Tetrahedron Letters No. 33, pp 3075 - 3078, 1973. Pergamon Press. Printed in Great Britain.

HOMOTROPILIDENES II.[1] ORIENTATION EFFECTS IN DIHYDROAZABULLVALENES.

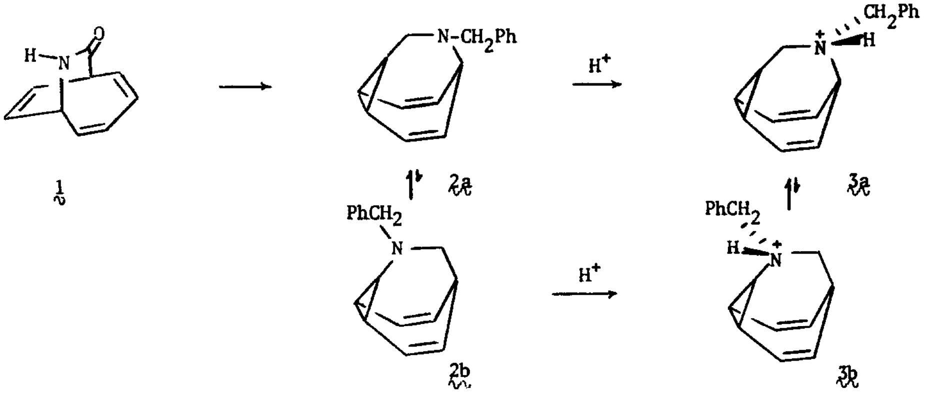
Grant R. Krow and James Reilly

Department of Chemistry, Temple University
of the Commonwealth of Penna., Philadelphia, Pa. 19122

(Received in USA 12 June 1973; received in UK for publication 28 June 1973)

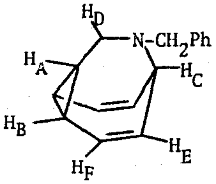
Accumulation of evidence concerning substituent effects on equilibrium preferences of bridged homotropilidenes is currently the object of experimental[1-5] and theoretical effort.[6] Since theoretical predictions of substituent preferences have revolved around the concept of π-donor and π-acceptor interactions with homotropilidene orbitals, it seemed of interest to determine the effect on the homotropilidene equilibrium of converting a π-donor heteroatom to a substituent in which the π-donating ability was removed. This situation is realized when the lone electron pair of an amine is protonated to form an ammonium ion. We here report the results of such a structural study with N-benzyldihydroazabullvalene **2** and its conjugate acid **3**.

In the synthetic approach bicyclic lactam **1**[2a] was converted in 38% overall yield to **2** by a sequence of steps involving N-benzylation, conversion to thioamide, acetone-sensitized photorearrangement[2a] and lithium aluminum hydride in ether reduction.[7] A structural assignment to **2** was possible based on the the pmr spectrum in conjunction with spin-decoupling information (Table I). The appearance of the downfield resonance H_c as a triplet coupled only to olefinic protons H_E uniquely identifies **2a** as the favored tautomer. No observable pmr averaging process was observed between **2a** and its tautomer **2b** in 1-chloronaphthalene as solvent from 30-160°.



Incremental additions of trifluoroacetic acid to 2a resulted in gradual changes in the pmr spectrum as the equilibrium shifted from the free base to the protonated form 3. Most dramatic of the changes were (a) the shift of the H_c triplet resonance downfield from H_D with 0.32 eq. of acid, (b) the merging of the H_A and H_B resonances and the collapse of the H_D doublet to a broad singlet $W_{1/2}$ = 14 Hz after 0.63 eq. of acid, (c) the observation of separate patterns for H_D and $H_{D'}$, after 1.26 eq. of acid, and (d) a gradual broadening of the benzyl resonance and collapse to a higher order pattern at 1.88 eq. of acid.

Table I - Pmr Spectrum^a of 2a

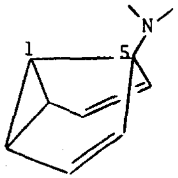


Assignment^b	δ	Appearance^c
H_A	1.94	m (J_{AD} = 4.0 Hz, J_{AB} = 9.0 Hz)
H_B	2.52	m
H_C	3.14	t (J_{CE} = 8.0 Hz)^d
H_D	3.20	d
H_E	5.28	dd (J_{EF} = 9.0 Hz)
H_F	5.88	m^e
CH_2	3.56	s
Ph	7.22	s

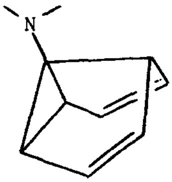
a) $CDCl_3$ (75 mg of 2 in 0.5 ml solvent), b) Integrated areas are consistent with the assignments c) Reported J were where necessary obtained with the aid of decoupling experiments using a Varian XL-100 instrument, d) Discernible upon shifting caused by addition of 18 mg trifluoracetic acid, e) Irradiation of H_F results in collapse of H_B to a doublet with small < 1.0 Hz additional coupling.

Since in the pmr spectrum of the protonated amine (Table II) the downfield proton H_C is coupled only to the vinyl proton H_E, the tautomer 3a with the cyclopropyl and amino groups separated by a methylene unit is indicated. The pmr spectrum of 3a gave no evidence of an averaging process with **3b** when raised to 70°, but after ten minutes at this temperature some decomposition had occurred.

Theoretical predictions[6] based on analysis of substituted semibullvalenes indicate that the planar geometry of bisected amine **4a**, which may serve as a model for **2a**, is 0.12 eV more stable with the nitrogen at C_5 away from the cyclopropyl ring than is **4b** with the nitrogen at C_1. Although calculations are available for both trigonal perpendicular and bisected carbonium ions substituted at C_1 and C_5 of semibullvalene[6], such species are not isoelectronic with the

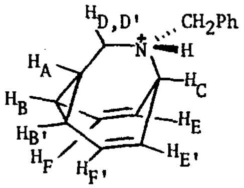


4a



4b

Table II - Pmr Spectrum[a] of **3a**



Assignment	δ	Appearance
$H_A, H_{B,B'}$	2.27	m
H_C	3.95	t(J_{CE} = 8 Hz)
$H_{D,D'}$	3.59, 3.83	m[b]
$H_{E,E'}$	5.81	q($J_{E,F}$ = 11 Hz)
$H_{F,F'}$	6.23	m[b]
CH_2	4.13	m
Ph	7.39	s

a) $CDCl_3$ (75 mg of **2** in 0.5 ml solvent with 160 mg CF_3COOH), b) Coupled to 2.27 region ammonium ion and so do not serve as satisfactory models. The orientation of nitrogen at C_5 of the dihydroazabullvalenes might be attributed to an adverse electron withdrawing effect associated with having a cyclopropyl carbon ($sp^{2.27}$) at C_1 adjacent to an electronegative nitrogen either as its free base or conjugate acid.[2a,8] The bridgehead carbon C_5 ($S_p{}^3$) is better able to satisfy the electronic requirements of electronegative groups by an inductive mechanism.[2a]

Acknowledgements: Cyclooctatetraene was provided by BASF.

References

1. G. R. Krow and K. C. Ramey, Tetrahedron Lett., 3141 (1971).
2. a) L. A. Paquette, J. R. Malpass, G. R. Krow, and T. J. Barton, J. Amer. Chem. Soc., 91, 5296 (1969); b) L. A. Paquette, S. Kirschner, and J. R. Malpass, ibid., 91, 3970 (1969).
3. M. J. Goldstein, R. C. Krauss, and S. H. Dai, ibid., 94, 680 (1972).
4. a) J. F. M. Oth, R. Merenyi, H. Röttele, and G. Schröder, Tetrahedron Lett., 3941 (1968); b) J. F. M. Oth, E. Machens, H. Röttele, and G. Schröder, Justus Liebigs Ann. Chem., 745, 112 (1971); c) J. F. M. Oth, R. Merenyi, J. Nielsen, G. Schröder, Chem. Ber., 98, 3385 (1965); d) G. Schröder and J. F. M. Oth, Angew. Chem. Intern. Ed., 6, 414 (1967).
5. J. C. Barborak, S. Chari, and P. V. R. Schleyer, J. Amer. Chem. Soc., 93, 5275 (1971).
6. R. Hoffmann and W. D. Stohrer, ibid., 93, 6491 (1971).
7. C, H, and N analyses of all isolated compounds agreed with expectation to within ± 0.3%. Experimental procedures were routine and will be reported in the full paper.
8. V. Buss, R. Gleiter, and P. V. R. Schleyer, J. Amer Chem. Soc., 93, 3927 (1971).