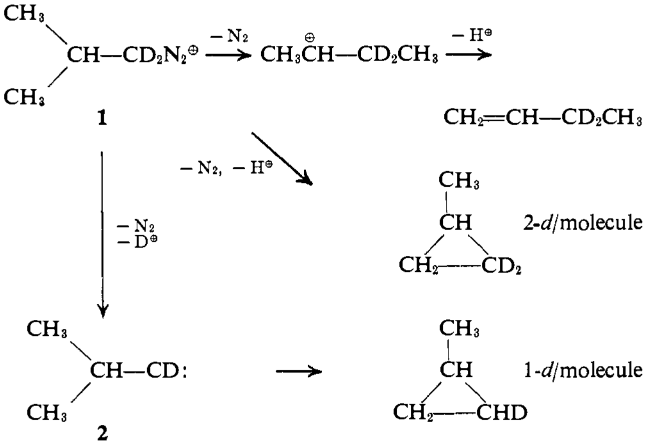
Mechanism of Cyclopropane Formation *via* Diazotization of Aliphatic Amines[1]

Sir:

Aprotic diazotization of aliphatic amines affords hydrocarbons in increased yield: olefins with a minimum of skeletal rearrangement and double-bond migration and relatively large amounts of cyclopropanes.[2] These results have been interpreted as arising from poorly solvated (*i.e.*, unstabilized) cationic intermediates. However, aliphatic carbenes also give, *via* intramolecular processes, nonrearranged olefins and cyclopropanes.[3] The possibility of carbenic and cationic processes occurring concurrently during the diazotization process has been raised but not adequately resolved.[4a,b] The following experiments clearly demonstrate that under conditions of protic and aprotic diazotization, carbenic intermediates are not involved.

For example, 1,1-d_2-isobutyldiazonium ion (**1**) can yield, by loss of nitrogen, migration of methyl, and loss of proton, 3,3-d_2-1-butene. Similarly methylcyclopropane arising directly from **1** would also contain two deuterium atoms per molecule. If the carbene intermediate (**2**) were involved, methylcyclopropane derived from it could only contain one deuterium atom. Inasmuch as significant amounts of hydrogen–deuterium exchange occur during the aprotic diazotization process,[5] an absolute deuterium determination of the methylcyclopropane obtained is of questionable value. However, since 1-butene can only arise from **1** *via* a cationic process,[2,3] the difference in absolute deuterium content of the 1-butene and methylcyclopropane formed from 1,1-d_2-isobutylamine (**3**) is a measure of the amount of **2** involved. This correlation is valid only if it is assumed that cyclopropane formation can occur by loss of one of the methyl protons in either a concerted process or *via* a protonated methylcyclopropane.



Diazotization of **3**-d_2[6] in chloroform or in DOAc–D_2O (1:1) gave hydrocarbon mixtures which were separated (glpc), trapped, and analyzed.[7,8] In each case the deuterium content of the 1-butene and the methylcyclopropane were found to be essentially the same (Table I). However, the minor differences (~1–2% less deuterium in methylcyclopropane) can be attributed to either the intermediacy of **2** or an equilibrating methylcyclopropane which is capable of losing a portion of its deuterium in its conversion to methylcyclopropane but not to 1-butene.[9] The extensive *loss* of deuterium in system 3 is the result of protium–deuterium exchange occurring during the reaction.[5] The results are in excellent agreement with the extent of deuterium *incorporation* observed in the system isobutylamine-d_2–DOAc–$HCCl_3$.[5] The seemingly anomalous results obtained from the reaction **3**-d_2–DOAc–$HCCl_3$[9] are also best explained as resulting from protium–deu-

Table I. Diazotization of $(CH_3)_2CHCD_2ND_2$[a]

System	Acid–solvent	Deuterium content[b]								
								 [c]		
		d_0	d_1	d_2	d_0	d_1	d_2	d_0	d_1	d_2
1	DOAc–D_2O	0	4	96	0	3	97			
2	HOAc–H_2O	0	5	95	0	3	97	0	16	84
3	HOAc–$HCCl_3$	10	40	50	8	38	54	16	44	40
4	DOAc–$HCCl_3$	0	17	83	0	15	85	2	29	69
5	DOAc–hexanol-*d*	0	9	91	0	8	92			
6	DCl–$HCCl_3$[d]	0	5	95	0	3	97			

[a] Amine [3% **1**-d_1, 97% **1**-d_2] (1 equiv), H(D)OAc (1 equiv), and octyl-ONO (1.1 equiv) and solvent at reflux. [b] Low-voltage mass spectrometry. [c] Loss of deuterium relative to 1-butene and methylcyclopropane can be best explained by a 1,2-hydride shift followed by loss of deuterium or hydrogen. This phenomenon is presently being studied using 2-*d*-isobutylamine. [d] *Cf.* ref 5, footnote 14b.

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(1) Financial support (Grant No. GP-3976) from the National Science Foundation is gratefully acknowledged.

(2) J. H. Bayless, F. D. Medicino, and L. Friedman, *J. Am. Chem. Soc.*, **87**, 5790 (1965).

(3) W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, Chapter 3.

(4) (a) M. S. Silver, *J. Am. Chem. Soc.*, **82**, 2971 (1960). (b) Cyclopropane formed *via* deoxidation of 1-d_2-propanol apparently occurs *via* the propyl cation: P. S. Skell and I. Starer, *ibid.*, **84**, 3963 (1962).

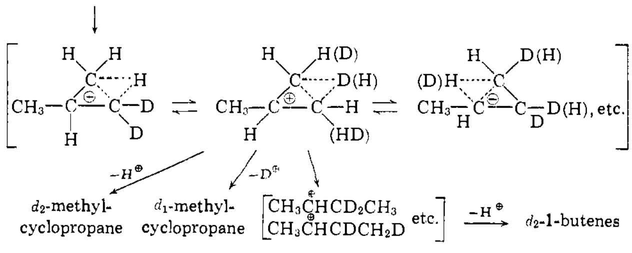
(5) J. H. Bayless and L. Friedman, *ibid.*, **89**, 147 (1967).

(6) 1,1-d_2-Isobutylamine was prepared by the reduction of isobutyronitrile with lithium aluminum deuteride. Attempts to prepare the amine by a modified Beauveault–Blanc reduction (V. L. Hansley, *Ind. Eng. Chem.*, **39**, 55 (1947)) on isobutyronitrile led to deuterium exchange at the tertiary carbon, and as a result the amine obtained was approximately 15% d_1, 50% d_2, and 35% d_3 (*t*-H:*t*-D ~ 60:40) species.

(7) The isomer hydrocarbon composition was essentially the same as that observed previously.

(8) Low-voltage mass spectrometry.

(9) The possibility of an equilibrating protonated methylcyclopropane can account for the minor differences in deuterium content of 1-butene and methylcyclopropane. The 1-butene can result either by methyl migration and loss of a proton or *via* an equilibrating protonated cyclopropane followed by loss of the methyl proton. No deuterium, however, can be lost in either process.



terium exchange—a result of the experimental difficulty of creating an absolutely proton-free environment and of protium generation during olefin formation. The amount of exchange is reduced when diazotization is effected in excess hexanol-*d* (system 5) as a result of swamping the reaction with exchangeable deuterium (*i.e.*, dilution of protium).

The intermediacy of a carbene can be eliminated or restricted to a maximum level of involvement of *ca.* 0.1%. However, considering the wide range of experimental conditions and the excellent internal consistency in relative deuterium content of the methylcyclopropane and 1-butene, a better explanation for the differences observed is the *limited* involvement of an equilibrating deuterated (or protonated) methylcyclopropane.[10]

(10) (a) A. A. Aboderin and R. L. Baird, *J. Am. Chem. Soc.*, **86**, 2300 (1964). (b) An equilibrating protonated cyclopropane was postulated by these authors to account for the extensive retention of deuterium in the cyclopropane isolated. These conflicting data may be a result of the difference in (1) reaction conditions (35% aqueous perchloric acid[10a] would more effectively stabilize the cation) and (2) the nature of the cation(s) produced. Unpublished work in these laboratories show that there are only minor changes in deuterium content with wide variation of protic reaction conditions.

Anthony T. Jurewicz, Lester Friedman
Department of Chemistry, Case Institute of Technology
Cleveland, Ohio 44106
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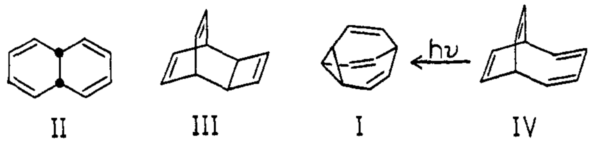
The Synthesis of Bicyclo[4.2.2]deca-2,4,7,9-tetraene. New Sources of *cis*- and *trans*-9,10-Dihydronaphthalene and Bullvalene[1]

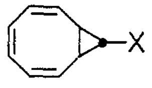
Sir:

The energy surface on which several $C_{10}H_{10}$ hydrocarbons exist features a number of paths between the isomers accessible either photochemically or thermally. The interconversion of bullvalene (I) and *cis*-9,10-dihydronaphthalene (II) and the thermal conversion of Nenitzescu's hydrocarbon, tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (III), to II have been described by Doering and Rosenthal.[2] We have previously added the photochemical conversion of I to III and a second hydrocarbon, as yet of unknown structure.[3] We wish to further enrich the known minima on this energy surface by adding the hitherto unknown bicyclo[4.2.2]deca-2,4,7,9-tetraene (IV). In addition, a new source of *cis*- and *trans*-9,10-dihydronaphthalene has been found. Finally, although we plan to report at length on the properties of IV later, we cannot resist describing its facile conversion to bullvalene.

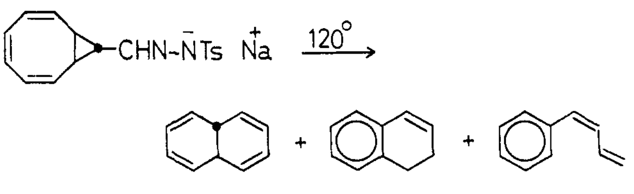


II III I IV

In a procedure previously described by Boekelheide[4,5] and others,[6,7] diazoacetic ester was decomposed thermally in the presence of cyclooctatetraene[8] and a small amount of cupric sulfate. This procedure led to methyl bicyclo[6.1.0]nona-2,4,6-triene-9-carboxylate (Va). Nuclear magnetic resonance (nmr) spectroscopy showed that the rearrangements noted in this system[4–7] had been avoided. Conversion of Va to the salt of the tosylhydrazone Ve was accomplished *via* the acid Vb, the acid chloride Vc, and the aldehyde Vd by unexceptional steps. Decomposition of the dry salt of Ve at 90–120° led not to the conventional[9] product bicyclo[6.2.0]deca-2,4,6,9-tetraene (VI) but to a complex mixture of $C_{10}H_{10}$ products. These compounds, in order of their elution from a 2-m, 20% Dow-Corning 710 silicone oil column, are: *trans*-9,10-dihydronaphthalene (20.0%),[10] II (11.6%),[10] *cis*-1-phenylbuta-1,3-diene (4.6%),[10] IV (37.8%), and 1,2-dihydronaphthalene (13.3%). Cyclooctatetraene (12.7%) and small, variable amounts of naphthalene were also formed. All compounds save IV were identified by comparison of spectra with those of authentic samples.



Va, X = $COOCH_3$
b, X = COOH
c, X = COCl
d, X = CHO
e, X = CHN-NH-Ts



II + IV

The structure of IV remains to be proved. In particular, it must be carefully differentiated from the isomeric VI. The 100-Mcps nmr spectrum[11] of IV shows two multiplets integrating for two protons each at 604 and 565 cps from tetramethylsilane, a symmetrical four-line pattern centered at 546 cps integrating for four protons, and a two-proton multiplet centered at 312 cps. On irradiation of the 312-cps signal, the four-line pattern at 546 cps collapses to a sharp singlet. Thus this signal can be assigned to the four protons on the ethylene bridges of IV. Norbornadiene shows a similar four-line pattern and identical behavior on decoupling of the bridgehead protons.[11] It is most difficult to reconcile this behavior with structure VI.

The ultraviolet spectrum showed maxima at $\lambda_{\max}^{\mathrm{EtOH}}$ 280, 268, and 258 mμ (ϵ 2900, 4200, and 4200, re-

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(1) We wish to express our gratitude to the Lilly Research Laboratories for their generous support of this work.

(2) W. von E. Doering and J. W. Rosenthal, *J. Am. Chem. Soc.*, **88**, 2078 (1966).

(3) M. Jones, Jr., unpublished work.

(4) K. F. Bangert and V. Boekelheide, *J. Am. Chem. Soc.*, **86**, 905 (1964).

(5) K. F. Bangert and V. Boekelheide, *ibid.*, **86**, 1159 (1964).

(6) S. Akiyoshi and T. Matsuda, *ibid.*, **77**, 2476 (1955).

(7) D. D. Phillips, *ibid.*, **77**, 5179 (1955).

(8) We thank the Badische Anilin und Soda Fabrik for a sample of cyclooctatetraene.

(9) W. Kirmse and K.-H. Pook, *Chem. Ber.*, **98**, 4022 (1965).

(10) We thank Professor W. von E. Doering and Mr. J. W. Rosenthal for spectra of *cis*-9,10-dihydronaphthalene, Professor E. E. van Tamelen for spectra of *trans*-9,10-dihydronaphthalene, Professor M. Pomerantz for spectra of *cis*-1-phenybuta-1,3-diene, and Dr. W. Grimme for spectra of bicyclo[4.2.1]nona-2,4,7-triene.

(11) We are most grateful to Professor M. Robert Willcott of the University of Houston who determined the 100-Mcps nmr spectra.