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Hydroxymetallocenes

BY RICHARD E. BENSON AND RICHARD V. LINDSEY, JR.

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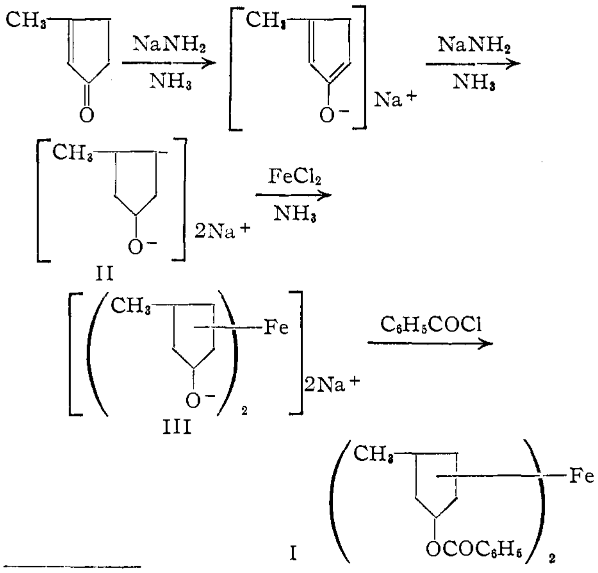
Bis-(1-hydroxy-3-methylcyclopentadienyl)-iron (IV), the first example of a ferrocene derivative having a hydroxyl group directly attached to a cyclopentadienyl ring, was synthesized by the reaction of 3-methyl-2-cyclopentenone with sodium amide and ferrous chloride in liquid ammonia. Some reactions of the bis-(hydroxy) compound were investigated, and its dibenzoate I was separated into two isomeric substances, presumably the *meso* and racemic forms. Bis-(1-hydroxy-3-methylcyclopentadienyl)-cobalt-III reineckate also has been prepared.

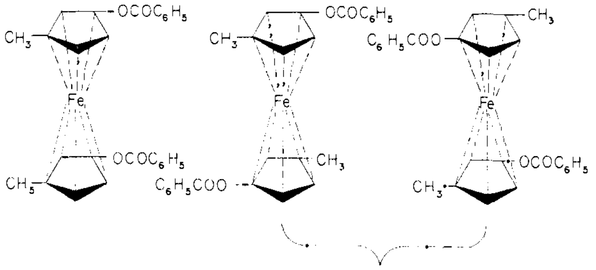
In connection with some studies of ferrocene derivatives it became of interest to prepare a hydroxy-substituted ferrocene to compare its behavior with that of phenol in a number of typical substitution reactions. The known derivatives of ferrocene[1] that might be considered as intermediates to a hydroxy compound are those which contain amino, sulfo and halo substituents. At the time of our work, the halogen derivatives[2] had not yet been reported, and the amino compound had been obtained only by an arduous series of reactions,[3] although a more satisfactory synthesis has since been reported.[4] The results of a few attempts to convert the sulfonic acid[5] to a hydroxy compound made this route look unattractive. Accordingly, attention was turned to more direct routes. Since hydroxycyclopentadienes, which would be required for a direct synthesis, have not been reported, a synthesis based on an enolizable cyclopentenone was developed.

3-Methyl-2-cyclopentenone reacted with two moles of sodium amide in liquid ammonia to give disodium hydroxycyclopentadiene (II) which was treated, without isolation, with anhydrous ferrous chloride. The resulting disodium bis-(1-hydroxy-3-methylcyclopentadienyl)-iron (III) was extremely sensitive to air, but conversion to the dibenzoate I with benzoyl chloride gave a stable, crystalline derivative in over-all yields of 28–35%. The dibenzoate I was obtained in over-all yields of 27 and 11% when sodium amide was replaced by potassium amide and lithium amide, respectively.



The yields are surprisingly high in view of the numerous side reactions of the ketone that can take place, such as polymerization, addition of the amide ion and reaction with ammonia. In addition, the formation of a doubly charged anion (II) might be expected to have a high energy barrier. The energy requirement in this case, however, is compensated by the formation of the resonance-stabilized hydroxycyclopentadienyl dianion.

The dibenzoate I was obtained as yellow-orange crystals (m.p. 100–120°) and was shown to be a mixture of isomers, presumably *meso* and racemic.



meso racemic

Fractional crystallization yielded the high-melting (125.5–127°) and low-melting (104–105°) diastereomers. This represents the first example of the isolation of such isomers in ferrocene-type compounds, although their existence had been predicted earlier by Pauson.[6a,b] The purity of the two fractions was not established, but the addition of approximately 5% of the high-melting fraction depressed the melting point of the low-melting fraction to 93–103°. The infrared spectra of solutions of the two isomers were remarkably similar. This result constitutes additional evidence for the free rotation of the cyclopentadienyl rings in ferrocene compounds.[1]

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(1) P. L. Pauson, *Quart. Rev.*, **9**, 391 (1955). This is an excellent review of ferrocene and related compounds.

(2) A. N. Nesmeyanov, E. G. Perevalova and O. A. Nesmeyanova, *Doklady Akad. Nauk S.S.S.R.*, **100**, 1099 (1955); *C. A.*, **50**, 2558 (1956).

(3) F. S. Arimoto and A. C. Haven, Jr., THIS JOURNAL, **77**, 6295 (1955).

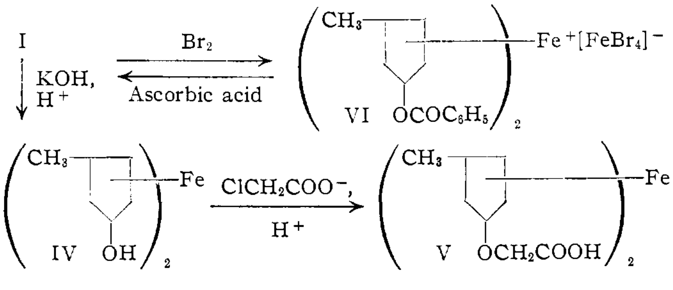
(4) A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya and L. S. Shilovtseva, *Doklady Akad. Nauk S.S.S.R.*, **102**, 535 (1955); *C. A.*, **50**, 4925 (1956).

(5) V. Weinmayr, THIS JOURNAL, **77**, 3009 (1955).

(6a) Reference 1, p. 413.

(6b) ADDED IN PROOF.—Two additional examples of this type of stereoisomerism have been reported recently. Thus, diacetylation of bis-(1-methylcyclopentadienyl)-iron yielded two pairs of isomers, designated "*cis*"- and "*trans*"-bis-(1-acetyl-2-methylcyclopentadienyl)-iron and "*cis*"- and "*trans*"-bis-(1-acetyl-3-methylcyclopentadienyl)-iron: L. K. Rinehart and K. L. Motz. Abstracts of Division of Organic Chemistry, XVIth International Congress of Pure and Applied Chemistry, Paris, July, 1957, p. 132.

Alkaline hydrolysis of the dibenzoate I in an oxygen-free atmosphere yielded bis-(1-hydroxy-3-methylcyclopentadienyl)-iron (IV) as a sublimable, yellow solid. Alkaline solutions of IV, which were initially yellow-red, rapidly became green on exposure to air and ultimately deposited iron oxide. The initial oxidation did not appear to involve the formation of the ferricinium ion, since the green color was not discharged by the addition of a reducing agent.



The reaction of the bis-(hydroxy) compound IV with chloroacetic acid yielded bis-(1-carboxymethyloxy-3-methylcyclopentadienyl)-iron (V) as a mixture of isomers. The latter was sensitive to air when moist but stable when dry. The bis-(acid) V was converted to the *p*-phenylphenacyl ester. The reaction of benzenesulfonyl chloride with the bis-(hydroxy) compound IV yielded the corresponding sulfonate.

Attempts to effect nuclear substitution of bis-(1-hydroxy-3-methylcyclopentadienyl)-iron (IV) or of the dibenzoate I were unsuccessful. Bromination of the dibenzoate yielded the tetrabromoferrate VI, analogous to the result obtained with dicyclopentadienyliron.[7] The structure of the tetrabromoferrate was confirmed by reconversion to the dibenzoate I by ascorbic acid. Attempts to effect a number of reactions of the dibenzoate I including nitration, acylation and Fries rearrangement were unsuccessful. Similarly, the bis-(hydroxy) compound IV could not be brominated nor made to undergo the Reimer–Tiemann reaction under the conditions examined.

The synthesis of hydroxymetallocenes by the reaction of 3-methyl-2-cyclopentenone with alkali amides and metal chlorides was extended to the cobalt analog by the use of cobaltous chloride. The product was isolated as the stable cobalt(III) derivative in the form of the reinecke salt. It has been reported that dicyclopentadienylcobalt reacts with water to give hydrogen and dicyclopentadienylcobalt(III) ion.[8] The use of water in the workup procedure presumably accounts for the formation of the cobalt(III) hydroxy compound. Dicyclopentadienylcobalt(III) ion is reported to be very stable.[9]

Experimental

Bis-(1-hydroxy-3-methylcyclopentadienyl)-iron is extremely sensitive to oxidation by air and all operations involving the compound were conducted in a nitrogen atmosphere with deaerated solvents.

Bis-(1-benzoyloxy-3-methylcyclopentadienyl)-iron (I).—To a stirred suspension of sodium amide in liquid ammonia, prepared from 9.4 g. (0.408 g.-atom) of sodium and approximately 250 ml. of liquid ammonia, was added dropwise over 20 minutes 19.2 g. (0.2 mole) of 3-methyl-2-cyclopentenone.[10] A reddish-brown solid separated immediately and the resulting mixture was stirred for 1 hr. Ferrous chloride[11] (12.7 g., 0.1 mole) was added in small portions during 15 minutes. The resulting black mixture was stirred for 2 hr. and the ammonia was allowed to evaporate overnight. A solution of 5 g. of sodium hydroxide in 250 ml. of water was added carefully to the black mixture. The solid was broken up, the mixture was stirred for about 15 minutes, and the insoluble material was removed by pressure filtration. The yellow-red filtrate was treated with benzoyl chloride under Schotten–Baumann conditions to give an orange-yellow solid that was collected by filtration, washed with dilute sodium hydroxide solution, sodium bicarbonate solution and finally with water. The crude product weighed 15.3 g. (34%) after drying in air, m.p. 100–120°. Recrystallization from acetic acid yielded fine yellow needles, m.p. 121–123.5°.

Anal. Calcd. for $C_{28}H_{22}O_4Fe$: C, 68.74; H, 4.88; Fe, 12.29. Found: C, 68.86; H, 5.00; Fe, 12.54.

The infrared spectrum determined in carbon tetrachloride solution showed strong bands at 5.75 (carbonyl), 3.25 (saturated CH bonding) and 3.4–3.5 μ (unsaturated CH bonding). Also, sharp bands were present at 7.0, 7.3, 7.6, 8.5, 8.8, 9.3, 9.4, 9.75 and 14.2 μ. The compound dissolved readily in methylene chloride, carbon disulfide, carbon tetrachloride, benzene, ethyl alcohol and acetone to give yellow-red solutions.

Isomer Separation.—Fractional crystallization of a crude product of initial melting point 100–120° yielded two fractions of unknown isomer purity. The higher melting isomer was obtained by crystallizing the crude product several times from acetic acid to give fine needles, m.p. 123.5–125°. This product was dissolved in *n*-heptane, allowed to crystallize partially, and the solvent was decanted carefully. Fresh solvent was added to the solid and the crystallization process was repeated. The product separated as thick clusters of fine, yellow-orange crystals, m.p. 125.5–127° (A).

The acetic acid filtrates were combined, concentrated by distillation and allowed to stand. The crystals that separated were isolated by filtration, m.p. 99–103°. The product was recrystallized three times from *n*-heptane to give fine, long, yellow-orange needles which melted at 104–105° (B). About equal amounts of A and B were isolated. Addition of approximately 5% of A to B depressed the melting point to 99–103°. The infrared spectra of A and B, determined in saturated carbon tetrachloride solution, were remarkably similar with all variances but two being attributable to concentration effects. However, slight variations of relative absorption intensity occurred in the 8.25 and 10.5–10.6 μ regions. These may indicate slight isomer impurity in either or both samples.

Bis-(1-hydroxy-3-methylcyclopentadienyl)-iron (IV).—To a solution of 60 ml. of absolute ethyl alcohol and 15 ml. of water was added 3.0 g. of the dibenzoate I and 2.0 g. of potassium hydroxide. The solution was heated to reflux for 1.5 hr., the alcohol was removed by distillation and water was added. The resulting red solution was cooled and acidified with excess hydrochloric acid to give a yellow-orange solid. The solid was separated by pressure filtration under nitrogen, washed first with water and then with sodium bicarbonate solution and dried in a nitrogen atmosphere. Small samples of the product were sublimed by placing them in 38 cm., 8 mm. o.d. tubes containing solid carbon dioxide to displace the air. Sublimation at 130–140° (0.1 mm.) yielded a yellow solid that was extremely sensitive to air. The hydroxy compound was soluble in methylene chloride and insoluble in carbon tetrachloride and *n*-heptane. A small sample dissolved in deaerated water yielded a yellow solution which, on exposure to air, rapidly became bluish-green. The color was not discharged by the

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(7) R. B. Woodward, M. Rosenblum and M. C. Whiting, THIS JOURNAL, **74**, 3458 (1952).

(8) G. Wilkinson, P. L. Pauson and F. A. Cotton, *ibid.*, **76**, 1970 (1954).

(9) G. Wilkinson, *ibid.*, **74**, 6148 (1952).

(10) R. M. Acheson and R. Robinson, *J. Chem. Soc.*, 1127 (1952). The ketone was purified by distillation.

(11) P. Kovacic and N. O. Brace, THIS JOURNAL, **76**, 5491 (1954).

addition of ascorbic acid, indicating that the ferricinium ion was probably not formed.

Bis-(1-carboxymethyloxy-3-methylcyclopentadienyl)-iron (V).—The product from the reaction of 28.8 g. (0.3 mole) of 3-methyl-2-cyclopentenone, 19 g. (0.15 mole) of anhydrous ferrous chloride and sodium amide (from 15 g. of sodium) was treated with 250 ml. of water containing 10 g. of sodium hydroxide, filtered, and the red filtrate was acidified with hydrochloric acid. The aqueous layer was decanted from the oil that separated, and 5% aqueous sodium hydroxide was added until most of the oil had redissolved. The mixture was transferred to a 3-necked flask equipped with a nitrogen inlet tube, stirrer and condenser. A solution of sodium chloroacetate, prepared from 35 g. (0.37 mole) of chloroacetic acid, 15 g. of sodium hydroxide and 150 ml. of water, was added with stirring to the solution of the hydroxy compound. The resulting solution had a *p*H of 9–10. The solution was heated and stirred on a steam-bath for 3 hr. to yield a yellow-red solution of *p*H approximately 7. About 5 ml. of 5% sodium hydroxide solution was added and the resulting solution was heated for an additional 8 hr. with stirring.

On standing, a considerable amount of yellow solid separated. The mixture was acidified and stirred for 1 hr. The solid was removed by filtration, washed with water and allowed to dry. The product was washed with ether to obtain 17.4 g. (33% yield) of yellow-orange solid, m.p. 110–150° dec. The product was recrystallized from water with considerable loss to give 10.7 g. (20% yield) of yellow-orange solid, m.p. 128–136° dec. An analytical sample was obtained by crystallization from glacial acetic acid, m.p. 123–130° dec. The melting point range of this and other derivatives prepared in this work is undoubtedly due to the presence of geometrical isomers.

Anal. Calcd. for $C_{16}H_{18}O_6Fe$: C, 53.06; H, 5.01; Fe, 15.42. Found: C, 53.02; H, 5.05; Fe, 15.72.

The acid was converted to the bis-(*p*-phenylphenacyl ester), which was crystallized from ethyl alcohol to give fine, yellow-orange needles, m.p. 128–155°.

Anal. Calcd. for $C_{44}H_{38}O_8Fe$: C, 70.40; H, 5.10. Found: C, 70.42; H, 5.13.

The dry acid was stable in air, but moist crystals turned green. Aqueous solutions in deaerated water were initially yellow-orange but rapidly became green on exposure to air. This color was not altered by the addition of ascorbic acid, indicating that the color was not due to the formation of the ferricinium ion. The compound was soluble in glacial acetic acid, methanol, ethyl alcohol and acetone and was insoluble in methylene chloride, chloroform, toluene and ether.

Bis-(1-phenylsulfonyloxy-3-methylcyclopentadienyl)-iron.—An alkaline solution of crude bis-(1-hydroxy-3-methylcyclopentadienyl)-iron was allowed to react with benzenesulfonyl chloride under Schotten–Baumann conditions. The solid product was washed with dilute sodium hydroxide and water and allowed to dry. The product was taken up in methylene chloride, filtered from a small amount of insoluble material, and the methylene chloride was removed by distillation. The resulting oil was recrystallized twice from methanol to give fine, yellow needles, m.p. 108–118°. The product was soluble in *n*-heptane. An analytical sample was obtained by crystallization from benzene–cyclohexane, m.p. 117–123°.

Anal. Calcd. for $C_{24}H_{22}O_6S_2Fe$: C, 54.76; H, 4.21; Fe, 10.61. Found: C, 55.41; H, 4.40; Fe, 10.80.

Bis-(1-benzoyloxy-3-methylcyclopentadienyl)-iron Tetrabromoferrate (VI).—A solution of 4.1 g. (0.00905 mole) of bis-(1-benzoyloxy-3-methylcyclopentadienyl)-iron in 25 ml. of methylene chloride was cooled in an ice-bath, and a solution of 2.9 g. (0.018 mole) of bromine in 30 ml. of cold methylene chloride was added dropwise with stirring over 15 minutes. The resulting red solution was stirred for 0.5 hr. and allowed to warm to room temperature during 1.5 hr. Sufficient carbon tetrachloride was added to produce a faint turbidity that was removed by warming slightly, and the resulting solution was cooled and allowed to stand. The glistening, black crystals that separated were removed by filtration and washed with carbon tetrachloride, m.p. 111–114°, weight 2.6 g. Concentration of the initial filtrate yielded an additional 0.7 g. of fine, red crystals, m.p. 101–105°, making the total yield 3.3 g. (88%). The product was soluble in methylene chloride, chloroform and warm benzene to give yellow-red solutions. It was insoluble in carbon tetrachloride and ether. The compound is dichroic, black in the gross crystalline state and red when finely divided. Some decomposition occurred during attempted recrystallization, and the crude product was analyzed without further purification.

Anal. Calcd. for $C_{26}H_{22}O_4Fe_2Br_4$: C, 37.63; H, 2.67; Br, 38.52. Found: C, 37.43; H, 2.66; Br, 39.07.

A small amount of the tetrabromoferrate was dissolved in warm water to yield a bluish-green solution. The addition of ascorbic acid resulted in separation of a yellow solid which was recrystallized from methanol and from *n*-heptane to give fine, yellow-orange crystals, m.p. 120–125°. The product did not contain bromine and a mixture of the solid with an authentic sample of the dibenzoate I melted at 119–125°.

Attempts to Form Nuclear-substituted Derivatives. A. From Dibenzoate (I).—Nitration with aqueous nitric acid resulted in rupture of the carbon–iron bond. The use of copper nitrate in acetic anhydride at 0–10° gave a small amount of nitrogen-containing product that decomposed during recrystallization from benzene to give an inorganic solid. Attempts to acylate the dibenzoate in acetic acid with phosphoric acid catalyst yielded unchanged starting material if a small amount of phosphoric acid was used or oils that did not crystallize when excess phosphoric was used. These products did not give a positive carbonyl test with 2,4-dinitrophenylhydrazine reagent. The Fries reaction with aluminum chloride and deaerated tetrachloroethane yielded a product that contained iron and was soluble in methylene chloride and insoluble in *n*-heptane. The product was insoluble in 10% sodium hydroxide solution and did not give a positive carbonyl test with 2,4-dinitrophenylhydrazine reagent. Heating the dibenzoate I in refluxing tetrachloroethane gave a dark green solution, the infrared spectrum of which showed a carbonyl band of the ketone type (5.9 μ) and a new ester band (5.7 μ). In addition, there was a weak band at 2.85 μ that could be due to the presence of a hydroxyl group.

B. From Bis-(1-hydroxy-3-methylcyclopentadienyl)-iron.—Bromination of the hydroxy compound IV in dilute aqueous solution with bromine–potassium bromide reagent gave an oil that contained bromine but not iron. The aqueous layer gave an excellent test for the ferric ion, indicating that carbon–iron bond rupture had taken place. The Reimer–Tiemann reaction was examined under conditions described for β-naphthol.[12] Some 3-methyl-2-cyclopentenone was isolated from the reaction by conversion to the 2,4-dinitrophenylhydrazone, but none of the expected product was obtained.

The Bis-(1-hydroxy-3-methylcyclopentadienyl)-cobalt(III) Reineckate.—Sodium amide was prepared from 10.0 g. (0.435 g.-atom) of sodium and 250 ml. of ammonia, and 19.2 g. (0.2 mole) of 3-methyl-2-cyclopentenone was added dropwise during 20 minutes. The resulting mixture was stirred for 45 minutes, and treated with 13.0 g. (0.1 mole) of cobaltous chloride[13] over a period of 10 minutes to give a black mixture which was stirred at −33° for 2.5 hr. The ammonia was allowed to evaporate, and 250 ml. of anhydrous ether was added. The mixture was allowed to stand under a slow stream of nitrogen overnight. Deaerated water (350 ml.) containing 25 g. of sodium hydroxide was added carefully with cooling to the resulting green mixture. The mixture was stirred for 15 minutes and filtered under nitrogen. As the result of a number of preliminary tests, it was concluded that the divalent cobalt compound had undergone oxidation to the cation derivative despite the fact that operations had been conducted under nitrogen. Accordingly, the filtrate was acidified with hydrochloric acid and treated with hydrogen peroxide to oxidize any of the unchanged divalent cobalt compound to the cation derivative. The addition of an aqueous solution of reinecke salt $[NH_4Cr(NH_3)_2(SCN)_4 \cdot H_2O]$ to the filtrate yielded the reineckate as an orange-brown solid, weight 3.5 g., m.p. 154–157° dec. The product was recrystallized from ace-

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[12] A. Russel and L. B. Lockhart, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 463.

[13] H. Hecht, *Z. anorg. Chem.*, **254**, 37 (1947).

tone–water to give an orange-brown powder, m.p. 154–162° dec. The melting point range is probably due to the presence of isomers.

Anal. Calcd. for $C_{16}H_{20}O_2N_6S_4CoCr$: C, 33.86; H, 3.55; N, 14.81. Found: C, 33.82; H, 3.94; N, 14.68.

The infrared spectrum of this product was compared with that of the reinecke salt of dicyclopentadienylcobalt(III) cation. The spectrum of the hydroxy derivatives is in accord with the proposed structure.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Stereochemistry and Mechanism of the Bromodecarboxylation of Unsaturated Carboxylate Ions[1]

BY JOSEPH D. BERMAN[2a] AND CHARLES C. PRICE[2b]

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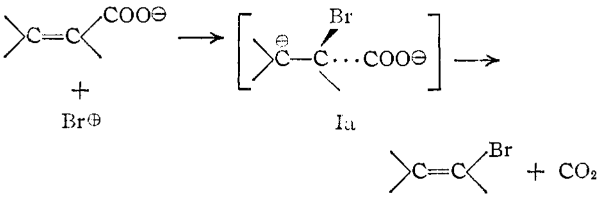
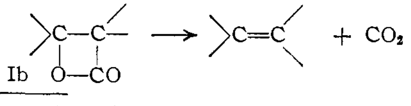
The addition of bromine to warm aqueous solutions of the sodium salts of *p*-anisic, α-thenoic, phenylacetic, *m*-methoxyphenylacetic, *cis*- and *trans*-cinnamic, *cis*- and *trans*-stilbene-α-carboxylic and *dl*- and *d*-hydratropic acids led to rapid replacement of the carboxylate group by bromine. No geometric isomerization of the *cis-trans*-stilbene pair occurred. The *d*-hydratropic acid produced *dl*-bromide, but it was shown independently that the *d*-bromide was completely racemized under the reaction conditions. Under the same conditions, the sodium salts of benzoic, hydrocinnamic, *p*-nitro- and *p*-methoxyphenylacetic and trimethylacetic acids did not react with bromine, and the acids were recovered in essentially quantitative yield. A mechanism is proposed involving intermediate addition of bromine cation to the α-carbon of α,β-unsaturated acids or the γ-carbon of β,γ-unsaturated acids, followed by expulsion of carbon dioxide.

Some examples of the bromodecarboxylation of sodium salts such as those of salicylic,[3] cinnamic[4] and α-phenylcinnamic acids[5] have long been known.[6] From our study of a number of sodium salts, it appears that those unsaturated acids with a readily available pair of π-electrons, on the α-carbon for α,β-unsaturated acids and on the γ-carbon for β,γ-unsaturated acids, consume bromine in a few minutes at 50–60° with rapid evolution of carbon dioxide. The π-electrons may be either part of a reactive aromatic system or a double bond.

Examples of the former are *p*-anisic and α-thenoic acids, as well as salicylic acid.[3] In contrast, benzoic acid fails to react. Examples of the latter are the cinnamic acids.

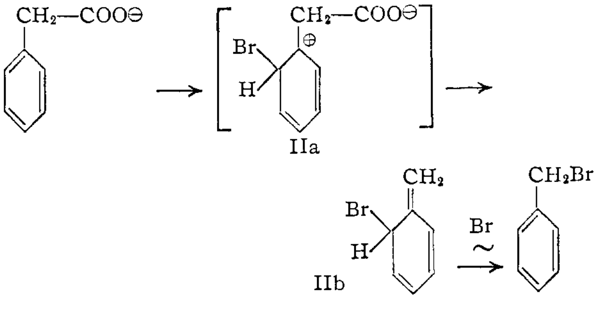


Since *cis*-stilbene-α-carboxylate produces only α-bromo-*cis*-stilbene and the *trans*-isomer only α-bromo-*trans*-stilbene, it seems obvious that Ia is not a stable intermediate but must be extremely short-lived, perhaps even the transition state. It does not seem likely that the configuration of the β-carbon atom is preserved in a stable β-lactone intermediate Ib, which then loses carbon dioxide.



Although such a reaction can occur for β-lactones on heating in inert media, in water they are normally converted to β-hydroxy acids.[7] Furthermore, in the case of *cis*-cinnamate, some 60% of the bromodecarboxylation product was the *trans* isomer. The isomerization occurred during or after bromination, since the acid recovered in 17% yield was not isomerized. One would expect that the much greater difference in energy between *cis*- and *trans*-β-bromostyrene than between *cis*- and *trans*-α-bromostilbene would provide a far greater driving force for isomerization in the former case.

Since phenylacetate also undergoes bromodecarboxylation readily and rapidly but benzoate and hydrocinnamate do not, we believe the same type of transition involving a carbonium ion beta to the carboxylate can occur here by *ortho* attack in the ring.



The carboxymethyl group would direct electrophilic attack by bromine cation to the *ortho* (or *para*) positions of the ring as indicated, producing the transition state IIa. Elimination of carbon dioxide would then produce the intermediate IIb. In the polar medium of the reaction, the final step of allylic rearrangement of IIb to benzyl bromide should occur rapidly. Actually, a 70% yield of benzyl bromide was isolated. A course similar to that of phenylacetate to IIb probably is involved[8]

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(1) Presented at the 127th A.C.S. Meeting, Cincinnati, Ohio, March 30, 1955.

(2) (a) Harpur College, Endicott, New York; (b) Department of Chemistry, University of Pennsylvania, Phila. 4, Pa.

(3) A. Cahours, *Ann.*, **52**, 338 (1844).

(4) C. Glaser, *ibid.*, **154**, 169 (1870).

(5) R. Miller, *Ber.*, **26**, 664 (1893).

(6) For a recent review, see R. G. Johnson and R. K. Ingham, *Chem. Revs.*, **56**, 219 (1956).

(7) See, *e.g.*, A. Basler, *Ber.*, **16**, 3001 (1883); H. Johansson and S. M. Hagman, *ibid.*, **55**, 647 (1922); H. Staudinger, *ibid.*, **41**, 1355 (1908); H. Solkowski, *J. prakt. Chem.*, **106**, 253 (1923).

(8) E. E. van Tamelen and M. Shamma, THIS JOURNAL, **76**, 2315