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THE DISTINCTIVELY DIFFERENT CHEMICAL PROPERTIES OF BICYCLO [3.1.0]HEX-1-ENES AND SINGLET TRIMETHYLENEMETHANES

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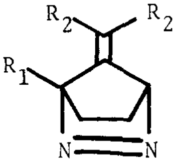
The present paper explores a region on the borderline of covalency, where the structural problem is to distinguish a very weak bond from one that is effectively broken. In previous reports[1-3], we have expressed concern that the bicyclic hydrocarbons 2a and 3a might play some role in the system of reactive intermediates generated by deazetation of the diazene 1a.



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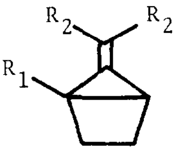

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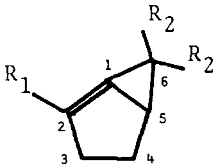

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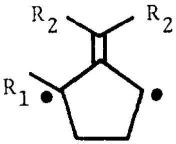


4

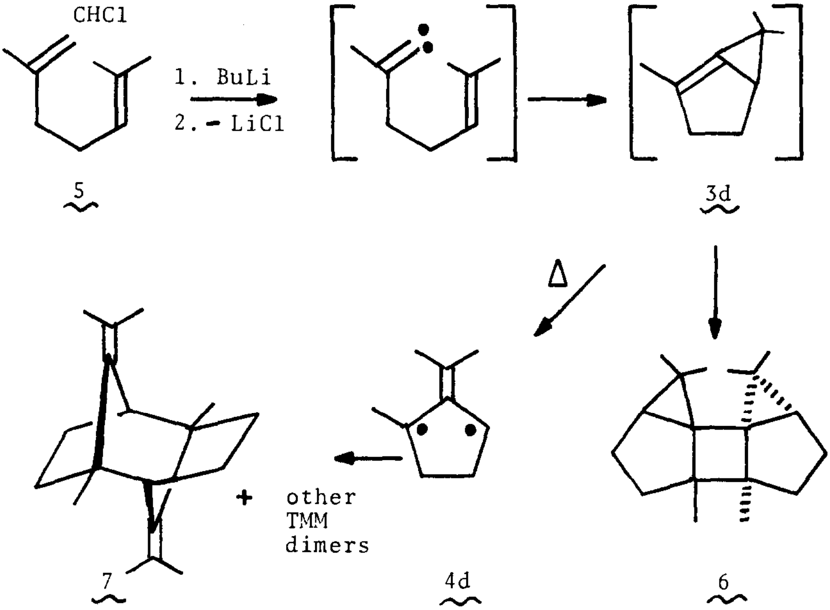
a: $R_1 = H$, $R_2 = Me$
b: R_1, $R_2 = H$
c: $R_1 = Me$, $R_2 = H$
d: R_1, $R_2 = Me$

We have provided physical evidence from low temperature flash photolysis[3]that there must be a structural difference between a true singlet 2-methylenecyclopenta-1,3-diyl (4) and a bicyclic isomer of it (2 or 3), but this leaves open the question of how this difference expresses itself in chemical reactivity. We now find that the chemistry of two bicyclo[3.1.0]hex-1-ene derivatives, 3c and 3d, is quite different from that of TMM singlet diyls 4a and 4b.

Studies by Köbrich[4-6] showed that 2,6,6-trimethylbicyclo[3.1.0]hex-1-ene, 3d, apparently was generated by treatment of the vinyl chloride 5 with BuLi at low temperature. Compound 3d was not isolated, but three dimers of it were reported among the products: the [2+2] adduct, 6, the doubly bridged substance, 7, which is formally a TMM dimer, and a product "of lower symmetry," which was not further described. We now have characterized the latter material in more detail by NMR and mass spectroscopy[7] and find it to consist of a mixture of dimers of the TMM 4d analogous to those of 4a observed[1] in the thermal deazetation of the diazene 1a. As Köbrich reported[5,6], there is a marked temperature-dependence of the ratio of the [2+2] adduct 6 to the TMM adducts. When the reaction is carried out at low temperature (< −40°), 6 is the major product, but predominant amounts of TMM dimers are formed at 0°. We also find a concentration-dependence, with 6 being favored by high concentration. These results are consistent with the formation of 3d from 5 and with a conversion of 3d to the TMM 4d that requires an activation energy (Scheme I).

The effect of replacement of the gem-dimethyl groups of this series by hydrogens is illustrated in Scheme II. Treatment of 1,1-dibromo-2-methyl-1,5-hexadiene, 8a[8], with BuLi or MeLi in diethyl ether or tetrahydrofuran at low temperature gives a 90% yield[10] of three dimers of 2-methylbicyclo[3.1.0]hex-1-ene, 3c. The structural assignments are based upon the spectroscopic

Scheme I



properties[11-15] of the dimers and of their decadeuterio analogues prepared from the pentadeuterio dibromide 8c. In addition to 11, which like 6 in Scheme I, is derived by [π+π] dimerization of the bicyclo[3.1.0]hex-1-ene, two new types of dimers are found. Compound 10 results from an ene reaction of two moles of 3c, and compound 9 is formally a product either of capture of the TMM 4c by the bicyclic olefin 3c or of a [σ+π] dimerization of 3c with itself.

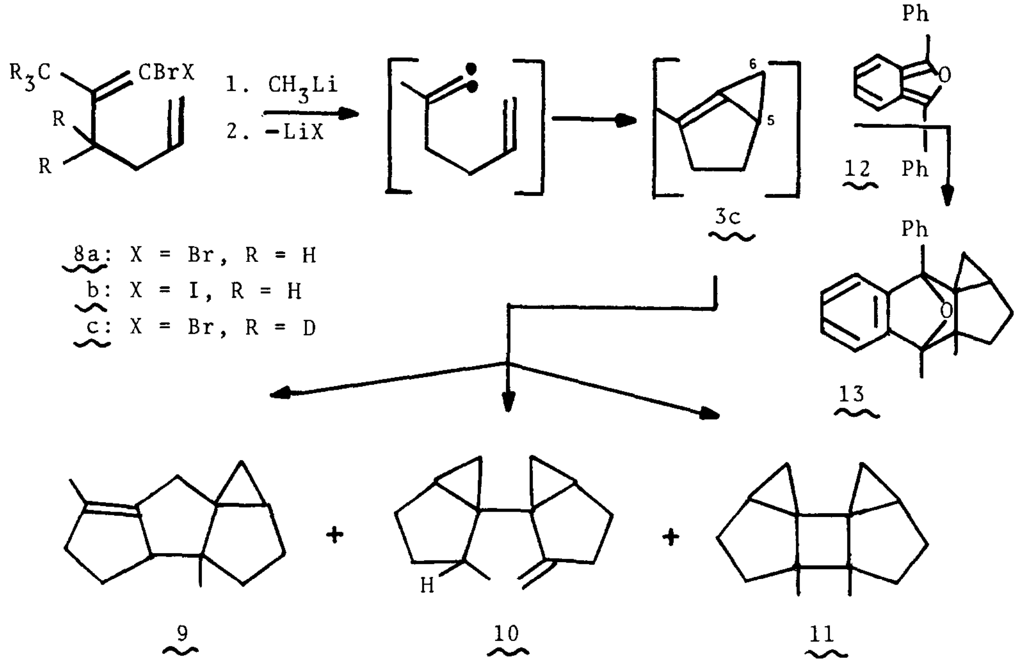
The course of these reactions can be followed at low temperature by effecting metal-halogen exchange between the iodobromo compound 8b and CH_3Li in diethyl ether-d_{10} at −110° in the probe of the 270 Mhz NMR spectrometer. The intermediate bromolithium derivative decomposes at −90° with the simultaneous appearance of NMR absorptions characteristic of 9, 10, and 11. No signals that could be attributed to 3c or to dimers of the TMM 4c are observed.

The product ratio 9:10:11 is 5:2.5:1 and is invariant over a reaction temperature range of −90° to 0° and an initial concentration range (at 0°) of the dihalide 0.1 to 3×10^{-4} M.

Diphenylisobenzofuran (12) traps 3c at 0° in < 5% yield to give a 2:1 mixture of two stereoisomeric Diels-Alder adducts (13)[16]. Thermal deazetation of the diazene 1b in the presence of 12 gives a mixture of TMM dimers and perhaps other products but no Diels-Alder adducts of the hypothetical bicyclo[3.1.0]hex-1-ene, 3b.

We interpret the temperature and concentration invariance of the dimeric products from 3c to mean that these reactions do not require the intervention of the ring-opened form, the TMM 4c. In particular, dimer 9 is more reasonably formulated as a [σ+π] cycloadduct. The extraordinary ease of this process, which is rapid at −90°, must be the consequence of relief of enormous ring strain in 3c. One of the few model [σ+π] cycloadditions involving strained single bonds is the reaction of bicyclo[2.1.0]pentane with maleic anhydride, which is slow at +120°[17].

Scheme II



The gem-dimethyl group of 3d apparently causes a steric retardation of the $[\sigma+\pi]$ and ene reactions, leaving the [2+2] cycloaddition as the only self-reaction. Ring-opening to the TMM 4d now has a chance to compete, and the authentic TMM dimers are formed at higher temperatures (Scheme I).

We conclude that in bicyclo[3.1.0]hex-1-ene derivatives, there is a finite activation energy associated with cleavage of the C_5-C_6 bond. The chemistry of these species is not the same as that of the capturable singlet intermediates obtained by deazetation of diazenes such as 1[18,19].

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References and Notes

1. J. A. Berson, R. J. Bushby, J. M. McBride, and M. Tremelling, J. Am. Chem. Soc., 93, 1544 (1971).

2. J. A. Berson, L. R. Corwin, and J. H. Davis, J. Am. Chem. Soc., 96, 6177 (1974).

3. M. S. Platz, D. R. Kelsey, J. A. Berson, N. J. Turro, and M. Mirbach, J. Am. Chem. Soc., 99, 2009 (1977).

4. The elegant investigations[5,6] of the chemistry of bicyclo[3.1.0]hex-1-enes

begun by the late Professor Gerd Kobrich and his co-workers at the University of Hanover were interrupted by his untimely death.

5. G. Köbrich and H. Heinemann, *Chem. Comm.*, 493 (1969).

6. G. Köbrich, *Angew. Chem. Internat. Ed., English*, **12**, 464 (1973).

7. The NMR spectrum shows vinylic hydrogens at δ1.9-1.6. The mass spectral fragmentation pattern is virtually identical to that of **7** and of the dimers of **4a**[1], showing the base peak at the mass of the monomer. The other dimers **6**,**9**,**10** and **11**, show no peak at the mass of the monomer.

8. Prepared by dibromomethylenation[9] of 5-hexen-2-one.

9. G. H. Posner, G. L. Loomis, and H. S. Sawaya, *Tetrahedron Lett.*, 1373 (1975).

10. Gas chromatographic (gc) analysis with dodecane internal standard on γ-methyl γ-nitropimelonitrile, 85°. Preparative gc on γ,γ and Carbowax 20M.

11. Compound **9**: ^{1}H NMR (δ); 1.638 (3H,s) allylic CH_3; 1.255 (1H,m,*J* = 5.148, 8.089), endo cyclopropyl[14]; 0.902 (3H,s) quaternary CH_3; 0.592 (1H,pseudo t *J* = 5.148, 4.412), endo cyclopropyl. [^{13}C] 143.252 (1C) quaternary olefinic C; 125.672 (1C) quaternary olefin C; 52.219 – 11.664 (12c) aliphatic C. Mass spec.: m/e = 188.15563, calcd. for $C_{14}H_{20}$: 188.15660.

12. Compound **10**[15]: ^{1}H NMR: 4.967 (1H,s), 4.816 (1H,s) = CH_2; 1.327 (1H,m), 1.022 (1H,s,*J* = 4.412, 8.089) cyclopropylmethines; 0.976 (3H,d,*J* = 6.619), tertiary CH_3; 0.760 (3H,m,*J* = 4.412), 8.089 cyclopropyl CH_2; 0.447 (1H, pseudo t,*J* ≅ 4.412), endo cyclopropyl; 0.207 (1H,q,*J* = 5.5148, 8.089), exo cyclopropyl. [^{13}C] 154.555 (1C) quaternary olefinic C; 103.275 (1C) secondary olefinic C; 37.936-9.572 (12C) aliphatic C. Mass spec.: m/e = 188.15509, calcd. for $C_{14}H_{20}$: 188.15660.

13. Compound **11**[15]: ^{1}H NMR: 1.109 (6H,s) quaternary CH_3; 0.499 (2H,q,*J* = 5.148, 8.089) exo cyclopropyl; 0.237 (2H, pseudo t, *J* = 4.413, 5.147) endo cyclopropyl. ^{13}C NMR (partial) 53.739 (2C); 42.877 (2C); 36.032 (2C), 30.866 (2C); 23.117 (2C); 18.726 (2C); 11.60 (2C). Mass spec.: m/e = 188.15563, calcd for $C_{14}H_{20}$: 188.15660.

14. Based on the known relative coupling constants within cyclopropyl groups: (a) K. B. Wiberg, D. E. Barth, and P. H. Schertler, *J. Org. Chem.*, **38**, 378 (1973); see also (b) W. G. Dauben and W. T. Wipke, *ibid.*, **32**, 2976 (1967).

15. Although all three reactions appear to be highly regio and stereospecific, the spectra do not distinguish the structure shown from that of another regioisomer in which the locations of a methyl and a cyclopropyl group have been interchanged.

16. Major isomer of **13**: ^{1}NMR; 1.037 (m,*J* = 4.412) exo cyclopropyl; 0.977 (3H,s), quaternary CH_3; 0.710 (1H,q,*J* = 5.148, 4.412), endo cyclopropyl. Minor isomer of **13**: 1.143 (1H,q,*J* = 5.883, 8.089), exo cyclopropyl; 0.830 (3H,s), quaternary CH_3; 0.569 (1H,q,*J* = 5.883, 3.677), endo cyclopropyl. The mass spectrum of the mixture showed a parent peak at m/e = 364.18135; calcd. for $C_{27}H_{24}O$: 364.18283.

17. P. G. Gassman, K. T. Mansfield and T. J. Murphy, *J. Am. Chem. Soc.*, **90**, 4746 (1968).

18. [2+2] dimers analogous to **6** and **11** are not found among the TMM dimers from diazenes **1a**[1] or **1b**[19]. Moreover, the reactions of singlet **4a**[2] and **4b**[19] with olefins and dienes give cycloadducts derived exclusively from the open TMM forms, not from the closed forms **3a** and **3b**.

19. R. Siemionko, Ph.D. Thesis, Yale University, 1978.

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