

nickel sulfate hexahydrate and 14 g of cobaltous sulfate heptahydrate per 100 ml of water through the inner jacket. This solution permitted the following wavelength distribution to pass through: 6% 2967 Å, 20% 3025 Å, 62% 3130 Å, 10% 3340 Å. All studies were made at room temperature. Samples in 13-mm Pyrex test tubes were degassed to  $5 \times 10^{-3}$  mm in three freeze-thaw cycles and then sealed. Benzophenone-benzhydrol actinometry<sup>34</sup> was used for quantum yield determinations with the thiabicyclic ketones. Reliably reproducible output rates of  $4.86 \times 10^{16}$  quanta  $\text{sec}^{-1}$  were recorded. For the oxabicyclic ketones, a 2-hexanone solution was used as the chemical actinometer. An actinometer quantum yield of 0.33 was used<sup>49</sup> which gave a reproducible lamp

output of  $2.01 \times 10^{16}$  quanta  $\text{sec}^{-1}$ . After the irradiation the degree of reaction was determined by quantitative vapor phase chromatography. The conversions were run to 15% or less. The mass balance in these runs was generally better than 90%.

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## Cycloaddition of Azides to Hexamethyl(Dewar benzene)<sup>1</sup>

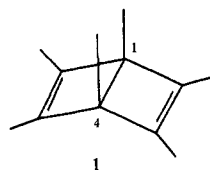
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**Abstract:** The cycloaddition of various aryl azides and methyl azidoformate to hexamethyl(Dewar benzene) (**1**) results in exclusive exo bonding of the dipolar species. The stereochemistry of triazoline formation was adumbrated by nmr considerations and confirmed by X-ray crystal structure analysis of the *p*-bromophenyl derivative (**14**). Adduct **14** was noted to possess a very long internal cyclobutene  $\sigma$  bond (1.61 Å) and other interesting spatial features. No skeletal rearrangement of the diene occurred and attack from the exo direction was evidently not deterred by the presence of the 1- and 4-methyl groups at the corner positions of **1**, nor by the large steric demands of the concerted addition. Comparison is made with the behavior of 7,7-dimethylnorbornene. Hydrolysis of phenyltriazoline adduct **7** and the derived (photochemically) exo aziridine **11** in dilute aqueous acid affords unrearranged diol of unknown stereochemistry. Heating of this diol at its melting point (155°) results in dehydration and rearrangement to 5-acetyl-1,2,3,4,5-pentamethylcyclopentadiene.

Hexamethyl(Dewar benzene) (**1**), readily available from the bicyclic trimerization of 2-butyne in the presence of aluminum chloride,<sup>4</sup> is indeed a re-



markable molecule. Despite the fact that its central bond is the longest on record (1.63 Å)<sup>5</sup> and its stability is 60 kcal/mol less than that of hexamethylbenzene,<sup>6</sup> the conversion of **1** to its aromatic counterpart occurs with a sizable activation energy (31–37 kcal/mol).<sup>6,7</sup> Woodward and Hoffmann have attributed the reluctance of central bond cleavage in **1** to orbital symmetry imposed barriers.<sup>8</sup> Additionally,

protonation studies of **1** in "super acidic" media have indicated that several interesting carbonium ions of rearranged structure are generated therein.<sup>9</sup> Of considerable synthetic and mechanistic import have been the recent findings that a number of these cations can actually be trapped in addition reactions to **1**.<sup>10</sup>

Presently, the most vexatious problem in hexamethyl(Dewar benzene) chemistry is full understanding of the causative factors behind the *seemingly* divergent directions of attack on the hydrocarbon by various reagents. To illustrate, electrophilic addition of chlorosulfonyl isocyanate to **1** appears to proceed by preferential endo attack to give ion **2**, which subsequently rearranges to **3** by migration of the central bond and ultimate C–N bond formation.<sup>10a,b</sup> In antithetical fashion, ethyl *N*-sulfonylcarbamate is believed to bond to **1** from the

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(2) (a) The Ohio State University; (b) National Institutes of Health Predoctoral Fellow, 1966–1970.

(3) Iowa State University. Work performed in part in the Ames Laboratory of the U. S. Atomic Energy Commission.

(4) W. Schäfer, *Angew. Chem.*, **78**, 716 (1966); *Angew. Chem. Int. Ed. Engl.*, **5**, 669 (1966).

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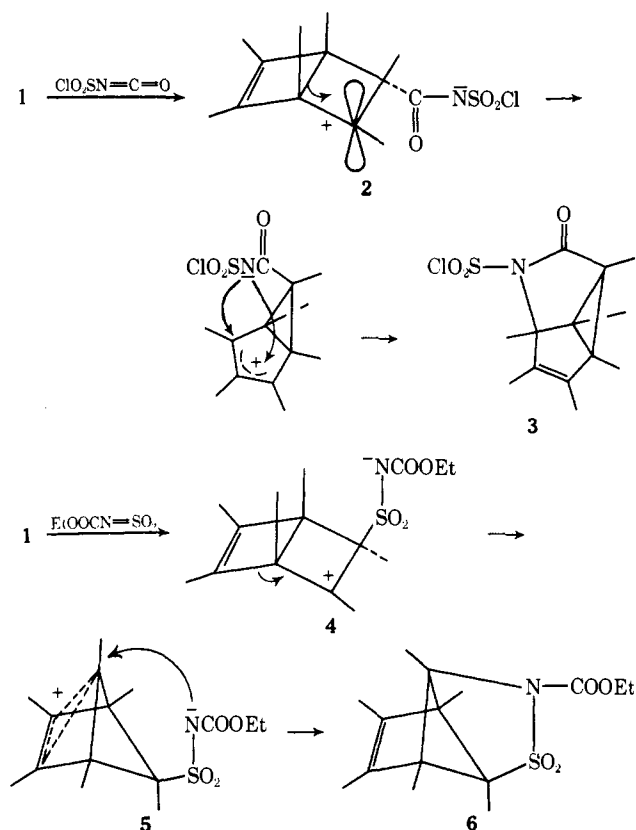
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(9) (a) L. A. Paquette, G. R. Krow, J. M. Bollinger, and G. A. Olah, *J. Amer. Chem. Soc.*, **90**, 7147 (1968); (b) H. Hogeveen and H. C. Volger, *Recl. Trav. Chim. Pays-Bas*, **87**, 385, 1042 (1968).

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exo face to give **4** which presumably rearranges *via* **5** to produce **6**.<sup>10g</sup> The addition of 4-phenyl-1,2,4-triazoline-3,5-dione to **1** may actually follow a similar path.<sup>10d</sup> Catalytic hydrogenation and cyclopropanation of the permethylated bicyclo[2.2.0]hexadiene is also claimed to result in reaction from the exo direction.<sup>10e,11</sup> Unfortunately, the addition reactions of protonic electrophiles are not stereochemically interpretable because of the insurgence of structural rearrangements which void the directional features of the initial bonding mode.<sup>10c</sup>

Although reservations can be expressed that the number and types of reactions studied are not yet sufficiently varied, the previously advanced suggestion<sup>10a,12</sup> that the varying exo/endo rate ratios may be the result of offsetting electronic and torsional effects would appear to offer at least a partial solution to the dilemma. To provide greater substance to this theory, however, it becomes necessary to subject hexamethyl(Dewar benzene) to a broader examination of its inherent steric features. Accordingly, we have undertaken a study of the stereochemistry of addition of selected azides to **1**.

1,3-Dipolar additions of azides to olefins are considered to be multicentered cycloaddition processes.<sup>13</sup>

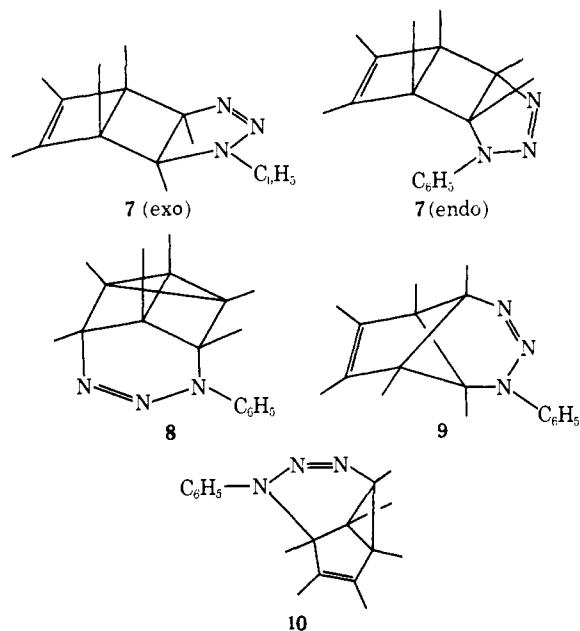
(11) E. Müller and H. Kessler, *Tetrahedron Lett.*, 3037 (1968); see also H. Prinzbach and E. Druckrey, *ibid.*, 4285 (1968).

(12) In brief, the theory<sup>10a</sup> is founded on the premise that, because the flap angle between the rings in **1** is 124° and the terminal methyl groups extend 16° out of the cyclobutene planes away from the bridge,<sup>5</sup> the p orbitals of the two  $\pi$  bonds are held in close proximity on the lower surface of the hydrocarbon with the result that a greater concentration of electron density resides in the endo cavity. From the steric viewpoint, whereas exo attack generates torsional strain because of electrophile-methyl (C) eclipsing, endo attack engenders nonbonded compression of two methyl groups.

(13) For recent reviews, consult: (a) R. Huisgen, *Angew. Chem.*, 75, 741 (1963); *Angew. Chem. Int. Ed. Engl.*, 2, 633 (1963); (b) R. Huisgen, R. Grashey, and J. Sauer in "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, London, 1964, pp 806-878; (c) G. L'Abbe, *Chem. Rev.*, 69, 345 (1969); (d) P. Scheiner, *Selec. Org. Transform.*, 1, 327 (1970).

The independence of solvent polarity,<sup>14</sup> the very negative entropies of activation,<sup>14,15</sup> and the stereospecificity<sup>16</sup> and regiospecificity (in unsymmetrical examples)<sup>16,17</sup> point to a highly ordered transition state in which both new bonds are simultaneously formed, but not to the same extent.<sup>13</sup> The azide-olefin addition is evidently also a reaction of rather large steric requirements. For example, whereas phenyl azide and its derivatives react readily with norbornene from the exo direction, both the exo and endo faces of 7,7-dimethylnorbornene are apparently hindered sufficiently to completely deter cycloaddition to this olefin.<sup>18,19</sup> Hexamethyl(Dewar benzene) differs sterically from 7,7-dimethylnorbornene in the sense that the greatest nonbonded interactions will be experienced at the corners of the molecule rather than at the midpoint of the double bonds. As the transition state nears, therefore, the immediate effect on an approaching azide molecule will most certainly be different in magnitude. But will it also be different in direction?

To answer such questions, excess **1** was heated in refluxing hexane with phenyl azide for 142 hr. There was obtained in 65% yield a lone 1:1 adduct which exhibits an 100-MHz nmr spectrum consisting (apart from phenyl proton absorption) of singlets at  $\delta$  1.71 (6 H), 1.26, 1.24, 0.96, and 0.94 (3 H each). Of the mechanistically reasonable possibilities (7-10), structure **8**



was immediately removed from consideration since it lacks  $sp^2$ -bound methyl groups. Also, the highly

(14) (a) P. Scheiner, J. H. Shomaker, S. Deming, W. J. Libbey, and G. P. Nowack, *J. Amer. Chem. Soc.*, 87, 306 (1965); (b) R. Huisgen, H. Stangl, H. J. Sturm, and H. Wagenhofer, *Angew. Chem.*, 73, 170 (1961).

(15) (a) R. Huisgen, L. Möbius, G. Müller, H. Stangl, G. Szeimies, and J. M. Vernon, *Chem. Ber.*, 98, 3992 (1965); (b) R. Huisgen, G. Szeimies, and L. Möbius, *ibid.*, 100, 2494 (1967); (c) A. S. Bailey and J. E. White, *J. Chem. Soc. B*, 819 (1966).

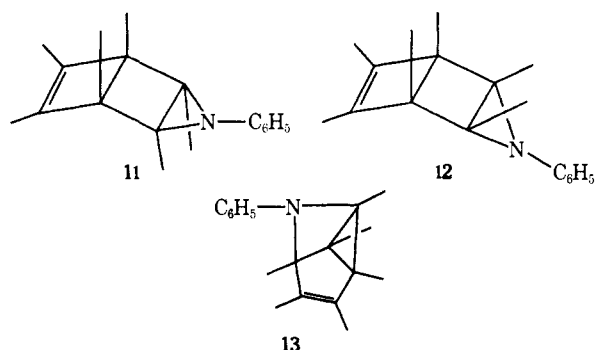
(16) See, for example, P. Scheiner, *J. Amer. Chem. Soc.*, 90, 988 (1968).

(17) (a) P. Scheiner, *Tetrahedron*, 24, 349 (1967); (b) R. Fusco, G. Bianchetti and D. Pocar, *Gazz. Chim. Ital.*, 91, 933 (1961); (c) R. S. McDaniel and A. C. Oelschlager, *Can. J. Chem.*, 48, 345 (1970).

(18) K. Alder and G. Stein, *Justus Liebigs Ann. Chem.*, 501, 1 (1933); 515, 165, 185 (1935).

(19) For a discussion of steric factors relating to other additions which proceed through cyclic transition states, see H. C. Brown, J. H. Kawakami, and S. Ikegami, *J. Amer. Chem. Soc.*, 92, 6914 (1970).

symmetrical adduct **9** would be expected to give rise to *two* six-proton singlets and *one* pair of slightly separated singlets, each of area 3. Since this was not observed, this structure was dismissed. To distinguish between **7** and **10**, the adduct was irradiated in acetone solution through Vycor optics with a 200-W Hanovia lamp. Nitrogen was rapidly evolved (measured volumetrically) and a single substance (>95% purity) was produced. Significantly, the nmr spectrum of this material consisted of three sharp singlets at  $\delta$  1.66, 1.27, and 1.03 (6 H each) in addition to the aromatic region. Clearly, the structural feature inherent in the triazoline which gives rise to the dissimilarity between the members of each pair of upfield methyl groups had been removed, with the result that the photoproduct is symmetrical (three pairs of equivalent methyl groups). In addition, the close similarity of the various absorptions in the photoproduct to the chemical shifts of the triazoline suggested that no skeletal rearrangement had accompanied the loss of nitrogen. These results support the conclusion that the photolysis involved the conversion of **7** into aziridine **11** or **12** and not the generation of azetidine **13** from **10**.



A closer examination of the methyl chemical shift data for **1**, **7**, and its derived aziridine, and several related triazolines (**14**–**16**) suggested that the nitrogen substituents were exo fused to the bicyclo[2.2.0]hexene ring (Table I). In particular, the differing degree of

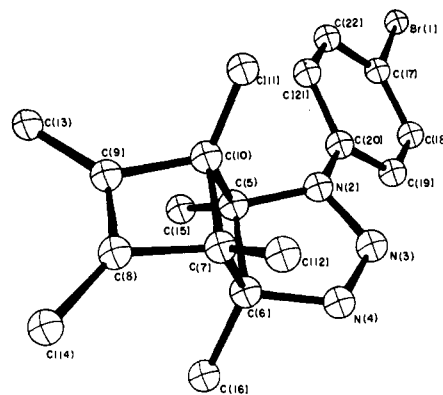
**Table I.** Methyl Chemical Shift Data (60 MHz,  $\text{CDCl}_3$ ,  $\delta$  Units)

Compound	$=\text{CCH}_3$	$>\text{NCCH}_3$	$\text{CCH}_3$
<b>1</b> <sup>a</sup>	1.6		1.1
<b>7</b> <sup>b</sup>	1.71	1.24, 1.26	0.94, 0.96
<b>11</b>	1.66	1.27	1.03
<b>14</b>	1.71	1.23, 1.27	0.90, 0.94
<b>15</b>	1.74	1.27, 1.29	0.94, 0.97
<b>16</b>	1.69	1.30, 1.36	0.88

<sup>a</sup> Taken from ref 4. <sup>b</sup> At 100 MHz.

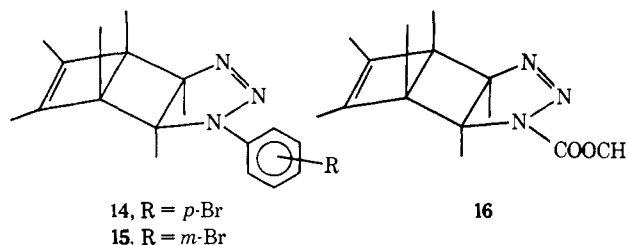
shielding experienced by the two bridgehead methyl groups in **7**, which effect is attributable to differences in the magnetic anisotropy of the two termini of the triazo linkage,<sup>20</sup> would seem to require the nitrogen bridge to lie in a position (exo) where such "through space" interaction could realistically be expected to occur.

(20) The operation of a purely inductive electron-withdrawal effect by the nitrogen atoms would appear to be discounted since the chemical shift differences between the two  $>\text{NCCH}_3$  absorptions and the two  $\text{CCH}_3$  singlets in **7** are essentially equal. If the effect of the nitrogen was being transmitted through the  $\sigma$  framework to the more remote site, the former absorptions would be expected to be more widely separated since inductive effects are diminished with distance. Secondly, the bridgehead absorptions are upfield shifted from their position in **1**, an effect opposite to that expected from inductive electron drain toward nitrogen.



**Figure 1.** A structural view of **14** as determined by X-ray analysis showing the conformation of the molecule.

To confirm this stereochemical analysis, the *p*-bromophenyl azide adduct of **1** (**14**) was prepared and its

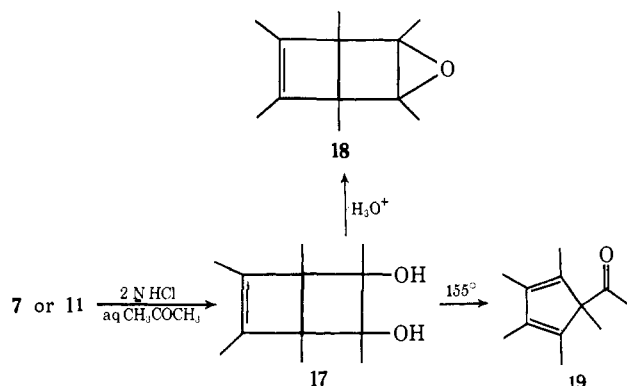


molecular geometry was established by X-ray crystal structure analysis. Microscopic examination revealed clear acicular needles with sharply defined faces. Preliminary photographs displayed the  $2/m$  Laue symmetry appropriate for the monocyclic crystal class. Systematic extinctions on  $0k0$  (for  $k = 2n + 1$ ) and  $h0l$  (for  $l = 2n + 1$ ) uniquely determined the space group as  $P2_1/c(C_{2h}^2)$ . Intensity data were collected on a crystal having approximate dimensions of  $0.15 \times 0.10 \times 0.10$  mm. A least-squares fit of diffractometer measured  $\theta$  values gave  $a = 15.932 \pm 0.005$  Å,  $b = 7.291 \pm 0.003$  Å,  $c = 14.434 \pm 0.005$  Å and  $\beta = 95.88 \pm 0.05^\circ$ . All of the data in the  $hkl$  and  $\bar{h}kl$  octants with  $\theta \leq 30^\circ$  were collected on a fully automated Hilger-Watts diffractometer with Zr-filtered Mo  $K\alpha$  radiation (0.7107 Å). After correction for Lorentz and polarization factors 1322  $F_o^2$  were judged observed (i.e.,  $F_o^2 > 3\sigma(F_o^2)$ ). A three-dimensional Patterson synthesis revealed the Br position and the remaining 21 hydrogen atoms were located in the subsequent Br-phased electron density synthesis. Full-matrix least-squares refinements in which all atoms had anisotropic temperature factors lowered the conventional discrepancy index to its present minimum of 0.096 for the observed reflections. A computer generated drawing of the final X-ray model is given in Figure 1.

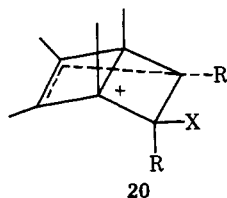
As can clearly be seen from the drawing, addition had occurred in an exo fashion and no skeletal rearrangement of the bicyclo[2.2.0]hexadiene ring system had taken place. Unfortunately, decomposition lowered the accuracy of the final X-ray model. Estimated standard deviations are approximately 0.01 Å for carbon-carbon bond lengths and  $1.0^\circ$  for carbon bond angles. Nevertheless, some features are quite striking. The central bond in the Dewar benzene moiety is quite stretched (1.61 Å), and the other internal bonds are also longer than expected. Conversely, the bonds connect-

ing the four saturated carbons to their methyl group are all shortened to  $1.49 \pm 0.02 \text{ \AA}$ . The dihedral angle between the plane of the triazolone portion and the cyclobutyl ring is  $113.3^\circ$ . The cyclobutene and triazolone rings are parallel with a dihedral angle of approximately  $1.0^\circ$ . The dihedral angle between the cyclobutane and cyclobutene rings is  $111.2^\circ$ . The other bond lengths agree well with generally accepted values.

Given the exo stereochemistry of triazolone **7** and aziridine **11**, we were led to examine their behavior toward aqueous acid.<sup>21</sup> Both **7** and **11** were rapidly decomposed by 2 *N* hydrochloric acid in aqueous acetone to diol **17**, which was likewise produced from epoxide **18** under these conditions.<sup>22</sup> No rearrange-



ment products were detected. These results are in striking contrast to the general observation that Wagner–Meerwein rearrangements normally follow from such acid-promoted reactions.<sup>10</sup> The preservation of structural integrity in the bicyclo[2.2.0]hexene ring can be accommodated by solvent capture after ionization at rates which are greater than those of carbon–carbon migration. This is realizable perhaps because of homoallylic stabilization as in **20**; however, in the absence



of data pertaining to the configuration of the oxygenated functions in **17** and **18**, this proposal must be considered tentative.

We have also noted that heating of diol **17** at its melting point ( $155^\circ$ ) results in ready dehydration. Structural rearrangement accompanies the thermolysis and ketone **19** is produced in quantitative yield.

## Conclusions

The results demonstrate that normal azides undergo cycloaddition to **1** without skeletal bond reorganization, presumably due chiefly to the concerted nature of the reaction. In this connection, Anastassiou and Eacchus<sup>10j</sup> have shown that enhancement of the dipolar electrophilic character of the azide results in the incursion of rapid bond reorganization in the hexa-

methyl(Dewar benzene) molecule. For example, the reaction of **1** with cyanogen azide was found to be time and temperature dependent and to give rise to adducts possessing three distinctly different carbon frameworks.

A second important consideration is that azide attack occurs exclusively from the exo direction despite the large spatial demands of such concerted cycloadditions.<sup>19</sup> In this respect, **1** resembles the far less congested hexafluorobicyclo[2.2.0]hexa-2,5-diene molecule which when functioning as a dipolarophile undergoes only exo bonding.<sup>23</sup> The presence of the 1,4-dimethyl substituents in **1** clearly does not bring about a change in direction of preferential attack of azide reagent from exo to endo. Apparently, therefore, such one-stage addition reactions involving cyclic transition states are not deterred by the positioning of methyl groups at the corners of the bicyclic structures to the extent where this mode of bonding is disfavored. Brown's results with 7,7-dimethylnorbornene<sup>19</sup> suggest that the placement of a similar group over the middle of the double bond exerts a much larger rate-retarding effect. In one sense this is rather surprising, since the large R substituent attached to the azide group must ultimately position itself at a corner site. This apparent incongruousness is receiving additional experimental evaluation.

## Experimental Section

**1,2,3,4,5,6-Hexamethyl-7-phenyl-7,8,9-triazatricyclo[4.3.0.0<sup>2,5</sup>]-nona-3,8-diene (7, exo).** A solution of 30 g (0.185 mol) of **1** and 10 g (0.084 mol) of phenyl azide in 60 ml of hexane was heated at reflux with stirring and exclusion of light. After 142 hr, all of the phenyl azide had been consumed (ir analysis), and the solvent was removed *in vacuo*. The product was filtered from excess **1**, washed with cold pentane, and sublimed [ $75^\circ$  (0.02 mm)] to give 15.47 g (65.5%) of **7** as white crystals, mp  $115\text{--}116.5^\circ$ , from hexane;  $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$  288 ( $\epsilon$  7900) and 302 nm (8090). *Anal.* Calcd for  $\text{C}_{18}\text{H}_{23}\text{N}_3$ : C, 76.83; H, 8.24. Found: C, 77.11; H, 8.31.

**1,2,4,5,6,7-Hexamethyl-3-phenyl-3-azatricyclo[3.2.0.0<sup>2,4</sup>]-hept-6-ene (11).** Irradiation of a solution of 3.05 g (10.85 mmol) of **7** in 400 ml of acetone through Vycor optics with a 200-W Hanovia lamp resulted in the evolution of one equivalent (244 ml) of nitrogen over a period of 25 min. Solvent removal afforded 2.87 g of **11** as a white solid imbedded in a small amount of orange oil. Neither sublimation nor chromatography on silica gel or alumina effected removal of the oily contaminant (<5% by nmr analysis). Upon exposure to air, however, the impurity soon decomposed to a non-volatile orange-brown gum from which pure **11** was separated by elution through charcoal with hexane. Subsequent sublimation [ $70^\circ$  (20 mm)] gave **11** as a white solid, mp  $105\text{--}106.5^\circ$ ;  $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$  252 ( $\epsilon$  14,800) and 287 sh nm (1630); *m/e* calcd for  $\text{C}_{18}\text{H}_{23}\text{N}$ : 253-18303960; found: 253.18241441.

*Anal.* Calcd for  $\text{C}_{18}\text{H}_{23}\text{N}$ : C, 85.32; H, 9.15. Found: C, 85.18; H, 9.14.

**1,2,3,4,5,6-Hexamethyl-7-*p*-bromophenyl-7,8,9-triazatricyclo[4.3.0.0<sup>2,5</sup>]-nona-3,8-diene (14).** *p*-Bromophenyl azide<sup>24</sup> (7.25 g, 33.6 mmol) and **1** (27.0 g, 0.166 mol) were dissolved in 70 ml of reagent grade hexane and refluxed for 18 hr. The solution was cooled in an ice bath and the residue filtered to give 7.6 g (63%) of adduct, mp  $146.5\text{--}148^\circ$  dec. Recrystallization from hexane gave material of mp  $151\text{--}151.5^\circ$  dec.

*Anal.* Calcd for  $\text{C}_{18}\text{H}_{22}\text{BrN}_3$ : C, 60.00; H, 6.16; N, 11.66. Found: C, 59.90; H, 6.42; N, 11.68.

**1,2,3,4,5,6-Hexamethyl-7-*m*-bromophenyl-7,8,9-triazatricyclo[4.3.0.0<sup>2,5</sup>]-nona-3,8-diene (15).** A solution of *m*-bromophenyl azide<sup>25</sup> (7.25 g, 33.6 mmol) and **1** (27.0 g, 0.166 mol) in 70 ml of reagent grade hexane was refluxed for 28 hr when all of the azide

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**Table II.** Final Fractional Coordinates for Nonhydrogen Atoms<sup>a</sup>

Atom	x/z	y/b	z/c
Br	-0.0002 (1)	0.6112 (2)	0.1442 (1)
N(1)	0.2290 (6)	1.277 (15)	-0.0300 (7)
N(2)	0.2405 (7)	1.3034 (19)	0.0060 (8)
N(3)	0.2675 (7)	1.4147 (16)	-0.0470 (10)
C(1)	0.2504 (7)	1.1197 (17)	-0.1262 (9)
C(2)	0.2771 (7)	1.3254 (18)	-0.1388 (10)
C(3)	0.3675 (7)	1.2641 (17)	-0.1423 (8)
C(4)	0.3826 (8)	1.2158 (20)	-0.2417 (9)
C(5)	0.3593 (8)	1.0354 (20)	-0.2348 (10)
C(6)	0.3392 (7)	1.0538 (16)	-0.1326 (10)
C(7)	0.3783 (9)	0.9259 (18)	-0.0617 (10)
C(8)	0.4346 (8)	1.3539 (21)	-0.0780 (10)
C(9)	0.3524 (10)	0.8708 (21)	-0.3016 (10)
C(10)	0.4142 (10)	1.3285 (23)	-0.3174 (10)
C(11)	0.1824 (8)	1.0446 (18)	-0.1975 (10)
C(12)	0.2378 (9)	1.4474 (21)	-0.2153 (12)
C(13)	0.0706 (9)	0.7853 (31)	0.0903 (10)
C(14)	0.0615 (10)	0.9719 (24)	0.1036 (12)
C(15)	0.1144 (8)	1.0841 (22)	0.0608 (9)
C(16)	0.1743 (9)	1.0093 (18)	0.0102 (10)
C(17)	0.1834 (9)	0.8235 (22)	0.0000 (10)
C(18)	0.1285 (9)	0.6984 (23)	0.0387 (12)

<sup>a</sup> Estimated standard deviations, shown in parentheses, are right adjusted to the least significant digit of the preceding number.

appeared to be consumed (ir analysis). The solution was reduced in volume, adsorbed on silica gel, and chromatographed on silica gel using 20% ether in hexane. The eluted triazoline was recrystallized from hexane to give 1.85 g (15.3%) of white crystals, mp 116–117°.

Anal. Calcd for C<sub>18</sub>H<sub>22</sub>BrN<sub>3</sub>: C, 60.00; H, 6.16; N, 11.66. Found: C, 60.03; H, 6.17; N, 11.85.

**1,2,3,4,5,6-Hexamethyl-7-carbomethoxy-7,8,9-triazatricyclo-[4.3.0.0<sup>2,5</sup>]nona-3,8-diene (16).** A solution of 20.0 g (0.123 mol) of **1** and 12.4 g (0.123 mol) of methyl azidoformate in 50 ml of pentane was allowed to stand for 10 days in a stoppered flask in the dark. The precipitated crystals were removed by filtration and sublimed [85° (0.02 mm)] to give 17.8 g (55%) of **16** as a white powder. Recrystallization of this material from ether-pentane afforded small colorless crystals, mp 126–128° dec;  $\nu_{\text{max}}^{\text{KBr}}$  1720 cm<sup>-1</sup>;  $\nu_{\text{max}}^{\text{CHCl}_3}$  1725 cm<sup>-1</sup>;  $\lambda_{\text{max}}^{\text{OH}}$  241 nm ( $\epsilon$  3920).

Anal. Calcd for C<sub>14</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub>: C, 63.85; H, 8.04; N, 15.91. Found: C, 63.87; H, 8.07; N, 16.12.

**1,2,3,4,5,6-Hexamethylbicyclo[2.2.0]hex-5-ene-2,3-diol (17).** A. From Triazoline **7**. Hydrochloric acid (3.6 ml of 2 N, 7.2 mequiv) was added dropwise to a stirred solution of 2.06 g (7.3 mmol) of **7** in 50 ml of acetone at ambient temperature. Gas evolution was observed during the course of the addition. After 30 min, the reaction mixture was neutralized with saturated aqueous sodium bicarbonate solution, the solvent evaporated *in vacuo*, and the residue partitioned between ether and water. Evaporation of the dried ethereal layer gave an orange-colored mixture of oil and solid (1.58 g). Nmr examination of this residue revealed the presence of aniline and **17** with the signals from the latter contributing ca. 70% of the total peak area. The residue was washed with two 5-ml portions of pentane to give 345 mg of tan solid which was taken up in ether and decolorized with charcoal. Recrystallization of the resulting white solid from hexane afforded 306 mg (21.4%) of **17** as fine, white fibers, mp 153–155° dec (lit.<sup>22</sup> mp 155–157°). The infrared and nmr spectra were identical with those reported for **17**.

B. From Aziridine **11**. To a stirred acetone solution (30 ml) of **11** (637 mg, 2.51 mmol) was added dropwise at room temperature 1.3 ml (2.6 mequiv) of 2 N hydrochloric acid. Processing as above gave 371 mg (75.2%) of the diol.

In another experiment, a drop of 60% aqueous perchloric acid was added to a solution of **11** in acetone-*d*<sub>6</sub> in an nmr tube and the tube was shaken to ensure mixing. Repeated nmr scans at brief intervals showed the clean conversion of **11** to **17**. The reaction was complete after 5 min. No further change was noted when the spectrum was recorded after an additional 30 min at the probe temperature.

**Pyrolysis of 17.** 5-Acetyl-1,2,3,4,5-pentamethylcyclopenta-1,3-diene (**19**). A sample of **17** (27.5 mg, 0.14 mol) was placed in an nmr tube and the tube was partially immersed in an oil bath preheated to 155°. Upon melting, evolution of water vapor began

**Table III.** Selected Bond Distances<sup>a</sup>

Atoms	Distance (angströms)	Atoms	Distance (angströms)
Br-C(13)	1.92 (1)	C(3)-C(8)	1.49 (2)
N(1)-N(2)	1.39 (1)	C(5)-C(9)	1.54 (2)
N(2)-N(3)	1.22 (1)	C(4)-C(10)	1.49 (2)
C(1)-N(1)	1.46 (1)	C(1)-C(11)	1.52 (2)
C(2)-N(3)	1.50 (2)	C(2)-C(12)	1.50 (2)
C(1)-C(2)	1.57 (2)		
C(2)-C(3)	1.51 (2)	C(13)-C(14)	1.38 (2)
C(3)-C(4)	1.52 (2)	C(14)-C(15)	1.37 (2)
C(4)-C(5)	1.37 (2)	C(15)-C(16)	1.37 (1)
C(5)-C(6)	1.55 (2)	C(16)-N(1)	1.39 (1)
C(6)-C(1)	1.51 (1)	C(16)-C(17)	1.37 (2)
C(3)-C(6)	1.61 (2)	C(17)-C(18)	1.42 (2)
C(6)-C(7)	1.48 (2)	C(18)-C(13)	1.40 (2)

<sup>a</sup> The estimated standard deviations are shown in parentheses.

**Table IV.** Selected Bond Angles<sup>a</sup>

Atoms	Angle (deg)	Atoms	Angle (deg)
Br-C(13)-C(18)	111.4	C(1)-C(2)-C(3)	89.5 (0.9)
Br-C(13)-C(14)	121.4 (1.2)	C(2)-C(3)-C(4)	110.1 (1.0)
C(18)-C(13)-C(14)	127.2 (1.4)	C(2)-C(3)-C(8)	118.2 (1.1)
C(13)-C(14)-C(15)	116.6 (1.3)	C(2)-C(3)-C(6)	90.1 (0.8)
C(14)-C(15)-C(16)	119.8 (1.2)	C(1)-C(6)-C(7)	119.5 (1.0)
C(15)-C(16)-C(17)	122.4 (1.2)	C(1)-C(6)-C(3)	88.6 (0.8)
C(16)-C(17)-C(18)	121.1 (1.3)	C(1)-C(6)-C(5)	112.0 (1.1)
C(17)-C(16)-N(1)	119.3 (1.1)	C(3)-C(6)-C(7)	124.1 (1.0)
C(15)-C(16)-N(1)	118.3 (1.0)	C(3)-C(6)-C(5)	85.0 (1.1)
C(16)-N(1)-C(1)	125.9 (1.0)	C(6)-C(3)-C(8)	123.6 (1.1)
C(16)-N(1)-N(2)	118.7 (1.0)	C(6)-C(3)-C(4)	86.2 (0.9)
C(1)-N(1)-N(2)	110.9 (0.9)	C(7)-C(6)-C(5)	119.5 (1.0)
N(1)-N(2)-N(3)	114.8 (1.0)	C(8)-C(3)-C(4)	121.0 (1.2)
N(2)-N(3)-C(2)	109.8 (1.1)	C(3)-C(4)-C(10)	131.3 (1.2)
N(3)-C(2)-C(1)	104.9 (1.0)	C(3)-C(4)-C(5)	94.8 (1.0)
C(2)-C(1)-N(1)	99.4 (1.0)	C(6)-C(5)-C(4)	94.0 (1.0)
N(3)-C(2)-C(12)	108.6 (1.1)	C(6)-C(5)-C(9)	131.1 (1.1)
N(3)-C(2)-C(3)	110.0 (1.1)	C(5)-C(4)-C(10)	133.9 (1.2)
N(1)-C(1)-C(1)	116.0 (0.9)	C(4)-C(5)-C(9)	134.8 (1.2)
N(1)-C(1)-C(6)	112.6 (1.0)		
C(2)-C(1)-C(11)	116.5 (1.1)		
C(2)-C(1)-C(10)	91.7 (0.8)		
C(1)-C(2)-C(12)	123.5 (1.1)		

<sup>a</sup> The standard deviation is calculated from the inverse matrix of least-squares refinement.

and continued for 2 min after which time the tube was cooled and the product dissolved in the appropriate amount of carbon tetrachloride (insoluble water droplets were clearly visible). The nmr spectrum of the solid product was identical with that reported for **19**.<sup>22</sup> The contents of the tube were diluted with ether and dried over anhydrous magnesium sulfate. Filtration followed by solvent removal afforded 24.7 mg (39%) of **19** as a colorless oil which solidified upon refrigeration. The infrared spectrum of the product was, like the nmr, identical with that reported for **19**.<sup>22</sup>

**Preliminary Crystallographic Examination of 14.** Microscopic examination revealed clear acicular crystals with well-defined faces. A crystal with approximate dimensions 0.15 × 0.10 × 0.10 mm was used for intensity and preliminary work. The 2/m Laue symmetry allowed assignment to the monoclinic crystal class and systematic extinctions on *h0l* (*l* = 2*n* + 1) and *0k0* (*k* = 2*n* + 1) uniquely determine the common space group *P*2<sub>1</sub>/*c*(*C*<sub>2h</sub><sup>5</sup>). Calculated and measured densities of 1.45 g/cm<sup>3</sup> indicated *Z* = 4 or one molecule per asymmetric unit.

A crystal mounted along the *b* axis was transferred to a fully-automated Hilger-Watts four-circle diffractometer. A least-squares refinement of accurately measured  $\theta$  values gave *a* = 15.932(5), *b* = 7.291(3), *c* = 14.343(5) Å and  $\beta$  = 95.88(5)°. Data were collected at room temperature using Zr-filtered Mo K $\alpha$  radiation (0.7107 Å). All data within a 2 $\theta$  sphere of 60° were collected for the *hkl* and *hkl* octants. A  $\theta$ -2 $\theta$  scan technique was used and backgrounds were measured at  $\theta_{hkl} \pm (0.25 + 0.01 \times \theta_{hkl})$ . Check reflections were monitored periodically to assess crystal and electronic stability. There was a gradual decline of ~10% in the

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  $\sigma(F) = \{[I + \sigma(I)]/L_p\}^{1/2} - (I/L_p)^{1/2}$ .<sup>26</sup> 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.<sup>27</sup> 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.*<sup>28</sup> In Table II are listed the final X-ray coordinates and their standard deviations.<sup>29</sup> In Tables III and IV are listed

the final bond distances and bond angles, respectively, along with their standard deviations.<sup>30</sup> Figure 1 is a computer generated drawing of the final X-ray model.<sup>31</sup>

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(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  $F_o$  for the "unobserved reflections" greater than  $3\sigma(F_o)$ . No abnormally short intermolecular contacts were observed.

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## Thermolysis of 1,2,3,4,5,6-Hexamethyl-7-phenyl-7,8,9-triazatricyclo[4.3.0.0<sup>2,5</sup>]nona-3,8-diene. Synthetic Entry to the 1,2,3-Triazonin Ring System<sup>1</sup>

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**Abstract:** Thermolysis of the title compound (**2**) in refluxing decalin (195°) affords as the major product (42%) the theoretically interesting 10 $\pi$  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  $\Delta^2$ -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.<sup>3</sup> However, when the grouping in question is phenyl, for example, elevated temperatures are required

and the decomposition usually develops added complexity.<sup>4</sup> 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<sub>1</sub>-N<sub>2</sub> bond.<sup>4,5</sup> The ensuing modes of decomposition of zwitterions such as **1** appear to be somewhat structurally dependent and to involve cleavage of the N<sub>8</sub>-C<sub>4</sub> or the C<sub>4</sub>-C<sub>5</sub> bond.

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