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INTRAMOLECULAR AZIDE CYCLOADDITION TO A PHOTOCHEMICALLY GENERATED ZWITTERION

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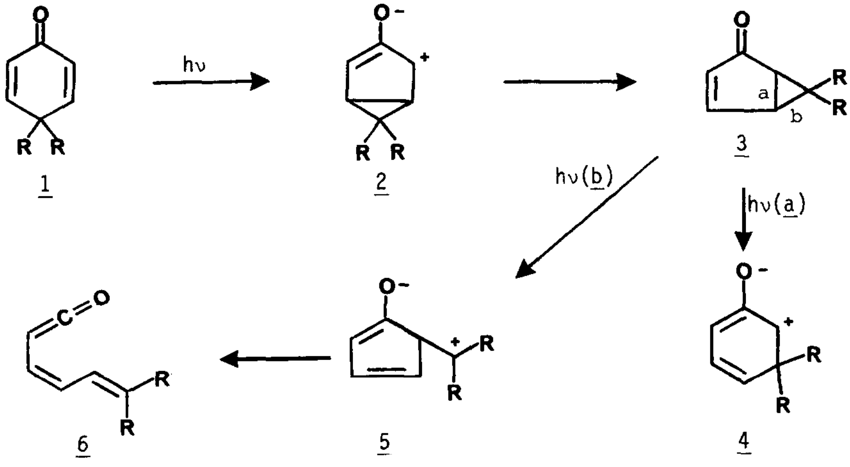
Photochemical rearrangements of 2,5-cyclohexadienones 7a and 7b to bridged triazenes 11a and 11b *via* zwitterions 10a and 10b are described.

Photorearrangements of 2,5-cyclohexadienones, 1, generally occur from the n → π* excited triplet state.[1] Reorganization of electrons gives zwitterion 2, from which a [1,4] sigmatropic shift produces bicyclo[3.1.0]hex-3-en-2-one 3. Solvent[2] and diene trapping[3,4] studies with 4-methyl-4-trichloromethylcyclohexa-2,5-dienone provide direct experimental evidence for the involvement of zwitterions[5] of type 2, as originally postulated by Zimmerman and Schuster.[6]

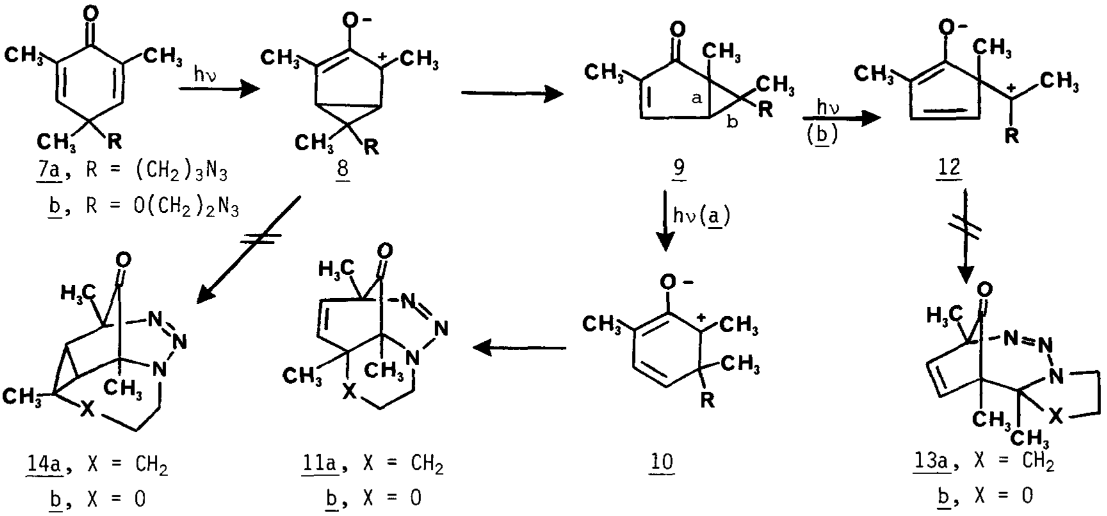
Bicyclo[3.1.0]hexenones 3 undergo secondary photorearrangements to give phenolic compounds and derivatives of diene ketenes.[1] Products from these rearrangements are dependent



on the solvent character and are believed to arise by initial cleavage of either cyclopropane bond a with formation of zwitterion 4 or bond b to give zwitterion 5.[7] [1,2] Shifts provide phenols from 4, while 5 can open to diene ketene 6. Recently, Williams and coworkers have reported the intramolecular addition of a proximate alcohol and carbonyl group to a zwitterion of type 4.[8]

We report the discovery of an intramolecular cycloaddition of an alkyl azide to a photochemically generated zwitterion of type 4; e.g., 10 → 11. The overall photochemical conversions of 4-azidoalkyl-2,5-cyclohexadienones 7 to bicyclic triazenes 11 demonstrate that photorearrangements of 2,5-cyclohexadienones can occur in the presence of the photoreactive azide group by selective irradiation of the long wavelength UV absorption band of the dienone chromophore. These observations provide direct evidence for the intermediacy of zwitterions of type 4 (i.e., 10) in the photochemistry of bicyclo[3.1.0]hex-3-en-2-ones. Of additional importance is the implication that the azido group may be generally useful for cycloaddition to transient oxyallyl intermediates.[9]

Irradiation of azide 7a[10] (42 mg, 0.19 mmol) in THF (10 mL) with a 366 nm light source[11] for 2 h, followed by flash chromatography (45% ethyl acetate in hexane) gives 11a (27 mg, 64%, mp 87-88°C; Anal. Calcd. for $C_{12}H_{17}N_3O$: C, 65.72; H, 7.82; N, 19.16. Found: C, 65.77; H, 7.89; N, 19.16). Similar irradiation of 7b in benzene solution gives 11b (75%, mp 101-102°C, decomposition).



The structures of 11a and 11b are assigned on the basis of chemical composition and well defined spectral data,[12] within the context of the three possible isomeric intramolecular cycloaddition products 11, 13, and 14.[13] Cyclopropane 14 must be considered in light of the successful intermolecular trapping of the type 2 zwitterion generated from photorearrangement of 4-methyl-4-trichloromethylcyclohexa-2,5-dienone,[3,4] but may be rejected on the basis of, among other observations, an absence of olefinic functionality required by ^{1}H and ^{13}C NMR data.[12] That the intramolecular cycloaddition 8 → 14 does not occur may be the result of the expected short lifetime of zwitterion 8 relative to that derived from the C(4) electron deficient 4-methyl-4-trichloromethylcyclohexa-2,5-dienone[1f] and/or a relatively unfavorable transition state leading to 14.

The remaining structures 11 and 13 require the reasonable assumption[1] that the zwitterion 8 derived bicyclohexenone 9 undergoes a secondary photorearrangement to zwitterions 10 (bond a cleavage) or 12 (bond b cleavage). An essential difference between intramolecular cycloaddition products 11 and 13 is that in 11 the carbonyl group resides in a bicyclo[3.3.1] ring system, while in 13 the carbonyl group bridges a bicyclo[4.2.1] system. The carbonyl group absorption frequency of 1727 and 1728 cm^{-1} for 11a and 11b is consistent with a bicyclo[3.3.1] ring system, but not with a bicyclo[4.2.1] system.[14] Furthermore, the ^{13}C NMR chemical shift of δ 197.43 and 201.76 for the carbonyl group of 11a and 11b is appropriate for a bridging cyclohexanone, but not at the lower field of ~218 commonly found for cyclopentanones.[15] Finally, the olefinic coupling constant of 9.3 and 9.6 Hz for 11a and 11b is typical of six membered ring olefins (8.8-11.0 Hz),[14] but not five membered ring olefins (5.1-7.0 Hz).[15]

Efforts to 1) further elucidate the mechanism of triazene formation, 2) study the chemistry of bridged triazenes 11, and 3) intercept other oxyallyl species[9] *via* dipolar and related cycloadditions is in progress.

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References and Notes

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3. (a) Samuel, C. J. J. Chem. Soc., Chem. Commun. 1979, 275. (b) Samuel, C. J. J. Chem. Soc., Perkin 2 1981, 736.

4. Stereochemistry observed in the zwitterion trapping experiments with cyclopentadiene reported by Samuel (reference 3) are consistent with the observations of Zimmerman, H. E.; Crumrine, D. S. J. Am. Chem. Soc. 1968, 90, 5612 and Brennan, T. M.; Hill, R. K. J. Am. Chem. Soc. 1968, 90, 5614 that the [1,4] shift 2 → 3 occurs with inversion of configuration at the migrating carbon atom.

5. Further supporting evidence for the intermediacy of zwitterions of type 2 include the observation of very long-lived blue transients attributed to zwitterions on irradiation of 2,5-cyclohexadienones at 100 K in EPA glasses: Fisch, M. H.; Richards, J. H. J. Am. Chem. Soc. 1968, 90, 1547; Fisch, M. H. J. Chem. Soc., Chem. Commun. 1969, 1472. For an examination of the importance of zwitterionic intermediates in the gas phase photorearrangements of 2,5-cyclohexadienones and bicyclo[3.1.0]hexenones, see Swenton, J. S.; Saurborn, E.; Srinivasan, R.; Sonntag, F. I. J. Am. Chem. Soc. 1968, 90, 2990.

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7. For examples, see (a) Zimmerman, H. E.; Keese, R.; Nasielski, J.; Swenton, J. S. J. Am. Chem. Soc. 1966, 88, 4895. (b) Kropp, P. J. J. Am. Chem. Soc. 1964, 86, 4053 and reference 1d.

8. Williams, J. R.; Moore, R. H.; Li, R.; Blount, J. F. J. Am. Chem. Soc. 1979, 101, 5019; Williams, J. R.; Moore, R. H.; Li, R.; Weeks, C. M. J. Org. Chem. 1980, 45, 2324. Prior evidence for zwitterionic intermediates in bicyclo[3.1.0]hexenone photochemistry was presented by Zimmerman, H. E.; Epling, G. A. J. Am. Chem. Soc. 1972, 94, 7806.

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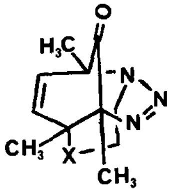
10. The preparation of 7a is described in detail in A. G. Schultz and S. O. Myong, J. Org. Chem. 1983, 48, 2432. The preparation of 7b follows a similar route and will be reported in detail in a full paper describing the intramolecular cycloaddition chemistry of 7b and related compounds.

11. A Hanovia 450-W medium-pressure Mercury-arc lamp in a Pyrex immersion well fitted with Corning color filters 0-25 and 7-54 was employed as the 366 nm light source.

12. Spectral data for 11a: IR (film): 1727, 1433 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.87 (s, 3H), 1.38 (s, 3H), 1.57 (s, 3H), 1.14-1.84 (m, 4H), 3.52 (m, 1H), 4.21 (m, 1H), 5.39 (d, 1H, J = 9.3 Hz), 5.56 (d, 1H, J = 9.3 Hz); ^{13}C NMR (CDCl$_3$) δ 12.93 (q), 18.41 (q), 23.95 (q), 24.97 (t), 33.45 (t), 47.44 (t), 51.96 (s), 63.94 (s), 70.59 (s), 128.14 (d), 138.00 (d), 201.96 (s). 11b: IR (film): 1728 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.07 (s, 3H), 1.51 (s, 3H), 1.60 (s, 3H), 3.5-4.1 (m, 4H), 5.64 (d, 1H, J = 9.6 Hz), 5.91 (d, 1H, J = 9.6 Hz); ^{13}C NMR (CDCl$_3$) δ 12.28, 18.29, 23.00, 46.79, 64.35, 64.90, 72.09, 86.14, 130.28, 136.14, 197.43; chemical ionization m/e 222 (M+1, 100%).

13. The available spectroscopic data do not allow a rigorous exclusion of the orientational isomer of 11 shown here. However, the transition state required for this mode of cyclization would appear to be considerably less favorable that leading to 11.



14. The carbonyl absorption frequency for bicyclo[4.2.1]nona-2,4,7-trien-9-one is: (film) 1780 cm^{-1} (Press, J. B.; Shechter, H. J. Org. Chem. 1975, 40, 2446) and that for bicyclo[3.3.1]nona-2,6-dien-9-one is: (KBr) 1720 cm^{-1} (Aumann, R.; Kencht, J. Chem. Ber. 1976, 109, 174).

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