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CIS-AZOXY ALKANES. I. SYNTHESIS

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Although trans-azoxy alkanes have been known for some time,[2] there are to our knowledge only eight recorded examples of genuine unconjugated cis-azoxy derivatives,[3,4,9] five of which are highly substituted dihydropyrazoline oxides.[9] The molecular structure of this functionality was recently defined and shown to be consistent with simple assymetric oxidation of the cis-azo moiety.[4]

A simple "one pot" oxidative hydrolysis of easily obtained precursors appears to be a general synthetic route to bicyclic cis-azoxy alkanes. Triazoline-dione 1 (R = C_6H_5) reacts with a wide variety of dienes to provide in excellent yields easily purified crystalline adducts.[5] The hydrogenated adduct 2 is refluxed with excess potassium hydroxide in ethylene glycol-water (1:1) from one to twenty-four hours under nitrogen. At the conclusion of the hydrolysis excess 30% aqueous hydrogen peroxide is added and the solution refluxed for

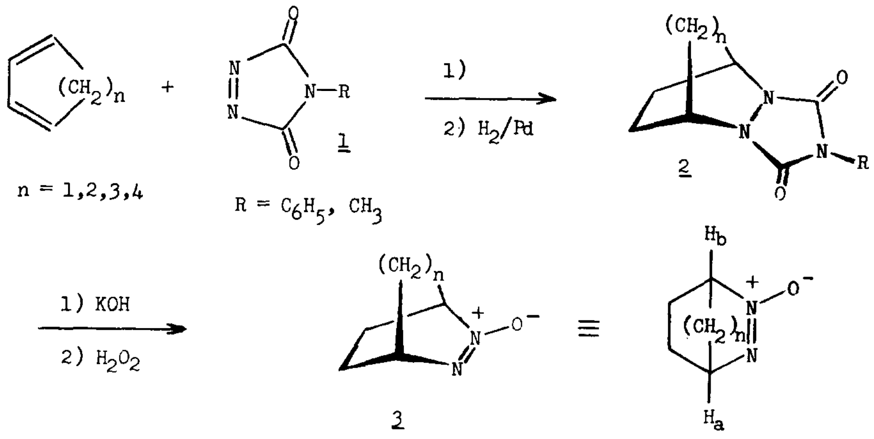
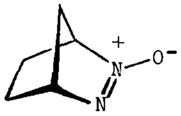
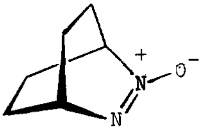
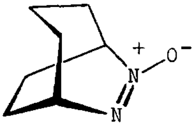
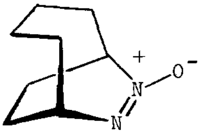
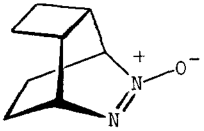
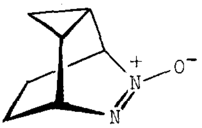
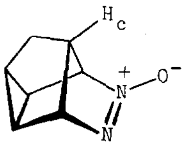


TABLE I

cis-Azoxy Alkanes

		Yield, % (unoptimized)	mp (uncorr.)	ir(KBr), cm^{-1}	NMR(CDCl$_3$),τ,60MHz[a]
1		73	93-95	1517 (s)	5.32 (2H, broad s, hw = 10 Hz) 7.6-8.5 (6H, m)
2		50	150-152	1510 (s)	5.49 (2H, broad s, hw = 14 Hz) 8.13 (8H, broad s)
3		21	176-177	1510 (s)	5.53 (2H, broad s, hw = 12 Hz) 7.5-8.3 (10H, m)
4		98	133-134	1510 (s)	5.33 (2H, broad s, hw = 14 Hz) 7.4-8.6 (12H, m)
5		82	149-150	1484 (s)	5.50 (2H, broad s, hw = 15 Hz) 7.0-8.6 (10H, m)
6		8	135-136	1502 (s)	5.23 (2H, broad s, hw = 11 Hz) 8.30 (6H, m) 8.90 (2H, m)
7		15	54-56	1509 (s)	5.38 (2H, doublet, hw = 6 Hz) 7.27 (1H, broad s) 7.97 (3H, s) 8.06 (2H, s)

a) hw = width at half height

an additional two hours. Steam distillation of aniline followed by workup affords the azoxy product in unoptimized yields ranging from 21 to 98%. (See Table 1)

Azoxy-alkanes 5, 6 and 7 were prepared **likewise** from cyclooctatetraene dibromide, cycloheptatriene and norbornadiene in the indicated yields. Decomposition during oxidation was minimized in the preparation of compound 7 by utilization of N-methyl triazolinedione (1, R = CH_3) in place of the phenyl derivative.

Bicyclic *cis*-azo derivatives corresponding to molecular skeletons 1-7 have resisted synthesis or have been prepared with difficulty.[6] These can be obtained easily by subjecting the unoxidized hydrolyzate of 2 to a cupric halide workup.[7] The appropriate *cis*-azo compound is subsequently liberated from its cupric complex with base. All new compounds return satisfactory analyses and register consistent spectroscopic properties.

As pointed out by Greene and Hecht[4] protons H_a and H_b *alpha* to *cis*-azoxy moiety in 1 accidentally experience very similar if not identical NMR chemical shifts. Similarly compounds 2-6 exhibit both bridgehead protons from τ5.2-5.6 as a broad singlet 10-15 Hz wide at **half** height. Resolution is not improved at 100MHz. H_a and H_b of azoxy 7 are found as a doublet at τ5.38 (J = 2.1 Hz; half width = 5.5 Hz). Decoupling experiments demonstrate that the doublet character of this band arises from coupling with the bridgehead proton H_c situated above the azoxy unit.[8]

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1) To whom inquiries should be addressed.

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