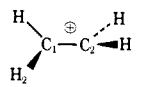
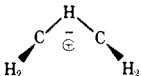


**Table I.** Calculated Carbon Chemical Shifts

Molecule	$\sigma$ , ppm	$\Delta\sigma^a$ (calcd)	$\Delta\sigma$ (exptl)	Energy, <sup>b</sup> hartrees
CH <sub>4</sub>	222.1	0.0	0	-40.13976
CH <sub>5</sub> <sup>+</sup> ( <i>D</i> <sub>3h</sub> )	253.4	31.3		-40.31506
CH <sub>5</sub> <sup>+</sup> ( <i>C</i> <sub>4v</sub> )	250.2	28.1		-40.31891
CH <sub>5</sub> <sup>+</sup> ( <i>C</i> <sub>s</sub> )	173.1	-49.0		-40.32206
C <sub>2</sub> H <sub>4</sub>	105.5	0.0	0.0	-77.92189
	C <sub>1</sub>	+68.1	+49 <sup>c</sup>	-78.19498
	C <sub>2</sub>	-232.8	-193 <sup>c</sup>	
		73.2	-32.3	-78.18414

<sup>a</sup> CH<sub>5</sub><sup>+</sup> shifts are relative to CH<sub>4</sub>; C<sub>2</sub>H<sub>5</sub><sup>+</sup> shifts are relative to C<sub>2</sub>H<sub>4</sub>. <sup>b</sup> Taken from ref 9. <sup>c</sup> Estimated from data on similar systems given in ref 2.

classical form of the ethyl cation from experimental data reported by Olah and White<sup>2</sup> on other stable classical cations. We report these estimates under the "experimental" entry of the table.

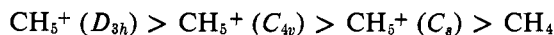
The problem for C<sub>2</sub>H<sub>5</sub><sup>+</sup> is one of determining whether the actual structure may be represented by a rapidly equilibrating pair of ions or by a static ion with a hydrogen bridge. It can be seen from the table that the results for the CH<sub>3</sub> and CH<sub>2</sub> resonances of the classical form of the ethyl cation are in moderately good agreement with the experimental estimates. If the ion may be represented by a rapidly equilibrating pair of ions, then the <sup>13</sup>C shift will be the average of  $\sigma(C_1)$  and  $\sigma(C_2)$ . This average is calculated to be -82.3 ppm (relative to C<sub>2</sub>H<sub>4</sub>), in good agreement with the value of -72 ppm estimated from the results of Olah and White.<sup>2</sup> The <sup>13</sup>C shift in the hydrogen-bridged structure, on the other hand, is predicted to be about 50 ppm to high field of this average value. Thus if the ethyl cation could be observed directly, <sup>13</sup>C chemical shift measurements would be capable of distinguishing between the possible structures. The calculated results also support the conclusions of Olah and White<sup>2</sup> on similar types of ions (*e.g.*, the 2-butyl cation).

Carbon chemical shifts were also calculated for the trigonal-bipyramidal (*D*<sub>3h</sub>), square-pyramidal (*C*<sub>4v</sub>), and less symmetrical (*C*<sub>s</sub>) structures of CH<sub>5</sub><sup>+</sup> given in ref 7. All three forms show sizable shifts from CH<sub>4</sub>. The <sup>13</sup>C resonance of the *C*<sub>s</sub> structure is shifted 49 ppm downfield from CH<sub>4</sub>, while the *C*<sub>4v</sub> and *D*<sub>3h</sub> structures are predicted to give upfield resonances of 28.1 and 31.3 ppm, respectively. Estimation of experimental results for CH<sub>5</sub><sup>+</sup> is less straightforward. However, as Olah has pointed out, "onium-type" carbons are to be found in bridged species, *e.g.*, the 2-norbornyl, 7-norbornenyl, and 7-norbornadienyl cations.<sup>13</sup> In these three cations, the bridging carbon chemical shifts range from -43 to -23 ppm relative to CH<sub>4</sub>.<sup>13</sup> It is perhaps worthy of note that these values are quite close to the calculated value for CH<sub>5</sub><sup>+</sup> (*C*<sub>s</sub>). Thus, if CH<sub>5</sub><sup>+</sup> exists as a static ion these results suggest that <sup>13</sup>C nmr would be able to distinguish between the less symmetrical (*C*<sub>s</sub>) and the other two (*C*<sub>4v</sub> and *D*<sub>3h</sub>) structures. However, it should be noted that the activation energy for hydro-

(13) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 6883 (1969).

gen rearrangement within the ion is only about 2 kcal/mol.

It is of interest to briefly examine the origin of the shifts in these systems. Decreasing the negative charge on carbon usually leads to an overall contraction of the carbon valence atomic orbitals. Such contraction results in an increased paramagnetic contribution to magnetic shielding and a low-field shift. Although there is a contraction of carbon orbitals as we go from the *D*<sub>3h</sub> to the *C*<sub>s</sub> structure, the total charges (as measured by Mulliken<sup>14</sup> gross populations) on carbon in CH<sub>5</sub><sup>+</sup> and CH<sub>4</sub> are in the order



and thus it appears that the shifts cannot be rationalized in terms of such charge effects alone.

In addition to charge effects, the shielding at a nucleus will also depend upon the extent to which the electrons can be perturbed by the magnetic field. Some measure of this is given by the availability of excited singlet states. It is likely that all four systems have excited states of approximately the same (relatively high) energy. However, it is important to note that for CH<sub>4</sub>, CH<sub>5</sub><sup>+</sup> (*D*<sub>3h</sub>), and CH<sub>5</sub><sup>+</sup> (*C*<sub>4v</sub>), contributions from many of these excited states are zero by symmetry. In contrast, contributions from all excited singlet states of CH<sub>5</sub><sup>+</sup> (*C*<sub>s</sub>) will have finite values and this together with the more contracted carbon valence functions in the *C*<sub>s</sub> structure may explain the larger paramagnetic value.

Similar ideas may be used to explain the shifts in the various structures for the ethyl cation. The carbon orbitals of the CH<sub>2</sub> center are rather more contracted than those of the CH<sub>3</sub> group due to the greater positive charge on this center. However, all the trends cannot be explained in terms of charge effects alone. It is worthy of note that some excitations are mainly localized on the CH<sub>2</sub> center and will probably further increase the paramagnetic contribution for C<sub>2</sub> while leaving that for C<sub>1</sub> almost unchanged.

**Acknowledgments.** This work was initiated while we were members of Professor J. A. Pople's group at Carnegie-Mellon University, and we thank him for financial support. We also wish to thank Dr. Leo Radom for useful discussions and a referee for several useful comments on the manuscript.

(14) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

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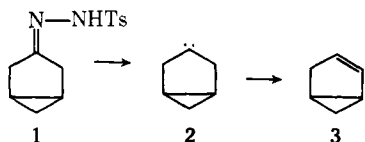
### The Reactions of *exo*- and *endo*-8-Carbenetricyclo[3.2.1.0<sup>2,4</sup>]octane<sup>1</sup>

Sir:

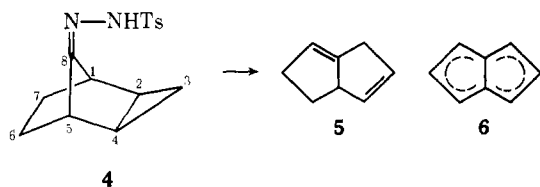
Several years ago we reported on the methoxide ion induced decomposition of the tosylhydrazone of

(1) Financial support from the National Science Foundation and the Air Force Office of Scientific Research is gratefully acknowledged.

3-bicyclo[3.1.0]hexanone (**1**), which generates bicyclo[3.1.0]hexene-2 (**3**) in 91% yield, most probably as a result of a 1,2-hydrogen migration of 3-carbenabicyclo[3.1.0]hexane (**2**).<sup>2</sup> Thus, any trishomocyclopropenyl character which might actually be present in 3-carbenabicyclo[3.1.0]hexane is not revealed. If one were to bridge 3-carbenabicyclo[3.1.0]hexane across the C-2-C-4 positions with a small bridging unit, hydrogen migration would be prevented and transannular interactions might be revealed. With this as our goal, we chose to investigate *exo*- and *endo*-8-carbenatricyclo[3.2.1.0<sup>2,4</sup>]octane.



Decomposition of the tosylhydrazone of *exo*-8-tricyclo[3.2.1.0<sup>2,4</sup>]octanone in bis(2-ethoxyethyl) ether (3.3 equiv of NaOCH<sub>3</sub>) at 160° gives a 20% yield of volatile hydrocarbons, composed of 65% of bicyclo[3.3.0]octa-1,6-diene (**5**) and 35% of a mixture of two isomeric bicyclo[3.3.0]octadienes (**6**).<sup>3</sup> Two reasonable reaction



courses can be suggested: migration of C-2 (**7** → **8** → products), with **8** undergoing either a concerted ( $\sigma_{2s} + \sigma_{2a}$  fission at bonds a or at bonds b)<sup>4</sup> or biradical ring opening to products (fission at a, b, or c) or migration of C-7 (**9** → **10** → **11** → products), with **10** undergoing a vinylcyclopropane rearrangement to **11** and **11** opening by a partly concerted (fission at bonds a), partly biradical (fission at b or b + a), or a completely biradical process.<sup>5,6</sup>

In sharp contrast, the decomposition of the tosylhydrazone of *endo*-8-tricyclo[3.2.1.0<sup>2,4</sup>]octanone (**12a**) in diglyme (5.74 equiv of NaOCH<sub>3</sub>) at 155° produces *endo-anti*- (**13**, 11%) and *endo-syn*-tricyclo[3.2.1.0<sup>2,4</sup>]octan-8-yl methyl ether (**14**, 1%), *endo*-tricyclo[3.3.0.0<sup>4,6</sup>]octan-2-yl methyl ether (**15**, 51%), tetracyclo[3.3.0.0<sup>2,8</sup>.0<sup>4,6</sup>]octane (**16**, 33%), and tricyclo[3.3.0.0<sup>4,6</sup>]oct-2-ene (**17**, 4%) in an overall yield of 80%. The

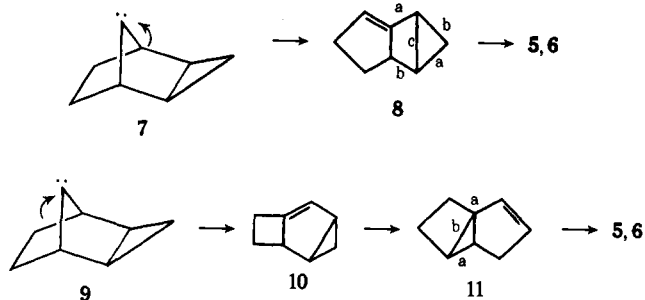
(2) P. K. Freeman and D. G. Kuper, *J. Org. Chem.*, **30**, 1047 (1965).

(3) The nmr, infrared, and elemental analyses of 1,6-diene **5** and mixture **6** were consistent with the structural assignments. Both the 1,6-diene and the mixture of isomeric dienes were hydrogenated to *cis*-bicyclo[3.3.0]octane. All other product structures have been identified by spectral comparison with authentic standards.

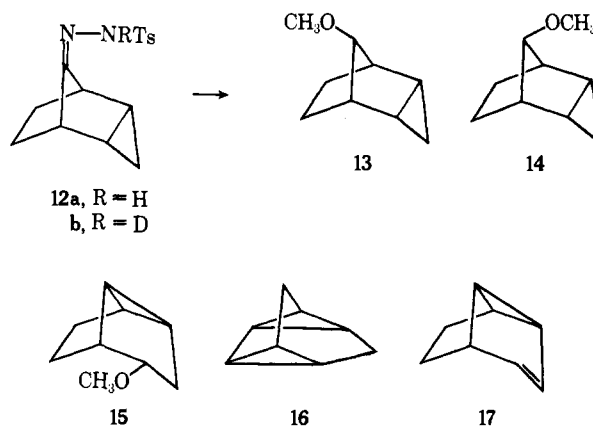
(4) For evidence supporting a  $\sigma_{2s} + \sigma_{2a}$  process for the bicyclo[2.1.0]pentene to cyclopentadiene reaction, see J. E. Baldwin and A. H. Andrist, *Chem. Commun.*, 1561 (1970).

(5) The analogies found in carbonium ion chemistry with (a) the deamination of *syn*-7-norbornenylamine (H. Tanida, T. Tsuji, and T. Irie, *J. Org. Chem.*, **31**, 3941 (1966)), (b) the solvolysis of *syn*-7-norbornenyl tosylate (S. Winstein and E. T. Stafford, *J. Amer. Chem. Soc.*, **79**, 505 (1957)), and (c) the deamination of *exo-syn*-8-tricyclo[3.2.1.0<sup>2,4</sup>]octylamine, which yields *exo*-2-tricyclo[4.2.0.0<sup>3,5</sup>]octanol (K. W. Pober, Ph.D. Thesis, University of Idaho, 1967), suggest that the initial step is **9** → **10**.

(6) R. A. Moss and J. R. Whittle (*Chem. Commun.*, 341 (1969)) have observed a similar 1,2-alkyl shift for 7-carbenanorbornane.



formation of methyl ethers **13**, **14**, and **15** suggests that the methanol of neutralization formed in the re-



action of tosylhydrazone with sodium methoxide may have converted **18** to **19**, providing two major reaction routes, a carbonium ion pathway (from **19**) as well as a carbene pathway (from **18**).<sup>7</sup> By using either deuterated or undeuterated tosylhydrazone, various quantities of methanol-*d*, and taking advantage of the isotope effect, it is possible to separate the carbene and carbonium ion components of the reaction (Table I). Thus, we find that keeping the concentration

Table I. Decomposition of Tosylhydrazone **12** in Diglyme-NaOCH<sub>3</sub>-CH<sub>3</sub>OH(D)

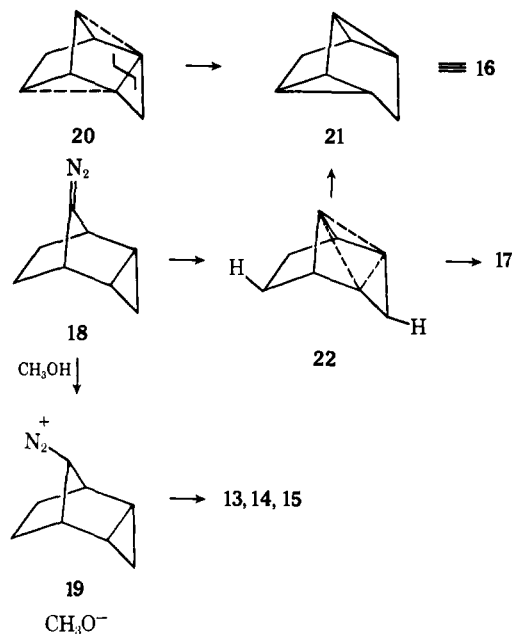
Run	<b>12</b> , equiv	NaOCH <sub>3</sub> , equiv	CH <sub>3</sub> OD, <sup>b</sup> equiv	<b>15</b> , <sup>c</sup> %	<b>13</b> , <sup>c</sup> %	<b>16</b> , <sup>c</sup> %	<b>17</b> , <sup>c</sup> %
1	1.00 <b>12b</b> <sup>a</sup>	5.82		6	3	81	10
2	1.00 <b>12a</b>	5.92	1.00	64	13	21	2
3	1.00 <b>12a</b>	5.75	11.9	81	11	7	1
4	1.00 <b>12a</b>	6.20	81.7	81	16	3	0

<sup>a</sup> 97% *d*<sub>1</sub>. <sup>b</sup> 83% methanol-*d*. <sup>c</sup> ± 2%.

of the proton source to a minimum and using the fact that  $k_H/k_D > 1$ ,<sup>8</sup> it is possible to retard the route **18** → **19** to such an extent that the carbene component is 91% (run 1, products **16** and **17**), whereas a concentration of nearly 82 equiv of methanol-*d* using undeuterated tosylhydrazone **12a** results in a process which proceeds principally through **19** and a carbonium ion (97%) (run 4, products **13** and **15**).

(7) R. H. Shapiro, J. H. Duncan, and J. C. Clopton, *J. Amer. Chem. Soc.*, **89**, 471, 1442 (1967).

(8) Similar isotope effects have been noted, ref 7 and K. B. Wiberg and J. M. Lavanish, *ibid.*, **88**, 5272 (1966); F. Cook, H. Shechter, J. Bayless, L. Friedman, R. L. Foltz, and R. Randall, *ibid.*, **88**, 3870 (1966).



Thus, decomposition of diazo compound **18** generates a bivalent intermediate, which rearranges *via* bond formation between C-2 and C-8, fission at C-2-C-4, and bonding between C-4 and C-6, with concomitant hydrogen migration (**20**) to generate **21** (equivalent to **16**). Therefore, it seems clear that the carbene intermediate rearranges with transannular trishomocyclopropenyl participation. It would also seem likely that delocalization is present in the intermediate.<sup>9</sup> Whether or not this interaction is chemically significant is a matter to be determined by further experimentation. Representing the intermediate as **22**, the formation of tetracyclic **16** by a C-6  $\rightarrow$  C-8 hydrogen shift is a symmetry-allowed process ( $\sigma_{2a} + \omega_{2a} + \omega_{0a}$ ).<sup>10</sup> In harmony with this, in run I (Table I) it is found that tetracyclic **16** contains 23%  $d_1$ ; therefore a simple C-6  $\rightarrow$  C-8 shift represents the major reaction pathway, although perhaps not the sole pathway.<sup>11</sup>

It appears, therefore, that *exo*-8-carbenatricyclooctane rearranges by 1,2-alkyl migration and *endo*-8-carbenatricyclooctane rearranges *via* a trishomocyclopropenyl interaction with loss of a proton either from C-6 to form **16** or from C-3 to form tricyclooctene **17**.

(9) R. Gleiter and R. Hoffmann, *ibid.*, **90**, 5457 (1968).

(10) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, pp 169-173.

(11) An intermolecular process for conversion of **22** to **16**, involving loss of a proton from **22**, generation of a carbanion related to **16**, and subsequent protonation, would be expected to exhibit a deuterium isotope effect near unity for deuterium incorporation; K. B. Wiberg, *Chem. Rev.*, **55**, 713 (1955).

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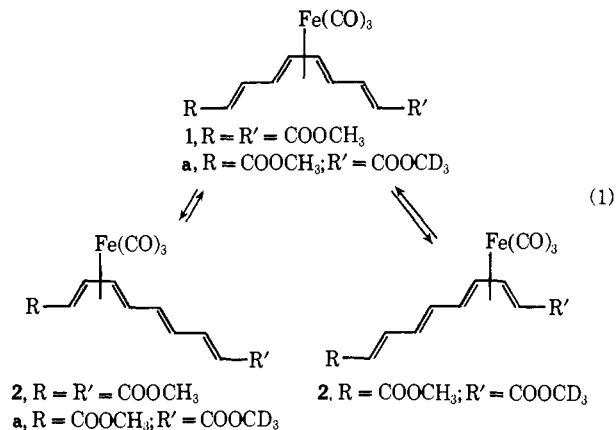
Peter K. Freeman,\* R. S. Raghavan, Donald G. Kuper  
 Department of Chemistry, Oregon State University  
 Corvallis, Oregon 97331  
 Department of Chemistry, University of Idaho  
 Moscow, Idaho 83843  
 Received May 25, 1971

### Shift Isomerization and Racemization of Some Polyene-Tetrahaptoiron Tricarbonyl Complexes

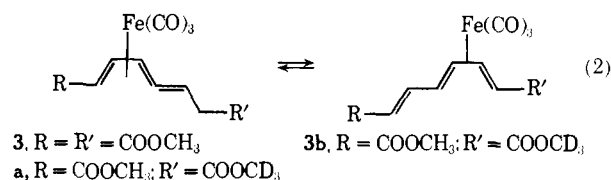
Sir:

We have studied the relationship between racemization and shift isomer interconversion in two series

of polyene-tetrahaptoiron tricarbonyl complexes: optically active and deuterated complexes of 1,8-dicarbomethoxy-1,3,5,7-octatetraene (eq 1) and optically active

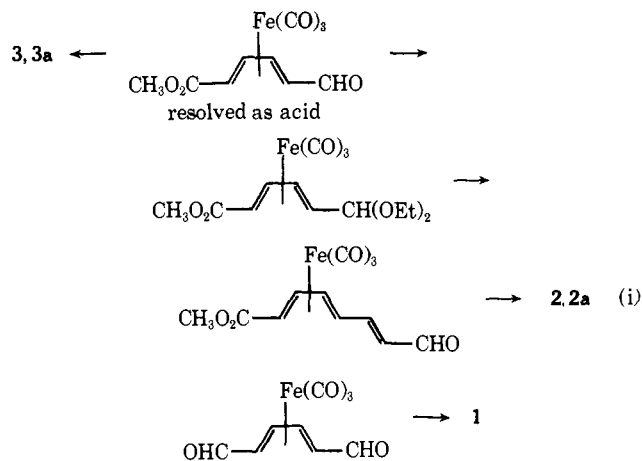


and deuterated complexes of 1,6-dicarbomethoxy-1,3,5-hexatriene (eq 2).<sup>1</sup> For the octatetraene complexes



rates of the following processes were determined: interconversion of middle (1) and end (2) shift isomers; interconversion of the two end isomers (**2a** and **2b**); racemization of the optically active end isomer (-)-**2**. For the hexatriene complexes rates of the following processes were measured: interconversion of the two deuterated complexes **3a** and **3b**; racemization of optically active (-)-**3**. All of the above reactions followed

(1) These complexes were prepared from the appropriate aldehyde and carbomethoxymethylenetriphenylphosphorane by general procedures described earlier (eq i).<sup>2,3</sup> All had the expected analytical and spectral properties: **1**, mp 107.5-109°; nmr (C<sub>6</sub>D<sub>6</sub>) 3.46 (OCH<sub>3</sub>); **2**, mp 123-125°; nmr  $\delta$  3.37 (OCH<sub>3</sub>), 3.48 (OCH<sub>3</sub>); **3**, mp 97-98°; nmr  $\delta$  3.40 (OCH<sub>3</sub>), 3.47 (OCH<sub>3</sub>). In **2a** the resonance at  $\delta$  3.48 was absent, while in **3a** the resonance at  $\delta$  3.47 was absent.



(2) H. W. Whitlock and Y. N. Chuah, *J. Amer. Chem. Soc.*, **87**, 2606 (1965).

(3) H. Whitlock, C. R. Reich, and W. D. Woessner, *ibid.*, **93**, 2483 (1971).