these compounds is due to one mole of crystal water, retained in most of the samples (*cf.* Table I). The absorption frequency attributable to *intra*molecular hydrogen bonding in the hydroxyaldehyde Schiff bases should appear near 3200–3300 cm.$^{-1}$, and would thus overlap the intense water O–H stretching absorption. The infrared evidence for the lack of strong intermolecular hydrogen bonding is in agreement with other physical properties of these substances (*e.g.*, some of the Schiff bases are soluble in dioxane and even chloroform). In view of the experimental evidence given above, the structures of the hydroxyaldehyde Schiff bases must be those indicated by formulas XXIII and XXIV. According to this interpretation, the neighboring carboxylate groups participate in binding the proton in a bifurcated hydrogen bond. Thus, the proton would be completely surrounded by electron donor sites, and the approach of a second molecule of the Schiff base to form an intermolecular hydrogen bond would be prevented. The structures thus indicated for the two principal tautomeric forms of a representative Schiff base contain the hydrogen atom bound in a manner very similar to what would be expected for the metal chelates formed by these Schiff bases.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILL.]

Organic Chemistry of Ferrocene. V.[1a] Cyclization of ω-Ferrocenylaliphatic Acids

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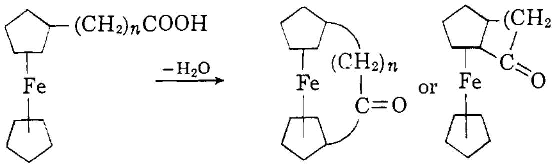
The effect of aliphatic chain length on cyclization has been studied in the series β-ferrocenylpropionic acid (Ib), γ-ferrocenylbutryic acid (Ic), δ-ferrocenylvaleric acid (Id) and ε-ferrocenylcaproic acid (Ie). The first member gives the heteroannularly bridged 1,1′-(α-ketotrimethylene)-ferrocene (IIb) while the second and third members give the homoannularly cyclized products IIIc and IIId and ε-ferrocenylcaproic acid gives only a polymer (XVII) of low molecular weight. Synthetic methods employed and some of the reactions of the mono-bridged compound are discussed, as are a pair of geometrical isomers (XIVa and XIVb) obtained from ferrocene-1,1′-dibutyric acid (XIII).

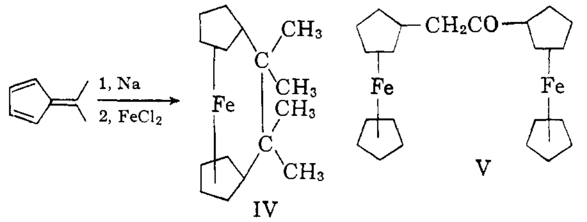
Homoannular and heteroannular cyclizations of ω-ferrocenylaliphatic acids (I) were reported previously in a short note,[2] while the synthesis of those acids was the subject of an earlier paper in this series.[3] The present paper describes details of these cyclizations and presents improved methods of synthesis of certain of the acids. The work described was undertaken to establish what the steric requirements are for cyclization of ω-ferrocenylaliphatic acids (I) to heteroannular or homoannular products (II or III, respectively).



I^{a-e} II^{a-e} III^{a-e}

Ia, IIa, IIIa: $n = 1$
Ib, IIb, IIIb: $n = 2$
Ic, IIc, IIIc: $n = 3$
Id, IId, IIId: $n = 4$
Ie, IIe, IIIe: $n = 5$

Ferrocenylacetic Acid.—Although it would have been quite surprising had ferrocenylacetic acid[3,4] (Ia) undergone either homoannular or heteroannular cyclization, this possibility was tested by treating ferrocenylacetic acid with polyphosphoric acid for 19 hours at 40°; only starting material was recovered. Heteroannular cyclization would have required linking the two rings by a 2-carbon bridge. Although a 2-carbon bridge is possible, as shown by the isolation of 1,1′-tetramethylethyleneferrocene (IV),[5a] the latter compound was prepared by cyclization around the central iron atom by a pre-formed bridge. It is doubtful that a 2-carbon bridge (IIa) can be formed by electrophilic substitution on an intact ferrocene molecule, reaction with 1,2-dichloroethane or oxalyl chloride in the presence of aluminum chloride giving 1,1-diferrocenylethane[5b] and diferrocenyl ketone,[5c] respectively. It is even less likely that the fused 5-4 ring system (IIIa) can be formed by the present methods. Indeed, intermolecular reaction has been observed to predominate in the reaction of ferrocenylacetyl chloride with excess ferrocene



IV V

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[1] (a) Paper IV, L. Westman and K. L. Rinehart, Jr., *Acta Chem. Scand.*, in press. (b) Alfred P. Sloan Foundation Fellow. (c) Undergraduate Research Participant supported by a grant (NSFG-8521) from the National Science Foundation.

[2] K. L. Rinehart, Jr., and R. J. Curby, Jr., *J. Am. Chem. Soc.*, **79**, 3290 (1957).

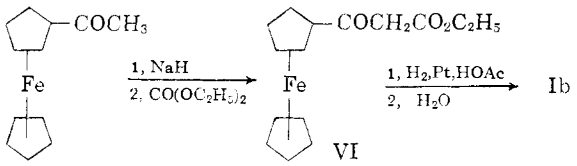
[3] K. L. Rinehart, Jr., R. J. Curby, Jr., and P. E. Sokol, *ibid.*, **79**, 3420 (1957).

[4] Although the ferrocenylacetic acid employed in this study was prepared by the Willgerodt reaction (in 25% yield from acetylferrocene),[3] the method of choice is undoubtedly the reaction of N,N-dimethylaminomethylferrocene methiodide with potassium cyanide, followed by nitrile hydrolysis (90% yield from methiodide) [D. Lednicer, J. K. Lindsay and C. R. Hauser, *J. Org. Chem.*, **23**, 653 (1958)], and this method has been used in later work from this Laboratory.[6]

[5] (a) K. L. Rinehart, Jr., A. K. Frerichs, P. A. Kittle, L. F. Westman, D. H. Gustafson, R. L. Pruett and J. E. McMahon, *J. Am. Chem. Soc.*, **82**, 4111 (1960). (b) K. L. Rinehart, Jr., P. A. Kittle and A. F. Ellis, *ibid.*, **82**, 2082 (1960). (c) S. I. Goldberg, *J. Org. Chem.*, **25**, 482 (1960).

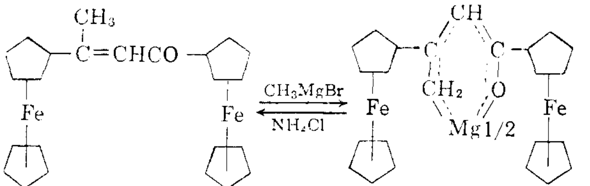
under Friedel-Crafts conditions to give deoxyferrocoin (V) in good yield.[6]

β-Ferrocenylpropionic Acid.—Of considerably more promise in cyclization reactions was β-ferrocenylpropionic acid (Ib). This compound has been prepared by a number of methods in the past: by the Willgerodt reaction (4% yield from propionylferrocene[3]); by hydrolysis and decarboxylation of ferrocenylmethylmalonic ester[7], in turn prepared from N,N-dimethylaminomethylferrocene methiodide and sodiomalonic ester (56% yield of Ib from methiodide); by the hydrogenation of β-ferrocenylacrylic acid, in turn prepared from ferrocenecarboxaldehyde and malonic acid (75% yield of Ib from the aldehyde)[8]; and by the hydrogenolysis and hydrolysis of ethyl ferrocenoyl acetate (VI).[3,9] The latter compound in turn has been prepared by the Friedel-Crafts reaction of ferrocene and carbethoxyacetyl chloride (71% yield)[9] and by the carbethoxylation of acetylferrocene employing sodium amide[3] or potassium amide[10] in liquid ammonia (65% yield).[10] In the present study sodium hydride (mineral oil dispersion) suspended in benzene was employed for the carbethoxylation of acetylferrocene, and the resulting keto ester was hydrogenolyzed over platinum oxide in acetic acid to give, after hydrolysis Ib in 70-78% yield over-all from acetylferrocene.

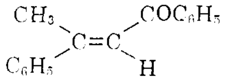


VI

During the present preparation of ethyl ferrocenoylacetate (VI), a small amount (4% or less) of 1,3-diferrocenyl-2-buten-1-one (VII), the aldol condensation product of two moles of acetylferrocene, was obtained under certain conditions. This material was identified by elemental analyses, and its infrared spectrum which contains carbonyl absorption at 1640 cm.$^{-1}$ and olefinic absorption at 1595 cm.$^{-1}$. An interesting aspect of the chemistry of VII is its lack of reactivity toward the Grignard reagent. When VII was treated with methylmagnesium bromide in ether a brilliant blue color was obtained, presumably due to the enolate ion VIII. Enolization was indicated by the observation that normal work-up of the reaction mixture gave only recovered starting material, even with a tenfold molar ratio of methylmagnesium bromide; no product corresponding to either 1,2- or 1,4-addition was observed. The failure of VII to add methylmagnesium bromide is rather surprising, since dypnone (IX), the benzene analog from acetophenone condensation, reacts with methylmagnesium bromide to give predominantly 1,2-addition and with other Grignard or lithium reagents to give 1,2- or 1,4-addition.[11]

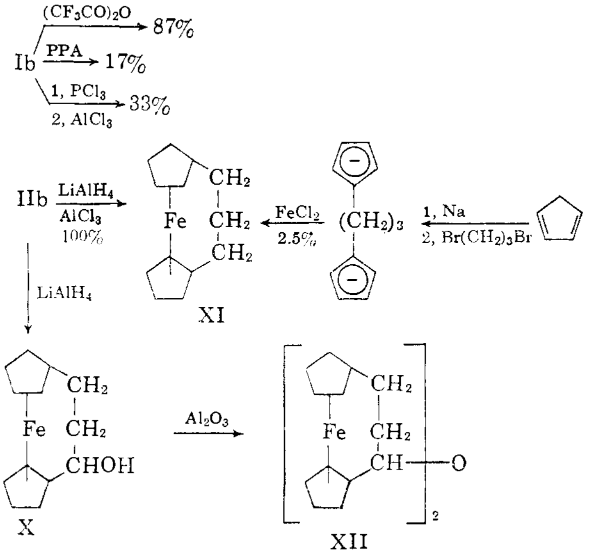


VII VIII



IX

Three methods were investigated for the self-condensation of β-ferrocenylpropionic acid; the reagent of choice proved to be trifluoroacetic anhydride. When this reagent was employed in carbon tetrachloride solution, 1,1′-(α-ketotrimethylene)-ferrocene (IIb) was obtained in yields as high as 87%,[12] lower yields being obtained with the neat reagent. The same product was obtained in 17% yield from treatment of Ib with polyphosphoric acid, and in 33% yield from treatment of β-ferrocenylpropionyl chloride with aluminum chloride.



XI X XII

The structure of IIb was assigned from its molecular weight (monomeric), and its infrared spectrum (*cf.* Table I) in which the bands at 1110 and 1004 cm.$^{-1}$, characteristic of an unsubstituted ring[9b,14,15] and to be expected for a homoannular

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(6) K. L. Rinehart, Jr., C. J. Michejda and P. A. Kittle, *J. Am. Chem. Soc.*, **81**, 3162 (1959).

(7) C. R. Hauser and J. K. Lindsay, *J. Org. Chem.*, **22**, 1246 (1957).

(8) K. Schlögl, *Monatsh.* **88**, 603 (1957).

(9) (a) R. B. Woodward and E. Csendes, personal communication. (b) Properties are reported in the Ph.D. thesis of M. Rosenblum, Harvard University, 1953.

(10) C. R. Hauser and J. K. Lindsay, *J. Org. Chem.*, **22**, 482 (1957).

(11) J. P. Freeman, *ibid.*, **22**, 1608 (1957).

(12) This reagent neat was first employed for the cyclization of β-ferrocenylpropionic acid by Woodward and Csendes,[9a] who apparently obtained the same bridged ketone,[9b] and who tentatively assigned the correct structure to the compound.[9a] The use of a dilute solution was later investigated by Hill and Richards, who reported a 69% yield of ketone.[13] We are indebted to Dr. Richards for information on this procedure in advance of publication.

(13) E. A. Hill and J. H. Richards, *J. Am. Chem. Soc.*, **83**, 4216 (1961).

(14) K. L. Rinehart, Jr., K. L. Motz and S. Moon, *J. Am. Chem. Soc.*, **79**, 2749 (1957).

(15) M. Rosenblum and R. B. Woodward, *ibid.*, **80**, 5443 (1958).

TABLE I

INFRARED ABSORPTION BANDS OF ACYLFERROCENES[a]

Acylferrocene	Absorption peaks, cm.$^{-1}$			
1,1′-(α-Ketotrimethylene)- (IIb)	1682	1266	..	..
1,2-(α-Ketotetramethylene)- (IIIc)	1679	1281	1109	1003
1,2,1′,2′-Bis-(α-ketotetramethylene)- (XIV) (low melting isomer)	1673	1285	..	..
1,2,1′,2′-Bis-(α-ketotetramethylene)- (XIV) (high melting isomer)	1678	1290	..	..
1,2-(α-Ketopentamethylene)- (IIId)	1655	1290	1110	1004

TABLE II

ULTRAVIOLET ABSORPTION MAXIMA OF ACYLFERROCENES[b]

λ_{max}, mμ	ϵ_{max}
225	12,240
265	3,840
335	1,080
226	17,600
270	7,500
227	22,700
268	17,400
232	19,400
269	17,400
227	15,500
269	7,400

[a] Carbon disulfide solutions. [b] In 95% ethanol.

cyclization product, were absent. Of particular interest is the ultraviolet spectrum of IIb, since the extinction coefficients of the maxima near 225 and 265 mμ are much lower (12,240 and 3,840, respectively (*cf.* Table II)) than those of acetylferrocenes[14,15] which are approximately 15,000–18,000 near 225 mμ and 5,000–7,000 near 265 mμ. This is attributed to lack of coplanarity between the cyclopentadienyl ring and the carbonyl group in 1,1′-(α-ketotrimethylene)-ferrocene (IIb).

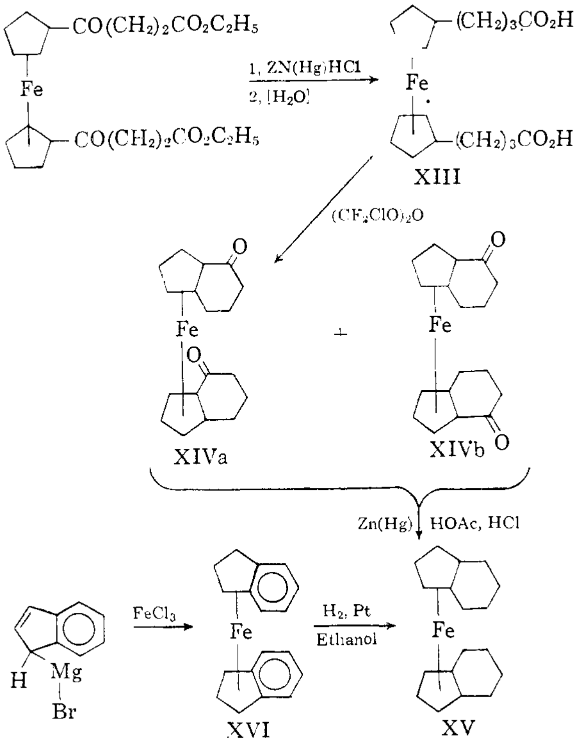
An occasional by-product of the trifluoroacetic anhydride reaction was β-ferrocenylethyl methyl ketone identified by analyses, infrared spectrum and basic hydrolysis to Ib.

Reduction of the ketone IIb with lithium aluminum hydride gave the corresponding alcohol X,[16] while reduction with lithium aluminum hydride–aluminum chloride[17] gave a nearly quantitative yield of the unsubstituted bridged compound. 1,1′-trimethyleneferrocene (XI). The latter compound has been obtained elsewhere by hydrogenolysis of the ketone IIb over platinum in acetic acid,[16,18] and by ring closure of the bis-1,3-dicyclopentadienylpropane dianion about a central iron nucleus.[19] The latter route of course provides independent proof of the structure of IIb.

The alcohol X appears to be singularly resistant to dehydration. Reaction with phosphorus oxychloride–pyridine gave unchanged starting material as the only identifiable product, while an attempt to dehydrate the alcohol over alumina[20,21] yielded a small amount (7–10%) of the corresponding ether XII, together with much recovered alcohol X. No olefin was isolated in either case.

Ferrocene Mono- and Dibutyric Acids.—γ-Ferrocenylbutyric acid (Ic)[3] was prepared from β-ferrocenoylpropionic acid using a modified procedure of Thomson.[22] Treatment of γ-ferrocenylbutyric acid with either trifluoroacetic anhydride of polyphosphoric acid gave the homoannular cyclization product 1,2-(α-ketotetramethylene)-ferrocene (IIIc); yields of 63–83% and 15%, respectively, were obtained.

$$\mathrm{Ic}\ \begin{matrix}\xrightarrow{\mathrm{PPA}} 15\% \\ \xrightarrow{(\mathrm{CF_3CO})_2\mathrm{O}} 63\text{–}83\%\end{matrix}\ \mathrm{IIIc}$$



The infrared and ultraviolet spectral data for this compound are presented in Tables I and II. The infrared spectrum of IIIc is essentially a composite of the spectra of ferrocene itself and of the symmetrically disubstituted compound XIV (*cf.* below) as would be expected from the earlier proposed "Infrared Rule of Annular Independence."[23,24] The latter rule states that the infrared spectrum of any ferrocene with differently

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(16) Apparently the first preparations of X and XI also were effected by Woodward and Csendes.[9a,b]

(17) R. F. Nystrom and C. R. A. Berger, *J. Am. Chem. Soc.*, **80**, 2896 (1958).

(18) K. Schlögl and H. Seiler, *Tetrahedron Letters*, **No. 7**, 4 (1960).

(19) A. Lüttringhaus and W. Kullick, *Angew. Chem.*, **70**, 438 (1958).

(20) (a) G. L. K. Hoh, Ph.D. Thesis, University of Kansas, 1960; (b) D. E. Bublitz, Ph.D. Thesis, University of Kansas, 1961.

(21) K. Schlögl and A. Mohar, *Naturwiss.*, **48**, 376 (1961).

(22) J. B. Thomson, *Chemistry & Industry*, 1122 (1959).

(23) M. Rosenblum, *ibid.*, 953 (1958).

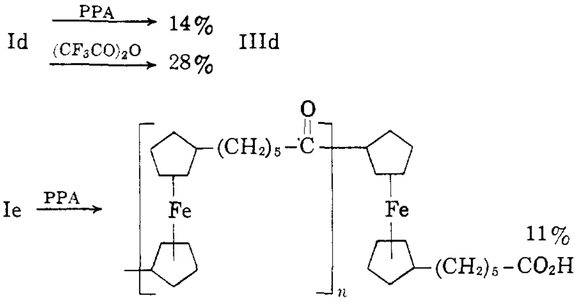
(24) K. L. Rinehart, Jr., 135th Meeting, American Chemical Society, Boston, Mass., April, 1959; *cf.* abstracts, p. 29-O.

ubstituted rings A and B is a composite of the spectra of two ferrocenes—one with two rings A and the other with two rings B. The well known "9–10 Rule,"[9b,15,24] is a corollary of this more general statement since the infrared spectrum of ferrocene, where the two rings A are unsubstituted, contains strong bands at 1110 and 1004 cm.$^{-1}$ (9 and 10 μ). In agreement with the homoannular cyclization structure in which the carbonyl group is coplanar with the cyclopentadienyl ring, the ultraviolet spectrum of IIc contains a very high maximum (ϵ 17,600) at 226 mμ (*cf.* Table II).

Similarly, treatment of 1,1′-ferrocenedibutyric acid (XIII) with trifluoroacetic anhydride led to homoannular cyclization, as has been reported earlier for the reaction of XIII with polyphosphoric acid by Nesmeyanov, Volkenau and Vilchevskaya.[25] The melting point of the crude product was the same as that reported earlier (130°).[25] The latter authors established homoannular cyclization by reduction of the product to 1,2,1′,2′-bis-(tetramethylene)-ferrocene (XV), identical in ultraviolet spectrum with the reduction product from bis-indenyliron (XVI). The diketone XV must exist as geometrical isomers XIVa and XIVb and, while these were not obtained by the earlier authors, fractional crystallization of the product in the present work led to the expected two isomers, m.p.'s 135.0–135.5° (16%) and 167–168° (8%). Assignment of structures as *meso* and D,L is not yet possible, however. The ultraviolet spectrum of the low melting isomer has maxima at 227 and 268 mμ with ϵ 22,700 and 17,400, respectively, while the high melting isomer has maxima at 232 mμ (ϵ 19,400) and 269 mμ (ϵ 17,400). The infrared spectrum of the low melting isomer has absorption peaks at 1673 and 1285 cm.$^{-1}$, while the high melting isomer has absorption peaks at 1678 and 1290 cm.$^{-1}$. The dibutyric acid starting material was prepared by Clemmensen reduction of the bis-ketoester obtained from disuccinylation of ferrocene.[26]

δ-Ferrocenylvaleric Acid.—This acid (Id)[3] was treated with both trifluoroacetic anhydride and with polyphosphoric acid. Both gave only the homoannularly cyclized product, 1,2-(α-ketopentamethylene)-ferrocene (IIId). The infrared spectrum of the compound has the expected 1110 and 1004 cm.$^{-1}$ bands for an unsubstituted cyclopentadienyl ring and its carbonyl band (Table I) occurs at a lower frequency than in IIIe, an effect already observed for the corresponding benzenoid compounds, 2,3-benzocycloheptanone and 2,3-benzocyclohexanone.[27] Similarly, the extinction coefficient of the ketone IId in the ultraviolet is lower than in IIIc, again analogous to the corresponding benzenoid systems.[28]

ϵ-Ferrocenylcaproic Acid.—Were this acid (Ie)[3] to condense intramolecularly and homoannularly (as Ic and Id), it would lead to an eight-membered ketone ring. Similarly, heteroannular intramolecular condensation would give a nine-membered ketone, if one counts the two ferrocene carbons and one iron as three members. Medium-sized rings (8–11 atoms)[29] are in general quite difficult to form and it is not surprising, then, that both modes of reaction are avoided in Ie and that the acid condenses intermolecularly. The resulting product is a keto acid, XVII, where the chain length *n* is approximately 2–3; the name polymer is not quite applicable and the term oligomer is suggested. In keeping with its structure the infrared spectrum of XVII contains weak carboxyl bands at 1725, 2700 and 2620 cm.$^{-1}$ and strong ketone absorption at 1660 cm.$^{-1}$.



XVII

Experimental[30]

Ferrocenylacetic Acid (Ia) and Polyphosphoric Acid.—A mixture of 50 mg. of ferrocenylacetic acid (Ia) and a large excess of polyphosphoric acid was heated at 40°, with occasional manual stirring. Small samples of the mixture were removed from time to time and decomposed with ice and equilibrated between bicarbonate and ether. Even after 19 hours at this temperature no color was observed in the organic layer and the experiment was discontinued.

The reaction was also attempted at higher temperature (56°), but no neutral product was ever obtained and decomposition was observed under these conditions.

Preparation of Ethyl Ferrocenoylacetate (VII).—A solution of 58.7 g. (0.25 mole) of acetylferrocene[31] in 500 ml. of anhydrous benzene was added dropwise during 90 minutes to a stirred mixture of 60.7 g. (0.515 mole) of diethyl carbonate, 23.9 g. of a mineral oil dispersion of sodium hydride (51.8%, corresponding to 0.515 mole) and 200 ml. of benzene.

The mixture was maintained at reflux under nitrogen for 24 hours, then cooled. Absolute ethanol (25 ml.) was then added to destroy excess sodium hydride, and the mixture was poured over ice drenched with a slight excess of hydrochloric acid. The aqueous layer was extracted with benzene until the extract was colorless and the combined benzene extracts and original organic layer were washed with water and dried over sodium sulfate. Removal of benzene on a rotary evaporator left a biphasic oil. The crude product crystallized after 2 hours at room temperature. Residual

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(25) A. N. Nesmeyanov, N. A. Volkenau and V. D. Vilchevskaya, *Doklady Akad. Nauk, S.S.S.R.*, **111**, 362 (1956).

(26) P. J. Graham, R. V. Linsey, G. N. Parshall, M. L. Peterson and G. M. Whitman, *J. Am. Chem. Soc.*, **79**, 3416 (1957).

(27) W. M. Schubert and W. A. Sweeney, *ibid.*, **77**, 4172 (1955).

(28) G. D. Hedden and W. G. Brown, *ibid.*, **75**, 3744 (1953).

(29) *Cf.* V. Prelog, in "Perspectives in Organic Chemistry," A. R. Todd, editor, Interscience Publishers, Inc., New York, N. Y., 1956, p. 96.

(30) Melting points were determined either on a Kofler micro hot-stage or in a Hershberg melting point apparatus and are uncorrected. Ultraviolet spectra were determined on approximately 10^5 *M* solutions in ethanol. Infrared spectra were obtained in the Spectroscopy Laboratory, by Messrs. O. W. Norton, R. Johnson and their associates; microanalyses in the Microanalytical Laboratory under Mr. J. Nemeth; all of the University of Illinois.

(31) Acetylferrocene has been prepared by various procedures in this Laboratory, but the method of choice seems to be that involving acetic anhydride and phosphoric acid (P. J. Graham, R. V. Lindsey, G. W. Parshall, M. L. Peterson and G. M. Whitman[26]). We are also grateful to Dr. E. O. Brimm of the Linde Air Products Co. for a generous sample of acetylferrocene at the start of our studies.

diethyl carbonate was decanted to leave 64 g. (83%) of the β-ketoester VII, m.p. 49–53° (lit.[10] m.p. 50–51°).[32]

Isolation of 1,3-Diferrocenyl-2-buten-1-one (VII).—In another run, the above carbethoxylation was carried out in 500 ml. of ether using 60.7 g. of diethylcarbonate, 23.9 g. of sodium hydride–mineral oil dispersion and 58.7 g. of acetylferrocene. Usual work-up of the reaction mixture gave a dark red oil which was dissolved in a minimum amount of benzene and chromatographed over 500 g. of Florex; development and elution were with benzene–cyclohexane (1:1).

The first fraction from the column yielded, after solvent removal on a rotary evaporator, 55.5 g. of a deep red oil, which was rechromatographed over the same Florex column after the column had been cleaned by washing with methanol followed by benzene. Elution with 50% ether in benzene and crystallization from hexane yielded 5.0 g. (4.4%) of 1,3-diferrocenyl-2-buten-1-one, m.p. 123–124°.

Anal. Calcd. for $C_{24}H_{22}Fe_2O$: C, 65.79; H, 5.06; Fe, 25.49. Found: C, 65.64; H, 5.12; Fe, 25.62.

The infrared spectrum of VII (potassium bromide pellet) contains strong bands at 1640 and 1595 cm.$^{-1}$, while the electronic spectrum (ethanol) contains absorption maxima at 319 (ϵ 5120), 388 (ϵ 1450) and 505 mμ (ϵ 1740). In base (0.0111 *N* sodium hydroxide) in ethanol the maxima are at 319 (ϵ 2422), 384 (ϵ 682) and 505 mμ (ϵ 606).

The second fraction from the column yielded, after solvent removal on a rotary evaporator, 13.4 g. (17.3%) of ethyl ferrocenoylacetate, m.p. 49–51°.

Reaction of Methylmagnesium Iodide with 1,3-Diferrocenyl-2-buten-1-one.—A solution of 388 mg. (0.9 mmole) of 1,3-diferrocenyl-2-buten-1-one in 100 ml. of ether was added dropwise to a stirred solution of 1 millimole of methylmagnesium iodide in 40 ml. of absolute ether under argon. With the first drop the solution turned brilliant blue. The ultraviolet spectrum of the blue solution contained maxima at 253, 296 and 371 mμ. After completion of addition, the solution was heated for 6 hours under reflux, cooled and hydrolyzed with saturated ammonium chloride. Workup then yielded 415 mg. of crude recovered starting material, m.p. 112–115°, infrared spectrum nearly identical to starting material. Chromatography over alumina (Merck, activity I, ether eluent) gave a single band, which upon evaporation and recrystallization yielded pure VII, m.p. 124–126.5°, undepressed on admixture with authentic compound.

Anal. Found: C, 66.09; H, 5.23.

The reaction was repeated with an ethereal solution of 190 mg. (0.4 mmole) of ketone and 4 mmoles of methylmagnesium iodide. The blue solution stood overnight at room temperature; then the ether was distilled and tetrahydrofuran was added to the blue solid mass. The deep wine colored tetrahydrofuran solution was heated for 7 hours under reflux (52°), cooled and worked up as before to give 169 mg. of crude starting material, identified by melting point (110–120°) and infrared spectrum.

Preparation of β-Ferrocenylpropionic Acid(Ib).—A solution of 13.4 g. (0.445 mole) of ethyl ferrocenoylacetate in 150 ml. of glacial acetic acid was stirred for 45 hours under hydrogen at room temperature and atmospheric pressure with 2.0 g. of platinum oxide (pre-reduced *in situ*).[33] The catalyst was filtered, the filtrate was diluted with water, and a small amount of ascorbic acid was added to reduce any ferricinium ion formed. The resulting solution was extracted repeatedly with ether and the combined ether extracts were worked up to give 11.9 g. (93%) of the reduced ester as a pale yellow oil whose infrared spectrum (smear) contained a single carbonyl band at 1745 cm.$^{-1}$.

The crude saturated ester was saponified during 2 hours in a refluxing solution of 0.5 *N* sodium hydroxide in 50% aqueous ethanol. The solution was then cooled, diluted with water, extracted with ether, and cooled in an ice-bath. Acidification with hydrochloric acid to *p*H 3 precipitated β-ferrocenylpropionic acid (Ib), which was filtered and air-dried; yield 9.50 g. (88% from crude saturated ester, 82% from keto ester), m.p. 119–120° (lit.[3,7] m.p. 115–116°), undepressed on admixture with an authentic[3] sample.

Preparation of 1,1'-(α-Ketotrimethylene)-ferrocene (IIb). A. **Trifluoroacetic Anhydride Method.**—The procedure employed was essentially that of Richards and Hill[12,13]: a mixture of 9.50 g. (36.8 mmoles) of β-ferrocenylpropionic acid (Ib), 95 g. (450 mmoles) of trifluoroacetic anhyride and 400 ml. of carbon tetrachloride was stirred for 4.5 hours under nitrogen at room temperature in a sealed flask wrapped with aluminum foil. The mixture was then poured into excess sodium bicarbonate solution and the resulting aqueous layer was extracted with methylene chloride. The combined organic phases were then washed with water, 2 *N* potassium hydroxide, and water, and dried over magnesium sulfate. Removal of solvent left 7.90 g. (90%) of crude bridged ketone IIb, m.p. 138–143°. Recrystallization from hexane yielded 7.06 g. (81%) of pure 1,1'-(α-ketotrimethylene)-ferrocene, m.p. 146–147° (lit.[2] m.p. 145.5–146.5°).

Anal. Calcd. for $C_{13}H_{12}FeO$: C, 65.03; H, 5.04; Fe, 23.26; mol. wt., 240. Found: C, 64.50; H, 5.04; Fe, 23.98; mol. wt., 281 (ebull., benzene).

The reaction was repeated several times under identical conditions: yields of the crystallized ketone varied from 68–87%. In one run, the mother liquor from crystallization was concentrated to a very small volume. Chromatography of this concentrate over alumina then gave in 4% yield **β-ferrocenylethyl trifluoromethyl ketone**, m.p. 34.5–35°. The infrared spectrum of this compound contained a carbonyl band at 1760 cm.$^{-1}$ and unsubstituted cyclopentadienyl ring bands at 1110 and 1003 cm.$^{-1}$. The ketone etches Pyrex on ignition with calcium oxide followed by heating with sulfuric acid while a blank failed to etch Pyrex.

Anal. Calcd. for $C_{14}H_{13}F_3FeO$: C, 54.19; H, 4.19; Fe, 18.06. Found: C, 54.03; H, 4.38; Fe, 17.68.

In another run in which no carbon tetrachloride solvent was employed, 2.6 g. of β-ferrocenylpropionic acid was treated with 75 ml. of trifluoroacetic anhydride for 16 hours at 5°. The mixture was extracted with three 75-ml. portions of ether and the combined ether extracts were washed with excess saturated sodium bicarbonate and water, then dried over magnesium sulfate. Ether was removed and the product was chromatographed over an acid-washed alumina column. Benzene was employed as eluent. The deep red ketonic fractions were combined and solvent was removed. The product obtained, m.p. 143.5–145°, weighed 0.73 g. (30%). Upon recrystallization from pentane pure 1,1'-(α-ketotrimethylene)-ferrocene was obtained, m.p. 145.5–146.5°.

B. **Friedel–Crafts Method.**—A mixture of 2.6 g. (0.01 mole) of β-ferrocenylpropionic acid and 25 ml. of cold phosphorus trichloride was stirred overnight at room temperature. Excess phosphorus trichloride was removed under water aspirator pressure and the residue was dissolved in methylene chloride. An infrared spectrum of the crude material (obtained from an aliquot of the methylene chloride solution evaporated to dryness) contained a strong acid chloride carbonyl band at 1790 cm.$^{-1}$ and a weak carboxyl carbonyl band at 1705 cm.$^{-1}$.

The acid chloride–methylene chloride solution was added dropwise to a stirred cooled mixture of 1.5 g. (0.011 mole) of anhydrous aluminum chloride and 100 ml. of methylene chloride. After the addition was complete the mixture was allowed to stand overnight at room temperature and was then poured over ice. The aqueous phase was extracted repeatedly with methylene chloride and the combined organic portions were washed with water, saturated sodium sulfate, filtered, concentrated and transferred to a column of acid-washed alumina, 25 mm. × 45 cm.

The chromatogram was developed with benzene and eluted with methylene chloride–pentane (2:1); two bands appeared. The first fraction, an orange band, was crystallized from pentane after removal of the eluting solvent; wt. 0.8 g. (33%) of 1,1'-(α-ketotrimethylene)-ferrocene,

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[32] An additional advantage of the sodium hydride carbethoxylation is in few by-products. In one carbethoxylation of acetylferrocene by sodium amide in liquid ammonia (in this Laboratory performed by W. E. Adcock), the product was contaminated with two crystalline forms of diethyl imidodicarboxylate $[NH(COOC_2H_5)]$, m.p. 51–52, 74–75°, identified by its elemental analysis (Calcd.: C, 44.80; H, 6.84; N, 8.69. Found: C, 45.07; H, 6.89; N, 8.69) and infrared spectrum (3439, 2960, 1800, 1725, 1500, 1320, 1160, 1100 cm.$^{-1}$ in chloroform).

[33] Hydrogenolyses of larger samples (50–100 g.) of the keto ester were carried out in a large Parr bomb apparatus during 48–72 hours at room temperature and 200 p.s.i. Workup in this case consisted of filtration of the catalyst and removal of acetic acid on a rotatory evaporator. Yields were comparable to those described for the smaller runs.

m.p. 145°, undepressed by mixture with an authentic sample.

The purple aqueous phase from the original Friedel-Crafts reaction was made strongly acidic with concentrated hydrochloric acid, and 50 g. of stannous chloride was added. The blue-violet color gradually turned yellow-green and a yellow precipitate appeared. The mixture was extracted with ether and the yellow ether extract was washed repeatedly with water, then dried over sodium sulfate, filtered and evaporated on a steam-bath. The residue was crystallized from cyclohexane to yield 0.1 g. (4%) of recovered β-ferrocenylpropionic acid.

C. **Polyphosphoric Acid Method.**—A mixture of 2.6 g. of finely ground β-ferrocenylpropionic acid and 60 g. of polyphosphoric acid was stirred occasionally during 43 hours at room temperature. The viscous mass was poured over ice and extracted with ether. The ether extracts were washed successively with water, saturated sodium bicarbonate solution and water, then dried over sodium sulfate. The solution was concentrated and transferred to an acid-washed alumina chromatographic column, 25 mm. × 30 cm., which was eluted with methylene chloride–pentane (2:1). A single band was eluted from the column; removal of the solvent and crystallization from pentane gave 0.40 g. (17%) of 1,1′-(α-ketotrimethylene)-ferrocene, m.p. 145.5°. Acidification of the bicarbonate wash gave 37.5 mg. (1%) of recovered β-ferrocenylpropionic acid, m.p. 113°.

Preparation of 1,1′-(α-Hydroxytrimethylene)-ferrocene (X).—A solution of 2.0 g. of 1,1′-(α-ketotrimethylene)-ferrocene (IIb) in 150 ml. of anhydrous ether was added during 30 minutes to 160 ml. of a stirred stock solution of lithium aluminum hydride (*ca.* 1 *N*).[34] The mixture was stirred an additional 45 minutes at room temperature, then excess lithium aluminum hydride was decomposed by slow addition of ethyl acetate. The yellow suspension was poured over ice–dilute hydrochloric acid and the resulting organic layer was washed with water, dried and concentrated. Addition of pentane yielded 1.27 g. (63%) of the yellow alcohol X, melting 133–143°. Recrystallization from pentane gave pure 1,1′-(α-hydroxytrimethylene)-ferrocene, m.p. 159° (reported[9b] m.p. 153–154.5°.)

Anal. Calcd. for $C_{13}H_{14}FeO$: C, 64.50; H, 5.79; Fe, 23.15. Found: C, 64.60; H, 5.93; Fe, 23.36.

Attempted Dehydrations of 1,1′-(α-Hydroxytrimethylene)-ferrocene.—In a procedure identical to that of Schögl and Mohar[21] a mixture of 400 mg. of the alcohol, 2.5 g. of alumina (Woelm, acidic, activity I) and 12 ml. of dry benzene was stirred for 30 minutes under nitrogen. The alumina was filtered and washed repeatedly with ether. The combined ether and benzene phases were evaporated and the residual solid was chromatographed over alumina (Merck, neutral, activity III). No olefin was obtained; however, elution with 1% ether in hexane removed 37 mg. (10%) of bis-α-(1,1′-trimethyleneferrocene) oxide (XII), the diether derived from the alcohol X, and elution with 20% ether in hexane removed 0.340 g. 85%) of starting material. The crude ether melted 145–165°; after recrystallization from benzene–hexane it had m.p. 220–223° dec.

Anal. Calcd. for $C_{26}H_{26}Fe_2O$: C, 67.00; H, 5.62, Found: C, 67.22; H, 5.92.

Treatment of the alcohol with pyridine–phosphorus oxychloride at 0° and the usual work-up gave recovered starting material as the only identifiable product.

Preparation of 1,1′-Trimethyleneferrocene (XI) was by the method of Nystrom and Berger.[17] A solution of 6.0 g. (0.045 mole) of aluminum chloride in 60 ml. of dry ether was added dropwise, under nitrogen, to a stirred slurry of 1.14 g. (0.030 mole) of lithium aluminum hydride in 50 ml. of ether; then the mixture was stirred for 15 minutes more at room temperature. A solution of 7.16 g. (0.030 mole) of 1,1′-(α-ketotrimethylene)-ferrocene (IIb) in 350 ml. of dry ether was added and the mixture was then heated for 3.5 hours at reflux, cooled in an ice-bath. Excess reagent was decomposed with wet ether, then water, and the resulting aqueous layer was extracted with ether. The combined ether extracts were washed, then dried and concentrated to give 7.1 g. (quantitative) of 1,1′-trimethyleneferrocene, m.p. 103.5–106.0°. Recrystallization from petroleum ether (b.p. 30–60°) gave 7.0 g. (99%) of bright yellow plates, m.p. 107.5–108.0° (lit.[19] m.p. 106–107°).

Preparation of γ-Ferrocenylbutyric Acid (Ic).[22]—A mixture of 200 g. of zinc dust, 25 g. of mercuric chloride, 10 ml. of concentrated hydrochloric acid and 250 ml. of water was shaken for 10 minutes. The zinc amalgam was collected by filtration and washed with 3 ml. of 3% hydrochloric acid. The zinc amalgam was then placed in a 2-liter round-bottom flask, and there were added 230 ml. of water, 230 ml. of concentrated hydrochloric acid, 230 ml. of benzene and 43 g. of β-ferrocenylpropionic acid[25] (Ic) dissolved in 230 ml. of methanol. The mixture was heated overnight at reflux. The reaction was considered complete when all the color appeared in the organic phase. The organic layer was washed four times with 100 ml. of water, dried over magnesium sulfate, evaporated to 30 ml. and passed through an alumina column. Elution with benzene removed one yellow band. The yellow methyl ester residue after evaporation of the benzene was hydrolyzed with 60 ml. of 10 *N* sodium hydroxide by heating on a steam-bath for 30 minutes. Careful acidification of the solution to *p*H 2 with phosphoric acid gave 36 g. (88%) of γ-ferrocenylbutyric acid, m.p. 115–116° (lit.[3] m.p. 115–116°).

Preparation of 1,2-(α-Ketotetramethylene)-ferrocene (IIIc). A. Trifluoroacetic Anhydride Method.—γ-Ferrocenylbutyric acid (Ic, 9.84 g.) was dissolved in 40 g. of trifluoroacetic anhydride which had been cooled previously to −70°. The solution was stirred for 75 minutes at 0°, then poured over ice. The aqueous layer was extracted repeatedly with ether and the ether extracts were in turn washed with water, sodium carbonate solution and water, then dried and concentrated. The residual red oil was chromatographed over alumina. Elution with benzene–ether gave in the major band 7.88 g. (86%) of the ketone, which after recrystalliztion from ether weighed 7.20 g. (79%), m.p. 87.5–88.5°. Infrared and ultraviolet spectral data are presented in Tables I and II, respectively.

Anal. Calcd. for $C_{14}H_{14}FeO$: C, 66.19; H, 5.55. Found: C, 66.59; H, 5.69.

B. **Polyphosphoric Acid Method.**—γ-Ferrocenylbutyric acid (0.5 g.) was treated with polyphosphoric acid at room temperature for 4 hours with occasional stirring. The gummy, thick solution was poured over ice. The mixture was extracted with ether, which in turn was extracted with sodium carbonate solution and this with ether again. The combined ether solution was dried over sodium sulfate and condensed on a steam-bath. The remaining solution was transferred to a chromatography column, and eluted with benzene. Benzene was taken off under diminished pressure and red crystals (75 mg. 15%) obtained, m.p. 84.0–84.5°. Found: C, 66.59; H, 5.69. The ultraviolet spectrum has λ_{max} 226 mμ, ϵ_{max} 17,600; λ_{max} 270 mμ, ϵ_{max} 7,500.

Preparation of Ferrocene-1,1′-dibutyric Acid (XIII).—Diethyl ferrocene-1,1′-bis-(γ-ketobutyrate) was prepared by the method of Graham, *et al.*[26]

The bis-ketoester was then subjected to Clemmensen reduction by a procedure modified from that of Nesmeyanov, Volkenau and Vilchevskaya.[24] Diethyl 1,1′-ferrocene-bis-(γ-ketobutyrate), 4.0 g., m.p. 135–136° (lit.[13] m.p. 134–136°), was dissolved in 30 ml. of ethanol and 25 ml. of benzene; the solution was refluxed for 4 hours, with 20 g. of amalgamated zinc, 15 ml. of hydrochloric acid and 15 ml. of water. The benzene layer was washed with water, with sodium bicarbonate solution, and with sodium sulfate solution. The aqueous layer was extracted twice with benzene and the benzene layers were washed and dried. The combined benzene solutions were concentrated and chromatographed on alumina with benzene. The ester came down in one broad band, leaving a band of unreduced keto-ester at the top of the column. The center part of the ester band was evaporated and saponified by heating with sodium hydroxide in ethanol. The solution was diluted with water and extracted with ether; no unsaponified ester was observed in the ether layer. The sodium hydroxide solution was acidified with phosphoric acid and extracted with ether. The ether solution was washed with water and dried over sodium sulfate; then the acid was crystallized by displacement of the ether by hexane; the yield was 0.45 g. (14% from *bis*-ketoester), m.p. 109–110° (lit.[1] 109.5–110.5°).

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[34] W. G. Brown, in "Organic Reactions," Vol. 6, R. Adams, ed., John Wiley and Sons, Inc., New York, N. Y., 1951, p. 469.

Preparation and Separation of the Isomeric 1,2,1′,2′-Bis(α-ketotetramethylene)-ferrocenes XIVa and XIVb.—Ferrocene-1,1′-dibutyric acid (XIII, 0.45 g.) was added to 5.0 g. of trifluoroacetic anhydride at −70°. The orange suspension was swirled in an ice-bath for 30 minutes, allowed to come to room temperature during 1 hour, and finally poured over ice-sodium hydroxide. The aqueous solution was extracted with ether and the ether extract was washed, dried, filtered and transferred to an alumina column. Elution with 5% acetone in ether removed 5.6 mg. (1%) of 1,2-(α-ketotetramethylene)-ferrocene (IIIc) from monoacid impurity in the starting di-acid, while elution with 20% acetone in ether gave 0.176 g. (47%) of a mixture of isomeric diketones XIVa and XIVb.

Recrystallization of the product from ether–acetone gave 31.6 mg. of material melting 153–161° dec., which after two further recrystallizations from ether–acetone had constant m.p. 167–168°. The infrared spectrum (potassium bromide pellet) has bands at 3100, 2970, 1678, 1480, 1455, 1350, 1290, 1253, 1175, 1025, 985 and 840 cm.$^{-1}$, while the ultraviolet spectrum has λ_{max} 232 mμ (ϵ 19,400) and λ_{max} 269 mμ (ϵ 17,400).

Anal. Calcd. for $C_{18}H_{18}FeO_2$: C, 67.10; H, 5.63; Fe, 17.33. Found: C, 66.99; H, 5.61; Fe, 17.37.

The mother liquor from the first crystallization was concentrated and the acetone–ether was displaced by hexane. Crystallization at −70° gave 104.6 mg. of orange–red crystals, m.p. 134.0–135.5°. Repeated recrystallization from hexane gave 69.4 mg. of the pure isomer, m.p. 135.0–135.5°. The infrared spectrum contains essentially the same bands as those given for the other isomer, while the ultraviolet spectrum has λ_{max} 227 mμ (ϵ 22,700) and λ_{max} 268 mμ (ϵ 17,400).

Preparation of 1,2-(α-Ketopentamethylene)-ferrocene (IIId). A. Polyphosphoric Acid Method.—A mixture of a small amount (500 mg.) of δ-ferrocenylvaleric acid (Id)[3] and polyphosphoric acid stood for 4 hours with occasional manual stirring. It was then poured over ice and extracted with ether, which was in turn washed with sodium carbonate and water, dried and concentrated to small volume. The remaining solution was chromatographed over alumina (Merck, basic). Elution with benzene gave a single band, which on concentration under reduced pressure gave 70 mg. (14%) of red crystals, m.p. 61–63°.

Anal. Calcd. for $C_{15}H_{16}FeO$: C, 67.19; H, 6.02. Found: C, 66.99; H, 6.18.

B. **Trifluoroacetic Anhydride Method.**—To 10 ml. of trifluoroacetic anhydride was added slowly 0.30 g. (0.001 mole) of δ-ferrocenylvaleric acid (Id).[3] The reaction mixture was cooled to 5°, allowed to stand for 16 hours with occasional shaking, and finally poured over ice. Workup as in method A gave 80 mg. (28%) of 1,2-(α-ketopentamethylene)-ferrocene (IIId) as red crystals, m.p. 57–58°, infrared spectrum nearly identical to that of the product from method A.

Reaction of ε-Ferrocenylcaproic Acid with Polyphosphoric Acid.—A purple mixture of 1.09 g. of ε-ferrocenylcaproic acid and 21 g. of polyphosphoric acid was stirred occasionally for 10 hours at room temperature and 4 hours at 56°, then cooled and poured over ice. The product–acid mixture was extracted successively with ether and methylene chloride; there remained undissolved an orange precipitate in the aqueous layer. This was filtered, washed with water, and digested with acetone, then dried for 24 hours at 1 mm. and room temperature; yield, 0.12 g. (11%). The orange solid did not melt below 200°, but decomposed slowly above that temperature. Its analytical values and infrared spectrum (strong ketone carbonyl at 1660 cm.$^{-1}$ and weak carboxyl carbonyl at 1725 cm.$^{-1}$) indicated that it was an intermolecular condensation product.

Anal. Calcd. for $(C_{16}H_{18}FeO)n$: C, 68.14; H, 6.43; Fe, 19.80. Calcd. for $C_{16}H_{20}FeO_2$: C, 64.03; H, 6.72; Fe, 18.61. Calcd. for $H(C_{16}H_{18}FeO)_2OH$: C, 66.0; H, 6.53; Fe, 19.2. Calcd. for $H(C_{16}H_{18}FeO)_3OH$: C, 66.8; H, 6.49; Fe, 19.4. Found: C, 66.7; H, 6.58; Fe, 18.09, 18.30.

Both the original ether and methylene chloride extracts were worked up in the same way: washed with water, sodium carbonate, water, dried, evaporated, chromatographed over alumina. From the ether extract were obtained two small neutral chromatographic bands, while the major portion of the methylene chloride extract appeared to be recovered, starting acid and only very little neutral material was found.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY, HARVARD UNIVERSITY, CAMBRIDGE 38, MASS.]

Peresters. IX. Di-*t*-butyl Monoperoxycarbonate

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Di-*t*-butyl monoperoxycarbonate (IV) decomposes at 100° in cumene to yield a mole of carbon dioxide, 0.06 mole of methane, 0.82 mole of bicumyl and *t*-butyl alcohol and acetone in a ratio of about 15 to 1. For the decomposition of this perester $\Delta H^{\ddagger} = 35.4$ kcal. and $\Delta S^{\ddagger} = 14.6$ e.u. It is about 100 times faster than di-*t*-butyl peroxide at 100°, and about 10^5 times slower than di-*t*-butyl diperoxyoxalate (I) at 45°. The absence of di-*t*-butyl peroxide in the decomposition products of the peroxycarbonate, and of the latter in the decomposition products of the diperoxyoxalate, shows that there is no cage effect in either of these decompositions.

Introduction

In the decomposition of di-*t*-butyl diperoxyoxalate (I) in cumene at 25–45° the only products are *t*-butyl alcohol and carbon dioxide[1] and there is no cage effect.[2] The corresponding monoperoxyoxalate, (II) however,[3] yields 37–44% di-*t*-butyl carbonate (III) and only about half of the radicals are scavengeable. From these results it is clear that two *t*-butoxy radicals do not recombine with a low enough activation energy for their coupling to be diffusion controlled. To explain the nonoccurrence of di-*t*-butyl monoperoxycarbonate (IV) among the products from I there were two possibilities: (1) the monoperoxycarbonate was not formed because the carbo-*t*-butylperoxy radical V, unlike the carbo-*t*-butoxy radical VI, did not survive even the few collisions necessary for cage recombination; or (2) the monoperoxycarbonate

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(1) P. D. Bartlett, E. P. Benzing and R. E. Pincock, *J. Am. Chem. Soc.*, **82**, 1762 (1960).

(2) P. D. Bartlett and T. Funahashi, *ibid.*, **84**, 2596 (1962).

(3) P. D. Bartlett, B. A. Gontarev and H. Sakurai, *ibid.*, **84**, 3101 (1962).