that of benzophenone but also showed weak carbonate absorption (5.60 μ).

When benzpinacol (3 mmoles) was oxidized with potassium permanganate (5 mmoles) in acetic acid and acetic anhydride, with added potassium acetate, no crystalline product was obtained from the diluted reaction mixture. Concentration of the solution and extraction with benzene gave an oil which was shown to be benzophenone (infrared).

Potassium permanganate oxidation of trans-1,2-bis(p-chlorophenyl)-1,2-diphenylethylene. The *trans* olefin (0.70 g.) was oxidized with potassium permanganate in the same manner as I. Work-up of the dark brown mixture afforded 0.12 g. (16%) of diastereomeric epoxides, m.p. 193–206°, whose infrared spectrum showed that both *meso-* and *dl*-epoxides were present, the latter in greater amount.

Chromyl chloride oxidation of tetraphenylethylene. A solution of 1.9 g. (12.3 mmoles) of chromyl chloride in 75 ml. of acetic acid and 25 ml. of acetic anhydride was added dropwise (1 hr.) to a hot (90–95°) stirred solution of 1.66 g. (5 mmoles) of I in 85 ml. of acetic acid and 15 ml. of acetic anhydride. After 10 min. more, 100 ml. of water was added (highly exothermic) and the dark green solution allowed to cool. Filtration afforded 0.49 g. of an ochre-yellow, low melting (100°) solid, which gave a positive Beilstein test). Chromatography over alumina, with benzene as eluant, produced white crystals, m.p. 162–174°; this material was shown to be a mixture of mainly II and the corresponding chlorohydrin (?) by infrared examination, there being no carbonyl absorption and only four peaks not found in the spectrum of pure II. When the filtrate was concentrated and extracted with benzene in the usual manner,. and the oily residue examined by infrared, no carbonate absorption (5.60 μ) was detected, benzophenone being the sole component. The presence of small amount of tetraphenylethylene chlorohydrin in the solid products (above) was inferred from the positive halogen test and the fact that refluxing the 162–174° solid briefly with ethanolic potassium hydroxide gave fairly pure II, m.p. 197–201°, which did not depress the melting point of authentic tetraphenylethylene oxide.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Structure of Distyrinic Acid

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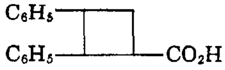
Distyrinic acid (I), the chief saturated acidic product from the treatment of cinnamic acid with 50% sulfuric acid at reflux, had previously been assigned the structure 2,3-diphenylcyclobutanecarboxylic acid (IA). We wish to report that the correct structure is IB, the compound being the mechanistically reasonable 1-phenyl-2-carboxy-3-methylindane.

In 1882 Fittig and Erdmann[1] reported that treatment of cinnamic acid with hot 50% sulfuric acid yielded a mixture of saturated acids, which they called "distyrenic acid." In 1923 Stoermer and Becker[2] reinvestigated this substance and separated it into two pure compounds, a major component, distyrinic acid, and a minor isomer, distyranic acid. Their structural investigation was confined to distyrinic acid, available in 2.6% over-all yield from cinnamic acid, and the evidence they report seems unambiguous. They found that drastic oxidation of the compound yielded benzil, establishing that there are two unsubstituted phenyl rings on adjacent carbons, and that pyrolysis of the calcium salt of the compound yielded ethylstilbene, again supporting the idea that there are adjacent phenyl groups. Both the pyrolysis product and the analytical data establish the presence of a ring, furthermore, and on the basis of this evidence they assigned distyrinic acid the structure (Ia).



Ia

We have reinvestigated this substance for two reasons: (1) the mechanism by which this compound might be formed is intriguing, since any simple scheme would predict the predominant 1,3-arrangement of phenyls, electrophilic attack being expected of course on the β-carbon of a styrene system; (2) the reaction offers a fairly convenient route to an otherwise difficultly accessible cyclobutane derivative. Accordingly, we repeated the procedure of Stoermer and Becker and obtained distyrinic acid in an over-all yield of 3.4%, confirming at least this aspect of their report. There is no doubt that we have obtained their substance, since the preparation was repeated according to their description and fractional distillation of the mixed methyl esters from the acidic reaction product, as they described, gave the methyl ester of distyrinic acid, m.p. 72.5–73° (lit., m.p. 73°). Hydrolysis afforded distyrinic acid, m.p. 153–154° (lit., m.p. 147°). We have also prepared the corresponding amide, m.p. 208° (lit., m.p. 205°). Furthermore, our analytical data correspond to those reported for both the acid and the ester. However, it soon became obvious that the previously assigned structure is incorrect.

The most convincing evidence that structure (Ia) cannot be correct comes from our studies on nitric acid oxidation of methyl distyrinate. Thus oxidation with refluxing 30% nitric acid, conditions which would certainly not rearrange a compound which had been prepared by three days' refluxing in 50% sulfuric acid, furnished *o*-benzoylbenzoic acid.

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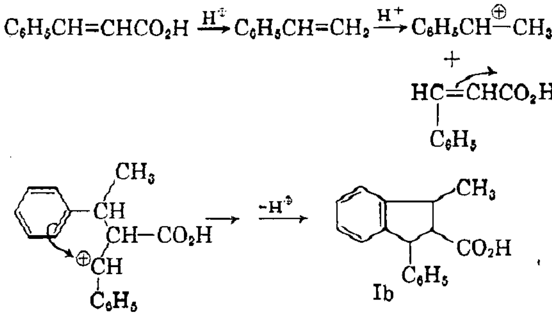
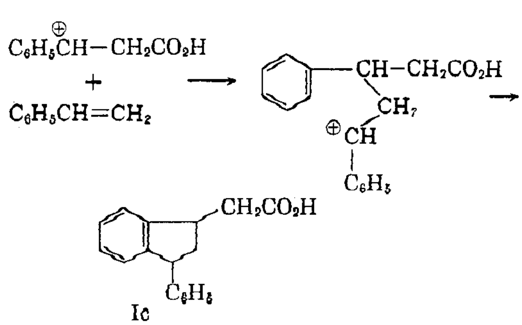
[1] R. Fittig and E. Erdmann, *Ann.*, **216**, 179 (1882).

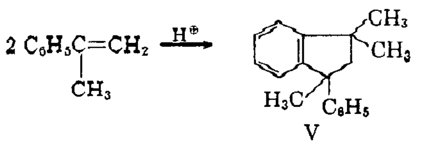
[2] R. Stoermer and W. Becker, *Ber.*, **56**, 1440 (1923).

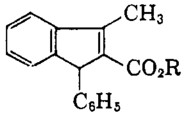
This shows that only one of the phenyl groups is unsubstituted, the other being *o*-disubstituted, and is in direct contradiction to the previous report that benzil is obtained on oxidation with permanganate; we have attempted to repeat this latter experiment unsuccessfully.

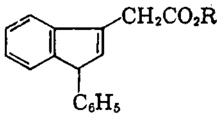
In order to degrade the molecule further we have introduced a double bond by the use of *N*-bromosuccinimide. With one mole of this reagent an unsaturated ester (II) is formed from the methyl ester of (I), and the formula $C_{18}H_{16}O_2$ corresponds simply to the loss of two hydrogen atoms, but an excess of the reagent affords a dibromo-unsaturated ester (III), $C_{18}H_{14}O_2Br_2$. Strikingly, on zinc debromination this is reconverted to II, the loss of the two bromines being accompanied by an uptake of two hydrogens. Nitric acid oxidation of II also yields *o*-benzoylbenzoic acid, confirming the results on I itself. Ozonization of the acid corresponding to II yields IV, $C_{16}N_{14}O_3$, a keto acid. A positive iodoform test establishes that the keto function is an acetyl group.

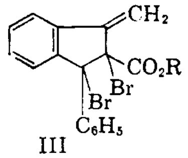

(1)

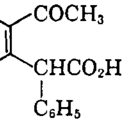

(2)


(3)


IIb


IIc


III


IV

All of this is consistent with structures Ib or Ic for distyrinic acid. These are the two likely structures for a saturated product from acid treatment of cinnamic acid in any case, since their formation can be rationalized easily in terms of the following mechanisms, and since α-methylstyrene with acid has been found to yield V.[3]

The structures of II based on these two formulas are IIb and IIc, the positions of the double bonds being as indicated since ozonization must lead to IV, which results from oxidative decarboxylation in the one case and from oxidation of the aldehyde function and decarboxylation of the β-keto acid group in the other case. The structure assigned to IV is consistent with its NMR spectrum (as the methyl ester), with unsplit methyl and methoxyl groups, aromatic hydrogens, and a single hydrogen at rather low field for the C—H with three electron withdrawing substituents.

The choice between IIb and IIc is easily made. Thus II has its carbonyl absorption in the infrared shifted to 5.89 μ, which indicates a conjugated ester group, as in IIb. The ultraviolet spectrum also indicates a cinnamic ester chromophore. Furthermore the NMR spectrum of II shows a split methyl group, a methoxyl group, a single broadened hydrogen signal at lower field, and the aromatic band. This is consistent only with IIb; the C—H signal from a group surrounded by two phenyls and a vinyl group is found at relatively low field, and no other hydrogen (*e.g.* vinyl hydrogen) can be detected. Thus the structure of distyrinic acid is Ib.

A consideration of the properties of compound III adds further support to these assignments. This is the compound obtained by the action of an excess of *N*-bromosuccinimide on the ester of I, and it can also be prepared from II by the action of this reagent, and reconverted to II with zinc and alcohol. However the infrared absorption band at 5.85 μ and the ultraviolet absorption at 253 mμ are suggestive of a styrene chromophore rather than a cinnamic ester derivative. Most important, the NMR spectrum reveals only the aromatic hydrogens, the methoxyl, and two hydrogens in the vinyl region which are coupled to each other. The only reasonable interpretation is that the methyl group of I and of II has been converted to a methylene group here; this has been confirmed by the isolation of formaldehyde on ozonization of III. This structure shown for III explains the zinc reaction, for debromination of III would lead to a fulvene which would be easily reduced further,[4] and the observed uptake of two hydrogen atoms during the debromination is thus accounted for.

The only alternative structure for IV would be IV′. However the derived structure for distyrinic

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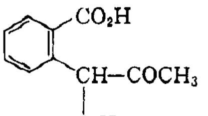
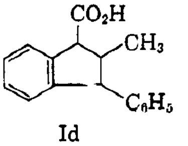
(3) E. Bergmann, H. Tanbadel, and H. Weiss, *Ber.*, **64**, 1493 (1931).

(4) *Cf.* K. Ziegler, H. Gellert, H. Martin, K. Nagel, and J. Schneider, *Ann.*, **589**, 91, (1954).

acid, Id, cannot be reasonably obtained from cinnamic acid and, more seriously, no structure can be drawn for III on this basis, since its exocyclic methylene group must be part of a styrene system, from the spectroscopic evidence. We are unable to account for the previous report of Stoermer and Becker, in such startling disagreement with our own. It is apparent, however, that the assigned structures uniquely fit our observations.



IV′



Id

EXPERIMENTAL[5]

Distyrinic acid (I). Cinnamic acid (800 g.) was refluxed with aqueous sulfuric acid (3300 g. water, 3200 g. sulfuric acid) for 72 hr. An ether extract was then washed thoroughly with sodium bicarbonate solution, the bicarbonate solution was acidified, and the resulting yellow solid was taken up in ether and treated with an excess of diazomethane solution. The resulting neutral ester mixture was fractionally distilled, and the fraction boiling 135–165° (0.8 mm.) was collected and allowed to stand. It crystallized after several weeks, and on repeated recrystallization from aqueous methanol there was obtained 24.3 g. (3.37%) of *methyl distyrinate*, m.p. 72.5–73° (lit.,[2] m.p. 72°).

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.18; H, 6.81. Found: C, 81.29; H, 6.91.

In the infrared the compound showed carbonyl absorption at 5.79 μ. In the ultraviolet it showed only weak aromatic absorption, and the compound did not decolorize permanganate solution in the standard test for unsaturation.

On hydrolysis this ester yielded *distyrinic acid*, m.p. 153–154° (lit.,[2] m.p. 147°).

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 81.11, H, 6.44.

The acid was converted to the corresponding amide by the published procedure, m.p. 208–210° (lit.,[2] m.p. 205°).

Nitric acid oxidation of methyl distyrinate. Methyl distyrinate (1 g.) was refluxed overnight with 30 ml. of 30% nitric acid. Isolation of the acid products by suitable extractions yielded 0.7 g. of a compound, m.p. 97–122°, whose infrared spectrum indicated it to be impure *o*-benzoylbenzoic acid (m.p. 122°). After esterification with diazomethane and chromatography methyl *o*-benzoylbenzoate was isolated, identified by its melting point (49–51°) and mixed melting point with an authentic sample, and by the identity of its infrared spectrum with that of an authentic sample.

Methyl dehydrodistyrinate (II). Reaction of 5.0 g. of methyl distyrinate with 3.75 g. of *N*-bromosuccinimide in 125 ml. of refluxing carbon tetrachloride for 5 hr., followed by the addition of 15 ml. of pyridine and a further 0.5-hr. reflux, yielded, after chromatography of the product on alumina, 1.29 g. (27%) of *methyl dehydrodistyrinate*, m.p. 95–96°.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 82.17; H, 6.08.

In the infrared the compound showed carbonyl absorption at 5.89 μ and in the ultraviolet it had maxima at 230 mμ (18,700) and 291 mμ (15,000). In the NMR spectrum (60 megacycles; carbon tetrachloride solution; shifts relative to an external benzene capillary) there was a broad aromatic band at −33, a small broadened band at 112, a sharp band at 185, and a doublet at 239 and 241 c.p.s. Since the 185 band is due to the methoxyl group, the areas correspond to nine, one, three, and three hydrogens, respectively.

Nitric acid oxidation of this ester, as described for distyrinic acid, yielded *o*-benzoylbenzoic acid, identified by comparison of the acid and its methyl ester with authentic samples. Hydrolysis of methyl dehydrodistyrinate yielded *dehydrodistyrinic acid*, m.p. 223–225°.

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.83; H, 5.77.

Methyl dibromodehydrodistyrinate (III). When methyl distyrinate (5 g.) was treated with an excess (10 g.) of *N*-bromosuccinimide in 250 ml. of refluxing carbon tetrachloride for 75 hr., during which time hydrogen bromide was evolved, the product was *methyl dibromodehydrodistyrinate* (6.5 g.; 82%), m.p. 113.5–114° (from acetone-water).

Anal. Calcd. for $C_{18}H_{14}O_2Br_2$: C, 51.21; H, 3.11; Br, 37.86. Found: C, 51.46; H, 3.35; Br, 38.65.

In the infrared the compound showed carbonyl absorption at 5.85 μ, and in the ultraviolet it had a maximum at 253 mμ (21,000). The NMR spectrum had the large aromatic band at −54, a one proton doublet at 91 and 100, a one proton doublet at 134 and 143, and the three proton methoxyl at 174 c.p.s.

The same compound was formed when II was treated with an excess of *N*-bromosuccinimide.

Ozonolysis of III in ethyl acetate and aqueous decomposition of the product yielded formaldehyde as its dimedon derivative (3.4%), identical with an authentic sample.

Reduction of III. A solution of III (0.5 g.) in three parts alcohol and one part acetone (25 ml.) was added dropwise under nitrogen to a refluxing mixture of activated (ammonium chloride) zinc (1.1 g.) and hydroquinone (0.025 g.) in 25 ml. of ethanol with stirring. After 27 hr. further reflux the mixture was cooled and filtered, and the filtrate was concentrated to 10 ml. Addition of water caused separation of methyl dehydrodistyrinate (II), m.p. 95–96°. Yields varied from 68 to 87%, and this procedure proved the most convenient synthesis of II.

Ozonolysis of dehydrodistyrinic acid. Dehydrodistyrinic acid (0.59 g.) was ozonized in ethyl acetate at −60°. The ozonide was decomposed with hydrogen peroxide, and the acidic product isolated. The crude product, m.p. 114–124° (0.26 g.) gave pure *o*-acetyldiphenylacetic acid (IV), m.p. 125–128°, on recrystallization from aqueous methanol.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.58; H, 5.55. Found: C, 75.49; H, 5.39.

With diazomethane this was converted to its *methyl ester*, m.p. 81–82°.

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 75.37; H, 5.90.

The NMR spectrum of this methyl ester confirmed the assigned structure, with aromatic hydrogens at −33, a single peak at 55, a three proton methoxyl peak at 185, and an unsplit methyl peak at 255 c.p.s.

Under the standard test conditions the compound yielded iodoform, identified by direct comparison.

NEW YORK, N. Y.

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[5] Ultraviolet spectra in 95% ethanol; infrared spectra in chloroform, performed on a calibrated Perkin-Elmer 221-G spectrophotometer.