would not be appreciably populated in cases in which the ion is formed from a variety of precursors using electrons of a broad energy range, however.

In order to demonstrate the ease of application of this reaction to structural problems, various compounds which produce abundant C_3H_6 radical cations in their mass spectra were studied. Examples undergoing reactions 1 and 2 are presented in Table I. The C_3H_6 ions produced by the ionization of cyclopropane and the fragmentation of tetrahydrofuran react identically with ammonia at both high and low ionizing energies. These results demonstrate the equivalence of the C_3H_6 ions, a fact consistent with thermochemical measurements.[9]

Table I. Relative Abundance of *m*/*e* 30 and 31 Produced in Reactions 1 and 2[a]

$V - E$, eV[b]	c-C_3H_6		THF		Cyclohexanone		Hexamethylene oxide	
10	0.075	0.065	0.079	0.070	0.052	0.040[c]	0.040	0.02
7	0.073	0.065	0.075	0.068	0.055	0.040	0.041	0.02
3	0.10	0.08	0.12	0.09				
1.1	0.18	0.12	0.16	0.10	0.16	0.08	0.19	0.05

[a] $P = 1 \times 10^{-5}$ Torr, mixture of 4:1 NH_3:C_3H_6X. Column 1 is $I_{30}/(I_{42} + I_{30} + I_{31})$, column 2 is $I_{31}/(I_{42} + I_{30} + I_{31})$. [b] V = electron energy. E = appearance potential of C_3H_6. [c] Corrected for trace of *m*/*e* 31 found in single-resonance spectrum of cyclohexanone.

The high-resolution mass spectrum of cyclohexanone shows that *m*/*e* 42 is approximately 70% $C_3H_6\cdot^+$,[10] consistent with the somewhat lower abundances of *m*/*e* 30 and 31 relative to the total *m*/*e* 42 ions. In hexamethylene oxide, metastable ions are found which indicate that $C_3H_6\cdot^+$ is produced from both *m*/*e* 72 ($C_4H_8O\cdot^+$) and *m*/*e* 70 ($C_5H_{10}\cdot^+$).[11] Since various C_5H_{10} ions (1-pentane and cyclopentene) produce C_3H_6 ions which are unreactive with ammonia (*vide infra*), the lower abundance of *m*/*e* 30 and 31 can be also understood.

The increased product-ion abundance of *m*/*e* 30 and 31 at lower ionizing energies (Table I) has been previously observed for other ion–molecule reactions[12] and is consistent with the intermediacy of a collision complex which decays relatively more rapidly to starting materials than to products at higher internal energies.

A variety of compounds produce $C_3H_6\cdot^+$ in their unimolecular fragmentation which are unreactive with ammonia. In addition to propene, these are 1-chloropropane, cyclopentane, 1-pentene, 2,5-dihydrofuran, and 2,3-dimethylbutane. The result for 1-chloropropane is in contrast to the behavior shown by 1-chlorobutane-*3,3*-d_2, in which 93% 1,3 elimination takes place.[13] However, in 1-chloropropane, the formation of cyclic $C_3H_6\cdot^+$ would involve the loss of a primary hydrogen atom, which is known to be less favored than loss of a secondary. It is also possible that rearrangement occurs during or after the production of a cyclic $C_3H_6\cdot^+$.

Of course all C_3H_6 ions exhibiting the same reactivity (or lack of reactivity) to NH_3 are not necessarily of identical structure. For example, $C_3H_6\cdot^+$ produced from the compounds in Table I could possess either a cyclic or an acyclic structure ($\cdot CH_2CH_2CH_2^+$), and some isomerization to produce a propene-like ion could have taken place. Further studies are underway to clarify these points and to test the generality of this reaction involving other cyclic hydrocarbons and other nucleophiles.

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Carbon-13 Chemical Shifts in 1-Substituted Bicyclo[2.2.2]octanes[1]

Sir:

The ideas of *field effects* and *through-space effects* have long been of interest in the study of substituent effects on reactivity[2] in organic chemistry. However, these ideas and their relationships to the concepts of *resonance effects* and *inductive effects* have been difficult to define precisely or to demonstrate clearly by experiments. Probably the most promising experimental approaches have employed bicyclic compounds.[3]

Chemical reactivity parameters and the language of organic substituent effects have been applied extensively in nmr interpretations, especially for the proton, ^{19}F, and ^{13}C nuclei.[4] Recent developments in the techniques, equipment,[5] and theory[6] of ^{13}C nmr guarantee

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[1] Supported by Grant No. PRF 3310-A4,5 from the Petroleum Research Fund, administered by the American Chemical Society.

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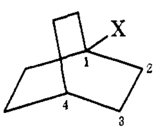
Table I. ^{13}C Chemical Shifts of 1-Substituted Bicyclo[2.2.2]octanes[a]

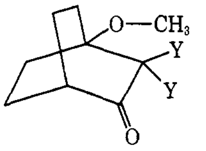
Substituent	Carbon atom[b] 1	2	3	4	CH_3CH_2X[c] CH_2	CH_3
H	3.01	0.89	0.89	3.01	0.0	0.0
OCH_3	−45.35 (−48.36)[d]	−2.36 (−3.25)	0.00 (−0.89)	2.69 (−0.32)	−62.5	−9.4
F	−65.47 (−68.48)	−4.30 (−5.19)	−0.38 (−1.27)	2.74 (−0.27)	−73.4	−6.7
Cl	−39.26 (−42.27)	−9.25 (−10.14)	−1.25 (−2.14)	3.64 (+0.63)	−33.5	−12.0
Br	−35.88 (−38.89)	−10.61 (−11.50)	−2.14 (−3.03)	4.22 (+1.21)	−22.5	−14.5

[a] Shifts reported here in parts per million with respect to 5% internal cyclohexane and were determined to ±0.01 ppm. Positive shifts correspond to larger shieldings. [b] The numbering of carbons corresponds to structure I. [c] ^{13}C chemical shifts of the corresponding ethyl compounds with respect to ethane. These numbers were derived from ref 12 except for the methoxy substituent for which data were obtained in this work. [d] Values in parentheses are differences between observed values for a given substituent and the corresponding value for the unsubstituted hydrocarbon, RH.

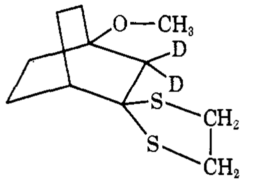
an important role for ^{13}C approaches in the study of substituent effects. Accordingly, we have undertaken a systematic ^{13}C nmr study of certain aspects of this area and here report preliminary results on 1-substituted bicyclo[2.2.2]octanes (I), a system of the type frequently chosen for the study of field effects.



I = RX; X = F, Cl, Br, OCH_3, H



IIa, Y = H, H
b, Y = D, D



III

Bicyclo[2.2.2]octane, RH, was obtained from Chemical Samples Company. All of the other compounds were prepared from the intermediate, 4-methoxybicyclo[2.2.2]octan-2-one (IIa). The undeuterated materials were prepared from IIa *via* 1-methoxybicyclo-[2.2.2]octane, $ROCH_3$, which was obtained by a Wolf–Kischner reduction.[7] The 1-halobicyclo[2.2.2]-octanes, RF, RCl, and RBr, were prepared from $ROCH_3$ by reactions with acetyl fluoride, chloride, and bromide, respectively, under previously reported conditions.[7,8] The 2,2-dideuterio analogs of I were prepared from IIa by first introducing deuterium α to the carbonyl in a basic D_2O exchange reaction, and converting the resulting 2,2-dideuterioketone to the thioketal III with ethanedithiol.[9] Compound III was converted by Raney nickel reduction to 2,2-dideuterio-1-methoxybicyclo[2.2.2]octane, which served as an intermediate analogous to $ROCH_3$ in the conversion to the dideuterio analogs of RCl and RBr.

Carbon-13 spectra were obtained in natural abundance at 25.144 MHz with pseudo-random noise-modulated proton decoupling, using a center-band-sweep, ^{19}F-lock spectrometer system.[5] The samples were 2 *m* in CCl_4, with 5% cyclohexane added as an internal standard. The results are given in Table I. The assignments of signals to carbons 1 and 4 and to carbons 2 and 3 were based upon off-resonance proton decoupling.[10] For the cases X = Cl, Br, and OCH_3, the assignments of carbons 2 and 3 were based upon spectra of the corresponding compounds with deuterium replacing hydrogen on carbon 2, the splittings due to deuterium clearly identifying the carbons to which they were attached. In no case were additional deuterium splittings observed on carbon atoms other than carbon 2.

The remaining assignments were inferred from the cases unequivocally assigned and in the case of X = F from the long-range J_{CF} values ($|^1J_{CF}| = 185.3$ Hz, $|^2J_{CF}| = 18.4$ Hz, $|^3J_{CF}| = 9.4$ Hz, and $|^4J_{CF}| = 3.3$ Hz, based upon these assignments for carbons 2 and 3).[11]

The chemical shifts in Table I show substantial ranges within each column. As one might expect, these ranges decrease in magnitude in the order $C_1 > C_2 > C_3 > C_4$, reflecting a decreasing magnitude of substituent effect with increasing separation from the substituent. While there is no theory now available that is capable of accounting for these data quantitatively, some interesting patterns emerge on which tentative interpretations can be based.

The order of shieldings for C_1 is the same as that reported previously for CH_2 in the analogous ethyl compounds.[12] This order is presumably due both to the immediate electronic distribution about the C_1 atoms and the neighbor anisotropy effect exerted by the substituent. Also, the chemical shifts of the C_2 carbons follow the same order, except for the methoxy substituent,[13] as that reported previously for CH_3 in the analogous ethyl compounds.[12,13] Thus, these two sets of shifts also reflect similar substituent effects, in which the neighbor anisotropy effect is presumably grossly diminished. Furthermore, the chemical shifts of the C_3 carbons in I follow the same order as those of C_2, indicating substantially similar mechanisms by

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which the substituent exerts its influence on the shieldings of these carbons. An attenuation factor of about 4 seems to apply to the substituent effects at these two carbons; this does not seem unreasonable for a mechanism that is propagated through a σ-carbon network.[14]

In view of the relationship between the shieldings of C_2 and C_3, it is noteworthy that the C_4 shieldings do not follow the same order. Indeed, except for X = H, the C_4 shieldings follow the opposite order from that of C_2 and C_3. These results seem to point toward one of two possibilities: either there is a through-bond, substituent-effect mechanism that is merely attenuated between C_2 and C_3 but changes sign between C_3 and C_4, or else a substantially different mechanism is operative at C_4, perhaps a field effect. Additional experiments and theoretical approaches aimed at clarifying this point are under way.

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Catalysis of Symmetry-Restricted Reactions by Weak Lewis Acids

Sir:

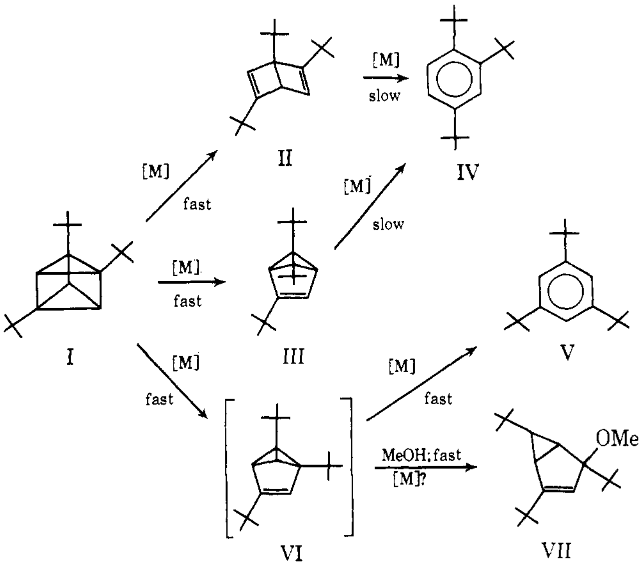
We report evidence that, for a sufficiently strained system, reactions which are thermally symmetry restricted (${}_{\sigma}2_a + {}_{\sigma}2_a$ and ${}_{\sigma}2_s + {}_{\sigma}2_s$) can be catalyzed, quite dramatically in some cases, by a large number of substances which all share the features of being moderate to weak Lewis acids.

These reactions have been investigated for the tri-*tert*-butylprismane I[1] which, together with the tri-*tert*-butyl(Dewar benzene) II,[1] the tri-*tert*-butylbenzvalene III,[1] and 4-methoxy-2,4,6-tri-*tert*-butylbicyclo[3.1.0]-hex-2-ene (VII) have been prepared and characterized by Kaplan and Wilzbach and their collaborators.[2-4]

In the absence of acid or other catalysts the prismane was relatively stable thermally; it decomposed only slowly in pyridine at 110° to give the benzenes IV and V in a 1:1 ratio ($t_{1/2}$ = 18 hr).

In contrast, catalytic quantities (*ca.* 0.01 *M*) of a large number of metal complexes at 25–30° in methanol converted I into the Dewar benzene II, the benzvalene III, and, probably, also into the benzvalene VI[1] (see Table I and Scheme I). Some of the catalysts ($AgNO_3$, $SnCl_2$, Na_2PdCl_4, and $[Rh(CO)_2Cl]_2$) also isomerized II and III to IV in slower subsequent steps. These reactions are also thermally symmetry restricted and will be discussed later.

Scheme I



The benzvalene VI is unstable and isomerizes readily to V, or, in the presence of methanol, gives the bicyclohexene VII.[4] Since the latter was frequently detected in the catalyzed reactions and the benzene V was obtained in the $AgNO_3$-catalyzed reactions, we presume that both of these compounds arose from VI here too. These reactions may also have been accelerated by the catalysts used.

The prismane I also reacted with protonic acids; however, 0.003 *M* hydrochloric acid in methanol at 30° only isomerized I to IV ($t_{1/2}$ = 35 min). Since both II and III were unchanged under *these* conditions, they cannot be intermediates in the formation of IV which presumably involves a protonation step. As the asymmetric benzene IV was formed in only negligible amounts in the other reactions (see Table I), these isomerizations were not due to the adventitious presence of traces of acid.

All the metal-catalyzed reactions (except, possibly, those where $t_{1/2} < 1$ min, which were not studied) appear, from our preliminary data, to be first order in I. This has been rigorously established for the $\{Rh(CO)_2Cl\}_2$-catalyzed reaction in methanol, which is also approximately first order in catalyst (pseudo-first-order rate constant for the disappearance of I is $4.4 \pm 0.6 \times 10^{-4}$ sec^{-1} at 37°, $[\{Rh(CO)_2Cl\}_2] = 3 \times 10^{-4}$ mol l.$^{-1}$, [I] = 6×10^{-2} mol l.$^{-1}$).

The most remarkable feature of the results is that such a wide variety of catalysts, including Hg(II), Sn(II), Zn(II), and Pb(II) salts and *sym*-trinitrobenzene, are effective. Although pyridine, when used as solvent, deactivated some catalysts completely ($ZnCl_2$, $Pb(OAc)_2$, $[Cu(OAc)_2]_2$, and $Co(acac)_3$), others, such as $HgCl_2$, $AgNO_3$, or $SnCl_2$, were still active, though at a somewhat reduced rate. This inhibition is not unexpected; since pyridine is a good ligand to most metals there will be competition between it and I for the catalyst.

The product distribution varied with the catalyst; some ($HgCl_2$, $SnCl_2$) favored formation of the Dewar benzene II, others ($AgNO_3$, $Co(acac)_3$), the benzvalene III (or VI). If concerted, these reactions would be examples of (${}_{\sigma}2_s + {}_{\sigma}2_s$) and (${}_{\sigma}2_a + {}_{\sigma}2_a$) reactions, respectively.

A number of examples of the catalysis of symmetry-restricted (${}_{\sigma}2_s + {}_{\sigma}2_s$)[5-11] and (${}_{\sigma}2_a + {}_{\sigma}2_a$)[12,13] reactions

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(1) The systematic names for the compounds are 1,3,5-tri-*tert*-butyltetracyclo[$2.2.0.0^{2,6}.0^{3,5}$]hexane (I), 1,2,5-tri-*tert*-butylbicyclo[2.2.0]-hexa-2,4-diene (II), 1,3,6-tri-*tert*-butyltricyclo[$3.1.0.0^{2,6}$]hex-3-ene (III), and 1,2,4-tri-*tert*-butyltricyclo[$3.1.0.0^{2,6}$]hex-3-ene (VI).

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