both norbornadiene and 7-substituted norbornadienes enter into equilibria of the type **4** $\rightleftharpoons$ **5** $\rightleftharpoons$ **6** and that the position of equilibrium is influenced by the substituents.

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Electrochemical Generation of Stereoisomeric Vinyl Radicals

Sir:

Products isolated from the electrochemical reduction of alkyl halides are generally indicative of carbanion intermediates.[1] A mechanism often suggested for the over-all process involves initial formation of a free radical, which is reduced to the carbanion in a subsequent step (eq 1). Relatively little unambigous evidence has

$$\mathrm{RX} + e^- \longrightarrow \mathrm{X}^- + \mathrm{R}\cdot \xrightarrow{e^-} \mathrm{R}^- \longrightarrow \text{products} \qquad (1)$$

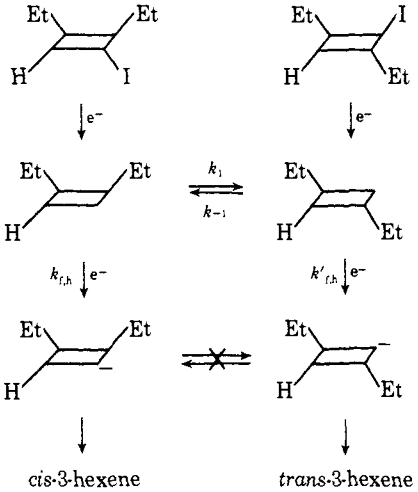
been cited for existence of radical intermediates in these reductions, and at least one investigator[1b] has preferred a concerted two-electron reduction directly to the carbanion. Isolation of alkylmercuric compounds in a few cases[1c,e] would appear, however, to be more consistent with the intermediacy of radicals in such cases. We wish to report direct stereochemical evidence for the existence of vinyl radicals, during the electrochemical reduction of stereoisomeric vinyl iodides, on a time scale sufficiently long to allow partial equilibration before further reduction to the carbanion. Electrochemical reduction of the stereoisomeric 3-iodo-3-hexenes[2] in dimethylformamide (DMF) containing tetraethylammonium bromide (TEAB) affords in each case a mixture of *trans*- and *cis*-3-hexene (total yields 89–92%) (Table I). *trans*-3-Hexene is the predominant product in each case, but it is formed in distinctly higher yields from *trans*-3-iodo-3-hexene than from the *cis*-iodide. Furthermore, electrochemical reduction in the presence of a tenfold excess of phenol (an excellent carbanion trapping agent in DMF)[3] results in exactly the same product ratios as in the absence of phenol. This indicates that isomerization of vinyl carbanions cannot be a significant pathway by which stereochemistry of the starting materials is lost on the way to products. Rates of isomerization of vinyl radicals, on the other hand, are very high[4] and hence the results are consistent with Scheme I involving radical intermediates.

Table I. Stereochemistry of Products from Electrochemical Reduction of the Stereoisomeric 3-Iodo-3-hexenes at 25°[a–d]

Substrate (0.01 *M*)	Phenol concentration, *M*	Relative % products[e] *trans*-3-Hexene	*cis*-3-Hexene
trans-3-Iodo-3-hexene	0	94	6
trans-3-Iodo-3-hexene	0.1	94	6
cis-3-Iodo-3-hexene	0	70	30
cis-3-Iodo-3-hexene	0.1	70	30

[a] The iodides were purified by preparative vpc (1/4 in. by 3 ft column, 20% SF-96 on Fluoropak 80, 110°) immediately before electrochemical experiments. [b] Product analyses were by vpc (1/8 in. by 20 ft column, 25% 1,2,3-tris(β-cyanoethoxy)propane, 30°). [c] Each iodide possesses a single well-developed polarographic wave at −1.35 V *vs.* Ag–AgBr; limiting currents were proportional to the square root of the mercury column height, indicating diffusion control, and values of the diffusion current constant, $I_\mathrm{d} = i_\mathrm{d}/\mathrm{cm}^{2/3}t^{1/6}$, indicated an over-all two-electron reduction. [d] The stereoisomeric 3-hexenes and 3-iodo-3-hexenes were stable to the reaction conditions. [e] Relative and absolute yields were reproducible to ±2%.

Scheme I



Isolation of partially equilibrated products implies that *isomerization rates are comparable in magnitude to rates of reduction* ($k_{f,h}$,$k'_{f,h}$) *of the radicals to carbanions.*[5] It is not normally possible to measure high electron-transfer rates under conditions where, as must certainly be true for $k_{f,h}$ and $k'_{f,h}$, mass transport is the rate-limiting step. We wish to point out that when values for the high rates of isomerization of vinyl radicals become available, the data of Table I and similar experiments should allow rather close estimates of the high rates of electron transfer to vinyl radicals. Stereochemical evidence of this sort may be made the basis of a general procedure for indirect measurement of rates of

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[1] (a) R. E. Erickson, R. Annino, M. D. Scanlon, and G. Zon, *J. Amer. Chem. Soc.*, **91**, 1767 (1969); (b) M. R. Rifi, *Tetrahedron Lett.*, 1043 (1969); (c) C. K. Mann, J. L. Webb, and H. M. Walborsky, *ibid.*, 2249 (1966); (d) A. J. Fry and R. H. Moore, *J. Org. Chem.*, **33**, 1283 (1968); (e) J. W. Sease and R. C. Reed, Abstracts, Electrochemical Society Meeting, New York, N. Y., May 1969, No. 134, p 328.

[2] G. Zweifel and R. B. Steele, *J. Amer. Chem. Soc.*, **89**, 5085 (1967).

[3] (a) P. H. Given and M. E. Peover, *J. Chem. Soc.*, 385 (1960); (b) A. J. Fry and M. A. Mitnick, *J. Org. Chem.*, in press; (c) tetraethylammonium bromide is the proton donor, *via* Hoffmann elimination, in the absence of phenol.

[4] (a) R. M. Fantazier and J. A. Kampmeier, *J. Amer. Chem. Soc.*, **88**, 5219 (1966); (b) L. A. Singer and N. P. Kong, *ibid.*, **89**, 6805 (1967).

[5] These results constitute the second unequivocal experimental interception of stereoisomeric vinyl radicals; the first such report[6] utilized a reaction (the isomeric 3-chloro-3-hexenes plus sodium naphthalenide) similar in its gross aspects to the electroreductions reported here. The stereospecific reduction of vinyl halides by dissolving metals[7] may also involve radical intermediates.

[6] G. D. Sargent and M. W. Browne, *J. Amer. Chem. Soc.*, **89**, 2788 (1967).

[7] M. C. Hoff, K. W. Greenlee, and C. E. Boord, *ibid.*, **73**, 3329 (1951).

fast electrode processes when such rates are not accessible by conventional means.

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Tricarbonyliron Complexes of Functional 1,2-Disubstituted Cyclobutadienes

Sir:

The recent discovery that free cyclobutadiene can be generated and intercepted as a transient intermediate by oxidative degradation of the corresponding tricarbonyliron complex[1] has presented the possibility that the chemistry of cyclobutadienes and cyclobutadienoid systems may at last be vulnerable to systematic development.[2] A major barrier to full elaboration of this approach is the scarcity of general methods for synthesizing metal complexes of specifically substituted cyclobutadienes possessing functional groups. Most current methods suffer from either lack of generality or difficultly accessible precursors for the complexation step,[3] with the result that at the present time only tricarbonyliron complexes of a series of monosubstituted cyclobutadienes, which have been prepared by electrophilic substitution reactions on the parent complex in conjunction with conventional manipulation of functionality,[4] are available *via* a general route. We have initiated a program directed toward preparation and study of a variety of cyclobutadiene-related systems by the metal complex route and describe the first results herein. Initial effort has been directed toward functional 1,2-disubstituted cyclobutadienes and this report is concerned with the synthesis of a series of tricarbonyliron complexes of this type. The availability of complexes with this particular substitution pattern is of special interest since it will not only permit potential experimental studies of a large number of theoretically interesting 1,2-disubstituted cyclobutadienes,[5] but also provide possible access to complexes of many equally interesting cyclobutadienoid systems through cyclization reactions involving adjacent substituents.

Irradiation of a dioxane solution of dichloromaleic anhydride, a threefold excess of *trans*-1,2-dichloroethylene, and benzophenone as sensitizer under nitrogen with a Hanovia 450-W high-pressure lamp through Pyrex afforded, after aqueous work-up and esterification of the resulting diacid with diazomethane, tetrachloro diester **1**[6,7] [mp 92–93°; $\nu_{\mathrm{max}}^{\mathrm{CCl}}$ 1765 (sh), 1755, and 1725 cm^{-1}; $\delta_{\mathrm{TMS}}^{\text{acetone-}d_6}$[8] 3.85 (s, 3 H, $-\mathrm{OC}H_3$), 3.95 (s, 3 H, $-\mathrm{OC}H_3$), and 5.10 (AB quartet, 2 H, $\Delta\nu_{\mathrm{AB}} = 25.5$ cps, $J_{\mathrm{AB}} = 9.0$ cps, $-\mathrm{C}H\mathrm{ClC}H\mathrm{Cl}-$)] in 32% yield. Treatment of the latter with activated zinc and recently prepared diiron nonacarbonyl[9] in refluxing 10% (v/v) acetic acid in ether under nitrogen led in 7–9% yield to 1,2-bis(carbomethoxy)cyclobutadieneiron tricarbonyl (**2a**)[10] [yellow needles, mp 105–106.5°; *m/e* 308, 280, 252, and 224; ν_{max}^{KBr} 1723, 1985, and 2063 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 3.77 (s, 6 H, $-\mathrm{OC}H_3$) and 4.77 (s, 2 H, ring protons)].

From this key intermediate a series of complexes was prepared by standard methods. Thus hydrolysis ($\mathrm{KOH{-}CH_3OH}$) could be effected either completely to diacid **2b**[11] [yellow amorphous powder, 208–214° dec; $\nu_{\mathrm{max}}^{\mathrm{dioxane}}$ 1705 (sh), 1723 (sh), 1740, 1990, 2060, and 2500–3400 cm^{-1} (br); $\delta_{\mathrm{TMS}}^{\text{acetone-}d}$ 5.20 (s, 2 H, ring protons) and 5.85 (bs, 2 H, $\mathrm{CO_2}H$)] or partially to half-ester **2c**[13] [yellow needles, mp 130–137°; $\nu_{\mathrm{max}}^{\mathrm{CHCl_3}}$ 1670, 1735, 2010, 2075, and 2500–3400 cm^{-1} (br); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 3.86 (s, 3 H, $-\mathrm{OC}H_3$), 4.78 (s, 1 H, ring proton), 4.94 (s, 1 H, ring proton), and 10.06 (bs, 1 H, $-\mathrm{CO_2}H$)], a cyclobutadiene complex which is unique in this series in being potentially resolvable. Treatment of diacid **2b** with thionyl chloride and pyridine at room temperature yielded bis(acid chloride) **2d** [orange needles, mp 153–156°; $\nu_{\mathrm{max}}^{\mathrm{CHCl_3}}$ 1775, 2020, and 2080 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.13 (s)], a highly versatile intermediate in this series. In one sequence **2d** was converted to bis(amide) **2e** [yellow microcrystals, mp 297–298° (dec, sealed tube); $\nu_{\mathrm{max}}^{\mathrm{KBr}}$ 1606, 1625, 1660, 1674 (sh), 2000, 2080, 3170, and 3360 cm^{-1}; $\delta_{\mathrm{TMS}}^{\text{DMSO-}d_6}$ 5.08 (s, 2 H, ring protons), 7.40 (bs, 2 H, NH),

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(1) L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Amer. Chem. Soc.*, **87**, 3253 (1965).

(2) The value of this method in providing cyclobutadiene for mechanistic and synthetic studies has already been established: (a) G. D. Burt and R. Pettit, *Chem. Commun.*, 517 (1965); (b) L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Amer. Chem. Soc.*, **88**, 623 (1966); (c) J. C. Barborak and R. Pettit, *ibid.*, **88**, 1328 (1966); (d) J. C. Barborak and R. Pettit, *ibid.*, **89**, 3080 (1967); (e) W. Merk and R. Pettit, *ibid.*, **89**, 4787 (1967); (f) L. A. Paquette and L. D. Wise, *ibid.*, **89**, 6659 (1967).

(3) For recent reviews of methods of preparation of metal complexes of cyclobutadienes see: (a) M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967, Chapter 2; (b) P. M. Maitlis, *Advan. Organometal. Chem.*, 4, 95 (1966).

(4) J. D. Fitzpatrick, L. Watts, G. F. Emerson, and R. Pettit, *J. Amer. Chem. Soc.*, 87, 3254 (1965).

(5) For a discussion of theoretical aspects of some of the substituted cyclobutadienes pertinent to this work, see H. E. Simmons and A. G. Anastassiou in ref 3a, Chapter 12, pp 393–395.

(6) This cyclobutane synthesis is a direct extension of the photochemical cycloaddition of cyclic dihalomaleic acid derivatives to olefins developed by Scharf and Korte: (a) H. D. Scharf and F. Korte, *Chem. Ber.*, **98**, 764 (1965); (b) H. D. Scharf and F. Korte, *Angew. Chem.*, 77, 452 (1965).

(7) Compositional analyses of all new compounds reported herein for all elements except oxygen agreed within 0.3% of values expected of assigned structures.

(8) All nmr spectra were recorded at 60 Mcps at ambient temperatures.

(9) E. H. Braye and W. Hubel, *Inorg. Syn.*, 8, 178 (1966).

(10) Mechanistic considerations of this complexation step are clouded by the multiply heterogeneous conditions and by limited evidence that the necessity for the presence of zinc depends on the history of the diiron nonacarbonyl used. However, details of the procedure, which will be reported in the full paper, have been developed to the point that the stated yield range is consistently attained.

While the reaction could well involve preliminary dechlorination to a dichlorocyclobutene followed by complexation of the latter with diiron nonacarbonyl, other mechanisms cannot be ruled out at this time. Consequently, work is currently in progress to define through control experiments the product-forming intermediates involved in the reaction and thus to determine whether this approach represents a new reaction type or merely a variation of the dihalocyclobutene approach.

(11) It is of historical interest that **2b** is a metal complex of Perkin's "tetrenedicarboxylic acid," the objective of one of the first attempts to synthesize a cyclobutadiene.[12] The corresponding complex of the monoacid, "tetrenecarboxylic acid,"[12] has also been synthesized.[4]

(12) (a) W. H. Perkin, Jr., *J. Chem. Soc.*, 950 (1894); (b) W. H. Perkin, Jr., *Chem. Ber.*, 26, 2243 (1893).

(13) We are indebted to Mr. Frank Tsantes for developing a procedure for the preparation of this compound.