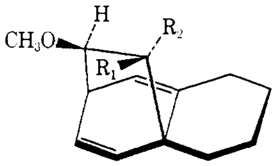
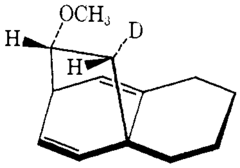
would appear that bond rotation and cleavage compete quite favorably. On this basis, the high levels of preservation of geometrical relationships which are evidenced in the thermolysis of **1** and **5** can be attributed in large measure to increased barriers to k_{rot} due to steric and ponderal factors. In the absence of at least one of these constraining features (*cf.* **4**, **8**, and **9**), 1,4-diradical intermediates exhibit little stereochemical preference. Such is not totally unexpected in view of the magnitude of the energy barrier associated with radical additions to benzene rings;[10] from microscopic reversibility considerations, there must exist a small but significant barrier for loss of a group from substituted cyclohexadienyl radicals.

Thus, loss of stereochemical integrity has been demonstrated for 1,4 diradicals in which k_{scis} has been appreciably enhanced relative to k_{rot}. We must therefore conclude that a singlet diradical of this type cannot accurately be described as a flat region atop an energy profile, *i.e.*, as a twixtyl. Instead the present results demand that those areas of potential energy space associated with semistabilized 1,4 radicals be more precisely characterized by maxima and minima which reflect such subtle intrinsic molecular features as steric demands and ponderal effects. This state of affairs would ensure significant passage of the reaction through the lowest energy conformation provided, of course, that the rates of ultimate bond scission for the various conformations are similar in magnitude. It may well be that under certain strictly specified conditions the diradical region will exhibit little deviation from the horizontal, but such twixtylic conditions need not always apply.

Finally, it should be noted that the available data do not rule out the possibility that portions of these fragmentations proceed by preliminary [1,3]sigmatropic rearrangement *via* intermediates of type **10** and subsequent stereospecific Diels–Alder fragmentation.[11] However, the high propensity of related dienes[12] for symmetry-allowed thermal [1,5]sigmatropic rearrangements suggests that this alternative does not gain importance.



10a, $R_1 = D; R_2 = H$
b, $R_1 = H; R_2 = D$



10c

Acknowledgment. This research was supported in part through National Cancer Institute Grant No. CA 12115. The authors are also indebted to Professor G. Closs for the deuterium-decoupled nmr spectra and to Dr. Stanley A. Lang for assistance with the 100-MHz spectra.

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(10) M. Szwarc and J. H. Binks, *Theor. Org. Chem. Pap. Kekule Symp., 1958*, 263 (1959).

(11) It would have to be assumed that **1** and **5**, which both have *syn*-methoxyl groups, undergo this rearrangement with high retention of configuration to give **10a** and **10b**, respectively. In contrast, **4**, which has an *anti*-methoxyl group, would have to react with some inversion of configuration to provide the appropriate mixture of **10b** and **10c**. Alteration in the retention–inversion pathways of thermal [1,3]sigmatropic bicyclo[3.2.0]hept-2-ene rearrangements upon introduction of an added methyl group has been noted previously; J. A. Berson and G. L. Nelson, *J. Amer. Chem. Soc.*, **92**, 1096 (1970).

(12) (a) J. A. Berson and M. R. Wilcott, III, *ibid.*, **88**, 2494 (1966); (b) J. A. Berson, P. W. Grubb, R. A. Clark, D. R. Hartter, and M. R. Wilcott, III, *ibid.*, **89**, 4076 (1967); (c) E. Ciganek, *ibid.*, **89**, 1458 (1967); (d) V. Rautenstrauch, H. J. Scholl, and E. Vogel, *Angew. Chem., Int. Ed. Engl.*, 7, 288 (1968); (e) L. A. Paquette, D. E. Kuhla, and J. H. Barrett, *J. Org. Chem.*, **34**, 2879 (1969).

(13) Philips Petroleum Fellow, 1970–1971; University Dissertation Fellow, 1971–1972.

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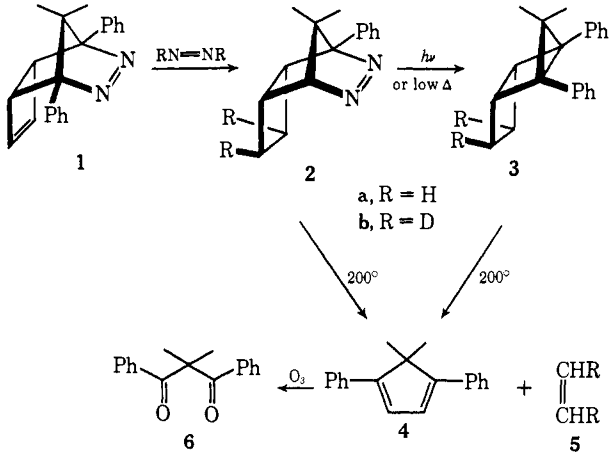
Received June 25, 1971

Pyrolysis of *anti*-Tricyclo[3.2.0.0^{2,4}]heptanes. The Role of 2,4 Substitution in the Operation of σ Bond Assisted Cyclobutane Fragmentations

Sir:

We wish to report discovery of the first example in which highly stereoselective cycloreversion of a cyclobutane to olefinic products according to the $[{}_\sigma2_s + {}_\sigma2_s]$ mode becomes energetically accessible and possibly concerted due to the suprafacial fragmentation of a third proximate σ bond. The resulting novel $[{}_\sigma2_s + {}_\sigma2_s + {}_\sigma2_s]$ fragmentation follows a least motion path and contrasts with the severe distortions associated with the $[{}_\sigma2_a + {}_\sigma2_s]$ pathway otherwise demanded of concerted cyclobutane fragmentations.[1,2] The results to be described demonstrate that the proper juxtaposition of a relatively weak σ bond effectively obviates the necessity of twisting the four-membered ring at the transition state as well as the need for generating 1,4-diradical intermediates.

The synthetic scheme outlined below afforded a convenient route not only to **3a** but also to its 6,7-cis,exo dideuterio analog **3b**. Diimide readily (90%) reduced tricyclic azo compound **1**[3] to **2a**, mp 97–99° dec;[4] subsequent photolysis (100%, 200-W lamp, ether, Pyrex optics) or pyrolysis (>95%, 140°, 5 hr, $CHCl_3$) of **2a** gave **3a**, a colorless viscous oil.[4,5] An identical



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(1) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, p 65 ff.

(2) L. A. Paquette and J. A. Schwartz, *J. Amer. Chem. Soc.*, **92**, 3215 (1970), and pertinent references cited therein.

(3) L. A. Paquette and L. M. Leichter, *ibid.*, **92**, 1765 (1970); in press.

(4) Satisfactory spectral and analytical data were obtained for each new compound footnoted.

(5) For **3a**: $\delta_{\mathrm{max}}^{\mathrm{CDCl_3}}$ 7.67 (m, 10), 3.60 (m, 2), 1.82 (m, 4), 0.85 (s, 3), and 0.22 (s, 3). In **3b**, the multiplets at 3.60 and 1.82 are significantly sharpened and the 1.82 absorption displays a relative intensity of 2 H.

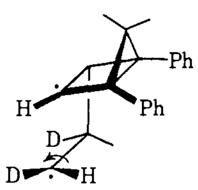
Table I. Deuterated Ethylenes from Pyrolysis at 210°

		Products, % yield				
		Absolute			Relative	
Run no.	Reactant	$CH_2{=}CHD$[a]	$^{D}_{H}{>}C{=}C{<}^{D}_{H}$	$^{D}_{H}{>}C{=}C{<}^{H}_{D}$	$^{D}_{H}{>}C{=}C{<}^{D}_{H}$	$^{D}_{H}{>}C{=}C{<}^{H}_{D}$
1	**2b**	10.2	82.1	7.7	91.4	8.6
2	**2b**	11.5	79.0	9.5	89.3	10.7
3	**3b**	9.8	82.0	8.2	90.9	9.1
4	**3b**	10.7	81.0	8.4	90.7	9.3

[a] Consistently, *ca.* 10% monodeuteration was encountered in the DN=ND reduction of **1** (mass spectral analysis of **2b** and **3b**); no prodution of **2a** and **3a** was noted. The ethylene analyses are in full agreement with the mass spectral data. The chemical shift for the protons in the $CH_2{=}CHD$ (double irradiation conditions) is found at 533.4 Hz.[8]

preparation of **3a** starting with dideuteriodiimide proceeded with equal efficiency.[5] When heated to 200°, **3** underwent ready fragmentation exclusively to ethylene and 1,4-diphenyl-5,5-dimethylcyclopentadiene (**4**), mp 96–98°.[4,6] At this temperature, the **2** $\rightarrow$ **3** conversion is so rapid that the product mixture is independent of which of the two is used as reactant. The stereochemistry attending the production of ethylene was studied by pyrolysis of **2b** and **3b** in sealed tubes. The results are summarized in Table I. For analysis, the 1,2-dideuterioethylene produced was transferred on a high-vacuum line to an nmr tube containing CCl_4–10% TMS (0.3 ml). The relative proportions of *cis*- and *trans*-**5b** were then determined by deuterium-decoupled proton nmr spectroscopy.[7] The relative intensities of the absorptions due to *cis*- (532.1 Hz)[8] and *trans*-1,2-dideuterioethylene (532.7 Hz)[8] indicated that 90 ± 1% of the cis isomer was present in the pyrolysis mixtures. Previous studies have shown that cis–trans isomerization of 1,2-dideuterioethylene is negligible at temperatures as high as 450° under similar conditions.[9] Some minor amount of equilibration in **2b** and **3b** cannot be summarily dismissed; however, nmr monitoring of these reactions indicated that such interconversions are not significant if operative.

These results show that opening of the *anti*-tricycloheptane nucleus occurs in highly stereoselective fashion with a preference for double retention of approximately 9. This ratio is substantially greater than the corresponding $({}_{\sigma}2_s + {}_{\sigma}2_s)/({}_{\sigma}2_a + {}_{\sigma}2_s)$ ratio found with 7,8-*cis,exo*-dideuterio-*cis*-bicyclo[4.2.0]octane (*i.e.*, 0.75),[9] in agreement with the simplistic orbital symmetry analysis given above. Also, the product distribution appears sufficient to dismiss the intervention of diradical intermediates such as **7** and **8**. If formed, such species would be expected[9,10] to undergo rather extensive bond rotation[11] (*cf.* arrows—no directional preference intended) with resultant disruption of the stereochemical sense of the fragmentation. This interpretation is further bolstered by the established need for phenyl substitution at C_2 and/or C_4.



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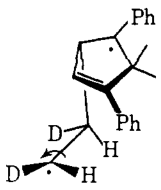

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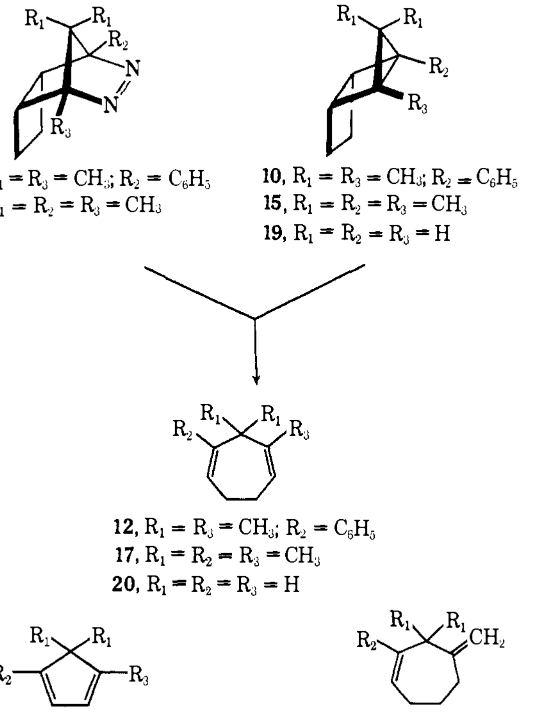
For example, although pyrolysis (210°, 4 hr, neat) of **9** or **10** did result in cycloreversion to ethylene and cyclopentadiene **11**,[4] this pathway in this instance represents only 55% of the total reaction. There was also obtained a difficultly separable mixture of **12** (~15%), **13** (~15%), and a remaining uncharacterized substance (~15%). In the case of **14**[4] and **15**[4] (210°, 1.5 hr, neat), the extent of cyclopentadiene production decreased still further to <2.5%. The formal rearrangement products consisted of **17**[4] (50%) and **18**[4] (21%); tricycloheptane **15** was also recovered (29%).



9, $R_1 = R_3 = CH_3$; $R_2 = C_6H_5$
14, $R_1 = R_2 = R_3 = CH_3$

10, $R_1 = R_3 = CH_3$; $R_2 = C_6H_5$
15, $R_1 = R_2 = R_3 = CH_3$
19, $R_1 = R_2 = R_3 = H$

12, $R_1 = R_3 = CH_3$; $R_2 = C_6H_5$
17, $R_1 = R_2 = R_3 = CH_3$
20, $R_1 = R_2 = R_3 = H$

11, $R_1 = R_3 = CH_3$; $R_2 = C_6H_5$
16, $R_1 = R_2 = R_3 = CH_3$

13, $R_1 = CH_3$; $R_2 = C_6H_5$
18, $R_1 = R_2 = CH_3$

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(6) Confirmation of the latter structural assignment was derived from ozonolysis to diketone **6** of unequivocal constitution: A. B. Evnin, D. R. Arnold, L. A. Karnischky, and E. Strom, *J. Amer. Chem. Soc.*, **92**, 6218 (1970).

(7) This elegant method of analysis was first suggested to us by Professor G. Closs, whom we also thank for the spectral determinations cited herein.

(8) Downfield from TMS at 100 MHz.

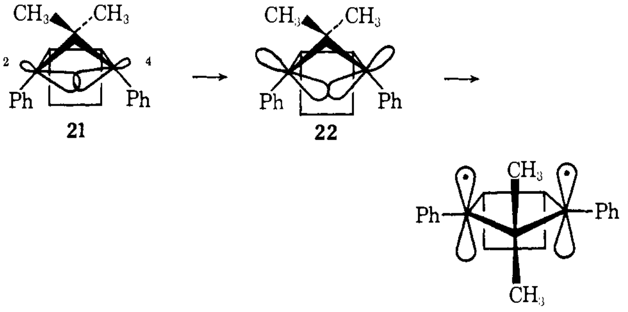
(9) J. E. Baldwin and P. W. Ford, *J. Amer. Chem. Soc.*, **91**, 7192 (1969).

(10) L. A. Paquette and G. L. Thompson, *ibid.*, **93**, 4920 (1971).

(11) There exists no apparent reason why k_{rot} (either direction) should not be competitive with k_{scis} in these intermediates: H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968); L. M. Stephenson and J. I. Brauman, *J. Amer. Chem. Soc.*, **93**, 1988 (1971).

As expected,[12] the parent *anti*-tricyclo[3.2.0.0^{2,4}]heptane (**19**) gave rise only to 1,4-cycloheptadiene (**20**) when heated at 173° for 15 min.

The subtle role played by the phenyl groups at C_2 and C_4 may be rationalized in stereoelectronic terms. Such aryl substituents are certain to weaken the C_2–C_3 bond of the tricycloheptane nucleus (*cf.* **21**). As fragmentation of this bond commences, progressive rehybridization in the sp^2 direction[13] will lead through **22** to **23**. Whether the two cyclobutane bonds rupture at intermediate stage **22** where the orbitals of the C_2–C_4 bond have become well canted but not yet completely severed (leading to a concerted reaction) or only after diradical **23** is formed (formally now a stepwise process) is of course not known. The data require only that the two edge bonds in the four-membered ring break essentially simultaneously. The inability of alkyl groups or hydrogen atoms to accomplish a similar end result may be associated with the fact that the C_1–C_5 and C_2–C_4 bonds in these molecules undergo rupture at approximately the same rate because their inherent dissociation energies are quite similar. The phenyl groups can be expected to weaken the C_2–C_4 bond. Surprisingly, however, such substitution provides little acceleration (estimated $\Delta H^{\ddagger} \sim 39$ kcal/mol for **3** → **4** + **5**)[14] suggestive perhaps of substantial steric hindrance to proper orientation of the phenyl rings.



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22

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Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

[12] H. Tanida, S. Teratake, Y. Hata, and M. Watanabe, *Tetrahedron Lett.*, 5345 (1969). These workers have reported the conversion of **19** into a 10:1 mixture of two compounds under these conditions. The minor product in our runs was found to be unreacted **19**.

[13] Such hybridization will accord maximum stabilization to the odd electron centers.

[14] We thank Professor John Brauman for his comments on this point.

[15] National Institutes of Health Predoctoral Fellow, 1969–present.

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Received June 25, 1971

Potential of Ion Cyclotron Resonance Spectroscopy for the Study of the Intrinsic Properties and Reactivity of Transition Metal Complexes in the Gas Phase. Ion–Molecule Reactions of Iron Pentacarbonyl

Sir:

Ion cyclotron resonance spectroscopy (icr) has proven to be a powerful technique for studying ion–molecule reactions.[1] With the exception of several hydrides,[1–7] however, relatively little research has been concerned with inorganic compounds, and, in particular, transition metal complexes have not been examined. We wish to report the gas-phase ion chemistry of iron pentacarbonyl, both alone and in binary mixtures, indicating the tremendous potential of icr studies for illuminating certain aspects of inorganic and organometallic chemistry.

The volatile iron pentacarbonyl is a logical choice for initial icr studies of metal complexes. The icr spectrum of $\mathrm{Fe(CO)_5}$[8] at low pressure is in qualitative agreement with previous electron[9–12] and photon[13] impact results; the ions present at an electron energy of 70 eV include most prominently the species $\mathrm{Fe(CO)}_n^+$ (n = 0–5). Within the mass range of the present instrument (∼260 amu), ion–molecule reaction products are observed at higher pressures in $\mathrm{Fe(CO)_5}$ at *m/e* 224 and 252, corresponding to $\mathrm{Fe_2(CO)_4^+}$ and $\mathrm{Fe_2(CO)_5^+}$, respectively. Double-resonance experiments indicate reactions 1–4 to be responsible for the formation of these binuclear species.

$$\mathrm{Fe^+ + Fe(CO)_5 \longrightarrow Fe_2(CO)_4^+ + CO} \qquad (1)$$

$$\mathrm{FeCO^+ + Fe(CO)_5 \longrightarrow Fe_2(CO)_4^+ + 2CO} \qquad (2)$$

$$\mathrm{FeCO^+ + Fe(CO)_5 \longrightarrow Fe_2(CO)_5^+ + CO} \qquad (3)$$

$$\mathrm{Fe(CO)_2^+ + Fe(CO)_5 \longrightarrow Fe_2(CO)_5^+ + 2CO} \qquad (4)$$

Binary mixtures of $\mathrm{Fe(CO)_5}$ with $\mathrm{CH_3F}$, $\mathrm{H_2O}$, $\mathrm{NH_3}$, and HCl were examined principally to delineate the occurrence of ligand displacement reactions. For example, the ligand substitution reactions of eq 5 are

$$\mathrm{Fe(CO)}_n^+ + \mathrm{CH_3F} \longrightarrow \mathrm{Fe(CH_3F)(CO)}_{n-1}^+ + \mathrm{CO}\ (n = 1\text{–}4) \qquad (5)$$

observed when $\mathrm{CH_3F}$[14] is added to $\mathrm{Fe(CO)_5}$. At the highest $\mathrm{CH_3F}$ pressures employed, 2×10^{-4} Torr, only one CO group is replaced in any of the $\mathrm{Fe(CO)}_n^+$ (n = 1–4) ions, and $\mathrm{Fe(CO)_5^+}$ remains inert toward substitution of CO by $\mathrm{CH_3F}$. Additional reaction products observed are $\mathrm{CH_3Fe(CO)_4^+}$ and $\mathrm{CH_3Fe(CO)_5^+}$, derived primarily from the dimethylfluoronium ion[14] in reactions 6 and 7. Reaction 6 is an example of an

$$\mathrm{(CH_3)_2F^+ + Fe(CO)_5} \longrightarrow \begin{cases} \mathrm{CH_3Fe(CO)_5^+ + CH_3F} & (6) \\ \mathrm{CH_3Fe(CO)_4^+ + CO + CH_3F} & (7) \end{cases}$$

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[1] For a description of the instrumental techniques employed, see D. Holtz, J. L. Beauchamp, and J. R. Eyler, *J. Amer. Chem. Soc.*, **92**, 7045 (1970).

[2] D. Holtz and J. L. Beauchamp, *ibid.*, **91**, 5913 (1969).

[3] R. Dunbar, *ibid.*, **90**, 5676 (1968).

[4] W. T. Huntress, Jr., M. M. Mosesman, and D. D. Elleman, *J. Chem. Phys.*, **54**, 843 (1971).

[5] S. E. Buttrill, Jr., *J. Amer. Chem. Soc.*, **92**, 3560 (1970).

[6] J. Brauman and K. Smyth, *ibid.*, **91**, 7778 (1969).

[7] J. L. Beauchamp and S. E. Buttrill, Jr., *J. Chem. Phys.*, **48**, 1783 (1968).

[8] The only difficulty encountered in handling iron pentacarbonyl in the icr spectrometer was the formation of conducting paths between the filament and the adjacent trapping plate. This was controlled by machining the filament support block such that iron shadowed from the filament did not form a complete conducting pathway.

[9] R. E. Winters and R. W. Kiser, *Inorg. Chem.*, **3**, 699 (1964).

[10] A. Foffani, S. Pignataro, B. Cantone, and F. Grasso, *Z. Phys. Chem. (Frankfurt am Main)*, **45**, 79 (1965).

[11] D. R. Bidinosti and N. S. McIntyre, *Can. J. Chem.*, **45**, 641 (1967).

[12] G. A. Junk and H. J. Svec, *Z. Naturforsch. B*, **23**, 1 (1968).

[13] Reliable thermochemical data on the ions formed are provided in G. Distefano, *J. Res. Nat. Bur. Stand., Sect. A*, **74**, 233 (1970).

[14] For a description of the gas-phase ion chemistry of $\mathrm{CH_3F}$, see A. G. Marshall and S. E. Buttrill, Jr., *J. Chem. Phys.*, **52**, 2752 (1970).