Mechanistic Details of the Photoinduced Formation and Thermal Rearrangement of 3-Methoxy-4-aza-6,7-benzotricyclo[3.3.2.$0^{2,8}$]deca-3,6,9-triene (Benzazabullvalene A)[1]

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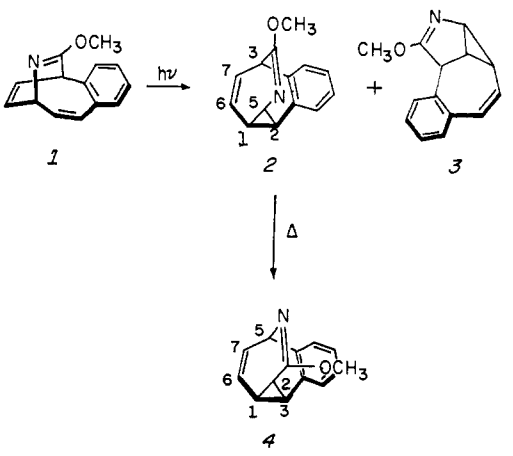
Abstract: Addition of chlorosulfonyl isocyanate to 3,5,6,8-tetradeuteriobenzocyclooctatetraene (**17**) and subsequent hydrolysis of the resulting N-(chlorosulfonyl) lactam afforded 2,3-benzo-8-methoxy-7-azabicyclo[4.2.2]deca-2,4,7,9-tetraene (**14**) with hydrogen labels at C_5 and C_9. Acetone-sensitized or direct photolysis of **1A** gave benzazabullvalene A **8** with protons at C_1 and C_7. Of the various mechanisms possible for this transformation, the labeling result uniquely identifies the process as a di-π-methane rearrangement with initial vinyl–vinyl bonding. Thermal rearrangement of **8** and alternatively labeled benzazabullvalene A **26** led to specifically deuterium-labeled benzazabullvalenes **22** and **29**, respectively. It is seen that two mechanisms can account for these observations. First, a route involving a series of Cope rearrangements with initial rupture of the imino ether function, followed by participation from the benzene ring with loss of aromatic character, and a final [3,3] sigmatropic shift to reestablish this delocalization could be operative, or the formal diradical equivalent initiated by homolytic rupture of the C_1C_5 bond followed by migration of $C(OCH_3)$ to C_7 and phenyl shift to C_5 is involved. These two routes are considered in detail from the mechanistic viewpoint. The 100-MHz nmr spectrum of unlabeled benzazabullvalene B (**4**) is analyzed with the aid of double resonance techniques.

In earlier reports, we demonstrated that photorearrangement of imino ether **1** afforded primarily benzazabullvalene A (**2**)[2] and some benzisoazabullvalene (**3**).[3] Additionally, we showed that **2** underwent an irreversible thermal rearrangement at 125–150° to benzazabullvalene B (**4**) in high yield. It is readily



1 2 3 4

seen that several mechanistic pathways are available in the photochemical isomerization of **1** to **2** as well as in the thermal rearrangement of **2** to **4**. The present research was initiated in order (a) to determine precisely whether the conversion of **1** to **2** occurs by di-π-methane rearrangement or by $2\sigma + 2\pi$ bond reorganization; (b) to see which of the several alternatives within each rearrangement type is in fact operative; (c) to establish if the thermal transformation of **2** to **4** is the result of homolytic bond cleavage reactions with subsequent rebonding or a series of Cope rearrangements involving, at one stage, temporary destruction of the aromaticity in the fused benzene ring; and (d) last, to achieve a complete analysis of the nmr spectrum of benzazabullvalene B.

Structural Aspects of Photorearrangement of 1. The problem of elucidating the correct mechanism operative in the photolysis of **1** was especially intriguing because it represents the first bicyclo[4.2.2]deca-2,4,7,9-tetraene derivative to be examined in detail. *A priori*, three distinctly different pathways are possible, each of which is supported by literature precedence; however, the influence of unsymmetrically positioned heterocyclic substituents on the course of each of these three mechanisms had not previously been examined. Earlier, the Zimmerman group had shown that the conversion of barrelene to semibullvalene is the result of a di-π-methane rearrangement involving vinyl–vinyl bonding.[4] Interestingly, benzobarrelene is transformed into benzosemibullvalene preferably *via* the vinyl–vinyl bonding route and not by the alternative benzo–vinyl bonding mechanism.[5] However, di-π-methane rearrangements which do involve benzo–vinyl bridging have been recently recognized in several systems.[6] Also, a substantial number of $\sigma^2_a + \pi^2_a$ photorearrangements are known,[7] and it is entirely

(1) Unsaturated Heterocyclic Systems. LXV. For previous paper in this series, see L. A. Paquette and R. J. Haluska, *J. Org. Chem.*, **35**, 132 (1970).

(2) The terminology "benzazabullvalene A" and "benzazabullvalene B" is employed herein simply as a convenient device to differentiate between isomeric structures 2 and 4, respectively.

(3) L. A. Paquette, J. R. Malpass, G. R. Krow, and T. J. Barton, *J. Am. Chem. Soc.*, **91**, 5296 (1969); L. A. Paquette and J. R. Malpass, *ibid.*, **90**, 7151 (1968).

(4) H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *ibid.*, **89**, 3932 (1967); H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *ibid.*, **91**, 3316 (1969).

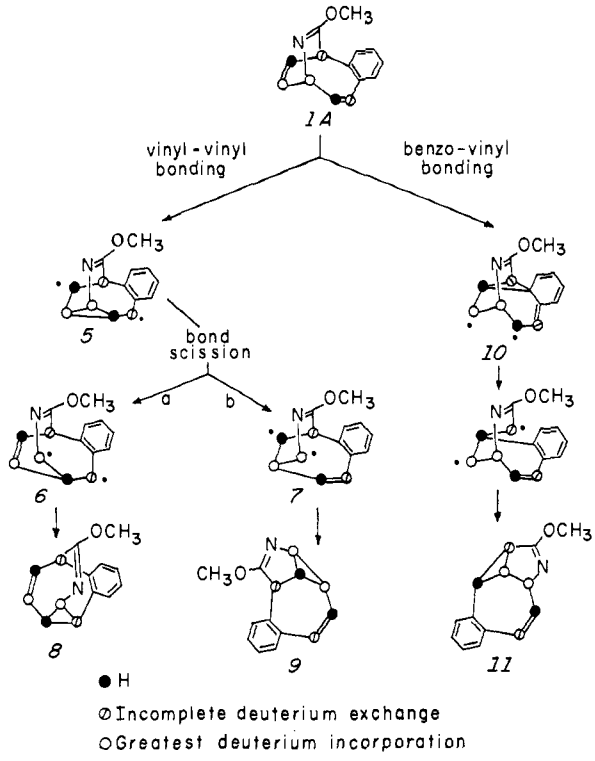
(5) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *ibid.*, **90**, 4191, 6096 (1968).

(6) (a) E. Ciganek, *ibid.*, 88, 2882 (1966); (b) P. W. Rabideau, J. B. Hamilton, and L. Friedman, *ibid.*, **90**, 4465 (1968); (c) J. R. Edman, *ibid.*, 88, 3454 (1966); (d) H. Hart and R. K. Murray, Jr., *ibid.*, **91**, 2183 (1969); (e) R. C. Hahn and L. J. Rothman, *ibid.*, **91**, 2409 (1969); (f) J. Ipaktschi, *Tetrahedron Letters*, 215 (1969); (g) G. R. Ziegler and G. S. Hammond, *J. Am. Chem. Soc.*, **90**, 513 (1968).

(7) For a partial listing of examples, see L. A. Paquette and J. R. Malpass, *ibid.*, **90**, 7151 (1968).

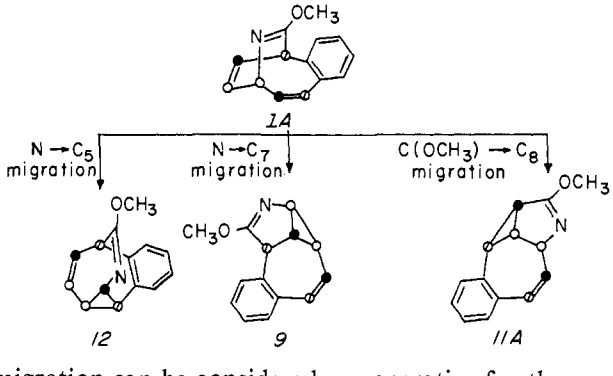
reasonable that **1** could be rearranging by one or more of these symmetry-allowed intramolecular cycloadditions.[8]

Scheme I. Possible Di-π-methane Mechanisms for the Photorearrangement of **1A**



Two di-π-methane bonding processes are seen to be possible in **1**, as illustrated in Scheme I. Nevertheless, initial benzo–vinyl bonding clearly does not occur, as revealed by the fact that **11** is not produced during the photochemical reaction.[3,9] Of the three possible $\sigma^2_a + \pi^2_a$ mechanisms (Scheme II), the $C(OCH_3) \rightarrow C_8$

Scheme II. Possible σ^2_a and π^2_a Mechanisms for the Photorearrangement of **1A**

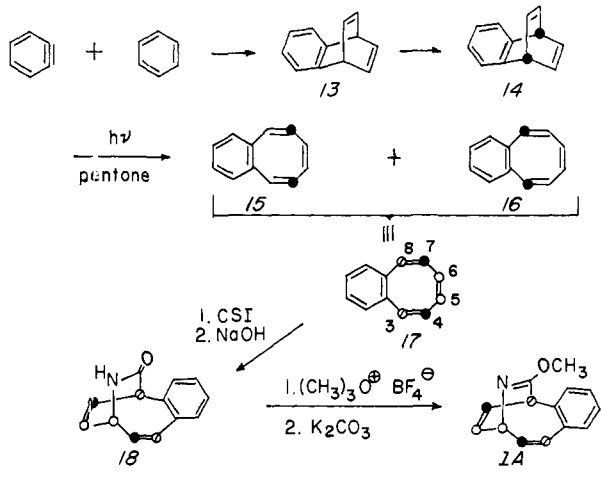


migration can be considered nonoperative for the same reason. If **1** were deuterium labeled as indicated in these schemes (*i.e.*, **1A**), it can be seen that the distribution of hydrogen in the resulting partially deuterated benzazabullvalene A depends on whether vinyl–vinyl bonding or $\sigma^2_a + \pi^2_a$ bond migration occurs. Whereas the first mechanism leads to a benzazabullvalene A hydrogen labeled at C_1 and C_7 (**8**), the second mechanism would afford **12** with hydrogen labels at C_5 and C_7. Parenthetically, it should be noted that the labeling in benzisoazabullvalene **9** produced from either pathway is identical, a fact which does not allow for unequivocal assignment of mechanistic detail to the process leading to this minor product.

The route to **1A** began with the synthesis of benzobarrelene (**13**) according to the procedure of Friedman.[10] Treatment of this hydrocarbon with N,N-dideuteriocyclohexylamine–lithium N-deuteriocyclohexylamide resulted in exchange of the aromatic and vinyl protons without affecting the sp^3-bound bridgehead protons. In our hands, however, the exchange did not proceed as readily as Zimmerman describes;[5] after five deuteration passes and silica gel chromatography to remove unwanted naphthalene, the crystalline sample of **14** was only 72.1 ± 0.6% deuterated at the aryl and vinyl sites (nmr analysis). The distribution of residual hydrogen between aryl and vinyl positions was calculated by the method of Zimmerman;[5] 39.6 ± 0.6% of the aryl positions and 16.2 ± 0.6% of the vinyl positions were found to bear hydrogen. This extent of deuterium exchange was more than sufficient for our intended purposes, however, and this sample of **14** was utilized for the subsequent experiments.

Irradiation of a 0.1% solution of **14** in pentane for 320 min yielded a mixture consisting of **17** (90%) and unchanged **14** (10%) (Scheme III). Further photol-

Scheme III. Preparation of 2,3-Benzo-8-methoxy-7-azabicyclo[4.2.2]deca-2,4,7,9-tetraene, Partially Deuterated as **1A**



ysis did not appear to alter this ratio. Preparative scale vpc served to remove **14** and afforded **17** in 75% isolated yield. The deuterated benzocyclooctatetraene (**17**) possessed the nonaromatic hydrogen atom distribution shown in Table I; as noted earlier,[5] most of the hydrogen label resides at C_4 and C_7 (because **15** is present to the extent of 94%), with lesser amounts at the C_3 and C_8 positions, and still less at C_5 and C_6. These three pairs of carbon atoms have been labeled ●, ⊘, and ○, respectively, in the various formulas to denote the decreasing hydrogen content at the several positions. It is particularly noteworthy that the experimental and calculated values of Table I are in excellent agreement. A consequence of the presence of

(8) For a summary of discussion on this point, see R. Hoffmann, Abstracts of the 21st National Organic Chemistry Symposium, Tempe, Arizona, 1969, pp 116–120.

(9) In actuality, intermediate **10** may undergo bond reorganization in an alternative manner. However, since this alternative does not lead to ultimate reestablishment of benzenoid aromaticity, we discount the likelihood of its operation and have not illustrated the process in Scheme I.

(10) L. Friedman and D. F. Lindow, *J. Am. Chem. Soc.*, **90**, 2329 (1968).

Table I. Hydrogen Atom Distribution in **17** (60 MHz Spectrum, CCl_4 Solution)

Chemical shift, δ	Multiplicity and assignment	Hydrogen atom distribution Exptl values[a]	Calcd values[b]
6.7–7.2	Multiplet, aryl protons	1.584 (±0.024)	1.584
6.48	Doublet, J = 10.5 Hz, H_3 and H_8	0.460 (±0.012)	0.444
5.93	Broad singlet, H_4 and H_7	1.880 (±0.012)	1.880
5.80	Broad singlet, H_5 and H_6	0.332 (±0.012)	0.324

[a] All integrations were measured at a sweep width of 250 Hz and the values are relative to the aryl area. [b] These calculations are founded on the basis of a 94:6 distribution of **15** and **16**.

Table II. Hydrogen Atom Distribution in **18** (60 MHz Spectrum, $CDCl_3$ Solution)

Chemical shift, δ	Multiplicity and assignment	Hydrogen atom distribution Exptl values[a]	Calcd values[b]
7.60	Broad singlet, >NH	2.584 (±0.105)	2.584
7.30	Broad singlet, aryl protons		
5.7–6.4	Complex vinyl absorption	2.220 (±0.079)	2.276
4.25	Multiplet, bridgehead protons	0.391 (±0.026)	0.396

[a] All integrations were measured at a sweep width of 500 MHz and the values are relative to the aryl area. [b] These calculations are founded on the logical assumption that the protium content of the aryl group will remain invariant in this chemical transformation.

Table III. Hydrogen Atom Distribution in **1A** (60 MHz Spectrum, $CDCl_3$ Solution)

Chemical shift, δ	Multiplicity and assignment	Hydrogen atom distribution Exptl values[a]	Calcd values[a]
7.23	Broad singlet, aryl protons	1.584	1.584
5.6–6.5	Complex multiplets, vinyl protons	2.400 (±0.128)	2.276
4.57	Broad doublet, J = ~8 Hz, H_6	0.160 (±0.026)	0.166
4.10	Broad doublet, J = 5.6 Hz, H_1	0.205 (±0.051)	0.230
3.62	Singlet, methoxyl protons	3.140 (±0.102)	3.000

[a] The criteria of Table II also apply to these data.

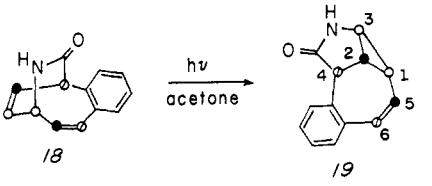
6% of **16** in the sample of benzocyclooctatetraene is that the deuterium content at C_3C_8 differs significantly from that at C_5C_6, a fact which later proved to be of substantial value in following the fate of the individual carbon atoms.

Addition of chlorosulfonyl isocyanate (CSI) to **17** at 80–85° in the absence of solvent, followed by hydrolysis under the predescribed alkaline conditions,[11] gave rise in high yield to lactam **18**. Subsequent treatment of **18** with trimethyloxonium fluoroborate resulted in efficient conversion to **1A**. The data of Tables II and III clearly reveal that the observed deuterium distribution in both **18** and **1A** fits precisely with that predicted on the basis of the mechanism advanced earlier for the CSI–cyclooctatetraene cycloaddition.[11]

Irradiation of **1A** both under sensitized conditions in acetone solution (Pyrex filter) and directly in ether solution through a Vycor filter proceeded smoothly to give deuterium-labeled benzazabullvalene A. This gross structural assignment follows from the physical and spectral properties of the substance in conjunction with earlier work from this laboratory[3] and from the results summarized in Table IV. Quantitative comparison of the experimental observations with the deuterium distribution calculated to result from the di-π-methane and $\sigma^2_a + \pi^2_a$ mechanisms (Table IV) clearly established that the photoproduct was in fact **8** and not **12**. The obtention of **8** can be uniquely reconciled with the di-π-methane pathway which must proceed in its initial stages exclusively by vinyl–vinyl bonding (Scheme I).

Photorearrangement of Lactam 18. Because small additional quantities of **18** were available, the detailed nature of the photoisomerization of this lactam was studied. The photolysis of unlabeled **18** has earlier been shown to give **19** as the major product.[3] In the present work, **18** was irradiated under sensitized conditions and the crude photolysate was recrystallized to give **19** with the hydrogen distribution shown in Scheme IV. The quantitative aspects of these results

Scheme IV. Location of Hydrogen Label in Deuterium-Substituted Lactam **19**



18 19

are summarized in terms of normalized integration values in Table V. As already mentioned, no distinction is possible between the di-π-methane and $\sigma^2_a + \pi^2_a$ rearrangements in this instance. However, the distribution of hydrogen found in **19** unequivocally restricts the number of mechanistic possibilities to the above-mentioned two. Further comments on these two alternatives is deferred to the Discussion. The minor component of the photolysis mixture proved not to be separable in pure form on this small scale.

Structural Aspects of the Thermal Rearrangement of 2. The introduction of a fused benzene ring onto fluxional molecules such as bullvalene and semibullvalene has been previously assumed to preclude the operation of Cope rearrangements.[12] In this context, it is of special interest to consider the fact that benzazabullvalene A (**2**) undergoes irreversible rearrangement to benzazabullvalene B (**4**) at relatively low temperatures (125–150°).[3] Mechanistic passage of **2** to **4** can be the result of the operation of five different mechanisms: (i) homolysis of the C_1C_2 bond, followed by migration of $C(OCH_3)$ to C_7 and migration of N from C_5 to C_2 (path a_1); (ii) homolysis of the C_1C_2 bond, followed by phenyl migration to C_7 and migration of N from C_5 to C_2

(11) L. A. Paquette, J. R. Malpass, and T. J. Barton, *J. Amer. Chem. Soc.*, **91**, 4714 (1969).

(12) (a) G. Schröder and J. F. M. Oth, *Angew. Chem. Intern. Ed. Engl.*, **6**, 414 (1967); (b) J. A. Elix, M. V. Sargent, and F. Sondheimer, *J. Am. Chem. Soc.*, **89**, 5081 (1967).

Table IV. Hydrogen Atom Distribution in Deuterium-Labeled Benzazabullvalene A (8) Resulting from Irradiation of 1A (60 MHz Spectrum, $CDCl_3$ Solution)

Chemical shift, δ	Multiplicity and assignment	Hydrogen atom distribution: Experimental values[a] Sensitized irradiation	Experimental values[a] Direct irradiation	Calculated values[a] Di-π-methane (*i.e.*, **8**)	Calculated values[a] $\sigma^2_a + \pi^2_a$ (*i.e.*, **12**)
7.10	Broad singlet, aryl protons	1.584	1.584	1.584	1.584
5.85	Broad singlet, H_6 and H_7	1.102 (±0.100)	1.095 (±0.115)	1.106	1.106
Ca. 3.8	Shoulder, H_5			0.166	0.940
3.57	Singlet, methoxyl protons	3.400 (±0.059)	3.510 (±0.138)	3.000 (3.396)	3.000 (4.170)
Ca. 3.48	Shoulder, H_3			0.230	0.230
2.68	Broad absorption, H_2	0.221 (±0.028)	0.222 (±0.069)	0.230	0.230
2.15	Broad absorption, H_1	0.975 (±0.038)	0.970 (±0.054)	0.940	0.166

[a] The criteria of Table II also apply to these data.

(path a_2); (iii) homolysis of the C_1C_5 bond, followed by migration of $C(OCH_3)$ to C_7 and phenyl shift from C_2 to C_5 (path b_1); (iv) homolysis of the C_1C_5 bond, followed by a double phenyl shift (path b_2); and (v) Cope rearrangement involving initial rupture of the imino ether function, followed by participation from the benzene ring with loss of aromatic character, and a final [3,3] sigmatropic shift to reestablish this delocalization (path c).[13] The complete rearrangement scheme for deuterium-labeled benzazabullvalene A (**8**) is given in Scheme V. It is apparent that in the particular case of **8**, definition of the deuterium-labeling pattern in the benzazabullvalene B produced upon thermal rearrangement would disclose the particular mechanistic pathway, the only unclear point being the fact that deuterated structure **22** could arise not only by the Cope rearrangement process (path c) but also by its formal diradical equivalent (path b_1).

The deuterated benzazabullvalene A **8** was rearranged by heating in tetrachloroethylene solution at temperatures up to 200°. Alumina chromatography and recrystallization from hexane afforded colorless crystals of benzazabullvalene B, mp 124–126°. Nmr analysis (100 MHz) showed that this substance was highly enriched with hydrogen label at positions 2 and 6 (Table VI). Consideration of the quantity of residual hydrogen at the remaining sites would seem to confirm that **22** was actually produced. However, because the final decision between isomers **20** and **22** rests ultimately on the small, albeit readily measurable, hydrogen content difference of H_5 in these two isomers, the decision was made to investigate this rearrangement by means of an alternate deuterium-labeling scheme which would clearly distinguish between path a_1 on the one hand, and paths b_1 and c on the other. Convincingly, the information available at this stage of the investigation rules out the possibility that paths a_2 and b_2 are operative, at least to an extent measurable by the nmr technique.

(13) In point of fact, a sixth mechanistic alternative can be written. However, it is readily seen that this rearrangement pathway requires that the nitrogen atom ultimately become part of a three-membered ring. The formation of such an intermediate is considered to be an energetically unfavorable process and is, in fact, not at all operative in the more highly fluxional methoxyazabullvalene molecule.[3] In view of these considerations, this mechanism has not been included in Scheme V. Moreover, this energy demanding alternative would lead to **21** which is later shown not to be produced.

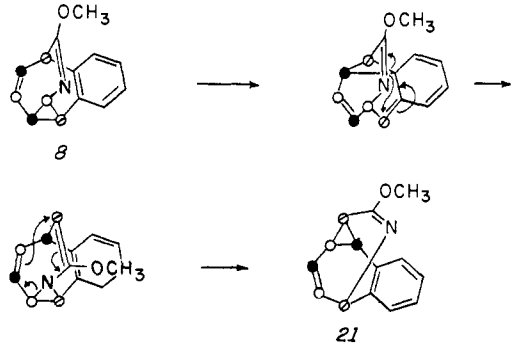


Table V. Hydrogen Atom Distribution in Deuterium-Labeled **19** Resulting from Irradiation of **18** (60 MHz Spectrum, DMSO-d_6 Solution)

Chemical shift, δ	Multiplicity and assignment	Hydrogen atom distribution: Exptl values[a]	Values Calcd for **19**[a]
8.00	Broad singlet, NH	0.94 (±0.66)	1.00
7.22	Broad singlet, aryl protons	1.584	1.584
6.50	Broad absorption, H_6	0.250 (±0.021)	0.230
5.93	Broad singlet, H_5	0.946 (±0.088)	0.940
3.90	Broad singlet, H_4	0.229 (±0.069)	0.230
3.02	Broad absorption, H_3	0.163 (±0.053)	0.166
2.10	Broad singlet, H_2	0.920 (±0.128)	0.940
1.58	Broad absorption, H_1	0.159 (±0.067)	0.166

[a] The criteria of Table II also apply to these data.

The synthesis of the second requisite deuterium-labeled benzazabullvalene A (**26**) began with the preparation of 4,5,6,7-tetradeuteriobenzocyclooctatetraene (**24**) according to the method of Merk and Pettit[14] (Scheme VI). The conversion of **24** to **1B** was carried out as previously described. Examination of the nmr spectrum of **1B** showed that H_1 and H_4 contain 100% hydrogen label while 34% residual hydrogen resided at each of the remaining nonaryl protons, the

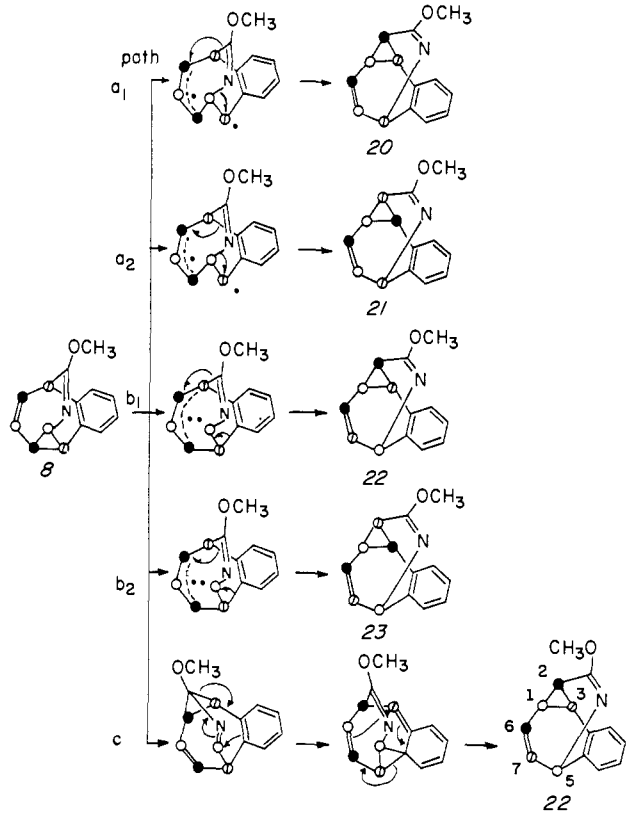
(14) W. Merk and R. Pettit, *J. Amer. Chem. Soc.*, **90**, 814 (1968). We thank Professor Pettit for providing us with advice on the preparation of **24** prior to publication.

Table VI. Hydrogen Atom Distribution in the Deuterium-Labeled Benzazabullvalene B (22) Resulting from Thermal Rearrangement of 8 (100 MHz Spectrum, $CDCl_3$ Solution)

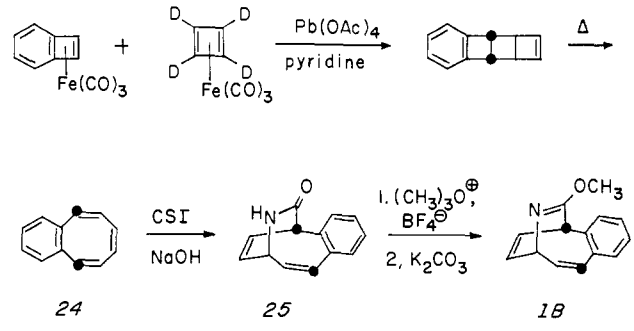
Chemical shift, δ	Multiplicity and assignment	Hydrogen atom distribution: Exptl values[a]	Calcd values for 20	21	22	23
7.19	Multiplet, aryl protons	1.584	1.584	1.584	1.584	1.584
5.92	Broad singlet, chiefly H_6[b]	1.145 (±0.045)	1.106	1.106	1.170	1.170
4.60	Singlet, H_5	0.152 (±0.032)	0.230	0.230	0.166	0.166
3.54	Singlet, methoxyl protons	3.170 (±0.195)	3.000	3.000	3.000	3.000
2.84	Multiplet, H_3	0.258 (±0.032)	0.230	0.940	0.230	0.940
2.59	Singlet, H_2	0.890 (±0.110)	0.940	0.230	0.940	0.230
2.29	Broad, H_1	0.142 (±0.051)	0.166	0.166	0.166	0.166

[a] The criteria of Table II also apply to these data. [b] The much smaller protium content at position 7 was indicated by the presence of a small shoulder on the low-field side of this absorption.

Scheme V. Complete Scheme of Possible Thermal Rearrangements of Deuterium-Labeled Benzazabullvalene A (8)

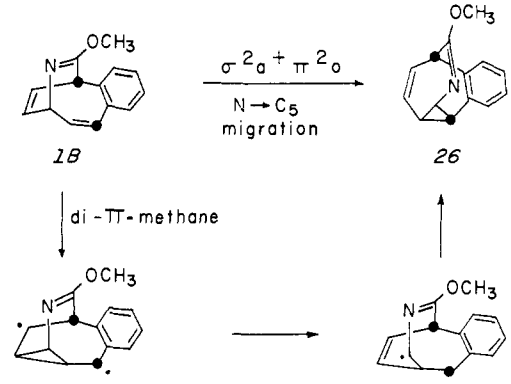


Scheme VI. Preparation of 2,3-Benzo-8-methoxy-7-azabicyclo[4.2.2]deca-2,4,7,9-tetraene, Partially Deuterated as 1B



l tter observation being a consequence of the incomplete exchange realized earlier in the preparation of the perdeuteriocyclobutadieneiron tricarbonyl. The above isotopic distribution is based on the simple and logical presumption that the aryl protons in **1B** constitute a four-proton absorption. Scheme VII concisely illustrates the point that little information concerning the photorearrangement mechanism is derivable from this series since the di-π-methane and $\sigma^2_a + \pi^2_a$ routes both give rise to the identical isotopic labeling pattern. However, quantitative assay of the hydrogen distribution in **26** was mandatory in order to provide the isotopic distribution values required for the subsequent thermochemical work and to substantiate our earlier mechanistic conclusions on the photoinduced rearrangement of **1**. Nmr analysis of **26** provided the quantitative results given in Table VII. The agreement realized between the experimental data and the values calculated for **26** were again very acceptable in this instance.

Scheme VII. Location of Hydrogen Label in 26 Produced upon Photoisomerization of 1B



After heating a saturated tetrachloroethylene solution of **26** at 160° for several hours and replacing the solvent with $CDCl_3$, the spectrum (100 MHz) of the product was recorded at ambient temperature. It is clearly seen from the quantitative data of Table VIII that C_3 and C_7 are the sites of the protium-labeled carbon atoms. Thus, the resulting benzazabullvalene B must be **29** and pathway a_1 (Scheme VIII), as well as pathways a_2 and b_2, need not be considered further. It remained now to decide between mechanisms b_1 and c, and this point is taken up in the Discussion.

Table VII. Hydrogen Atom Distribution in Deuterium-Labeled Benzazabullvalene A (**26**) Resulting from Irradiation of **1B** (60 MHz Spectrum, $CDCl_3$ Solution)

Chemical shift, δ	Multiplicity and assignment	Hydrogen atom distribution: Exptl values[a]	Hydrogen atom distribution: Calcd values
7.1	Multiplet, aryl protons	4.0	4.0
5.9	Multiplet, vinyl protons	0.79	0.68
3.56	Singlet, methoxyl protons with shoulders due to H_3 and H_5	4.12	4.34
2.68	Broad multiplet, H_2	0.98	1.0
2.15	Broad absorption, H_1	0.38	0.34

[a] Hydrogen distribution calculated from nmr integrations with the assumption that the aryl integral equals 4.0 H.

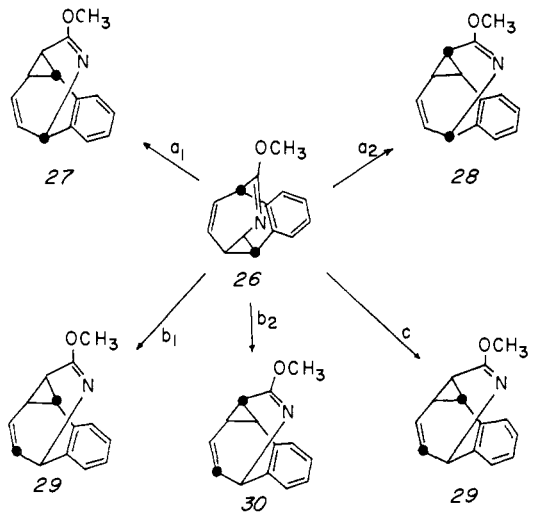
clear from spin decoupling that H_7 is situated at the more downfield position (δ 6.01). Thus, irradiation of H_5 (δ 4.60) is seen to result in removal of $J_{5,7}$ (7.2 Hz) with resultant simplification of the low-field portion of the vinyl multiplet; simultaneously, allylic coupling to H_6 ($J_{5,6}$ = 1.8 Hz) is also lost, as revealed by significant sharpening of the upfield signals due to this proton. Significantly, irradiation of H_1 (δ 2.30) produces exactly the opposite effect ($J_{1,6}$ = 7.0 Hz; $J_{1,7}$ = 1.8 Hz). That H_1 is the cyclopropyl proton at highest field was easily deduced from the observation that double irradiation of the H_6H_7 pair affected only the multiplet centered at δ 2.30. Since spin decoupling of H_5 had no visible effect on the cyclopropyl region, it would appear that no spin information of any measurable magnitude is transmitted from H_5, H_6, or H_7 to H_2 and H_3.

Table VIII. Hydrogen Atom Distribution in Deuterium-Labeled Benzazabullvalene B (**29**) Resulting from Thermal Rearrangement of **26** (100 MHz Spectrum, $CDCl_3$ Solution)

Chemical shift, δ	Multiplicity and assignment	Hydrogen atom distribution: Exptl values[a]	Calcd values for **27**	**28**	**29**	**30**
7.19	Multiplet, aryl protons	4.00	4.00	4.00	4.00	4.00
6.01	Broad, chiefly H_7[b]	1.19 (±0.09)	0.68	0.68	1.34	1.34
4.60	Broad, H_5	0.37 (±0.05)	1.00	1.00	0.34	0.34
3.54	Singlet, methoxyl protons	2.93 (±0.12)	3.00	3.00	3.00	3.00
2.84	Broad, H_3	1.04 (±0.18)	1.00	0.34	1.00	0.34
2.60	Broad, H_2	0.33 (±0.08)	0.34	1.00	0.34	1.00
2.30	Broad, H_1	0.29 (±0.06)	0.34	0.34	0.34	0.34

[a] Hydrogen distribution calculated from nmr integrations with the assumption that the aryl integral equals 4.0 H. [b] The much smaller protium content at position 6 was indicated by the presence of a small shoulder on the high-field side of this absorption.

Scheme VIII. Complete Scheme of Possible Thermal Rearrangements of Deuterium-Labeled Benzazabullvalene A (**26**)



Analysis of the Nmr Spectrum of 4. Because accurate nmr chemical shift assignment to the various protons of benzazabullvalene B (**4**) was necessary for reliable quantitative evaluation of the hydrogen atom distributions in partially deuterated isomers **22** and **29**, the 100-MHz spectrum of **4** was carefully analyzed by application of the double resonance technique (Figure 1). Although the two vinyl protons are relatively closely spaced, it is

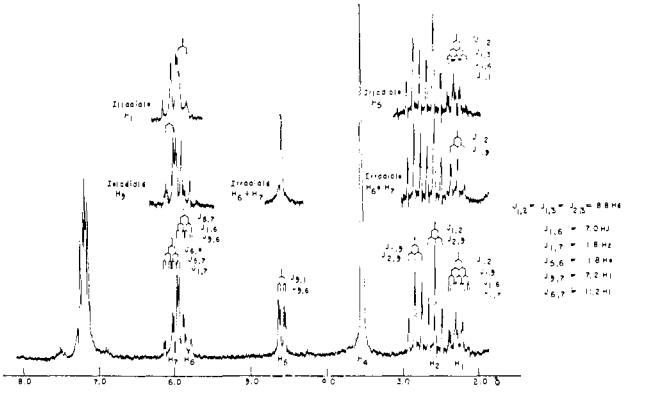
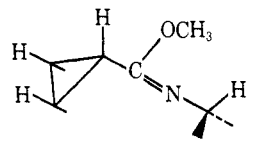
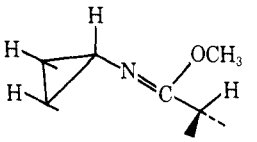


Figure 1. 100-MHz spectrum of **4** in $CDCl_3$ solution. Because the multiplicities of the peaks due to H_6 and H_7 are not strictly first order, the splitting diagrams in this region are necessarily simplified.

It now remained to distinguish unequivocally between H_2 and H_3 in **4**, and this was realized from a study of the changes in chemical shift (Δδ) which occur upon protonation of molecular fragments **31** and **32**. In both examples, the shift shown by the α-cyclopropyl proton on acidification was expected to differ markedly



31

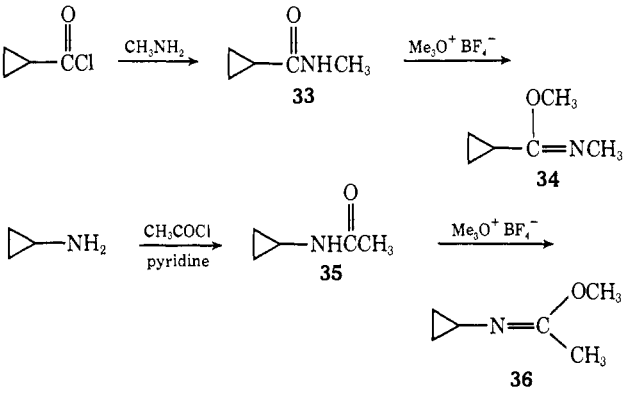


32

from the $\Delta\delta$'s exhibited by the β-cyclopropyl protons. Additionally, since the seat of protonation (nitrogen atom) is closer to the three-membered ring in **32**, the magnitudes of these changes in the two systems were likewise expected to differ.[15] Barring unforeseen problems due to molecular geometry, the strong likelihood existed that the magnitude of these $\Delta\delta$'s would be characteristic of the various proton types. At least in the present instance, this expectation has been realized.

The model systems chosen, *i.e.*, **34** and **36**, were prepared by standard methods as illustrated in Scheme IX. The 100 MHz nmr spectra of **34** and **36** in chloroform solution are characterized by complex multiplets for the β-hydrogens. Upon irradiation of the α-proton, however, each multiplet collapses to an AA'BB' pattern; the centers of the two halves of these simplified patterns are the values cited in Table IX. The chemical shifts realized upon protonation of these two imino ethers with trifluoroacetic acid (see Experimental Section for methodology) are also summarized in Table IX. As noted, only relatively small changes were observed when the solutions were subjected to a twofold dilution; continued dilution produced no further changes. Similar data obtained with benzazabullvalene A (**2**) and benzazabullvalene B (**4**), together with their respective deuterated congeners **8**, **22**, **29**, are summarized in Table X. The "C-cyclopropyl" derivatives **4**, **22**, **29**, and **34** were recovered unchanged from the acidification experiments. Although the major recovered products in the "N-cyclopropyl" series were the starting substances, slight impurities were seen to be formed with time. The chemical nature of these changes was not pursued.

Scheme IX. Synthesis of Imino Ethers **34** and **36**



It may be recalled that in **4** both H_2 and H_3 appear as identical triplets in neutral solution. The unambiguous assignment of which proton shifts to δ 2.90 and 4.12 upon acidification was made possible by examination of the deuterated structures **22** and **29**. Clearly revealed was the fact that the proton resonating at δ 2.62 shifts to 2.93 upon addition of trifluoroacetic

(15) A study of cyclopropyl carbonium ions and protonated cyclopropyl ketones has revealed that large, albeit regular, downfield shifts are experienced by both the α- and β-hydrogens, with the α-proton always appearing at lower field. These results indicate that a large amount of charge delocalization does pass into the three-membered ring [C. U. Pitmann, Jr., and G. A. Olah, *J. Am. Chem. Soc.*, 87, 5123 (1965)].

Table IX. Nmr Shifts of **34**, **36**, and Their Trifluoroacetate Salts (100 MHz Spectrum, $CHCl_3$ Solution)

Compd	Chemical shift, δ multiplicity, and assignment	Chemical shift, δ on acidification ~1.0 *M*	~0.5 *M*[a]	$\Delta\delta$, Hz, at 100 MHz ~1.0 *M*	~0.5 *M*
34	0.87[b]	1.30	1.36	43	49[c]
	0.67[b] (AA'BB' pattern,[b] β-protons)	doublet (J = 6.0 Hz) with additional small coupling		63	69
	1.61 (complex multiplet, α-proton)	1.91	1.91	30	30
		pentuplet (J = 6.0 Hz)			
	3.07 (singlet, NCH_3)	3.26	3.32	19	25
		singlet			
	3.46 (singlet, $-OCH_3$)	3.99	4.11	53	65
		singlet			
36	0.65[b]	0.93	0.96	28	31
	0.48[b] (AA'BB' pattern,[b] β-protons)	complex multiplet		45	48
	2.61 (complex multiplet, α-proton)	2.89	2.90	28	29
		complex multiplet			
	1.94 (singlet, CCH_3)	2.50	2.50	56	56
		singlet			
	3.51 (singlet, $-OCH_3$)	4.08	4.13	57	62
		singlet			

[a] No changes were observed on further dilution. [b] All of these measurements were recorded while the α-proton was simultaneously spin decoupled. [c] No attempt has been made to distinguish between the protons *cis* and *trans* to the α-hydrogen.

Table X. Nmr Shifts of **2**, **4**, **8**, **22**, **29** and Their Trifluoroacetate Salts (100 MHz, $CDCl_3$ Solution)

Compd	Proton	Chemical shift, δ	Trifluoroacetate salt, chemical shift, δ[a]	$\Delta\delta$, Hz at 100 MHz
2	H_1	2.17	2.46	29
	H_2	2.76	3.02	26
	H_3	3.38	3.83	45
	$-OCH_3$	3.57	4.21	64
	H_5	3.77	4.21[b]	44
	H_6, H_7	5.87	5.83, 6.16	4, 29
8	H_1	2.17	2.47	30
	$-OCH_3$	3.57	4.22	65
	H_7	5.87	5.84	3
4	H_1	2.30	2.91	61
	H_2	2.62	2.91	29
	H_3	2.88	3.43	55
	$-OCH_3$	3.56	4.12	56
	H_5	4.61	5.01	40
	H_6	5.90	6.16	26
	H_7	6.06		10
22	H_2	2.62	2.93	31
	$-OCH_3$	3.56	4.13	57
	H_6	5.90	6.16	26
29	H_3	2.88	3.40	52
	$-OCH_3$	3.56	4.13	57
	H_7	6.06	6.16	10

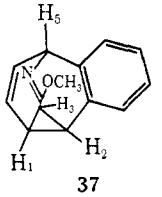
[a] The concentration levels were approximately 30 mg/0.4 ml. [b] Presence established by spin decoupling techniques.

acid, whereas the proton at 2.88 is responsible for the 3.40 absorption.

The answer to whether H_2 (as shown) or H_3 is adjacent to the methoxyl-bearing carbon in **4** now follows from a consideration of the $\Delta\delta$ values. Five relevant points require brief discussion.

(1) The methoxyl group always suffers a large downfield shift (53–65 Hz). Actually, this characteristic behavior can be used to differentiate between the O-methyl and N-methyl substituents in **34** (Table IX).

(2) The protons α to a methoxyl-bearing carbon suffer a large downfield shift when *not* in a cyclopropyl ring, *e.g.*, 56 Hz in **36** and 45 Hz in **2**. In contrast, a noticeably smaller shift is seen when this hydrogen resides on a three-membered ring (30 Hz in **8** and **34**, 29 Hz in **2**). The observed shift of 29 Hz for H_2 in **4** would nicely fit this generalization, whereas an incongruity would develop if H_3 ($\Delta\delta$ 55 Hz) were to be positioned on the cyclopropane ring next to the methoxyl-bearing carbon atom (*cf.* **37**).



37

(3) Furthermore, if H_3 were situated as in **37**, then the shifts exhibited by H_1 and H_2 would necessarily be 61 and 29 Hz, respectively (Table X). There exists no reason to believe that there should exist in this fixed structure a significant difference in the shifts observed for H_1 and H_2 on protonation. This premise is substantiated by the behavior of **2**, **34**, and **36** in which the various β-protons (whether *cis* or *trans* to the imino ether function) are seen to shift to equal extents. We conclude therefore that these data likewise confirm that H_2 is positioned as shown in **4**; in this structure, the allylic (H_1) and benzylic (H_3) protons are shifted nearly equal amounts (61 and 55 Hz, respectively). These $\Delta\delta$ values are larger than the corresponding shifts in **2** (29 and 26 Hz), suggesting that greater electron-withdrawing demands are placed on the cyclopropane ring when the nitrogen atom is positioned β, rather than α, to it. This behavior is also seen with the **34**–**36** isomer pair.

(4) Further evidence for structure **4** rather than **37** can also be gained from the nmr spectra of the free bases. In each of the imino ethers examined, the difference in chemical shift between a proton α to the nitrogen and a proton adjacent to the methoxyl-bearing carbon is reasonably constant. Thus, whereas the N-methyl group in **34** is displayed at δ 3.07, the C-methyl group in **36** appears at δ 1.94—an upfield shift of 113 Hz. In the isomeric series **2** and **4**, upfield shifts of 123 (bridgehead position) and 100 Mz (cyclopropyl position) are seen, in good agreement with an average value of 115 Hz. If **4** actually were **37**, the shift would be 89 Hz, a much smaller value.

(5) Finally, let us consider the effects produced on the β-cyclopropyl hydrogens by the two modes of attachment of the imino ether functionality. In passing from **34** to **36**, the β-protons experience a 19–22-Hz *upfield* shift. Similarly, in going from **4** to **2**, H_1 shifts 13 Hz in the *upfield* direction while the H_3 to H_2 difference is 12 Hz in the same direction. If structure **37** were correct, a comparison between H_2 substituents would be required; this shift is seen to be 14 Hz *downfield*—a totally different order of magnitude.

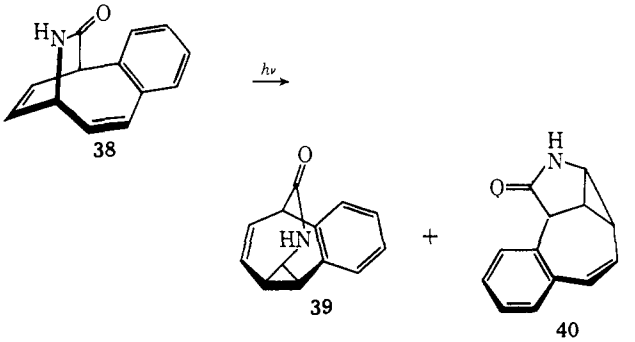
Although these arguments are admittedly tortuous, they do serve to define clearly the relative positions of H_2 and H_3 and provide the necessary proof that the deuterium labeling indicated earlier in this paper is correct.

Discussion of Results

The Photorearrangement of 1 and 18. In view of the fact that acetone sensitization is required for the high yield (93%) conversion of **1** to **2** (>95%) and **3** (<5%),[3] it may be concluded that this photoisomerization proceeds most efficiently from the triplet state of **1**. Because direct irradiation of **1** also leads to **2** (20%), but also to much polymer, intersystem crossing from the excited singlet state of **1** to its triplet manifold must be relatively inefficient. The question concerning the possible direct low yield conversion of singlet **1** to **2** cannot be answered unequivocally with the data at hand. Nevertheless, it is clear that should a singlet photoreaction be operative, the identical di-π-methane rearrangement must be followed.

The deuterium-labeling results show that photoexcitation of **1** leads to an activated species which undergoes vinyl–vinyl bonding to produce diradical **5**. An appreciable activation energy most certainly is associated with this bridging process; in any case, the mechanism involving benzo–vinyl bonding is not utilized presumably because this pathway is even more energetically demanding. The further rearrangement of **5** is highly selective. That **6** is the major product can be interpreted most simply to mean that scission of bond a is favored as a consequence of odd-electron stabilization by the benzene ring. This electronic effect results in a 20-fold greater yield of **8** relative to **9**.[16]

The case of **38** now becomes particularly intriguing to consider, for this lactam gives rise to both **39** and **40** on sensitized irradiation, with the latter photoisomer



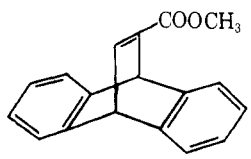
38 **39** **40**

predominating by a factor of 3.[3] Since the vinyl–vinyl bonding mechanism is likewise followed in this instance,[17] the source of this dramatically different electronic preference must reside in the amide function.

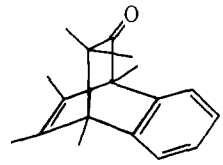
(16) As we have noted above, the $\sigma^2_a + \pi^2_a$ mechanism involving $N \rightarrow C_7$ migration would also explain the labeling pattern in **9**. We deem it very unlikely that the excited state of **1** would partition itself uniquely between these two widely differing mechanisms, particularly since Scheme I nicely accounts for *all* the facts (Ockham's razor).

(17) Although the deuterated counterpart of **39** was not obtained pure from the irradiation of **18**, the nmr spectrum of this material clearly revealed that it was directly related to **8**.

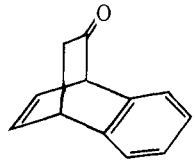
A possible factor which may contribute to the preferred formation of **40** over **39** may be a direct interaction of the lactam carbonyl with the nonbenzylic radical center [*cf.* **7** with $-N{=}C(OCH_3)-$ replaced by $-NHCO-$]. Because a limited number of examples which display somewhat related selectivity are known, *e.g.*, **41–43**, a complete evaluation of such factors is not possible at the present time.



41[6a,b]



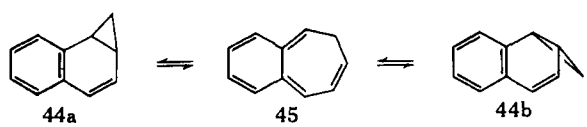
42[6d]



43[6f]

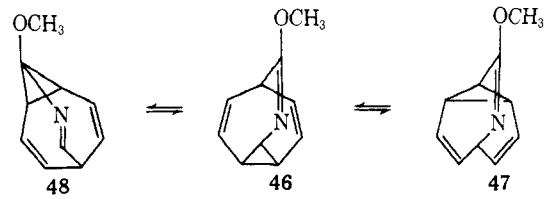
The Thermal Rearrangement of 2. Thermal rearrangement of two differently deuterium-labeled benzazabullvalene A's (**8** and **26**) has established that the formation of benzazabullvalene B (**4**) is the result either of a Cope rearrangement sequence (path c) or its formal diradical equivalent (path b_1). Mechanistic passage to **4** *via* path b_1 requires initial homolysis of the C_1C_5 bond, followed by migration of $C(OCH_3)$ to C_7 and phenyl shift from C_2 to C_5 (Scheme II). At first glance, this process would appear to parallel the thermal behavior (500–600°) of methoxyazabullvalene, at least in its early stages.[18] Closer examination reveals, however, that the bond preferentially ruptured in methoxyazabullvalene corresponds to the C_1C_2 bond in **2**. Yet we now know that paths a_1 and a_2 (Scheme V) where such an event would formally occur are not operative. Nevertheless, it may be argued convincingly that the presence of the benzene ring could alter the preference exhibited by the parent substance.

Irrespective of these considerations, a roughly quantitative means of deciding between paths b_1 and c is available from an analysis of the reaction profiles of somewhat related Cope rearrangements. Thus, the activation energy for the rearrangement of benzonorcaradiene **44** to benzocycloheptatriene **45** has been determined to be 19.4 kcal/mole.[19] In the azabullvalene series, **46** and **47** are separated by an activation



44a **45** **44b**

energy of approximately 12 kcal/mole,[20] a value commonly seen in such systems.[21] The dramatic dampening effect of the imino ether bridge on the fluxional nature of this molecule (compared to bullvalene) is perhaps best reflected in the relatively large energy barrier (~15–20 kcal/mole)[20] which separates **46** from **48**. The conversion of **46** to **48** has an exact parallel in



48 **46** **47**

the first step of pathway c (Scheme V); as the reaction progresses, disruption of benzenoid aromaticity is incurred.

The activation energy for the first bond reorganization is given a value of 18 kcal/mole in view of the very close similarity to the **46** ⇋ **48** reaction. Since the initial intermediate is not detectable by nmr at 125–150°,[3] it is at least 2 kcal/mole less stable than benzazabullvalene A. Since the total energy of activation for this rearrangement is 26.6 kcal/mole,[3] the activation energy required to destroy the aromaticity of the benzene ring in the second step of the rearrangement must be less than 24.6 kcal/mole. We conclude that the reasonable correspondence between the energetics of these two reactions speaks strongly in favor of mechanism c, especially when considered in light of the much higher energy barriers expected from the alternative homolytic process (path b_1).[22,23]

Experimental Section[24]

Deuteration of Benzobarrelene. To 50 ml of N,N-dideuteriocyclohexylamine was added under nitrogen 4.4 ml (5.2 mmoles) of 1.18 *M* *n*-butyllithium in pentane. After 30 min, 1.30 g (8.43 mmoles) of benzobarrelene[10] dissolved in pentane was added and the resulting solution stirred for 88 hr at *ca.* 70°. Additional portions of butyllithium were added after 18 hr (5.2 mmoles), 20 hr (2.89 mmoles), and 26 hr (6.64 mmoles). After cooling, the solution was quenched with D_2O (5 ml) and the mixture was poured into 250 ml of 10% HCl and extracted twice with hexane. The hexane was washed with 250 ml of 10% HCl, twice with water, dried, and evaporated leaving colorless needles of partly deuterated benzobarrelene.

A solution of 40 ml of N,N-dideuteriocyclohexylamine and 6.6 ml (6.6 mmoles) of *ca.* 1 *M* *n*-butyllithium in pentane was stirred under nitrogen for 30 min and the partly deuterated benzobarrelene was added in pentane. The solution was stirred at 75° for 70 hr. Additional portions of the butyllithium were added after 6 hr (6.6 mmoles), 22 hr (7.8 mmoles), and 47 hr (7.8 mmoles). The solution was quenched with D_2O (10 ml) and worked up to give a slightly yellow oily solid (1.7 g) which was 32% deuterated in the aryl and vinyl positions.

A third pass was performed on the deuterated benzobarrelene in 40 ml of N,N-dideuteriocyclohexylamine containing 1.7 *M* *n*-butyllithium in pentane (7.0 mmoles) at 75–80° for 70 hr. Further 7.0-mmole portions of *n*-butyllithium were added after 8.5, 26, and 50 hr. On work-up, the benzobarrelene was shown to be 50% deuterated in the aryl and vinyl positions.

A fourth pass was performed on the benzobarrelene in 50 ml of N,N-dideuteriocyclohexylamine containing *n*-butyllithium in pentane (6.0 mmoles). The mixture was stirred at 75° for 86 hr; further 6.0-mmole samples of butyllithium were added after 6, 21, 45, 56.5, 71, 73, and 76 hr. The benzobarrelene was isolated in the usual way and contained 60.5% deuterium in the aryl and vinyl

(18) L. A. Paquette, G. R. Krow, J. R. Malpass, and T. J. Barton, *J. Am. Chem. Soc.*, **90**, 3600 (1968); L. A. Paquette, G. R. Krow, and J. R. Malpass, *ibid.*, **91**, 5522 (1969).

(19) E. Vogel, D. Wendisch, and W. R. Roth, *Angew. Chem.*, **76**, 432 (1964); *Angew. Chem. Intern. Ed. Engl.*, **3**, 443 (1964).

(20) H. Klose and H. Günther, *Chem. Ber.*, **102**, 2230 (1969).

(21) G. Schröder, J. F. M. Oth, and R. Merenyi, *Angew. Chem.*, 77, 774 (1965); *Angew. Chem. Intern. Ed. Engl.*, 4, 752 (1965).

(22) A recent discussion of a somewhat related diradical reaction, the conversion of norcaradienes to toluenes, considers the energetics of such processes.[23]

(23) E. Ciganek, *J. Am. Chem. Soc.*, **89**, 1458 (1967).

(24) Melting points were determined with a Thomas-Hoover melting point apparatus and are corrected, while boiling points are uncorrected. The nmr spectra were determined with Varian A-60A and HA-100 spectrometers.

positions. The oily solid contained significant amounts of hydrocarbon impurity and was chromatographed on a 55 × 3.5 cm column of silica gel (Baker) which had been packed in 1% ether–hexane, then washed with 800 ml of hexane. The sample was introduced in hexane and elution continued with this solvent. Fractions of 100-ml size were collected; fractions 3–5 contained partly deuterated naphthalene plus other oily compounds; fractions 6–12 contained pure benzobarrelene (0.676 g).

The benzobarrelene (0.676 g) was added to a mixture of N,N-dideuteriocyclohexylamine and 1.33 *M* *n*-butyllithium in pentane (7.4 ml, 9.85 mmoles) which had been stirred for 30 min under nitrogen. Stirring was continued at 75° for 41 hr, and further 7.4-ml portions of butyllithium were added after 10, 14, 22, and 34 hr. On work-up, the product was shown to be *ca.* 72% deuterated by nmr.

Purification by column chromatography as described above yielded benzobarrelene (0.582 g, mp 64–65°) which was homogeneous on vpc analysis. Nmr sepctroscopy on the pure sample confirmed that deuterium was incorporated to the extent of 72.1% on the aryl and vinyl positions.

Direct Irradiation of Deuterated Benzobarrelene (14). To a solution of 572 mg of **14** in 420 ml of purified pentane was added 66 mg of cyclooctane as an internal standard. This solution was irradiated with a 450-W Hanovia lamp surrounded by a Vycor filter and housed in a standard photochemical well. The progress of the photolysis was followed by periodic removal of small aliquots and analysis of these by vpc. After 320 min, the reaction had proceeded to 90% completion and the experiment was terminated. The solvent was carefully evaporated and the residue was subjected to preparative scale vpc on a 5 ft × 0.25 in. column of 10% SF 96 on Chromosorb G at 118°. There resulted 435 mg (76%) of benzocyclooctatetraene **17**. The hydrogen atom distribution in **17** (see Table I) was calculated by the method of Zimmerman.[25]

Reaction of 17 with CSI. Hydrolysis to Deuterated Lactam 18. Redistilled chlorosulfonyl isocyanate (CSI) (240 μl) was added dropwise under nitrogen to **17** (370 mg) previously heated to 65°. The temperature was increased to 80–85° for 3 hr at which time the mixture appeared as a dark solid. This solid was dissolved in dry acetone and added to 4 *N* NaOH in aqueous acetone at pH 6–8 in the predescribed manner.[3] The mixture was extracted thoroughly with dichloromethane, and the combined organic layers were dried and evaporated. The pale yellow solid which resulted was washed with pentane and dried (421 mg, 89% yield). Recrystallization of this material from methanol–acetone afforded colorless crystals, mp 225–227°, of **18** (lit.[3] mp 226–227°). The nmr data for **18** are given in Table II.

Conversion of 18 to 1A. Lactam **18** (200 mg) was dissolved in dry methylene chloride (15 ml) and Meerwein's reagent (244 mg) was added under nitrogen. The mixture was stirred overnight at room temperature and worked up as before.[3] The resulting yellowish oil was immediately passed through a very short column of alumina (Merck, neutral, activity I) in ether solution. The yield of somewhat oily crystals was 202 mg (94%). Three recrystallizations from benzene–hexane gave colorless crystals of **1A**, mp 74–77° (lit.[11] mp 76–80°). The nmr data for **1A** are summarized in Table III.

Acetone-Sensitized Photolysis of 1A. A 65-mg sample of purified **1A** was dissolved in 20 ml of dry acetone and this solution was irradiated for 145 min (Hanovia 450-W source, Pyrex optics). After evaporation of the acetone, the residue was dissolved in ether and this solution was passed down a short alumina column. Evaporation of the eluate yielded 66 mg of a colorless oil which when crystallized from hexane gave 38 mg of benzazabullvalene A **8**, mp 107–112° (lit.[3] mp 113–114°). The nmr data for **8** are summarized in Table IV.

Direct Photolysis of 1A. A solution of 45 mg of purified **1A** in 18 ml of anhydrous ether was irradiated (Hanovia 450-W source, Vycor optics) for 45 min. Work-up as above yielded needles of **8**, mp 113–114° (23 mg). The nmr data for this material may be found in Table IV.

Photorearrangement of Lactam 18. A solution of 84 mg of **18** in 28 ml of dry acetone was photolyzed (Hanovia 450-W source, Pyrex optics) for 375 min. The solvent was evaporated and the residue was recrystallized from absolute ethanol. There was obtained 25 mg of crystalline **19**, mp 247–252° dec (lit.[3] 253–254° dec). The nmr data are summarized in Table V.

Thermal Rearrangement of 8. A solution of 38 mg of **8** in tetrachloroethylene was sealed in a Pyrex tube. The sample was heated at temperatures up to 200° for 3 hr. After cooling, the solvent was evaporated, a solution of the residue in ether was passed through a column of alumina, and the residue was recrystallized from hexane. There was obtained 22 mg of **22**, mp 124–126° (lit.[3] mp 127–128°). The nmr data for **22** are summarized in Table VI.

Tetradeuteriocyclobutadieneiron Tricarbonyl. Cyclobutadieneiron tricarbonyl[26] (1.8 g) was dissolved in 15 ml of deuteriotrifluoroacetic acid under a nitrogen atmosphere at 0°. After stirring at room temperature for 3.5 hr, the mixture was poured onto cracked ice (25 g) and extracted with 15-ml portions of pentane. This cycle was repeated two more times and 1.2 g (33%) of incompletely exchanged cyclobutadieneiron tricarbonyl was obtained.

4,5,6,7-Tetradeuteriobenzocyclooctatetraene (24).[13] To a solution of 31 g (0.7 mole) of lead tetraacetate in 125 ml of pyridine maintained at 10° with ice cooling was added gradually a solution of 1.05 g (0.053 mole) of tetradeuteriocyclobutadieneiron tricarbonyl and 1.4 g (0.57 mole) of benzocyclobutadieneiron tricarbonyl[27] in 15 ml of the same solvent. After stirring at room temperature for 4 hr, the mixture was poured into water and extracted several times with pentane. The combined pentane extracts were washed with dilute acetic acid to remove residual pyridine. The dried solution was evaporated and the residual tetracyclic adduct was heated to 140° to give 146 mg (17%) of **24**.

Reaction of 24 with CSI. Hydrolysis to Deuterated Lactam 25. Chlorosulfonyl isocyanate (210 mg, 1.48 mmoles) was heated neat at 82° with 207 mg (1.31 mmoles) of **24** for 3 hr. The resulting dark solid was dissolved in acetone and hydrolyzed as above. The crude lactam **25** so obtained (240 mg, 89%) was not purified.

Conversion of 25 to 1B. Treatment of the above sample of **25** with 300 mg of trimethyloxonium fluoroborate in methylene chloride solution (15 ml) at room temperature overnight, followed by the predescribed work-up, afforded 151 mg (54%) of **1B**, mp 74–76°. Careful nmr analysis of the spectrum of this material indicated that H_1 and H_4 contain 100% hydrogen label, whereas 34% residual hydrogen label resided at each of the remaining nonaryl protons.

Acetone-Sensitized Irradiation of 1B. A solution of 67 mg of **1B** in 30 ml of acetone was irradiated as above for 2 hr. After evaporation of the solvent, the residue was dissolved in ether and this solution was passed down a short alumina column. Removal of the solvent afforded 37 mg of benzazabullvalene A (**26**), mp 108–112°. The nmr data for **26** are summarized in Table VII.

Thermal Rearrangement of 26. The sample of **26** was dissolved in approximately 0.75 ml of tetrachloroethylene and this solution was sealed into an nmr tube. The sample was heated at temperatures up to 160° for 3 hr. After cooling, the solvent was evaporated, the residue was clarified by passing an ether solution through a short alumina column, and the eluate was evaporated to give 22 mg of **29**, mp 124–126°. The nmr data for **29** are summarized in Table VIII.

N-Methylcyclopropanecarboxamide (33). To a solution of 5 ml of methylamine in 20 ml of dry benzene cooled to 0° was added slowly dropwise a solution of 1.05 g of cyclopropanecarboxylic acid chloride in 5 ml of the same solvent. The mixture was stirred for 3 hr at room temperature and evaporated *in vacuo*. Hexane was added and the precipitated hydrochloride was removed by filtration. Recrystallization of the resulting oily crystals from hexane was achieved with difficulty to give 320 mg of white needles, mp 54–57° (lit.[28] mp 55–57°).

Imino Ether 34. Amide **33** (208 mg) was dissolved in dry methylene chloride (10 ml) and stirred overnight with trimethyloxonium fluoroborate (390 mg). The usual work-up[3] gave a methylene chloride solution of **34** which was carefully concentrated, but not completely evaporated. Preparative vpc isolation (65°, 5 ft × 0.25 in. column packed with 10% SF96 on Chromosorb W) gave a colorless oil, ν_{max}^{neat} 1678 cm^{-1}.

Anal. Calcd for $C_6H_{11}NO$: C, 63.68; H, 9.80; N, 12.39. Found: C, 63.42; H, 9.79; N, 12.42.

N-Acetylcyclopropylamine (35). Cyclopropylamine (1.174 g) and pyridine (1.60 g) were stirred together in benzene (25 ml) and

(25) For all of the quantitative nmr data cited in this paper, the integrals quoted are averages of at least five to ten measurements. The deviations in the values listed are estimated simply from the extreme integral values obtained for each proton.

(26) L. A. Paquette and L. D. Wise, *J. Am. Chem. Soc.*, 89, 6659 (1967).

(27) G. F. Emerson, L. Watts, and R. Pettit, *ibid.*, 87, 131 (1965).

(28) R. P. Neighbors, U. S. Patent 3,227,107 (Oct 4, 1966); *Chem. Abstr.*, 66, 11174 (1967).

cooled slightly. Acetyl chloride (1.584 g) in benzene (5 ml) was added dropwise and the mixture was stirred at room temperature for 3 hr. The benzene layer was decanted from an oily solid residue which was rinsed with additional benzene. The combined benzene solutions were evaporated to give oily crystals of the amide. This material was recrystallized with difficulty from hexane to yield 300 mg of colorless needles, mp 44–48°.

Imino Ether 36. Amide **35** (201 mg) was treated as above with 400 mg of Meerwein's reagent in dry methylene chloride to give **36** as a colorless oil after preparative scale vpc purification, ν_{max}^{neat} 1680 cm^{-1}.

Anal. Calcd for $C_6H_{11}NO$: C, 63.68; H, 9.80; N, 12.39. Found: C, 63.33; H, 9.65; N, 12.44.

Protonations with Trifluoroacetic Acid. To a solution of the imino ether in chloroform was added a slight excess of trifluoroacetic acid. The excess acid and solvent were removed *in vacuo* during 1–2 days. The residue was then dissolved in the appropriate solvent.

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Additions to Bicyclic Olefins. I. Stereochemistry of the Hydroboration of Norbornene, 7,7-Dimethylnorbornene, and Related Bicyclic Olefins. Steric Effects in the 7,7-Dimethylnorbornyl System[1]

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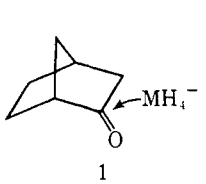
Abstract: A systematic study of addition reactions of norbornene, 7,7-dimethylnorbornene, and related bicyclic olefins has been undertaken in order to define more precisely the role of steric effects in controlling the stereochemistry of the additions and the nature of the intermediates in such addition reactions. The addition of borane to norbornene proceeds almost exclusively *exo* (99.5%), whereas the corresponding addition to 7,7-dimethylnorbornene proceeds preferentially *endo* (78%). Similarly, hydroboration of 2-methylenenorbornane gives preferentially *exo* (85%), whereas 2-methylene-7,7-dimethylnorbornane gives preferentially (85%) *endo* product. Similar results were realized with 1-methylnorbornene, 2-methylnorbornene, bornene, and 2,7,7-trimethylnorbornene. Consequently, hydroboration of norbornene, 1- and 2-methylnorbornene, and 2-methylenenorbornane goes predominantly *exo*, evidently reflecting the greater steric availability of the *exo* position in this bicyclic system. However, the presence of 7,7-dimethyl substituents causes the addition to proceed preferentially from the *endo* direction. Consequently, in hydroboration the 7,7-dimethyl substituents alter the normal direction of addition to olefins of the norbornane structure, irrespective of whether the double bond is endocyclic, directly under the 7,7-substituents, or exocyclic, located to the side of the substituents.

A major argument for the σ-bridged norbornyl cation is the almost exclusive *exo* substitution realized in the solvolysis of 7,7-dimethylnorbornyl derivatives.[3,4] The reduction of norcamphor by sodium borohydride[5] or lithium aluminum hydride[6] proceeds preferentially from the *exo* direction (**1**) to give the *endo* alcohol predominantly. On the other hand, the reduction of camphor or apocamphor takes place preferentially from the *endo* direction (**2**) to give the *exo* alcohol.



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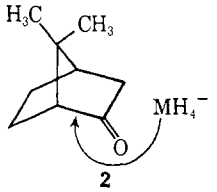

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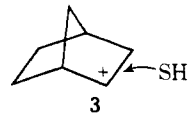
On the other hand, solvolyses of both norbornyl (**3**) and apobornyl (**4**) derivatives give the *exo* products almost exclusively. It was argued that the failure of the



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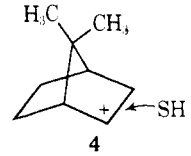

4

7,7-dimethyl substituents to control the stereochemistry of substitution in the cation, in the same manner that these substituents control the direction of attack by the complex hydrides, required something "special,"[3] σ bridging in the cation.

This is a reasonable argument. However, as was pointed out earlier,[7] it rests upon largely unexplored foundations. Implicit in the proposed argument is the assumption that because the 7,7-dimethyl substituents cause an inversion in the direction of attack by complex hydrides on the carbonyl group of apocamphor, these substituents should be expected to cause a similar

(1) Hydroboration. XXX.
(2) Graduate research assistant on grants (G 19878 and GP 6492X) supported by the National Science Foundation.
(3) J. A. Berson, "Molecular Rearrangements," P. de Mayo, Ed., Part I, Interscience Publishers, New York, N. Y., 1963, Chapter 3.
(4) S. Winstein, *et al.*, *J. Am. Chem. Soc.*, 87, 376, 378, 379, 381 (1965).
(5) H. C. Brown and J. Muzzio, *ibid.*, 88, 2811 (1966).
(6) S. Beckmann and R. Mezger, *Ber.*, 89, 2738 (1956).
(7) H. C. Brown, *Chem. Brit.*, 2, 199 (1966).