intensity of the check reflections. The intensities were corrected for Lorentz and polarization factors and $\sigma[I]$ was estimated from $[(\text{total count}) + (\text{background}) + 5\%(\text{total count})^2 + 5\%(\text{background})^2]^{1/2}$. The estimated deviation of F, $\sigma(F)$, was calculated from $\sigma(F) = \{[I + \sigma(I)]/L_p\}^{1/2} - (I/L_p)^{1/2}$.[26] All reflections with $F \leq 3\sigma(F)$ were judged unobserved. A total of 1322 reflections were judged observed. No correction was made for absorption or decomposition.

Solution and Refinement. A three-dimensional Patterson synthesis revealed the Br position unambiguously.[27] The remaining 21 nonhydrogen atoms were easily located in the subsequent Br-phased electron density synthesis. Full-matrix least-squares refinements with anisotropic temperature factors for all atoms (198 variables) reduced the conventional discrepancy index, R, to its present minimum of 0.096. The scattering factor tables were those of Hanson, *et al.*[28] In Table II are listed the final X-ray coordinates and their standard deviations.[29] In Tables III and IV are listed the final bond distances and bond angles, respectively, along with their standard deviations.[30] Figure 1 is a computer generated drawing of the final X-ray model.[31]

Acknowledgment. The authors at The Ohio State University thank the National Institutes of Health, National Science Foundation, and Eli Lilly and Company for their support of this research. The authors at Iowa State University thank the Ames Laboratory of the U.S. Atomic Energy Commission for support.

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(26) D. E. Williams and R. E. Rundle, *J. Amer. Chem. Soc.*, **86**, 1660 (1964).

(27) J. Rodgers and R. A. Jacobson, a general FOURIER program in PL1 for triclinic, monoclinic, and orthorhombic space groups, U. S. Atomic Energy Commission Report 15-2155, Iowa State University of Science and Technology, Ames Institute for Atomic Research, 1969.

(28) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, 17, 1040 (1964).

(29) W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Least-Squares Program," U. S. Atomic Energy Commission Report ORNL-3794, Oak Ridge National Laboratory, Tenn., 1965.

(30) W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Function and Error Program," U. S. Atomic Energy Commission Report ORNL-TM-306, Oak Ridge National Laboratory, Tenn., 1964.

(31) The table of structure factors and the final thermal parameters will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche. Briefly, in no case was F_c for the "unobserved reflections" greater than $3\sigma(F_o)$. No abnormally short intermolecular contacts were observed.

Thermolysis of 1,2,3,4,5,6-Hexamethyl-7-phenyl-7,8,9-triazatricyclo[4.3.0.0^{2,5}]nona-3,8-diene. Synthetic Entry to the 1,2,3-Triazonin Ring System[1]

Leo A. Paquette* and Robert J. Haluska[2]

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received May 5, 1971*

Abstract: Thermolysis of the title compound (**2**) in refluxing decalin (195°) affords as the major product (42%) the theoretically interesting 10π electronic triazonin **3**. The bicyclic valence tautomer of **3**, **4**, is also isolated (14%) but is shown not to be a primary product. Rather, **4** arises from the rearrangement of a precursor (believed to be **8**) on the alumina adsorbent employed in the chromatographic separation. Heating of **4** to 80° results in ready conversion to **3**. Lastly, the azanorbornadiene **5** is formed in 12% yield. Mechanistic rationalizations for the production of **3–5** are presented. The key physical and chemical properties of triazonin **3** are tabulated and examined in the light of aromatic or polyenic character for this heterocyclic system. The conclusion is reached that this first example of a polyheteronin is decidedly aromatic.

The 1-substituted Δ^2-triazolines which result from 1,3-cycloaddition of azides to olefins are recognized to undergo thermally induced loss of nitrogen especially readily when the 1 substituent is strongly electron withdrawing.[3] However, when the grouping in question is phenyl, for example, elevated temperatures are required and the decomposition usually develops added complexity.[4] Since enhancement of solvent polarity has been found to cause significant increases in the rates of these decompositions, and because apparent Wagner–Meerwein rearrangement products are occasionally formed, the expulsion of nitrogen is viewed as proceeding through diazonium–betaine intermediates (*e.g.*, **1**) *via* initial heterolytic cleavage of the N_1–N_2 bond.[4,5] The ensuing modes of decomposition of zwitterions such as **1** appear to be somewhat structurally dependent and to involve cleavage of the N_3–C_4 or the C_4–C_5 bond.

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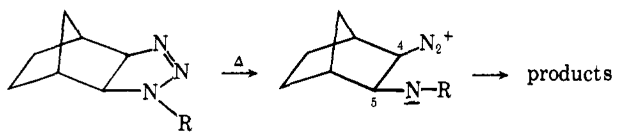
(1) Unsaturated Heterocyclic Systems. LXXXIV. For the previous paper in this series, see L. A. Paquette, R. J. Haluska, M. R. Short, L. K. Reed, and J. Clardy, *J. Amer. Chem. Soc.*, **94**, 529 (1972).

(2) National Institutes of Health Predoctoral Fellow, 1966–1970.

(3) (a) F. D. Marsh and M. E. Hermes, *J. Amer. Chem. Soc.*, **86**, 4506 (1964); (b) F. D. Marsh, M. E. Hermes, and H. E. Simmons, *ibid.*, **87**, 2996 (1965); (c) A. C. Oehlschlager, P. Tillman, and L. H. Zalkow, *Chem. Commun.*, 596 (1965); (d) A. C. Oehlschlager and L. H. Zalkow, *J. Org. Chem.*, **30**, 4205 (1965); (e) A. G. Anastassiou, *ibid.*, **31**, 1131 (1966); (f) K. D. Berlin, L. A. Wilson, and L. M. Raff, *Tetrahedron*, **23**, 965 (1967); (g) R. Huisgen, L. Möbius, G. Müller, H. Stangl, G. Szeimies, and J. M. Vernon, *Chem. Ber.*, **98**, 3992 (1965); (h) A. C. Oehlschlager, R. S. McDaniel, A. Thakore, P. Tillman, and L. H. Zalkow, *Can. J. Chem.*, **47**, 4367 (1969); (i) R. L. Hale and L. H. Zalkow, *Tetrahedron*, **25**, 1393 (1969).

(4) (a) K. Alder and G. Stein, *Justus Liebigs Ann. Chem.*, **501**, 1 (1933); **515**, 165, 185 (1935); (b) R. S. McDaniel and A. C. Oehlschlager, *Tetrahedron*, **25**, 1381 (1969).

(5) (a) R. Fusco, G. Bianchetti, and D. Pocar, *Gazz. Chim. Ital.*, **91**, 849, 933 (1961); (b) I. Brown and O. E. Edwards, *Can. J. Chem.*, **43**, 1266 (1965); (c) K. D. Berlin and L. A. Wilson, *Chem. Ind. (London)*, 1522 (1965); (d) A. L. Logothetis, *J. Amer. Chem. Soc.*, **87**, 749 (1965).



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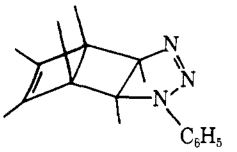
In the accompanying paper,[1] the preparation of *exo*-triazoline **2** was described; its thermal behavior is now



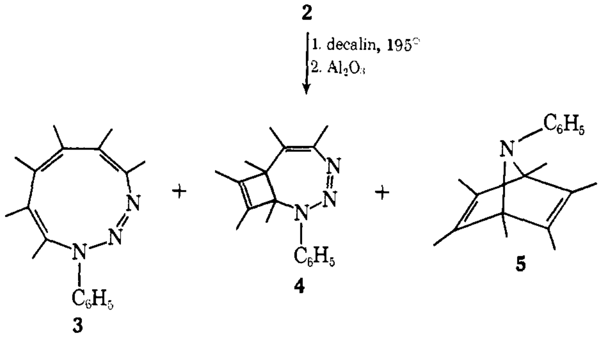
2

reported. In its initial stages, the thermolysis of **2** could take at least three widely divergent pathways. In the first of these alternatives, the high level of strain present in the permethylated bicyclo[2.2.2]hexenyl moiety could be relieved by kinetically controlled scission of the central bond.[6] Such a reaction would have no parallel in triazoline chemistry. The second option would involve initial rupture of the heterocyclic ring as in **1**. In this eventuality, loss of nitrogen would generate a highly interesting dipolar intermediate which would in all probability be subject to structural rearrangement prior to intramolecular collapse. In many respects, this carbonium ion would resemble those species initially produced upon electrophilic addition of hexamethyl(Dewar benzene) where skeletal bond reorganizations abound.[7] Lastly, the possibility exists that the excessively strained nature of **2** would cause the three constituent rings to undergo a more or less synchronous isomerization of unprecedented type. Accordingly, **2** represents an interesting molecule capable of providing an assessment of the relative importance of ring strain on competitive modes of triazoline decomposition.

Results

Heating a solution of **2** in decalin at reflux (195°) for 25 min resulted in the complete disappearance of the triazoline (tlc analysis). Column chromatography of the golden yellow pyrolysate on alumina resulted in the separation of three components. The major product (42%), a yellow-orange solid, exhibited a moderately intense infrared band (KBr) at 1640 cm^{-1} suggestive of an enamine double bond. In addition, extended π-electron conjugation was indicated by absorption maxima observed in the ultraviolet and visible regions [ethanol, 222 (ϵ 28,000) and 353 nm (3780); isooctane, 224 (ϵ 28,600) and 358 nm (4390)]. The nmr spectrum (60 MHz, $CDCl_3$) of the material displayed sharp singlets at δ 2.17 and 2.20 (6 H total) and a broadened singlet (12 H) at 1.99 (partially resolved into a multiplet at 100 MHz) along with the usual downfield phenyl absorptions (δ 6.6–7.4; 5 H). The implication from such chemical shift data is that the product contains six sp^2-bound methyl groups, two of which are positioned on carbon bearing a nitrogen atom. Further, elemental analysis and high-resolution mass spectral molecular weight determination showed conclusively that the substance was isomeric with **2** ($C_{18}H_{23}N_3$)!

Two structural formulations compatible with these observations are triazonin **3** and azepine **6**. In order for **6** to give rise to the observed nmr spectrum, however, the two α-methyl groups would have to be magnetically nonequivalent by reason of restricted rotation about the triazene N_2–N_3 single bond. Alternatively, it is possible that the lower field pair of singlets are in fact an unresolved multiplet arising from homoallylic coupling of equivalent α-methyl groups with the β-methyl substituents, the corresponding multiplet of the latter being masked under the broadened singlet at δ 1.99. With regard to the possibility of magnetically nonequivalent α-methyl groups, it has recently been demonstrated[8] that such a phenomenon does appear in the nmr spectra of 3,3-dimethyltriazenes below (and in one instance at room temperature). In all instances, mild warming was found to cause coalescence. That the proton resonance spectrum of the pyrolysis product was unchanged to 118° made it unreasonable then to conclude that the observed spectrum was caused by such behavior in **6**. In addition, careful examination of these spectra at both 60 and 100 MHz clearly showed that the two lower field singlets are not due to spin–spin coupling but in fact are attributable to two distinct methyl groups.[9] In contrast, the triazonin formulation would be expected to display the observed spectral features. These data, as well as its formation from heating of **4**, are taken as confirmatory evidence for **3**.



The second component to be eluted from alumina (14%) exhibited infrared absorptions at 1650 and 1625 cm^{-1} and ultraviolet maxima in ethanol at 218 (ϵ 19,700) and 330 nm (2180) and in isooctane at 222 (ϵ 20,500) and 333 nm (2520). In the nmr ($CDCl_3$), the substance showed, aside from phenyl absorptions, a singlet at δ 2.51 (3 H), a pair of singlets at δ 2.06 and 1.97 (6 H each), and another singlet of area 3 at δ 1.29. The above data, along with an empirical formula of $C_{18}H_{23}N_3$, suggested the compound to be **4**. In confirmation of this assignment, **4** was found to be smoothly transformed into **3** at 80° during 100 min in tetrachloro-

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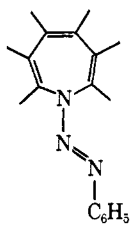
(6) Retro-Diels–Alder fragmentation such as is observed with the phenyl azide adduct of norbornadiene[3g] was not considered likely in the present instance because of the necessity that tetramethylcyclobutadiene be formed concomitantly with dimethylphenyltriazole.

(7) (a) L. A. Paquette, *Tetrahedron Lett.*, 2133 (1968); (b) L. A. Paquette and G. R. Krow, *ibid.*, 2139 (1968); (c) W. Schäfer and H. Hellmann, *Angew. Chem. Int. Ed. Engl.*, **6**, 518 (1967); (d) L. A. Paquette, G. R. Krow, J. M. Bollinger, and G. A. Olah, *J. Amer. Chem. Soc.*, **90**, 7147 (1968); (e) H. Hogeveen and H. C. Volger, *Recl. Trav. Chim. Pays-Bas*, **87**, 385, 1042 (1968); (f) L. A. Paquette and G. R. Krow, *J. Amer. Chem. Soc.*, **91**, 6107 (1969); (g) A. G. Anastassiou and S. W. Eachus, *Chem. Commun.*, 429 (1970); (h) R. Criegee and H. Grüner, *Angew. Chem.*, **80**, 447 (1968); *Angew. Chem. Int. Ed. Engl.*, **7**, 467 (1968); (i) M. Kunz and W. Lüttke, *Chem. Ber.*, **103**, 315 (1970).

(8) (a) G. Koga and J.-P. Anselme, *Chem. Commun.*, 894 (1969); (b) M. H. Akhtar, R. S. McDaniel, M. Feser, and A. C. Oehlschlager, *Tetrahedron*, **24**, 3899 (1968).

(9) At 60 MHz (CCl_4), the difference in chemical shift between these peaks was found to be 3.55 Hz while at 100 MHz it was seen to be 5.9 Hz.



6

ethylene solution. Such cyclobutene ring openings are well documented.[10]

The marked thermal lability of **4** made it apparent, however, that this substance could not be a direct thermal product of **2**. Rather, **4** must have been formed by rearrangement of an isomeric structure during the chromatographic procedure. This premise was experimentally verified by heating a sample of **2** as above in decalin and, after solvent removal, recording the nmr spectrum of the product mixture. Clearly present were, *inter alia*, **3** and **5**, but no **4**. Treatment of this mixture in pentane with alumina resulted in the appearance of **4** with no change in the proportions of **3** and **5**. The structure of the precursor to **4** remains unknown (however, see Discussion), but it is certain that neither **2** nor **3** gives rise to **4** in this way. The triazoline was recovered completely unchanged after standing in contact with the adsorbent for several hours, while **3** was seen to slowly darken and decompose under similar conditions.

The spectral data obtained on the third component (12%) revealed that it was the azanorbornadiene **5**. Thus the nmr spectrum consisted apart from phenyl absorptions of two sharp singlets at δ 1.70 (12 H) and 1.39 (6 H). The ultraviolet spectrum (see Experimental Section) was a composite of that expected from a norbornadiene and an aniline derivative.[11]

Thermolysis of **2** in tetrachloroethylene at 121° for 65 min resulted in complete loss of starting material (tlc, nmr) and formation of a reaction mixture approximately 80% of which was **3**. The presence of neither **4** or **5** was indicated, but the former was generated by elution of the material through Florisil. The absence of **4** was considered to be a function of the lower pyrolysis temperature but attempted verification of this by analogous thermolysis in a sealed tube at 195° caused complete decomposition to black tarry materials with no recognizable products being present (nmr analysis).

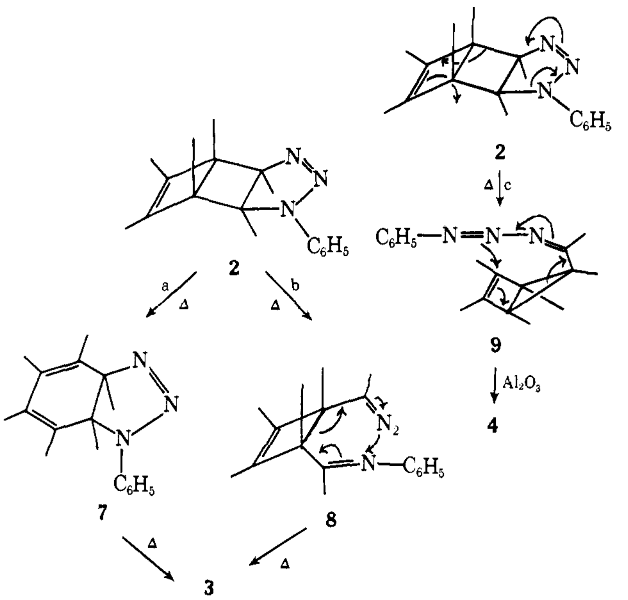
Attempts to induce paramagnetic shifts in the nmr spectrum of **3** with trisdipivalomethanatoeuropium(III)[12] met with failure; no change was observed in the spectrum over a substantial concentration range of the shift reagent. Apparently, none of the nitrogen centers is sufficiently basic for effective complex formation. The triazonin (**3**) does not undergo cycloaddition with 4-phenyl-1,2,4-triazoline-3,5-dione and it resists catalytic hydrogenation and photoinduced rearrangement or nitrogen expulsion.

Somewhat interestingly, exposure of **4** to the triazolinedione in CDCl$_3$ at 40° resulted in quantitative conversion to **3** during 20 min.

Discussion

A striking feature of the thermolysis of **2** is the absence of nitrogen expulsion in the principal rearrangement pathways. The conversion of **2** to **3** is considered to be the result either of disrotatory cyclobutene ring opening to give **7** and subsequent [3,3] sigmatropic shift (path a, Scheme I) or heterocyclic ring fragmentation to imino diazoalkane **8**[13] and subsequent bond reorganization (path b). Particular interest is attached to the mechanism of formation of **4**. A conceivable pathway could involve backside participation of the olefinic π system in **2** with simultaneous rupture of the triazoline ring to afford bicyclopentane **9** (path c, Scheme I). This type of electronic shift finds a convincing parallel in the thermal behavior of several norbornene derivatives of type **10**. For example, Meinwald and coworkers[14a] have reported the formation of *exo*-epoxide **10a** and its rapid rearrangement at room temperature to **11a**. The latter was found by Rey and Dreiding[14b] to exist in mobile equilibrium with **12a**. In addition, Schleyer[15a] and Brown[15b] have shown that **11b** spontaneously rearranges to **12b**. Also, the reaction of norbornadiene with benzenesulfonyl azide[3d] and cyanogen azide,[3f] not unexpectedly, gives no directly observable triazoline or aziridine formation (because of their thermal lability), but rather eventuates in the rapid production of **12c** and **12d**, respectively. These rearrangements have been visualized as occurring *via* Cope rearrangement of intermediates **11c** and **11d** which result in turn from bond relocations illustrated in **10**.[16]

Scheme I



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(10) L. A. Paquette and J. H. Barrett, *J. Amer. Chem. Soc.*, **89**, 3979 (1967).

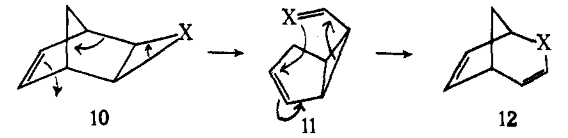
(11) (a) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Wiley, New York, N. Y., 1963, p 138; (b) M. B. Robin and N. A. Kuebler, *J. Chem. Phys.*, **44**, 2664 (1966); (c) R. Hoffmann, E. Heilbronner, and R. Gleiter, *J. Amer. Chem. Soc.*, **92**, 706 (1970); (d) A. T. Bottini and G. P. Nash, *ibid.*, **84**, 734 (1962).

(12) J. K. M. Sanders and D. H. Williams, *ibid.*, **93**, 641 (1971), and references therein.

(13) (a) J. E. Baldwin, G. V. Kaiser, and J. A. Romersberger, *ibid.*, **87**, 4114 (1965); (b) M. Regitz, *Angew. Chem. Int. Ed. Engl.*, **6**, 733 (1967); (c) W. Carpenter, A. Haymaker, and D. W. Moore, *J. Org. Chem.*, **31**, 789 (1966); (d) R. Fusco, G. Bianchetti, D. Pocar, and R. Ugo, *Chem. Ber.*, **96**, 802 (1963). We thank Dr. P. Scheiner for calling this set of references to our attention.

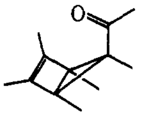
(14) (a) J. Meinwald, S. S. Labana, L. L. Labana, and G. H. Wahl, Jr., *J. Amer. Chem. Soc.*, **87**, 1789 (1965); (b) M. Rey and A. S. Dreiding, *Helv. Chim. Acta*, **48**, 1985 (1965).

(15) (a) C. Cupas, W. E. Watts, and P. von R. Schleyer, *Tetrahedron Lett.*, 2503 (1964); (b) J. M. Brown, *Chem. Commun.*, 226 (1965).



a, X = O; **b**, X = CH_2; **c**, X = $NSO_2C_6H_5$; **d**, X = NCN

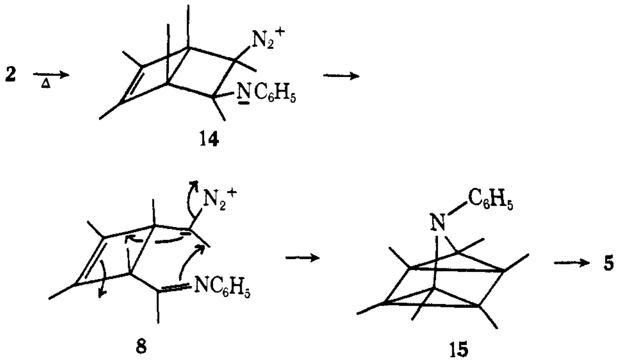
In order for **9** to be the unidentified precursor to **4**, its thermal stability would have to be assumed. In this regard, it is significant to note that ketone **13**, which corresponds structurally to **9**, is generated at 210° and is unchanged (nmr) upon prolonged heating at 120°.[17,17a] The conversion of **9** to **4** on alumina is viewed as analogous to the transformation of **11** to **12**.



13

Azanorbornadiene **5** is presumed to arise *via* azaquadricyclane **15** (Scheme II). Intermediates **14** and **8** bear formal analogy to those suggested to account for the thermal behavior of certain triazolines,[4b,13] while a conversion of the type **8** to **15** has been proposed earlier[31] for a similar norbornadiene reaction.[18] Additionally, quadricyclanes are well known to give rise thermally to norbornadienes.[19]

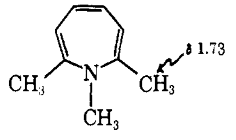
Scheme II



The above observations provide uncontestable evidence that the strain inherent in **2** promotes rather unique thermal rearrangement and decomposition pathways in this triazoline. Of perhaps overriding importance, however, is the awareness that the theoretically interesting triazonin **3** now becomes readily available by virtue of two synthetic manipulations. This molecule represents the first example of a polyheteronin for which Hückel molecular orbital theory predicts aromatic stability because of its closed shell configuration of $(4n + 2)$ π electrons ($n = 2$). A question central to this issue is whether the structure possesses sufficient electronic stabilization to compensate for the energetic disadvantages customarily forced upon medium-sized ring systems, *i.e.*, planarity and bond angle strain. Several criteria are available for evaluating the potential aromatic character of such a molecule. Although the permethylated nature of **3** does serve to lessen somewhat the sensitivity of the existing methods, the evidence obtained to date is most reasonably interpreted by representing triazonin **3** as decidedly aromatic.

Firstly, the triazonin is unchanged upon heating to elevated temperatures and prolonged standing in the presence of air under ordinary conditions. Such enhanced thermodynamic stability relative to oxonin,[20] 1*H*-azonin,[21] and derivatives of the latter heterocycle[22] which are appreciably more thermally labile can be rationally construed as evidence of aromaticity. Although it may be argued that the extensive substitution on **3** would lessen its propensity for valence bond isomerization, intermolecular cycloaddition, and like chemical transformations, the impressive photochemical stability of the triazonin would appear to support the initial conclusion.

Secondly, the spectral properties of **3** are consistent with the operation of extended electronic delocalization. Comparison of chemical shifts of the ring methyl groups of **3** with those of the nonaromatic, polyenic azepine **16**[23] on the one hand and those of the methylpyrroles (**17**),[24] picoline (**18**),[24] and methylpyridazines (**19**)[25] on the other indicates that the triazonin exhibits some degree of diamagnetic circulation around the ring. Specifically, the ring methyl chemical shifts in **3** occur at considerably lower field positions than do their



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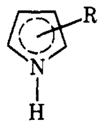
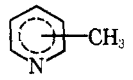
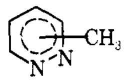


17, 2-CH_3: δ 2.16
3-CH_3: δ 2.05



18, 2-CH_3: δ 2.55
3-CH_3: δ 2.32
4-CH_3: δ 2.37



19, 3-CH_3: δ 2.74
4-CH_3: δ 2.40

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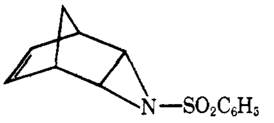
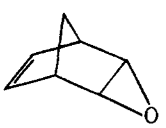
(16) Significantly, *endo*-aziridine i [A. C. Oehlschlager and L. H. Zalkow, *Can. J. Chem.*, 47, 461 (1969)] and *endo*-epoxide ii [J. T. Lumb



i



ii

and G. H. Whitham, *J. Chem. Soc.*, 1189 (1964)] have been found to be thermally stable and not prone to isomerization. Thus, such rearrangements would appear to be facilitated by backside participation of the transannular double bond.

(17) M. Klaus, H. Prinzbach, and H. Achenbach, *Angew. Chem.*, 81, 899 (1969); *Angew. Chem. Int. Ed. Engl.*, 8, 880 (1969).

(17a) Note Added in Proof. The structural assignment to 13 has recently been revised: B. C. Baumann, M. Rey, J. Markert, H. Prinzbach, and A. S. Dreiding, *Helv. Chim. Acta*, 54, 1589 (1971). The molecule is currently believed to be hexamethyl-2-oxabicyclo[3.2.0]-hepta-3,6-diene.

(18) J. E. Franz and C. Ozuch, *Chem. Ind. (London)*, 2058 (1964).

(19) L. A. Paquette and L. M. Leichter, *J. Amer. Chem. Soc.*, 92, 1765 (1970), and references therein.

(20) (a) A. G. Anastassiou and R. P. Cellura, *Chem. Commun.*, 903, 1521 (1969); 484 (1970); (b) S. Masamune, S. Takada, and R. T. Seidner, *J. Amer. Chem. Soc.*, 91, 7769 (1969).

(21) A. G. Anastassiou and J. H. Gebrian, *Tetrahedron Lett.*, 825 (1970).

(22) (a) S. Masamune, K. Hojo, and S. Takada, *Chem. Commun.*, 1204 (1969); (b) A. G. Anastassiou and J. H. Gebrian, *Tetrahedron Lett.*, 5239 (1969); (c) A. G. Anastassiou, S. W. Eachus, R. P. Cellura, and J. H. Gebrian, *Chem. Commun.*, 1133 (1970).

(23) L. A. Paquette, D. E. Kuhla, J. H. Barrett, and R. J. Haluska, *J. Org. Chem.*, 34, 2866 (1969).

(24) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, New York, N. Y., 1969, pp 173–174.

(25) K. Tori and M. Ogata, *Chem. Pharm. Bull.*, 12, 272 (1964).

counterparts in **16**, in a region of the spectrum approaching that normally reserved for methyl groups on aromatic substances as in **17–19**. The nmr criterion is also provisionally supported by the ultraviolet spectrum of **3** which exhibits (in isooctane) maxima at 224 and 358 nm. On the cautious assumption that the uv spectral characteristics of the triazonin ring system will bear appreciable similarity with those of 1*H*-azonins [*e.g.*, for 1*H*-azonin, $\lambda_{\max}^{\text{hexane}}$ 252 (ϵ 20,500) and 335 nm (2700)[22c]], a significant bathochromic shift in the lowest energy band is noted. According to existing theory,[26] such a change is associated with an increase in planarity (and therefore also stability) of the heteronin. The excellent correlations previously recorded in the azonin series[22c] suggest this type of analysis to be a reliable criterion for evaluating a gradual transition from polyenic to aromatic character.

The inherent implication in the conclusion that **3** enjoys appreciable electronic stabilization is that the nitrogen atom at position 1 effectively contributes its unshared electrons to the ring. The inability of **3** to complex with $(DPM)_3Eu$ supports the concept of decreased electronegativity for this heteroatom.

Experimental Section

Thermolysis of 2 in Refluxing Decalin. A solution of 2.90 g (10.3 mmol) of **2**[1] in 60 ml of decalin was immersed in an oil bath preheated to 200° where it was maintained for 25 min. Elution of the cooled reaction mixture through alumina (activity III) without prior solvent removal afforded three major fractions (after decalin elution).

The first fraction, a golden yellow oil (1.21 g), was subjected to molecular distillation [50° (0.02 mm)]. After 121 mg of an oily forerun[27] had distilled, the remainder of the material sublimed to a slightly moist crystalline mass. Resublimation [75° (0.02 mm)] afforded, after a minute oily forerun, pure **3** as a yellow-orange powder, mp 78.5–79.5°, which resisted all attempts at crystallization: $\nu_{\max}^{\text{KBr}}$ 1640, 1590, 1490, 1365, 1350, and 1130 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ (60 MHz), 6.6–7.4 (m, 5, aryl) and singlets at 2.20 (3 H), 2.17 (3 H), and 1.99 (br, 12 H); $\delta_{\max}^{\text{C}_2\text{Cl}_4}$ (100 MHz) 6.5–7.4 (m, 5, aryl), 2.17, and 2.11 (s, 3 each), and 1.87–1.97 (m, 12); $\lambda_{\max}^{\text{C}_2\text{H}_5\text{OH}}$ 222 (ϵ 28,000) and 353 nm (3780); $\lambda_{\max}^{\text{isooctane}}$ 224 (ϵ 28,600) and 358 nm (4390); *m/e* calcd, 281.1891872; found, 281.1898193.

Anal. Calcd for $C_{18}H_{23}N_3$: C, 76.83; H, 8.24. Found: C, 76.69; H, 8.24.

Pure **3** (nmr, ir) was also obtained by preparative thick-layer chromatography on silica gel (2:3 ether in hexane) of the first sublimate. It was necessary to quickly extract the material from the adsorbent with ether to minimize decomposition. Triazonin isolated in this manner, however, did not crystallize even after sublimation.

The second fraction obtained from the column (412 mg) was shown by analytical tlc to be composed mainly of **4** contaminated with small amounts of **3** and **5**. Molecular distillation [80° (0.02 mm)] served only to increase the proportion of **3** in the sample. Isolation of pure **4** was achieved by two successive preparative thick-layer chromatographies (see above for conditions and precautions) and high-vacuum drying. The golden yellow oil did not crystallize on prolonged standing: $\nu_{\max}^{\text{film}}$ 1650, 1625, 1590, 1490, 1430, 1365, 1345, and 1130 cm^{-1}; $\delta_{\text{TM}}^{\text{CDCl}_3}$ 7.1–7.5 (m, 3, aryl), 6.8 (m, 2, aryl), and singlets at 2.51 (3 H), 2.06, and 1.97 (12 H), and 1.29 (3 H); in C_2Cl_4, these signals appeared at 7.0–7.4, 6.5–6.7, 2.48, 2.02, 1.93, and 1.24 with the same multiplicities and relative areas; $\lambda_{\max}^{\text{C}_2\text{H}_5\text{OH}}$ 218 (ϵ 19,700) and 330 nm (2180); $\lambda_{\max}^{\text{isooctane}}$ 222 (ϵ 20,500) and 333 nm (2520); *m/e* calcd, 281.1891872; found, 281.1895554.

The material isolated in the third fraction (319 mg) gave after molecular distillation [60° (0.02 mm)] 259 mg of **5** contaminated with small amounts of **3** and **4** (tlc). These impurities were removed by elution of the mixture through charcoal with pentane. Solvent removal and sublimation [50° (0.05 mm)] afforded **5** as a white solid: mp 76.5–78°; $\nu_{\max}^{\text{KBr}}$ 1590 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 6.6–7.2 (m, 5, aryl), 1.70 (s, 12, allyl), and 1.39 (s, 6, bridgehead methyls); $\lambda_{\max}^{\text{C}_2\text{H}_5\text{OH}}$ 220 sh (ϵ 8580), 241 sh (4390) and 276 sh nm (1210); *m/e* calcd, 253.18303960; found, 253.18285239.

Thermal Isomerization of 4 to 3. A solution of **4** in tetrachloroethylene sealed *in vacuo* in a thick-walled nmr tube was suspended in an oven at 80° with periodic removal for nmr analysis of the contents. During 100 min, **4** was cleanly converted to **3**.

Treatment of Pyrolysate with Alumina: The Origin of 4. A solution of 200 mg of **2** in 5 ml of decalin was refluxed (195°) for 15 min. After cooling, the solvent was removed *in vacuo* (bath temp <50°). The nmr spectrum of the residual orange-brown oil revealed the presence of **3** and **5** (ratio *ca.* 5:1), but no **4**.[28] The $CDCl_3$ was removed under reduced pressure and the pyrolysis mixture was dissolved in 10 ml of pentane to which 500 mg of alumina was then added. The resulting slurry was stirred for 20 min at room temperature, filtered, and evaporated. The nmr spectrum of the golden residue unequivocally indicated the presence of **4**. The relative amounts of **3** and **5** were not noticeably changed, but the intensity of the unidentified absorptions decreased. Repetition of the alumina treatment further increased the amount of **4** without affecting the **3**:**5** ratio.

Pyrolysis of 2 in Tetrachloroethylene as Monitored by Nmr. A solution of **2** in C_2Cl_4 was sealed *in vacuo* in a thick-walled nmr tube and the tube was suspended in an oven at 118° from which it was periodically removed for nmr analysis of the contents. Over a period of 65 min at 118°, **2** was converted smoothly into a pyrolysis mixture approximately 80% of which was **3**. The presence of neither **4** nor **5** was detected. An additional 15 min at the same temperature caused no further change. Analytic tlc of the contents confirmed the presence of **3** and the absence of **4**. At least five other very minor components were noted.

A similar solution heated at 195° for 10 min gave rise to black, tarry decomposition products.

Preparative Scale Pyrolysis of 2 in Tetrachloroethylene. A solution of 1.89 g of **2** in 15 ml of C_2Cl_4 was refluxed until nmr analysis of an aliquot indicated total consumption of the starting material (approx 2 hr). Solvent removal *in vacuo* gave 1.91 g of brown oil, the nmr of which indicated >80% of **3**, and no **4** or **5**. Preparative tlc as above was effective in the isolation of pure **2**. Chromatography of a portion of the crude mixture on Florisil led to the generation of some **4**.

Conversion of 4 to 3 in the Presence of *N*-Phenyl-1,2,4-triazoline-3,5-dione. To a $CDCl_3$ solution of **4** in an nmr tube was added a slight excess of 4-phenyl-1,2,4-triazoline-3,5-dione.[29] The tube was shaken to ensure mixing and inserted into the probe of the nmr instrument (40°). Periodic scans revealed that **4** was being transformed into **3**. Reaction was complete in 20 min.

Acknowledgment. The authors wish to take this opportunity to thank the National Science Foundation and Eli Lilly and Company for their partial support of this research.

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(26) H. E. Simmons, personal communication cited in footnote 9 of reference 22c.

(27) The nmr spectrum of this material indicated the presence of an ethyl group but no aromatic ring. It was not further investigated.

(28) The relative intensities of other absorptions suggests that **3** and **5** comprise approximately 80% of the reaction mixture.

(29) J. C. Stickler and W. H. Pirkle, *J. Org. Chem.*, 31, 3444 (1966).