The Reaction of Cycloheptatriene with Methoxycarbonylnitrene: Synthesis of 2,3- and 4,5-Homo-1*H*-azepines

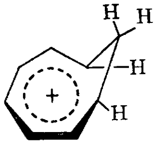
By LEO A. PAQUETTE* and ROBERT J. HALUSKA

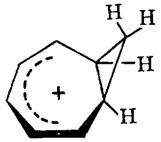
(*Department of Chemistry, Ohio State University, Columbus, Ohio* 43210)

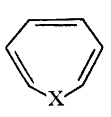
CONSIDERABLE attention has been paid to 6π-electron homoaromatic systems, principally the homotropylium cation (I), wherein the cationic portion of the molecule is stabilized by a "pseudo-aromatic" sextet of electrons, two of which in the classical structure (II) form part of the cyclopropyl ring.[1] Such orbital overlap is at present recognized to be intermediate between that of the customary σ- and π-types.

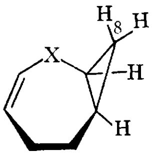
Heterotropylidenes such as 1*H*-azepine (IIIa), oxepin (IIIb), and thiepin (IIIc) have in common the property of being cyclic 8π-electron molecules which, if planar, could in actuality be antiaromatic. It was reasoned that "homo"-derivatives of (III) *e.g.* (IV) and (V), should constitute suitable substrates for study of homoantiaromaticity should this phenomenon exist. Further, removal of two electrons from (IV) and (V) could possibly lead to heterocyclic homotropylium dications; conversely, donation of two electrons to these molecules could give rise to interesting monocyclic 10π-electron entities.

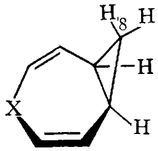
We report the preparation of homoazepine derivatives (IVa) and (Va) by reaction of cycloheptatriene with methoxycarbonylnitrene.[2,3] Heating a 7% solution of methyl azidoformate in cycloheptatriene at 127—128° for 4 hr. led, after recovery of the excess of hydrocarbon, to a mixture of nitrene insertion products from which a 35% yield of (IVa) and (Va) could be isolated by careful distillation [b.p. 67—74° (0·2 mm.)]. The ratio of (IVa) to (Va) was approximately 2·2 : 1 (v.p.c. analysis); final separation was achieved by preparative scale gas chromatography (20% SE30 on Chromosorb W at 118°).

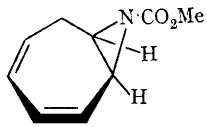

(I)

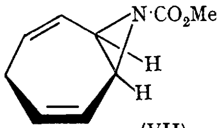

(II)

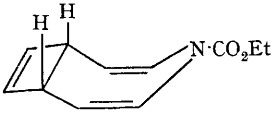

(IIIa) X=NH
(IIIb) X=O
(IIIc) X=S


(IV) X=N·CO_2Me


(V) X=N·CO_2Me


(VI)


(VII)


(VIII)

The 2,3-homoazepine (IVa) was obtained as a very pale yellow liquid which exhibits the following spectral properties: ν_{max} (film) 1730 ($>$C=O), 1655 and 1635 cm.$^{-1}$ ($>$C=C$<$); λ_{max} (EtOH) 262 mμ (ϵ 8430); δ_{Me_4Si}($CDCl_3$) 6·65 (d, *J* 9·5 Hz, H-7), 6·12 (d, *J* 11·1, 3·1 Hz, H-4), 5·66 (dd, *J* 11·1, 6·6 Hz, H-5), 5·10 (dd, *J* 9·5, 6·6 Hz, H-6), 3·80 (s, OMe), 3·15 (m, H-2), 1·1—1·6 (m, H-3 and *anti*-proton at C-8), 0·1—0·4 (m, *syn*-proton at C-8).[4]

The 4,5-homoazepine (Va) was likewise isolated as a faint yellow oil displaying the following spectra: ν_{max} (film) 1725 ($>$C=O) and 1670 cm.$^{-1}$ ($>$C=C$<$); λ_{max} (EtOH) 231 mμ (ϵ 11,430); δ_{Me_4Si}($CDCl_3$) 6·65 (d, *J* 9·8 Hz, H-2 and H-7), 5·15 (br d, *J* 9·8 Hz, H-3 and H-6), 3·86 (s, OMe), 1·0—1·6 (m, H-4, H-5, *anti*-proton at C-8), 0—0·3 (m, *syn*-proton at C-8).[4]

The minor products from the reaction appear to be a mixture of air-sensitive cycloheptatrienyl urethanes on the basis of infrared and n.m.r. spectra. These substances have not been investigated further.

The homo-1*H*-azepines (IVa) and (Va) most likely result from valence bond rearrangement of initially formed methoxycarbonylaziridines (VI) and (VII), respectively. The overall reaction is therefore reminiscent of the preparation of 1*H*-azepines from aziridinobenzene intermediates[5] and of (VIII) from the ethoxycarbonyl nitrene adduct of cyclo-octatetraene.[6]

The temperature invariant n.m.r. spectra of (IVa) and (Va) attest to the fact that the internal cyclopropyl bond in these structures is not prone to delocalization or to valence bond isomerization. The homo-1*H*-azepines, therefore, fail to exhibit antiaromaticity. However, the ready availability of (IVa) and (Va) now makes possible a study of their chemical properties.

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[1] For a recent review, see S. Winstein, "Aromaticity", *Chem. Soc. Special Publ.*, No. 21, 1967, pp. 25—32.

[2] This reaction represents an adaptation of the method of K. Hafner and C. König (*Angew. Chem.*, 1963, **75**, 89) and R. J. Cotter and W. F. Beach (*J. Org. Chem.*, 1964, **29**, 751.

[3] A recent report of an analogous reaction has appeared: W. H. Okamura, W. H. Snider, and T. J. Katz, *Tetrahedron Letters*, 1968, 3367.

[4] J. G. Traynham, J. S. Dehn, and E. E. Green, *J. Org. Chem.*, 1968, **33**, 2587.

[5] L. A. Paquette and D. E. Kuhla, *Tetrahedron Letters*, 1967, 4517, and references therein.

[6] S. Masamune and N. T. Castellucci, *Angew. Chem.*, 1964, **76**, 569 (*Angew. Chem. Internat. Edn.*, 1964, **3**, 582).