

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

DIHALOCYANOACETYL DERIVATIVES OF MESITYLENE

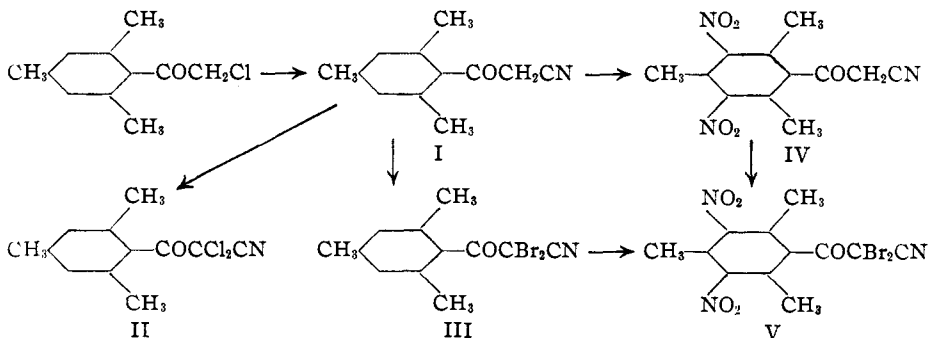
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It has been shown that the halogenation of methyl phenyl ketones by solutions of hypohalites becomes possible when the action of the alkali on the carbonyl group is hindered by the presence of ortho substituents in the benzene ring. Thus when acetomesitylene is shaken for two days with an aqueous solution of sodium hypobromite, tribromoacetylmesitylene is formed.¹ Although the trihaloacetyl compounds so obtained are stable to cold alkali, they can be cleaved in the normal manner by long treatment with hot concentrated solutions of alkali. Work on the cleavage of these and similar trihalomethyl compounds will be reported elsewhere.²

A natural extension of this study of halogenation by solutions of hypohalites was its application to ketones having active methylene groups adjacent to the hindered carbonyl. Of these the cyanomethyl ketones offered particular interest because of the remarkable activity of the methylene group. In α -cyanoacetophenone, for example, the hydrogens of the methylene group enolize so readily as to render the compound soluble in alkali. It was to be expected from this that halogenation might proceed much more rapidly with this type of ketone than with those previously examined.



Accordingly, cyanoacetylmesitylene (I) and di-(cyanoacetyl)-mesitylene (VI) have been prepared and their reaction with hypohalite solutions has been studied. When chloroacetylmesitylene, obtained from mesitylene and chloroacetyl chloride by the method of Collet,³ is treated with potassium cyanide, cyanoacetylmesitylene (I) is obtained in good yield.

¹ Fuson and Walker, *THIS JOURNAL*, **52**, 3269 (1930).

² In a recent article Houben and Fischer, *Ber.*, **63B**, 2458 (1930), reported the cleavage of trichloroacetylmesitylene by boiling with a 40% sodium hydroxide solution for two hours.

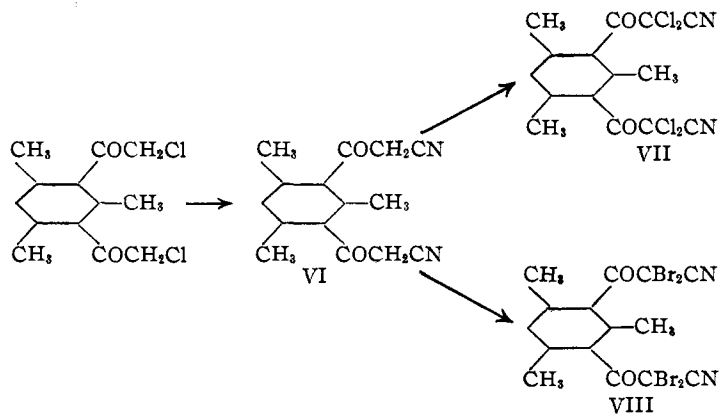
³ Collet, *Bull. soc. chim.*, [3] **17**, 510 (1897).

The cyano ketone is sufficiently acid to decompose potassium cyanide and for this reason it is necessary in the preparation to employ two molecular proportions of the salt for one of the chloro compound.

In an exactly similar fashion, di-(cyanoacetyl)-mesitylene (VI) is obtained from the corresponding dichloro compound.⁴ Here, of course, four molecular proportions of potassium cyanide are necessary for every mole of di-(chloroacetyl)-mesitylene used. Both the cyano and the dicyano compounds are readily soluble in aqueous alkali and this property has been used in separating them from impurities such as the unchanged chloro compounds.

The action of hypohalite solutions on these cyano ketones is remarkable because of its rapidity. When the cyano ketone is added to a solution of sodium hypochlorite, for example, the crystals dissolve immediately but the material is almost at once reprecipitated in the form of the chlorinated derivative, dichlorocycanoacetylmesitylene (II). Both this compound and the dibromocycanoacetylmesitylene (III), obtained in an exactly similar manner, are stable to cold solutions of alkalis and are obtained in good yields even when the hypohalite solution is strongly alkaline.

The position of the two bromine atoms in dibromocycanoacetylmesitylene has been checked by the use of dinitrocycanoacetylmesitylene (IV). This compound, which was obtained from cyanoacetylmesitylene by direct nitration, was found to give dinitrodibromocycanoacetylmesitylene (V) when treated with a solution of sodium hypobromite. This same dinitrodibromo compound was obtained when dibromocycanoacetylmesitylene (III) was treated with fuming nitric acid. There can be no doubt then that the two bromine atoms in dibromocycanoacetylmesitylene are situated in the acetyl group.



⁴ The dichloro compound was prepared by the method of Breed (Bryn Mawr College Monographs, 1, No. 1, p. 7).

Di-(cyanoacetyl)-mesitylene (VI) when treated with solutions of sodium hypochlorite and sodium hypobromite yielded, respectively, di-(dichloroacetyl)-mesitylene (VII) and di-(dibromocycanoacetyl)-mesitylene (VIII). This process, however, presented a rather puzzling phenomenon. The crystals of the dicyano compound when added to a solution of a sodium hypohalite first dissolved completely. Then after a few seconds the solution became milky as though the neutral tetrahalo compound were being precipitated. However, this precipitate redissolved rapidly and finally the expected tetrahalo compound separated and remained insoluble. This process is being studied.

Experimental

Cyanoacetylmesitylene⁵ (I).—Ten grams of chloroacetylmesitylene was dissolved in 300 cc. of alcohol by boiling under a reflux condenser. Four and a half grams of potassium cyanide was dissolved in a small amount of water and the solution was added through the condenser. After the solution had boiled for four hours, the alcohol was evaporated and the residue dissolved in 200 cc. of water. The crude material was precipitated by adding hydrochloric acid. After filtering, the material was dissolved in methyl alcohol and clarified by boiling with bone black. It was recrystallized from dilute methyl alcohol. The compound melted at 108–109° and the yield was 50 to 60% of the theoretical.

Anal. Calcd. for $C_{12}H_{13}ON$: C, 77.0; H, 7.0. Found: C, 76.8; H, 6.8.

Dibromocycanoacetylmesitylene (III).—A solution of sodium hypobromite was made by slowly adding 15 g. of bromine to a cold solution of 15 g. of sodium hydroxide in 150 cc. of water. To this solution 1 g. of cyanoacetylmesitylene was added. A white crystalline substance formed and after being filtered it was recrystallized from dilute methyl alcohol. The substance melted at 81–82° and the yield was 50 to 60% of the theoretical.

Anal. Calcd. for $C_{12}H_{11}ONBr_2$: Br, 46.4. Found: Br, 46.3.

Dichlorocycanoacetylmesitylene (II).—A solution of sodium hypochlorite was prepared by bubbling chlorine through a cold solution of 15 g. of sodium hydroxide dissolved in 150 cc. of water. One gram of cyanoacetylmesitylene was added to this solution. A white crystalline substance formed which went into solution on shaking. The solution was allowed to stand for twenty-four hours and was then filtered. The material was recrystallized from dilute methyl alcohol. The substance melted at 38–39° and the yield was 45 to 50% of the theoretical.

Anal. Calcd. for $C_{12}H_{11}ONCl_2$: Cl, 27.7. Found: Cl, 27.6.

Dinitrodibromocycanoacetylmesitylene (V).—One gram of dibromocycanoacetylmesitylene was added to 20 cc. of cold fuming nitric acid (sp. gr. 1.49–1.50). After being allowed to stand for fifteen minutes, the solution was poured into ice water and filtered. The compound was recrystallized from dilute methyl alcohol; it melted at 97–98°. The yield was 85% of the theoretical.

Dinitrocycanoacetylmesitylene (IV).—One gram of cyanoacetylmesitylene was added to 20 cc. of cold fuming nitric acid (sp. gr. 1.49–1.50). The mixture was allowed to stand for a few minutes, was poured into ice water and filtered. The compound was recrystallized from dilute methyl alcohol. It melted at 170.3 to 171.3° (corr.) and the yield was 35% of the theoretical.

⁵ This preparation was first carried out by Mr. A. E. Knauf.

Anal. Calcd. for $C_{12}H_{11}O_3N_3$: C, 52.0; H, 4.0. Found: C, 51.8; H, 3.7.

Dinitrodibromocycanoacetylmesitylene.—One gram of dinitrocycanoacetylmesitylene was added to a solution of sodium hypobromite. The solution was allowed to stand for twenty-four hours and then filtered. The substance was recrystallized from aqueous methyl alcohol and melted at 94–95°. The yield was 45% of the theoretical.

Anal. Calcd. for $C_{12}H_9O_3Br_2N_3$: Br, 36.8. Found: Br, 36.6.

Di-(cyanoacetyl)-mesitylene (VI).—Ten grams of di-(chloroacetyl)-mesitylene was dissolved in 300 cc. of alcohol by boiling under a reflux condenser. Five and a half grams of potassium cyanide dissolved in a small amount of water was added through the condenser. After boiling for four hours the alcohol was evaporated and the residue dissolved in 200 cc. of water. The substance was precipitated by adding hydrochloric acid. After filtering, the crude material was dissolved in alcohol and clarified by boiling with bone black. The substance was recrystallized from dilute alcohol and melted at 156–157° (corr.). The yield was 70 to 80% of the theoretical.

Anal. Calcd. for $C_{15}H_{14}O_2N_2$: C, 70.9; H, 5.5. Found: C, 70.6; H, 5.3.

Di-(dichlorocycanoacetyl)-mesitylene (VII).—A solution of sodium hypochlorite was prepared by bubbling chlorine through a cold solution of 15 g. of sodium hydroxide dissolved in 150 cc. of water until the solution became yellow. One gram of di-(cyanoacetyl)-mesitylene dissolved in sodium hydroxide was added to this solution. A white substance formed but went into solution on shaking. The solution was allowed to stand for twenty-four hours and then filtered. The substance was recrystallized from dilute methyl alcohol. It melted at 52–53° and the yield was 50 to 60% of the theoretical.

Anal. Calcd. for $C_{15}H_{10}O_2N_2Cl_4$: Cl, 36.2. Found: Cl, 36.0.

Di-(dibromocycanoacetyl)-mesitylene (VIII).—A solution of sodium hypobromite was prepared by slowly adding 15 g. of bromine to a cold solution of 15 g. of sodium hydroxide dissolved in 150 cc. of water. One gram of di-(cyanoacetyl)-mesitylene dissolved in sodium hydroxide was added to this solution. After being allowed to stand for a few minutes the substance was filtered and recrystallized from methyl alcohol. The compound melted at 121.2–122.2° (corr.). The yield was 30 to 35% of the theoretical.

Anal. Calcd. for $C_{15}H_{10}O_2N_2Br_4$: Br, 56.1. Found: Br, 55.9.

Summary

1. Cyanoacetylmesitylene and di-(cyanoacetyl)-mesitylene have been prepared from chloroacetylmesitylene and di-(chloroacetyl)-mesitylene, respectively, by treatment with potassium cyanide.

2. Cyanoacetylmesitylene when treated with solutions of sodium hypochlorite and sodium hypobromite has been found to yield, respectively, dichlorocycanoacetylmesitylene and dibromocycanoacetylmesitylene.

3. Dinitrodibromocycanoacetylmesitylene has been prepared, (a) by nitration of dibromocycanoacetylmesitylene and (b) by treating dinitrocycanoacetylmesitylene with a solution of sodium hypobromite.

4. Di-(dichlorocycanoacetyl)-mesitylene and di-(dibromocycanoacetyl)-mesitylene have been obtained from di-(cyanoacetyl)-mesitylene by treatment of the latter with solutions of sodium hypochlorite and sodium hypobromite, respectively.

5. All of these dihalocycanoacetyl compounds have been found to be stable to cold solutions of alkalis.