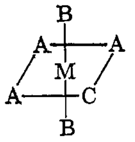
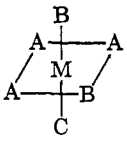
reacts with mercuric chloride to give *p*-tolylmercuric chloride, mp and mmp 236–238°. Unlike the corresponding dichlorotris(pyridine)benzylchromium(III),[1] the σ-bonded *p*-tolylchromium compound absorbs only weakly in the visible region (λ_{max} (THF) 445 mμ (ϵ 137)), is rapidly hydrolyzed, and does not reduce Fe^{III} salts in perchloric acid solution. The pure, crystalline solid is stable under nitrogen, only undergoing decomposition between 130 and 190° to give *p,p'*-ditolyl as the main organic product.

The crystals of dichlorotris(tetrahydrofuran)-*p*-tolyl chromium(III) are orthorhombic with a = 10.396, b = 18.447, c = 22.396 A, d_m = 1.315, Z = 8, d_c = 1.331; the space group is Pbca. Since the crystals are unstable to the atmosphere, they were sealed in Lindemann glass capillaries before exposure to X-rays. The intensities were measured with the aid of a Hilger and Watts linear diffractometer; the 2661 strongest reflections produced by Mo Kα radiation were used in the analysis. The structure was solved by three-dimensional Patterson and Fourier methods. The current value of R is 0.136.

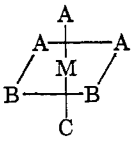
There are three possible isomers of octahedrally coordinated compounds of the type MA_3B_2C. The configuration of the present compound is depicted by I.



I



II



III

The molecule projected down the a axis is shown in Figure 1. In the solid state the ligands adopt an orientation which precludes the symmetry $\bar{1}$ or m in the molecule, and so, since the space group contains symmetry centers and glide planes, there are equal numbers of *d* and *l* molecules in the unit cell. The *p*-tolyl group is σ bonded to the chromium through one carbon atom. The bond lengths in the octahedron at the chromium atom are at present: $Cr{-}O_1$ = 2.04, $Cr{-}O_2$ = 2.05, $Cr{-}O_3$ = 2.21, Cr–C = 2.01, $Cr{-}Cl_1$ = 2.31, $Cr{-}Cl_2$ = 2.33 A. Refinement is continuing and final details of the molecular structure will be published.

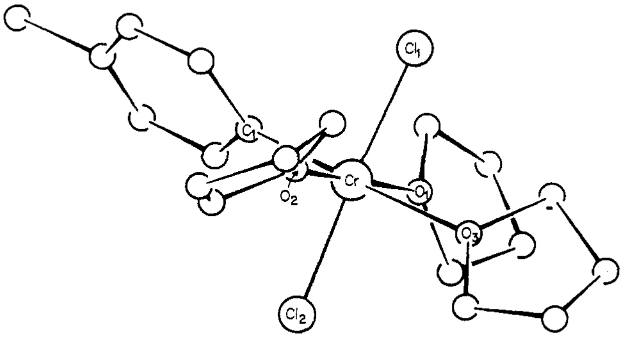


Figure 1.

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The Reaction of Chloroformates with Silver Fluoroborate in Chlorobenzene

Sir:

The unique chemistry of diazonium ions[1] (I) and isocarboxonium ions[2] (II) has been of continuing practical and theoretical interest. We wish to report attempts to generate carboxylium ions[3] (III), another member of this family, by the reaction of chloroformates with silver fluoroborate in chlorobenzene. Our results suggest that the formalism relating I and III has chemical significance.[4]

$$\underset{\mathrm{I}}{[\mathrm{R{-}N{\equiv}N}]^+} \qquad \underset{\mathrm{II}}{[\mathrm{R{-}O{=}C}]^+} \qquad \underset{\mathrm{III}}{[\mathrm{R{-}O\overset{-\,-}{-}C{\equiv}O}]^+}$$

The classic work of Bartlett and Knox[5] established that deamination of 1-aminoapocamphane yields bridgehead substitution products whereas the corresponding 1-chloroapocamphane is remarkably inert even to forcing conditions.[6] This difference in reactivity has generally been ascribed to the exceptional behavior of the diazonium ion.[1,7]

We have found that treatment of 1-apocamphane chloroformate (IV) with an equimolar amount of silver fluoroborate in chlorobenzene at room temperature for 8 hr also yields bridgehead substitution products. Under these conditions the products are silver chloride (92%), carbon dioxide (70%), 1-fluoroapocamphane (V; 52%), and isomers of 1-chlorophenylapocamphane (VI; 24%). The chloroformate IV was stable in chlorobenzene in the absence of silver fluoroborate, and 1-chloroapocamphane was unreactive toward boron trifluoride and silver fluoroborate in chlorobenzene. The fluoride V was identified by infrared, proton, and

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(1) H. E. Zollinger, "Azo and Diazo Chemistry, Aliphatic and Aromatic Compounds," Interscience Publishers, Inc., New York, N. Y., 1961.

(2) P. S. Skell and I. Starer, *J. Am. Chem. Soc.*, **81**, 4117 (1959), and subsequent references; J. Landgrebe, *Tetrahedron Letters*, 105 (1965).

(3) Carbalkoxylium ions[3c] have been postulated as intermediates in the reaction of chloroformates with silver nitrate to give nitrate esters: (a) R. Boschan, *J. Am. Chem. Soc.*, **81**, 3341 (1959); see, however, D. N. Kevill and G. H. Johnson, *Chem. Commun.*, 235 (1966); in the solvolysis of chloroformates: (b) M. Green and R. F. Hudson, *J. Chem. Soc.*, 1076 (1962), and earlier work; A. Kivinen, *Acta Chem. Scand.*, **19**, 845 (1965); and in the hydrolysis of N,N'-dicarbalkoxy-N,N'-dialkoxyhydrazines: (c) R. J. Crawford and R. Rapp, *J. Org. Chem.*, **28**, 2419 (1963). These ions can be considered as a ramification of some of the mechanistic proposals for the rearrangement and eliminations of chloroformates: (d) E. S. Lewis and W. C. Herndon, *J. Am. Chem. Soc.*, **83**, 1961 (1961); K. L. Oliver and W. G. Young, *ibid.*, **81**, 5811 (1959); K. B. Wiberg and T. M. Shryne, *ibid.*, **77**, 2774 (1955); and in the Friedel-Crafts reactions of chloroformates: (e) W. H. Coppock, *J. Org. Chem.*, **22**, 325 (1957); (f) C. Friedel and J. M. Crafts, *Compt. Rend.*, **84**, 1450 (1877); F. A. Drahowzal, "Friedel-Crafts and Related Reactions," Vol. II, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 644.

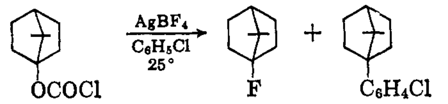
(4) In this context chemical significance implies a reactant-product analogy and not a mechanistic analogy. The carboxylium ions which may be proposed to rationalize the following results are at best a unifying concept which represents a starting point for more detailed mechanistic work.

(5) P. D. Bartlett and L. H. Knox, *J. Am. Chem. Soc.*, **61**, 3184 (1939).

(6) The reaction of a structurally similar bridgehead chloride has been achieved with aqueous silver nitrate at 205° for 19.5 hr: W. von E. Doering and E. F. Schoenewaldt, *J. Am. Chem. Soc.*, **73**, 2333 (1951). However, the same chloride is stable toward ethanolic silver nitrate at 160° for 21 hr and toward aqueous zinc chloride at 205° for 91 hr. The recently reported reaction of 1-chloronorbornane with antimony pentafluoride in sulfur dioxide appears to be unique: P. von R. Schleyer, W. E. Walts, R. C. Fort, Jr., M. B. Comisarow, and G. A. Olah, *ibid.*, **86**, 5679 (1964).

(7) For recent discussions see (a) D. Y. Curtin, B. H. Klanderman, and D. F. Tavares, *J. Org. Chem.*, **27**, 2709 (1962); (b) K. V. Scherer, Jr., R. S. Lunt, III, and G. A. Ungefug, Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p 27P.

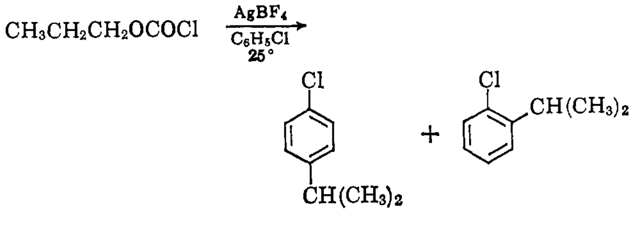
fluorine magnetic resonance, and mass spectrometry. The mixture of isomers VI was identified by spectral data and by dechlorination[8] to the known hydrocarbon.[9]



IV V VI

Treatment of the chloroformate IV with excess boron trifluoride in chlorobenzene at room temperature gave 1-chloroapocamphane (48%) and isomers of 1-chlorophenylapocamphane (18%). These reactions of apocamphane chloroformate (IV) clearly demonstrate the importance of the elements of carbon dioxide in this process.

It has been known for 90 years that chloroformates are precursors for alkylarenes in the Friedel–Crafts reaction[3f] and the alkylation of arenes by amines under diazotization conditions has recently been shown to give products which are usually similar to those obtained in Friedel–Crafts reactions.[10] In the present case the similarity of the reactions is demonstrated by the observation that cyclohexyl chloroformate and cyclohexyl chloride each yield *o*-cyclohexylchlorobenzene (33%) and *p*-cyclohexylchlorobenzene (44%) upon reaction with an equimolar amount of silver fluoroborate in chlorobenzene at room temperature. Attempts to detect cyclohexene and *meta*-substituted products established that there was less than 5% of each of these products formed. Reaction of *n*-propyl chloroformate with silver fluoroborate in chlorobenzene occurred at room temperature to give *o*- and *p*-isopropylchlorobenzene in 30 and 34% yield, respectively, while a similar reaction using *n*-propyl chloride gave the same products in yields of 3% each.[11] These results demonstrate a qualitative similarity of Friedel–Crafts, diazotiazation, and chloroformate–silver ion alkylations.



Aromatic diazonium salts exhibit remarkable stability relative to the aliphatic ions.[1] In an attempt to generate a carbaroxylium ion, phenyl chloroformate (VII) was allowed to react with equimolar silver fluoroborate. The reaction required reflux for 2 hr to give silver chloride (96%), boron trifluoride (63%), and phenyl fluoroformate (VIII; 46%). The latter was identified by comparison with an infrared spectrum of an authentic sample[12] and by reaction with methanol to give methyl phenyl carbonate. Ethanolysis of the reaction mixture after the silver chloride had precipitated gave 82% ethyl phenyl carbonate; this provides a more accurate estimate of the actual yield of VIII than does the isolated yield. Attempts to find fluorobenzene and monochlorinated biphenyls or aryl esters[3e] showed that less than 5% of each compound was present. Phenyl chloroformate was stable to lithium fluoroborate in refluxing chlorobenzene. Formation of the fluoroformate VIII is similar to the reaction of acylium ions with fluoroborate to give acid fluorides and boron trifluoride.[13]

$$C_6H_5{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Cl \xrightarrow[C_6H_5Cl\ \Delta]{AgBF_4} C_6H_5{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}F$$

VII VIII

Although these reactions may be conveniently rationalized by the intermediacy of carboxylium ions, neither these results nor the formal analogies constitute evidence for these ions. Possible alternatives vary with the structure of the reactant chloroformate or intermediate fluoroformate and range from concerted and radical processes to ion-pair and ionic formulations. Nonetheless, the reactions reported here may be of synthetic utility and suggest an alternative entry to species similar in reactivity to diazonium ions. Extensions to a variety of leaving groups, substituents, counterions, solvents, and Lewis acids are presently under investigation.

Acknowledgment. J. B. M. and P. Y. J. were recipients of National Science Foundation undergraduate fellowships. We are also grateful to the Public Health Service (GM-10696 and GM-12595) for support of this work.

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[8] P. Bruck, *Tetrahedron Letters*, 449 (1962).

[9] D. I. Davies and C. Waring, *Chem. Commun.*, 263 (1965).

[10] (a) G. A. Olah, N. A. Overchuk, and J. C. Lapierre, *J. Am. Chem. Soc.*, **87**, 5785 (1965); (b) A. T. Jurewicz, J. H. Bayless, and L. Friedman, *ibid.*, **87**, 5788 (1965).

[11] The rearrangement of the propyl group observed in this alkylation of chlorobenzene is different from the lack of rearrangement reported by Jurewicz, *et al.*,[10b] for the alkylation of benzene in 0.5–1.6% yield by *n*-propylamine under diazotization conditions.

[12] W. A. Sheppard, *J. Org. Chem.*, **29**, 1 (1964). We are grateful to Dr. Sheppard for providing this spectrum.

[13] F. Seel, *Z. Anorg. Allgem. Chem.*, **250**, 331 (1942); G. Olah and S. Kuhn, *Ber.*, **89**, 866 (1956). The acylium ion could be considered to be formally analogous to I, II, and III. For example, G. A. Olah, W. S. Tolgyesi, S. J. Kuhn, M. E. Moffatt, I. J. Bastien, and E. B. Baker (*J. Am. Chem. Soc.*, **85**, 1328 (1963)) have reported generation of carbonium ions by loss of carbon monoxide from acylium ions, and the reverse process, the Koch synthesis of acids, is well known. The ions postulated to be intermediates in oxidative decarboxylations of carboxylic acids would be another member of this family: E. J. Corey and J. Casanova, Jr., *ibid.*, **85**, 165 (1963); E. J. Corey, N. L. Bauld, R. T. LaLonde, J. Casanova, Jr., and E. T. Kaiser, *ibid.*, **82**, 2645 (1960).

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A Benzobicyclo[2.1.1]hexene

Sir:

We wish to report the first synthesis of a benzobicyclo[2.1.1]hexene derivative, the smallest bridged benzocyclene yet prepared. The compound of this ring system is of considerable interest in view of its being a benzo analog of bicyclo[2.1.1]hexene, the successful synthesis of which has long been awaited in connection with the important results of practical and theoretical significance produced by the studies of saturated bicyclo[2.1.1]hexanes.[1-3]

Treatment of 2-benzonorbornenone (I) with selenium

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[1] J. Meinwald and J. K. Crandall, *J. Am. Chem. Soc.*, **88**, 1292 (1966), and preceding papers in the series.

[2] K. Ebisu, L. B. Batty, J. M. Higaki, and H. O. Larson, *ibid.*, **88**, 1995 (1966), and references cited therein.

[3] K. B. Wiberg and F. Fenoglio, *Tetrahedron Letters*, 1273 (1963), and references cited therein.