mining the rates of substitutions at hard electrophilic centers. Since H for N_3^- is 6.46 while that for Cl^- is about -3 one can see how azide ion could be much more reactive in substitutions at this type of center than chloride ion.

Experimental Section

Preparation and Purification of Materials. The preparation and purification of the various α-disulfones have been described in an accompanying paper,[11] as was the purification of the dioxane used as solvent. Lithium bromide, sodium bromide, and sodium fluoride were all reagent grade and were recrystallized from distilled water and dried before using. Sodium acetate, sodium nitrite, acetic acid, and sodium azide were all reagent grade and were used without further purification. The various amines were of the highest purity obtainable from Matheson Coleman and Bell and were further purified by distillation from barium oxide before use.

Reaction of 2b with Sodium Azide. *p*-Tolyl α-disulfone (**2b**), 0.62 g (2.00 mmoles), and sodium azide, 0.33 g (5.0 mmoles), were dissolved in 400 ml of 60% dioxane (v/v) and the solution was heated for 5 hr at 60°. The solution was then evaporated to dryness under reduced pressure. The residue was treated with a mixture of water and ether. The ether layer was washed first with dilute sulfuric acid, then with dilute sodium hydroxide, and finally with water. The ether layer was then dried over anhydrous magnesium sulfate and the ether was evaporated under reduced pressure. The residue crystallized upon being cooled and scratched with a stirring rod: yield, 0.35 g (90%) of *p*-toluenesulfonyl azide; mp 22° (lit.[18] mp 22°); infrared spectrum identical with that of a known sample prepared by the method of Curtius.[18]

Procedure for Kinetic Runs on the Catalysis of the Hydrolysis of 2 by Added Nucleophiles. The exact procedure depended on the temperature at which the run was to be carried out. For those runs carried out at temperatures *higher* than 21.3° the procedure was as follows. A standard solution of the α-disulfone was prepared in dioxane and the proper volume of this solution was pipetted into the reaction flask of the same apparatus used in an accompanying paper[11] to study the uncatalyzed hydrolysis of **2**. The proper volumes of standard aqueous solutions of the other reagents required were then pipetted into the same reaction vessel, and the solutions were thoroughly mixed. From this point on, the procedure was the same as that used for following the uncatalyzed hydrolysis.[11]

For the runs at 21.3° the apparatus employed was that used by Kice and Guaraldi[19] in studying the hydrolysis of **1** in 60% dioxane. To make a run, 3 ml of a standard solution of the α-disulfone in freshly distilled dioxane was placed in chamber A of this apparatus, and 2 ml of an aqueous solution containing all the remaining reagents was placed in chamber B. The apparatus was then immersed in the constant-temperature bath. After 5 min the two solutions were rapidly mixed, and the resulting solution was transferred to chamber C of the apparatus, a 1-cm spectrophotometer cell. The apparatus was then immediately placed in a thermostated cell holder inside a Cary Model 15 spectrophotometer, and the progress of the hydrolysis of **2** was monitored spectrophotometrically at the same wavelengths used[11] for the uncatalyzed hydrolysis.

Procedure for Kinetic Studies of the Reaction of Azide with 2b. The general procedure was the same as for the runs at 21.3° with the catalyzed hydrolysis. However, because of the absorption of sodium azide in the 240-mμ range, the kinetics of the disappearance of **2b** were followed at 275 mμ, rather than at 258 mμ. At 275 mμ **2b** still has an appreciable absorption but azide does not.

Procedure for Kinetic Studies of the Reaction of Amines with 2b. The general procedure was exactly the same as that used for studying the other reactions of **2b** at 21.3°. The disappearance of the α-disulfone was followed spectrophotometrically at 270 mμ. The 1:1 RNH_2–RNH_3^+ buffer solutions were prepared by adding the calculated amount of standard hydrochloric acid solution to a standard solution of the amine in water.

(18) T. Curtius and G. Kraemer, *J. Prakt. Chem.*, **125**, 323 (1930).

(19) J. L. Kice and G. Guaraldi, *J. Am. Chem. Soc.*, **89**, 4113 (1967).

Pyrolysis of Azabullvalenes and 7-Azabicyclo[4.2.2]deca-2,4,7,9-tetraenes. Unsaturated Heterocyclic Systems. LXII[1,2]

Leo A. Paquette, Grant R. Krow, and John R. Malpass

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Abstract: 8-Methoxy-7-azabicyclo[4.2.2]deca-2,4,7,9-tetraene (**1a**) and methoxyazabullvalene (**2a**) heated at 600° in the gas phase give an identical mixture containing quinoline (75%), 2-methoxyquinoline (10%), 1-methoxyisoquinoline (7%), and 3-methoxyisoquinoline (1%), in addition to several very minor products. Under the same conditions, the 2- and 9-methyl derivatives of **1a** and the methyl homolog of **2a** yield chiefly methylquinolines (>95%). Most notably, methyl-**2a** affords all seven possible methylquinolines, with 2-methylquinoline predominating (32%). In contrast, the 2- and 9-methyl derivatives of **1a** give only six methylquinolines, the 2 isomer being totally absent. The thermal aromatization of **1a** and **2a** is one which most likely passes through a common intermediate; this intermediate, however, must become nonidentical when a single methyl group is placed on the two structures, despite the fact that considerable methyl scrambling occurs. A mechanistic scheme is proposed to account for these interesting and unprecedented observations.

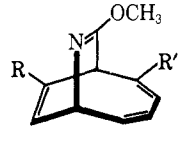
Mechanistically intriguing thermal rearrangements of polyunsaturated hydrocarbons have recently gained the attention of numerous researchers.[3,4] Current interest in such interconversions has been heightened by the awareness that orbital symmetry factors[5] may

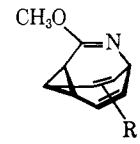
(1) For the previous paper in this series, see L. A. Paquette, J. R. Malpass, G. R. Krow, and T. J. Barton, *J. Am. Chem. Soc.*, **91**, 5296 (1969).

(2) The authors are grateful to the National Institutes of Health, the Alfred P. Sloan Foundation, and the Lilly Research Laboratories for grants which contributed to the financial support of this research.

(3) (a) G. Schröder, *Chem. Ber.*, **97**, 3140 (1964); (b) E. E. van

control the various bond reorganizations to a substantial degree. Transformations of molecules of the formula $(CH)_{10}$ have been most widely studied and are most clearly understood at the present time. In view of the ready synthetic availability of derivatives of certain $(CH)_9N$ heterocycles,[1,6] we have investigated the thermal behavior of **1a**, **2a**, and several of their mono-





1a, R = R′ = H
b, R = CH_3; R′ = H
c, R = H; R′ = CH_3

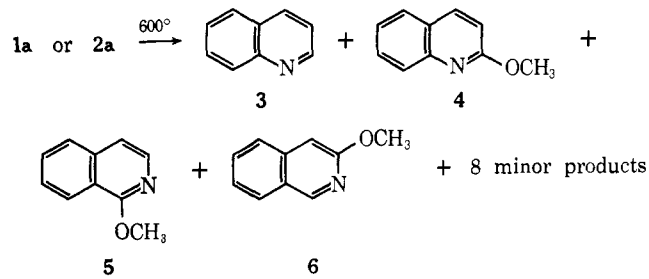
2a, R = H
b, R = CH_3

methyl analogs.[7] In the cases of **1a** and **2a**, the nitrogen center and the methoxy-bearing carbon atom can serve as internal probes of the various bond reorganization processes. This sort of atomic labeling was anticipated to shed considerable light on the various mechanistic possibilities for the pyrolysis reactions. In addition, the methyl substituents in **1b**, **1c**, and **2b** were expected to assist in defining more precisely the true reaction pathway by reducing further the number of mechanistic alternatives. This goal has been realized.

Results

Sublimation of **1a** into a glass-bead packed quartz tube (28 cm × 16 mm) at 600° (12 mm) resulted in almost total conversion to a mixture of 12 products in high yield. Interestingly, **2a** afforded an identical product mixture under these conditions. Preparative-scale gas chromatography permitted the isolation and characterization of the four major products which together comprised 93% of the pyrolysate (Scheme I). Chief among the products was quinoline (**3**, 75%) which was identified by comparison of vpc, infrared, nmr, and picrate melting point (203°) data with those of an authentic sample. Similar criteria were employed

Scheme I



3 **4** **5** **6**

+ 8 minor products

to confirm the isolation of 2-methoxyquinoline (**4**, 10%), 1-methoxyisoquinoline (**5**, 7%), and 3-methoxyisoquinoline (**6**, 1%). The previously uncharacterized **6** was prepared independently by methylation of 3-hydroxyisoquinoline with 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 shown by independent synthesis that 5-methoxyquinoline[8] and 6-methoxyisoquinoline[9] had not been produced in detectable quantities. Also, the various methoxy-substituted quinolines and isoquinolines were stable to the pyrolytic conditions, thereby indicating that quinoline was not an artifact of these thermal reorganizations.[10]

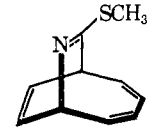
In order to gain further insight into the nature of this thermal process, the pyrolytic behavior of **1b**, **1c**, and **2b** was studied. At approximately 600°, decomposition of **1b** and **1c** led in >95% yield to the formation of all possible monomethylquinolines *except 2-methylquinoline* (Table I).[11] Pyrolysis of **2b** afforded also a

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

Products	Substrate pyrolyzed: **1b**	**1c**	**2b**
	Percentage composition[a]		
8-Methylquinoline	13	19	11
7-Methylquinoline	28	19	16
6-Methylquinoline	11	17	9
5-Methylquinoline	21	15	12
4-Methylquinoline	22	15	11
3-Methylquinoline	5	15	9
2-Methylquinoline	*b*	*b*	32

[a] Percentage composition values were obtained by a combination of vpc and nmr techniques and are reliable to ±3%. [b] Not observed (<0.5%).

mixture of methylquinolines (~95% yield), but, in contrast, *2-methylquinoline was now the major product* (Table I). The 2- and 8-methylquinolines were readily separable from the mixture by preparative vpc on a column packed with 20% Apiezon L–KOH (4:1) on



i

In this instance, however, the foul-smelling minor products were not characterized.

(11) The limit of detectability of 2-methylquinoline was less than 0.5%.

Tamelen and B. Pappas, *J. Am. Chem. Soc.*, 85, 3296 (1963); (c) C. D. Nenitzescu, M. Avram, I. I. Pogany, G. D. Mateescu, and M. Farcasiu, *Acad. Rep. Populare Romine Studii Ceretari Chim.*, 11 (1), 7 (1963); (d) W. von E. Doering and J. W. Rosenthal, *J. Am. Chem. Soc.*, 88, 2078 (1966); (e) M. Jones, Jr., and L. T. Scott, *ibid.*, 89, 150 (1967); (f) E. E. van Tamelen and T. L. Burkoth, *ibid.*, 89, 151 (1967); (g) W. von E. Doering and J. W. Rosenthal, *Tetrahedron Lett.*, 349 (1967); (h) S. Masamune, C. G. Chin, K. Hojo, and R. T. Seidner, *J. Am. Chem. Soc.*, 89, 4804 (1967); (i) S. Masamune, H. Zenda, M. Wiesel, N. Nakatsuka, and G. Bigam, *ibid.*, 90, 2727 (1968); (j) S. Masamune, R. T. Seidner, H. Zenda, M. Wiesel, N. Nakatsuka, and G. Bigam, *ibid.*, 90, 5286 (1968); (k) W. Grimme, H. J. Riebel, and E. Vogel, *Angew. Chem. Intern. Ed. Engl.*, 7, 823 (1968); (l) M. Jones, Jr., and B. Fairless, Jr., *Tetrahedron Lett.*, 4881 (1968).

(4) (a) G. Schröder, *Chem. Ber.*, 97, 3131 (1964); (b) G. Schröder and W. Martin, *Angew. Chem. Intern. Ed. Engl.*, 5, 130 (1966); (c) J. N. Labows, Jr., J. Meinwald, H. Röttele, and G. Schröder, *J. Am. Chem. Soc.*, 89, 612 (1967); (d) K. Grohmann and F. Sondheimer, *ibid.*, 89, 719 (1967); (e) G. Schröder and J. F. M. Oth, *Angew. Chem. Intern. Ed. Engl.*, 6, 414 (1967); (f) G. Schröder, W. Martin, and J. F. M. Oth, *ibid.*, 6, 870 (1967); (g) M. Jones, Jr., and S. D. Reich, *J. Am. Chem. Soc.*, 89, 3935 (1967); (h) P. Radlick and W. Fenical, *Tetrahedron Lett.*, 4901 (1967); (i) J. Daub and P. von R. Schleyer, *Angew. Chem. Intern. Ed. Engl.*, 7, 468 (1968); (j) M. Jones, Jr., and L. O. Schwab, *J. Am. Chem. Soc.*, 90, 6549 (1968).

(5) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1, 17 (1968).

(6) (a) L. A. Paquette and T. J. Barton, *J. Am. Chem. Soc.*, 89, 5480 (1967); (b) L. A. Paquette, T. J. Barton, and E. B. Whipple, *ibid.*, 89, 5481 (1967); (c) L. A. Paquette, J. R. Malpass, and T. J. Barton, submitted for publication.

(7) A preliminary communication of these results has appeared: L. A. Paquette, G. R. Krow, J. R. Malpass, and T. J. Barton, *ibid.*, 90, 3600 (1968).

(8) L. Bradford, T. J. Elliott, and F. M. Rowe, *J. Chem. Soc.*, 437 (1947).

(9) R. A. Robinson, *J. Am. Chem. Soc.*, 69, 1934, 1939 (1947).

(10) When thiomethyl imino ether i was pyrolyzed under the stated conditions, quinoline was again found to be the major product (80%).

Chromosorb W and were indentified on the basis of the previously adopted criteria (nmr, infrared, and picrate melting point comparisons). The next peak to be eluted from this column was a mixture of 3-, 6-, and 7-methylquinolines, and the final peak was a mixture of the 4- and 5-methyl isomers. These mixtures could not be fractionated gas chromatographically on the wide variety of columns which were examined. However, the presence of the indicated quinolines was clearly demonstrated by a combination of infrared and nmr spectoscopic comparisons with authentic samples.[12]

Resubmission of each methylquinoline to the pyrolysis procedure resulted in no scrambling of the methyl substituent. Therefore, the alkylquinolines are the result of aromatization reactions arising directly from thermal bond reorganization and loss of methanol.

Mechanistic Consideration. Having established that pyrolysis of **1a** and **2a** leads chiefly to **3** and in lesser quantities to **4**, **5**, and **6**, and that substantial methyl scrambling attends the thermal rearrangements of **1b**, **1c**, and **2b**, it is appropriate to consider what pathways seem likely for these transformations. Of considerable relevance to these mechanistic considerations are the recent reports describing the ease with which the bicyclo[4.2.2]deca-2,4,7,9-tetraene system (**7**) undergoes rapidly reversible degenerate thermal valence isomerization at moderately elevated temperatures.[3k,l] The results strongly implicate tetracyclo[4.4.0.0^{2,10}.0^{5,7}]deca-3,8-diene (**8**) as an intermediate in these interconversions. Additional convincing evidence has been derived from

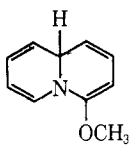
7 8 9

the observation that photochemically generated **8** undergoes quantitative conversion to **7** at −15 to −20°.[3j] Apparently, **8** passes at a much slower rate to *cis*-9,10-dihydronaphthalene (**9**).[3l]

Thus, it is conceivable that **1a** undergoes initial symmetry-allowed intramolecular (4 + 2)π cycloaddition at the more electron deficient of the two isolated double bonds to produce **10** which is subject to a slower nonconcerted reverse (4 + 4)π cycloaddition leading to **11** (Scheme II). In **11**, the added stabilization of the imino ether linkage has been lost, a fact which could result in rapid passage to all-*cis* 2-methoxyazacyclodecapentaene (**12**). At the elevated temperatures, **12** could not be expected to survive, but four distinct thermal disrotatory cyclizations leading to **13–15** and to **11** (retrogression) are available to this polyene.[3f,13]

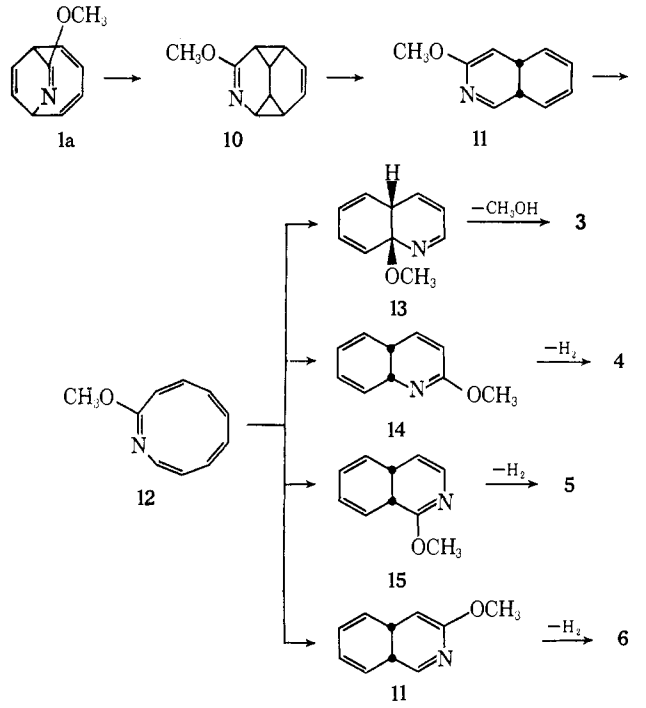
(12) The nmr studies of the methylquinoline mixtures were conducted at different concentrations (CCl_4) solutions) in view of the substantial and highly informative concentration dependence of the spectra. The ratio of 3-, 6-, and 7-methylquinolines was determined by integration of the three methyl singlets at 100-Hz sweep width. In the final fraction which contained the 4- and 5-methylquinolines, the methyl signals were not separated; rather, integration of the two characteristic low-field one-proton signals at δ 8.65 and 8.82, respectively, gave the ratio of the two isomers.

(13) A fifth ring closure leading to ii is possible, but aromatization is



ii

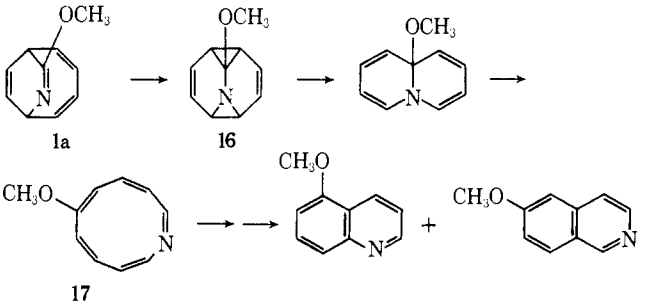
Scheme II



The conversion of **12** *via* **13** to quinoline (**3**) involves cleavage of a tertiary C–H (~90 kcal/mole) and a C–O bond (~84 kcal/mole). The lesser amount of energy required to expel methanol from **13** (~174 kcal/mole) is quite likely related to the fact that quinoline formation predominates since aromatization of **11**, **14**, and **15** demands the loss of molecular hydrogen (~180 kcal/mole).[14] In addition, the low yield of 3-methoxyisoquinoline (**6**) may be a reflection of the less favored disrotatory cyclization of **12** to **11** (and also expulsion of hydrogen directly from initially formed **11**)[15a] due to the requisite forfeiture of imino ether stabilization which must be incurred.[15b]

Alternatively, thermal isomerization of **1a** could proceed by intramolecular Diels–Alder cycloaddition involving the imino ether linkage to give **16** which can hypothetically lead to all-*cis* 6-methoxyazacyclodecapentaene (**17**, Scheme III). However, because disrotatory

Scheme III



obviously precluded in this instance; if produced, reversal to **12** would be its most likely fate.

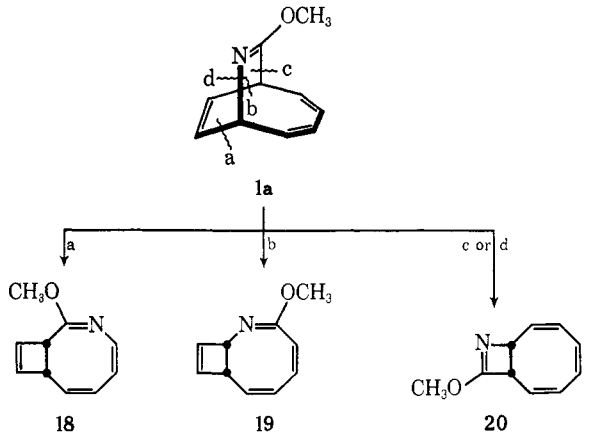
(14) These bond energy values are obviously approximations which do not take account of the stabilized radical produced in these examples. However, since the same general type of radical is formed in the various cases, the difference of 6 kcal/mole appears to be a reliable "order of magnitude."

(15) (a) However, see Scheme V which bypasses the necessity of involving preformed **11**. (b) In all of these considerations, the logical assumption is made that the requisite transition states resemble products.

cyclization of **17** and *in situ* dehydrogenation of the resulting two dihydro derivatives can lead only to 5-methoxyquinoline and 6-methoxyisoquinoline (not observed), this pathway must be considered nonoperative.

The thermal rearrangement of **1a** can also be formulated as arising by initial symmetry-allowed suprafacial shifts of order [1,5],[16] four of which are possible (Scheme IV). In view of the ease with which bicyclo[6.2.0]deca-2,4,6,9-tetraene can be thermally isomerized to *trans*-9,10-dihydronaphthalene in quantitative yield,[3h] azalogs **18–20** can likewise be expected to pass readily into the *trans* isomers of **11**, **13–15**, and then into the derived quinolines and isoquinolines.

Scheme IV



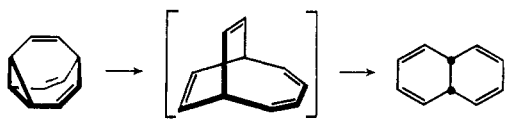
18 19 20

Although the mechanistic pathways in Scheme IV correctly predict the structures of the products which are formed in the pyrolysis of **1a**, it is readily seen that **1b** can only give rise to 4- and 7-methylquinolines by these routes. In the case of **1c**, only the 2-, 5-, 6-, and 7-methylquinolines would be produced. Thus, Scheme IV not only fails to explain the formation of a number of methylquinolines, but **1c** is stated to lead in part to the 2-methyl isomer which is not observed. These serious shortcomings clearly indicate the particular considerations in this scheme to be less than satisfactory.

The elimination of Schemes III and IV from further consideration causes Scheme II to become the only attractive remaining mechanistic rationalization. However, the specific scrambling of the methyl group between positions 3, 4, 5, 6, 7, and 8 of the resulting alkylquinolines cannot be explained within the confines of the illustrated rearrangement pathway. Rather, the observed scrambling indicates that an additional series of thermal reorganizations must necessarily be incorporated into Scheme II. Furthermore, since the 2-methoxyazabullvalene (**2a**) gives the identical pyrolysis product distribution as **1a**, a common intermediate must intervene. Yet, in the methyl-tagged series (**1a** and **1b** *vs.* **2b**) the results require that this intermediate be not totally identical, but that it differ in some fashion which preserves the integrity of the carbon atom adjacent to the nitrogen center when entering from the azabicyclo[4.2.2]decatetraene direction.

Central to the final solution of this mechanistic question was the observation what when **2a** was pyrolyzed at a temperature below that at which quinoline formation began to be observed above trace quantities, *i.e.*, 500°, partial conversion to **1a** was achieved. In a typical run under these conditions, **2a** was recovered in 67% yield; the remaining 33% consisted of **1a** (31%) and aromatics (2%). When **2b** was heated in similar fashion (450, 460, and 585°), a mixture of monomethylazabicyclo[4.2.2]decatetraenes was produced, with recovery decreasing as the temperature was raised (correspondingly greater quantities of quinolines were produced). Although this isomeric mixture could not be separated into its components, infrared and nmr spectral analysis provided definitive evidence on the gross structural assignments. Not unexpectedly, carefully controlled pyrolysis of **1a**, **1b**, and **1c** gave no evidence of thermal conversion to methoxyazabullvalenes. In addition, it was noted that **1b** and **1c** were not interconverted at elevated temperatures, nor did nonspecific methyl scrambling to other methylazabicyclo[4.2.2]decatetraenes take place.

At first glance, these results do not appear to parallel completely the thermal behavior of bullvalene (**21**) which gives 9,10-dihydronaphthalene (**23**) as the first isolable product at 350°.[3d] However, this apparent



21 22 23

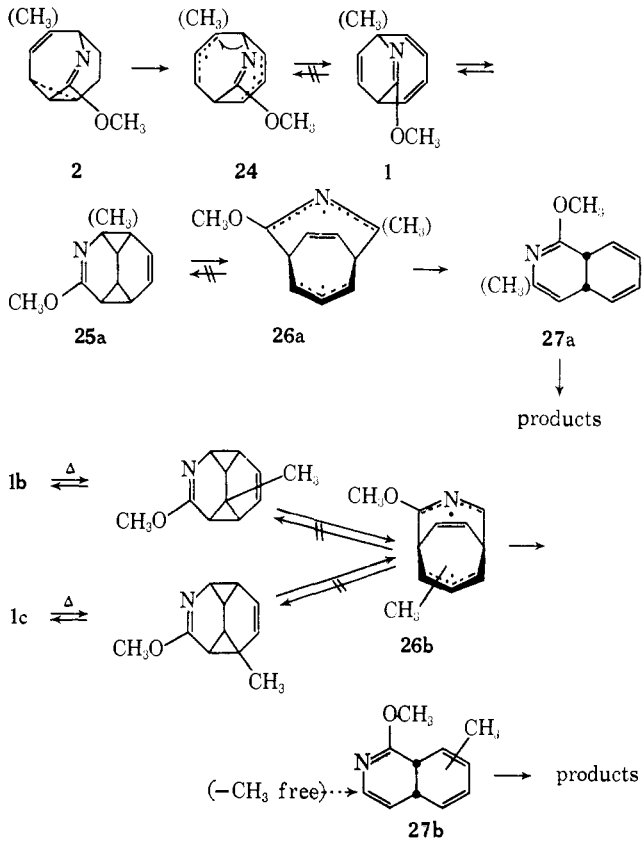
discrepancy with the all-carbon system is believed to result simply from the fact that bicyclo[4.2.2]deca-2,4,7,9-tetraene (**22**) is much less thermally stable than its nitrogen analog **1**, conversion of **22** to **25** occurring as low as 245°.[3g,i] Isolation of **22** from the pyrolysis of **21** under such circumstances would obviously be precluded.

Scheme V proposes a reasonable pathway for the formation of azabicyclo[4.2.2]decatetraenes from azabullvalenes. Thus, diallylic diradical **24** is formed from **2** by homolytic rupture of a cyclopropyl bond. Subsequent migration of nitrogen leads to **1**. Because **2b** gives rise chiefly to 2-methylquinoline, 1,2 shift of nitrogen from the bridgehead carbon atom (which does not become involved in the averaging process and therefore is not likely to carry the methyl group[1]) to a methyl-substituted carbon center must occur to an appreciable extent. Since the methyl group in **2b** earlier has been shown to undergo averaging among the seven peripheral carbons,[1] the likehood of the transportation of **24** to **1** is clearly evident. The scheme is not meant to be restricted to this particular migration; rather, a combination of all possible processes probably is operative. Significantly, however, this mechanism accounts for placement of a methyl group adjacent to nitrogen.

Consideration must now be given to the detailed mechanism which can account for the selectivity of methyl scrambling (no 2-methylquinoline produced) in the azabicyclo[4.2.2]decatetraenes. Initially, it it seen that intramolecular $(4 + 2)\pi$ cycloaddition in **1b** and **1c** leads to two structurally distinguishable azatetracyclo[4.4.0.0^{2,10}.0^{5,7}]deca-3,8-dienes (Scheme V). Reverse (3 + 3 + 2) cycloaddition of these intermediates would give biradical **26b**. The most obvious way to preserve the structural integrity of the triatomic nitrogen-containing bridge while allowing for scrambling of the methyl substituent among the remaining seven positions

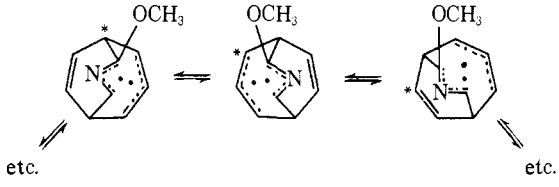
(16) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, 87, 2511 (1965).

Scheme V



is to invoke a rotation of the heteroatomic bridge about a seven-atom "rim". In the parent series, this rotation would be completely degenerate (Scheme VI); in the

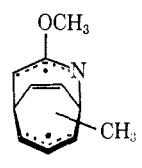
Scheme VI



case of **1b** and **1c**, scrambling of the methyl substituent to all the rim positions occurs with preservation of the absence of alkyl labeling on the carbon atom of the pivoting bridge. Although the aforementioned bond reorganization will hypothetically also be operative in **26a**, it should be noted that in certain of the structures (*ca.* 30% based on 2-methylquinoline isolated) the methyl substituent has already found its way to the pivoting bridge due to earlier nitrogen migration.[17,18]

(17) It is interesting to compare the effect of benzo fusion on other possible diradical intermediates such as **26**; see ref 1 and L. A. Paquette and J. R. Malpass, *J. Am. Chem. Soc.*, **90**, 7151 (1968).

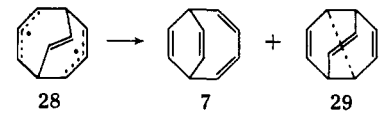
(18) It is recognized that there are two possible retrograde (3 + 3 + 2) cycloadditions available to intermediates of type **25**, the alternative bond cleavage giving rise to diradical iii. The passage of **25** to iii can be considered nonoperative since both **1b** and **1c** should give 2-methylquinoline as a result of methyl scrambling in iii. Likewise, the conversion of **2** directly into iii or **26a** (*via* a Cope rearrangement product) is considered to be much less likely than conversion to **24** because of the previously recognized limited fluxional nature of **2**, as evidenced by the reluctance of nitrogen to occupy bridgehead and cyclopropyl sites.[1] The result is that the bond cleaved homolytically in passing from **2** to **24** is the weakest link.



iii

Complete skeletal scrambling in **2** might be invoked to account for the formation of *all* methylquinolines. However, such a process would logically result also in the formation of methylisoquinolines, and these were not observed. This further supports the limited fluxional nature of **2**.

The combination of Schemes II, V, and VI constitutes the simplest formal representation of the pyrolytic aromatization of the azabicyclo[4.2.2]decatetraenes and azabullvalenes which is entirely compatible with the whole of the interlocked framework of data. In particular, the mechanistic sequence provides a ready demonstration of why a common intermediate in the unsubstituted series should suddenly become nonidentical when a single methyl group is added to the various structures, despite the fact that considerable methyl scrambling occurs. Certain minor limitations to the extensiveness of the scheme deserve mention. Firstly, although diradical **26** could conceivably cyclize to an azabullvalene, it does not appear to do so. This behavior is paralleled by **28** which cyclizes to **7** and **29**, but



not to bullvalene (**21**).[3i] Secondly, since **1b** and **1c** do not scramble when pyrolyzed, then **1** must not revert to **24**. Further **26** must not be capable of retrogression to **25** which by analogy to hydrocarbon analogs is expected to be in equilibrium with the azabicyclo[4.2.2]-decatetraene system under these conditions. Finally, it is interesting to conjecture that the passage of **25** to diradical **26** is favored not only because direct opening to **11** (Scheme II) would cause disrupture of imino ether stabilization but also because of the homoconjugative stability which may be available to **26**.

Experimental Section[19]

General Pyrolysis Procedure. The sample was slowly sublimed into a quartz tube (28 cm × 16 mm) packed with glass beads maintained at the desired temperature. The pressure in the system was maintained at 8–12 mm. The pyrolysis product was collected in a trap cooled in a Dry Ice–acetone bath. The yellow-brown oils were analyzed by vpc on 12 ft × 0.25 in. aluminum columns packed with 20% Apiezon L–KOH (4:1) on 60–80 mesh Chromosorb W.

Product Characterization from the Pyrolysis of 1a and 2a. Quinoline picrate, mp 203°, was prepared from a commercial sample. 2-Methoxyquinoline (**4**) was prepared by heating 2-chloroquinoline with excess sodium methoxide in methanol;[20] picrate mp 183–184.5° (from ethanol).

Isoquinoline N-oxide was converted to 1-chloroisoquinoline by the procedure of Robinson.[21] The latter was transformed into 1-methoxyisoquinoline (**5**) by the method of Robison and Robison;[22] picrate mp 160–162° (lit.[22] mp 163.5–165.5°).

3-Hydroxyquinoline was prepared from commercially available 3-methylquinoline according to literature directions.[23] To 700 mg of diazomethane in 70 ml of ether, 15 ml of dimethylformamide, 30 ml of *t*-butyl alcohol, and 40 ml of chloroform cooled to −20°

(19) Melting points are corrected. The nmr spectra were determined with Varian A-60 and A-60A spectrometers purchased with funds made available through the National Science Foundation.

(20) D. M. Clugston and D. B. Maclean, *Can. J. Chem.*, **44**, 781 (1966).

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(22) M. M. Robison and B. L. Robison, *ibid.*, **80**, 3443 (1958).

(23) (a) C. E. Teague, Jr., and A. Roe, *ibid.*, **73**, 688 (1951); (b F. H. Case, *J. Org. Chem.*, **17**, 471 (1952); (c) J. H. Boyer and L. T, Wolford, *ibid.*, **21**, 1297 (1956); (d) H. E. Baumgarten and J. E. Dirks, *ibid.*, **23**, 900 (1958).

Table II

Compd	Sample wt, mg	Pyrolysis temp, °C	Pressure, mm	Yield of products, mg (%)
1b	246	600–610	12	203 (100)[a]
1c	228	580–600	12	186 (100)[a]
2b	170	615	8–9	135 (97.5)[a]

[a] According to vpc analysis, these mixtures consisted chiefly (95%) of methylquinolines.

was added 675 mg of 3-hydroxyisoquinoline. The solution was stirred for 5 hr at −10 to −20° and was allowed to come to room temperature overnight. The solution was concentrated by directing a stream of air at its surface; dimethylformamide was removed *in vacuo*, and the residual oil was molecularly distilled. Pure **6** was isolated by preparative vpc; $\delta_{TMS}^{CDCl_3}$ 8.7 (singlet, 1 H), 7.36 (multiplet, 4 H), 6.78 (singlet, 1 H), and 3.90 (singlet, 3 H). Its picrate melted at 197–198°.

Anal. Calcd for $C_{16}H_{12}N_4O_8$: C, 49.47; H, 3.12; N, 14.43. Found: C, 49.54; H, 3.30; N, 14.48.

Product Characterization from the Pyrolysis of 1b, 1c, and 2b. 2-Methylquinoline picrate, mp 194–195°, was prepared from a commercial sample (lit.[24] mp 195°). 3-Methylquinoline was prepared from aniline and α-methylacrolein (Skraup) according to the procedure of Manske, *et al.*;[24] picrate mp 189° (lit.[24] mp 190°). 4- and 6-methylquinolines were commercially available. 5- and 7-methylquinolines were obtained from reaction of *m*-toluidine and glycerol under the conditions described by Palmer.[25] The isolated 8-methylquinoline afforded a picrate, mp 202–204° (lit.[26] mp 202–204°).

Some representative pyrolysis experiments are summarized in Table II (results and product ratios were consistently reproducible).

Partial Pyrolyses. The partial pyrolyses indicated in Table III were studied.

Table III

Compd	Temp, °C	Product ratio, %: 1	2	Aromatics
1a	500	75[b]	..	25[c]
1b	505	32[d]	..	68[e]
1c	580–600	3.5[f]	..	96.5[e]
2a	500	31[b]	67[g]	2[c]
2b	460	17.5[h]	52[i]	30.5[e]

[a] Percentage composition values were obtained directly from vpc analyses. [b] Exclusively **1a**. [c] A mixture of **3–6**. [d] Exclusively **1b**. [e] A mixture of methylquinolines. [f] Exclusively **1c**. [g] Exclusively **2a**. [h] A mixture of methylated derivatives. [i] Exclusively **2b**.

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The Involvement of Oxygenated Functions in the Acetolysis of 7-Oxygenated Norbornyl Tosylates

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Abstract: Acetolyses of *exo*- and *endo*-2-tosyloxybicyclo[2.2.1]heptan-7-one ethylene glycol ketal have been studied. Whereas the *exo*-tosylate gave *exo*-acetate as the major product, the predominant reaction path followed by the *endo* isomer was one of ring cleavage to yield substituted cyclohexenes. The *exo*-tosylate solvolyzed eleven times faster than the *endo* isomer. Although the rates of solvolysis were similar to *endo*-2-tosyloxybicyclo[2.2.1]heptane, the dramatic change in product ratios showed that more than one mechanism was involved.

Few intermediates in the history of chemistry have received more attention than the norbornyl cation. In attempts to define the nature of this unusual cation, investigators have pursued a remarkably singular mode of attack. This commonly accepted approach has been to functionalize generously the norbornyl skeleton with groups which could stabilize an incipient cation (relative to stabilization by hydrogen) by either their electron-donating ability or through resonance. In view of the interest in this problem it is surprising that only a few examples of norbornyl systems bearing electron-withdrawing substituents have been studied.[2–5] Unfortunately even among these few cases there is no clear-cut example which allows a rigorous comparison of the behavior of *exo*- and *endo*-arenesulfonates. Roberts and coworkers[2,6] and Wilt and Wagner[5] studied only *exo*-tosylates. The investigations of Gassman and Marshall on derivatives of 7-ketonorbornane were complicated by the change in hybridization at C-7 and by the possibility that the carbonyl group might be exerting an unprecedented influence on the developing carbonium ion center. In the solvolysis of the 7,7-dimethoxy-2-tosyloxynorbornanes, the interpretation of the results was complicated by the fact that the *endo*-tosylate **1** solvolyzed with MeO-4 neighboring group participation,[3] while the *exo*-tosylate **2** appeared to solvolyze without participation of the neighboring methoxyl func-

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