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THE HETERO-PSEUDOAROMATIC, CYCLOÖCTA[c]FURAN

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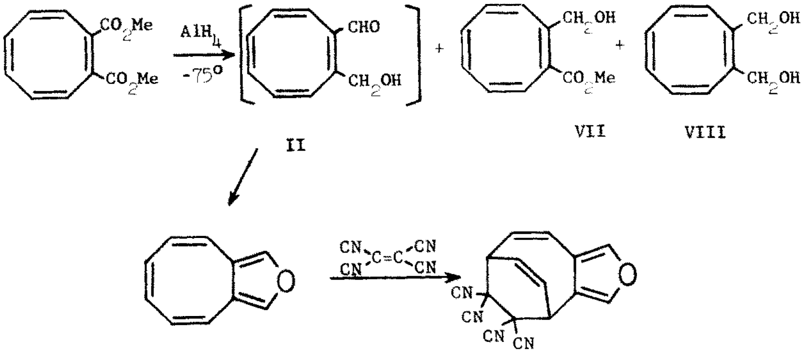
Because of their interesting theoretical electron arrangement, pseudoaromatic compounds (i.e. unsaturated cyclic systems containing 4n π-electrons) have recently received considerable attention. Several recent publications describe the isolation of the hetero-pseudoaromatics azepin (1) and oxepin (2). We report here the preparation of a new bicyclic hetero-pseudoaromatic, cycloöcta[c]furan, I.

Aluminum hydride ($LiAlH_4$ + $AlCl_3$) reduction of 1,2-dicarbomethoxycycloöctatetraene (3) at -75° affords a colorless material (presumed to be II)(4) which, in ether solution or more rapidly on silicic acid, is converted to I.



I

VI

Cycloöcta[c]furan, I, is a bright yellow-orange mobile liquid which reacts rapidly with oxygen forming a white polymeric solid. The infrared spectrum (in CCl_4) of I shows strong absorption at 1064, 880, and 662 cm^{-1}, medium absorption at 3009, 1645, 1533, 1141 cm^{-1} and weak absorption at 1635, 1218, 822, 629 cm^{-1}. Among the multitude of peaks produced in the mass spectrum of

I, the parent peak at m/e 144 ($C_{10}H_8O$) is present in addition to peaks at m/e 118($C_8H_6O^+$), 115 ($C_9H_7^+$) and 89($C_8H_5^+$) for which the speculative structures III, IV, and V are consistent. These assignments are supported by meta-stable peaks (via the relationship $m^* = m^2_{daughter}/m_{parent}$) (5) in the range m/e 92-97 and 67-69. The U.V.-visible spectrum (in cyclohexane) exhibits the typical long tailing absorption of a cyclooctatetraene (6) with a peak at 244 mμ (ε 9100) and weak shoulders at 462 mμ (ε 20) and 500 mμ (ε 7.5).

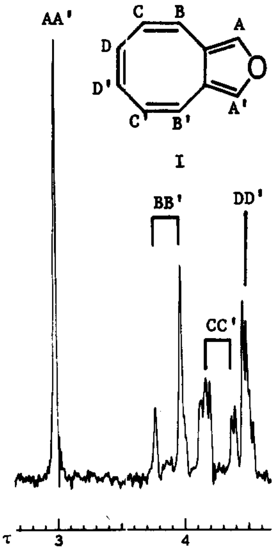
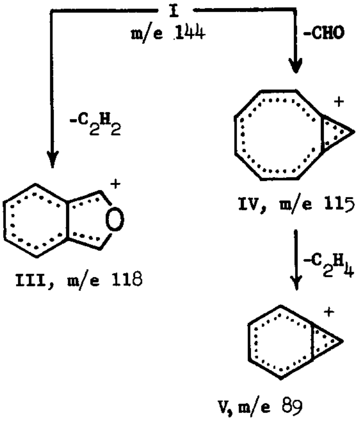


Fig. I

P.M.R. Spectrum of I



First order analysis (with the help of the computer program LAOCOON II) (7) of the p.m.r. spectrum of I (in CCl_4) indicates that the expected proton pattern of AA'BB'CC'DD' is observed, Fig. 1. The furano protons, AA', occur as a sharp singlet at τ 2.98 (2.1 H) while the protons on the eight-membered ring occur as a complex with BB' at τ 3.92 (2.0 H), CC' at τ 4.25 (2.1 H), and DD' at τ 4.50 (1.8 H). The proton coupling constants across the olefinic bonds, $J_{BC} = J_{B'C'} \cong J_{DD'} = 12 \pm 1$ c.p.s., are in the correct range for vicinal couplings in cyclic-C_8 olefins (cyclooctatetraene J = 11.8)(8). Satisfactory values for the other coupling constants, J_{AC}, J_{BC}, etc. have not as yet been obtained, however, they appear to be small within the range of ± 4 c.p.s.

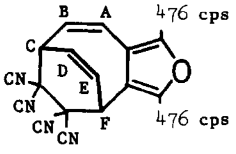
The electronic and magnetic resonance spectra suggest that cycloöcta[c]-furan is not a planar molecule but probably has a "tub" shape similar to cycloöctatetraene.

Cycloöcta[c]furan, in addition to reacting rapidly with oxygen, is instantly converted to a dark violet gel upon treatment with a strong acid (trifluoroacetic). It forms very weak π-complexes with trinitrofluorenone and trinitrobenzene; these appear to be stable only in the solid phase. I is not affected by prolonged heating with tributylphosphine. Tetracyanoethylene (TCNE) reacts slowly with I forming a monoadduct. The U.V. spectrum (in CH_3CN) of this adduct shows a single maximum at 253 mμ (ε 8170) while in the I.R. spectrum (KBr) the nitrile absorption occurs as a very weak doublet at 2290 and 2255 cm^{-1}. Of the numerous structures possible for a monoadduct of I and TCNE, only VI, the adduct resulting from Diels-Alder addition of TCNE across two of the double bonds of the eight-membered ring, is wholly consistent with the p.m.r. The p.m.r. spectrum (in acetone) of this adduct reveals a sharp singlet at τ 2.08 (2.0 H), olefinic peaks at τ 3.0 - 3.3 (0.92 H) τ 3.4 - 3.7 (1.90 H), τ 3.7 - 4.2 (1.1 H), and allylic peaks at τ 5.0 - 5.2 (0.98 H), τ 5.4 - 5.8 (1.2 H). If the absorption at τ 2.08 is the result of coincidental overlap of the apparently chemically different furano protons,

TABLE I

Best Calculated Chemical Shifts (ν) and Coupling Constants (J) for Proton Magnetic Resonance Spectrum of VI

ν (cps)	A = 406.4	C = 263.7	E = 384.7
	B = 361.3	D = 384.7	F = 295.1
J (cps)	AB = 11.8	BC = 9.3	CD = 6.9
	AC = -0.2	BD = 0.0	CE = 0.1
	AD = 0.0	BE = 0.0	CF = 0.0
	AE = 0.0	BF = 0.0	DE = 10.1
	AF = 0.0	EF = 7.2	DF = 0.1



VI

ν in c.p.s. from $Me_4Si(\nu_0$ = 60 Mc/sec.

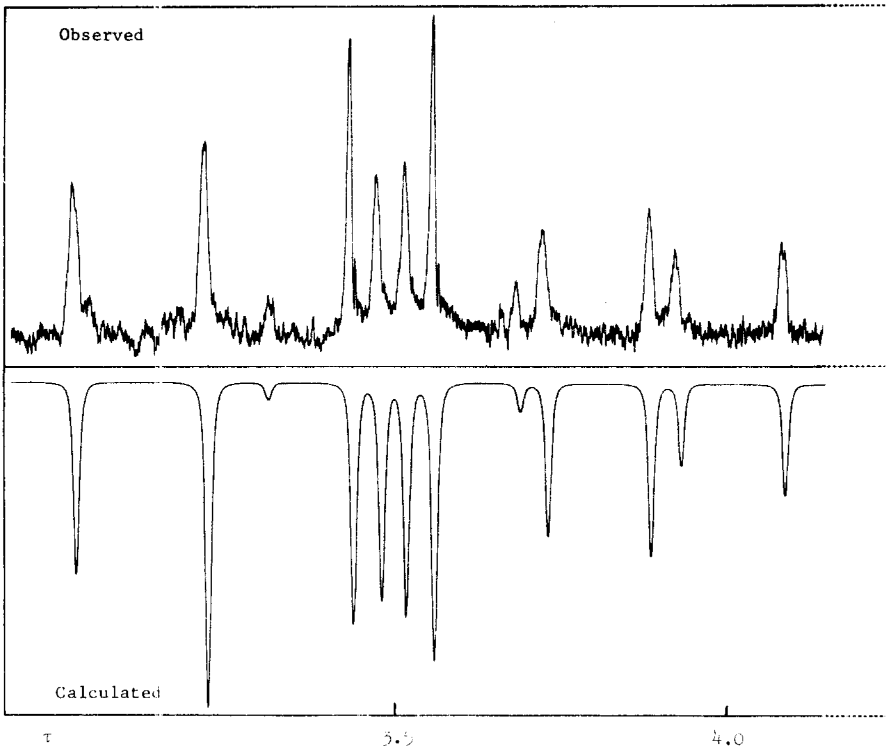


Fig. II

P.M.R. Spectrum of VI (Olefinic Protons)

computer analysis of the remaining olefinic (Fig. II) and allylic (Fig. III) protons as a complex ABCDEF using LAOCOON II-PLOT (9) convincingly confirms this assignment and firmly establishes the structure VI. The computed coupling constants and chemical shifts are tabulated in Table I.

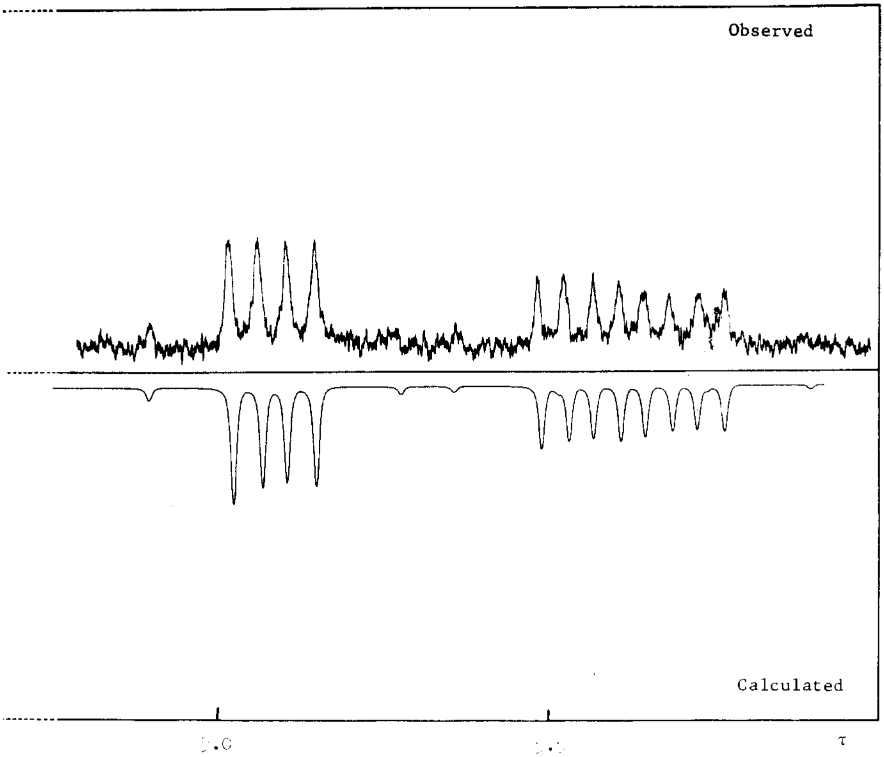


Fig. III

P.M.R. Spectrum of VI (Allylic Protons)

Preparation of Cycloöcta[c]furan: To a mixture of 10 mmol. of $LiAlH_4$ in 75 ml. of ether was added 3.3 mmol. of anhydrous $AlCl_3$. After stirring for 1 hour the suspension was cooled to -75° and 5.0 mmol. of 1,2-dicarbomethoxycyclooctatetraene in 30 ml. of ether was added over 2 minutes. After stirring for 45 minutes 30 ml. of a saturated aq. NH_4Cl solution was added over 5 minutes while the reaction mixture was allowed to warm slowly to room temperature. The ether layer was separated, combined with 2 x 50 ml. washings of the aqueous layer, and dried over $MgSO_4$ for 15 minutes. The ether was rapidly stripped at 35°. The residue (0.92 g.) was dissolved in a small amount of deaerated chloroform, placed on a silicic acid column (25 g.) prepared with deaerated chloroform and allowed to stand for 3-1/2 hours. Elution with deaerated chloroform and stripping of the solvent afforded: cycloöcta[c]furan (48%), then unreacted 1,2-dicarbomethoxycycloöctatetraene (17%), followed by an unstable semi-solid the I.R. of which was consistent with VII (15%), and lastly the diol VIII (18%).

If the above reduction is carried out at room temperature, only the diol VIII (in 94% yield) is obtained. VIII is a pale yellow hygroscopic liquid which solidifies a little below room temperature; p.m.r.: τ 4.09, 4.15 (6 olefinic protons), 5.81 (4 methylene protons) 6.55 (2 hydroxyl protons).

Tetracyanoethylene Adduct of VI: Allowing a nitrogen-flushed dichloromethane solution of I and excess tetracyanoethylene stand at room temperature for 2 days affords a 49% yield of a white crystalline solid, VI, m.p. 246-248° ($HCCl_3$). Calcd. C, 70.59; H, 2.96. Found C, 70.73; H, 3.02.

References and Footnotes

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9. We wish to thank Dr. D. Jung for use of his modification of LAOCOON II which records the data from this program as a smooth curve (lower curves in Figs. II and III). These programs were run on an I.B.M. 7090 using a resolution factor of 0.6 c.p.s. band width at half-height.