# 183. *Volume Effects of Alkyl Groups in Aromatic Compounds. Part IV. The Dinitration of 2-Chlorocymene.*

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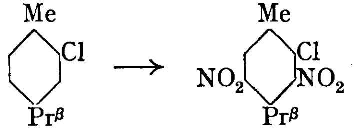
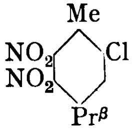
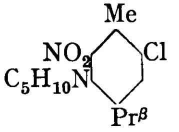
The dinitration of 2-chloro-*p*-cymene (I) with cold fuming nitric acid was considered, for reasons given in Part I (J., 1933, 977), to give the derivative (II). Lubs and Young (*J. Ind. Eng. Chem.*, 1919, **11**, 1131), however, have recorded that by using mixed acids they obtained (1) a solid, m. p. 108—109°, apparently identical with the chlorodinitrocymene (m. p. 109—110°) of Fileti and Crosa (*Gazzetta*, 1888, **18**, 289), to which they assign formula (III); (2) a chlorodinitro-compound, $C_7H_6O_4N_2Cl$ (*sic*), m. p. 88—89°; and (3) an oil, described as a mixture of these two solids.



(I.) (II.)



(III.)

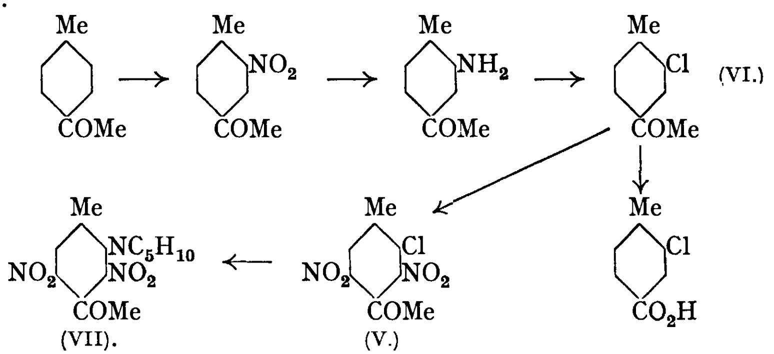


(IV.)

Since their conclusion and experimental results are opposed to our experience of concentrated nitric acid acting alone as nitrating agent, we have re-examined this substitution under the conditions prescribed by Lubs and Young, by Fileti and Crosa (*loc. cit.*), and by one of us (*loc. cit.*).

*The Conditions of Formation and the Constitution of the Compound, m. p.* 88—89°.—The production of terephthalic acid during Lubs and Young's experiment led us to suspect that the substance, m. p. 88—89°, was an oxidation product. A possible cause of its formation was the presence of 3-chlorocymene in the "2-chlorocymene" of Lubs and Young, which was obtained by direct halogenation of cymene from crude spruce turpentine. Since 3-chlorocymene is relatively more easily oxidised to the corresponding chlorodinitromethylacetophenone during nitration than is 2-chlorocymene (Ganguly and Le Fèvre, preceding paper), a probable consequence of using the mixed initial material indicated would be the isolation of 2-chloro-3 : 5-dinitro-4-methylacetophenone (*i.e.*, the oxidation product of 3-chlorocymene); this ketone has m. p. 91—92°. Pure 2-chlorocymene, prepared from recrystallised 2-cymidine hydrochloride by the Sandmeyer reaction and subjected as exactly as possible to the conditions used by Lubs and Young, gave none of the substance, m. p. 88—89°.

Since the substance, m. p. 88—89°, might be the ketone (V), this was synthesised. From 3-nitro-4-methylacetophenone (Errera, *Gazzetta*, 1891, **21**, 92), *via* the amine, 3-chloro-4-methylacetophenone (VI) was obtained; this on oxidation with alkaline potassium permanganate gave 3-chloro-4-methylbenzoic acid (von Gerichten, *Ber.*, 1878, **11**, 365) and therefore was correctly oriented. Solution of (VI) in cold fuming nitric acid afforded 3-chloro-2 : 6-dinitro-4-methylacetophenone (V), m. p. 97—98°, the positions of the nitro-groups being proved by its quantitative transformation into 2 : 6-*dinitro*-3-*piperidino*-4-*methylacetophenone* (VII).



Lubs and Young state that the substance, m. p. 88—89°, in boiling alcohol gives an intense blue colour with a trace of sodium carbonate. In this test, we obtained negative results with the pure halogenodinitrocymenes, but blue solutions with the halogenodinitromethylacetophenones described in this and the preceding paper.

*The Constitution of the Compound, m. p.* 108—109°.—This substance was prepared, from pure 2-chlorocymene, both by the process of Lubs and Young and (better) by nitration with fuming nitric acid alone. If it were (III), it should react with hot piperidine to form the chloronitropiperidinocymene (IV) (compare Le Fèvre and Turner, J., 1927, 1113); instead, it gives 3 : 5-dinitro-2-piperidino-*p*-cymene (Le Fèvre, J., 1933, 977) quantitatively, and therefore undoubtedly has the constitution (II).

We cannot explain the *o*-diamine reactions reported by Lubs and Young for the amine prepared from this compound, but would point out that (a) the diamine was not analytically pure (they record N, 13·7, 13·5, instead of 14·1%) and (b) of the six qualitative tests applied, in only two were solids produced (no analyses or other data for either of these are recorded), while of the remaining four, one was a positive, and three were blank, colour reactions.

## EXPERIMENTAL.

2-*Cymidine*.—2-Nitrocymene (76 g.) was heated under reflux on the water-bath for 10 hours with activated iron filings (80 g.), water (250 c.c.), and a little hydrochloric acid or ferric chloride. Steam distillation, extraction of the distillate with light petroleum (b. p. 40—60°), drying (sodium sulphate), and evaporation of the solvent afforded the base, b. p. 234—238°/750 mm. (yield, about 70% of the nitrocymene).

2-*Chloro*-p-*cymene*.—Recrystallised 2-cymidine hydrochloride (43 g.), suspended in 120 c.c. of concentrated hydrochloric acid diluted with 80 c.c. of water, was diazotised (sodium nitrite, 15 g.), and the solution heated for 2 hours with cuprous chloride (from crystallised copper sulphate, 120 g., sodium chloride, 60 g., and water, 2 l.) in concentrated hydrochloric acid (200 c.c.). 2-Chlorocymene was isolated by steam distillation, dried (calcium chloride), and distilled twice, a fraction (26 g.), b. p. 216—218°/762 mm., being collected; $d_{4°}^{17°}$ 1·152, $n_D^{17°}$ 1·51776, whence $[R_L]_D$ 44·2 (calc., 44·4).

*Dinitration of* 2-*Chlorocymene*.—(a) *With fuming nitric acid.* The chlorohydrocarbon (5 g.) was added to nitric acid (60 g., *d* 1·5) below 0° during ½ hour. Dilution with ice and one crystallisation of the solid product from acetic acid gave pure 2-chloro-3 : 5-dinitro-*p*-cymene, m. p. 109·5—110·5° (Found : C, 46·6; H, 4·2. Calc. : C, 46·4; H, 4·2%).

(b) *With mixed acids.* 2-Chlorocymene (14 g.) was added drop by drop to a mixture of sulphuric acid (*d* 1·8, 24 g.) and oleum (32·5 g., 20% $SO_3$) cooled by ice–salt and mechanically stirred. Into the resulting liquor, fuming nitric acid (*d* 1·5, 12 g.), diluted with concentrated sulphuric acid (24 g.) and oleum (32·5 g., 20% $SO_3$), was run so that the temperature did not rise above 0°. The acid mixture was poured on ice (300 g.), and the solid separated, washed with water, and twice crystallised from dilute acetic acid; it then had m. p. 109·5—110·5° (alone or mixed with authentic 2-chloro-3 : 5-dinitrocymene) (Found : C, 46·2; H, 4·2%). The yield (4·7 g.) was considerably lower than that obtained by method (a).

From the acid solution left after separation of the solid chlorodinitrocymene, ether extracted a thick syrup. This, though left in the ice-chest for a month, gave no solid as described by Lubs and Young (*loc. cit.*). Further, a piperidino-derivative could not be obtained from it.

3 : 5-*Dinitro*-2-*piperidinocymene*.—The chlorodinitro-compounds (m. p. 109·5—110·5°) mentioned in the last two sections were heated under reflux with piperidine (5 parts) for 20 minutes on the steam-bath. Dilution with water and crystallisation from acetic acid gave in each case yellow needles, m. p. 122—123° (alone or mixed with an authentic specimen) in yields equal to the weights of outgoing materials respectively.

*Synthesis of* 3-*Chloro*-4-*methylacetophenone* (VI).—4-Methylacetophenone (55 g.) was dissolved during 1½ hours in nitric acid (*d* 1·5, 370 c.c.) below 0°. Dilution with ice and water to about 2 l. afforded 3-nitro-4-methylacetophenone (65 g.), m. p. 62° after crystallisation from alcohol (300 c.c.). The nitro-derivative (50 g.) was heated on the steam-bath for 5 hours with alcohol (150 c.c.), iron filings (51 g.), and concentrated hydrochloric acid (7 c.c.). Cooling, filtration, and evaporation then gave 30 g. of the amine, m. p. 79—80° after crystallisation from petroleum. 3-Amino-4-methylacetophenone hydrochloride (30 g.), obtained by passing hydrogen chloride into an alcoholic solution of the base, was submitted to the Sandmeyer reaction. Steam distillation of the product gave crystalline 3-chloro-4-methylacetophenone, m. p. 40—43°, which was used without further purification for the next step.

3-*Chloro*-2 : 6-*dinitro*-4-*methylacetophenone*.—The crude halogenohydrocarbon (5 g.) was added in ½ hour to nitric acid (*d* 1·5, 75 g.) below 0°. Dilution by addition to ice and crystallisation of the solid product from methyl alcohol (30 c.c.) gave a white crystalline substance (7 g.), m. p. 97—98°. This (0·7 g.), when heated with piperidine (2 g.), gave 2 : 6-*dinitro*-3-*piperidino*-4-*methylacetophenone*, m. p. 113—114° after crystallisation from acetic acid (Found : C, 54·7; H, 5·4. $C_{14}H_{17}O_5N_3$ requires C, 54·7; H, 5·5%).

*Oxidation of the Ketone* (VI).—The ketone (5 g.) was added to a mixture of 10% sodium hydroxide solution (40 c.c.), water (200 c.c.), and 5% aqueous potassium permanganate (250 c.c.). After 10 hours' boiling, decoloration with sulphur dioxide, and cooling, a white solid, m. p. 228° (after two crystallisations from toluene), was obtained which appeared to be 2-*chloro*-4-*acetylbenzoic acid* (Found: C, 54·1; H, 3·3. $C_9H_7O_3Cl$ requires C, 54·4; H, 3·5%). This acid (0·5 g.), treated with a boiling mixture of 10% sodium hydroxide solution (4 c.c., diluted to 25 c.c. with water) and 5% potassium permanganate solution for 5 hours, gave chloroterephthalic acid, m. p. 320° (Fileti and Crosa, *Gazzetta*, 1888, **18**, 313, record m. p. 300°; Ahrens, *Ber.*, 1886, **19**, 1637, gives m. p. " oberhalb 300° ").

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