

b.p. 60–65° (30 mm.), which was identified by its strong lachrymatory properties and by its vigorous reaction with concentrated ammonium hydroxide solution to form 3.4 g. of benzamide, m.p. and mixed m.p. 126.5–127°.

The solid obtained from the sodium acetate treatment was washed with ether, combined with the residue from the steam distillation and recrystallized from benzene to give 42.6 g. (90%) of the boron difluoride complex of dibenzoylmethane (VII), m.p. and mixed m.p. 189–190°. The ether wash solution was extracted with sodium bicarbonate solution to yield, on acidification, 2.5 g. of benzoic acid, m.p. 119.5–121.5°. On the basis that this acid resulted from hydrolysis of benzoyl fluoride, the total yield of the acid fluoride is 35%.

Self-condensation of the Enol Acetate of Ethyl Acetoacetate (IX) with Boron Trifluoride.—A solution of 34.4 g.

(10) G. T. Morgan and R. B. Tunstall, *J. Chem. Soc.*, **125**, 1963 (1924).

(0.2 mole) of the enol acetate of ethyl acetoacetate (b.p. 102.5–104.5° at 17 mm.)¹¹ in 35 ml. of ethylene chloride was saturated with boron trifluoride at 0–5° in 30 minutes. The mixture was stirred for 5 hours at ice-bath temperature, then for one hour at room temperature, and decomposed by stirring with 200 ml. of 3.7 molar sodium acetate solution for 45 minutes. The aqueous mixture was extracted with ether, the extracts washed with sodium bicarbonate solution, and dried over Drierite. On distillation there were obtained ethyl acetoacetate and 15.5 g. (90%) of ethyl diacetylacetate (X), b.p. 90–93.5° (12 mm.) (reported b.p. 95–97° at 12 mm.)¹² The product was further identified by its blue copper salt, m.p. 150–152°.¹³ This same result was obtained independently by two workers.

(11) L. Claisen and E. Haase, *Ber.*, **33**, 1244 (1900).

(12) A. Spassow, in "Organic Syntheses," **21**, 46 (1941).

(13) H. Böhme and H. Fischer, *Ber.*, **76B**, 106 (1943).

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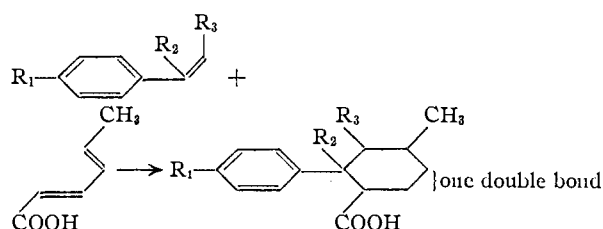
The Diels-Alder Reaction between Sorbic Acid and Substituted Styrenes

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The Diels-Alder reactions of sorbic acid with styrene and nine substituted styrenes have been studied. All adducts were proven to have structures in which the carboxyl and phenyl groups are ortho to each other. Difficulties with both the polar and biradical mechanisms for the Diels-Alder reaction are presented.

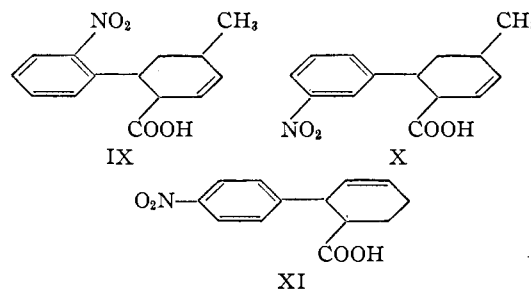
To further test polar mechanisms of the Diels-Alder reaction,^{1–5} the reaction between sorbic acid and a series of styrenes has been studied. The yield and properties of the adducts are summarized in Table I. In general the reaction product consisted of approximately equal amounts of a single crystalline isomer and a non-crystalline mixture of isomers. In all cases the carboxyl group in the crystalline product was proved to be ortho to the phenyl group as illustrated in equation (1). A comparison of the yields of crystalline product to total adduct, as given in Table I, shows that the major portion of most of the adducts have the car-



	R ₁	R ₂	R ₃
Ia and Ib	H	H	H
II	H	CH ₃	H
III	<i>i</i> -C ₃ H ₇	CH ₃	H
IV	Cl	H	H
V	Cl	CH ₃	H
VI	OCH ₃	CH ₃	H
VII	OCH ₃	H	CH ₃
VIII	NO ₂	H	H

bon skeleton indicated. In several cases the non-crystalline adduct was also shown to contain at least in part adducts of the same carbon skeleton. It is probable that structures other than I–X are present in only minor amounts.

The adducts from sorbic acid with *o*- and *m*-nitrostyrene were also studied and found to possess structures IX and X. All adducts can be correlated with polar mechanisms except VIII and IX, which are clearly exceptional. These two closely resemble the exception to polar mechanisms reported by Ropp and Coyner,⁶ who found that 1-(*p*-nitrophenyl)-butadiene and acrylic acid yielded XI.



Position of double bond unproven in IX and X

Proofs of Structures.—The adduct (II) from α -methylstyrene was dehydrogenated with sulfur to give 2-phenyl-4-methylbenzoic acid as previously described.⁷ The 145° adduct (Ia) from styrene plus sorbic acid was similarly converted to 2-phenyl-4-methylbenzoic acid.

The *p*-isopropyl- α -methylstyrene adduct (III) was dehydrogenated with sulfur accompanied by loss of the angular methyl group. The resulting acid was cyclized to the corresponding fluorenone,

(1) B. J. F. Hudson and R. Robinson, *J. Chem. Soc.*, 715 (1941).

(2) R. Robinson and H. N. Rydon, *ibid.*, 1398 (1939).

(3) M. J. S. Dewar, "Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, pp. 150–156.

(4) A. E. Remick, "Electronic Interpretations of Organic Chemistry," 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 447.

(5) W. E. Bachmann and N. C. Deno, *THIS JOURNAL*, **71**, 3062 (1949).

(6) G. A. Ropp and E. C. Coyner, *ibid.*, **72**, 3960 (1950).

(7) N. C. Deno, *ibid.*, **72**, 4057 (1950).

m.p. 120° (which was not further investigated) and 169° (Ib) were isolated in small amounts. Most of the adduct was a non-crystalline mixture of isomers. When the reaction was conducted at 180° without solvent, a new acid melting at 145° (Ia) was isolated in 26% yield. Alder and co-workers⁸ obtained apparently the same 169° adduct (Ib) from methylsorbat and styrene. The carbon skeleton of Ib was demonstrated by sulfur dehydrogenation to 2-phenyl-4-methylbenzoic acid.⁸ The carbon skeleton of Ia was demonstrated in an identical manner. Although neither Ia nor Ib was isomerized by refluxing with sodium methoxide in methanol for 24 hours, Ia could be partially isomerized to Ib by conversion to the methyl ester and treating with triphenylmethylsodium. Both Ia and Ib rapidly absorbed bromine and gave similar ultraviolet absorption spectra (Table II). The position of the double bond cannot be assigned on the above evidence, but the bromine absorption indicates a slight preference for a position β, γ to the carboxyl group. The assignment of the double bond in adduct II, which was made in a previous paper,⁷ was unwarranted.

TABLE II
ULTRAVIOLET ABSORPTION SPECTRA OF Ia AND Ib

λ , m μ		log ϵ
220		4.04
260	min.	2.62
262	max.	2.64
267	min.	2.40
269	max.	2.48
280		1.25

Difficulties with the Polar Mechanism.—Many products from Diels–Alder reactions have proven structures which are contrary to those which would have been predicted assuming a polar mechanism.^{9,10} It may be significant that most exceptions are either in the category of cyclic dimerizations or formation of dihydropyrans.

Difficulties with the Biradical Mechanism.—Although the adducts from many unsymmetrical dienes and olefins have proven structures, the biradical theory can be tested with only a limited number because of the lack of knowledge on selectivity in free radical reactions. However, two exceptions have been previously noted.⁹ To these can be added two examples of head-to-tail cyclic dimerizations, formation of dipentene from

isoprene¹¹ and dimerization of chloroprene.¹² Reference to the original papers will show that in each case the structure of the adduct would require biradical intermediates containing a primary and secondary free radical, in spite of the fact that a biradical involving a primary and tertiary free radical is possible. These discrepancies may be removed when rules governing orientation of free radicals are better understood.

There are two other objections to the biradical theory from a different basis. It is difficult to see how the biradical mechanism^{9,13} can account for either of the two Alder rules: the rule of *cis* addition and the rule of "maximum accumulation of double bonds."¹⁴

A second difficulty arises when the relative rates of the Diels–Alder reaction and linear polymerization are compared. The biradical theory implies that both reactions will go through the same biradical intermediate.¹³ However, many observations have been made that the presence of polymerization inhibitors increases the yields of Diels–Alder adducts at the expense of polymerization.¹⁵

These above difficulties are derived from specific examples so that it is still possible that certain Diels–Alder reactions involve biradical intermediates or transition states.^{3,4}

Experimental

The yields and properties of the Diels–Alder adducts are listed in Table I. The following experimental details apply to all the Diels–Alder reactions conducted unless otherwise noted in Table I.

The reactions were conducted in a flask with an air condenser sealed on to eliminate hot joints. A carbon dioxide atmosphere was used throughout. This was introduced by adding several grams of Dry Ice through the condenser and allowing the air and excess carbon dioxide to vent out through a mercury trap. About 1% by weight of hydroquinone was added to inhibit polymerization. The reaction mixtures were heated at 170–190° for 100 to 200 hours unless otherwise noted in Table I.

The reaction mixture was in all cases a clear yellow or brown gum. Three volumes of benzene were added after cooling. It was usually necessary to warm the mixture to 100° to effect solution. The benzene solution was extracted with an excess of 10% aqueous potassium hydroxide in order to separate the Diels–Alder adduct and copolymer from the neutral polymer. The aqueous layer was washed with ether, and the ether and benzene extracts discarded. Altering the order of using ether and benzene or using other solvents usually led to precipitation of gums and formation of emulsions.

The aqueous layer was heated to 100° to expel dissolved ether. At 100° a slight excess of acetic acid was added with stirring. The precipitated tan gum was chilled and rinsed with water. In some cases a crop of crystals could be obtained by crystallizing the gum from acetone. In all cases the uncrystallizable material was dissolved in a small amount of acetone to facilitate the transfer to a distillation flask. The short-path distillation was conducted at 0.3–1 mm. at a temperature of 140–220°. Although different adducts distilled at different temperatures in this range, no advantage was noted when cuts over smaller temperature ranges were taken. The final products (except with IV) were obtained

(8) K. Alder, K. H. Decker and R. Lienau, *Ann.*, **570**, 224 (1950).

(9) C. W. Smith, D. G. Norton and S. A. Ballard, *THIS JOURNAL*, **73**, 5273 (1951). In addition to the exceptions listed by these authors, there are several more which are all of the cyclic dimerization type: olefins to cyclobutanes (A. L. Henne and R. P. Ruh, *ibid.*, **69**, 279 (1947); E. C. Coyner and W. S. Hillman, *ibid.*, **71**, 324 (1949)), diene to a divinylcyclobutane (H. W. B. Reed, *J. Chem. Soc.*, 685 (1951)), dienes to vinylcyclohexenes (J. L. Charlsh and W. H. Davies, *ibid.*, 1385 (1950); K. Alder and W. Vogt, *Ann.*, **570**, 190 (1950)), and dienes to cyclooctadienes (A. C. Cope and W. R. Schmitz, *THIS JOURNAL*, **72**, 3056 (1950)). Several exceptions listed by Smith, Norton and Ballard do not seem to be exceptions to us. The correlation with polar mechanisms of the adduct from citraconic anhydride with either 1-vinylnaphthalene or its 6-methoxy analog are explained in ref. 5. The addition of 1-(*p*-bromophenyl)-butadiene to acrylic acid gives an adduct fitting polar mechanisms as indicated by the original authors (ref. 6).

(10) H. R. Snyder and G. I. Poos, *THIS JOURNAL*, **72**, 4104 (1950).

(11) T. Wagner-Jauregg, *Ann.*, **488**, 176 (1931).

(12) A. C. Cope and W. R. Schmitz, *THIS JOURNAL*, **72**, 3056 (1950).

(13) G. B. Kistiakowsky, *et al.*, *J. Chem. Phys.*, **5**, 682 (1937); *ibid.*, **7**, 725 (1939).

(14) For a summary of these rules see M. C. Kloetzel, "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 10.

(15) Many references could be quoted but perhaps the most direct is G. B. Bachman and C. G. Goebel, *THIS JOURNAL*, **64**, 787 (1942).

as colorless needles or prisms by crystallization of the distillate from acetone with or without addition of ethanol.

2-Phenyl-4-methylbenzoic Acid from 2-Phenyl-4-methylcyclohexenecarboxylic Acid (Ib).—A mixture of 0.5 g. of the acid and 0.15 g. of sulfur was heated at 230–240° for two hours. The mixture was distilled at 0.5 mm. up to 170°. The distillate was partitioned between ether and sodium bicarbonate solution. The aqueous solution was acidified with acetic acid and extracted with ether. Evaporation of the ether gave yellow granules (m.p. 152–159°). Recrystallization from methanol-water gave 52 mg. (11%) of colorless granules, 2-phenyl-4-methylbenzoic acid, m.p. 163–166°, undepressed when mixed with an authentic sample. As further proof, the 2-phenyl-4-methylbenzoic acid was cyclized to 3-methylfluorenone.⁷

When the uncrystallized monomeric adduct was similarly dehydrogenated, and the crude acidic product directly cyclized with sulfuric acid, 3-methylfluorenone was obtained in 8% yield. This result suggests that the uncrystallized monomeric adduct is composed of compounds either isomeric with Ia or formed by hydrogen disproportionation of Ia.

Isomerization of Ia to Ib.—Three hundred mg. of the acid (Ia) was esterified with diazomethane and the ester treated with a slight excess of triphenylmethylsodium in ether for two hours. When the solution was worked up, 270 mg. of acidic product was obtained, m.p. 148–153°. Four recrystallizations from acetone gave 35 mg. of Ib, m.p. 165.5–167°.

2-Isopropyl-6-methylfluorenone from 2,4-Dimethyl-2-(4'-isopropylphenyl)-cyclohexenecarboxylic Acid (III).—One gram of the acid was dehydrogenated with a 10% excess of sulfur at 225–230° for two hours. Distillation at 160–170° and 0.5 mm. gave an orange gum. This was dissolved in concentrated sulfuric acid to give a dark green solution. After standing for two hours at room temperature the solution was poured over ice. The orange gum was dissolved in ether, washed with 10% sodium hydroxide solution, and the ether removed. The yellow gum was dissolved in pentane and chromatographed through a column of alumina followed by elution with benzene to give 395 mg. (46%) of viscous yellow oil, 2-isopropyl-6-methylfluorenone, identified as its phenylhydrazone, bright yellow needles, m.p. 142.2–143°.

Anal. Calcd. for C₂₃H₂₂N₂: C, 84.62; H, 6.79; N, 8.58. Found: C, 84.4; H, 7.03; N, 8.68.

When the uncrystallized monomeric adduct was dehydrogenated and cyclized, 2-isopropyl-6-methylfluorenone was obtained in 6% yield.

3-Methylfluorenone from 2-(4'-Chlorophenyl)-4-methylcyclohexenecarboxylic Acid (IV).—A large excess of sodium was added to a solution of 0.5 g. of the uncrystallized acid in 75 ml. of absolute ethanol and the solution refluxed for one hour after the sodium had reacted. Water was added and the alcohol removed on the steam-bath. The reaction mixture was acidified with acetic acid and extracted with ether. The ether was removed and the residual gum distilled up to 140° at 0.5 mm. to give 435 mg. of colorless gum that could not be crystallized. Dehydrogenation and cyclization gave 129 mg. (33% over-all yield) of 3-methylfluorenone, m.p. 68–69°, no depression when mixed with an authentic sample.

2-Phenyl-2,4-dimethylcyclohexenecarboxylic Acid (II) from 2,4-Dimethyl-2-(4'-chlorophenyl)-cyclohexenecarboxylic Acid (V).—One-half gram of the acid (V) was reduced with metallic sodium by the method used above. The acidic product was crystallized from acetone to give 232 mg. (56%) of colorless needles, m.p. 183–185.5°, no depression when mixed with a sample of compound II.

2-Methoxy-6-methylfluorenone from 2,4-Dimethyl-2-(4'-methoxyphenyl)-cyclohexenecarboxylic Acid (VI).—One gram of the acid (VI) was dehydrogenated and cyclized by the method used above. Crystallization of the product from ethanol-water gave yellow needles, m.p. 80–87°. Two recrystallizations from acetone gave 54 mg. (6%) of yellow needles of 2-methoxy-6-methylfluorenone, m.p. 93.4–94.2°.

Anal. Calcd. for C₁₅H₁₂O₂: C, 80.33; H, 5.40. Found: C, 79.80; H, 5.27.

When the uncrystallized monomeric adduct was dehydrogenated and cyclized, 2-methoxy-6-methylfluorenone was obtained in 3% yield.

2-Methoxy-5,6-dimethylfluorenone from 2-(4'-Methoxyphenyl)-3,4-dimethylcyclohexenecarboxylic Acid (VII).—One gram of the acid (VII) was dehydrogenated and cyclized by the method used above to give on crystallization from acetone 36 mg. (4%) of yellow plates of 2-methoxy-5,6-dimethylfluorenone, m.p. 130.2–130.6°.

Anal. Calcd. for C₁₆H₁₄O₂: C, 80.65; H, 5.92. Found: C, 80.48; H, 5.67.

2-Phenyl-4-methylcyclohexenecarboxylic Acid (Ib) from 2-(3'-Nitrophenyl)-4-methylcyclohexenecarboxylic Acid (X).—Twenty ml. of 3 N hydrochloric acid was added to a mixture of 0.5 g. of mossy tin, 20 ml. of ethanol and 472 mg. of the acid (X). The mixture was refluxed for five hours and the ethanol then removed on the steam-bath. The solution was cooled to 5° and 5 ml. of 50% hypophosphorous acid added. A solution of 0.5 g. of sodium nitrite in 10 ml. of water was added with stirring and the temperature kept at 0–5° for one hour. The solution was allowed to come to room temperature and stand for five hours. Extraction with ether and crystallization from acetone gave 54 mg. (14%) of tan granules, m.p. 150–165°. Recrystallization from acetone raised the m.p. to 168–170°, no depression when mixed with a sample of 2-phenyl-4-methylcyclohexenecarboxylic acid (Ib).

2-Phenyl-4-methylcyclohexenecarboxylic Acid (Ib) from the 2-(4'-Nitrophenyl)-4-methylcyclohexenecarboxylic Acid (VIII).—Reduction and deamination of 175 mg. of the acid (VIII) by the method used above gave 12 mg. (8%) of 2-phenyl-4-methylcyclohexenecarboxylic acid (Ib), m.p. 163–168°.

3-Methylcarbazole from 2-(2'-Nitrophenyl)-4-methylcyclohexenecarboxylic Acid (IX).—Two drops of concentrated hydrochloric acid were mixed with 50 mg. of the acid (IX) and heated at 90° for two hours followed by distillation up to 180° at 0.5 mm. The distillate was partitioned between ether and 5% sodium hydroxide solution. Evaporation of the ether layer and crystallization from methanol-water gave 2 mg. (4%) of 3-methylcarbazole, m.p. 196–201°.

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