95. Studies on Tropolone Derivatives. X. On *p*-Aminotropolone (II).¹⁾

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A brief report has already been made on *p*-aminotropolone (I) by the present authors¹⁾²⁾. Further reactions were carried out on this substance and comparisons were made with aryl amines results of which are described briefly in the following.

Bromination of (I) in ethanol does not yield a crystalline substance but the bromination of *p*-acetylaminotropolone (IIa)²⁾ yields its monobromo derivative (A), m.p. 201–204° (Anal. Calcd. for $C_9H_8O_5NBr \cdot C_2H_5OH$: C, 43.43; H, 4.64. Found: C, 43.77; H, 4.42)³⁾. Treatment of (A) with acetic anhydride gives a diacetate, m.p. 166–167°, which shows no depression of the melting point when fused with the diacetate⁴⁾ of *p*-amino-*o*-bromotropolone obtained previously from *o*-bromotropolone via the azo compound. Bromination of the diacetate (IIb) of (I) in chloroform also gives the same substance (A) as recrystallized from ethanol. In these cases, therefore, bromine is seen to enter the ortho position.

Nitration of (I), (IIa), (IIb) and the methyl ether (IIc)²⁾ of (II) by the application of 1 or 2 moles of nitric acid to their acetic acid solution resulted in the formation of a purplish black resinous substance with a very small amount of the recovery of unreacted substances. Nitration of these compounds in conc. sulfuric acid also ended in the recovery of unreacted substances.

Benzoylation of (I) by the Schotten-Baumann method gave *N*-benzoyl-*p*-aminotropolone, as colorless scales, m.p. 181–182° (Anal. Calcd. for $C_{14}H_{11}NO_5$: C, 69.69; H, 4.59; N, 5.81. Found: C, 69.40; H, 4.36; N, 5.64).

Condensation of (I) in a mixture of ethanol and acetic acid with various aryl aldehydes, such as benzaldehyde, salicylaldehyde, anisaldehyde, vanillin and *p*-nitrobenzaldehyde, did not proceed easily, only *p*-nitrobenzaldehyde alone giving a condensation product⁵⁾. *p*-Nitrobenzylidene derivative: m.p. 202–204° (decomp.) (Anal. Calcd. for $C_{14}H_{10}O_4N_2$: N, 10.37. Found: N, 10.41). This condensate gives red coloration to the organic solvent layer with ferric chloride, is insoluble in water and is easily hydrolyzed by the heating of its aqueous solution.

Diazotization of (I) in conc. sulfuric acid, followed by dilution

with water and heating to 80° yields p-hydroxytropolone (III), as yellow needles, m.p. 251° (decomp., blackening at 245°). (Anal. Calcd. for $C_7H_6O_2$: C, 60.87; H, 4.38. Found: C, 60.25; H, 4.27). (III) is soluble in acetone, ethanol and acetic acid, insoluble in benzene and ether, and is sublimable (5 mm.-Hg; bath temperature, 170 – 180°). It gives water-insoluble yellow sodium salt, purplish black ferric complex salt, and yellow copper complex salt. These salts do not melt even above 350° . Heating (III) with acetic anhydride and treatment with water gives an acetyl derivative as yellow scales, m.p. 87 – 88° which colors red with ferric chloride. (Anal. Calcd. for $C_9H_8O_4$: C, 59.99; H, 4.48. Found: C, 59.40; H, 3.99).

For the elimination of the amino group in the para position, (I) was diazotized in ethanol and heated to 70° but unexpectedly, the product proved to be p-ethoxytropolone, colorless needles, m.p. 135.0 – 135.5° . (Anal. Calcd. for $C_9H_{10}O_3$: C, 65.06; H, 6.06. Found: C, 65.05; H, 5.69). This compound is soluble in ethanol, acetone, ether and benzene and is insoluble in petroleum ether. It gives yellow sodium salt and yellowish green copper complex. The organic solvent layer colors red with ferric chloride.

The formation of halogen derivatives from (I) by the Sandmeyer reactions has been reported previously¹⁾, but by subsequent examination it has become necessary to correct the melting point of p-chloro and p-iodo compounds in the previous report. p-Chlorotropolone, m.p. 181.5 – 183° . (Anal. Calcd. for $C_7H_5O_2Cl$: C, 53.73; H, 3.22. Found: C, 53.63; H, 3.21). p-Iodotropolone, m.p. 185 – 186° , which liberates iodine when left in air. (Anal. Calcd. for $C_7H_5O_2I$: C, 33.90; H, 2.03. Found: C, 33.73; H, 2.56).

Treatment of (I) and phenylisothiocyanate in ethanol gives p-phenylthiocarbamylaminotropolone (IV), i.e. N-phenyl-N'-p-tropolonyl-thiourea, as yellow prisms, m.p. 150 – 151° (decomp.). (Anal. Calcd. for $C_{14}H_{12}O_2N_2S$: C, 61.76; H, 4.41. Found: C, 61.66; H, 4.60).

(IV) $X = C_6H_5NHCS-$

(V) $X = CH_3CONHC_6H_4SO_2-$

(VI) $X = C_6H_2(NO_2)_3-$

Application of p-acetylaminobenzenesulfonyl chloride to (I) in pyridine yields p-(p-acetylaminophenylsulfamino)-tropolone (V), as yellow needles, m.p. 224 – 225° (decomp.) (Anal. Calcd. for $C_{15}H_{14}O_5NS_2$: C, 53.88; H, 4.22. Found: C, 54.30; H, 3.89.).

Application of methyl iodide to (I) in methanol in the presence of potassium carbonate gives a compound assumed to be p-dimethylaminotropolone methiodide (i.e. p-tropolonyltrimethylammonium iodide) as pale yellow scales, m.p. 215–218°. Application of picryl chloride to (I) in methanol in the presence of sodium acetate gives p-picrylamino tropolone (VI) as reddish orange scales, m.p. 249–251° (decomp.). (Anal. Calcd. for $C_{13}H_5O_3N_4$: N, 16.09. Found: N, 16.07).

For comparison with aryl amines, reaction of (I) with urea, nitrourea, carbon disulfide and dicyandiamide, was attempted but all ended in the recovery of (I).

The aqueous solutions of alkali salts of (I) rapidly colors reddish brown when left in air. Hydrochlorides of (I) are obtained in various compositions. A substance (B), m.p. 223–224° (decomp.), obtained by the addition of the excess of hydrochloric acid to (I) and evaporated to small volume, is assumed from its analytical values to be a complex of p-aminotropolone and hydrochloric acid in 2:3 molar ratio. (Anal. Calcd. for $2C_7H_5O_3N \cdot 3HCl$: C, 43.82; H, 4.46. Found: C, 44.30; H, 4.78.) The crystals of m.p. 115–117° obtained by the addition of hydrochloric acid to the aqueous solution of the sodium salt of (I) to pH 5 shows the composition of 1:1:1 molar ratio of p-amino-tropolone, hydrochloric acid and water. (Anal. Calcd. for $C_7H_5O_3N \cdot HCl \cdot H_2O$: C, 43.87; H, 5.26; N, 7.31. Found: C, 43.60; H, 4.92; N, 7.18). Besides the above, some crystals showing m.p. 180–185° are also obtained but its composition is still undetermined.

In order to obtain thiourea derivatives, potassium thiocyanate was applied to (B) and yellow needles of m.p. 128–130° were obtained but from its analytical values, this is assumed to be a peculiar rhodanate of p-aminotropolone. (Anal. Calcd. for $2C_7H_5O_3N \cdot HSCN \cdot H_2O$: C, 51.25; H, 4.84; N, 11.96; HSCN, 16.7. Found: C, 51.33; H, 4.92; N, 12.10; HSCN (gravimetric determination as AgSCN), 17.6).

In short, p-aminotropolone behaves to some extent like aryl amines such as aniline and gives halogen and hydroxyl compounds by diazotization but their yield is rather poor. Condensation with aryl aldehyde is decidedly difficult and the condensate is very easily hydrolyzed. It also differs from aryl amines in that it hardly reacts with urea, etc.

These facts may be explained by the assumption that the basicity of p-aminotropolone decreases due to the resonance contribution of ionic structure (X_2). Moreover, the presence of tautomeric imino-form (Y) may be possible.

No definite confirmation has been obtained as to the presence of a substance corresponding to p-tropoquinone³⁾ structure proposed in the case of hinokitiol.

Very recently, Cook and the others⁹⁾ reported on the formation of γ (or p)-aminotropolone and γ (or p)-hydroxytropolone, which seem to be identical with (I) and (III) obtained by the present authors. These facts prove the advisability of making some specific regulation as to the nomenclature of substituent positions in tropolone nucleus.

The fact that p-aminotropolone forms a special kind of hydrochlorides and rhodanate should be worthy of notice together with the formation of a specific complex compounds during bromination of tropolone¹⁰⁾.

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- 4) T. Nozoe, Y. Kitahara, K. Yamane, and A. Yoshikoshi, *Proc. Japan Acad.*, **27**, 18 (1951).
- 5) Reaction with benzaldehyde is very difficult, only once a product of m.p. 127–128° was obtained.
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