mechanisms were, at that time, considered equally satisfying.

We consider the isolation of bromonium salt **3** clear evidence that carbene **6** attacks bromophenol **2** to afford the reactive bromonium ylide **5**, which subsequently affords diphenoquinones **7**, **8**, and **9**. The formation of **7**–**9** upon regeneration of ylide **5** (or **5a**) by treatment of salt **3** with triethylamine is corroborative evidence for this view. Clearly, salt **3** is a convenient source of bromonium ylides **5** and **5a** and offers an unambiguous approach to the study of these remarkable intermediates. Halonium ylides may prove to be of unusual synthetic utility;[16] accordingly, this area is being further investigated.

Acknowledgment. This research was supported by grants in aid from Du Pont and Rohm and Haas and stimulated by discussions with Professor J. C. Martin.

[16] For example, protonation of the bromonium ylide presumed to arise upon photolysis of **1** in isopropyl bromide might lead to an isolable alkylarylbromonium salt, a type of compound not yet synthesized. See J. B. Dence and J. D. Roberts, *J. Org. Chem.*, 33, 1251 (1968).

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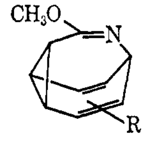
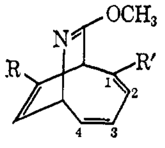
Pyrolysis of Azabullvalenes and 7-Azabicyclo[4.2.2]deca-2,4,7,9-tetraenes[1,2]

Sir:

Recently the first member of the azabullvalene class of fluxional heterocycles (**1a**) was described.[3,4] The four-step synthesis began with the 1,4 addition of chlorosulfonyl isocyanate to cyclooctatetraene followed by hydrolysis of this (N-chlorosulfonyl)lactam, conversion of the resulting lactam to imino ether **2a**, and irradiation of **2a**. In the present communication we describe the thermal behavior **1a** and **2a** and several of their monomethyl analogs.



1a, R = H
b, R = CH_3



2a, R = R′ = H
b, R = CH_3; R′ = H
c, R = H; R′ = CH_3

This study was prompted by reports that heating bicyclo[4.2.2]deca-2,4,7,9-tetraene (**3**) (245°, 4 hr) gave rise to *cis*-9,10-dihydronaphthalene (**4**) (20%) and naphthalene (80%)[5] and that partial decomposition of bullvalene (**6**) (350°, flow system) afforded **4** as the only product.[6] Although Doering and Rosenthal implicated novel mechanistic pathways in these thermal interconversions, they were not able to define the precise mechanism(s) in the absence of more definitive evidence.

In the cases of **1a** and **2a**, the nitrogen- and methoxyl-bearing carbon atoms can serve as internal probes of the various reorganization processes; the behavior of these imino ethers at elevated temperatures then becomes of particular interest because the nature of the pyrolysis products could effectively limit the number of mechanistic possibilities. The additional methyl substituent of **1b**, **2b**, and **2c** can be expected to reduce further the number of alternatives. We propose to demonstrate herein that this goal has been attained.

Methoxyazabullvalene (**1a**) proved to be remarkably stable; below 500°, this substance could be sublimed into a glass-bead packed quartz tube (28 cm × 16 mm) at 20 mm and be recovered quantitatively. When this procedure was repeated at 550°, or better, at 600° (almost total conversions), **1a** was cleanly converted in high yield to a mixture of 12 products. Interestingly, **2a** afforded the identical product mixture under these conditions. Preparative-scale gas chromatography (8 ft × 0.25 in. stainless steel column packed with 20% Apiezon L-KOH (4:1) on 60–80 mesh Chromosorb W) permitted the isolation and complete characterization of quinoline (75%; picrate mp 203°), 2-methoxyquinoline (10.3%; picrate mp 183–184.5°), 1-methoxyisoquinoline (6.6%; picrate mp 160–162°),[7] and 3-methoxyisoquinoline (∼1%; picrate mp 197–198°). 3-Methoxyisoquinoline was prepared independently from 3-hydroxyisoquinoline[8] and diazomethane in a DMF–*t*-BuOH–ether–$CHCl_3$ solvent system. The remaining eight products (combined yield, 7%) were not characterized because of limited quantities; however, it was established by independent synthesis that 5-methoxyquinoline[9] and 6-methoxyisoquinoline[10] had not been produced in detectable quantities. The various methoxy-substituted quinolines and isoquinolines are stable to the conditions of pyrolysis, thereby indicating that quinoline is not an artifact of these thermal reorganizations.

Investigation of the pyrolytic behavior of **1b**, **2b**, and **2c** has provided still more interesting results. At ∼600°, decomposition of **2b** and **2c** leads to the formation (∼95% yield) of all possible monomethylquinolines *except 2-methylquinoline* (Table I). Furthermore, the yields of the individual nitrogen aromatics are quite similar in the two cases. Each product was identified by comparison of infrared curves, nmr spectra, and vpc retention times with those of authentic samples; in addition, each quinoline was resubmitted to the pyrolysis procedure and was recovered unaltered.

Pyrolysis of **1b** affords again a mixture of methylquinolines (∼95% yield), but, in contrast, *2-methylquinoline* (picrate mp 194–195°) *is now the major product* (Table I).

Mechanistic considerations denote clearly that several modes of thermal isomerization are available to **1** and **2**, the most precedented of which[5,6,11,12] include: (a)

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[1] Unsaturated Heterocyclic Systems. XLII. For the previous paper in this series, see L. A. Paquette and M. Rosen, *J. Org. Chem.*, in press.

[2] The authors wish to express their gratitude to the National Institutes of Health and the Alfred P. Sloan Foundation for their generous financial support of this work.

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

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

[5] W. von E. Doering and J. W. Rosenthal, *Tetrahedron Letters*, 349 (1967).

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

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[8] J. H. Boyer and L. T. Wolford, *J. Org. Chem.*, **21**, 1297 (1956).

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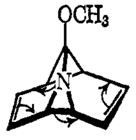
Table I. Product Data for the Pyrolysis (600°) of **1b**, **2b**, and **2c**.

	Substrate pyrolyzed		
	2b	**2c**	**1b**
Products	Percentage composition		
8-Methylquinoline	15	20	10
7-Methylquinoline	25	20	15
6-Methylquinoline	10	15	10
5-Methylquinoline	20	15	10
4-Methylquinoline	20	15	10
3-Methylquinoline	10	15	10
2-Methylquinoline	*a*	*a*	35

[a] Not observed.

intramolecular symmetry allowed $((4 + 2)\pi)$ cycloaddition involving the imino ether linkage of **2** to give **7** which can hypothetically lead to 6-methoxyazacyclodecapentaene (**8**); (b) a similar Diels–Alder addition involving the isolated olefinic bond to afford **9** which can give rise to 2-methoxyazacyclodecapentaene (**10**); (c) four distinct suprafacial sigmatropic shifts of order [1,5][13] in **2**; (d) rearrangement of the azabullvalene structure to common intermediate **9** (as indicated)



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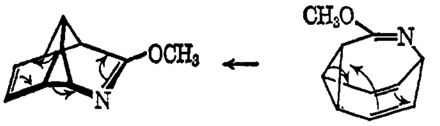

2 **1**

prior to more extensive rearrangement.

Because disrotatory cyclization of **8** and *in situ* dehydrogenation of the resulting two dihydro derivatives can only lead from **2a** to 5-methoxyquinoline and 6-methoxyisoquinoline (not observed), pathway a must be considered nonoperative. Of direct bearing on mechanisms b and c is the realization that these pathways correctly predict the structures of the products which are produced in the pyrolysis of **2a**.[14] However, **2b** can give rise uniquely to 4- and 7-methylquinolines by these routes. In the case of **2c**, only the 2-, 5-, 6-, and 7-methylquinolines would be expected to be produced. Thus, in the last two examples, mechanisms b and c not only fail to predict the formation of a number of methylquinolines, but **2c** is stated to lead in part to the 2-methyl isomer, which is not observed.

Although the methyl group of **1b** is recognized to prefer bonding to sp^2-hybridized carbon over the temperature range 30–195°,[15] more extensive positional scrambling of this substituent at 600° is anticipated. It is not surprising therefore that all seven methylquinolines are observed in this instance.

Such an analysis of the data indicates that the mechanistic speculation which has been applied to thermal interconversions of isomeric $C_{10}H_{10}$ hydrocarbons, although founded on the theoretical considerations of Hoffmann and Woodward,[13,16] has serious shortcomings when applied to the aza analogs and therefore must be considered equivocal and less than satisfactory at this time. Discussion of the mechanistic implications of the present results is deferred to the full paper.

Acknowledgment. We wish to thank Badische Anilin und Soda Fabrik for a generous gift of cyclooctatetraene which made this study possible.

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[13] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 2511 (1965).

[14] The predominance of quinoline can be rationalized on the basis that the requisite transition state resembles product, and loss of methanol is more facile (by approximately 13 kcal/mol) than ejection of molecular hydrogen.

[15] J. R. Malpass, unpublished observations.

[16] R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965).

[17] National Institutes of Health Postdoctoral Fellow, 1967.