

## Electronic Structure of Tricyclo[4.1.0.0<sup>2,7</sup>]hept-3-enes. Correlation with the Regioselectivity of Electrophilic Attack<sup>1</sup>

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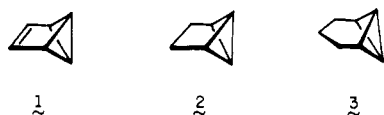
Received February 10, 1978

The photoelectron spectra of tricyclo[4.1.0.0<sup>2,7</sup>]hept-3-ene (4) and several methyl-substituted derivatives have been recorded in an effort to gain further detailed information relating electronic structure to various fixed conformations of bicyclobutane rings. In the case of 4 and its congeners, the experimental data reveal the Walsh-type bicyclobutane orbital to be the HOMO in each instance, the conclusions being supported by MINDO/3 calculations. This finding contrasts in a striking way with the orbital ordering previously established for benzvalene. The origins of this difference are discussed and the chemical manifestations of this ordering are demonstrated by rearrangement of these molecules with H<sup>+</sup>, D<sup>+</sup>, and Ag<sup>+</sup>.

That the chemical reactivity of some molecules can be rationalized by frontier orbital considerations is now extensively documented.<sup>4</sup> As a consequence, orbital sequencing can play a key role in the predictive capability of modern theoretical organic chemistry and there exists a need to develop in full our understanding of varied electronic interactions. In the special case of small cyclic molecules such as cyclopropane,<sup>5</sup> cyclobutane,<sup>6</sup> and bicyclobutane,<sup>7</sup> simple ZDO models have been widely accepted as suitable descriptors of their electronic structure.

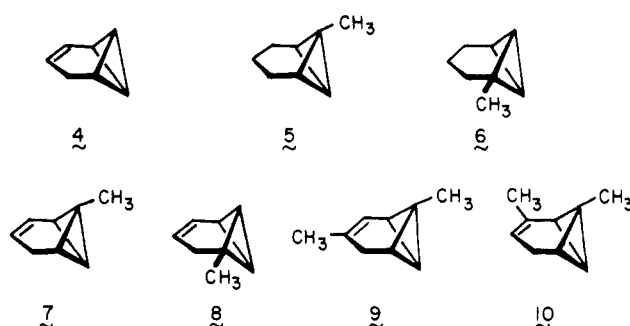
By assuming the validity of Koopmans' theorem,<sup>8</sup> one can experimentally check the calculated orbital sequencing of a molecule by means of photoelectron (PE) spectroscopy. The results of such investigations have recently increased our insight into, and improved our understanding of, cyclopropane and cyclobutane chemistry. We endeavor to establish that the somewhat more complicated bicyclobutane system can be treated analogously.

In this connection, we have previously investigated the electronic structure of benzvalene (1), tricyclo[3.1.0.0<sup>2,6</sup>]-



hexane ("dihydrobenzvalene", 2), and tricyclo[4.1.0.0<sup>2,7</sup>]heptane (3) by PE spectroscopy. This series of molecules can be regarded as independent check points for the electronic structure of the bicyclobutane system at various fixed conformations. The experimental evidence fully corroborates the results of theoretical investigations and establishes that the postulated orbital sequence in 1 (4b<sub>2</sub>, 10a<sub>1</sub>, 1a<sub>2</sub>, and 6b<sub>1</sub>) is due principally to two effects: (1) a strong interaction between the b<sub>2</sub>(π) orbital of the ethylene unit and the b<sub>2</sub>(σ) orbital of the adjacent bicyclobutane ring, and (2) a considerably smaller dihedral angle θ between the two fused cyclopropane rings in 1 (105°)<sup>10</sup> as compared to θ in the parent bicyclobutane (121.7°).<sup>11</sup>

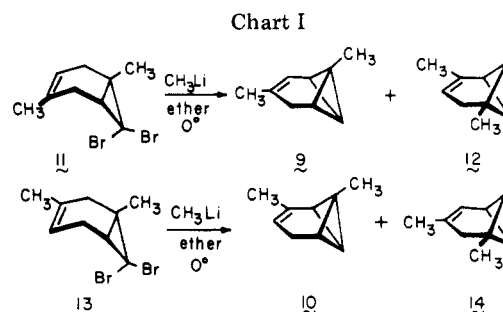
The aim of the present study was to develop additional support for the conclusions arrived at earlier on the basis of rather limited information. To do so, the PE spectrum of tricyclo[4.1.0.0<sup>2,7</sup>]hept-3-ene (4) was recorded, together with those of a series of methyl and dimethyl derivatives of both 3 and 4. The structures of the hydrocarbons are illustrated. Whereas 4, 7, and 8 were available from a prior study,<sup>12</sup> 9 and 10 were prepared from dibromobicycloheptenes 11 and 13, respectively (Chart I). Treatment of 11 with methyl lithium in ether at 0 °C resulted in intramolecular C-H insertion to give 9 and 12 in a ratio of approximately 7:1, in compliance



with the generalization that angular 1-methyl groups direct carbenoid capture preferentially to the more proximal α carbon.<sup>12b</sup> The regioselectivity observed upon similar cyclization of 13 proved to be entirely comparable. In this instance, 10 was found to dominate over 14 by a factor of 6. The identities of these dimethyltricycloheptenes were established by their characteristic <sup>1</sup>H NMR spectra as described in the Experimental Section. Interestingly, the preferred formation of 9 and 10 is also in line with MINDO/3 calculations according to which methyl substitution of the tricyclo[4.1.0.0<sup>2,7</sup>]heptane or tricyclo[4.1.0.0<sup>2,7</sup>]hept-3-ene skeleton in position 1 is predicted to be more stable than in position 6 (see Figure 2).

The PE spectra of 3, 4, and 7 which are considered representative for this class of compounds are shown in Figure 1. As regards 3, and the saturated compounds 5 and 6 as well, the recorded spectra all exhibit one highly distinctive band at an ionization energy of about 8.5 eV. The lack of any marked vibrational fine structure indicates a considerable change of the equilibrium structure of the corresponding molecules during the ionization process. This has also been observed in the spectrum of the parent bicyclobutane molecule.<sup>13</sup> On the other hand, the spectra of the unsaturated compounds 4 and 7-10 show two close lying peaks below 9 eV (bands ① and ② of the corresponding spectra).

The measured vertical ionization potentials of all these



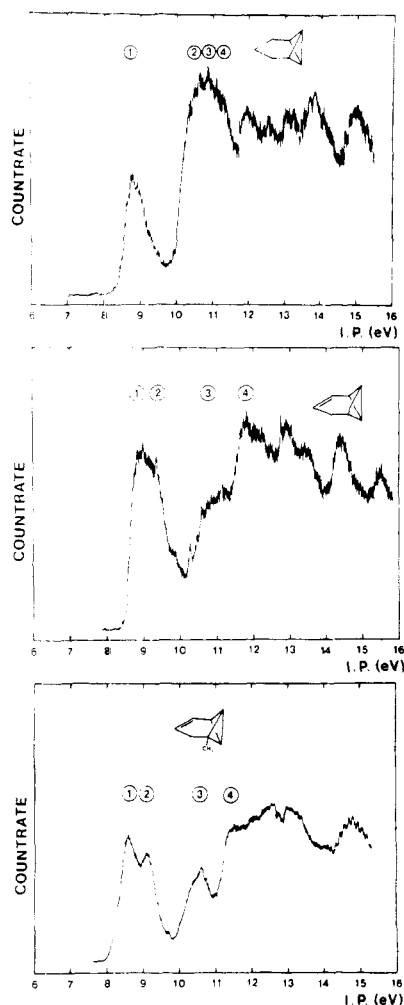


Figure 1. Photoelectron spectra of 3, 4, and 7.

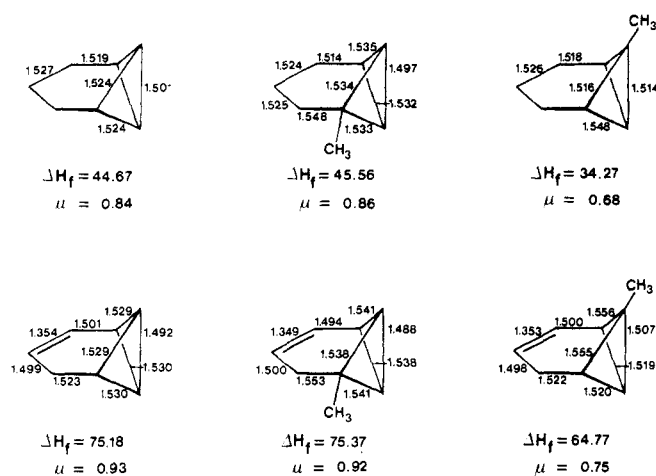


Figure 2. Calculated bond lengths, dipole moments (in Debye units), and heats of formation (kcal/mol) for 3-8 according to MINDO/3.

compounds are summarized in Table I where comparison is also made with calculated orbital energies resulting from MINDO/3 calculations.<sup>14</sup> Since the detailed three-dimensional structures of these molecules are not known, estimates were made by full geometry optimization of the individual molecules. The methyl substituents were assumed to have a local  $C_{3v}$  symmetry in order to avoid excessive calculations. The resulting structures for 3-8 are illustrated in Figure 2. The predicted structures of 1<sup>9</sup> and parent bicyclobutane<sup>11</sup> have been noted to be in close agreement with experiment. The

Table I. Comparison between Measured First Vertical Ionization Potentials of 3 to 10 with Calculated Orbital Energies (All Values in eV)

Compd	Registry no.	Band	$I_{V,J}$	Assignment	$\epsilon_J(\text{MIN-DO}/3)$
3	287-13-8	①	8.72	12a <sub>1</sub>	-8.66
		②	10.45	2a <sub>2</sub>	-9.85
		③	10.8	5b <sub>2</sub>	-10.03
		④	11.22	7b <sub>1</sub>	-10.49
4	35618-58-7	①	8.82	a <sub>1</sub> *	-8.66
		②	9.20	π	-8.77
		③	10.80	a <sub>2</sub> *	-10.05
		④	11.80	b <sub>1</sub> *	-10.50
5	32348-63-3	①	8.20	a <sub>1</sub> *	-8.53
		②	9.90	a <sub>2</sub> *	-9.64
		③	10.2	b <sub>2</sub> *	-9.87
		④	10.8	b <sub>1</sub> *	-10.45
6	66036-90-6	①	8.42	a <sub>1</sub> *	-8.63
		②	10.0	a <sub>2</sub> *	-9.67
		③	10.35	b <sub>2</sub> *	-9.96
		④	10.9	b <sub>1</sub> *	-10.42
7	61772-33-6	①	8.45	a <sub>1</sub> *	-8.51
		②	8.95	π	-8.73
		③	10.60	a <sub>2</sub> *	-9.87
		④	11.35	b <sub>1</sub> *	-10.45
8	61772-31-4	①	8.64	a <sub>1</sub> *	-8.64
		②	9.16	π	-8.75
		③	10.67	a <sub>2</sub> *	-9.81
		④	11.4	b <sub>1</sub> *	-10.41
9	66036-91-7	①	8.30	a <sub>1</sub> *	-8.48
		②	8.70	π	-8.61
		③	10.40	a <sub>2</sub> *	-9.84
		④	11.25	b <sub>1</sub> *	-10.30
10	66036-92-8	①	8.26	a <sub>1</sub> *	-8.46
		②	8.66	π	-8.65
		③	10.36	a <sub>2</sub> *	-9.87
		④	11.3	b <sub>1</sub> *	-10.33

prediction that 3 should possess  $C_{2v}$  symmetry is in accord with the general trend of MINDO/3 to underestimate puckering amplitudes of saturated cyclic systems.<sup>15</sup> But this failure is not expected to affect the qualitative conclusions reached in this investigation. Figure 2 also includes the calculated heats of formation ( $\Delta H_f$ ) as well as the calculated dipole moments ( $\mu$ ) of the individual molecules.

In the ensuing interpretative discussion, reasonable use shall be made of local symmetry terms. This is because all molecules except 3 and 5 actually have no symmetry at all, thereby making it difficult to differentiate between the various orbitals or electronic state symmetries. To obviate this problem, we have utilized local symmetry terms which are indicated by an asterisk (\*) in the corresponding symbols. Furthermore, the comparison between measured ionization potentials and calculated orbital energies at this level necessarily assumes the validity of Koopmans' theorem ( $-\epsilon_J = I_{V,J}$ ).<sup>8</sup>

## Discussion

In Figure 3, comparison is made of the measured band positions (left) and the calculated orbital energies for 3-8 (right). Clearly, the MINDO/3 calculations reproduce the general features very well except for the fact that the calculated gaps between bands ① and ② for the unsaturated species are too small in all cases. This tendency can be rationalized in terms of two effects: (1) Koopmans' defect in the sense that the excited state of the generated radical cation (i.e., corresponding to band ②) gains more electronic reorganization energy than its ground state (i.e., corresponding to band ①) and (2) a pseudo-Jahn-Teller effect acts to split nearly degenerate electronic states as witnessed in other context.<sup>16</sup> Both phe-

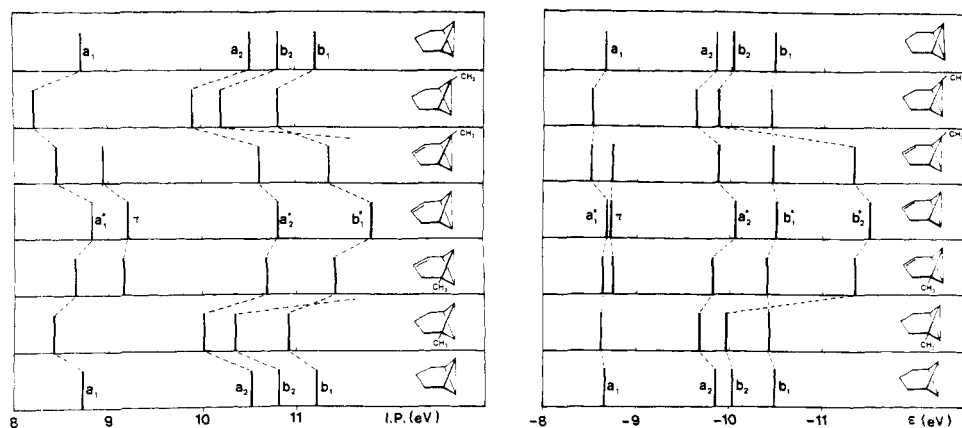


Figure 3. Comparison between the first bands in the PE spectra of 3-8 (left). Calculated orbital energies (MINDO/3) for 3-8 (right).

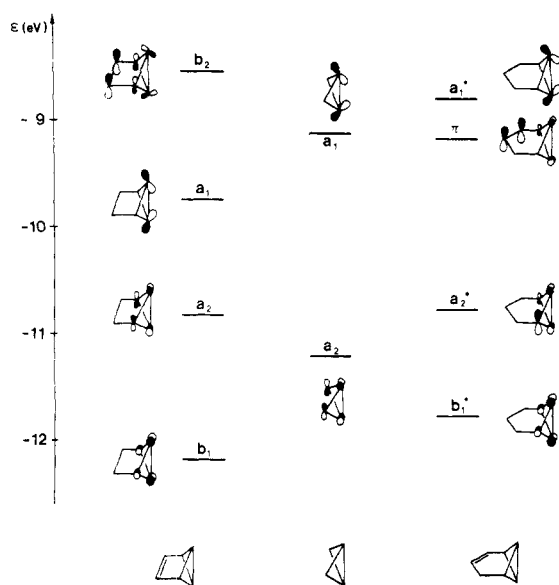


Figure 4. Comparison of the orbital sequences in benzvalene, bicyclobutane, and tricyclo[4.1.0.0<sup>2,7</sup>]hept-3-ene.

nomena parallel configuration interaction since the molecules have in fact no symmetry (see above), and both configurations therefore can mix to some extent to produce the observed energy levels.

The calculations for 3 suggest that  $a_1$  of the bicyclobutane unit is the HOMO of the molecule, well separated from the lower lying  $a_2$ ,  $b_2$ , and  $b_1$  orbitals. This interpretation has been confirmed by comparison with the corresponding levels in bicyclobutane and tricyclo[3.1.0.0<sup>2,6</sup>]hexane (2).<sup>9</sup> Methyl substitution to provide 5 and 6 caused these levels to shift toward lower ionization energies. In general, this effect is assumed to be proportional to the corresponding orbital density at the substituted center. However, this crude approximation (based on the assumption that its cause is purely due to the electron-donating effect of the alkyl substituent) is only valid if the shifted orbital appears at very low ionization energy, i.e., well separated from the  $\sigma$  region of common hydrocarbons. If this is not the case, then resonance effects with the  $\sigma$  orbitals of the methyl group ( $IP(\sigma, Me) \approx 12$  eV) begin to contaminate the simple model and the net effect cannot be quantitatively predicted by such perturbation arguments. Notwithstanding, the MINDO/3 method appears to reproduce the observed shifts quite accurately (see Figure 3).

The orbital sequence suggested by our interpretation for 4 (Figure 3) is compared with the orbital sequence of 1 and bicyclobutane in Figure 4. Both sequences can be derived qualitatively from a bicyclobutane fragment and a double

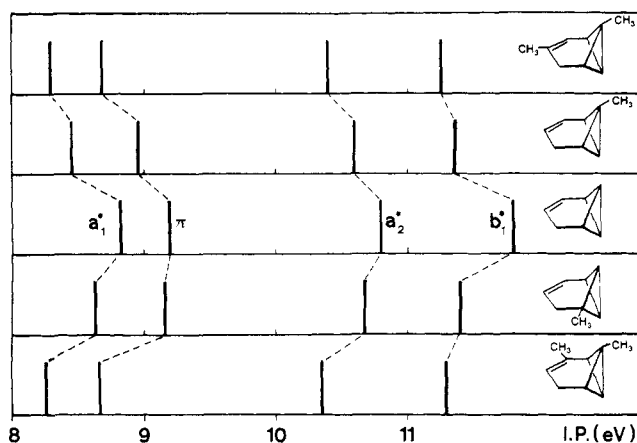
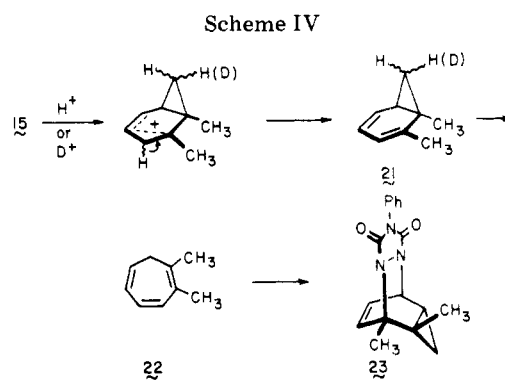
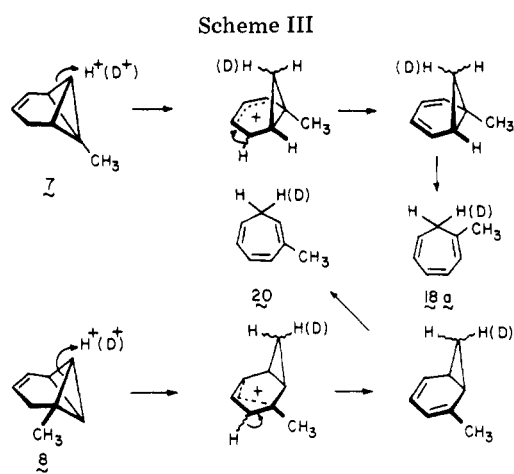
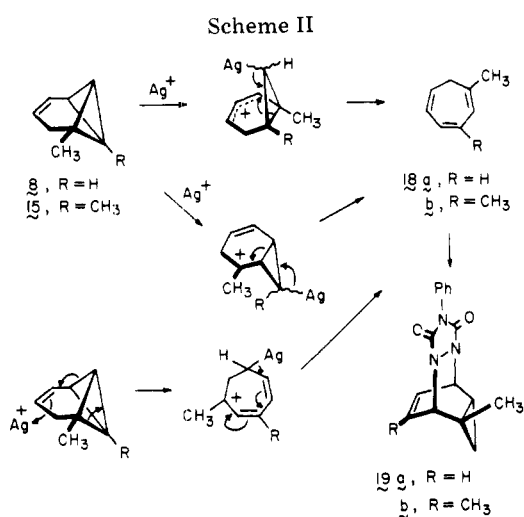
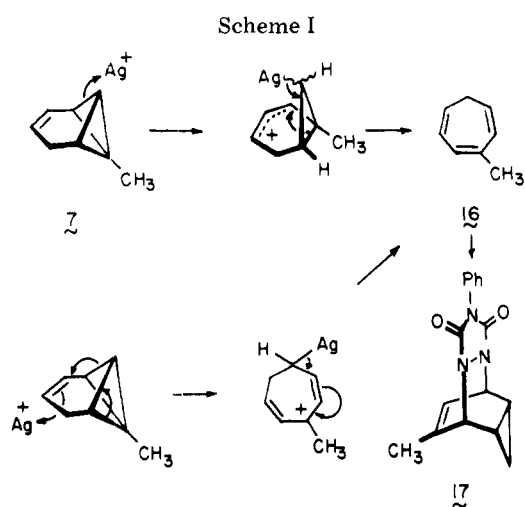


Figure 5. Comparison between the first bands in the PE spectra of 3 and 7-10.

bond or a propenyl moiety, respectively. In the case of 1, a strong interaction between the  $b_2(\pi)$  orbital of the ethylene bridge and the  $b_2$  orbital of the bicyclobutane part is encountered. As a result, the HOMO is a linear combination with large  $\pi$  character.<sup>9</sup> In contrast, the interaction between the double bond of the propenyl moiety and the orbitals of appropriate symmetry of the bicyclobutane part ( $a_2^*$  and  $b_2^*$ ) in 4 should be approximately half as large as in benzvalene due to the fact there is only one link between the interacting systems. Since 4 possesses a maximum  $C_s$  symmetry, one should expect a further mixing of this linear combination with many other orbitals. However, these interactions should be too small to override the  $a_1^*$  orbital as the HOMO of 4. This expectation is nicely corroborated by comparison of the spectra given by 7-10 as illustrated in Figure 5. For 9 and 10, the methyl group attached to the double bond shifts the band which is due to ionization out of the  $\pi$  orbital more strongly toward lower energy than the other bands, as expected.

The observation that the  $a_1^*$  level in tricyclo[4.1.0.0<sup>2,7</sup>]hept-3-ene and its various methyl substitution products lies above the  $\pi$  niveau leads, therefore, to the prediction that an electrophile should generally be directed to attack the bicyclobutane moiety. In 1, however, electrophilic capture should occur at the double bond. The latter conclusions appear to be in line with available experiment. Thus, reaction of 1 with such reagents as bromine,<sup>17</sup> *N*-phenyltriazolinedione,<sup>18</sup> chlorosulfonyl isocyanate,<sup>19</sup> benzenesulfonyl chloride,<sup>19</sup>  $Ag^+$ ,<sup>20</sup> and ozone<sup>21</sup> occurs by initial  $\pi$ -bond attack. In the ensuing section, the contrasting regioselectivity for electrophilic attack at a bicyclobutane edge bond is demonstrated.

**Electrophilic Reactions of Tricyclo[4.1.0.0<sup>2,7</sup>]hept-3-enes.** Although 7, 8, and 15<sup>12</sup> react exceedingly rapidly with



catalytic quantities of  $\text{Ag}^+$  and give rise quantitatively to methyl substituted cycloheptatrienes, the weight of evidence is insufficient to target specifically the site of electrophilic attack. The striking feature of these first experiments is the isomerically pure nature of the products, structural assignments to which follow from their  $^1\text{H}$  NMR spectra<sup>22</sup> and adduct formation with *N*-phenyltriazolinedione. The outcome of these rearrangements can be rationalized in terms of several different hypothetical mechanisms. For example, the isomerization of 7 to 3-methylcycloheptatriene might be viewed as the result of electrophilic attack at the less substituted allylic bicyclobutane edge bond, followed by deargentation<sup>23</sup> (Scheme I). Alternatively, the conversion to 16 might easily be imagined to proceed by initial attack at the  $\pi$  bond as illustrated.

No comparable steric differentiation between the upper and lower faces of the tricycloheptene nucleus exists in 8. However, the location of the methyl substituent can now be expected to cause the transient formation of allylic and tertiary carbocation intermediates to become more closely competitive. The same concession applies to 15 and this change in structure further complicates our analysis of the response of these molecules to  $\text{Ag}^+$  catalysis (Scheme II).

It is now apparent that our mechanistic inquiry would be greatly facilitated if the electrophilic reagent were to remain covalently bonded in the product. Such experiments take on double- (for 7 and 8) or triple-labeling characteristics (for 15) and permit, in principle, a clearer analysis of the regioselectivity of tricycloheptene capture by electrophiles. Experimentally,  $\text{D}^+$  is to be preferred in such circumstances and the

susceptibility of these highly strained molecules to acid-catalyzed rearrangement was therefore examined.

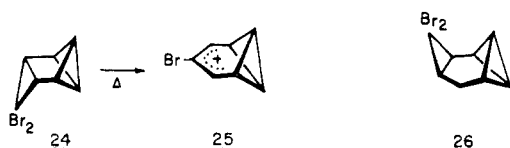
The addition of one drop of glacial acetic acid to an ethereal solution of 7 resulted in an immediate exothermic reaction and exclusive isomerization to 18a. Similar treatment with acetic acid- $d_4$  led to deuterium incorporation only at  $\text{C}_7$ , as indicated by the sizable reduction in the intensity of the  $\delta$  2.25 doublet,<sup>24</sup> an apparent decrease in the multiplicity of the olefinic quartet at 5.3 due to  $\text{H}_6$ , and mass measurement of the parent ion as  $m/e$  107 corresponding to  $\text{C}_8\text{H}_9\text{D}$ .

Under comparable conditions, 8 was quantitatively transformed to 2-methylcycloheptatriene (20).<sup>22</sup> The use of acetic acid- $d_4$  again resulted in incorporation of the isotopic label at  $\text{C}_7$  ( $^1\text{H}$  NMR analysis). In purely phenomenological terms, these transformations serve to rule out attack of  $\text{D}^+$  at the  $\text{C}=\text{C}$  bond present in 7 and 8.<sup>25</sup> Rather, considerations of product structure lead us to conclude that  $\text{H}^+$  and  $\text{D}^+$  prefer to attack 7 at the less substituted bicyclobutane edge bond and 8 at one of its nonallylic edge bonds (Scheme III). Deprotonation to deliver norcaradiene intermediates apparently precedes valence isomerization and ultimate formation of 18a and 20.

1,6-Dimethyltricyclo[4.1.0.0.2<sup>7</sup>]hept-3-ene (15) combines the structural features present in 7 and 8 and therefore holds especial interest as a substrate for acid-catalyzed isomerization. Its reaction with acetic acid resulted in rapid conversion to 1,2-dimethylcycloheptatriene (22), characterized both spectroscopically and by conversion to adduct 23 (Scheme IV). Addition of acetic acid- $d_4$  to a solution of 15 furnished 1,2-dimethylcycloheptatriene containing no detectable levels of isotopic label. However, as with the examples discussed earlier, deprotonation results in  $\text{H}^+$  being available in competition with  $\text{D}^+$ . Thus, 15 was added directly to neat acetic acid- $d_4$ , resulting now in incorporation of deuterium at  $\text{C}_7$ . These results suggest that 15 is attacked analogously to 8, proceeding via norcaradiene 21 to 22.

The mechanistic schemes proposed above concisely account for the product-forming transformations of the tricycloheptenes and, in particular, emphasize once again the interdependence of structural features and chemical reactivity in bicyclobutyl systems. A marked preference for electrophilic attack by D<sup>+</sup> at the edge bicyclobutane bonds in these molecules is apparent, in contradistinction to benzvalene which is  $\pi$ -olefinic reactive. These findings are in total agreement with the PE results. Whether other electrophiles (including Ag<sup>+</sup>) share in this regioselectivity remains to be established.

Finally, the divergent electronic interactions in tricycloheptenes and benzvalenes may serve to explain why the thermolysis of **24** in carbon tetrachloride proceeds exclusively with dibromocyclopropane ring opening to generate cation **25**,<sup>26</sup> while heating of **26** and related molecules leads to ther-



mal rearrangement in which the bicyclobutane moiety alone is ruptured.<sup>27</sup>

### Experimental Section

**7,7-Dibromo-1,4-dimethylbicyclo[4.1.0]hept-3-ene (11).** 1,4-Dimethyl-1,4-cyclohexadiene was prepared by sodium in liquid ammonia reduction of *p*-xylene according to Birch.<sup>28</sup> VPC analysis of the recovered hydrocarbon showed substantial quantities (50–75%) of unreacted *p*-xylene to be present. Since the aromatic compound caused no difficulty in the subsequent dibromocarbene addition, this mixture was not resubjected to further reduction as recommended by Fehnel<sup>29</sup> but utilized directly;  $\delta_{\text{Me}_4\text{Si}}^{\text{CDCl}_3}$  5.21 (m, 2), 2.48 (br s, 4), and 1.59 (br s, 6).

A stirred suspension of potassium *tert*-butoxide (12.96 g, 0.115 mol) and 1,4-dimethyl-1,4-cyclohexadiene (12.5 g, 0.115 mol, as 25% solution in *p*-xylene) in 250 mL of purified pentane cooled to 0 °C was treated dropwise during 1 h with 29.3 g (0.115 mol) of bromoform. Upon completion of the addition, the mixture was stirred at 0 °C for 1 h and then at room temperature for 2 h before being poured onto water (500 mL) and shaken. The layers were separated and the aqueous phase was extracted with pentane (100 mL). The combined organic solutions were washed with brine (100 mL), dried, and evaporated. The resulting oil was distilled to give 13.5 g (42%) of **11**: bp 79–80 °C (0.5 mm);  $\nu_{\text{max}}^{\text{neat}}$  2960, 2925, 2880, 2835, 1452, 1425, 1380, 1298, 1197, 1163, 1105, 1077, 1013, 988, 940, 796, and 755 cm<sup>-1</sup>;  $\delta_{\text{Me}_4\text{Si}}^{\text{CDCl}_3}$  5.32–5.05 (m, 1), 2.42–1.90 (br m, 5), 1.63 (s, 3), and 1.48 (s, 3); calcd for C<sub>9</sub>H<sub>14</sub><sup>79</sup>Br<sub>2</sub> *m/e* 277.9307, found 277.9312.

**Carbenoid Cyclization of 11.** A stirred solution of **11** (5.60 g, 20 mmol) in ether (60 mL) maintained at 0 °C under a nitrogen atmosphere was treated dropwise during 1 h with a solution of ethereal methylolithium (10.9 mL of 1.84 M, 20 mmol). The resulting solution was stirred at 0 °C for 1 h and at room temperature for 2 h. Water (30 mL) was carefully introduced, the layers were separated, and the aqueous phase was extracted with ether (30 mL). The combined organic solutions were dried over anhydrous sodium sulfate and carefully concentrated by distillation of ether at atmospheric pressure. Flash vacuum distillation of the residue gave a colorless distillate which was subjected directly to preparative VPC purification (12 ft  $\times$  0.25 in. 10% QF-1 on 60/80 mesh Chromosorb G, 85 °C). There was isolated 520 mg (22%) of **9** and 80 mg (3%) of **12**.

For 1,4-dimethyltricyclo[4.1.0.0<sup>2,7</sup>]hept-3-ene (**9**):  $\nu_{\text{max}}^{\text{neat}}$  3020, 2960, 2930, 2890, 2835, 1443, 1372, 1147, 934, 906, 838, 806, 790, 739, and 630 cm<sup>-1</sup>;  $\delta_{\text{Me}_4\text{Si}}^{\text{CDCl}_3}$  5.55–5.33 (m, 1), 2.33–2.15 (m, 2), 2.07–1.75 (m, 3), 1.57 (s, 3), and 1.48 (s, 3); calcd *m/e* 120.0939, found 120.0941. Anal. Calcd for C<sub>9</sub>H<sub>12</sub>: C, 89.94; H, 10.06. Found: C, 89.88; H, 10.17.

For 3,6-dimethyltricyclo[4.1.0.0<sup>2,7</sup>]hept-3-ene (**12**):  $\nu_{\text{max}}^{\text{neat}}$  3020, 2970, 2930, 2890, 2835, 1454, 1440, 1382, 1134, 1038, 910, 848, 836, 822, 806, 788, and 736 cm<sup>-1</sup>;  $\delta_{\text{Me}_4\text{Si}}^{\text{CDCl}_3}$  5.13–4.87 (m, 1), 2.33–2.13 (m, 1), 2.08–1.80 (m, 3), 1.70 (narrow m, 3), and 1.13 (s, 3); calcd *m/e* 120.0939, found 120.0941. Anal. Calcd for C<sub>9</sub>H<sub>12</sub>: C, 89.94; H, 10.06. Found: C, 89.63; H, 10.10.

**7,7-Dibromo-1,3-dimethylbicyclo[4.1.0]hept-3-ene (13).** 2,4-

Dimethyl-1,4-cyclohexadiene was prepared by sodium in liquid ammonia reduction of *m*-xylene according to Birch.<sup>28</sup> VPC analysis of the hydrocarbon so produced indicated 20–25% of unreacted aromatic to be present. This mixture was suitable for further use in this study. For pure diene:  $\delta_{\text{Me}_4\text{Si}}^{\text{CDCl}_3}$  5.40 (m, 2), 2.23 (br s, 4), and 1.63 (br s, 6).

2,4-Dimethyl-1,4-cyclohexadiene (16.6 g, 0.154 mol, as 83% solution in *m*-xylene) was allowed to react with potassium *tert*-butoxide (17.2 g, 0.154 mol) and bromoform (38.9 g, 0.154 mol) as described above. Distillation of the resulting oil gave 20.7 g (48%) of **13**: bp 91–92 °C (0.8 mm);  $\nu_{\text{max}}^{\text{neat}}$  2940, 2925, 2885, 2830, 1447, 1427, 1380, 1200, 1077, 1021, 979, 830, 793, and 748 cm<sup>-1</sup>;  $\delta_{\text{Me}_4\text{Si}}^{\text{CDCl}_3}$  5.33–5.07 (m, 1), 2.57–2.03 (br m, 5), 1.60 (s, 3), and 1.48 (s, 3); calcd for C<sub>9</sub>H<sub>14</sub><sup>79</sup>Br<sub>2</sub> *m/e* 277.9307, found 277.9312.

**Carbenoid Cyclization of 13.** A solution of **13** (5.60 g, 20 mmol) in 60 mL of ether was treated with methylolithium in the prescribed fashion. Flash distillation of the residual oil was followed by direct VPC purification on the QF-1 column. There was isolated 490 mg (20%) of **10** and 85 mg (3.5%) of **14**.

For 1,3-dimethyltricyclo[4.1.0.0<sup>2,7</sup>]hept-3-ene (**10**):  $\nu_{\text{max}}^{\text{neat}}$  3090, 3015, 2995, 2955, 2930, 2880, 2835, 1440, 1372, 1141, 1048, 922, 820, 782, and 734 cm<sup>-1</sup>;  $\delta_{\text{Me}_4\text{Si}}^{\text{CDCl}_3}$  5.07–4.83 (m, 1), 2.37–2.20 (m, 2), 2.08–1.83 (m, 3), 1.75–1.63 (m, 3), and 1.60 (s, 3); calcd *m/e* 120.0939, found 120.0941. Anal. Calcd for C<sub>9</sub>H<sub>12</sub>: C, 89.94; H, 10.06. Found: C, 89.47; H, 10.01.

For 4,6-dimethyltricyclo[4.1.0.0<sup>2,7</sup>]hept-3-ene (**14**):  $\nu_{\text{max}}^{\text{neat}}$  3090, 3025, 2965, 2930, 2870, 2815, 1445, 1405, 1380, 1132, 1088, 1040, 1005, 950, 928, 848, 796, and 735 cm<sup>-1</sup>;  $\delta_{\text{Me}_4\text{Si}}^{\text{CDCl}_3}$  5.68–5.47 (m, 1), 2.33–2.13 (m, 1), 1.98 (br s, 2), 1.87 (br s, 2), 1.68–1.52 (m, 3), and 1.15 (s, 3); calcd *m/e* 120.0939, found 120.0941. Anal. Calcd for C<sub>9</sub>H<sub>12</sub>: C, 89.94; H, 10.06. Found: C, 89.76; H, 10.22.

**General Procedure for Acid-Promoted Isomerizations.** A solution of **15** (500 mg, 4.2 mmol) in ether (15 mL) was treated with acetic acid (0.5 mL). After standing for 30 min, the solution was washed with saturated sodium bicarbonate (5 mL) and sodium chloride solutions (5 mL). After drying, concentration afforded 1,2-dimethylcycloheptatriene (**22**, 475 mg, 95%): <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  6.35 (m, 2), 6.00 (m, 1), 5.40 (pseudo q, *J* = 8 Hz, 1), 2.25 (d, *J* = 6 Hz, 2), 1.93 (s, 3), and 1.83 (s, 3); for C<sub>9</sub>H<sub>12</sub> *m/e* calcd 120.0939, found 120.0941.

To a solution of 120 mg (1.0 mmol) of **22** in ethyl acetate (5 mL) cooled to –78 °C was added dropwise a solution of *N*-phenyltriazolinedione in ethyl acetate until the color persisted. Evaporation of solvent, chromatography on silica gel (elution with ether–chloroform 9:1), and recrystallization from ethyl acetate afforded pure **23**: mp 148–149 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.40 (s, 5), 6.02 (m, 2), 5.21 (m, 1), 1.96 (s, 3), 1.47–1.28 (m, 1), 1.33 (s, 1), 0.54 (s, 1), 0.45 (d, 1). Anal. Calcd for C<sub>17</sub>H<sub>17</sub>N<sub>3</sub>O<sub>2</sub>: C, 69.13; H, 5.80; N, 14.23. Found: C, 68.82; H, 5.85; N, 14.23.

When **7** was similarly treated with acetic acid, the resulting lone hydrocarbon product (**18a**) was purified by preparative VPC (6 ft  $\times$  0.25 in. XF-1150 on 60/80 mesh Chromosorb G, 45 °C). Its <sup>1</sup>H NMR spectrum was identical to that illustrated in ref 22 for 1-methylcycloheptatriene.

Reaction of **18a** (28.8 mg) with *N*-phenyltriazolinedione (47.5 mg) in ethyl acetate at 0 °C afforded **19a**: mp 148–149 °C (from ethanol); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.42 (br s, 5), 6.17–5.85 (m, 2), 5.30–4.73 (m, 2), 1.40 (s, 3), 1.33–1.08 (m, 1), and 0.47–0.17 (m, 2). Anal. Calcd for C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>: C, 68.31; H, 5.38; N, 14.94. Found: C, 68.10; H, 5.46; N, 15.01.

Treatment of **8** in the prescribed manner led exclusively to **20**, identified by direct spectral comparison with 2-methylcycloheptatriene.<sup>22</sup>

**General Procedure for Ag(I)-Catalyzed Isomerizations.** A solution of **7** (93 mg, 0.87 mmol) in anhydrous benzene (5 mL) was treated with 0.1 mL of 0.2 M silver perchlorate in benzene solution. After standing for 30 min, the mixture was washed with brine (3  $\times$  10 mL), dried, and concentrated. Preparative VPC purification (XF-1150, 45 °C) afforded **16** as the sole product, identified by comparison of spectra.<sup>22</sup>

A solution of **16** (36 mg, 0.34 mmol) in ethyl acetate (2 mL) was treated at 0 °C with *N*-phenyltriazolinedione (59.5 mg, 0.34 mmol) in the same solvent (1 mL). The resulting solution was stirred for 1 h and evaporated. Recrystallization of the residue from ethanol gave **17** as colorless plates: mp 138.5–140 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.42 (br s, 5), 5.76–5.50 (m, 1), 5.17–4.83 (m, 2), 1.85 (d, *J* = 2 Hz, 3), 1.67–1.33 (m, 2), 0.57 (q, *J* = 7 Hz, 1), and 0.31–0.03 (m, 1); *m/e* calcd 281.1164, found 281.1172. Anal. Calcd for C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>: C, 68.31; H, 5.38; N, 14.94. Found: C, 68.28; H, 5.56; N, 14.99.

Analogous treatment of **8** (30 mg) with the silver perchlorate-

benzene reagent led exclusively to **18a**, identical to the sample obtained earlier.

From 500 mg (4.2 mmol) of **15**, **18b** was isolated in 97% yield:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  6.23 (d with fine splitting,  $J = 5$  Hz, 1), 6.00 (dd,  $J = 9$  and 5 Hz, 1), 5.82 (s, 1), 5.28 (m, 1), 2.30 (d,  $J = 7$  Hz, 2), 2.00 (s, 3), and 1.97 (d,  $J = 1.5$  Hz, 3);  $m/e$  calcd 120.0939, found 120.0941.

Cycloaddition of *N*-phenyltriazolinedione to **18b** in ethyl acetate solution at 0 °C gave **19b** as colorless needles: mp 118.5–120 °C (from ethyl acetate);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.37 (br s, 5), 5.70–5.42 (m, 1), 5.03 (t,  $J = 5.5$  Hz, 1), 4.62 (d,  $J = 2$  Hz, 1), 3.45 (s, 3), 1.33 (s, 3), 1.17 (m, 1), 0.43 (d,  $J = 2.5$  Hz, 1), and 0.33 (s, 1);  $m/e$  calcd 295.1321, found 295.1320. Anal. Calcd for  $\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_2$ : C, 69.13; H, 5.80; N, 14.23. Found: C, 69.04; H, 6.04; N, 14.16.

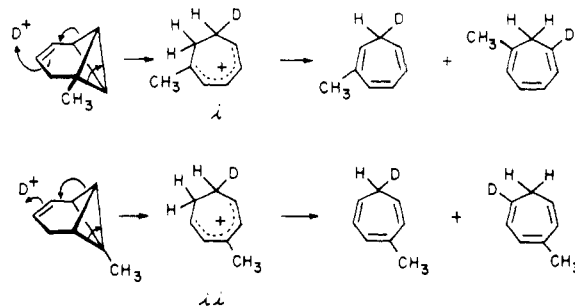
**Photoelectron Spectroscopy.** The PE spectra have been recorded on a Perkin-Elmer Ltd PS 18 instrument (Beaconsfield, England). The spectra were calibrated with Ar and a resolution of about 20 meV on the Ar line was obtained.

**Acknowledgment.** The work in Darmstadt was supported by the Fonds der Chemischen Industrie and the Otto Röhm Stiftung. The research at Ohio State was made possible by National Science Foundation support.

**Registry No.**—**11**, 66036-93-9; **12**, 66036-94-0; **13**, 66036-95-1; **14**, 66036-96-2; **15**, 61772-32-5; **16**, 3045-90-7; **17**, 66036-97-3; **18a**, 3045-88-3; **18b**, 61772-26-7; **19a**, 66036-98-4; **19b**, 66036-99-5; **22**, 66037-00-1; **23**, 66037-01-2; 1,4-dimethyl-1,4-cyclohexadiene, 4074-22-0; 2,4-dimethyl-1,4-cyclohexadiene, 4190-06-1; *N*-phenyltriazolinedione, 4233-33-4.

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- Because of the relative amount of  $\text{CD}_3\text{COOD}$  added and the liberation of  $\text{H}^+$  as the rearrangement proceeds, quantitative incorporation of 1 molar equiv of deuterium cannot be expected and is not seen.
- The following alternative mechanisms may be legitimately advanced for consideration:



However, they account neither for the exclusivity of product formation nor the absence of observable ( $^1\text{H NMR}$ )  $\text{sp}^2$ -bound deuterium (note particularly the latent symmetry of ii).

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## Isocyanide Reductions. A Convenient Method for Deamination<sup>1</sup>

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Received October 21, 1977

Dissolving metal reductions of a number of isocyanides are reported. Dissolving metal reduction of a chiral acyclic isocyanide leads to formation of racemic product. Some stereoselectivity is observed in the reduction of a chiral cyclopropyl isocyanide. Due to the ease of conversion of primary amines to isocyanides and the excellent yields obtained in the dissolving metal reduction of isocyanides, this method is recommended for deamination of primary amines. The mechanism of dissolving metal reduction is discussed.

Ugi and Bodesheim<sup>2</sup> observed the nearly quantitative reduction of isocyanides to their corresponding hydrocarbons by solutions of metals (lithium, sodium, potassium, and calcium) in liquid ammonia. They conjectured that the isocyanide accepted two electrons, by either a one-step or a two-step process, followed by cleavage of the carbon–nitrogen bond.



Later, Büchner and Dufaux<sup>3</sup> observed that the reductive cleavage of isocyanides occurred in tetrahydrofuran as a solvent as well as in liquid ammonia. These workers postulated a two-step mechanism in which the addition of the first electron leads to formation of an anion radical intermediate which can accept a second electron leading to the formation of a carbanion intermediate and cyanide ions.

