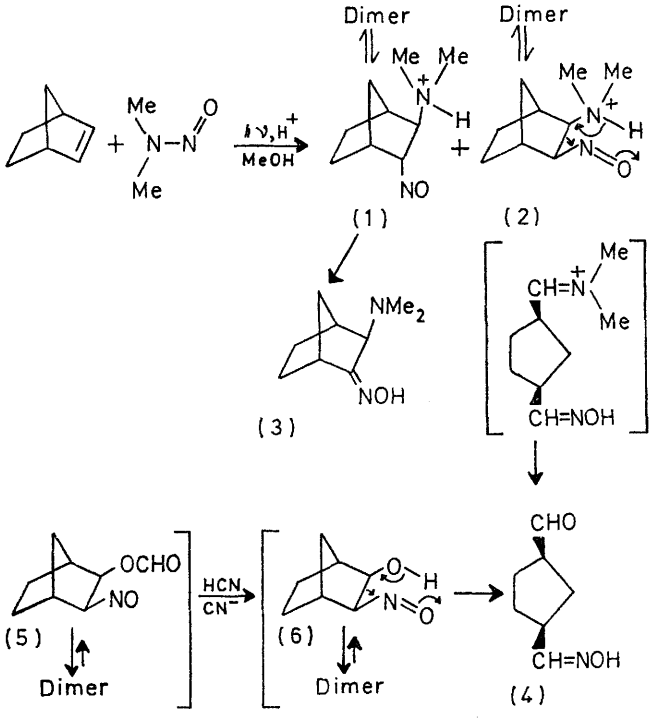
Nitrosamine Photoaddition to Norbornene and the Mechanism of Nitrosoalkane Cleavage

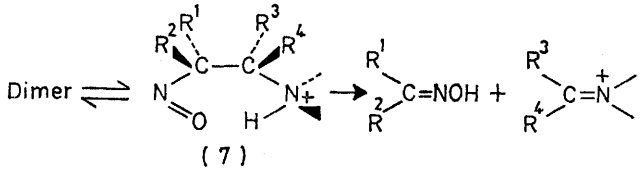
By YUAN L. CHOW,* SHI C. CHEN, and THOMAS MOJELSKY
(*Department of Chemistry, Simon Fraser University, Burnaby 2, B.C., Canada*)

Summary Evidence is presented that the facility of the functional groups to assume *cis*-coplanarity governs the cleavage of a 2-ammonio-1-nitrosoalkane which is obtained from nitrosamine photoaddition to an olefin.

WE have previously reported[1] that 2-ammonio-1-nitrosoalkanes obtained from the nitrosamine photoaddition to olefins may undergo a unique cleavage. Beside the fact that the cleavage occurs only when other reactions of the nitrosoalkanes are inefficient[2] the driving forces promoting this reaction remain obscure. We present evidence that a *cis*-coplanar orientation of the functional groups is a necessary stereochemical requirement and, in turn, that a cyclic transition state is the most likely mechanism for the cleavage.



On the basis of steric and torsional effects governing the stereochemistry of radical additions to norbornene,[3] the photoaddition of *N*-nitrosodimethylamine in methanolic HCl solution is expected[4] to give both the HCl salts of compounds (**1**) and (**2**). Under the conditions that permitted the isolation of the *C*-nitroso-dimers,[5] the photoaddition gave the *anti*-dimer of (**1**) [8·5% isolated as the free base, m.p. 112—113°; ν_{max} 1210 and 1150 cm^{-1}; τ 4·90 (2-H, t, J 4 Hz) and 7·10 (3-H, dd, J 1 Hz)]† without a trace of that derived from (**2**). Other addition products were the *exo*-3-dimethylaminonorbornanone oximes (**3**) [*anti*-oxime (2%); m.p. 72—73°; τ 6·67 (3-H, d, J 2·5 Hz): *syn*-oxime (9%); m.p. 142—143°; τ 6·58 (3-H $w_{\frac{1}{2}}$ 3·5 Hz)] and a large quantity of the "neutral" fraction which was shown to contain *cis*-1,3-diformylcyclopentane monoxime (**4**) [ν_{max}



2710, 1715, 1630, and 950 cm^{-1}; τ 0·36 (d, J 2 Hz), 2·68 (d, J 7 Hz); *m/e* 141] and its derivatives. The crude neutral fraction was quantitatively converted into the 2,4-dinitrophenylhydrazine derivative of (**4**) (m.p. 222—224°; lit.[6] 225—226°). Since the *anti*-dimer of (**1**) in a methanol solution containing 2N-HCl was exclusively tautomerized to the oxime (**3**), the cleavage products [(**4**) and others] were not derived from (**1**) but more likely from (**2**) which escaped detection.

In a desire to use compound (**6**) as the model compound for the cleavage of (**2**), the *anti*-dimer of the corresponding formyl derivative (**5**) was synthesized according to the published method.[7] The dimer (**5**) was stable in boiling methanol but in the presence of 0·02% NaOH rapidly decomposed to (**4**). A mild hydrolysis of the *anti*-dimer of (**5**) in methanol containing HCN (0·02N)–CN$^-$(0·02N) at 20° gave the sparingly soluble dimer of (**6**) [70%; m.p. 170—171°; ν_{max} 3390, 1235, and 1085 cm^{-1}; *m/e* (%) 282, 264, 142(63), and 93(100)]. In boiling methanol the dimer of (**6**) was exclusively converted into the mono-oxime (**4**) containing a trace amount of other products.

The cleavage of the rigid system in (**2**) and (**6**) presumably takes place readily because of the exact *cis*-coplanar orientation of the functional groups. This allows intramolecular proton transfer and concerted rearrangement. Such an explanation provides a rationale for the failure of the *trans*-derivative (**1**) or *trans*-2-dimethylamino-1-nitrosocyclohexane[5] to undergo cleavage. Only where a cyclic process is sterically feasible does cleavage compete effectively with other reactions of nitrosoalkanes such as dimerization and tautomerization.

† Those compounds with m.p.s. gave satisfactory analyses. All n.m.r. spectra were determined with a Varian A-60 spectrometer and the coupling constants with a Varian XL-100 spectrometer by decoupling experiments.

In the case of the flexible acyclic alkanes (**7**),[1,2,8] to assume the *cis*-coplanar orientation of the functional groups results in a conformation with eclipsings of the substituents R^1, R^2, R^3, R^4, and *N*-alkyl groups. The cleavage of such compounds is expected to require an additional activation energy to overcome the steric crowding and is accordingly slower than for (**2**).

(*Received*, 23*rd July* 1973; *Com.* 1056.)

[1] Y. L. Chow, C. J. Colon, and S. C. Chen, *J. Org. Chem.*, 1967, **32**, 2109.
[2] Y. L. Chow, S. C. Chen, and D. W. L. Chang, *Canad. J. Chem.*, 1970, **48**, 157.
[3] P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1967, **89**, 699, 701; F. R. Jensen, L. H. Gail, and J. E. Rodgers, *ibid.*, 1968, **90**, 5793; C. L. Osborn, T. V. Van Auken, and D. J. Trecker, *ibid.*, p. 5806.
[4] M. P. Lau, A. J. Cessna, Y. L. Chow, and W. R. Yip, *J. Amer. Chem. Soc.*, 1971, **93**, 3808.
[5] Y. L. Chow, S. C. Chen, and D. W. L. Chang, *Canad. J. Chem.*, 1971, **49**, 3069.
[6] R. H. Perry, jun., *J. Org. Chem.*, 1959, **24**, 829.
[7] H. C. Hamann and D. Swern, *J. Amer. Chem. Soc.*, 1968, **90**, 6481.
[8] W. Pritzkow and H. Thieme, *J. prakt. Chem.*, 1967, **36**, 180.