

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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Received March 4, 1970

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 perhalometalocenes. 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 heteroannularly¹ 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 ferrocene⁴ 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 authors³ 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 perhalometalocene, 1,1',2,2',-

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

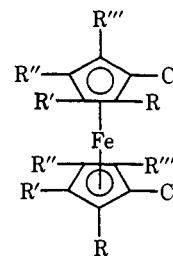
(2) A. N. Nesmeyanov, E. G. Perevalova, L. N. Yur'eva, and S. P. Gubin, *Izv. Akad. Nauk SSSR*, 909 (1965).

(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).

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 C₁₀Cl₁₀Fe: 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 C₁₀³⁶Cl₈³⁷Cl₂Fe: 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

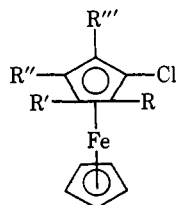
(6) R. L. Gay, T. F. Crimmins, and C. R. Hauser, *Chem. Ind. (London)*, 1635 (1966).

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

series was the fact that Ib and Ic both decomposed between 190 and 210° in air, while Id and Ie showed the same decomposition behavior in air as under nitrogen.

The potential utility of Ie for the synthesis of other perchloroferrocene derivatives was demonstrated by treating Ie with *n*-butyllithium at -40 to -70° to form the dilithiated intermediate (Ig), which, upon hydrolysis, afforded Id in quantitative yield. Ig was also carbonated to yield the corresponding 1,1'-perchloroferrocenedicarboxylic acid (Ie, R''' = COOH)⁷ and iodinated to give 1,1'-diiodoperchloroferrocene (Ie, R''' = I).⁷ Preliminary evidence indicates that Ie can also be directly substituted by nucleophilic attack with methoxide or ethoxide ion to give the corresponding mono- or dimethoxy as well as mono-, di-, tri-, or tetraethoxy derivatives.

That the polychlorination procedure could also be applied exclusively to a single ferrocene ring was shown by the synthesis of series IIb-IIe,⁷ utilizing a stepwise procedure analogous to that used for compounds Ib-Ie with chloroferrocene (IIa) as the starting material. One member of this series, IIb, was reported previously by Russian workers who prepared it by an alternate procedure.⁵



- IIa, 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

Full experimental details of the synthesis of all compounds, together with results of nmr, mass spectral, and crystallographic studies now in progress, will be presented in forthcoming publications.

(8) A. N. Nesmeyanov, B. A. Sazonova, and N. S. Sazonova, *Dokl. Akad. Nauk SSSR*, 176, 598 (1967).

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Received October 11, 1969

Cyclobutadiene via Dehalogenation of Dihalocyclobutenes

Sir:

Evidence for the existence of cyclobutadiene has recently been obtained through degradation of its iron carbonyl π complex^{1a-d} and by flash pyrolysis of α -photopyrone.² However, of the earlier efforts³ to

(1) (a) G. F. Emerson, L. Watts, and R. Pettit, *J. Amer. Chem. Soc.*, 87, 131 (1965); (b) L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, 87, 3253 (1965); (c) P. Reeves, J. Henerly, and R. Pettit, *ibid.*, 91, 5888 (1969); (d) W. Tyerman, M. Kato, P. Kebarle, S. Masamune, O. Strausz, and H. Gunning, *Chem. Commun.*, 497 (1967).

(2) E. Hedaya, R. Miller, D. McNeil, P. D'Angelo, and P. Schissel, *J. Amer. Chem. Soc.*, 91, 1875 (1969).

(3) For an excellent review of these early works dealing with attempted cyclobutadiene synthesis see M. P. Cava and M. J. Mitchell,

prepare the compound utilizing the more classical techniques of olefin synthesis, only the method employed by Nenitzescu and coworkers⁴ appears to have met with even qualified success. These latter workers observed that contact of *cis*-dichlorocyclobutene with lithium and sodium amalgam led to mixtures of *syn*- and *anti*-tricyclooctadienes (I and II); with lithium the *anti* isomer predominated while with sodium the *syn* compound was formed in greatest amount. It was considered possible that the first of these experiments involved coupling reactions of intermediate organolithium compounds leading to II, while in the case of the sodium amalgam the predominance of the *endo* isomer I conceivably arose through a Diels-Alder type dimerization of cyclobutadiene generated in the reaction. However, in this latter case, attempts to trap the conjectured cyclobutadiene intermediate with dienes or dienophiles were unsuccessful.



Another powerful classical method of olefin synthesis of course is the dehalogenation of vicinal dihalides with zinc.⁵ Dehalogenation with zinc proceeds more readily in the order iodides > bromides > chlorides and generally the preferred elimination is *trans*,⁶ hence for this method *cis*-dichlorocyclobutene would be the least attractive starting material for a cyclobutadiene synthesis. We report now the synthesis of *trans*-dibromo- and -diiodocyclobutene and present evidence that the dehalogenation of these with zinc and with lithium amalgam proceeds with generation of cyclobutadiene.

It was earlier shown that oxidative degradation of cyclobutadieneiron tricarbonyl (III) with ceric ion in the presence of lithium chloride afforded *trans*-dichlorocyclobutene (IV, X = Cl).^{1a} Similar decomposition in the presence of lithium bromide is now found to yield *trans*-dibromocyclobutene (IV, X = Br);⁷ the material is isolated as a colorless oil, bp 26° (0.05 mm), having an nmr spectrum consisting of two equal areas of absorption at τ 3.71 and 5.03. The *trans* nature of the compound is demonstrated by addition of bromine to yield *all-trans*-tetrabromocyclobutane⁸ (mp 104°, nmr τ 5.73 (s)). When lithium iodide is used in the reaction the decomposition of III gives rise to diiodocyclobutene (IV, X = I); this material has an nmr spectrum consisting of two equal areas of absorption centered at τ 3.70 and 4.82 and the nature of the substitution is assumed to be *trans* by analogy with that of the corresponding chloride and dibromide.⁹ The formation of

"Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967.

(4) M. Avram, I. G. Dinulescu, E. Marica, G. Mateescu, E. Sliam, and C. D. Nenitzescu, *Ber.*, 97, 382 (1964).

(5) For example the dehalogenation of vicinal dibromides with zinc in aqueous organic solvents has a value of $\Delta H \approx -70$ kcal/mol. In particular this method has been used to generate substituted cyclobutadienes, e.g., benzocyclobutadiene³ and tetramethylcyclobutadiene (C. E. Berkoff, R. C. Cookson, J. Hudec, and R. O. Williams, *Proc. Chem. Soc.*, 312 (1961)).

(6) S. Patai, "The Chemistry of Alkenes," Interscience, New York, N. Y., 1964, p 173.

(7) The elemental analyses for all new compounds reported here are in agreement with the proposed formula.

(8) M. Avram, L. Marica, and C. D. Nenitzescu, *Ber.*, 92, 1088 (1959).

(9) The molecular formula of the diiodo compound was obtained by