109. Tropone and Its Derivatives. VIII. On the Reaction of Halotropones.

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The authors have previously reported¹⁾ that the oxidation of the hydrochlorides of 2-hydrazinotropone (I) ($A: X_1 = \text{NHNH}_2$, $X_2 = \text{H}$) and of 7-bromo-2-hydrazinotropone (II) ($A: X_1 = \text{NHNH}_2$, $X_2 = \text{Br}$) with aqueous solution of cupric sulfate resulted in the substitution of the hydrazino group with chlorine and 2-chlorotropone (III) ($A: X_1 = \text{Cl}$, $X_2 = \text{H}$) and 7-bromo-2-chlorotropone (IV) ($A: X_1 = \text{Cl}$, $X_2 = \text{Br}$)

(A)

- I : $X_1 = \text{NHNH}_2$, $X_2 = \text{H}$
II : $X_1 = \text{NHNH}_2$, $X_2 = \text{Br}$

- III : $X_1 = \text{Cl}$, $X_2 = \text{H}$
IV : $X_1 = \text{Cl}$, $X_2 = \text{Br}$
V : $X_1 = \text{Br}$, $X_2 = \text{H}$
VI : $X_1 = \text{NHC}_6\text{H}_4\text{CH}_3$ (p), $X_2 = \text{H}$
VII : $X_1 = \text{SC}_6\text{H}_4\text{CH}_3$ (p), $X_2 = \text{H}$
VIII : $X_1 = \text{I}$, $X_2 = \text{H}$
IX : $X_1 = \text{H}$, $X_2 = \text{H}$
X : $X_1 = \text{Br}$, $X_2 = \text{Br}$
XI : $X_1 = \text{CN}$, $X_2 = \text{H}$

were obtained in a good yield. It had also been found by the present authors²⁾, and by Cook, et al.³⁾ that 2-chlorotropone (III) could also be obtained, although in a poor yield, by the application of thionyl chloride to tropolone. Later, the present authors obtained several kinds of halotropones by the decomposition of various hydrazino derivatives, and their properties and their reactions with cuprous cyanide, sodium compounds of acetoacetic ester, and of malonic ester were examined, which are described in the following.

Addition of the suspension of 2-hydrazinotropone (I) in hydrogen bromine solution (sp. gr. 1.41) to the boiling aqueous solution of cupric sulfate results in instant decomposition with vigorous generation of nitrogen. Extraction of the cooled reaction mixture with benzene, and sublimation of the residue under a reduced pressure yield 2-bromotropone (V) ($A: X_1 = \text{Br}$, $X_2 = \text{H}$) as colorless needles, m.p. 61–62° (Anal.⁴⁾ Calcd. for $\text{C}_7\text{H}_6\text{OBr}$: C, 45.40; H, 2.72. Found: C, 45.08; H, 3.10).

This substance, when admixed with 2-chlorotropone (III), m.p. 66–67°, showed no depression of the melting point, melting at 62–64°. Refluxing of (V) in cyclohexane with p-toluidine yields 2-p-

toluidinotropone (VI)⁵⁾, and treatment of (V) with the sodium salt of p-thiocresol gives 2-p-tolylmercaptotropone (VII)⁶⁾. These and analytical values confirm (V) to be 2-bromotropone.

Cook, and the others³⁾ obtained colorless leaflet crystals, m.p. 117–119°, by the application of phosphorus tribromide to tropolone, and described this compound as 2-bromotropone. However, this substance is distinctly different from the same substance obtained by the present authors and this point will require further examination.

Oxidative decomposition of hydrazino derivatives can also be carried out with ferric salts, such as ferric sulfate, besides cupric sulfate.

The same treatment of hydriodide of 2-hydrazinotropone (I) yields a small amount of 2-iodotropone (VIII) (A : X₁=I, X₂=H) as colorless granular crystals, m.p. 71–72°, and a fair amount of tropone (IX) (A : X₁=H, X₂=H).

The same treatment of 7-bromo-2-hydrazinotropone (II) hydrobromide yields 2,7-dibromotropone (X) (A : X₁=Br, X₂=Br) as colorless plates, m.p. 170–171°, which can also be obtained by the bromination⁷⁾ of tropone (IX) (Anal. Calcd. for C₇H₄OBr₂ : C, 31.83 ; H, 1.53. Found : C, 31.68 ; H, 1.28).

Passage of hydrogen chloride gas through the respective benzene solutions of 2-chlorotropone (III) and 2-bromotropone (V) precipitates their respective hydrochlorides which are both extremely hygroscopic, and addition of water to the salts liberates (III) and (V). 7-Bromo-2-chlorotropone (IV) and 2,7-dibromotropone (X) do not give a hydrochloride. The respective picrates of (III) and (V) are very unstable and liberate (III) and (V) during recrystallization. Addition of the ethanolic solution of silver nitrate to the ethanolic solution of (III) does not produce turbidity, but the precipitate of silver bromide occurs in the case of (V). In this case, bromine atom is seen to be more easily substituted than chlorine atom. Such is also the case in the reaction of these compounds with cuprous cyanide. Heating of 2-chlorotropone (III) with the cyanide at 170° does not induce any reaction, (III) being recovered, but 2-bromotropone (V) reacts with the cyanide when heated at 130°, and sublimation of the reaction product at 150° under 4 mm. pressure yields 2-cyanotropone (XI) (A : X₁=CN, X₂=H) as pale yellow needles, m.p. 138–139° (decomp.) (Anal. Calcd. for C₈H₅ON : C, 73.29 ; H, 3.84 ; N, 10.68. Found : C, 72.86 ; H, 3.36 ; N, 10.96).

Treatment of 7-bromo-2-chlorotropone (IV) with sodium hydroxide in dil. alcohol, at a room temperature, chiefly yields o-chlorobenzoic acid (XII) and 3-chloro-2-hydroxybenzaldehyde⁸⁾ (XIV), accompanied by a very minute amount of 3-bromotropolone (XIII).

From the experimental fact described above, it may be assumed that this reaction takes place as illustrated in the following schema.

The route (1) in the above schema is the well-known rearrangement in which the carbon in the carbonyl group (C_1) is attacked by the hydroxyl ion and, passing through an intermediate (B_1), and o-chlorobenzoic acid (XII) is formed with the liberation of Br anion. In the course (2), C_3 is attacked, by which, passing through the intermediate (B_2), 3-bromotropolone (XIII) is formed by the liberation of Cl anion. In the course (3), the attack of hydroxyl ion is assumed to occur at C_7 but, contrary to expectation, 3-chlorotropolone is not formed in this case and 3-chloro-2-hydroxybenzaldehyde (XIV) results. The reason for such a behavior is assumed to lie in the steric interference occurring due to the larger bromine atom in the intermediate (B_3) initially formed. In such a case, the tropone nucleus would slip out of its coplanar structure and the conjugation through $C_1, C_2, \dots, C_7$ would be weakened and consequently the negative charge of the polarized carbonyl may directly attack the C_6 situated at favorable position, whose hydrogen atom is expelled as the hydride ion. In this case, C_7 is positively charged by the severance of its bond with C_1 , at the same time becomes an acceptor of the hydride ion, and thereby the rearrangement to (XIV) occurs smoothly.

2-Chlorotropone (III) reacts easily with the sodium compound of ethyl acetoacetate in benzene solution and yellow scales (XV), m.p. 206–207° (decomp.), are obtained in a good yield (Anal. Calcd. for $C_{11}H_8O_3$: C, 70.20; H, 4.29. Found: C, 69.42; H, 3.94. Ultra-

violet absorption spectrum⁹⁾ in methanol: λ max., $[\log. \epsilon]$; 220 $m\mu$ [4.43], 248 $m\mu$ [4.18], 273 $m\mu$ [4.33], 418 $m\mu$ [4.26]). (XV) fails to give any coloration with ferric chloride, does not generate carbon dioxide from sodium bicarbonate, and sublimes in diminished pressure without any change. It gives a positive iodoform test, and gives an oxime of orange scales, m.p. 204–205° (decomp.) (Anal. Calcd. for $C_{11}H_9O_3N$: N, 6.89. Found: N, 6.81), a phenylhydrazone of violet scales, m.p. 164–166° (decomp.) (Anal. Calcd. for $C_{17}H_{14}O_2N_2$: C, 73.36; H, 5.07; N, 10.07. Found: C, 73.55; H, 5.14; N, 10.13), a semicarbazone of red scales, m.p. 240–245° (decomp.). From these results, this compound (XV) is assumed to possess the structure shown in (C).

Heating of (XV) with conc. hydrochloric acid results in a violet solution, which turns green upon standing the solution after correcting its reaction to pH 8 with sodium bicarbonate. Acidification of this solution yields a green precipitation. This is probably due to the scission of the lactone ring in (C) by the acid which undergoes condensation in a weak alkaline medium to the green (D), corresponding to a azulene derivative. This can probably be led to the azulene which fact is now being studied.

Treatment of 2-chlorotropone (III) with the sodium compound of ethyl malonate in ether solution yields yellow scales (XVI), m.p. 129–130° (Anal. Calcd. for $C_{12}H_{10}O_4$: C, 66.02; H, 4.62. Found: C, 65.82; H, 4.26). Treatment of (XVI) with methanolic ammonia at a room temperature gives what can be assumed as an amide of

yellow scales, m.p. 203–204° (decomp.) (Anal. Calcd. for $C_{10}H_7O_3N$: N, 7.45. Found: N, 6.84). (XVI) is assumed to be analogous to (XV), and to possess a structure as shown by (E). The mechanism of the formation of such a compound could be assumed to pass through an intermediate (F) in which the strongly negatively charged oxygen of the carbonyl, that is the characteristic of the

tropone nucleus, expels the ethoxyl of the ester group in the neighboring and favorable position as an ethoxide ion. This results in the facile formation of the lactone ring and (C) and (E) are thereby formed.

The parent skeleton (G) may be stabilized by the contribution of ionic structures which would be interesting in connection with sydnone¹⁰⁾ which has attracted much attention lately.

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