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CYCLIC AZOXY COMPOUNDS-RELATION OF STRUCTURAL CONSIDERATIONS TO NMR SPECTRA

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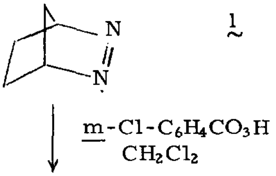
In connection with our work on the photolysis of azoxy compounds,[1] we oxidized 2,3-diazabicyclo(2.2.1)-2-heptene (1)[2] with meta-chloroperbenzoic acid. Except for



1

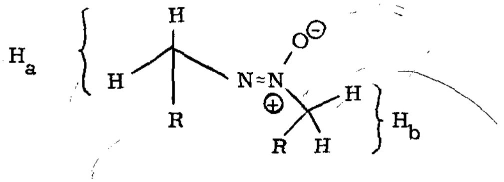
$C_5H_8N_2O$ 2 (57%)
molecular wt (cryoscopic in benzene)
found 122. calc'd 112.
Anal. in agreement with $C_5H_8N_2O$

2 mp 87-89°, white solid
ir ($CHCl_3$); 1500 cm^{-1} (s)
uv (EtOH); λ_{max} 228 mμ, ε (6000)
ms; m/e 112 (molecular ion)
68 (base peak)
nmr[3] ($CDCl_3$); 4.61 ppm, 2H,
SINGLET, width at half-height = 6 Hz
2.30-1.50 ppm, 6H, multiplet

the nmr spectrum, all data are consistent with the expected cis-azoxy structure for 2. Typical aliphatic trans-azoxy compounds show large differences in chemical shift between protons a and b (Table 1). Also, the average value of the chemical shifts of a and b is generally near that of the corresponding protons in the parent azo compound, or slightly further downfield.[4] However, in compound 2 the bridgehead hydrogens H_a and H_b appear at the same chemical shift,[5] and this singlet lies 0.5 ppm further upfield than the bridgehead hydrogens of 1.

Acyclic aliphatic cis-azoxy compounds have not been described in the literature

TABLE 1



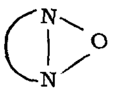
R	H_a	H_b	H^c
H^a	3.07^d	4.05	3.68
Ph^a	4.35	5.02	4.85
n-Pr^b	3.37	4.17	3.66

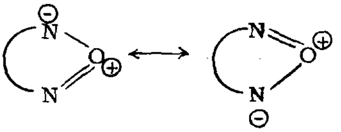
a) Reference 4; b) prepared by oxidation of azo-n-butane; c) H_a and H_b - parent azo compound; d) in ppm downfield from TMS.

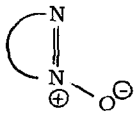
to our knowledge[6] although aromatic cis-azoxy compounds are known and appear to be moderately stable.[7] The cyclic cis-azoxy structure has been assigned to 1,4-dichloro-2,3-diazabicyclo(2.2.2)-2-octene-N-oxide,[8] but apparently without consideration of the possibilities indicated below. Thus, definitive information on cis-aliphatic azoxy compounds is lacking.

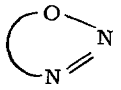
The nmr spectrum of 2 is consistent with three possibilities: 1) 2 is symmetrical, 2) 2 is unsymmetrical, but the chemical shifts of H_a and H_b are accidentally equivalent, or 3) 2 is unsymmetrical, but the chemical shifts of H_a and H_b appear to be equivalent because of rapid equilibration through a symmetrical intermediate.

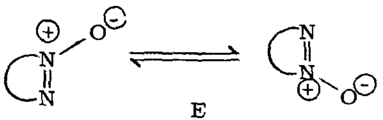
Structural Possibilities


A


B


C

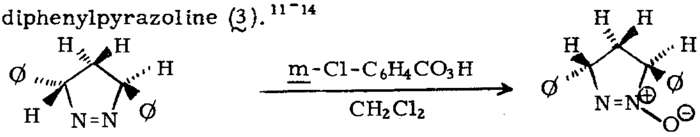

D


E

Structure A (the oxadiaziridine system!) is not in accord with the ultraviolet absorption of 2. The infrared and the thermal stability of 2 are also not in agreement with our present knowledge of oxadiaziridines. Structure **D** was eliminated by the lithium aluminum hydride reduction of **2** to a mixture of **1** and the corresponding hydrazo compound. The nmr of **2** showed little change over the solvent series CCl_4, CD_3COCD_3, D_2O, and CF_3COOH, or over the temperature range of -40° to +70° ($CDCl_3$). The spectrum remained the same at concentrations of 0.02 M and 1.0 M in CF_3COOH. These nmr data did not encourage us in possibility **E**.

Compound **1** was then oxidized with (+)peroxycamphoric acid,[9] affording **2** with $[\alpha]_D^{20} = 1.2°$ (CH_2Cl_2, 0.27 M), purified by glpc and identical in ir and mass spectrum with the **2** described above.[10] (The optical purity is not known.) This result excludes possibilities **A**, **B**, and **E**. Compound **2** is thus assigned the *cis*-azoxy structure **C**.

Further information on this type of system was sought from the oxidation of *trans*-3,5-diphenylpyrazoline (**3**).[11-14]



3

4

nmr ($CDCl_3$) 7.30 ppm, 10H broad singlet; 5.82 ppm, 2H, triplet; 2.07 ppm, 2H, triplet

mp 139-141° (yield, 70%)
ir ($CHCl_3$); 1500 cm^{-1} (s)
uv (EtOH); 225 mμ (broad shoulder, ϵ = 7000)
nmr ($CDCl_3$); 7.30 ppm, 10H, doublet; 5.57 ppm, 2H, overlapping doublet of doublets (broadened triplet) 2.80 ppm, 2H, multiplet (~10 lines)
Anal. in agreement with $C_{15}H_{14}N_2O$

Compound **4** does not have an A_2B_2 pattern, and thus cannot be of the same symmetry as the parent azo compound **3**, excluding possibilities **B** and **E**. Decoupling experiments support this conclusion. When **4** is irradiated at 2.80 ppm, the broadened triplet due to the benzylic protons collapses to a broad singlet (i.e., as with **2**, H_a and H_b of **4** are of comparable chemical shift). Irradiation at 5.57 ppm results in the collapse of the 2.80 ppm multiplet to an AB pattern (J = 14 Hz), consistent with structure **C**.[15]

We conclude that compounds **2** and **4** are simple cis-azoxy compounds (**C**) with ir absorption (1500 cm^{-1}) and uv absorption (225-228 mμ) similar to trans-azoxy compounds,[16] that the hydrogens adjacent to the azoxy groups are accidentally magnetically equivalent, in marked contrast to the corresponding hydrogens in trans-azoxy compounds, and that equilibration of type **E** does not occur under the conditions of our examination of **2** and **4**.

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2. S.G. Cohen, R. Zand, C. Steel, J. Amer. Chem. Soc. 83 2895 (1961) and references therein.
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5. Irradiation of the upfield multiplet at its center affords no change in the downfield singlet.
6. The compounds reported by B.T. Gillis and K.F. Schimmel, J. Org. Chem. 27 413 (1962) have been reassigned dimeric structures (see Ref. 15).
7. D.L. Webb and H.H. Jaffe, J. Amer. Chem. Soc. 86 2419 (1964).
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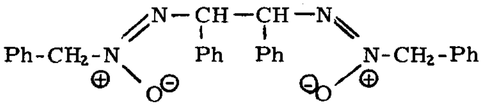
10. For a discussion of asymmetric synthesis see D.R. Boyd and M.A. McKervey, Quarterly Reviews 22 95 (1968).
11. C.G. Overberger and J-P. Anselme, J. Amer. Chem. Soc. 86 658 (1964). Sample kindly provided by Dr. Anselme, Univ. of Mass., Boston.
12. C.G. Overberger, J-P. Anselme, and J.R. Hall, J. Amer. Chem. Soc. 85 2752 (1963).
13. C.G. Overberger, N.M. Weinshenker, and J-P. Anselme, ibid. 87 4119 (1965).
14. Tautomerization to the 2-pyrazoline did not take place under these conditions.
15. Dimers of the type **F** have been observed as products from the oxidation of $PhCH_2N{=}NCH_2Ph$ (C.E. Wintner, Ph.D. Thesis, Harvard, 1963). Such a structure is precluded for **4** by nmr.



F

16. Typical trans-azoxy compounds show strong ir absorption at both 1500 and 1300 cm^{-1} and uv absorption at 221 mμ. Compounds **2** and **4** lack absorption at 1300 cm^{-1}.