

## Syntheses of and a Rearrangement in Tropone-Imine Systems

By D. S. WULFMAN,\* L. N. McCULLAGH, and J. J. WARD†

(Department of Chemistry, University of Missouri-Rolla, Rolla, Missouri, 65401)

**Summary** Tropyl azide (I) can be decomposed to form tropone-imonium azide (III) and *N*-tropylium-imonium azide (II); attempts to convert either salt or the corresponding fluoborates into tropone 2,4-dinitrophenylhydrazone leads to the corresponding benzaldehyde derivative.

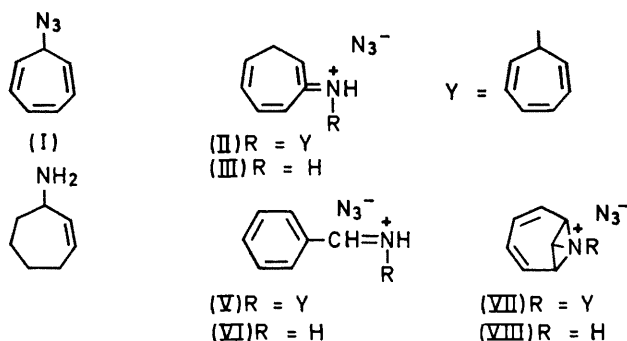
ATTEMPTS to elucidate the structure of an amine  $C_7H_7N$ , derivable from tropylium azide (I), have been complicated by the complexity of the reaction mixtures, low yields, and difficulty in obtaining reproducible results.<sup>1</sup> The compound  $C_{14}H_{14}N_4$  obtained here and that reported in ref. 1 differ in several significant areas;  $^1H$  n.m.r. chemical shift and i.r. spectrum. Usually, vapour-phase photolysis of (I) using low-intensity u.v. sun-lamps furnishes small amounts of a white solid  $C_7H_7N \cdot C_7H_7N_3$  (II) which exhibits  $\lambda_{max}$  (mull) 3.37, 3.42, 3.49, 4.74, 6.90, 7.03, 7.32, 7.98, 8.91, 9.34, 9.57, 11.2, 11.27, and 11.48  $\mu m$ ;  $\lambda_{max}$  (EtOH) 236 ( $\epsilon$  10,000), 287 (2000) 317 (5000), and 325 (5500) nm, and shows a narrow

tropone-imonium fluoborate identical in u.v. and i.r. spectra with a sample prepared by the method of Dauben.<sup>2</sup> The above appears to be consistent with the assignment of *N*-7-cycloheptatrienyltropone-imonium azide (II).

If a solution of (I) containing traces of (II) is allowed to stand several days at  $-20^\circ$ , a copious light tan to brown precipitate (III) forms to the extent of 2–5%. This material had previously been treated by the method of Merling<sup>3</sup> by one of us<sup>4</sup> and also by Looker.<sup>5</sup> Careful washing of (III) with cold pentane or methylene chloride ultimately freed it from traces of (I). This material showed a single structured singlet in the  $^1H$  n.m.r. spectrum ( $CD_3CN$ ) at  $\tau$ 2.35. The i.r. had  $\lambda_{max}$  (mull) 4.9, 6.1, 6.65, 6.7, 8.6 and 12.8  $\mu m$ , and the u.v. showed  $\lambda_{max}$  (EtOH) 236, 316, and 325 nm. Acidification failed to alter the n.m.r. spectrum appreciably. Reduction using  $NaBH_4$ - $PtO_2$ -EtOH furnished (IV), which was identified mass spectrometrically by comparison with an authenticated sample. The light tan solid can be readily converted into the fluoborate salt and other derivatives previously described by Bauld<sup>6</sup> and subsequently by Dauben<sup>2</sup> and having similar melting points and spectral properties. Conversion of (III) into tropone was readily realized and its i.r. and mass spectra were essentially identical with those from an authenticated sample and leads to the assignment of tropone-imonium azide for (III).

An attempt to determine if (V) or (VI) might be present [in principle to be expected from (VII) or (VIII)] was made using ethanolic phosphoric acid-2,4-dinitrophenylhydrazine reagent.<sup>7</sup> A fair yield of benzaldehyde 2,4-dinitrophenylhydrazone (X) was obtained. Repetition using tropone-imonium fluoborate and 7-*N*-tropylium-imonium fluoborate furnished similar results. These are in strong contrast with the observations of Nozoe *et al.*<sup>8</sup> with tropone and tropone oxime. A review of their reported melting points for the 2,4-dinitrophenylhydrazones and oximes from several tropones, and comparison with reported values for the expected rearrangement products, failed to uncover any ambiguous assignments. This type of rearrangement is not uncommon with tropylium salts in the presence of oxidants<sup>9</sup> or when an incipient carbonium ion is present on a carbon  $\alpha$  to C-7 in the tropylium series.<sup>10</sup> It does appear to be unique in the tropone, tropone-imine series.

We have yet to succeed in isolating the other product(s) formed when (I) is converted into (III).



multiplet in the  $^1H$  n.m.r. spectrum at  $\tau$  2.35 (6H) as well as highly structured peaks at  $\tau$  3.34 (2H), 3.89 (2H), 4.63 (2H), and 5.95 (1H). These latter peaks resemble in considerable detail typical tropylium n.m.r. spectra. Upon treatment of (II) with traces of acid (acetonitrile solution) a new peak occurs at  $\tau$  0.7 (7H). (The same location as tropylium ion.) Colorimetric analyses indicated the presence of one azide ion per molecule ( $C_{14}H_{14}N_4$ ). Treatment of (II) with ethanol, followed by reaction with fluoboric acid, furnished

† NDEA Predoctoral Fellow 1966–69, NSF Summer Fellow 1966.

We acknowledge partial support by NSF grants, the Tanner and Dr. P. V. Fennessey, Monsanto Company, St. Louis, Missouri, and the inadvertent support of Picatinny Arsenal, and the determination of mass spectra through the courtesy of O. P.

(Received, November 24th, 1969; Com. 1784.)

- <sup>1</sup> D. S. Wulfman and J. J. Ward, *Chem. Comm.*, 1967, 276.
- <sup>2</sup> H. J. Dauben, jun., and D. V. Rhoades, *J. Amer. Chem. Soc.*, 1967, **89**, 6764.
- <sup>3</sup> G. Merling, *Ber.*, 1891, **24**, 3108; W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, 1954, **76**, 3203.
- <sup>4</sup> C. E. Wulfman, F. Yarnell, and D. S. Wulfman, *Chem. and Ind.*, 1960, 1440; D. S. Wulfman, L. J. Durham, and C. E. Wulfman, *ibid.*, 1962, 859.
- <sup>5</sup> J. J. Looker, *J. Org. Chem.*, 1965, **30**, 638.
- <sup>6</sup> N. L. Bauld and Y. S. Rim, *J. Amer. Chem. Soc.*, 1967, **89**, 6763.
- <sup>7</sup> L. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. 1, p. 330, Wiley, New York, 1967.
- <sup>8</sup> T. Nozoe, T. Muckai, and T. Takase, *Sci. Reports Tohoku Univ. First Ser.*, 1956, **39**, 164; T. Nozoe, in D. Ginsberg, "Non-Benzenoid Aromatic Compounds," Interscience, New York, 1959; and references therein.
- <sup>9</sup> M. J. S. Dewar and R. Pettit, *Chem. and Ind.*, 1955, 199; *J. Chem. Soc.*, 1956, 2021 and 2026; W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, 1954, **76**, 3203; M. E. Vol'pin, and D. N. Kursanov, *Doklady Akad. Nauk S.S.S.R.*, 1959, **126**, 780 [*Chem. Abs.*, 1959, **53**, 21850].
- <sup>10</sup> W. von E. Doering and D. W. Wiley, *Tetrahedron*, 1960, **11**, 183.