1-Azatricyclo$[3,3,0,0^{2,8}]$octa-3,6-diene

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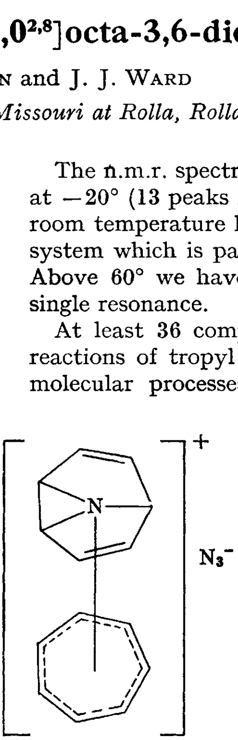
PREVIOUSLY we reported studies dealing with the formation of tropylium–azide ion pair from tropyl azide.[1] The structure of the ion-pair appeared to be an open-faced sandwich. It was not possible to tell whether the azide part was perpendicular or parallel to the plane defined by the tropylium ion.

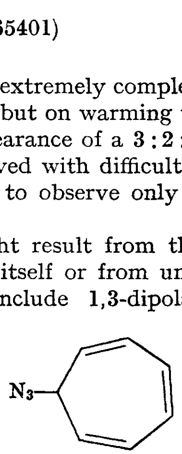
All n.m.r. spectra observed showed a single sharp resonance signal at τ 4·40 (τ 5·20 neat) accounting for 2—3% of the total signal. This signal was τ 0·06 up-field from the centre of gravity of the tropyl azide spectrum. We now assign the source of this signal as being due to the novel sandwich compound (I), resulting from the interaction of tropyl azide (II) and 1-azatricyclo-$[3,3,0,0^{2,8}]$octa-3,6-diene (IIIa). Treatment of (I) with trifluoroacetic acid furnishes tropylium ion and the ion (IIIb) as is shown by a decrease in the intensity of the resonance signal at τ 4·40* to one half and generation of a new signal at τ 0·73 [the location of the resonance of tropylium fluoroborate in the same solvent, CD_3CN, is τ 0·73] and a peak of variable position and intensity (a function of temperature and of the amount of trifluoroacetic acid) which we ascribe to $\equiv N^+$—H, HN_3, and $CF_3{\cdot}CO_2H$.

The n.m.r. spectrum of (I) is extremely complex at −20° (13 peaks in 7 c./sec.) but on warming to room temperature has the appearance of a 3 : 2 : 2 system which is partially resolved with difficulty. Above 60° we have been able to observe only a single resonance.

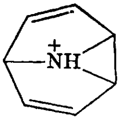
At least 36 compounds might result from the reactions of tropyl azide with itself or from unimolecular processes. These include 1,3-dipolar



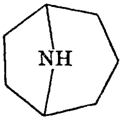
(I)



(II)



(IIIb)



(V)

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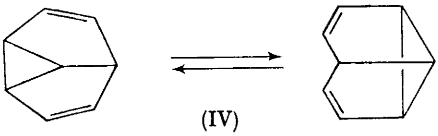
* Determined on a Varian A56—60 n.m.r. spectrometer at 60 Mc./sec. with tetramethylsilane as internal standard in trideuteromethyl cyanide.

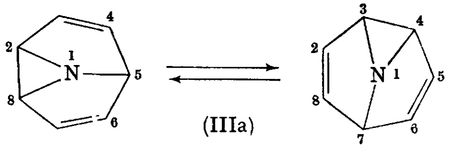
addition-type products,[2] with or without subsequent loss of nitrogen and nitrene reaction[3] products, and their possible valence isomerization products followed by possible interaction with tropyl azide. Of the structures considered, only (I) is consistent with the i.r., u.v., and n.m.r. spectral data. Comparison spectra have been examined in all cases by using tropyl azide, bistropyl ether, tropylidene, tropylium fluoroborate, and tropylium perchlorate.† The compound to which we assign the structure (I) possesses many spectral properties in common with these compounds except that the dissimilarities clearly preclude the presence of a free tropylium unit or the presence of a simple tropyl system. The u.v. spectra show λ_{max}(EtOH) 236 (ϵ 10,000), 326 (ϵ 5600), and λ_{max} 287 mμ (ϵ 2200) whereas tropyl compounds and tropylium ion show λ_{max} (EtOH) in the range 250—265 mμ (ϵ ~ 12,000—20,000).[4] However, the presence of a shoulder at 247 mμ (ϵ 8000) of approximately the same normalized intensity (16,000) as tropyl compounds suggests the presence of such a structural unit. The i.r. does not show any C=C stretching characteristic of tropylidene or tropyl azide. Experiments with tropyl azide show only a slight up-field shift in the proton resonance signal after treatment with tertiary amines. The single n.m.r. signal from tropylium perchlorate upon treatment with pyridine shifts from τ 0·73 to 4·35. When amines such as trimethylamine are used, a complex n.m.r. spectrum with multiple tropylium resonances occurring between τ 3·33 and 5·93 results.[5] The n.m.r. spectrum of (I) is not inconsistent with these observations but would seem to indicate the existence of rather special conditions to permit complex formation between (II) and (IIIa).

The n.m.r. spectral properties of (I) and (IIIa) and (IIIb) are highly suggestive of ready exchange and valence isomerization reactions.[6] It seems unlikely the 14 protons of (I) and the 7 C–H protons of (IIIa) and (IIIb) fortuitously occur at the same field strength.

It appears that (I) actually exists as a sandwich ion with or without the azide ion in close proximity but with at least time-average equivalence of both carbon rings. In (IIIa) and (IIIb) it appears that in contrast to tricyclo[3,3,0,$0^{2,8}$]octa-3,6-diene the valence isomerization process is not limited to the now classic homotropylidene rocking-type Cope rearrangements[7] (Scheme 1) but actually involves a hitherto unknown precessional or rotational-type Cope rearrangement (Scheme 2).


(IV)

SCHEME 1



(IIIa)

SCHEME 2

The u.v. spectrum is consistent with this assignment. The absorption maximum at 326 mμ is only present when the ring nitrogen bears a positive charge. This appears to be associated with interaction of the lone pair sp^3–σ^* orbital with the 4/π orbitals of the carbonoid system. The broad absorption maximum at 235 mμ is much more intense than that observed by Zimmermann[8] for tricyclo[3,3,0,$0^{2,8}$]octa-3,6-diene but falls at the same position. The disappearance upon acid treatment of the 326 mμ absorbance and shifting to maxima at 320 (ϵ 2500), 307 (ϵ 4100), and 293 mμ (ϵ 4200) appears to be the result of the more ready interaction between the nonbonded electron pair of nitrogen and the π-electrons of the two carbon–carbon double bonds.

Catalytic reduction of (I) over Adams catalyst at atmospheric pressure in absolute ethanol furnished a mixture which contained large amounts of cycloheptane and nortropane (V). Verification of the structure of (V) was accomplished by mass spectral analysis‡ (*m/e*, 111, 97, 96, 94, 91, 83, 82, 81, 80, 79, 67, 55, 43, 41, 39, 30, 29 amongst others). In addition small quantities of cycloheptyl amine were also obtained and verified mass spectrometrically. In addition, (I) should have a cryoscopic molecular weight of 119, we found 126 ± 15.§ Attempts to determine the percentage of ionic azide[9] were frustrated by the instability of

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† Test performed for D.S.W. by Hercules Inc., Bacchus, Utah, show dry tropylium perchlorate to be at least three times as sensitive to impact as nitroglycerin.

‡ Mass spectra were determined on a Consolidated Electrodynamic Corporation model 104 mass spectrometer with a gas chromatographic interface using an electron multiplier and scanning at 2 sec./octave. Interpretations were made on the basis of information in H. Budzikiewicz, C. Djerassi, and D. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day Inc., San Francisco, 1964.

§ Cryoscopic measurements were obtained using redistilled cyclohexanol.

the solid salt. Spectrophotometrically-obtained values ran 30—40% below theoretical.

Compound (I) was prepared at a low conversion (2—3%) by slow evaporation through a (75 cm. × 2·5 cm.) Vycor tube irradiated with G.E. Sunlamps at pressures below 3 mm. and collection of the distillate on a liquid nitrogen cold finger. Transfer and warming to 0° was carried out under a dry nitrogen atmosphere and (I) was isolated by trituration with cold pentane and centrifugation. Yields at this stage were 10—12 mg. per 8 g. of (II).

The i.r. spectrum of (I) showed peaks at 2976 s, 2857 s, 2110 s, 1449 m, 1418 m, 1368 w, 1253 vs, 1121 vs, 1081 m, 1046 mw, 894 s, 889 s, 873 s, 694 vs cm.$^{-1}$ in CH$_2$Cl$_2$.

The possibility that other tropylium ion derivatives might exist in the form (VI) was investigated for the series[10,11] y = O, S, Se, and Te. All of these compounds exist solely in the form (VII) and the only thing noteworthy about these compounds is that the C-7 proton resonance in the oxygen compound is τ 0·96 up-field from the position predicted on the basis of Huggin's electronegativities[12] and the C-6–C-1 proton resonances of the tellurium compound, unlike other tropylidene derivatives, are nicely resolved into a 1 : 1 : 2 : 2 : 1 : 1 sextet.

Work is currently under way to establish the exact structure of (I) by X-ray analysis and to determine unequivocally the character and energetics of the isomerization processes involving (I), (IIIa), and (IIIb).

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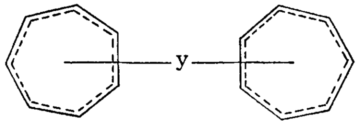
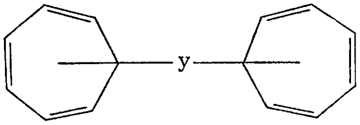


(VI)



(VII)

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[1] This Communication is the third in a series on "Tropylidene derivatives"; previous parts 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.

[2] The role of azides in 1,3 dipolar addition is discussed by R. Huisgen, *Angew. Chem. Internat. Edn.*, 1963, **2**, 565.

[3] A survey of nitrene reactions is given in L. Horner and A. Christmann, *Angew. Chem. Internat. Edn.*, 1963, **2,** 599.

[4] For tabulations of tropylium and tropylidene spectra see: T. Nozoe, "Non-Benzenoid Aromatic Compounds," ed. D. Ginsberg, Interscience, New York, 1959, p. 344, and G. Berson and R. Willcott, tert., *Rec. Chem. Prog.*, 1966, **27**, 139.

[5] Unpublished work D.S.W. and C. F. Seger, tert.

[6] W. von E. Doering and W. R. Roth, *Angew. Chem.*, 1963, **75**, 27; *Angew. Chem. Internat. Edn.*, 1963, **2**, 115; W. von E. Doering, *Zhur. Vsesoyuz. Khim. obshch im D. I. Mendeleeva*, 1962, **2**, 308; G. Schroeder, *Angew. Chem.*, 1963, **75**, 722; *Angew. Chem. Internat. Edn.*, 1963, **2**, 481; G. Schroeder, J. F. M. Oth, and R. Mereny, *Angew. Chem.*, 1965, **77**, 774; *Angew. Chem. Internat. Edn.*, 1965, **4**, 752.

[7] E. Vogel, *Angew. Chem. Internat. Edn.*, 1962, **2**, 1 and references therein.

[8] H. E. Zimmerman and G. L. Grunewald, *J. Amer. Chem. Soc.*, 1966, **88**, 183.

[9] A. Anton, J. G. Dodd, and A. E. Harvey, Jr., *Analyt. Chem.*, 1960, **32**, 1209.

[10] W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, 1957, **79**, 352.

[11] By method similar to L. Brandsma and H. J. Wijers, *Rec. Trav. chim.*, 1963, **82**, 68.

[12] B. P. Dailey and J. N. Schoolery, *J. Amer. Chem. Soc.*, 1955, **77**, 3977.