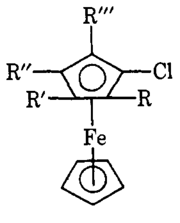
series was the fact that Ib and Ic both decomposed between 190 and 210° in air, while Id and Ie showed the same decomposition behavior in air as under nitrogen.

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.[8]



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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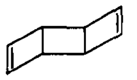
Cyclobutadiene *via* Dehalogenation of Dihalocyclobutenes

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 efforts[3] to prepare the compound utilizing the more classical techniques of olefin synthesis, only the method employed by Nenitzescu and coworkers[4] 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.


I


II

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*-tetrabromocyclobutane[8] (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

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(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. Henery, 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, "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 $\Delta H \simeq -70$ kcal/mol. In particular this method has been used to generate substituted cyclobutadienes, *e.g.*, benzocyclobutadiene[3] and tetramethylcyclobutadiene (C. E. Berkoff, R. C. Cookson, J. Hudec, and R. O. Williams, *Proc. Chem. Soc.*, 312 (1961)).

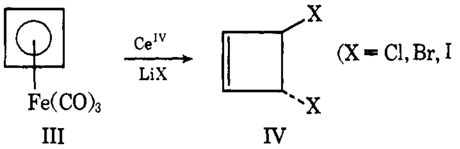
(6) S. Patai, "The Chemistry of Alkenes," Interscience, New York, N. Y., 1964, p 173.

(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

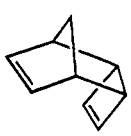
these three dihalocyclobutenes possibly stems from addition of the corresponding halogen to cyclobutadiene liberated in the oxidation of III; ceric ion rapidly oxidizes halide anions to the corresponding halogens; furthermore, when conducted in methanol the decomposition of the complex III with LiBr yields bromomethoxycyclobutene and tetrabromocyclobutane in addition to *trans*-dibromocyclobutene.

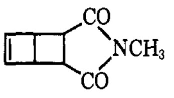


Treatment of either dibromocyclobutene or diiodocyclobutene with zinc dust in dimethylformamide at room temperature results in a vigorous exothermic reaction leading to the formation of the two cyclobutadiene dimers I and II (60% yield) with the former predominating (*vide infra*). Under similar conditions, using either the *cis*- or *trans*-dichlorocyclobutenes, no appreciable reaction with zinc occurs. A rapid exothermic reaction leading to a mixture of the hydrocarbons I and II also follows treatment of the two dihalides (IV, L = Br, I) with lithium amalgam in ether.

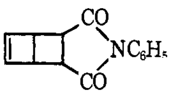
The simplest and most direct explanation for the formation of the hydrocarbons I and II in these reactions is that dehalogenation occurs to yield cyclobutadiene which then undergoes a Diels–Alder type dimerization. Other possible mechanisms could involve coupling reactions of either organozinc intermediates or of free radical species. However the formation of I and II occurs when acetic acid is used as a solvent and also occurs in solvents containing a 50 molar excess of phenol or hydroquinone; these data would then tend to eliminate mechanisms involving discrete organozinc intermediates or free radical species.

More convincing evidence for the generation of cyclobutadiene in these reactions is seen from experiments conducted in the presence of diene and dienophile trapping agents. Both dibromo- and diiodocyclobutene react with zinc dust in dimethylformamide containing cyclopentadiene to yield the hydrocarbon V.

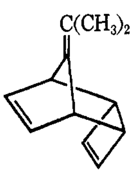

V



VI



VII



VIII

Compound V, the expected Diels–Alder adduct of cyclobutadiene and cyclopentadiene, is also produced when cyclobutadieneiron tricarbonyl is oxidatively decomposed in the presence of cyclopentadiene.[1a] In the presence of N-methyl- and N-phenylmaleimide the dehalogenation with zinc affords the two adducts VI (mp 47°, yield of purified material 34%) and VII (mp 136°), respectively.[11] The sterochemistry of the adducts VI and VII has not been determined; it is probably *endo* but in any event these identical compounds are also formed when cyclobutadiene is liberated from the complex III in the presence of the same dienophiles.

Particularly significant are the results obtained when dimethylfulvene is used as the trapping agent. Both the dehalogenation of dibromo- or diiodocyclobutene with zinc in the presence of dimethylfulvene and the oxidative decomposition of cyclobutadieneiron tricarbonyl (III) in the presence of dimethylfulvene lead to the formation of the hydrocarbon VIII.[12] The adduct VIII is again the product to be expected from a Diels–Alder addition of cyclobutadiene to dimethylfulvene. On the other hand, if intermediate organozinc compounds were involved in the reaction they would be expected to be nucleophilic in character and nucleophilic addition[13] (in particular, methyllithium) is known to occur at the terminal carbon atom of the exocyclic double bond of dimethylfulvene.

We have also found the hydrocarbon VIII to be present in the product mixture obtained from the dehalogenation of *cis*-dichlorocyclobutene with sodium amalgam in ether containing dimethylfulvene. Compound VIII is also formed when *cis*-dichlorocyclobutene is dehalogenated with lithium amalgam in benzene containing tetramethyethylenediamine and dimethylfulvene. The chelating amine is known to increase the anionic nature of lithium–carbon systems[14] and, in its presence, the reaction was anticipated to proceed similar to the sodium amalgam system with generation and entrapment of cyclobutadiene. It would appear then that at least part of this dehalogenation proceeds *via* cyclobutadiene and the failure of earlier attempts[4] to trap the material possibly arose from the incompatability of reactive dienophiles or dienes with sodium.

One interesting feature which remains to be explained concerns the ratio of *syn* to *anti* hydrocarbons (I and II) formed when the dihalides IV are dehalogenated under different conditions, particularly with varying solvent. For example, the dehalogenation of IV (X = Br or I) with zinc in dimethylformamide or pyridine affords a mixture of I and II in the ratio of approximately 100:1; this ratio drops to about 1:1 when acetic acid is used as a solvent. Similar behavior is also seen when cyclobutadiene is generated by oxidative decomposition of the iron carbonyl complex in different solvents; in dimethylformamide the ratio of the *syn* to *anti* dimers formed is approximately 100:1 and this value drops to about 2:1 when acetic acid is used as a solvent. The temperature and concentration under which the reactions are run also seem to affect the *syn*:*anti* ratio of the dimers, though the major factor appears to be the nature of the solvent. This feature of the present study remains to be explained satisfactorily although it should be noted that Berson and coworkers have previously reported a solvent effect on the *syn*:*anti*

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high-resolution mass spectroscopy. Also present in the reaction mixture is an isomer (nmr, τ 4.5 and 3.8) which, on standing, rearranges to the *trans*-diiodo compound mentioned in the text. Freedman and Doorakian[10] observed a similar facile rearrangement of bromotetraphenylcyclobutene.

(10) G. A. Doorakian and H. H. Freedman, *J. Amer. Chem. Soc.*, **90**, 3583 (1968).

(11) The nmr spectrum of the adduct VI consists of absorptions centered at τ 3.79 (m, 2), 6.31 (m, 2), 6.68 (m, 2), and 7.12 (s, 3), while adduct VII shows absorption centered at τ 2.66 (m, 5), 3.64 (m, 2), 6.21 (m, 2), and 6.49 (m, 2).

(12) The adduct VIII displays nmr absorptions centered at τ 4.14 (m, 4), 6.95 (m, 2), 7.19 (m, 2), and 8.51 (s, 6).

(13) K. Hafner, *et al.*, *Angew. Chem. Int. Ed. Engl.*, **2**, 123 (1963).

(14) A. W. Langer, *Trans. N. Y. Acad. Sci., Ser. II*, **27**, 741 (1965).

ratio in several Diels–Alder reactions.[15] In any event, since the two markedly different types of reactions[16] (dehalogenation of IV and oxidative decomposition of the complex III) give parallel results it seems likely that the phenomenon can be attributed to interactions involving cyclobutadiene liberated in the reactions.

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(15) J. A. Berson, Z. Hamlet, and W. A. Mueller, *J. Amer. Chem. Soc.*, **84**, 297 (1962).

(16) It was thought that the phenomenon could be attributed to hydrogen bonding of cyclobutadiene in protic solvents; thus the *syn* to *anti* ratio of the dimers formed upon dehalogenation of the diiodide with zinc is reduced from 125:1 to 30:1 upon changing from pure dimethylformamide to 20% water in dimethylformamide. However a low ratio (5:1) of *syn*:*anti* isomers is also found when dioxane is used as the solvent. Also the dehalogenation of *cis*-dichlorocyclobutene with sodium amalgam shows a similar variation with solvent; in ether the *syn*:*anti* ratio of dimers formed is approximately 30:1 and in pyridine it is 60:1.

(17) The authors thank the National Science Foundation, the Robert A. Welch Foundation, and the Petroleum Research Fund, administered by the American Chemical Society, for financial support. We also thank Badische Anilin und Soda Fabrik for a generous gift of cyclooctatetraene.

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Book Reviews

Acetylenes and Allenes. Addition, Cyclization, and Polymerization Reactions. By THOMAS F. RUTLEDGE, Atlas Chemical Industries, Inc. Van Nostrand-Reinhold Co., 450 West 33rd St., New York, N. Y. 1969. xvi + 432 pp. $21.50.

The author has undertaken the tremendous task of reviewing the addition, cyclization, and polymerization reactions of acetylenes and allenes in the present book, which has been preceded by a companion volume: "Acetylenic Compounds: Preparation and Substitution Reactions," Reinhold Book Corporation, 1968. The preparation of these books was certainly a timely undertaking because the most recent comprehensive text on acetylene chemistry was the elegant and most useful, but now outdated book by R. A. Raphael: "Acetylenic Compounds in Organic Syntheses," Butterworth and Co. (Publishers), London, 1955. As so often happens, the new book appeared almost simultaneously with a similar one; in this case, "Acetylene Chemistry," Marcel Dekker Inc., New York, 1969, a combined effort of an international group of authors under the editorship of H. G. Viehe. Fortunately the books are not competitive but nicely supplement each other. Rutledge's study has the advantage of being uniformly prepared, it easily allows a general orientation, while Viehe's production goes much more in depth and provides complete coverage of certain topics.

At first glance Rutledge's second book makes a favorable impression. The material is well organized and a large body of data has been brought together. Much useful information can be found on every page. When one starts reading, however, it appears that the writing is very condensed. This is an advantage if the style is clear and the wording precise, but in this respect the book is disappointing. One notes quite a number of misleading or even incorrect statements and sometimes the literature references are mixed up. An undue number of annoying printing errors both in the text and in the structural formulas at times makes reading difficult.

This is to be strongly regretted as more careful editing would have done better justice to the enormous amount of work involved in the collection of the literature data.

Despite these shortcomings the book is valuable and deserves to be consulted frequently not only by workers in the field of acetylenic compounds but by all synthetic organic chemists. There is hardly any domain in organic synthesis where acetylenic compounds cannot render useful service. This book and its companion volume are inexhaustible sources of inspiration.

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Utrecht, Netherlands

BOOKS RECEIVED, *March 1970*

THOMAS E. BARMAN. "Enzyme Handbook" (in two volumes, not sold separately). Springer-Verlag, New York, Inc., 175 Fifth Ave., New York, N. Y. 1969. 928 pp. $19.50.

FRANK A. BOVEY. "Polymer Conformation and Configuration." Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1969. 177 pp. $9.50.

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KENNETH B. WIBERG, Editor-in-Chief. "Organic Syntheses. An Annual Publication of Satisfactory Methods for the Preparation of Organic Chemicals." Volume 49. John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1969. 159 pp. $7.95.