric bromide of this oil was prepared and found to melt at 129.5–130.5°. The melting point of *n*-butylmercuric bromide is given as 129°.[11]

The residue remaining after the low boiling portion had been distilled from the reaction product was distilled at 3 mm. pressure. Most of it (29.5 g.) came over at 168–176°, and after solidification melted at 62–65°. After recrystallization from methanol there remained 26.5 g. (75% of the theoretical) melting at 69–70.5°. A mixed melting point with 3,5-dibromoisobutyrylmesitylene showed no depression.

(g) *n*-Amylmagnesium Chloride with α,3,5-Tribromoisobutyrylmesitylene.— The lower boiling portion of the residue was distilled with a water pump. (The residue of this distillation was saved for subsequent treatment.) The low boiling portion was redistilled at atmospheric pressure. As the first fraction, 7 g. was obtained at 120–130°; the second fraction distilled at 130–165° and amounted to 4.7 g. The second fraction was redistilled, and the portion distilling at 120–130° was added to the corresponding fraction of the first distillation. The total amount obtained at 120–130° was 9.6 g., or 63.5% of the theoretical. This oil was shown to be *n*-amyl bromide by preparing the mercuric bromide derivative, which melted at 123.5–124.5° after several recrystallizations from alcohol. The melting point of *n*-amylmercuric bromide has been given as 122°,[11] and as 127°.[12]

The residue from the water pump distillation was distilled at 3 mm. pressure. Most of it (31 g.) came over at 180–190°, and solidified on cooling. After several recrystallizations from methanol, there remained 28.5 g. (81.8% of the theoretical) which melted at 69.5–70.8°. This substance was shown to be 3,5-dibromoisobutyrylmesitylene by the mixed melting point method.

(h) Phenylmagnesium Bromide with α,3,5-Tribromoisobutyrylmesitylene.— The residue, a clear oil, was distilled at 3 mm. pressure. The lower boiling fraction was reserved for a later distillation at atmospheric pressure. The second fraction came over at 175–188°, and solidified on cooling. After several recrystallizations from methanol, there was 22.9 g. (65.8% of the theoretical) melting at 68–69°. By the method of mixed melting points this was shown to be 3,5-dibromoisobutyrylmesitylene.

The lower boiling fraction was redistilled at atmospheric pressure. Between 151 and 160° there was collected 11.3 g. (72% of the theoretical) of a clear liquid. Nitration of 3 cc. of this liquid yielded *p*-nitrobromobenzene, melting at 125–126°, which was identified by the mixed melting point method.

(i) *p*-Tolylmagnesium Bromide with α,3,5-Tribromoisobutyrylmesitylene.—The residue was a slightly brown, viscous oil. The solid which appeared on cooling was filtered. The filtrate was distilled at atmospheric pressure. The first fraction (2.3 g.) was obtained near the boiling point of toluene. The boiling temperature then rose rapidly to 178°, and 15.3 g. was obtained from that temperature to 183°. The residue was distilled at 24 mm. pressure, and came over as a solid (22 g.) around 210°.

The solid that had been filtered from the reaction product still contained *p*-bromotoluene. It was washed with ether, and the ether washings distilled at 2 mm. pressure, after the removal of the ether, to obtain the bromotoluene. The first fraction was redistilled at atmospheric pressure, 6.6 g. being obtained at 176–185°. The second fraction, 25.5 g. of a solid, came over at 160–190°.

Each portion of each product was identified. The *p*-bromotoluene was oxidized to

[11] Marvel, Gauerke and Hill, THIS JOURNAL, **47**, 3009 (1925).

[12] Slotta and Jacobi, *J. prakt. Chem.*, **120**, 249 (1929).

p-bromobenzoic acid, and the acid identified by the mixed melting point method. The mixed melting point method was also used to identify the solid product, 3,5-dibromoisobutyrylmesitylene. The total yield of p-bromotoluene was 21.9 g., or 68.4% of the theoretical. After a few recrystallizations from methanol, there remained 46.5 g. of the dibromo ketone melting at 69.5–71°, a yield of 71.5%.

Summary

The halogenation of hindered ketones by treatment with solutions of alkali hypohalites has been extended to include methyl, ethyl and isopropyl ketones as well as one 1,3-diketone.

The resulting α-halogen ketones have been described and certain reactions characteristic of the type have been studied.

Cleavage with alkali has been shown to be very difficult to effect. Only in the case of α,α,α-tribromoacetylmesitylene was the cleavage successfully carried out. In some cases the alkali acts as a dehalogenating agent.

It has been shown that these compounds are dehalogenated by treatment with phenol, p-halophenols being formed.

Dehalogenation has been effected also by treatment with the Grignard reagent. This reaction involves an interchange of radicals.

URBANA, ILLINOIS

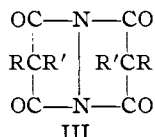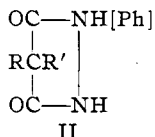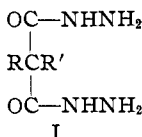## ALKYLATED DIKETOPYRAZOLIDINES AND TETRAKETOPYRAZOPYRAZOLES FROM ALKYLMALONIC ESTERS AND HYDRAZINE

BY ARTHUR W. DOX

Condensations of alkylmalonic acid derivatives with hydrazines have thus far yielded three types of products.

$$
\begin{array}{ccc}
\text{OC—NHNH}_2 & \text{OC—NH[Ph]} & \text{OC—N—CO} \\
| & | & | \quad | \\
\text{RCR}' & \text{RCR}' & \text{RCR}' \quad \text{R}'\text{CR} \\
| & | & | \quad | \\
\text{OC—NHNH}_2 & \text{OC—NH} & \text{OC—N—CO} \\
\text{I} & \text{II} & \text{III}
\end{array}
$$

Type I is the simple dihydrazide resulting from direct condensation between an alkylmalonic ester and hydrazine hydrate. A series of such dihydrazides has recently been prepared by de Graaf.[1]

Type II is represented by the "diethylmalonylhydrazine" which Einhorn and Feibelmann[2] obtained in the condensation of diethylmalonyl chloride with hydrazine; by the diethyl- and dipropyl-1-phenyl-3,5-"pyrazololidone" obtained by Conrad and Zart[3] from the dialkylmalonic esters and

[1] De Graaf, Dissertation, Leiden, 1930.

[2] Einhorn and Feibelmann, Ann., 359, 186 (1908).

[3] Conrad and Zart, Ber., 39, 2282 (1906).