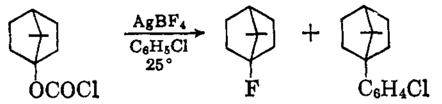
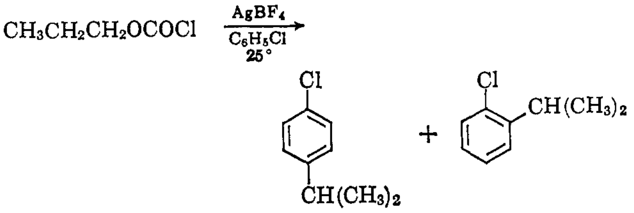
fluorine magnetic resonance, and mass spectrometry. The mixture of isomers VI was identified by spectral data and by dechlorination[8] to the known hydrocarbon.[9]


IV V VI

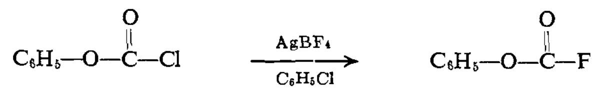
Treatment of the chloroformate IV with excess boron trifluoride in chlorobenzene at room temperature gave 1-chloroapocamphane (48%) and isomers of 1-chlorophenylapocamphane (18%). These reactions of apocamphane chloroformate (IV) clearly demonstrate the importance of the elements of carbon dioxide in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



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

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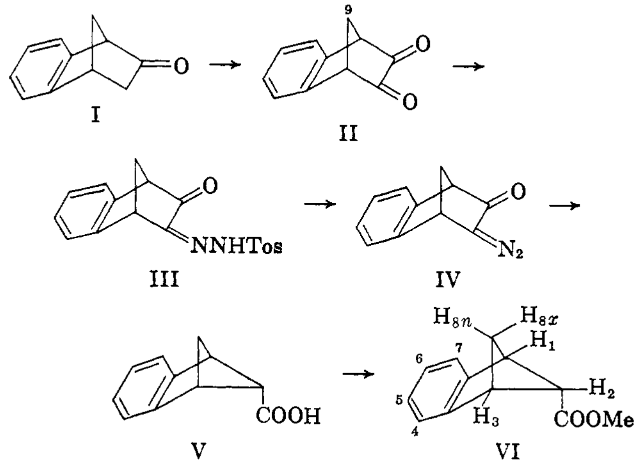
[1] J. Meinwald and J. K. Crandall, *J. Am. Chem. Soc.*, **88**, 1292 (1966), and preceding papers in the series.

[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.

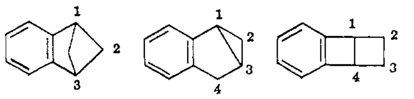
dioxide in boiling xylene for 16 hr produced in about 15% yield the yellow, crystalline diketone II, isolated by distillation at 120–122° (1 mm); mp 85° (cyclohexane); $\nu_{C=O}^{CCl_4}$ 1765 (s) and 1783 (sh) cm$^{-1}$; nmr in CCl$_4$[4]:



four Ar–H at $\tau$ 2.7 (A$_2$B$_2$ system), two C$_9$–H at $\tau$ 6.96 (dt) and 7.36 (dt), and two bridgehead H at $\tau$ 6.25 (t). *Anal.* Calcd for $C_{11}H_8O_2$: C, 76.73; H, 4.68. Found: C, 76.83; H, 4.87. The monotosylhydrazone III was generated *in situ* by dissolving II and tosylhydrazine in cold chloroform. The resulting solution was poured through a column of basic alumina, giving in the ether eluate good yields of the $\alpha$-diazo ketone IV of purity suitable for use in the next step.[5]

An aqueous dioxane solution of IV made weakly alkaline by NaHCO$_3$ was irradiated at room temperature under nitrogen atmosphere for about 25 hr (when evolution of nitrogen ceased) using a 300-w high-pressure mercury vapor lamp, giving an acidic material together with a neutral polymer. After esterification with diazomethane, the material was indicated by vpc to be a mixture of four compounds. The main compound VI was isolated by preparative vpc, followed by distillation, as colorless crystals, mp 58°, $\lambda_{max}^{n\text{-heptane}}$ 260.5 m$\mu$ ($\epsilon$ 630), 267 (850), and 274 (930) (no double bond conjugated with benzene ring), in about 10% yield from II. *Anal.* Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43; mol wt, 188. Found: C, 76.28; H, 6.64; mol wt, 186 (vapor phase osmometry, in chloroform). Catalytic hydrogenation of VI over PtO$_2$ in ethanol did not proceed.

In view of the chemical, nmr, and ultraviolet observation that VI is saturated, it must be derived from one of the three ring systems shown below. The method of preparation suggests that the system A is most probable.



A B C

Confirmatory evidence for the indicated structure VI was provided by the nmr spectrum, which showed in CCl$_4$ four Ar–H at $\tau$ 3.0 (A$_2$B$_2$ system), one H$_2$ at $\tau$ 6.38 (t), two H$_1$, H$_3$ at $\tau$ 6.62 (t), one H$_{8x}$ at $\tau$ 7.44 (A part of AB system, dt), and one H$_{8n}$ at $\tau$ 7.82 (B part of AB system, d), $J_{H_1,H_2}$ = 2.5, $J_{H_1,H_{8x}}$ = 2.5, $J_{H_1,H_{8n}} \cong 0$, and $J_{H_{8n},H_{8x}}$ = 6 cps. The presence of two protons at the bridgeheads, with the symmetrical signal pattern of aromatic protons, excludes the structures substituted at the bridgehead positions in all the systems. Because cyclopropane and its alkyl-substituted derivatives invariably have methylene nmr bands above $\tau$ 9.5, the lack of such a band in VI eliminates the system B, unless substituted in the 2 position. Completely symmetrical pattern of the triplet due to the bridgehead protons rules out the 2-substituted B and the 2- or 3-substituted C systems. Wiberg, *et al.*,[6] have reported the spectrum of methyl bicyclo[2.1.1]hexane-*endo*-5-carboxylate (VII). Although the spectrum of VI is considerably shifted to a lower field due to the effect of benzene ring, the shapes of signals and coupling constants of H$_1$, H$_2$, H$_3$, H$_{8n}$, and H$_{8x}$ correspond well to those of VII. Thus, having eliminated all other possible structures, we must conclude that the compound VI is methyl benzobicyclo-[2.1.1]hexene-2-carboxylate. The absence of a long-range coupling between H$_{8n}$ and the C$_2$ *endo* proton,[1,6] with the vicinal coupling constant $J_{H_1,H_2}$ = 2.5 cps, suggests predominantly *endo* configuration of the methoxycarbonyl group.

We plan to prepare derivatives suitable for the study of carbonium ion reactions of this system.

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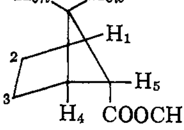
[4] For the description of nmr peaks, s = singlet, d = doublet, dt = doublet of triplets, etc.

[5] Substantially the same procedure was used by Meinwald[1] for the preparation of 3-diazonorcamphors.

[6] K. B. Wiberg, B. R. Lowry, and B. J. Nist, *J. Am. Chem. Soc.*, **84**, 1594 (1962). The shapes of signals and coupling constants in VII were reported: for H$_5$, a broad band at $\tau$ 7.68; for H$_1$, H$_4$, $\tau$ 7.30, t; for



VII

H$_{6x}$, a broad band at $\tau$ ~8.63; for H$_{6n}$, $\tau$ 9.25, d; $J_{H_1,H_{6x}}$ = 3.8 cps; $J_{H_{6n},H_{6x}}$ = 6.6 cps.

## A Versatile Synthesis of Cyclic Ketones

*Sir:*

We wish to report initial examples of a simple synthetic sequence leading to cyclohexanones and cyclopentanones, which may portend a general method for preparing cycloalkanones of various ring size. In essence, one allows 2,3-dichloropropene to react with a nucleophilic reagent to produce a $\beta$-chloroallyl derivative; an electrophilic center is subsequently generated in the latter, followed by its intramolecular attack on the vinyl chloride grouping and hydrolysis of the "masked" ketone. This is illustrated below in several examples,[1] wherein carbon nucleophiles are alkylated and a carbonium ion created for cyclization by treatment of derived alcohols or olefin with acid.

The solvolytic cyclization of **1** proceeded in *ca.* 65% yield to ketone **2**, and the 30% of **3** produced could itself be converted to **2** by treatment with 90% sulfuric acid. Thus **2** is obtainable in *ca.* 40% over-all yield

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[1] All new compounds gave satisfactory elemental analysis and were further characterized by spectroscopic methods.