44. Anionoid Substitution of 3-Bromotropolone¹⁾²⁾

By Tetsuo NOZOE and Yoshio KITAHARA

Chemical Institute, Faculty of Science, Tôhoku University, Sendai, Japan

(Comm. by R. MAJIMA, M.J.A., March 12, 1954)

Halotropolones, differing from halotropones, are in general stable to alkalis and other anionoid reagents unless under somewhat drastic conditions and resemble, in this respect, the aromatic halogen compounds. 3-Bromotropolone remains unchanged when heated in 2N aqueous sodium hydroxide solution but when reacted with alkali under more drastic conditions, it gives a hydroxy compound³⁾⁴⁾ and forms a cyano compound⁴⁾⁵⁾ by cuprous cyanide. Application of alkali sulfides and mercaptides results in comparatively facile displacement to give various mercaptotropolones.⁶⁾

It seemed of interest, therefore, to carry out the studies on the anionoid substitution of various bromotropolones, which do not undergo rearrangement as does halotropones, not only from the point of preparative application but also in examining the aromaticity of tropolones. The present paper describes the substitution of the most easily available 3-bromotropolone⁷⁾ (I, A: X=Br) with various anionoid reagents.

Some time ago, the writers reported³⁾ that when (I) is heated at 130–140° with 75% aqueous potassium hydroxide solution, it is converted to 3-hydroxytropolone (II, A: X=OH), m.p. 226–227°. Cook and others⁴⁾ isolated hydroxytropolone (III), m.p. 244° (decomp.), by using 50% aqueous sodium hydroxide solution. Since the alkali fusion of (III) gave salicylic acid, they also gave the structure of 3-hydroxytropolone (A: X=OH) to (III).

In the ultraviolet spectrum of (II), there can be found none of the fine structures in the longer wave length region (360–385 m μ) that are attributed to the hydrogen bond formation in the two hydroxyl groups and which appear in the ultraviolet spectrum of 7-hydroxyhinokitiol.⁸⁾ These fine structures rather appear in one of the products, 3-hydroxytropolone (IV),⁹⁾ m.p. 137°, of the persulfate oxidation of tropolone carried out later, that some doubts arose as to the authenticity of the structure of (II).

(I) was therefore reacted with aqueous potassium hydroxide solution, under conditions previously described, the product was sublimed, and the sublimate was separated into the benzene-soluble

and insoluble portions. The benzene-soluble portion yielded a minute

Fig. 1. Ultraviolet absorption spectra in methanol

- (a) 7-Hydroxyhinokitiol
- (b) 4-Hydroxytropolone (VI)
- (c) 4-Methoxytropolone (VII)
- (d) Dichlorotropone (VIII)

amount of colorless needles (V), m.p. 138.3–139.5° (from benzene-ethanol). Repeated recrystallization of the benzene-insoluble portion from acetic acid yielded a hydroxytropolone (VI) as colorless micro needles, m.p. 230–231°. No depression in the melting point occurred on admixture of (V) and 3-hydroxytropolone (IV), but the mixed fusion of (VI) and (II) gave an intermediate melting point, while a definite depression in the melting point occurred with (VI) and 5-hydroxytropolone,⁹⁾ m.p. 245° (decomp.).

(VI) was methylated with diazomethane and the oily mixture

of the dimethyl ethers thereby obtained was submitted to rearrangement reaction with sodium methoxide in absolute methanol but no rearrangement product was obtained, only giving a methoxytropolone (VII) as colorless scales, m.p. 95.5–96° (from methanol) (Anal. Calcd. for $C_9H_8O_3$: C, 63.15; H, 5.30. Found: C, 62.95; H, 5.65). (VII) gives red coloration in the ether layer with ferric chloride solution and shows depression of the melting point when admixed with 3- or 5-methoxytropolone.⁹⁾

Refluxing of (VI) with thionyl chloride in benzene for 5 hours gives, besides the recovered (VI), dichlorotropone (VIII), as colorless prisms, m.p. 67.5–68° (from cyclohexane-petroleum ether) (Anal. Calcd. for $C_7H_4OCl_2$: C, 48.03; H, 2.30. Found: C, 48.50; H, 2.17). Heating of (VIII) with 2N aqueous sodium hydroxide solution gives m-chlorobenzoic acid¹⁰⁾ as colorless scales, m.p. 149.5–150°. This indicates that (VIII) should be 2,6- or 2,4-dichlorotropone, and (VI), 4-hydroxytropolone (B: X=OH). Reexamination of the method of Cook and others⁴⁾ chiefly gave (VI).

It has already been reported⁴⁾⁵⁾ that the application of cuprous cyanide to (I) gives 3-cyanotropolone (A: X=CN), m.p. 175°. When the potassium salt of (I) is heated with potassium cyanide and absolute methanol in a sealed tube for 7 hours at 140–150° and the product purified through chromatography on silica gel as a benzene solution, besides unchanged (I), a cyanotropolone (IX) is obtained in

10-15% yield as pale yellow, fiber-like crystals, m.p. 191-193° (from benzene) (Anal. Calcd. for $C_8H_5O_2N$: N, 9.52. Found: N, 9.24). (IX) gives carboxytropolone (X), m.p. 217-218°, when heated with 75% sulfuric acid solution for 30 minutes at 150°. Both (IX) and (X) gave depression of the melting point on respective admixture with 3-cyanotropolone,⁵⁾ m.p. 174-175°, and 3-carboxytropolone,⁵⁾ m.p. 218-219° (decomp.). (X) was found by mixed fusion to be identical with 4-carboxytropolone,¹¹⁾ obtained by the decarboxylation of the anhydride of 3,4-dicarboxytropolone.¹¹⁾ It follows, therefore, that (IX) is 4-cyanotropolone (B: X=CN).

When (I) is heated in a sealed tube with sodium methoxide in absolute methanol at 140-150° for 20 hours, 3-hydroxy compound (V) is chiefly formed with a very small amount of 3-methoxytropolone⁹⁾ (XI), m.p. 79-80°. Even with the use of a well-purified methanol, (V) is chiefly formed in general.

When the copper complex salt (XII) of (I) is heated with cupric acetate in pyridine at 125-130° (bath temp.) for 20 hours, and the

copper complex formed is decomposed with hydrogen sulfide, 3-hydroxytropolone (V), is chiefly obtained, with a very minute amount of colorless prisms (XIII), m.p. 45.5-46°.

When (XII) and the potassium salt of phenylsulfonic amide is heated in pyridine at 135-140° (bath temp.) for 5 hours, phenylsulfonylamidotropolone (XIV) is obtained as pale yellow plates, m.p. 181-182° (from chloroform), in 70% yield (Anal. Calcd. for $C_{13}H_{11}O_4NS$: N, 5.05. Found: N, 5.32). On being heated with conc. sulfuric acid at 70°, (XIV) is easily converted into aminotropolone (XV) as yellow scales, m.p. 87-88° (from methanol), in almost quantitative yield (Anal. Calcd. for $C_7H_7O_2N$: N, 10.22. Found: N, 10.34). Picrate: Yellow prisms, m.p. 170.5-171°.

Some time ago, Cook and others¹²⁾ applied nitrous acid gas through the petroleum ether solution of tropolone and carried out catalytic hydrogenation of 3-nitrotropolone (XVI), thereby obtained in a small

Fig. 2. Ultraviolet absorption spectra in methanol
(a) 3-Cyanotropolone
(b) 4-Cyanotropolone (IX)
(c) 4-Carboxytropolone (X)

amount, from which they obtained 3-aminotropolone (XVII), m.p. 86° (micro method). The present writers also obtained 3-aminotropolone by the same manner and the mixed fusion of this 3-amino compound and (XV) failed to show any depression of the melting point. It follows, therefore, that (XIV) and (XV) are 3-substituted compounds. It had heretofore been found that azo coupling, nitra-

Fig. 3. Ultraviolet absorption spectra in methanol

- (a) 3-Phenylsulfonylamidotropolone (XIV)
(b) 3-Aminotropolone (XV)

tion, and nitrosation of tropolone chiefly occurred in the para(or 5)-position that 3-aminotropolone had been difficult to obtain but the present series of experiments have shown the easy way of getting this compound.

When (I) is heated with diethyl sodiomalonate in a small amount of methanol, in the presence of 4% cupric acetate, at $135-140^{\circ}$, and the product hydrolyzed with diluted sulfuric acid, some crystals (XVIII) of m.p.

$108-109^{\circ}$ are obtained (Anal.¹³) Found: C, 63.12; H, 5.65. U.V. max. of (XVIII) in methanol: 245, 325, 365 and $374\text{ m}\mu$. (XVIII) does not give any coloration in the ether or benzene layer but gives green coloration in the water layer with ferric chloride solution, and its alkaline hydrolysis for 8 hours failed to give any substance which gives red coloration with ferric chloride. The structure of (XVIII) will be reported later.

From the foregoing reactions, the reactivity of 3-bromotropolone lies in the intermediate stage between that of halobenzenes and alkyl halides, and corresponds to that of activated halobenzenes. The activation factor of this reaction is assumed to be the polarization of the carbonyl in tropolone.

Grateful acknowledgement is extended to Messrs. Kôzô Doi and Kahei Takase for their coöperation in these experiments.

References

- 1) The authors are indebted to Grant in Aid for Fundamental Scientific Research of the Ministry of Education and to Takasago Perfumery Co., Ltd. and Sankyô Co., Ltd. for financial support.
- 2) This work was presented at Symposium on Tropolone and Allied Compounds held by the Chemical Society of Japan in Tokyo, February 6, 1954.

- 3) T. Nozoe, Y. Kitahara, and S. Masamune: *Proc. Japan Acad.*, **27**, 649 (1951).
- 4) B. J. Abadir, J. W. Cook, J. D. Loudon, and D. K. V. Steel: *J. Chem. Soc.*, 2350 (1952).
- 5) T. Nozoe, Y. Kitahara, and S. Masamune: *Proc. Japan Acad.*, **29**, 17 (1953).
- 6) T. Nozoe, M. Satô, and K. Matsui: *Sci. Repts. Tôhoku Univ., First Ser.*, **37**, 211 (1953).
- 7) T. Nozoe, S. Seto, Y. Kitahara, M. Kunori, and Y. Nakayama: *Proc. Japan Acad.*, **26**, (7) 38 (1950).
- 8) T. Nozoe, Y. Kitahara, and K. Doi: *Ibid.*, **27**, 282 (1951).
- 9) T. Nozoe, S. Seto, S. Itô, M. Satô, and T. Katôno: *Sci. Repts. Tôhoku Univ., First Ser.*, **37**, 191 (1953).
- 10) W. Glund and R. Kempf: *J. Chem. Soc.*, **103**, 1530 (1913).
- 11) W. D. Crow, R. D. Haworth, and P. R. Jefferies: *Ibid.*, 3705 (1952).
- 12) J. W. Cook, J. D. Loudon, and D. K. V. Steel: *Chem. & Ind.*, 669 (1951).
- 13) Microanalyses were carried out by Mr. Onoe of the Sankyô Co., Ltd. (Tokyo) and by Miss Katô of this laboratory, to whom the authors express their gratitude.