(III). Both observations can be understood in terms of the preceding mechanism, written for the monodentate complex.

Step A would probably be rate determining. The intermediate I could then isomerize to the fumarato complex as in (**B**) or undergo intramolecular nucleophilic attack as in (C) to produce the novel chelated maleate complex (II). Step C is analogous to the mechanism of a recently reported amidolysis of glycine ethyl ester by a coordinate amide.[3]

In terms of the above mechanism, the failure of maleatopentaamminecobalt(III) to undergo the ligand reactions is explained by the absence of a coordinated water molecule. Furthermore, the greater prevalence of the observed ligand reactions in the Cr(III) system at lower acidities is readily explicable in view of the fact that the rate of ligand release from the complexes is acid catalyzed. Therefore, at lower acidity the lifetime of maleate in the first coordination sphere is longer and the extent of hydration and isomerization is correspondingly greater.

The nature of the unknown complex resulting from the direct reaction between maleic acid and hexaaquochromium(III) is not understood. Since it is neither the monodentate nor chelated form of the maleate complex, it seems necessary to assume that the ligand in the complex is hydrated. A striking aspect of the chemistry of the unknown complex is that it yields substantial amounts of maleic acid on aquation. This behavior is unexpected since $\Delta F°$ for free maleic acid going to malic acid in acidic solution is about -7 kcal/mol. Only a malate complex with substantial instability relative to hexaaquochromium(III) and free malic acid could exhibit the observed behavior. Intermediate II would not seem to have the requisite instability; tridentate attachment of malate would be more likely to satisfy the energy requirement.

Many of the experimental details are described elsewhere.[1,5] The analysis for the organic anions is, however, particularly germane to the results just reported and, accordingly, is described herewith.

The reaction mixture was charged onto a lithium-form cation exchange column which was then rinsed with water until all the carboxylic acids had been washed through. The eluent solution was charged onto a 18-mm diameter column containing 15 ml of AG1-X2, 200–400 mesh chloride-form resin.[6] Separation followed the scheme developed by Blaedel and Todd[7] for mixtures of maleic and fumaric acids. Elution of the column with 0.073 M HCl gave quantitative separation of the three acids, malic, fumaric, and maleic, appearing at the fractions 20–40, 75–125, and 150–300 ml, respectively (the actual volumes depend on the particular experimental arrangement, but are reported as support for the claim that separation was complete).

Maleic and fumaric acids were determined by direct measurement of the uv absorbance at 220 nm on the appropriate eluent fraction. Extinction coefficients of $4.5 \times 10^3\ M^{-1}\ \mathrm{cm}^{-1}$ for maleic acid and $1.03 \times 10^4\ M^{-1}\ \mathrm{cm}^{-1}$ for fumaric acid were measured in 0.073 M HCl. Malic acid was determined colorimetrically by the method of Goodban and Stark.[8] Samples containing 10–80 μg of malic acid in 1 ml could be determined with a precision of somewhat better than ±10%. Blank corrections were found necessary for each run.

Acknowledgment. Financial support for this research by the National Science Foundation, both for Grant No. GP 5322 and fellowships for M. V. O. from 1966–1969, are gratefully acknowledged.

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[5] M. V. Olson and H. Taube, submitted for publication.

[6] In some instances the resin could be used after only cursory preliminary rinsing. Other batches required prolonged rinsing with 6 M HCl before the effluent gave negligible uv absorbance at 220 nm.

[7] W. J. Blaedel and J. W. Todd, *Anal. Chem.*, **30**, 1821 (1958).

[8] A. E. Goodban and J. B. Stark, *ibid.*, **29**, 283 (1957).

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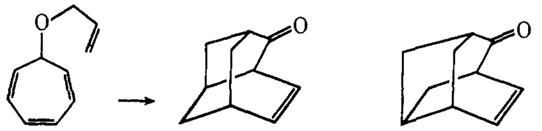
Multiple Thermal Rearrangements. The Pyrolysis of 7-Allyloxycycloheptatriene

Sir:

Cycloheptatriene and its derivatives have been found to undergo a variety of thermal unimolecular processes: (1) conformational ring inversion;[1] (2) valence tautomerization;[2] (3) [1,5]-hydrogen shift(s);[3] (4) [1,5]-carbon shifts(s).[4,5] One aspect of the thermal chemistry of cycloheptatriene which we felt had considerable synthetic potential was to examine the behavior of certain 7-substituted tropilidenes in which the substituent itself could undergo further reaction(s) with the ring double bonds of the tropilidene by virtue of hybridization changes (isomerization) attending [1,5]-sigmatropic hydrogen shift(s). We illustrate how multiple thermal rearrangements in the cycloheptatriene series may provide a facile entry to new polycyclic systems by the one-step high-yield synthesis (83%) of two unique tricyclic ketones from the pyrolysis of 7-allyloxycycloheptatriene (**1**; eq 1).



1 **10** **11** (1)

There are four possible tricyclic products **8–11** which could arise from **1** as a result of two sequential sigmatropic reactions[3a,6] followed by intramolecular cycloaddition reactions. That is, thermal rearrangement of **1** would first generate, *via* [1,5]-hydrogen shifts,

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[1] W. E. Heyd and C. A. Cupas, *J. Amer. Chem. Soc.*, **91**, 1559 (1969), and references therein cited.

[2] (a) For a review see G. Maier, *Angew, Chem. Int. Ed. Engl.*, **6**, 402 (1967); (b) M. Goerlitz and H. Gunther, *Tetrahedron*, **25**, 4467 (1969); (c) J. A. Berson, D. R. Hartter, H. Klinger, and P. W. Grubb, *J. Org. Chem.*, **33**, 1669 (1968); (d) E. Ciganek, *J. Amer. Chem. Soc.*, **89**, 1454 (1967), and previous papers; (e) D. Schoenleber, *Angew. Chem. Int. Ed. Engl.*, **8**, 76 (1969); (f) M. Jones Jr., *ibid.*, **8**, 76 (1969).

[3] (a) For a review see G. B. Gill, *Quart. Rev., Chem. Soc.*, **22**, 338 (1968); (b) A. P. Ter Borg and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **88**, 266 (1969), and previous papers; (c) K. W. Egger, *J. Amer. Chem. Soc.*, **90**, 1 (1968).

[4] J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968).

[5] For examples of thermal migration of other groups, see R. W. Hoffmann, K. R. Eicken, H. F. Luthardt, and B. Dittrich, *Tetrahedron Lett.*, 3789 (1969); J. A. Berson, P. W. Grubb, R. A. Clark, D. R. Hartter, and M. R. Willcott, *J. Amer. Chem. Soc.*, **89**, 4076 (1967); ref 2d.

[6] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968); S. I. Miller, *Advan. Phys. Org. Chem.*, **6**, 185 (1968); K. Fukui and H. Fujimoto in "Mechanisms of Molecular Migrations," Vol. 2, B. S. Thyagarajan, Ed., Wiley, New York, N. Y., 1969, pp 117–190.

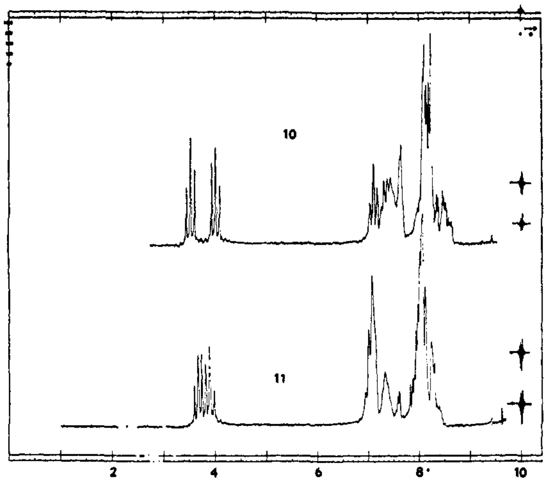
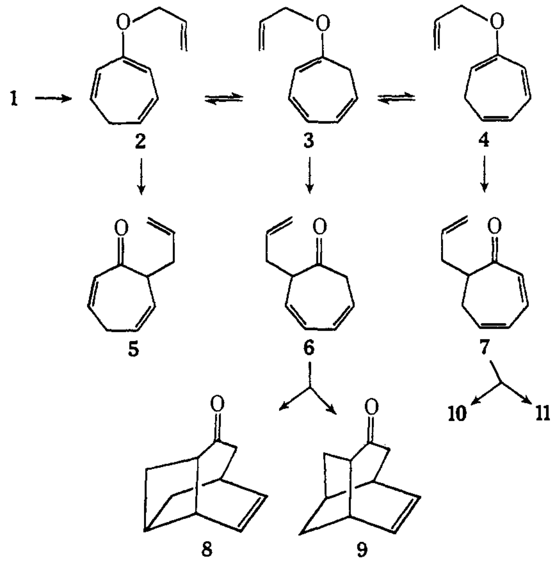
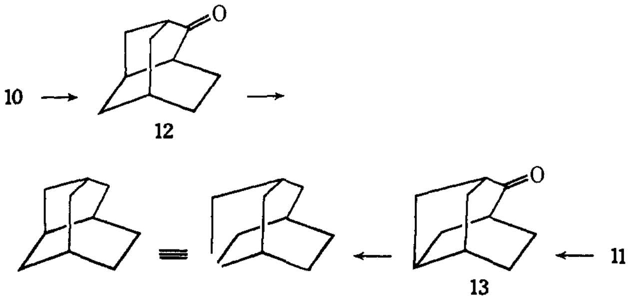


Figure 1. 100-MHz spectra of **10** and **11**.

the isomeric allyl vinyl ethers **2–4**, which would then undergo a Claisen rearrangement[7,8] to produce the isomeric allyl cycloheptadienones **5–7**, respectively.[9] Both **6** and **7**, however, should be capable of undergoing intramolecular Diels–Alder reactions to produce the tricyclic ketones **8–11**.



Heating **1**[10] (neat) at 200° for 24 hr in a sealed tube gives a 50:50 mixture of two isomeric ketones, **10** (mp 193–195°, $\nu_{max}^{CCl_4}$ 1736 cm^{-1}) and **11** (mp 175–177°, $\nu_{max}^{CCl_4}$ 1707 cm^{-1}).[11–14] The nmr spectra[16] of these compounds (Figure 1) showed that the desired intramolecular [4 + 2] cycloaddition had occurred (relative integrated area of olefinic protons = 2). The complexity of the high-field resonances, although consistent with **10** and **11**, precluded unambiguous structural assignments from the spectra alone. The structures of these ketonic products could be established, however, in the following way. The observed lack of deuterium incorporation (mass spectrum) in each ketone, under conditions (D_2O, K_2CO_3, dioxane, 100°) which should result in exchange of enolizable hydrogens,[17] rules out **8** and **9** as possible structures. Hydrogenation of **10** gave material identical with protoadamantanone **12**[17–20] while **11** gave a new ketone **13**[21] (mp 240–242°, $\nu_{max}^{CCl_4}$ 1712, 1699 cm^{-1}).[12] Wolff–Kishner reduction of **12** and **13** each gave the same compound which was identical with protoadamantane **14**.[17,19,20,22]



The isomerization of **1** to **10** and **11** provides the simplest entry to the tricyclo[4.3.1.0^{3,8}]decane carbon skeleton. Studies of the thermal behavior of other substituted cycloheptatrienes which should be capable

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[7] [3,3] sigmatropic change.

[8] For reviews, see A. Jefferson and F. Scheinmann, *Quart. Rev., Chem. Soc.*, 391 (1968); H. J. Hansen and H. Schmid, *Chem. Brit.*, 5, 111 (1969).

[9] Reaction to this stage has, in fact, been observed by Dreiding (E. Weth and A. S. Dreiding, *Proc. Chem. Soc.*, 59 (1964)). Heating 1 at 150° for 2 hr produces a mixture of 7-allyl-substituted 2,7- and 2,3-dihydrotropones. The latter isomer presumably arises by further [1,5]-hydrogen shifts in 6 and 7.

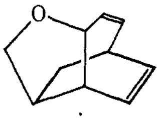
[10] Reaction of tropylium tetrafluoroborate at 25° for 3 hr with an equimolar amount of sodium allyl oxide using allyl alcohol as solvent gave 1 (85%, bp 48° (0.5 mm)).[9]

[11] IUPAC nomenclature: 10, tricyclo[4.3.1.0^{3,8}]dec-4-en-2-one; 11, tricyclo[4.3.1.0^{4,8}]dec-2-en-10-one.

[12] Satisfactory analyses were obtained for all new compounds.

[13] Separation of the ketones could be achieved by preparative gas chromatography on an 18% γ-methyl-γ-nitropimelonitrile column.[15]

[14] The tricyclic ether i is also formed as minor component (7%) in the pyrolysis of 1. This structural assignment, which is based on detailed nmr analysis, will be discussed in the full paper. Separation of i could be achieved either by glpc or by extracting an ethereal solution of the product mixture with aqueous silver nitrate.



i

[15] K. Conrow, *J. Amer. Chem. Soc.*, 83, 2343 (1961).

[16] Nmr spectra were obtained on a Varian HA-100 spectrometer. Spectra were obtained in CCl_4 with chemical shifts reported as τ in parts per million relative to internal TMS.

[17] H. W. Whitlock, Jr., and M. W. Siefken, *J. Amer. Chem. Soc.*, **90**, 4929 (1968).

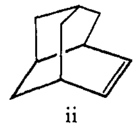
[18] L. A. Spurlock and K. P. Clark, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, No. ORGN-134.

[19] The nmr and infrared spectra and the glpc retention times of 12 and 14 were identical with authentic samples.[20]

[20] We thank Professor L. A. Spurlock, Brown University, Providence, R. I., for a sample of protoadamantanone (12) and Professor P. von R. Schleyer, Princeton University, Princeton, N. J., for a sample of protoadamantane (14).

[21] Tricyclo[4.3.1.0^{4,8}]decan-10-one. In view of the fact that there are six possible protoadamantanones,[17] we suggest the trivial name 10-protoadamantanone for 13.

[22] Wolff–Kishner reduction of 10 and 11 each gave protoadamantene (ii, mp 181–183°).[23]



ii

[23] Protoadamantene has been found to be a minor product in the deamination of 2-aminoadamantane: M. L. Sinnott, H. J. Storesund, and M. C. Whiting, *Chem. Commun.*, 1000 (1969).

of undergoing analogous multiple thermal rearrangements and the chemistry of **10** and **11** are in progress.

(24) National Science Foundation Undergraduate Research Participant.

(25) National Science Foundation Predoctoral Trainee, 1968–1969.

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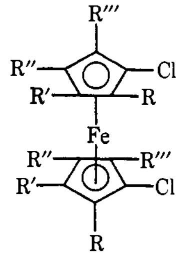
Oxidation-Resistant Metallocenes. Decachloroferrocene and Related Polychlorinated Ferrocenes

Sir:

Our interest in metallocene derivatives which might display a high degree of resistance toward oxidation has led us to investigate the synthesis and properties of a hitherto unknown class of organometallic compounds, the perhalometallocenes. Such a class would be expected to have considerable theoretical as well as practical importance. The present work was suggested by the known observation that the resistance of ferrocene toward chemical oxidation can be enhanced by the incorporation of electron-withdrawing substituents on the ferrocene ring. It has been shown that the effect of two such substituents on the oxidation potential of ferrocenes is roughly additive whether the substituents are located heteroannularly[1] or homoannularly.[2] Although this additive effect might be expected to diminish with additional electron-withdrawing substituents, substantial enhancement of oxidation resistance should result from complete substitution of the ferrocene rings by electron-withdrawing substituents. The only reported decasubstituted ferrocene derivatives, 1,1′,2,2′,3,3′,4,4′,5,5′-decamethyl-[3,4] and -decaethylferrocene,[5] contain solely electron-donating alkyl groups. The formation and high melting points of these compounds indicate, however, that there is no overwhelming steric barrier to decasubstitution in general. (The fact that decamethylferrocene is much more easily oxidized than ferrocene[4] also shows that decasubstitution does not necessarily protect the iron atom sterically against oxidation.) In the case of electron-withdrawing substituents, a second barrier to -decasubstitution which must be considered is their possible deleterious effect upon the metal-to-ring bonding. Some authors[3] have stated that π-cyclopentadienyl derivatives which are completely substituted with electronegative substituents do not appear to be stable.

In order to ascertain whether or not such compounds would possess both oxidative and thermal stability, the attention of the present authors has been centered upon the synthesis of perhalo and, specifically, decachloro and decafluoro derivatives of ferrocene and ruthenocene. In this communication, the preparation and properties of the first perhalometallocene, 1,1′,2,2′,3,3′,4,4′,5,5′-decachloroferrocene (Ie), a thermally stable metallocene derivative displaying unique oxidative stability, are described. In addition, the synthesis of two series of polychlorinated ferrocenes, Ib–Id and IIb–IIe, was carried out as part of the general investigation of polyhalogenated metallocene derivatives.



Ia, R, R′, R″, and R‴ = H
b, R = Cl; R′,R″, and R‴ = H
c, R and R′ = Cl; R″ and R‴ = H
d, R, R′, and R″ = Cl; R‴ = H
e, R, R′, R″, and R‴ = Cl
f, R = Li; R′, R″, and R‴ = H
g, R, R′, and R″ = Cl; R‴ = Li

The preparation of Ie was initiated by the reaction of 1,1′-dichloroferrocene (Ia) with *n*-butyllithium to give 1,1′-dichloro-2,2′-dilithioferrocene (If), followed by exchange chlorination of If with hexachloroethane, according to the method of Hauser and coworkers,[6] to give 1,1′,2,2′-tetrachloroferrocene (Ib).[7] By similar procedures, Ib was then converted to 1,1′,2,2′,3,3′-hexachloroferrocene (Ic),[7] Ic was converted to 1,1′,2,2′,3,3′,4,4′-octachloroferrocene (Id),[7] and Id was converted to Ie. *Anal.* Calcd for $C_{10}Cl_{10}Fe$: C, 22.64; Cl, 66.83; Fe, 10.53. Found: C, 22.61, 22.63; Cl, 66.90, 67.24; Fe, 10.21, 10.24. High-resolution mass spectrometry of Ie afforded a parent peak group with the required isotopic masses and distribution (Calcd for $C_{10}{}^{35}Cl_8{}^{37}Cl_2Fe$: 529.6175. Found: 529.6120). The infrared spectrum, in the region from 4000 to 250 cm^{-1}, showed only seven bands at 1350 (s), 1307 (m), 702 (s), 509 (w), 412 (m), 378 (m), and 368 cm^{-1} (m). No nmr signals were obtained.

The anticipated increased stability of the higher polychlorinated ferrocenes toward chemical oxidation was substantiated by treatment with strong oxidants. While Ib was destroyed immediately and Ic within 1 min by cold concentrated nitric acid, both Id and Ie, neat, were unaffected by heating either with concentrated nitric acid or concentrated sulfuric acid at 100° for 10 min. Id could be destroyed by stirring a carbon tetrachloride solution with cold concentrated nitric acid for 29 hr, whereas Ie was entirely unaffected by such conditions. No metallocene compound has been reported that exhibits stability toward nitric acid similar to that of Ie.

The thermal stability of compounds Ib–Ie was determined by the following decomposition points (obtained by differential scanning calorimetry at 5°/min under nitrogen): Ib (mp 147°), sublimes >200°; Ic (mp 191°) dec 254°; Id (mp 212°) dec 225°; Ie, dec 245°. Further evidence of the increasing oxidation resistance in the

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(1) E. G. Perevalova, S. P. Gubin, S. A. Smirnova, and A. N. Nesmeyanov, *Dokl. Akad. Nauk SSSR*, **155**, 857 (1964).

(2) A. N. Nesmeyanov, E. G. Perevalova, L. N. Yur'eva, and S. P. Gubin, *Izv. Akad. Nauk SSSR*, 909 (1965).

(3) R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, 8, 287 (1967).

(4) G. Illuminati, G. Ortaggi, and S. Scurro, *Rend. Accad. Naz. Lincei*, **43**, 364 (1967).

(5) K. Schlogl and M. Peterlik, *Monatsh. Chem.*, **93**, 1328 (1962).

(6) R. L. Gay, T. F. Crimmins, and C. R. Hauser, *Chem. Ind.* (London), 1635 (1966).

(7) Fully characterized by elemental, infrared, nuclear magnetic resonance, and mass spectral analysis.