Synthesis of 3-Aminotropone

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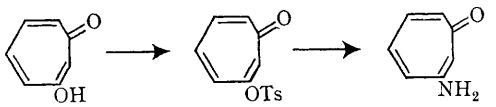
IN the unique troponoid aromatic system, 2-,[1] 3-,[2] and 4-hydroxytropone,[3] 2-[4] and 4-aminotropone[5] are known, which are vinylogues of carboxylic acid and of acid amide. We have synthesised 3-aminotropone (I) and are investigating its properties.

Toluene-*p*-sulphonation of 3-hydroxytropone with toluene-*p*-sulphonyl chloride in dry pyridine at room temperature overnight gave 3-toluene-*p*-sulphonyloxytropone (II) (64%), m.p. 92—92·3°, ν_{max} 1636, 1584, 1374, 1191, 1178, 1074, and 747 cm.$^{-1}$, λ_{max} 227 (log ϵ 4·33) and 298 mμ (3·73). Ammonolysis of (II) in saturated ammonia—methanol solution at 40° for 30 min. followed by chromatographic treatment on alumina gave (I) (57%), m.p. 188° (decomp.), ν_{max} 3340, 3120, 1645, 1580, 1540, 1505, 1480, and 1285 cm.$^{-1}$, λ_{max} 214 (log ϵ 3·87), 262 (4·14), 273 (4·06), 300 (3·45), and 312 mμ (3·42), pK_a 3·46 at 26°. Ammonolysis of (II) in liquid ammonia gave (I) in varying yields. Bromination of (I) in ethanol gave a monobromo-compound, m.p. 182—183° (decomp.), ν_{max} 3360, 3240, 3140, 1635, 1623, 1534, 1492, 1450, and 796 cm.$^{-1}$. Acetylation of (I) gave the *N*-acetyl compound, m.p. 172—173° (decomp.), ν_{max} 1711, 1546 vs, and 1522 vs cm.$^{-1}$.



(II) (I)

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[1] T. Nozoe, S. Seto, Y. Kitahara, M. Kunori, and Y. Nakayama, *Proc. Japan Acad.*, 1950, **26**, 38; J. W. Cook, A. R. Gibbs, R. A. Raphael, and A. R. Somerville, *J. Chem. Soc.*, 1951, 503; R. D. Harworth and J. D. Hobson, *ibid.*, p. 561; V. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, 1950, **72**, 2305; J. D. Knight and D. J. Cram, *ibid.*, 1951, **73**, 4136.

[2] R. B. Johns, A. W. Johnson, and M. Tisler, *J. Chem. Soc.*, 1954, 4605.

[3] T. Nozoe, T. Mukai, Y. Ikegami, and T. Toda, *Chem. and Ind.*, 1955, **66**; R. B. Johns, A. W. Johnson, A. Langemann, and J. Murray, *J. Chem. Soc.*, 1955, 309; R. S. Coffey and A. W. Johnson, *ibid.*, 1958, 1741; J Meinwald and O. L. Chapman, *J. Amer. Chem. Soc.*, 1958, **80**, 633.

[4] T. Nozoe, S. Seto, H. Takeda, S. Morosawa, and K. Matsumoto, *Sci. Reports Tôhoku Univ.*, 1952, **36**, 126; T. Nozoe, T. Mukai, and K. Takase, *ibid.*, 1956, **39**, 164.

[5] K. Doi, *Bull. Chem. Soc. Japan*, 1960, **33**, 887.