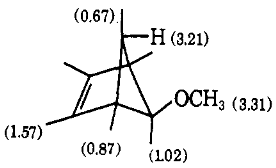
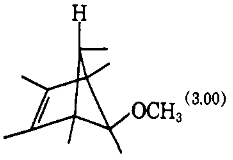
bicyclo[3.1.0]hexenyl cation **5**,[12] it likewise becomes possible to remove this structure from consideration.

The nmr spectra are entirely consistent, however, with the bicyclo[2.1.1]hexenyl cation structure **4** of which there exist two possible stereoisomers, one with a "quasiaxial" and the other with a "quasiequatorial" methyl group (relative to the cyclobutane ring). Corroborative evidence was obtained when the cold FSO_3H-SbF_5-SO_3 solution of **4** was quenched at −78° with excess sodium methoxide in methanol under conditions of rapid magnetic stirring. There was produced in 76% over-all yield the two methyl ethers **13** and **14** in a ratio of 75:25, respectively. These isomers proved to be difficult to separate and purify because of their high reactivity.[13] Careful fractional recrystallization of the mixture from methanol at low temperatures, however, ultimately resulted in the isolation of the major product, mp 44–45°, in 10–15% yield; on the basis of its nmr spectrum (δ values, CCl_4, internal TMS), this isomer has been assigned structure **13**. We have so far been unable to isolate a pure sample of **14**, and the indicated structural assignment must be considered tentative. Although it has not proven possible from the present data to state unequivocally which isomer of **4** predominates in the strongly acidic medium, the cation corresponding to isomer **13** seems most likely, particularly since the quenching is expected to be kinetically controlled under the conditions employed. The stereochemistry of the methoxyl groups in **13** and **14** follows from the customary steric considerations given to related ions.



13



14

Previously, the bicyclo[2.1.1]hexene system has proven very elusive; only recently has the first number of the series been described.[14] Should such quenching reactions prove to be general in nature, facile synthetic entry to a variety of bicyclo[2.1.1]hexene derivatives would be available.

Earlier work suggests implicitly that structures of types **3**–**7** constitute a set of $C_{12}H_{18}R^+$ cations[15] which exist on a single potential energy surface.[2–7] The various isomers are accessible by either thermal[2–7] or photochemical means.[11] The present findings [Dewar benzene and prismane routes] denote that the bicyclo[2.1.1]hexenyl cation (**4**) may be an energy minimum (with respect to the various cations) in strongly acidic media. Irradiation of **7** at −78° in FSO_3H gives **5**. Both **4** and **5** are subject to clean first-order conversion to **7**, but at greatly differing rates [for **4**, $k = 10.3 \times 10^{-4}$ sec^{-1} at 20.5° in HF–BF_3 solution;[7b,16] for **5**, $k = 1.15 \times 10^{-3}$ sec^{-1} at −34° in FSO_3H[11]]. Because **4** rearranges more slowly than **5**, it is not possible to examine the thermal interconvertibility of these cations by this technique. Nevertheless, the isomerization of **4** to **7** is perhaps best rationalized as proceeding *via* cation **5**.

Acknowledgment. The authors wish to thank Professor David Lemal for a generous gift of hexamethylprismane, and the Petroleum Research Fund administered by the American Chemical Society, for partial support of this work.

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[12] Protonation of **1** in neat FSO_3H [the solvent system used by Childs and Winstein;[11] shifts referred to internal CH_2Cl_2 (τ 4.70)] gives rise to an identical spectrum. The chemical shift values seen in FSO_3H–SbF_5–SO_3 solution [this work; reference point is capillary TMS (τ 10.00)] are approximately 0.15 ppm higher than the same values in FSO_3H (S. Winstein, personal communication).

[13] Silica gel chromatography converts **14** to hexamethylbenzene and partially transforms **13** into unidentified products. Both isomers readily add a second mole of methanol, and if the quenching is done in a methanol–potassium carbonate suspension without rapid stirring a dimethanol addition compound is produced to the extent of approximately 70%. We have not yet been able to assign a structure to this material.

[14] J. Meinwald and F. Uno, *J. Am. Chem. Soc.*, **90**, 800 (1968); F. T. Bond and L. Scerbo, *Tetrahedron Letters*, 2789 (1968).

[15] R need not necessarily be a proton but may also be a different electrophilic moiety.

[16] This rate is not significantly altered in FSO_3H (S. Winstein, personal communication).

[17] Considered as Stable Carbonium Ions. LXXVIII.

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Photochemical Transformations of 2-Methoxyazabullvalene[1,2]

Sir:

Interest in the ground- and excited-state properties of molecules with fluctuating bonds is at an all-time high. However, in spite of the relatively numerous accounts of photochemical routes to bullvalene,[3] semibullvalene,[4] and their derivatives, only in the case of bullvalene has more extensive photolysis of such a system been examined.[5] In this communication we wish to report our study of the photochemical transformations of 2-methoxyazabullvalene (**1**)[3e,6] under conditions of direct irradiation.

On exposure of methanol or tetrahydrofuran solutions of **1** to an unfiltered 450-W Hanovia lamp for 15 hr, a number of photoproducts result (Table I). The duration of the experiments was dictated by the fact that certain of the photoproducts were also unstable to ultraviolet light; under the stated conditions, the yields of the various components appeared to be maximized. Separation of the compounds was achieved by preparative-scale vpc separation at 160° on a 10-ft column

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[1] Unsaturated Heterocyclic Systems. XLVII. For the previous paper in this series, see I. C. Paul, S. M. Johnson, L. A. Paquette, J. H. Barrett, and R. J. Haluska, *J. Am. Chem. Soc.*, **90**, 5023 (1968).

[2] Partial support of this research by the National Institutes of Health and the National Science Foundation is gratefully acknowledged.

[3] For example, see (a) G. Schröder, *Angew. Chem.*, **75**, 722 (1963); *Angew. Chem. Intern. Ed. Engl.*, **2**, 481 (1963); (b) G. Schröder, *Ber.*, **97**, 3140 (1964); (c) W. von E. Doering and J. W. Rosenthal, *Tetrahedron Letters*, 349 (1967); (e) L. A. Paquette and T. J. Barton, *J. Am. Chem. Soc.*, **89**, 5480 (1967).

[4] (a) H. E. Zimmerman and G. L. Grunewald, *ibid.*, **88**, 183 (1966); (b) H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *ibid.*, **89**, 3932 (1967); (c) J. P. N. Brewer and H. Heaney, *Chem. Commun.*, 811 (1967); (d) R. S. H. Liu, *J. Am. Chem. Soc.*, **90**, 215 (1968).

[5] M. Jones, Jr., *ibid.*, **89**, 4236 (1967).

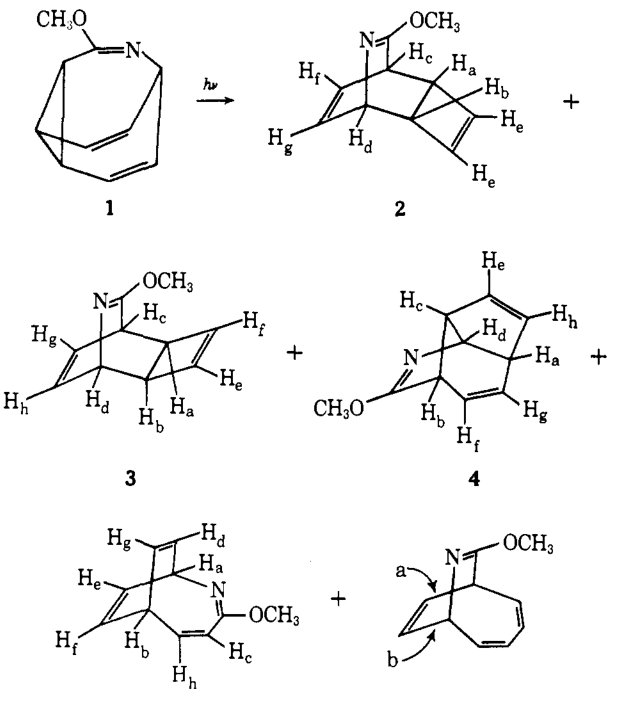
[6] L. A. Paquette, T. J. Barton, and E. B. Whipple, *ibid.*, **89**, 5481 (1967).

Table I. Product Compositions from the Irradiation of 2-Methoxyazabullvalene (**1**) in Methanol and Tetrahydrofuran Solutions for 15 Hr

Photoproduct	Retention time, min	Yield, %, MeOH	Yield, %, THF
2	14	9	2
3	15.5	9	7
4	18	9	5
5	21.5	7	10
6	21.5	1	*a*
Recovered **1**	32	57	55

[a] Not detected.

packed with 10% SF-96 on Chromosorb G. The most rapidly eluted substance (**2**) was readily identified as an unconjugated imino ether on the basis of its infrared ($\nu_{max}^{CHCl_3}$ 1650 cm^{-1}) and ultraviolet spectra [$\lambda_{max}^{CH_3OH}$ 267 mμ (ε 160)].[7] The 100-MHz nmr spectrum of this photoisomer (*Anal.* Found: C, 74.48; H, 7.03) consists of four sets of lone aliphatic proton signals [a triplet (J = 1.8 Hz) at δ 2.42, a triplet (J = 1.8 Hz) at 2.64, and multiplets at δ 3.46 and 4.58] and vinyl proton absorptions of area 2 at δ 6.20 (singlet) and *ca.* 6.47 (multiplet). Decoupling experiments permitted detailed analysis of the spectrum and measurement of the following coupling constants: $J_{ac} = J_{ab} = J_{bd}$ = 1.8 Hz, J_{cf} = 2.8 Hz, J_{cd} = 1.0 Hz, J_{dg} = 2.5 Hz, and J_{fg} = 3.7 Hz. The degree of unsaturation in **2** necessitates that the structure be tricyclic;[8] the *endo* configuration of the cyclobutene ring is assigned chiefly because of the identical chemical shift of the two vinylcyclobutene protons and the availability of the *exo* isomer (*i.e.*, **3**) for comparison.



The stereoisomeric nature of **3** (*Anal.* Found: C, 74.19; H, 6.99) follows from inspection of its spectra [$\nu_{max}^{CHCl_3}$ 1645 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 265 mμ (ε 60)]. Particularly revealing was the 100-MHz nmr spectrum which exhibited four mutually coupled aliphatic proton signals at δ 2.64, 2.79 (triplets) and 3.43, 4.59 (multiplets) and complex four-proton vinyl absorption in the δ 5.90–6.22 region. By means of spin decoupling, it proved possible to assign the following coupling constants: $J_{ab} = J_{ac} = J_{bd}$ = 1.8 Hz, J_{cd} < 0.5 Hz, $J_{cg} = J_{dh}$ = 3.2 Hz, J_{ef} = 1.3 Hz, and J_{gh} = 3.5 Hz. The proximity of H$_e$ and H$_f$ to the imino ether residue in **3** is very likely the causative factor behind their slightly different chemical shifts (δ 5.90 and 6.08).

Photoproduct **4** (m/e 161) proved to be unstable to ultraviolet light and to decompose upon storage at 0°. The substance was shown to be nonconjugated by its ultraviolet spectrum [$\lambda_{max}^{CH_3OH}$ 270 mμ (ε 50)], and the presence of an imino ether function was confirmed by a strong infrared band at 1620 cm^{-1} (CHCl$_3$). Its 100-MHz nmr spectrum showed single proton aliphatic absorptions at δ 2.56 (H$_a$, multiplet), 2.74 (H$_b$, triplet), 3.24 (H$_c$, multiplet), and 4.26 (H$_d$, triplet), and vinyl proton peaks of area 1 at δ 5.55 (H$_e$, doublet of doublets), 5.78 (H$_f$, multiplet), 6.05 (H$_g$, multiplet), and 6.60 (H$_h$, doublet of doublets); $J_{ad} = J_{ag} = J_{bf} = J_{bc}$ = 2.5 Hz, J_{ah} = 1.6 Hz, J_{ce} = 1.8 Hz, J_{cd} = 2.1 Hz, J_{eh} = 3.0 Hz, and J_{fg} = 4.5 Hz. With the identification of Hd as the proton on carbon attached to nitrogen, it becomes possible to assign the unique structure **4** from consideration of the measured coupling constants.

It was not possible to separate compounds **5** and **6** satisfactorily under a variety of conditions; however, the nmr spectrum of the mixture clearly showed the presence of known **6**.[3e] Perhaps significantly, the formation of **6** was not observed when tetrahydrofuran was employed as solvent; under these conditions, imino ether **5** could be obtained in a pure state (*Anal.* Found: C, 74.48; H, 7.04). The ultraviolet spectrum of **5** which exhibits a maximum in methanol at 250 mμ (ε 2200) is confirmatory for a conjugated system. The 100-MHz nmr spectrum displays only two saturated proton absorptions at δ 3.16 (H$_b$, multiplet) and 4.52 (H$_a$, triplet) in addition to six signals of equal area attributable to vinyl protons centered at δ 5.58, 5.86, 5.94, 6.12, 6.18, and 6.44; $J_{ad} = J_{ae}$ = 2.7 Hz, $J_{bf} = J_{bg}$ = 3.0 Hz, J_{bh} = 4.0 Hz, J_{ch} = 6.2 Hz, and $J_{dg} = J_{ef}$ = 4.5 Hz. The upfield protons are assigned on the basis that H$_a$ is doubly allylic and bonded to carbon attached to nitrogen and that H$_b$ is triply allylic. H$_c$ (δ 5.58), coupled only to H$_h$ (δ 6.44), must be vicinal to the methoxyl-bearing carbon because of its upfield position in the vinyl region. Structure **5** then is uniquely derivable from the observed coupling constants.

In order to gain added insight into the mechanistic course of these photorearrangements, the analogous irradiation of **6** in methanol was carefully monitored. After 1 hr all of the photoproducts observed in the photolysis of **1** were present except imino ether **4**, which was not formed until at least 3 hr had elapsed and the concentration of **1** had substantially increased. Under

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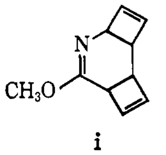
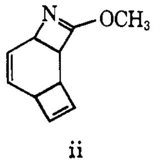
(7) Compare the ultraviolet spectra of 1 (strong end absorption only) and 6 [$\lambda_{max}^{CH_3CN}$ 271 mμ (ε 2000)].[3e]

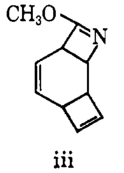
(8) The observed chemical shifts and coupling constants in 2 and 3 are inconsistent with alternative tricyclic structures such as i–iii.



i



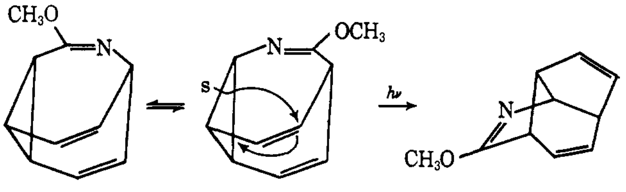
ii



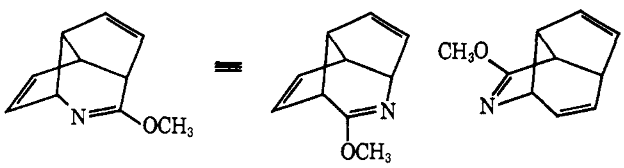
iii

the same conditions but with acetone as both solvent and sensitizer, the reaction rate was faster than that of the unsensitized runs *but* **1** *was the sole product.* Continued irradiation of **1** in this medium resulted in no further chemical change.

These results are congruent with the existence of a photoequilibrium between **1** and **6** under the conditions of direct irradiation. Further, the data are consistent with the formation of **2**, **3**, and **5** from singlet **6**. Symmetry-allowed disrotatory cyclization of the diene component in **6** gives **2** and **3** depending upon the direction of orbital rotation, while a concerted 1,3 suprafacial shift of bond a (see **6**) affords **5**.[9] Photoproduct **4** probably arises directly from singlet **1**; the simplest pathway leading to **4** is a 1,3 shift of cyclopropyl bond s in valence tautomer **7**. In this regard, it is particularly important to note that isomeric imino ethers **8** and **9** were not produced, despite the fact that these structures can also be derived from alternative vinylcyclopropane rearrangements in **1** and **7**.



1 **7** **4**

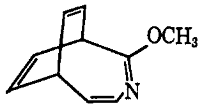


8 **9**

Finally, the significant sensitizing effect of acetone would seem to suggest that the singlet states of **1** and **6** cross to the corresponding triplet states with poor efficiency.

Acknowledgment. We wish to thank Badische Anilin and Soda Fabrik for a generous gift of cyclooctatetraene and Richard Cryberg for his assistance in obtaining the 100-MHz spectra.

(9) Here it is interesting that the formation of iv which could arise



iv

by a similar 1,3 suprafacial shift of bond b in **6** was not observed.

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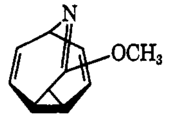
Benzazabullvalenes. Synthesis and Interconvertibility[1]

Sir:

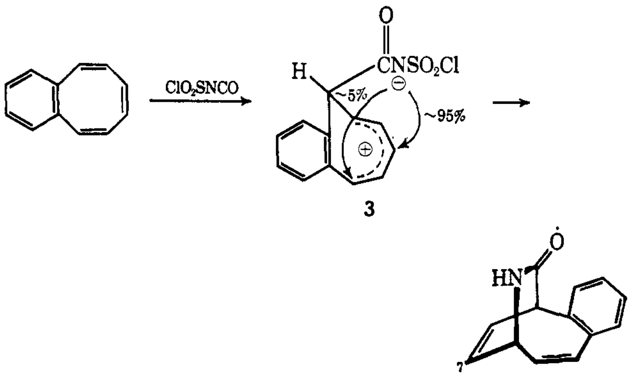
Previously we have shown that incorporation of an imino ether function into the bullvalene molecule (**1**) drastically diminishes the number of accessible structural arrangements from 1,209,600 in **1** to only 28 in **2**.[2,3] The simplicity of the averaging process in **2** has been attributed to the strong preference of the nitrogen atom for the imino ether bond. Equally significant was the observation that the aza substituent also exhibits preferential attachment to the "bridgehead" carbon (as shown in **2**). We now report the extension of this study to benzo derivatives of **2** in the course of which an especially intriguing structural dependence on photochemical reactivity and an unprecedented thermal rearrangement have been delineated.

1



2

Treatment of benzocyclooctatetraene[4] with chlorosulfonyl isocyanate (CSI) at 82° for 3 hr followed by hydrolysis of the resulting N-(chlorosulfonyl)lactam with aqueous NaOH in acetone gave in 82% yield amide **4**, mp 226–227°;[5] $\nu_{max}^{CH_2Cl_2}$ 3390 and 1680 cm^{-1}; $\lambda_{max}^{CH_3CN}$ 269 mμ (ϵ 9700). Electrophilic attack of CSI on benzocyclooctatetraene therefore proceeds to give dipolar benzotropylium cation **3**, addition occurring in the manner expected from protonation data.[6] Collapse of the zwitterion occurs chiefly by bonding to C-5; careful nmr analysis of the unpurified amide indicated that an upper limit of 7% cyclization to C-3 could have occurred.[7]



3

4

The crystalline imino ether **5**,[5] obtained in 96% yield from **4** by treatment with trimethyloxonium fluoroborate, exhibited ultraviolet absorption (in hexane) at 273.5 mμ (ϵ 8500) and nmr peaks for H_1 and H_6 at δ 4.10 (doublet, J = 5.6 Hz) and 4.56 (triplet, J = 6.0 Hz), respectively. Irradiation of **5** with acetone sensitization afforded in 93% yield primarily benzazabullvalene **6** (>95%), plus benzisoazabullvalene **7** (<5%).[8] The structures of **6** [mp 113–114°;[5]

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[1] Unsaturated Heterocyclic Systems. XLVIII. For the previous paper in this series, see L. A. Paquette and G. Krow, *J. Am. Chem. Soc.*, **90**, 7149 (1968).

[2] L. A. Paquette and T. J. Barton, *J. Am. Chem. Soc.*, **89**, 5480 (1967).

[3] L. A. Paquette, T. J. Barton, and E. B. Whipple, *ibid.*, **89**, 5481 (1967).

[4] W. Merk and R. Pettit, *ibid.*, **89**, 4787 (1967).

[5] Satisfactory elemental analyses were obtained for all new compounds.

[6] W. Merk and R. Pettit, *J. Am. Chem. Soc.*, **90**, 814 (1968).

[7] The limited available quantity of this minor isomer precluded its isolation and characterization.

[8] We herein propose the name *isobullvalene* to unknown hydrocarbon i in an effort to maintain some degree of constancy in nomencla-