Preparation and Thermal Rearrangement of an Aza-analogue of 4,5-Homotropone (Bicyclo[5.1.0]octa-3,5-dien-2-one)

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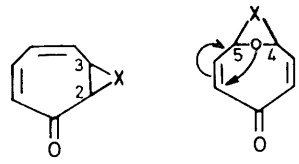
Summary Phthalimidonitrene adds to the 4,5-rather than the 2,3-double bond of tropone in accord with addition *via* the *syn*-arrangement (**6**) stabilised by two secondary interactions; thermal and photochemical rearrangement of the 8-azabicyclo[5.1.0]octadienone derivative (**2**; X = NR) at 80 °C proceeds by apparent C–C bond cleavage, to give (**3**).

EARLIER knowledge of 2,3-homotropone[1] (**1**; X = CH_2) (bicyclo[5.1.0]octa-3,5-dien-2-one; tropone numbering used throughout) and the 4,5-isomer[2] (**2**; X = CH_2) was recently extended[3] by preparation of the oxa-analogues (**1**; X = O) and (**2**; X = O). Both oxa-analogues underwent thermal conversion into simple benzenoid products; no products derived by C-4–C-5 bond cleavage in (**2**; X = O) could be found.[3] We describe preparation of the aza-analogue (**2**; X = NR) and its thermal and photochemical conversion into (**3**) involving apparent cleavage of the C-4–C-5 bond.

Although successful addition of nitrenes to tropone does not appear to have been observed, addition of lead tetra-acetate to *N*-aminophthalimide (**4**) (CH_2Cl_2, 0—5 °C) in the presence of a large excess of tropone (7·8 mol. equiv.) gave the adduct (**2**; X = NR) (52%), m.p. 144–145 °C (benzene),† formally derived by addition of phthalimidonitrene

† The reaction was worked-up in the usual way (ref. 7) and (**2**) was isolated by trituration with benzene.

(**5**) to the C-4–C-5 double bond of tropone. The n.m.r. spectrum of the adduct favours its formulation as (**2**; X = NR) [δ ($CDCl_3$) 3·42 (2H, H-4 and -5, m), 6·20 (2H, H-2 and -7, d, *J* 12 Hz), 6·92 (2H, H-3 and -6, d of m, *J* 12 Hz), 7·78 (4H, AA'BB' system)] rather than (**1**; X=NR).



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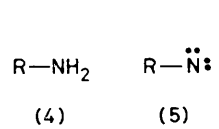

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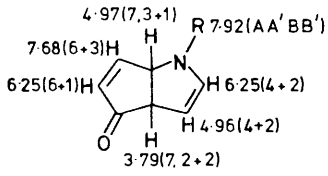

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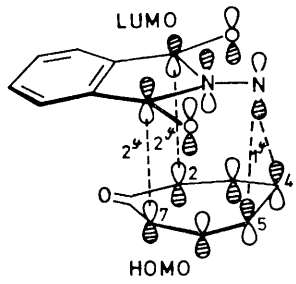

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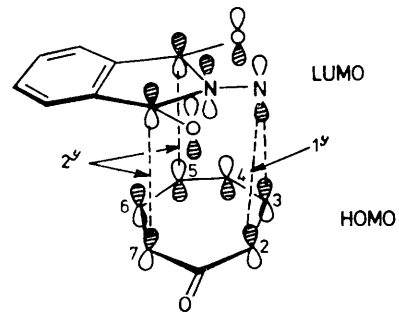

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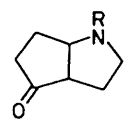

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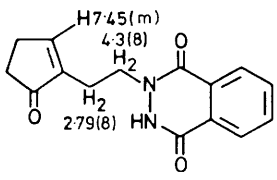

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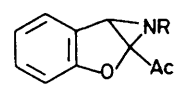

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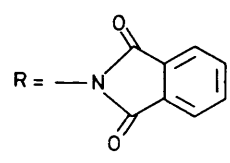

In the oxa-analogue (**2**; X = O), the equivalent protons H-2 and H-7 resonate at δ 6·32, and H-3 and H-6 at δ 6·94.[3] The n.m.r. spectrum of the crude reaction mixture failed to reveal any of the adduct (**1**; X = NR). Preferred nitrene addition to the 4,5- rather than the 2,3-double bond of tropone can be rationalised in terms of secondary M.O. interactions which explain the differing effectiveness of various nitrene traps,[4] as well as the *syn*-selectivity observed in the addition of amino-nitrenes to conjugated double bonds.[5] Addition of the *sp*-hybridised nitrene (**5**) to the 4,5-double bond of tropone *via* a *syn*-arrangement is pictured in (**6**). The tropone-HOMO[6] overlaps favourably at C-2 and C-7 with the nitrene-LUMO‡ giving two favourable secondary interactions (2^y) which support the primary (1^y) bond-forming interactions at C-4 and C-5 of tropone. As shown in (**7**) addition of the nitrene to C-2 and C-3 of tropone would result in a bonding 2^y-interaction at C-5 but a repulsive interaction at C-7.§

On heating in boiling benzene (**2**; X = NR) rearranged smoothly to (**3**) (75%); the same product was obtained by photolysis of (**2**; X = NR) (benzene solvent, medium-pressure mercury lamp, 20 °C). The n.m.r. spectrum of the rearrangement product [$(CD_3)_2SO$] is appended to structure (**3**) [δ-values (*J*/Hz)]. This spectrum and appropriate spin-decoupling experiments are fully consistent with the assigned structure. Reduction of (**3**) (H_2–Pt) gave the tetrahydro-derivative (**8**) which with NaOMe–MeOH underwent the expected easy β-elimination and Gabriel–Colman type ring-expansion to the phthalazine-1,4-dione (**9**),[7] $\nu_{C=O}$ 1695 cm^{-1} (cyclopentenone). The simple n.m.r. spectrum of the latter [see (**9**)] confirms assignment of structure (**3**) to the rearrangement product. Supporting formation of (**2**; X = NR) by addition of phthalimido-nitrene [rather than a nitrenoid, *e.g.*, protonated (**5**)] to tropone, the rearrangement product (**3**) is formed directly when the nitrene is generated by thermolysis of (**10**)[8] in boiling benzene containing tropone.

The easy rearrangement of (**2**; X = NR) by C-4–C-5 bond cleavage contrasts both with the failure of (**2**; X = O) to rearrange by a related path,[3] and the rearrangement by C–N bond-cleavage of simpler 2-vinylaziridines.[9] Although a formal 1,3-shift converts (**2**; X = NR) into (**3**) [see arrows in (**2**)] rearrangement could involve a biradical or a zwitterionic intermediate; the latter could explain the ease of this particular rearrangement. However, our present results do not distinguish between these and alternative mechanistic possibilities. When part of a concerted pericyclic process, C–C bond cleavage of an aziridine ring is well known.[10]

(*Received, 16th January* 1978; *Com.* 030.)

‡ I thank Dr. R. J. Bushby for Hückel calculations; only the relevant parts of the M.O.s are depicted.

§ The similar chemical shifts for the olefinic protons in (**2**; X = O) and (**2**; X = NR) suggest that our product is the expected, thermodynamically more stable *anti*-isomer, rather than the *syn*-isomer initially formed *via* transition state arrangement (**6**). Attempts to detect the first formed adduct at low temperature are continuing in an effort to overcome solubility problems.

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