125 ml. of water were added. The resulting solution was extracted with three 50-ml. portions of pentane. The pentane solution was washed with a dilute sodium bicarbonate solution, dried over magnesium sulfate, and decanted into a one-necked round-bottom flask. The pentane solution was concentrated at 45–50° through a 1-ft. Vigreux column. A 0.02–0.05-ml. sample was injected into a XF-1150 (silicon nitrile) on Chromosorb P column at 90°. After the *exo*-norbornyl acetate came off the column, the temperature was raised to 170°. The areas for the various peaks were measured by means of a disk chart integrator. All of the product analyses as well as the controls on the extraction procedure were done in this manner. The extraction procedure was found to be accurate to ±2% for three determinations. For the runs in aqueous ethanol, the 0.02–0.05-ml. sample of the pentane extract was injected into the column at 170°.

Stability Determinations.—In a typical experiment, 0.3124 g. of *exo*-norbornyl *p*-trifluoromethylthionbenzoate and 0.1823 g. of *exo*-norbornyl *p*-trifluoromethylthiolbenzoate were dissolved in 10 ml. of acetic acid. The solution was degassed and heated at 140.0° for 130 hr. This solution was analyzed by v.p.c. as described previously. The analysis showed 0.235 g. of thiol ester which corresponds to all of the added thiol ester as well as an additional 17% formed in the solvolysis reaction. All of the stability runs in acetic acid and with added lithium perchlorate were done in this manner.

To check the stability of *exo*-norbornyl *p*-trifluoromethylthiolbenzoate in aqueous ethanol, 0.7509 g. of the thiol ester was dissolved in 85% aqueous ethanol and the solution was heated at 125° for 13.5 days. The solution was analyzed by vapor phase chromatography as described previously. Only 75% of the original thiol ester was detected in this experiment.

Optical Stability of *exo*-Norbornyl *p*-Trifluoromethylthiolbenzoate.—A solution of 0.06 g. of optically active *exo*-norbornyl *p*-trifluoromethylthiolbenzoate and 0.272 g. of *exo*-norbornyl *p*-trifluoromethylthionbenzoate in 5 ml. of acetic acid, α +0.26 ±0.02°, was heated at 140° for 70 hr. at which time the optical rotation was 0.25 ± 0.02°. A 1-dm. polarimeter tube was used to determine the optical rotation.

Exchange.—A solution of 0.357 g. of *exo*-norbornyl *p*-trifluoromethylthionbenzoate and 0.615 g. of potassium thiobenzoate in 10 ml. of acetic acid was heated at 140° for 130 hr. By vapor phase chromatography, no *exo*-norbornyl thionbenzoate was detected under conditions such that 1% was easily observed.

Isolation of Thiol Ester.—A solution of 3.004 g. of optically active *exo*-norbornyl *p*-trifluoromethylthionbenzoate in 50 ml. of acetic acid, α +2.80°, was heated at 140° for 130 hr. The solution was cooled, 250 ml. of water was added, and the resulting solution was extracted with two 100-ml. portions of pentane. The pentane extract was washed with a dilute sodium bicarbonate solution, dried over magnesium sulfate, and decanted into a one-necked round-bottom flask. The pentane solution was concentrated to *ca.* 10 ml. at 45–50° through a 1-ft. Vigreux column. A 0.3–0.5-ml. sample was injected into an XF-1150 on Chromosorb P column at 170°. The *exo*-norbornyl *p*-trifluoromethylthiolbenzoate (0.314 g.) was collected and dissolved in 5 ml. of acetic acid. The resulting solution had an optical rotation of 0.00 ± 0.02° in a 1-dm. tube. The thiol ester was found to be optically stable under the v.p.c. conditions.

An Electron Impact Study of Norbornenyl and Nortricyclyl Chlorides

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An electron impact study of norbornene, *endo*- and *exo*-5-chloro-2-norbornene, and 3-chloronortricyclene is presented. The fragmentation pattern of each of these compounds is discussed. Appearance potentials of the major ions have been measured and are compared for each compound.

For the last 15 years bicyclo[2.2.1] systems have been the subject of extensive investigations; particular interest has centered around bicyclic cations as reactive intermediates.[2] There remain many questions about the nature of these species, one of the most fundamental of which concerns the ease of ionization or dissociation of the parent compound as a function of molecular structure and reaction environment. Electron impact studies at low pressures can furnish fundamental information about primary ionization and dissociation processes of these compounds in the absence of solvent and also provide useful thermochemical data.[3] Although gaseous ions can be expected to behave differently from ions in solution, many results from such investigations may be pertinent to reactions in condensed phases.

We have carried out an electron impact study of *exo*- and *endo*-5-chloro-2-norbornene and 3-chloronortricyclene, all of which have previously been investigated in solution. It has been observed, for instance, that the *exo*-chloronorbornene solvolyzes much more rapidly than its *endo* epimer, the products from both isomers being predominantly nortricyclic compounds.[4,5] In our work we have been concerned primarily with the fragmentation patterns of these chloro compounds and the relative appearance potentials of several ions, the most significant of which are $C_7H_9Cl^+$, $C_7H_9^+$, $C_6H_7^+$, and $C_5H_6^+$. Using our observed appearance potentials for the C_5H_6 cation, we have also estimated the heats of formation of the compounds.

Experimental

The mass spectra and appearance potentials were measured on a Consolidated Electrodynamics Model 21-103C mass spectrometer with the ion source at 225° and the inlet system at ambient temperature. A rhenium filament was used in the ion source. Mass spectra were obtained using 70-v. electrons and voltage scanning. The method of measuring appearance potentials has been previously described.[6]

An Aerograph Model A-90-P (Wilkens Instrument and Research, Inc.) was used for all gas chromatography. Infrared spectra were taken on a Perkin-Elmer Model 137B Infracord; samples were neat except for norbornene which was dissolved in carbon tetrachloride. N.m.r. spectra were obtained on a

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[1] To whom correspondence should be addressed: Department of Chemistry, Harvard University.

[2] For recent discussions of this subject, see the following: (a) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962; (b) J. Berson in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3; (c) G. D. Sargent, Ph.D. Thesis, Harvard University, 1964.

[3] (a) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York, N. Y., 1957; (b) S. Winstein and F. P. Lossing, *J. Am. Chem. Soc.*, **86**, 4485 (1964).

[4] J. D. Roberts, W. Bennett, and R. Armstrong, *ibid.*, **72**, 3329 (1950).

[5] J. D. Roberts and W. Bennett, *ibid.*, **76**, 4623 (1954).

[6] W. C. Steele, L. D. Nichols, and F. G. A. Stone, *ibid.*, **84**, 4441 (1962).

Varian A-60 spectrometer using deuteriochloroform as a solvent and tetramethylsilane as the internal reference.

Norbornene (practical grade, Matheson Coleman and Bell) was purified by gas chromatography[7] and identified by melting point (53°, lit.[8] m.p. 52–54°) and infrared spectrum (characteristic absorptions at 6.11, 6.20, and 6.39 μ[9]).

***exo*-5-Chloro-2-norbornene and 3-chloronortricyclene** were both prepared by addition of HCl to practical norbornadiene according to the method of Schmerling, *et al.*[10] The fraction boiling at 48–48.5° (20.5 mm.) [lit. b.p. 66–68° (43 mm.),[4] 38° (9 mm.)[10]], $n^{20}\text{D}$ 1.4948, $n^{25}\text{D}$ 1.4923 (lit. $n^{20}\text{D}$ 1.4949,[4] $n^{25}\text{D}$ 1.4909–1.4912[10]) was shown by gas chromatography[11] to be a 3:1 mixture of *exo*-5-chloro-2-norbornene and 3-chloronortricyclene. Samples of both compounds were purified by preparative gas chromatography and identified by elemental analysis and infrared and n.m.r. spectra.

Anal. Calcd. for C_7H_9Cl: C, 65.38; H, 7.05; Cl, 27.57. Found (for the norbornene derivative): C, 65.38; H, 7.26; Cl, 27.77. Found (for the nortricyclene derivative): C, 65.53; H, 7.09; Cl, 27.42.

The infrared spectrum of the chloronorbornene showed characteristic absorptions at 6.11, 6.37,[12] and 14.49 μ. The n.m.r. spectrum had multiplets centered at δ 6.06 (two vinyl H), 3.75 (one CHCl), 2.91 (two bridgehead H), and 1.70 (four C-6 and C-7 ring H). The infrared spectrum of the nortricyclene derivative was identical with that reported by Roberts for 3-chloronortricyclene.[5] The n.m.r. spectrum showed a single resonance at δ 3.87 for the proton on the carbon linked to chlorine. The remainder of the ring protons appeared as two unequal doublets with unresolved fine structure centered at δ 1.95 and 1.35.

***endo*-5-Chloro-2-norbornene.**—Synthesis was carried out by the Diels–Alder reaction between cyclopentadiene and vinyl chloride in a sealed tube.[5] The fraction boiling at 46.5° (16 mm.), $n^{25}\text{D}$ 1.4928 [lit.[5] b.p. 69–70° (40 mm.), $n^{25}\text{D}$ 1.4927], was shown by gas chromatography to contain approximately 40% *exo*- and 60% *endo*-5-chloro-2-norbornene. The latter was collected as eluted and identified by elemental analysis and infrared and n.m.r. spectra.

Anal. Calcd. for C_7H_9Cl: C, 65.38; H, 7.05; Cl, 27.57. Found: C, 65.31; H, 7.15; Cl, 27.52.

The infrared spectrum had characteristic bands at 6.10, 6.36,[13] and 14.31 μ.[9] The n.m.r. spectrum was the same as that reported for *endo*-5-chloro-2-norbornene.[13]

Stability of *endo*- and *exo*-5-Chloro-2-norbornene under Operating Conditions of the Mass Spectrometer.—Because the mass spectrum of *endo*-5-chloro-2-norbornene was essentially identical with that of the *exo* isomer, it was necessary to eliminate the possibility that rearrangement was occurring in the electron source of the mass spectrometer which was maintained at a block temperature of 225°. Pure samples of each isomer were injected into the gas chromatography with the temperature of the injector port at *ca.* 227° and that of the column and detector approximately the same as for preparative work. A major and a minor peak appeared in the chromatograms of each compound. The major component was collected and the infrared spectrum established that it was identical with the injected isomer. For the *exo*-5-chloro-2-norbornene, the fraction of total eluate represented by the small peak, presumably rearranged material, was never greater than 3% and frequently nearer 1–2% (injector temperature, 226–229°). For the *endo* compound, the small peak was *ca.* 1% at 227° (four runs) and 5% at 232° (one run).[14] Accordingly, the compounds were considered to have thermal stability adequate to our interpretations of the mass spectral data.

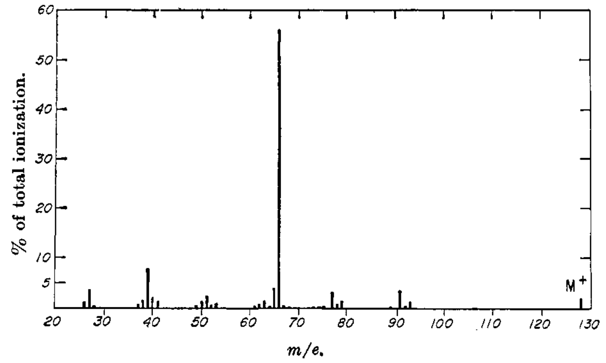

Figure 1.—The mass spectrum of *endo*-5-chloro-2-norbornene.

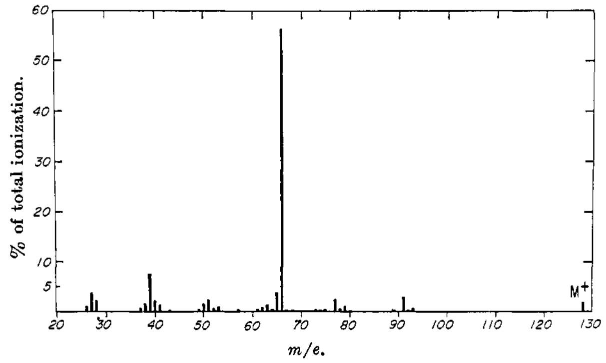

Figure 2.—The mass spectrum of *exo*-5-chloro-2-norbornene.

Results and Discussion

The mass spectra of the four compounds studied are illustrated in Figure 1–4. (The spectra have been corrected for *all* isotopes present.) The spectra indicate that the chlorinated compounds undergo primary decomposition according to the following scheme.

$$\begin{aligned} &\longrightarrow C_7H_9^+ + Cl && (1)\\ C_7H_9Cl^+ &\longrightarrow C_6H_7^+ + CH_2Cl && (2)\\ &\longrightarrow C_5H_6^+ + C_2H_3Cl && (3) \end{aligned}$$

Comparable reactions for norbornene are shown in eq. 4–6. Prominent secondary reactions (7–10) can be

$$\begin{aligned} &\longrightarrow C_7H_9^+ + H && (4)\\ C_7H_{10}^+ &\longrightarrow C_6H_7^+ + CH_3 && (5)\\ &\longrightarrow C_5H_6^+ + C_2H_4 && (6) \end{aligned}$$

deduced from metastable peaks at masses 89.0, 90.0, 75.1, and 64.0, respectively.

$$\begin{aligned} C_7H_9^+ &\longrightarrow C_7H_7^+ + H_2 && (7)\\ C_7H_8^+ &\longrightarrow C_7H_7^+ + H && (8)\\ C_6H_7^+ &\longrightarrow C_6H_5^+ + H_2 && (9)\\ C_5H_5^+ &\longrightarrow C_5H_4^+ + H && (10) \end{aligned}$$

Reverse Diels–Alder reactions (3 and 6), noted previously for norbornadiene[15] and $\Delta^{2,6}$-bicyclo[3.2.0]-

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[7] Column: 0.25 in. × 5 ft. containing DC-11 on Chromosorb W, 60–80 mesh (Wilkens Instrument and Research, Inc.); He carrier gas flow rate, 31 cc./min.; column temperature, 52°; detector temperature, 92°; injector temperature, 108°; retention time, 17 min.

[8] I. Heilbron and H. M. Banbury, "Dictionary of Organic Compounds," Eyre and Spottiswoode, London, 1953, p. 827.

[9] J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950); P. v. R. Schleyer, Thesis, Harvard University, 1954.

[10] L. Schmerling, J. P. Luvisi, and R. W. Welch [*J. Am. Chem. Soc.*, **78**, 2819 (1956)] estimated 80–84% *exo* chloride and 16–20% 3-chloronortricyclene based on infrared and hydrogenation data.

[11] Column: 0.25 in. × 10 ft. containing 10% Bentone 34 on Chromosorb W, 60–80 mesh (Wilkens Instrument and Research, Inc.); He carrier gas flow rate, 31 cc./min.; column temperature, 63°; detector temperature, 102°; injector temperature, 115°; retention times, *exo* chloride, 30 min., *endo* chloride, 45 min., and 3-chloronortricyclene, 41 min.

[12] P. v. R. Schleyer and M. M. Donaldson, *J. Am. Chem. Soc.*, **78**, 5702 (1956).

[13] P. Laszlo and P. v. R. Schleyer, *ibid.*, **85**, 2709 (1963).

[14] There was not enough material eluted under these peaks to allow identification but the retention times indicated *endo–exo* interconversion.

[15] S. Meyerson, J. D. McCollum, and P. N. Rylander, *J. Am. Chem. Soc.*, **83**, 1401 (1961).

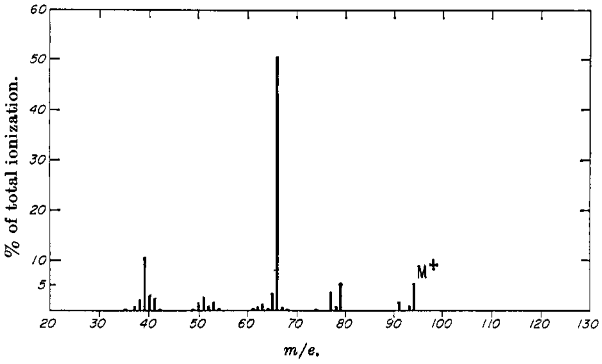

Figure 3.—The mass spectrum of norbornene.

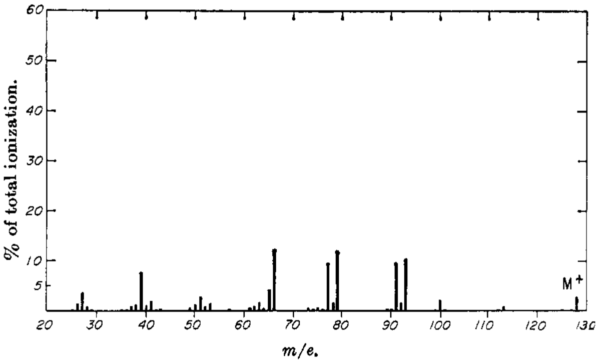

Figure 4.—The mass spectrum of 3-chloronortricyclene.

heptadiene,[16] dominate the spectra of norbornene and its chloro derivatives, all of which contain the C_5H_6 ring in the parent molecule. Since formation of the $C_5H_6^+$ ion from 3-chloronortricyclene requires a hydrogen shift as well as cleavage of a third carbon–carbon bond, fragmentation process (3) is less important for the tricyclic compound. Reactions 1 and 2 are less prominent for the bicyclic compounds than for the tricyclic derivative, the spectrum of which possesses marked peaks at both *m/e* 79 ($C_6H_7^+$) and 93 ($C_7H_9^+$). Analogous fragmentations for the unsubstituted hydrocarbon, reactions 4 and 5, are not peculiar to norbornene, for they have been observed for two other C_7H_{10} isomers, 1,3-cycloheptadiene and Δ^6-bicyclo[3.3.0]heptene.[16] The $C_6H_7^+$ ion is particularly abundant in the mass spectra of these latter two compounds, neither of which possess a five-membered ring.

All four compounds investigated in this study evidently undergo closely similar decomposition sequences. The mass spectra of the *endo–exo* pair are nearly identical; furthermore the spectrum of the parent hydrocarbon bears a striking resemblance to its chloro derivatives except for the position of the parent ions.

Energetics

To employ the semilog matching technique for the evaluation of appearance potential curves, the ionization efficiency curves of the ion in question must be parallel to that of the rare gas standard over the lower portion of the curve. Among the ions measured, this requirement is met only by ions formed through primary decomposition processes. Appearance potentials for such ions are generally reproducible to ±0.05 e.v. and may be considered reliable to ±0.15 e.v. Curves for other ions show some degree of tailing and consequently appearance potentials were obtained by conventional extrapolation of linear plots. While such curves show good reproducibility, accurate extrapolation is difficult and results are probably good only to ±0.3 e.v.

Appearance potentials of the selected ions are listed in Table I. The only compound studied for which an ionization potential has been previously reported is norbornene. In this case the present value is in good agreement with the result (9.05 e.v.) of Winstein and Lossing.[3] Substitution of chlorine in the 5 position results in an elevation of about 0.2 e.v. in the ionization potential of the bicyclic compound. Comparison with the tricyclic compound is complicated by the absence of a formal double bond as a source of the ejected electron.

TABLE I

APPEARANCE POTENTIALS[a] OF SELECTED IONS

Ion	*exo*	*endo*	Tricyclo	C_7H_{10}
$C_5H_6^+$	9.77	9.75	10.15	9.58
$C_6H_5^+$	13.0	13.0	12.7	13.8
$C_6H_7^+$	10.8	10.9	10.25	11.2
$C_7H_7^+$	12.6	12.5	12.2	13.6
$C_7H_9^+$	11.1	11.0	10.7	11.5
$C_7H_{10}^+$	. . .	. . .	. . .	8.95
$C_7H_9Cl^+$	9.15	9.1	9.51	. . .

[a] Given in electron volts.

Heats of formation of the parent compounds can be estimated by combining appearance potentials with known thermochemical data. For example, the following relation (11) can be used to estimate the heat of

$$\Delta H_f(\text{norbornene}) = \Delta H_f(C_5H_6^+) + \Delta H_f(C_2H_4) - A(C_5H_6^+) \quad (11)$$

formation of norbornene. Assuming that $C_5H_6^+$ produced from norbornene is the same as $C_5H_6^+$ resulting from electron impact ionization of cyclopentadiene, Lossing's value for the heat of formation of $C_5H_6^+$ (239 kcal. mole^{-1})[17] can be used together with the heat of formation of ethylene (12.5 kcal. mole^{-1})[18] and the appearance potential of $C_5H_6^+$ from norbornene (Table I) to give ΔH_f(norbornene) = 31 ± 4 kcal. mole^{-1}. This value agrees well with that (32 kcal. mole^{-1}) obtained from the heat of formation of norbornadiene (66.8 kcal. mole^{-1})[15] and its heat of hydrogenation to norbornene (−35 kcal. mole).[19]

Heats of formation of the chlorinated compounds can also be calculated by eq. 12. Thus, the values listed

$$\Delta H_f(C_7H_9Cl) = \Delta H_f(C_5H_6^+) + \Delta H_f(C_2H_3Cl) - A(C_5H_6^+) \quad (12)$$

in Table II are obtained through combination of the $C_5H_6^+$ appearance potential (Table I) with the heats of formation of $C_5H_6^+$ and of vinyl chloride (8.9 kcal. mole^{-1}).[20] The assumption is again made that the

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(16) C. Lifschitz and S. H. Bauer *J. Phys. Chem.*, **67**, 1629 (1963).

(17) A. G. Harrison, L. R. Honnen, H. J. Dauben, and E. P. Lossing, *J. Am. Chem. Soc.*, **82**, 5593 (1960). A somewhat lower value of ΔH = 231 kcal. mole^{-1} is suggested by F. H. Field and J. L. Franklin ("Electron Impact Phenomena," Academic Press Inc., New York, N. Y., 1957, p. 264, and references therein).

(18) F. D. Rossini, *et al.*, National Bureau of Standards Circular No. 500, U. S. Government Printing Office, Washington, D. C., 1952.

(19) R. B. Turner, W. R. Meader, and R. E. Winkler, *J. Am. Chem. Soc.*, **79**, 4116 (1957).

(20) J. R. Lacher, E. Emery, E. Bohmfalk, and J. D. Park, *J. Phys. Chem.*, **60**, 492 (1956).

TABLE II

CALCULATED HEATS OF FORMATION

Compd.	ΔH, kcal. mole^{-1}
exo	23 ± 4
endo	23
Tricyclo	15
C_7H_{10}	31

TABLE III

HEATS OF FORMATION[a] OF IONS

Ion	*exo*	*endo*	Tricyclo	C_7H_{10}
$C_5H_6^+$	(239)	(239)	(239)	(239)[b]
$C_6H_7^+$	243	245	222	257
$C_7H_9^+$	250	248	236	243
$C_7H_{10}^+$	...	...	...	238
$C_7H_9Cl^+$	234	233	234	...

[a] Given in kilocalories per mole. [b] See ref. 17.

$C_5H_6^+$ ions formed are identical with the $C_5H_6^+$ species produced by ionization of cyclopentadiene, presumably having the cyclopentadienide structure. Such an assumption is reasonable for norbornene and the chloronorbornenes. In the case of chloronortricyclene, however, formation of the cyclopentadienide cation would require cleavage of three carbon–carbon bonds and one hydrogen shift. Although this complex process is clearly less probable than the retro-Diels–Alder fragmentation of the three norbornenyl compounds, the energy required for formation of the $C_5H_6^+$ ion from the parent ion (reactions 3 and 6) is equal within experimental error for all four compounds (Table I).

Little thermochemical information is available for other ions whose appearance potentials are here reported. It is possible, however, to use the calculated heats of formation of the parent compounds together with the observed appearance potentials to estimate heats of formation of the ions. Several interesting results emerge. The sum of the ionization potential and the heat of formation of the compound yields a value (Table III) for the heat of formation of the parent ion which is the same within experimental error for all three chloro compounds. This agreement may result from an identity of the three parent ions or it may be only coincidental. The latter alternative would normally seem more reasonable in view of the large differences in mass spectra and energetics between the bicyclic and tricyclic chloro compounds.

The heat of formation of $C_6H_7^+$ produced according to reaction 2 or 5 can be calculated using the known heat of formation of CH_2Cl (29 kcal. mole^{-1})[21] or CH_3 (32 kcal. mole^{-1}),[18] respectively. The results show considerable scatter although that obtained from chloronortricyclene agrees well with the value given by Lifschitz and Bauer.[16] Results for $C_7H_9^+$ agree within experimental error for the three bicyclic compounds but the result for the tricyclic compound is somewhat lower.

The close similarity in both mass spectra and energetics of the ionization–dissociation processes for *exo-* and *endo*-5-chloro-2-norbornene indicates that these compounds dissociate under electron impact *via* common paths involving common ionic intermediates. This result is not surprising in view of the similar behavior of other sets of isomers such as those studied by Meyerson and co-workers.[22] 3-Chloronortricyclene, on the other hand, exhibits different behavior and, therefore, does not decompose solely through ionic intermediates common to the *exo–endo* pair.

Acknowledgment.—B. H. J. wishes to thank the Petroleum Research Fund of the American Chemical Society for financial support which helped make this work possible.

[21] A. G. Harrison and T. W. Shannon, *Can. J. Chem.*, **40**, 1730 (1962).

[22] See, for example, H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, Chapter 10.

Friedel–Crafts Reaction with Silicon-Containing Acid Chlorides as a Synthetic Route to Compounds and Polymers

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In the presence of aluminum chloride, β-trimethylsilylpropionyl chloride was found to undergo a facile elimination reaction yielding trimethylchlorosilane, ethylene, and carbon monoxide, or to acylate effectively an aromatic substrate, depending on reaction conditions. A detailed study of the elimination reaction was made. With ferrocene serving as a prototype aromatic and using trimethylsilyl-, dimethylchlorosilyl-, and methyldichlorosilyl-substituted organic acid chlorides with aluminum chloride catalyst, twenty-one new compounds and polymers were prepared and their structures corroborated by independent syntheses. In connection therewith, other new materials were formed as intermediates. The results with ferrocene indicate that the usefulness of these acid chlorides with aluminum chloride in Friedel–Crafts reactions extends to aromatics with reactivities in the toluene–benzene range, thus opening up a generally useful synthetic route for silylorgano aryl ketone intermediates. Qualitative correlations between acid chloride structures and their stability–reactivity under the Friedel–Crafts conditions used were made.

The literature on aluminum chloride catalyzed Friedel–Crafts reactions with silicon-containing organic acid chlorides appears to consist of one paper by Benkeser and Krysiak who reported the acylation of toluene with *m*- and *p*-trimethylsilylbenzoyl chlorides.[2] Their attempts with the *ortho* isomer were reported as unsuccessful, apparently owing to cleavage of the trimethylsilyl group. Moreover, one would ex-

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(1) To whom inquiries should be addressed.

(2) R. A. Benkeser and H. R. Krysiak, *J. Am. Chem. Soc.*, **76**, 599 (1954).