Tropones. Part III.[1] The Mechanism of the Production of *m*-Hydroxybenzaldehydes from 2-Chlorotropones

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Using a variety of oxidising agents, nitro-2-chlorotropones are converted into *m*-hydroxybenzaldehydes in which all the substituents of the original tropone are retained. Thus, 2-chloro-7-nitrotropone gives 4-chloro-3-hydroxy-2-nitrobenzaldehyde, and 2-chloro-5-nitrotropone gives 2-chloro-3-hydroxy-6-nitrobenzaldehyde. 2-Chloro-5,7-dinitrotropone, obtained by nitrating 2-chloro-5-nitrotropone, gives 2-chloro-3-hydroxy-4,6-dinitrobenzaldehyde as the sole aldehyde when treated with oxidising agents, but in aqueous acetic acid elimination of chloride competes with oxidation and 5-hydroxy-2,4-dinitrobenzaldehyde is obtained. Deuteriation studies have shown that when 2-chloro-7-nitrotropone is converted into 4-chloro-3-hydroxy-2-nitrobenzaldehyde, C-6 becomes the aldehyde carbon.

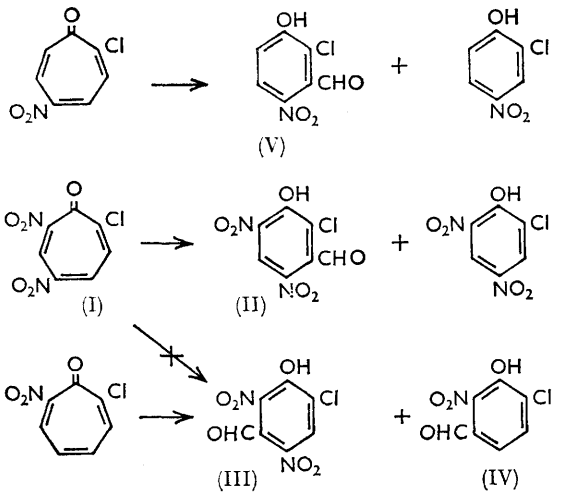
THE formation of 4-chloro-3-hydroxy-2,6-dinitrobenzaldehyde by the action of dilute acetic acid on 2-chloro-4,7-dinitrotropone [1] suggests that the chlorodinitrotropone is the immediate precursor of the aldehyde obtained when 2-chlorotropone was treated with nitric acid. It suggested also that 2-chloro-5,7-dinitrotropone might be the immediate precursor of the isomeric 2-chloro-3-hydroxy-4,6-dinitrobenzaldehyde. With a view to making this tropone and testing this hypothesis, we have synthesised 2-chloro-5-nitrotropone. The range of chloronitrotropones so obtained has enabled us to study the nature of the reactions involved in their oxidations to *m*-hydroxybenzaldehydes.

2-Chloro-5-nitrotropone was prepared by treating 5-nitrotropolone with thionyl chloride. The tropolone was prepared by oxidising 5-nitrosotropolone [2] with nitric acid, a more effective procedure than the direct nitration of tropolone.[3] The structure of the chlorotropone was established by its elemental analysis, spectral data, and by its conversion into *p*-nitrobenzoic acid using dilute alkali or, better, aqueous acetic acid.

In contrast to 2-chloro-7-nitrotropone,[1] 2-chloro-5-nitrotropone reacts smoothly with dinitrogen tetroxide in carbon tetrachloride, to give 2-chloro-5,7-dinitrotropone (I) as the major product. In addition, 2-chloro-3-hydroxy-4,6-dinitrobenzaldehyde (II) and 2-chloro-4,6-dinitrophenol were obtained, these probably arising as a result of moisture in the system.

The structure of 2-chloro-5,7-dinitrotropone was revealed as follows. It analysed for $C_7H_3ClN_2O_5$ and its spectral properties, closely resembling those of 2-chloro-5-nitrotropone (see Experimental), indicated that it was a tropone. The orientation of its substituents followed from its conversion into 2,4-dinitrobenzoic acid when it was treated with alkali.

When 2-chloro-5-nitrotropone was nitrated with nitric acid in acetic acid there was obtained 2-chloro-4,6-dinitrophenol and 2-chloro-3-hydroxy-4,6-dinitrobenzaldehyde (II).† No trace of the isomeric 4-chloro-3-hydroxy-2,6-dinitrobenzaldehyde (III) was found. This result taken with the formation of the aldehyde (II) and 2-chloro-5,7-dinitrotropone in the nitration described above suggested that the tropone (I) was the precursor of the aldehyde (II). This point was firmly established when the pure tropone (I) was treated with nitric acid. The aldehyde (II) was obtained as the sole pentasubstituted benzene together with the derived 2-chloro-4,6-dinitrophenol.



The conversion of chlorotropones into *m*-hydroxybenzaldehydes which retain the chlorine clearly involves an oxidation. The driving force for this ring contraction must be large, for, as we have shown,[1] 2-chloro-4,7-dinitrotropone rearranges to the aldehyde (III) with aqueous acetic acid, albeit in low yield. By using specific oxidising agents we have been able to raise the yields of *m*-hydroxybenzaldehydes considerably. Treatment of the readily available 2-chloro-7-nitrotropone with aqueous silver nitrate gave, as the major product, 4-chloro-3-hydroxy-2-nitrobenzaldehyde (IV), as was found earlier.[4] This aldehyde was identified on the basis of analytical and spectral data and by comparison with an authentic specimen.[1] It was noted that in the manner of *o*-nitrobenzaldehydes it was light-sensitive.[5] The

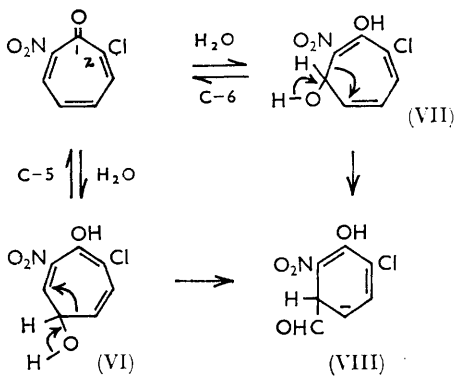
† The ease of nitration of 2-chloro-5-nitrotropone, in contrast to the stability of 2-chloro-7-nitrotropone, suggests that it is the precursor of the aldehyde (II) formed in the nitration of 2-chlorotropone with nitric acid.

[1] Part III, E. J. Forbes and D. C. Warrell, preceding paper.
[2] T. Nozoe and S. Seto, *Proc. Japan Acad.*, 1951, **27**, 188.
[3] J. W. Cook, J. D. Loudon, and D. K. V. Steel, *J. Chem. Soc.*, 1954, 530; W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, 1951, **73**, 828.
[4] T. Nozoe, T. Mukai, and K. Sakai, *Tetrahedron Letters*, 1965, 1041.
[5] G. Ciamician and P. Silber, *Ber.*, 1901, **34**, 2040.

oxidation with silver nitrate was erratic, for nitration sometimes accompanied oxidation, and the dinitro-aldehyde (III) was obtained in addition to the aldehyde (IV). This side-reaction could be avoided by using a variety of oxidising agents such as copper sulphate and potassium ferricyanide. The former gave the highest yields and cleanest reaction.

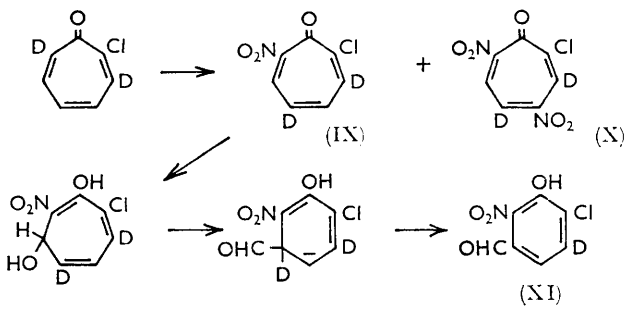
2-Chloro-5-nitrotropone was also easily oxidised; again copper sulphate was the best reagent. 2-Chloro-3-hydroxy-6-nitrobenzaldehyde (V) was thereby obtained, although the major product was 2-chloro-4-nitrophenol, this latter arising by deformylation of the aldehyde. This aldehyde (V) having electron-withdrawing substituents in the 2- and 6-positions can be expected to be more easily cleaved than the aldehyde (IV), whose formation from 2-chloro-7-nitrotropone was not accompanied by deformylated product.

The nature of the immediate precursors of the *m*-hydroxybenzaldehydes having been established, we can now formulate a mechanism for the ring contractions. They may be viewed as proceeding in three stages: first, nucleophilic attack by water to produce an anion (or its conjugate acid, as will certainly be the case when the oxidation is conducted in acidic media); secondly, rearrangement of this intermediate to produce a six-membered ring either by a bond migration or through a norcaradiene; and finally, oxidation of the carbanion so produced. This sequence is illustrated in detail for 2-chloro-7-nitrotropone.



As shown, attack by water can occur at either C-5 or -6 to produce intermediates (VI) or (VII), and migration of the appropriate bond then leads to the same carbanion (VIII). Migration of the alternative bonds leads to much less stable carbanions. If the rearrangement were controlled primarily by the stability of the rearranged carbanion (VIII) we would expect that both courses would be followed. If, on the other hand, charge density at the point of attack, and consequently the stability of the initial intermediate (VI) or (VII) (or their conjugate bases), was important, then attack would be expected to occur largely, if not exclusively, at C-6. This point has been settled by deuteriation studies based on the corollary that the aldehyde carbon derives from that carbon atom which is attacked by water.

[3,5,7-$^2H_3$]Tropolone was made by heating the sodium salt of tropolone with a large excess of deuterium oxide for 1 week. Its n.m.r. spectrum showed in the aromatic region a broadened singlet which integrated for two protons against the sharp singlet of the hydroxy-proton. When treated with thionyl chloride it gave 2-chloro-[3,5,7-$^2H_3$]tropone, which with nitric acid in acetic acid gave 2-chloro-7-nitro- and 2-chloro-4,7-dinitro-[3,5-$^2H_2$]tropone (IX) and (X).* When 2-chloro-7-nitro[3,5-$^2H_2$]tropone (IX) was heated with copper sulphate in deuterium oxide, it gave 4-chloro-3-hydroxy-2-nitro[5-^2H]benzaldehyde (XI). The position of the deuterium was revealed by its n.m.r. spectrum which showed equal singlets for one aromatic proton at τ 2·9 and the aldehyde proton at 0·4. That deuterium exchange does not occur during the course of the rearrangement was demonstrated by heating the non-deuteriated tropone with copper sulphate in deuterium oxide; the aldehyde so obtained had not incorporated any deuterium. Thus, the reaction is initiated by nucleophilic attack at C-6, showing that charge density on the ring carbon and/or the stability of the first intermediate is the controlling factor. Similar considerations applied to 2-chloro-5-nitro-, 2-chloro-4,7-dinitro-, and 2-chloro-5,7-dinitro-tropone suggest that these rearrange by nucleophilic attack at C-4, C-5 or -6, and C-4 respectively.



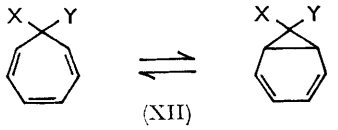
In conformity with earlier views [6] on the mechanisms of ring contractions which produce aldehydes, we have described the present rearrangement in terms of a bond migration in a cycloheptatriene, the driving force deriving from the stability of the anion so produced: that bond migrating which produces the most stable carbanion. However, even if allowance is made for the non-planarity of the cycloheptatriene ring, the migrating double bond must always be electron-deficient since it has a nitro-group attached to it. The ease of ring contraction is probably better accounted for by assuming the intermediacy of a norcaradiene, a route which appears to be the only acceptable one for reactions which produce benzoic acids.[6] That an equilibrium can exist between a cycloheptatriene and a norcaradiene at room temperature has been recently established by Ciganek [7]

* It is noteworthy that in this reaction no benzenoid compounds were obtained. This result is paralleled by our failure to rearrange 2-chloro-4,7-dinitro[3,5-$^2H_2$]tropone satisfactorily.

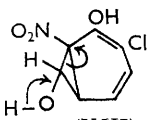
[6] E. J. Forbes, D. C. Warrell, and W. J. Fry, *J. Chem. Soc.*, 1967, 1693.

[7] E. Ciganek, *J. Amer. Chem. Soc.*, 1965, **87**, 652, 1149.

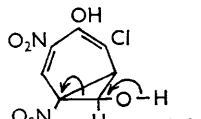
for the compound (XII; X = CF_3, Y = CN). It seems likely then that the norcaradiene could be formed in the present reactions where X and Y would be hydrogen and hydroxyl.* For 2-chloro-7-nitrotropone the intermediate (VII) collapses uniquely to the norcaradiene (XIII). Now, it will be seen that the bond which breaks is not only the one which produces the more stable carbanion, but also the one that is more polarised in the direction required to produce it. Similar considerations are equally convincing when applied to the dinitro-compounds; *e.g.*, attack by water at C-4 would lead to the intermediate (XIV) which would rearrange uniquely as shown.



(XII)

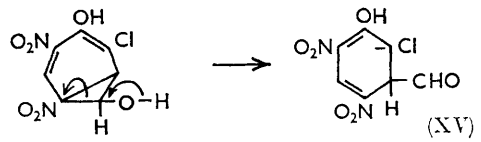


(XIII)

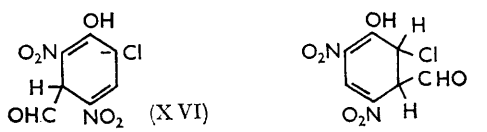


(XIV)

The final stage in the rearrangement, namely, the oxidation of the carbanion, requires little comment. The situation is analogous to that produced in nucleophilic aromatic substitution where hydride is formally the leaving group. It may, however, be better viewed as the donation of one or two electrons to the oxidising species (Ag^+, Cu^{2+}) followed by loss of a hydrogen atom or proton. The presence of carbanions was indicated in one of the reactions where loss of chloride accompanied ring contraction. When 2-chloro-5,7-dinitrotropone was treated with aqueous acetic acid it gave 5-hydroxy-2,4-dinitrobenzaldehyde as the major product, whereas with nitric acid it gave the expected 2-chloro-3-hydroxy-4,6-dinitrobenzaldehyde (II) and the derived 2-chloro-4,6-dinitrophenol. Loss of chloride under the poorly oxidising conditions prevailing requires that protonation of the carbanion (XV), and loss of hydrogen chloride, effectively competes with its oxidation. It is notable that under the same poorly oxidising conditions (aqueous acetic acid) 2-chloro-4,7-dinitrotropone rearranges without loss of chlorine. Loss of chloride would again require protonation at C-2 (XVI), but would be followed by a 1,4- rather than a 1,2-elimination. The different fates of the two formally similar carbanions probably derive from the greater facility of a 1,2- as compared with a 1,4-elimination rather than from the difference in the ease of protonation of the carbanions, since it has been shown recently that when equilibrated in base 1,2-dihydrobenzene predominates over 1,4-dihydrobenzene to no greater extent than *ca.* 7 : 3.[8] This difference in stability of the dienes is hardly sufficient to account for the clear-cut difference between the two reactions.



(XV)



(XVI)

The rearrangement then may be viewed as being initiated by nucleophilic attack of water at that carbon atom which allows the most stable anion (or its conjugate acid) to be formed. This point is probably also that at which charge density is lowest. Ring contraction then occurs through a norcaradiene rather than by a direct bond migration. Oxidation of the carbanion produced is facile, but may be precluded when its protonation leads to a 1,2-dihydrobenzene followed by elimination of chloride under poorly oxidising conditions.

EXPERIMENTAL

Ultraviolet spectra were recorded on a Unicam SP 800 spectrophotometer, and n.m.r. spectra were recorded at 60 Mc./sec. Light petroleum refers to the fraction b.p. 60—80°.

5-Nitrotropolone.—Finely powdered 5-nitrosotropolone [2] (5·5 g.) was added to concentrated nitric acid (100 ml.) at 0°. The suspension was stirred vigorously for 30 min., and then filtered. The residue (4·73 g.) was recrystallised from benzene, to give 5-nitrotropolone (2·82 g.), m.p. 199—201°.

2-Chloro-5-nitrotropone.—5-Nitrotropolone (3·4 g.) and thionyl chloride (1·6 ml.) were heated in benzene (100 ml.) under reflux for 6 hr. The solution was evaporated to dryness, to give a solid which was chromatographed first on silica gel in benzene and then on alumina in ether. Recrystallisation of the solid thereby obtained afforded *2-chloro-5-nitrotropone* (2·52 g.) as yellow needles from carbon tetrachloride, m.p. 143·5—145° (Found: C, 45·0; H, 2·4; N, 7·4. $C_7H_4ClNO_3$ requires C, 45·3; H, 2·2; N, 7·6%), $\nu_{max.}$ (CH_2Cl_2) 1644, 1614, 1538, 1326, 1122, 1031, 947, and 863 $cm.^{-1}$, $\lambda_{max.}$ (cyclohexane) 213, 250, and 353 mμ (ε 21,900, 23,200, and 10,000).

Rearrangement of 2-Chloro-5-nitrotropone.—(a) *With sodium hydroxide.* 2-Chloro-5-nitrotropone (99 mg.) was dissolved in 5% aqueous sodium hydroxide (50 ml.). After 3 hr., the solution was cooled in ice, acidified, and extracted with ether (5 × 50 ml.). The combined extracts were dried and evaporated. Chromatography of the residual solid (76 mg.) in ether on silica gel (4 g.) afforded, after

* The factors which determine the position of this equilibrium are not understood. When X = Y = CF_3 the compound exists entirely as a cycloheptatriene, and when X = Y = CN it exists entirely as a norcaradiene.[7] Size, however, is not the only factor, for when X = H and Y = phenyl, the compound exists as a norcaradiene (T. Mukai, personal communication) whereas cycloheptatriene exists entirely as a seven-membered ring.

[8] T. Yamaguchi, T. Ono, K. Nagai, C. C. Sin, and T. Shirai, *Chem. and Ind.*, 1967, 759.

recrystallisation from benzene–light petroleum, *p*-nitrobenzoic acid (39 mg.) as buff needles, m.p. and mixed m.p. 239—241°.

(b) *With acetic acid.* The tropone (298 mg.) was heated at 100° for 1 hr. in a mixture of water (2·5 ml.) and glacial acetic acid (12·5 ml.). Dilution of the solution with water, extraction with chloroform (2 × 30 ml.), and evaporation of the combined chloroform extracts afforded a pale yellow solid. Recrystallisation from benzene–ether gave *p*-nitrobenzoic acid as needles, m.p. and mixed m.p. 238—240°.

Nitration of 2-Chloro-5-nitrotropone.—(a) *With Dinitrogen tetroxide.* A solution of dinitrogen tetroxide (308 mg.) in dry carbon tetrachloride (22 ml.) was added to a solution of 2-chloro-5-nitrotropone (540 mg.) in carbon tetrachloride (200 ml.) at 0°. After 4 hr., the reaction mixture was filtered. Recrystallisation of the collected solid, first from benzene–light petroleum and then from carbon tetrachloride, afforded *2-chloro-5,7-dinitrotropone* (168 mg.) as yellow needles, m.p. 165—166° (Found: C, 36·5; H, 1·4; Cl, 15·5; N, 12·4. $C_7H_3ClN_2O_5$ requires C, 36·5; H, 1·3; Cl, 15·4; N, 12·2%), $\nu_{max.}$ (CH_2Cl_2) 1655, 1630, 1608, 1549, 1329, 1025, and 867 cm.$^{-1}$, $\lambda_{max.}$ (cyclohexane) 258 and 351 mμ.

Evaporation of the filtrate from the reaction mixture left an oil (323 mg.) which was chromatographed on silica gel (20 g.). Elution with 50% light petroleum–benzene afforded 2-chloro-4,6-dinitrophenol (15 mg.), obtained as yellow needles from light petroleum, m.p. and mixed m.p. 108—110°. Elution with 25% light petroleum–benzene afforded 2-chloro-3-hydroxy-4,6-dinitrobenzaldehyde (89 mg.), obtained as yellow needles, m.p. and mixed m.p. 109—110°.

(b) *With nitric acid.* Concentrated nitric acid (2 ml.) was added to a cold solution of 2-chloro-5-nitrotropone (205 mg.) in glacial acetic acid (20 ml.). The solution was left overnight, diluted with water (75 ml.), and extracted with ether (5 × 100 ml.). The combined ether layers were dried and evaporated. Distillation of benzene (400 ml.) from the residue left a yellow oil (221 mg.), which was chromatographed on silica gel. Elution with 50% light petroleum–benzene afforded, after crystallisation from n-hexane, 2-chloro-4,6-dinitrophenol (35 mg.). Elution with 25% light petroleum–benzene afforded, after crystallisation from carbon tetrachloride, 2-chloro-3-hydroxy-4,6-dinitrobenzaldehyde (45 mg.). Both substances were identified by comparison with authentic specimens. Elution with benzene afforded 2-chloro-5-nitrotropone (53 mg.).

Rearrangement of 2-Chloro-5,7-dinitrotropone.—(a) *With sodium hydroxide.* 2-Chloro-5,7-dinitrotropone (98 mg.) was dissolved in 5% sodium hydroxide (20 ml.). After 30 min. the solution was acidified and extracted with ether (6 × 25 ml.). The combined extracts were dried and evaporated, and the residue (34 mg.) was dissolved in benzene. Chromatography on silica gel (1 g.) using 2% ether–benzene as eluent afforded 2,4-dinitrobenzoic acid (12 mg.) as a solid, whose infrared spectrum, $\nu_{max.}$ (CH_2Cl_2) 1760, 1600, 1540, and 1100 cm.$^{-1}$, was superimposable on that of an authentic specimen.

(b) *With aqueous acetic acid.* A solution of the tropone (120 mg.) in acetic acid (4 ml.) and water (1 ml.) was heated on a steam-bath for 0·5 hr. The cooled solution was diluted with water (45 ml.) and extracted with chloroform (4 × 25 ml.). Evaporation of the combined and dried extracts yielded an oil (83 mg.) which was chromatographed on silica gel (3 g.). Elution with 25% light petroleum–benzene afforded an oil (51 mg.) which was treated with carbon tetrachloride. 5-Hydroxy-2,4-dinitrobenzaldehyde was thereby obtained as needles (22 mg.), m.p. 105—107°, undepressed on admixture with an authentic specimen [9] (Found: C, 39·8; H, 1·8; N, 13·0. Calc. for $C_7H_4N_2O_6$: C, 39·6; H, 1·9; N, 13·2%), $\nu_{max.}$ (CH_2Cl_2) 3220 (broad), 1705, 1630, 1592, 1536, 1335, 1140, 1110, 865, and 833 cm.$^{-1}$. Unreacted starting material (28 mg.) was also obtained.

(c) *With nitric and acetic acids.* A solution of the tropone (105 mg.) in a mixture of concentrated nitric acid (0·5 ml.) and glacial acetic acid (5 ml.) was left at room temperature for 2 hr. The solution was diluted with water and extracted with ether (5 × 50 ml.). Evaporation of the combined and dried ether extracts, and distillation of benzene (100 ml.) from the residue, left a yellow oil (116 mg.) which was chromatographed on silica gel (3 g.). Elution with 50% light petroleum–benzene gave 2-chloro-4,6-dinitrophenol (42 mg.), elution with 25% light petroleum–benzene gave, after crystallisation from carbon tetrachloride, 2-chloro-3-hydroxy-4,6-dinitrobenzaldehyde (36 mg.) as yellow needles, m.p. and mixed m.p. 108—109°.

Oxidation of 2-Chloro-7-Nitropropone.—(a) *With copper sulphate.* A solution of 2-chloro-7-nitrotropone (800 mg.) and copper sulphate (8 g.) in dioxan (10 ml.) and water (40 ml.) was heated at 100° for 5 hr. The cooled solution was filtered and the residue washed with water and chloroform. The filtrate and washings were acidified with conc. hydrochloric acid (10 ml.) and extracted with chloroform. The combined extracts were washed with water, dried, and evaporated. Chromatography of the residue (620 mg.) on silica gel (20 g.) gave, on elution with benzene, colourless crystals of 4-chloro-3-hydroxy-2-nitrobenzaldehyde (206 mg.), obtained as rhombs from carbon tetrachloride, m.p. 176—177°, undepressed on admixture with an authentic specimen obtained by chlorinating 3-hydroxy-2-nitrobenzaldehyde.

Further elution with benzene produced unreacted 2-chloro-7-nitrotropone (274 mg.). Yield of aldehyde, 40% on recovered starting material.

(b) *With silver nitrate.* The tropone (112 mg.) was heated, under reflux under nitrogen for 4 hr., with a solution of silver nitrate (2 g.) in water (18 ml.) and ethanol (2 ml.). The black precipitate was removed and washed with water. The combined aqueous solutions were extracted with ether (5 × 50 ml.). Evaporation of the combined (and dried) ether extracts afforded a semi-solid (85 mg.), which when chromatographed on silica gel in benzene afforded 4-chloro-3-hydroxy-2,6-dinitrobenzaldehyde (40 mg.) as flat yellow needles from carbon tetrachloride, m.p. and mixed m.p. 119—120°. Extraction of the precipitate from the reaction with chloroform and chromatography of the product obtained therefrom afforded 4-chloro-3-hydroxy-2-nitrobenzaldehyde (15 mg.) as flat needles, m.p. 175—177° (from cyclohexane–benzene).

(c) *With silver nitrate.* 2-Chloro-7-nitrotropone (354 mg.), silver nitrate (2 g.), water (18 ml.), and dioxan (5 ml.) were heated together under nitrogen for 15 hr. Work-up as described above yielded a red solid (267 mg.). Chromatography on silica gel (8 g.) gave, on elution with benzene, a yellow solid (155 mg.) and starting material (10 mg.). Crystallisation of the yellow solid from benzene–heptane (twice) afforded 4-chloro-3-hydroxy-2-nitrobenzaldehyde as

[9] H. H. Hodgson and H. G. Beard, *J. Chem. Soc.*, 1927, 2375.

colourless rhombs (120 mg.), m.p. and mixed m.p. 176—177°.

Action of Copper Sulphate on 2-Chloro-5-nitrotropone.—2-Chloro-5-nitrotropone (101 mg.) was heated with a solution of cupric sulphate (1 g.) in water (20 ml.) under reflux for 5 hr. The cooled filtered solution and the residue therefrom were extracted with ether, and the combined ethereal extracts were dried and evaporated. Chromatography of the residual oil (104 mg.) on silica gel (3 g.) gave, on elution with 20% light petroleum–benzene, 2-chloro-4-nitrophenol, obtained as colourless needles (30 mg.) (from light petroleum), m.p. 111—112°, undepressed on admixture with an authentic specimen,[10] $\nu_{max.}$ (CH_2Cl_2) 3500, 1590, 1520, 1330, and 1110 cm.$^{-1}$. Elution with benzene afforded 2-chloro-3-hydroxy-6-nitrobenzaldehyde (15 mg.), obtained as needles from n-hexane, m.p. and mixed m.p. 88—91°, i.r. spectrum ($\nu_{max.}$ 1710, 1585, 1520, 1330, and 1110 cm.$^{-1}$) superimposable on that of an authentic specimen.

Action of Alkali on 2-Chloro-3-hydroxy-6-nitrobenzaldehyde.—A solution of 2-chloro-3-hydroxy-6-nitrobenzaldehyde (203 mg.) in 5% sodium hydroxide (20 ml.) was set aside for 1 hr. Acidification and extraction with chloroform (3 × 80 ml.) afforded an oil (115 mg.). A solution of the oil in n-hexane deposited yellow needles (38 mg.) of 2-chloro-4-nitrophenol, m.p. and mixed m.p. 110—112°.

[3,5,7-$^2H_3$]*Tropolone.*—To a solution of tropolone (5 g.) in 4N-hydrochloric acid (50 ml.) was added 50% aqueous sodium hydroxide (300 ml.). The precipitated sodium salt was collected, washed with water (2 × 25 ml.), and recrystallised from aqueous ethanol. It was rigorously dried over phosphorus pentoxide at 110° *in vacuo*.

A suspension of the sodium salt (4·5 g.) in deuterium oxide (15 ml.) was heated at 150° for 8 days in a sealed hard-glass tube. The contents of the tube were treated successively with conc. hydrochloric acid (3 ml.) and water (150 ml.). Extraction with ether (5 × 100 ml.) afforded a solid (3·81 g.). A portion was recrystallised from n-hexane, to give colourless needles of [3,5,7-$^2H_3$]*tropolone*, m.p. 50—51°, undepressed on admixture with tropolone, $\nu_{max.}$ (CS_2) 1370, 1290, 1270, 1220, 1090, 970, 940, 880, and 810 cm.$^{-1}$; n.m.r. (MeCN) τ 0·8 (1H) and 2·7 (2H). The bulk of the trideuteriotropolone was used without further purification.

2-*Chloro*[3,5,7-$^2H_3$]*tropone.*—A solution of [3,5,7-$^2H_3$]-tropolone (3·61 g.) and thionyl chloride (3·56 g.) in benzene (75 ml.) was boiled under reflux for 1·5 hr. Distillation of the solvent left a solid (3·73 g.) which was extracted with hot light petroleum (b.p. 40—60°) (1 l.). The cooled extract afforded pale yellow needles (2·6 g.) of 2-*chloro*-[3,5,7-$^2H_3$]*tropone*, m.p. 63—64°, undepressed on admixture with 2-chlorotropone. Evaporation of the mother-liquors and chromatography of the residue on alumina (20 g.; Woelm activity III) gave a further crop of 2-chloro-[3,5,7-$^2H_3$]tropone (700 mg.), $\nu_{max.}$ (CS_2) 1370, 980, 960, 920, and 780 cm.$^{-1}$; n.m.r. (MeCN) τ 3·05 and 3·35; comparison with an integrated spectrum of a standard solution of dioxan showed two protons per molecule of the tropone.

Nitration of 2-*Chloro*[3,5,7-$^2H_3$]*tropone.*—To a solution of the tropone (1·93 g.) in acetic acid (10 ml.) was added a solution of nitric acid (10 ml.) in acetic acid (5 ml.). After 1·5 hr., the temperature of the reaction mixture rose to 60° and nitrous fumes were evolved. The solution was then cooled in ice, left for 1 hr., diluted with ice–water (100 ml.), and extracted with chloroform (6 × 50 ml.). Evaporation of the combined and dried extracts, and distillation of benzene (100 ml.) from the residue obtained gave a solid (1·19 g.). Chromatography on silica gel (60 g.) and elution with 50% light petroleum–benzene gave an oil (47 mg.) which was discarded. Elution with 15% light petroleum–benzene afforded a solid (207 mg.), which was recrystallised from benzene–hexane. 2-*Chloro-4,7-dinitro*[3,5-$^2H_2$]*tropone* was thereby obtained as yellow needles, m.p. 147—148°, undepressed on admixture with a specimen of 2-chloro-4,7-dinitrotropone, $\nu_{max.}$ (CH_2Cl_2) 2300, 1640, 1550, 1330, 1010, and 830 cm.$^{-1}$; n.m.r. (MeCN) τ 3·2 (singlet).

Elution with benzene afforded a yellow solid (450 mg.) which was recrystallised from carbon tetrachloride. 2-*Chloro-7-nitro*[3,5-$^2H_2$]*tropone* was thereby obtained as pale yellow needles (362 mg.), m.p. 121—122°, undepressed on admixture with 2-chloro-7-nitrotropone, $\nu_{max.}$ (CH_2Cl_2) 1640, 1540, 1500, 1360, 1090, 1010, and 820 cm.$^{-1}$; n.m.r. (MeCN) singlets at τ 2·5 (1H) and 3·1 (1H).

Rearrangement of 2-Chloro-7-nitrotropone with Copper Sulphate in Deuterium Oxide.—A solution of the tropone (243 mg.) and copper sulphate (0·5 g.) in a mixture of deuterium oxide (10 ml.) and dioxan (2 ml.) was boiled under reflux for 3 hr. The cooled solution was extracted with ether (5 × 20 ml.), to give an oil (134 mg.). Chromatography on silica gel (5 g.) and elution with benzene gave 4-chloro-3-hydroxy-2-nitrobenzaldehyde (91 mg.). Recrystallisation from benzene–hexane afforded a pure specimen, m.p. 176—177°, whose i.r. spectrum was superimposable on that of an authentic specimen.

Rearrangement of 2-*Chloro-7-nitro*[3,5-$^2H_2$]*tropone with Copper Sulphate.*—A solution of the tropone (242 mg.) and copper sulphate (2 g.) in water (20 ml.) and dioxan (2 ml.) was boiled under reflux for 3 hr. Work-up in the manner described in the above experiment afforded 4-*chloro-3-hydroxy-2-nitro*[5-^2H]*benzaldehyde* (75 mg.) as pale yellow needles from benzene–hexane, m.p. 176—177°, undepressed on admixture with a specimen of the undeuteriated aldehyde, $\nu_{max.}$ (CH_2Cl_2) 1700, 1590, 1530, 1330, 1110, and 1030 cm.$^{-1}$; n.m.r. (MeCN) singlets at τ +0·4 (1H) and 2·9 (1H).

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