The Synthesis of 4-Aminotropone

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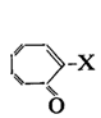
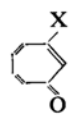
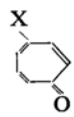
Tropolone[1] (I) and its isomers, 3-hydroxytropone[2] (II) and 4-hydroxytropone[3] (III) have been synthesized and their reactions have also been investigated. The amino homologues, of tropolones, 2-aminotropone[1] (IV) and derivatives, have already been synthesized and their reactions have been studied in detail. The isomeric 3-aminotropone (V) and 4-aminotropone (VI), on the other hand, have sofar not been prepared. The present communication deals briefly with the synthesis of the 4-isomer VI starting from 4-aminotropolone[4] (VII).



I: X=OH IV: X=NH_2

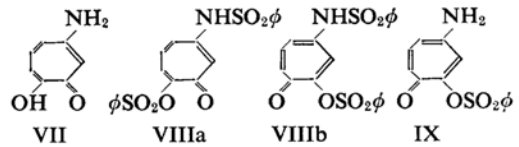


II: X=OH V: X=NH_2



III: X=OH VI: X=NH_2

Reaction of 4-aminotropolone sulfate and *p*-toluenesulfonyl chloride in pyridine afforded, with company of a di-*p*-toluenesulfonate (VIII), 4-amino-2-*p*-toluenesulfoxytropone (IX), of which hydrogenolysis[5] over 5% palladized charcoal gave easily 4-aminotropone (VI).



VII VIIIa VIIIb IX

The ultraviolet absorption of the aminotropone VI shows an tropone type of spectrum[6], having maxima at 228 mμ (log ε 4.35), 260 (3.89) and 365 (4.38) (Fig. 1).

The structure of the aminotropone VI is more reasonably assumed from the fact, that its infrared spectrum has two absorption bands,

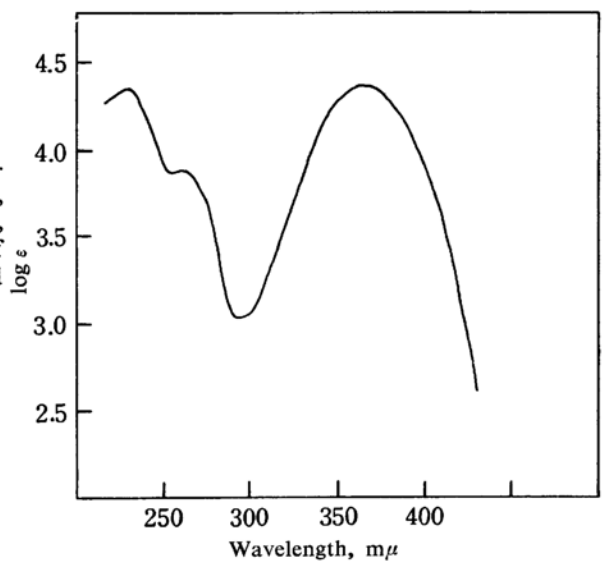


Fig. 1. Ultraviolet absorption spectrum of 4-aminotropone (VI) in methanol.

1) cf. P. L. Pauson, *Chem. Revs.*, 55, 9 (1955).
2) R. B. Johns, A. W. Johnson and M. Tisler, *J. Chem. Soc.*, 1954, 4605; A. W. Johnson and M. Tisler, ibid., 1955, 1841.
3) T. Nozoe, T. Mukai, Y. Ikegami and T. Toda, *Chem. & Ind.*, 1955, 66; R. B. Johns, A. W. Johnson, A. Langemann and J. Murray, *J. Chem. Soc.*, 1955, 309.
4) K. Doi, Abstracts of the 12th Annual Meeting of the Chemical Society of Japan, p. 230 (1959).
5) T. Nozoe, S. Seto, T. Sato and S. Ninagawa (to be published) have found the formation of tropones from 2-*p*-toluenesulfoxytropones with a similar hydrogenolysis procedure.
6) M. Tsuboi, This Bulletin, 25, 369 (1952).

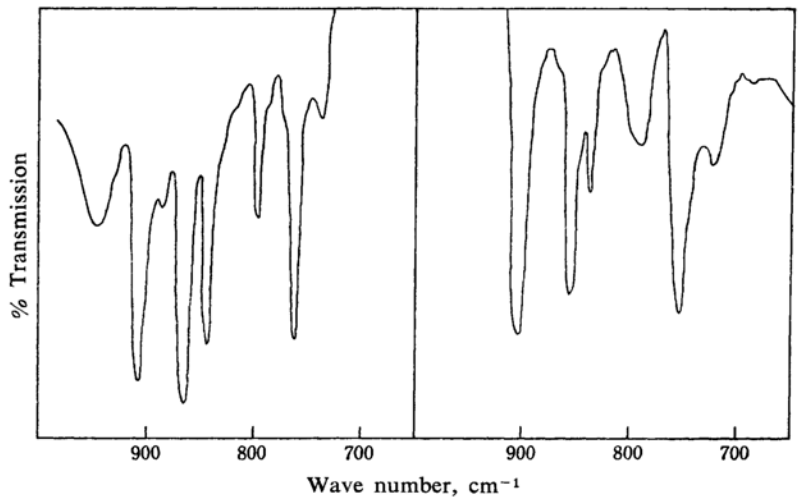


Fig. 2. Infrared absorption spectra of 4-aminotropone (VI, right) and 4-hydroxytropone (III, left).

790 and 903 cm^{-1}, which have been assigned[7] to the bands based on the CH out-of-plane vibrations of 4-substituted tropones. It may support the structural assignment above described, that the infrared spectrum of 4-hydroxytropone[7] (III) has two absorption bands, 797 and 865 cm^{-1}, and the features of the absorption in this region are closely ressembling to that of the aminotropone VI (Fig. 2).

Experimental

4-Amino-2-*p*-toluenesulfoxytropone (IX).—To a stirred solution of 4-aminotropolone sulfate[4] (2 g.) and pyridine (3 cc.), was added *p*-toluenesulfonylchloride (1.9 g.) for 3 min. at room temperature. After 30 min., dilution with water (20 cc.) and subsequent filtration afforded a pale yellow solid (2.6 g.), m. p. 199~200°C (decomp.), of which fractional recrystallization from methanol gave a less soluble product, a di-*p*-toluenesulfonate (VIII, 1.8 g.), m.p. 213°C (decomp.),

Found: C, 56.37; H, 4.54; N, 3.56. Calcd. for $C_{21}H_{19}O_6NS_2$: C, 56.61; H, 4.30; N, 3.14%.

and more soluble product IX (0.12 g.), yellow needles, m. p. 194°C (decomp.).

Found: C, 57.67; H, 4.41; N, 5.00. Calcd. for $C_{14}H_{13}O_4NS$: C, 57.73; H, 4.50; N, 4.82%.

4-Aminotropone (VI).—A mixture of IX (0.3 g.), sodium acetate trihydrate (0.15 g.), 5% palladized charcoal (50 mg.) and methanol (100 cc.) was shaken in the hydrogen atmosphere until absorption of hydrogen ceased. After 8 hr., the catalyst was removed and the filtrate was concentrated in vacuo. The residual solid, after chromatographic purification (ethyl acetate-alumina) followed by crystallization from ethyl acetate, afforded 4-aminotropone (VI, 20 mg.), yellow prisms, m. p. 218°C (decomp.).

Found: C, 69.08; H, 5.83; N, 11.63. Calcd. for C_7H_7ON: C, 69.40; H, 5.83; N, 11.56%.

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7) Y. Ikegami *Kagaku-no-Ryoiki* (*J. Japanese Chem.*), Extra No. 38, p. 33, Nankodo Co., Tokyo (1959).