Acid-Catalyzed Ring Opening of 3-Phenyl-1,2-bis(α-hydroxymethyl)cyclopropanes and 3-Phenyl-2-(α-hydroxydiarylmethyl)diphenylmethylenecyclopropanes[1a,b]

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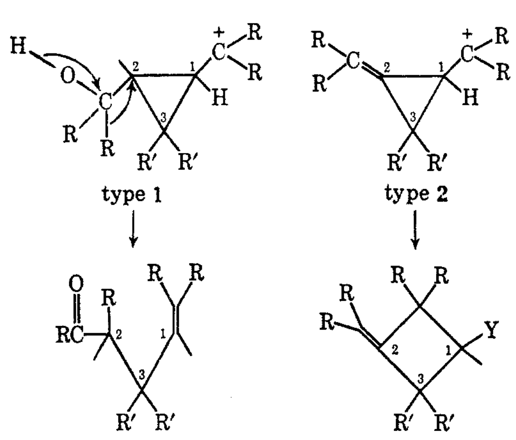
In contrast to similar compounds lacking a 3-phenyl substituent, 3-phenyl-1,2-bis(α-hydroxyphenylmethyl)-cyclopropane and 3-phenyl-1,2-bis(α-hydroxydiphenylmethyl)cyclopropane undergo acid-catalyzed ring opening between carbons 1 and 3, leading ultimately to substituted butadienes and benzaldehyde or benzophenone. A similar direction of ring opening occurs from 3-phenyl-2-(α-hydroxydiarylmethyl)diphenylmethylenecyclopropane to give vinylindenes.

Ring opening of cyclopropylcarbinyl cations of type **1** typically occurs between carbons 1 and 2. The major product is an unsaturated ketone **3** which arises from a pinacollike rearrangement. For example, the dehydrations of *trans*-[3] and *cis*-1,2-bis(α-hydroxydiphenylmethyl)cyclopropane[4] (**1**, R = C_6H_5; R′ = H)



type 1 type 2

3 4

Y = nucleophile

with acid have been reported to give 1,2,5,5-tetraphenylpenta-4-en-1-one (**3**, R = C_6H_5; R′ = H) in 75 and 76% yields, respectively; 21% bicyclic ether was also isolated from dehydration of the *cis* isomer. Similarly, acid dehydration of the methylenecyclopropanediol (**1**, R = C_6H_5; R′R′ = exocyclic methylene) gave the corresponding ketone (**3**, R = C_6H_5; R′R′ = methylene) in 73% yield.[5,6]

With the exception of those cases where one of the R′ groups is a carbinol, *vide ante*, the primary reaction of cyclopropylcarbinyl cations of type **2** also involves the bond between carbons 1 and 2. In this case the bond migrates to give the ring-expanded product **4**. An example of a type **2** system was recently reported by Nishimura, Kato, and Ohta[7] who examined the deamination of methylenecyclopropylcarbinylamine (**2**, R = R′ = H). In this case it was found that the reaction proceeded primarily (70%) by ring expansion in which the bond between C-1 and C-2 migrated to give **4** (R = R′ = H; Y = OAc,OH); neither the product of 1,3-ring expansion (2-methylenecyclobutanol) nor the product of 1,3-ring opening (2-methylenebut-4-en-1-ol) was observed.[8]

At this time, we would like to report our finding that substitution of a phenyl ring on carbon 3 of type **1** and type **2** systems alters the course of the reaction of both types of systems to yield products that result essentially exclusively from cleavage between carbons 1 and 3.

Type **1** systems that were examined include *trans*-3-phenyl-1,2-bis(α-hydroxyphenylmethyl)cyclopropane (**5a**) and *trans*-3-phenyl-1,2-bis(α-hydroxydiphenylmethyl)cyclopropane (**5b**), both of which were prepared in the obvious way from *trans*-3-phenyl-1,2-dibenzoylcyclopropane. Treatment of both diols with acid gave exclusively products that arose from cleavage between carbons 1 and 3. Thus, **5a** gave *trans,trans*-1,4-diphenylbutadiene **7a** (82% recrystallized) and benzaldehyde, whereas **5b** gave benzophenone and 1,1,4-triphenyl-butadiene **7b** (Scheme I). These products could arise either by concerted expulsion of the carbonyl compound from the cyclopropylcarbinyl cation **6** or by initial ring opening to give the benzyl cation **8** followed by loss of the aldehyde or ketone. Consistent with the latter possibility is the fact that **5b** gave, in addition to triphenylbutadiene, a small amount (at least 12%) of 1,1,4,4-tetraphenylbutadiene. This product is conveniently explained by hydroxyl exchange in the intermediate cation **8** followed by loss of benzaldehyde from the benzhydryl type of cation **9**.

Type **2** systems that were examined include **10a** and **10b** which were prepared by the addition of the appropriate Grignard reagent to **11** (Scheme II). Treatment of **10a** with a catalytic amount of sulfuric acid gave the indene **12a** in quantitative yield. Other methods of dehydration including iodine in CCl_4, chromatography on alumina, and pyrolysis on pyridine-impregnated alumina gave the same material in lower yields.

Although not demanding the indene structure, the analysis, molecular weight, ultraviolet spectrum (broad

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[1] (a) Supported in part by the National Science Foundation. (b) Taken in part from the Ph.D. Dissertation of A. W. Herriott, University of Florida, 1967.

[2] (a) NASA Trainee, 1963–1966. (b) Deceased Dec 7, 1966. (c) To whom correspondence should be addressed.

[3] R. A. Darby and R. E. Lutz, *J. Org. Chem.*, **22**, 1353 (1957).

[4] T. Shono, A. Oda, T. Morikawa, and R. Odu, *Bull. Chem. Soc. Jap.*, **38**, 940 (1965). Also see T. Shono, T. Yoshimura, and R. Oda, *J. Org. Chem.*, **32**, 1088 (1967).

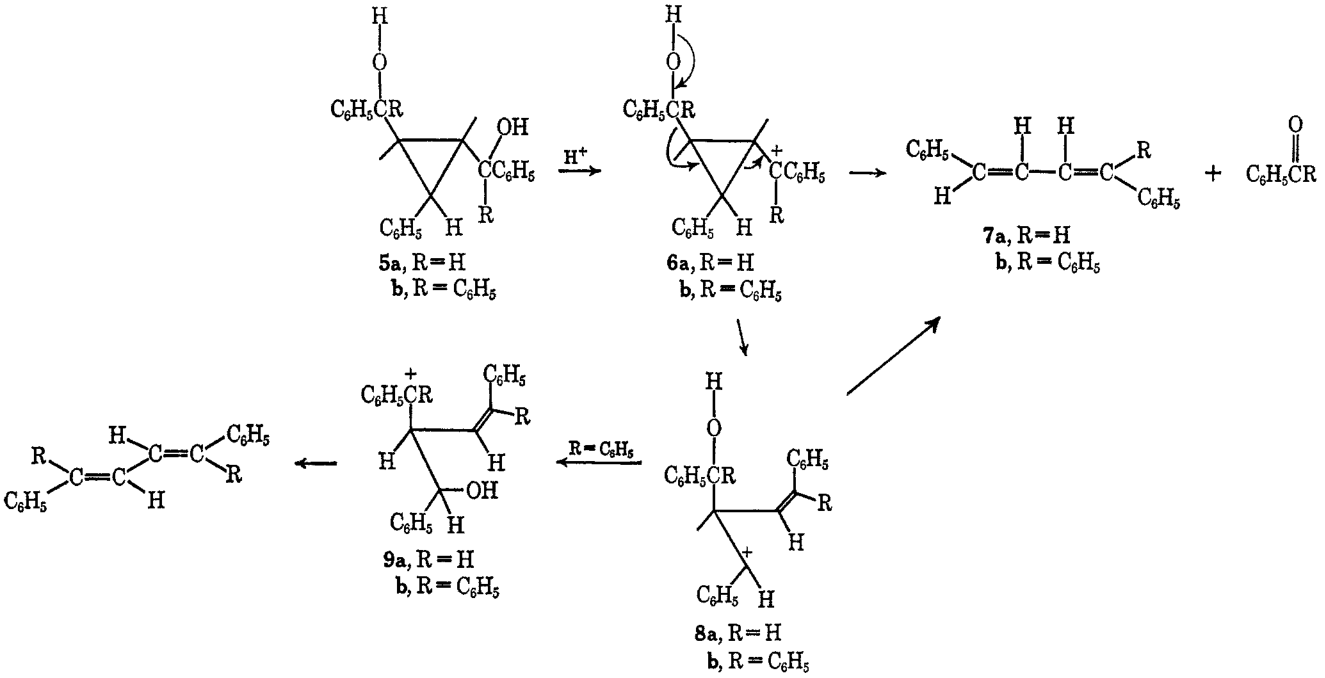
[5] R. R. Doyle and D. T. Longone, *ibid.*, **31**, 3868 (1966).

[6] For another example of a type **1** system, see T. Shono, T. Yoshimura, and R. Oda, *ibid.*, **32**, 1088 (1967), who studied the dehydration of *trans*-bis(α-hydroxydimethylmethyl)cyclopropane (**1**, R = CH_3; R′ = H). Although a multitude of products were observed, they again apparently derived from ring opening between carbons **1** and **2**. Furthermore, an interesting feature of this dehydration was the identification of two of the products as *cis*-cyclopropanes; this requires a ring-opened intermediate that is capable of reclosing to give the *cis* products.

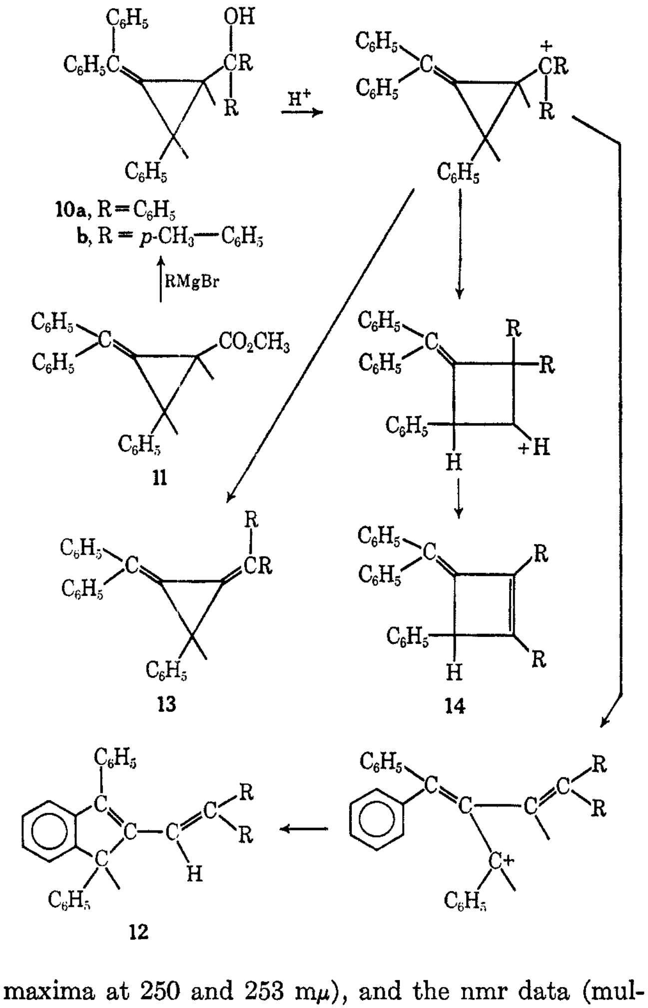
[7] A. Nishimura, H. Kato, and M. Ohta, *J. Amer. Chem. Soc.*, **89**, 5083 (1967).

[8] The acidic ring opening of 2,2,5,5-tetramethyl-4-isopropylidene-1-oxaspiro[2.2]pentane [J. K. Crandall and D. R. Paulson, *J. Org. Chem.*, **33**, 991 (1968)] may proceed *via* a methylenecyclopropylcarbinyl cation, but an alternate pathway not involving this intermediate was considered more likely.

SCHEME I

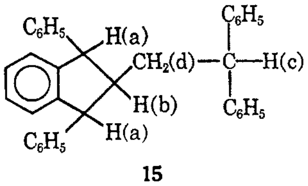


SCHEME II



maxima at 250 and 253 mμ), and the nmr data (multiplet centered at δ 7.1 and sharp singlet at 4.41 in a ratio of 25:1) are all consistent with it. However, at least two other structures are equally consistent with these data, the dimethylenecyclopropane **13** and the methylenecyclobutene **14**. That the structure is not the most direct dehydration product, the dimethylenecyclopropane, was suggested by the fact that ozonolysis of **10a** consistently gave between 70 and 79% of 1 equiv of benzophenone. Although this did not distinguish between **12** and **14** or, in fact, even conclusively exclude **13** as the structure, it did suggest a definitive experiment to afford a choice among these three possibilities. The *p*-methyl-substituted alcohol **10b** was treated with a catalytic amount of acid and the resulting yellow hydrocarbon whose properties were very similar to those of the previous dehydration product was ozonized. Ozonolysis of the dimethylenecyclopropane **13b** should produce both benzophenone and di-*p*-tolyl ketone. The methylenecyclobutene **14b** would give only benzophenone and the vinylindene **12b** would give only di-*p*-tolyl ketone. In fact, di-*p*-tolyl ketone was formed in 89% yield with no trace of benzophenone. Thus the vinylindene becomes the choice of the three.

The indene structure was supported by the fact that **12a** absorbs 2 mol of hydrogen to give a colorless product whose nmr spectrum is consistent with hydrocarbon **15**. Thus, it showed aromatic protons, a doublet at δ 4.50 [H(a)], a complex multiplet at 2.9–2.3 [H(b) and H(c)], and a quartet at 1.64 [H(d)]. The equivalency of the 1 and 3 indanyl protons [H(a)] supports a structure in which the two phenyls are *cis*.



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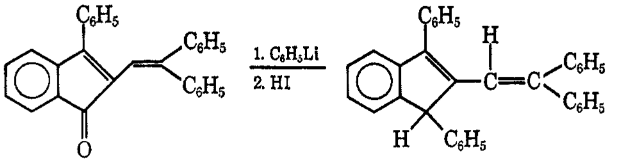
The structure of the hydrocarbon was finally unequivocally proved by alternate synthesis from the known 3-phenyl-2-(β,β-diphenylvinyl)indenone **16** by the steps outlined below. The resulting product was identical in every way (uv, nmr, and ir spectra and tlc) with 12a.



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Experimental Section[9]

5-Phenyl-3,4-dibenzoyl-2-pyrazoline.—A solution of phenyldiazomethane in ether was prepared by the method of Gutsche and Jason[10] on an 0.8-mol scale. The solution was stirred in an ice bath and *trans*-1,4-diphenyl-2-butene-1,4-dione (Eastman Practical Grade) was added in 3–5-g portions until the color changed from red to a greenish yellow; this required 60–70 g of the olefin. After stirring an additional 30 min, the solution was concentrated and cooled. The resulting yellow solid was recrystallized from methanol; the yield was 65–76 g (60–70% from the olefin) of the crude pyrazoline, mp 125–140°. Two more recrystallizations from methanol gave an analytic sample: mp 137.0–138.5°; ir, 3400 (N—H) and 1685 cm^{-1} (C=O); uv max (MeCN), 249 mμ (log ϵ 4.32) and 323 (4.13). The nmr spectrum showed aromatic multiplets at δ 8.1, 7.8, and 7.3 and an AB quartet (J = 9.0 Hz, $\delta_B - \delta_A$ = 6.3 Hz) at 5.19.

Anal. Calcd for $C_{23}H_{18}O_2N_2$: C, 77.95; H, 5.12; N, 7.90. Found: C, 77.79; H, 5.15; N, 8.04.

3-Phenyl-1,2-dibenzoylcyclopropane.—A solution of 25.0 g of 5-phenyl-3,4-dibenzoyl-2-pyrazoline (mp 125–140°) in 50 ml of N,N-dimethylaniline was heated at 150–155° for 1.5 hr, during which 90% of the theoretical amount of nitrogen was evolved. An additional hour at 165–170° gave another 10–15% of nitrogen. Benzene (150 ml) was added as the solution cooled to prevent the dark red mass from solidifying. The benzene solution was washed with 5% hydrochloric acid and then water, dried, and concentrated to *ca.* 40 ml, and the thick hot syrup was poured onto a 2.5 × 50 cm column of neutral alumina. Continuous elution with a 1:4 benzene–pentane solution gave, after 3 l. of solvent, 12 g (52%) of *trans*-3-phenyl-1,2-dibenzoylcyclopropane, mp 117–118°. An analytical sample recrystallized from ethanol had mp 121.5–122.0° (lit.[11] mp 116°); ir, 1680 cm^{-1} (C=O); uv max (MeCN), 247 mμ (log ϵ 3.91) and 315 (1.26). The nmr spectrum showed aromatic multiplets at δ 8.1 and 7.3 and an ABX pattern ($J_{AX} = J_{BX}$ = 6.0 Hz; J_{AB} = 10.0 Hz) with the X triplet at δ 4.25 and the AB portion centered at δ 3.66.

After all of the *trans* isomer had been eluted from the column, elution with 1:1 benzene–pentane gave a small amount (*ca.* 0.8 g) of the *cis* isomer: mp 150–152° (lit.[12] mp 151°); ir, 1690 and 1675 cm^{-1} (C=O). The nmr spectrum showed aromatic multiplets at δ 8.1 and 7.4 and an AB pattern (J = 7.5 Hz) with the benzyl proton at 3.59 and the other two protons at 3.42.

***trans*-3-Phenyl-1,2-bis(α-hydroxyphenylmethyl)cyclopropane (5a).**—To a stirred mixture of 0.760 g (21 mmol) of lithium aluminum hydride in 30 ml of anhydrous ether was added over 30 min a solution of 4.70 g (14.4 mmol) of *trans*-3-phenyl-1,2-dibenzoylcyclopropane in 120 ml of anhydrous ether. The mixture was refluxed overnight, then hydrolyzed with saturated sodium potassium tartrate solution, and worked up in the usual manner. The white solid was purified by precipitation from ether with pentane. The yield was 3.75 g (79%) of a mixture of diastereomers, mp 105–125° for the precipitate; further precipitation with pentane gave a solid, mp 111–113.5°, which was used for analysis and spectral data, ir 3400 cm^{-1} (OH). The nmr spectrum exhibited complex multiplets at δ 7.2 (aromatic protons), 4.1 (protons of hydroxymethyl group), and 2.5–1.5 (ring and hydroxy protons) in the area ratios of 15:2.0:5.1.

Anal. Calcd for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71. Found: C, 83.50; H, 6.73.

Reaction of *trans*-3-Phenyl-1,2-bis(α-hydroxyphenylmethyl)cyclopropane with Acid.—To a stirred solution of 900 mg (2.72 mmol) of the diol in 20 ml of chloroform was added 1 drop of concentrated sulfuric acid. After stirring for 15 min at room temperature, the solution showed ultraviolet maxima at 531, 333, and 322 mμ. The solution was washed with water, 7% sodium bicarbonate, and water; it was then extracted three times with saturated sodium bisulfite solution. The chloroform layer was dried and evaporated to give a white solid. Crystallization from methanol gave 460 mg (82%) of *trans,trans*-1,4-diphenylbutadiene, mp 151.5–152° (mmp 149.5–151°, with a commercial sample of mp 149–150°). The infrared and ultraviolet spectra were identical with those of an authentic sample.

The combined sodium bisulfite extracts were treated with concentrated hydrochloric acid until the solution was strongly acidic. Extraction with ether followed by drying of the organic layer and evaporation of the ether gave an oil whose odor and ultraviolet spectrum were identical with those of an authentic sample of benzaldehyde. The oil was refluxed with a solution of semicarbazide hydrochloride and sodium acetate in ethanol; addition of water gave a white precipitate which was recrystallized from ethanol–water to give 225 mg (51%) of benzaldehyde semicarbazone, mp 218–219° (lit.[12] mp 222°).

***trans*-3-Phenyl-1,2-bis(α-hydroxydiphenylmethyl)cyclopropane.**—To a solution of 1.0 g of *trans*-3-phenyl-1,2-dibenzoylcyclopropane in 50 ml of ether was added an excess of phenylmagnesium bromide. The mixture was allowed to remain at room temperature overnight and worked up in the usual manner to give the diol essentially quantitatively. The diol shows an unusual melting point behavior. The analytical sample appears to change its crystal form between 170 and 175° and the new solid material melts sharply at 184–185°. When the pure material is placed in a preheated bath at 177° it completely melts and then resolidifies. At 175° it simply appears to change its form without actually melting (lit.[11] mp 183°).

Reaction of *trans*-3-Phenyl-1,2-bis(α-hydroxydiphenylmethyl)cyclopropane with Acid.—To a solution of 0.50 g of the diol dissolved in chloroform was added 2 drops of concentrated sulfuric acid. The mixture was stirred at room temperature for 2 hr at which time the chloroform was washed successively with water, sodium bicarbonate, and water. The resulting solution was extracted with three portions of saturated sodium bisulfite solution. The bisulfite solution was then neutralized with concentrated hydrochloric acid and extracted with ether. Evaporation of ether after drying left 8 mg of oil which had a strong odor of benzaldehyde. The chloroform solution was taken to dryness. A thin layer chromatogram showed only two spots: one corresponding to benzophenone and the other, a bright blue fluorescent spot which moved almost with the solvent front (5% ether–pentane). Chromatography over neutral Woelm alumina (activity grade I) using 5% ether–pentane gave, in the early cuts, 0.21 g of white solid and, in later cuts, 0.168 g of an oil. The infrared spectrum of the oil indicated that it was primarily benzophenone. The white solid was dissolved in a small amount of methylene chloride followed by addition of pentane. Cooling over the weekend gave 35 mg of a white solid, mp 193.5–194.5°, whose nmr spectrum was identical with that of authentic 1,1,4,4-tetraphenylbutadiene, mp 202°. The filtrate was taken to dryness. Recrystallization of a portion of the residue from hot hexane gave a white solid, mp 99–100°, (lit.[13] mp 101.5–102° for 1,1,3-triphenylbutadiene). The nmr spectrum of the recrystallized material also implicated the triphenylbutatriene structure in that it showed phenyl hydrogens between δ 7.4 and 7.2 and olefin hydrogens (multiplet) between 6.9 and 6.7 in an area ratio of 15:2.9. The nmr spectrum of the crude residue from above indicated that the crude product was primarily the triphenylbutadiene contaminated with a small amount of tetraphenylbutadiene.

***trans*-3-Phenyl-2-diphenylmethylenecyclopropanecarboxylic Acid.**[14]—A stirred suspension of 1 g of electrolytic copper dust in 63.5 g (0.0237 mol) of 1,3,3-triphenylpropyne was purged with nitrogen and maintained at 150° (oil-bath temperature) while

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(9) Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. The nmr spectra were determined in deuteriochloroform on a Varian A-60A spectrometer with tetramethylsilane as an internal standard. Infrared spectra were determined as KBr pellets on an IR-10 spectrophotometer. Organic solutions were dried over anhydrous magnesium sulfate.

(10) C. D. Gutsche and E. F. Jason, *J. Amer. Chem. Soc.*, **78**, 1184 (1956).

(11) E. P. Kohler and W. N. Jones, *ibid.*, **41**, 1249 (1919).

(12) "Tables for Identification of Organic Compounds," Chemical Rubber Publishing Co., Cleveland, Ohio, 1960, p 71.

(13) H. Staudinger, *Ber.*, **42**, 4249 (1909).

(14) A. W. Herriott and W. M. Jones, *Tetrahedron Lett.*, 2387 (1967).

27 g (0.24 mol) of ethyl diazoacetate was added dropwise over 4 hr. After an additional hour at 150°, the mixture was allowed to cool; benzene was added to prevent solidification of the molten material. A solution of 20 g of potassium hydroxide in 60 ml of methanol was added and the mixture was refluxed overnight. After removal of the bulk of the solvent on a rotary evaporator, the dark sludge was shaken with ether and water; the aqueous layer was washed with ether, acidified with 10% hydrochloric acid, and extracted with chloroform. After being dried, the chloroform extracts were percolated through a column of Florex. Concentration of the solvent gave 21.5 g (28%) of a yellow solid, mp 150–160° dec. Recrystallization from benzene–heptane gave colorless crystals, mp 159–163° dec; two more recrystallizations from the same solvent gave mp 163.0–164.0° dec for an analytical sample. The physical properties have been previously reported.[14]

***trans*-Methyl 3-Phenyl-2-diphenylmethylenecyclopropanecarboxylate (11).**—A suspension of 7.2 g of 3-phenyl-2-diphenylmethylenecyclopropanecarboxylic acid in ether was treated with diazomethane, generated in the usual manner[15] from Diazald, until the solution remained yellow. The solution was concentrated to *ca.* 75 ml and allowed to stand overnight. The first crop of colorless crystals was 6.0 g, mp 134.0–135.5° dec; a second crop of 0.9 g with an identical melting point was obtained by concentration of the filtrate to give a total yield of 93%. Recrystallization from methanol for an analytical sample gave mp 135.5–137.0° dec, ir 1725 cm^{-1} (C=O). The nmr spectrum showed a multiplet at δ 7.25 (aromatic protons), a singlet at 3.70 (methyl protons), a partially obscured doublet at 3.62 (benzylic proton), and a doublet (J = 3.5 Hz) at 2.55 (other ring proton); the relative areas were 15:4.0:1.0 with the methyl and benzylic protons being integrated together.

Anal. Calcd for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.85; H, 5.72.

***trans*-3-Phenyl-2-(α-hydroxydiphenylmethyl)diphenylmethylenecyclopropane (10a).**—To an ether solution of phenylmagnesium bromide (30 mmol) was added 2.1 g (6.2 mmol) of the ester **11**. The mixture was stirred for 1 hr, hydrolyzed with ammonium chloride solution, and worked up in the usual manner. Crystallization of the resulting oil from methanol gave 2.05 g (71%) of pale yellow solid in two crops. Two recrystallizations from heptane gave colorless needles: mp 109.0–110.5°; ir 3500 cm^{-1} (OH). The nmr spectrum showed a multiplet at δ 7.18 (aromatic protons), an AB quartet (J = 4.5 Hz) centered at 2.89 (ring protons), and a singlet at 2.18 (hydroxyl proton) in area ratios of 25:2.0:1.0.

Anal. Calcd for $C_{35}H_{28}O$: C, 90.48; H, 6.07. Found: C, 90.24; H, 5.95.

1,3-Diphenyl-2-(β,β-diphenylvinyl)indene (12a).—To a stirred solution of 4.06 g (8.75 mmol) of 3-phenyl-2-(α-hydroxydiphenylmethyl)diphenylmethylenecyclopropane in 70 ml of methanol at 40° was added 1 drop of concentrated sulfuric acid. The solution immediately turned yellow and a solid began to separate. After 30 min the mixture was filtered to give 3.4 g of yellow solid, mp 121–126°; concentration of the solution gave a second crop of 430 mg, mp 125–135°, for a total yield of 98%. The product could not be readily recrystallized, but the melting point was raised to 130–132° by chromatography over Woelm neutral alumina. The uv spectrum (cyclohexane) showed maxima at 250 mμ (log ε 4.72) and 353 (4.62). The nmr spectrum (CCl_4) showed a multiplet at δ 7.08 (aromatic and vinyl protons) and a sharp singlet at 4.41 (1-indenyl proton) in area ratio of 25:1.0. The mass spectrum showed peaks at 448 (molecular ion M, intensity = 100), 372 (M − phenyl, 13), 360 (M − benzyl, 15), 193 (M − two phenyls, 38), 281 (M − benzhydryl, 10), 269 (M − β,β-diphenylvinyl, 9), 267 (triphenylvinyl cation, 10), 166 (benzhydryl cation, 31), and a multitude of fragments at *m/e* below 150.

Anal. Calcd for $C_{35}H_{26}$: C, 94.13; H, 5.87. Found: C, 94.23; H, 5.83.

Ozonolysis of 12a.—A solution of the indene in chloroform was treated at −30° with ozone (generated in about 6% concentration from a Welsbach generator) until a pale blue color persisted. The solvent was removed and the ozonide was decomposed in the usual manner with water, zinc dust, and a trace of acetic acid. Vpc analysis of the ether extract by the internal standard method indicated benzophenone as the only volatile product in a yield of 97 mg (77%). In a repeat experiment, treatment of the ether extract with 2,4-dinitrophenylhydrazine in ethanol containing sulfuric acid gave benzophenone 2,4-DNP in 62% yield, mp 230–236° (lit.[16] mp 239°).

Hydrogenation of 12a.—Platinum oxide (160 mg) was stirred in 25 ml of absolute ethanol under hydrogen atmosphere until adsorption ceased, and 220 mg (0.49 mmol) of the vinylindene in 60 ml of ethanol was added. After 20 hr of stirring at room temperature, the volume remained constant; 24.7 ml (2.1 equiv) of hydrogen was consumed. Filtration and concentration of the filtrate gave colorless feathery needles (110 mg, 49%), mp 138–142°. Two more recrystallizations from ethanol–ethyl acetate gave mp 147.5–148.0°.

The nmr spectrum showed multiplets at δ 7.2 and 6.48 (aromatic protons), a doublet (J = 7.5 Hz) at 4.50 (1 and 3 indanyl protons), a complex multiplet from 2.89 to 2.29 (2 indanyl proton and benzhydryl proton), and a doublet (J = 8.0 and 6.5 Hz) at 1.64 (methylene protons).

Anal. Calcd for $C_{35}H_{30}$: C, 93.29; H, 6.71. Found: C, 93.49, 93.31; H, 6.58, 6.66.

3-Phenyl-2-(α-hydroxydi-*p*-tolylmethyl)diphenylmethylenecyclopropane (10b).—The procedure for **10a** was followed using *p*-tolylmagnesium bromide. The oil obtained was chromatographed over deactivated silica gel to give alcohol **10b** in 28% yield, mp 100–110°; recrystallization from ethanol–water gave mp 105–111°. The nmr spectrum showed a multiplet at δ 7.1 (aromatic protons), an AB quartet (J = 3.8 Hz; $\delta_A - \delta_B$ = 9.5 Hz) centered at 2.85, a singlet at 2.22 (methyl groups), and a broad absorption at 1.8 (hydroxyl proton).

Anal. Calcd for $C_{37}H_{32}O$: C, 90.21; H, 6.55. Found: C, 90.04; H, 6.63.

1,3-Diphenyl-2-(β,β-di-*p*-tolylvinyl)indene (12b).—To a warm (*ca.* 50°) solution of 67 mg (0.13 mmol) of **10b** in 15 ml of methanol was added 1 drop of concentrated sulfuric acid. The solution immediately became yellow. After 1 hr a few drops of 10% sodium bicarbonate solution were added; stirring for an additional hour gave a yellow precipitate which was collected by filtration. This gummy material was chromatographed with 4:1 pentane–benzene over a short column of silica gel. Evaporation of the solvent and crystallization of the residue from methanol gave 54 mg (70%) of amorphous yellow solid: mp 130–133°; uv max (MeCN), 254 and 357 mμ. The nmr spectrum (CCl_4) showed a multiplet from δ 7.5 to 6.6 (aromatic and vinyl protons), a singlet at 4.38 (1-indenyl proton), a singlet at 2.42 (methyl group), and a singlet at 2.22 (methyl group).

Anal. Calcd for $C_{37}H_{30}$: C, 93.63; H, 6.37. Found: C, 93.38; H, 6.38.

Ozonolysis of 12b.—A solution of 33 mg (0.070 mmol) of the vinylindene in 25 ml of carbon tetrachloride was cooled to *ca.* −30° and treated with a stream of ozonized oxygen until the pale blue color persisted (about 5 min). Decomposition of the ozonide and analysis of the ether extract by vpc using the internal standard method indicated no benzophenone and 13 mg (89%) of di-*p*-tolyl ketone as the sole volatile product.

Alternate Synthesis of 12a.—A 1.0 *M* solution of phenyl lithium in ether was added dropwise to a stirred suspension of 103 mg of 3-phenyl-2-(β,β-diphenylvinyl)indenone[17] in ether until the red color disappeared. Hydrolysis and the usual workup gave a yellow oil: uv max (cyclohexane), 247 and 352 mμ; ir (neat), 3500 and 3400 cm^{-1} (OH). The oil was dissolved in 10 ml of acetic acid and 1 ml of 47% hydroiodic acid was added. After 5 min on a steam bath, the red solution was poured into ether and washed with thiosulfate and bicarbonate solutions. Drying and evaporating the ether layer gave a yellow gum whose tlc and spectral properties were completely identical with those of **12a** obtained by dehydration of **10a**.

Registry No.—**5a**, 17393-05-4; **10a**, 17414-44-7; **10b**, 17416-50-1; **11**, 17393-15-6; **12a**, 17448-10-1; **12a** saturated ($C_{35}H_{30}$), 17477-89-3; **12b**, 17448-11-2; 5-phenyl-3,4-dibenzoyl-2-pyrazoline, 17416-51-2; *trans*-

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(15) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley & Sons, Inc., New York, N. Y., 1967, p 191.

(16) Reference 12, p 96.

(17) P. J. Kim and N. Hagihara, *Bull. Chem. Soc. Jap.*, **38**, 2022 (1965). We are very grateful to Dr. Hagihara for a generous sample of this material.

3-phenyl-1,2-dibenzoylcyclopropane, 17393-16-7; *cis*-3-phenyl-1,2-dibenzoylcyclopropane, 17393-17-8; di-*p*-tolyl ketone, 611-97-2.

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Bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic Anhydride

J. R. Edman and H. E. Simmons

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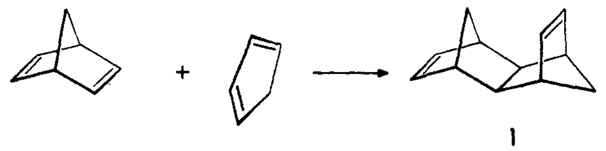
Bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic anhydride (norbornadiene-2,3-dicarboxylic anhydride) (**3**) has been synthesized and its Diels–Alder reactivity with butadiene, cyclopentadiene, and anthracene has been studied. The question of *exo* or *endo* attack on the norbornadiene ring is explored using deuterated cyclopentadiene and the pmr spectra of the adducts assigned. The photoisomerization of **3** to quadricyclane-2,3-dicarboxylic anhydride (**13**) and a cycloaddition reaction of **13** are reported.

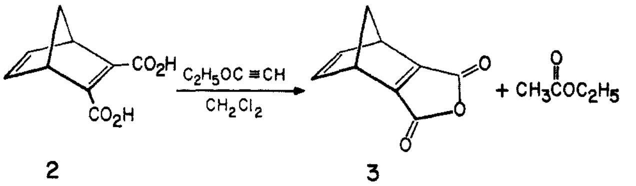
Stille and Frey[1] studied the Diels–Alder addition of cyclopentadiene to bicyclo[2.2.1]hepta-2,5-diene (norbornadiene) and established **1** as the structure of the major monoaddition product. They visualized this product as arising from *exo* addition with the methylene bridge of the cyclopentadiene ring directed away from the methylene bridge of norbornadiene. Such a mode of addition would be analogous to that of cyclopentadiene to norbornene.[2] Examination of models of norbornadiene and cyclopentadiene does not suggest why the proposed *exo* attack should be favored exclusively. The *endo*-5,6 protons which contribute to the *endo* steric hindrance in norbornene are no longer present in norbornadiene, and *endo* additions appear feasible in the latter. Furthermore, under the conditions that Stille and Frey ran their reactions (18 hr, 190°), the observed product **1** might simply represent the thermodynamically, but not kinetically, favored product.



1

We have synthesized bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic anhydride **3** and studied its reaction with cyclopentadiene. Anhydride **3** offers advantages over norbornadiene in that the two cyclopentene rings in the adduct can be chemically distinguished, and this allows assignment of the mode of cyclopentadiene addition. Anhydride **3** also reacts with cyclopentadiene at lower temperatures than norbornadiene, and there is better opportunity to distinguish between kinetically and thermodynamically controlled products.

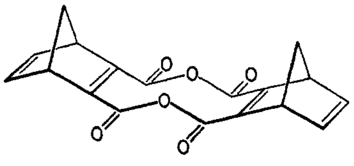
Synthesis and Reaction with Dienes.—Our preferred procedure for the synthesis of **3** is the dehydration of norbornadiene-2,3-dicarboxylic acid[3] in refluxing dichloromethane solution with ethoxyacetylene.[4] All other anhydride syntheses tried, including the carbodiimide method, gave poor yields. The crystalline anhydride **3** was obtained in a 70% yield and melts at 88–89°. It can be stored under nitrogen at −60° for at least 1 year, but slowly decomposes at room temperature.



2 3

The structure of **3** was established by its elemental analysis, molecular weight, infrared absorption spectrum (Figure 1a), pmr spectrum (Figure 1b), and photoisomerization to a quadricyclane anhydride. The characteristic infrared spectrum shows anhydride carbonyl absorptions at 1840 and 1770 cm^{-1}, with the carbonyl and hydroxyl absorptions found in **2** at 2540, 1700, and 1640 cm^{-1} missing.

In some runs a small amount of an ether-insoluble material was obtained which was assigned structure **4**.[5] The evidence for this structure is summarized in the Experimental Section.



4

The maleic anhydride double bond present in **3** readily undergoes Diels–Alder reactions with cyclopentadiene, butadiene, and anthracene.

The reaction with cyclopentadiene is unique in that it can occur in four distinct ways to give three isomeric adducts, **5**, **6**, and **7**. These additions are outlined in Scheme I.

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(1) J. K. Stille and D. A. Frey, *J. Amer. Chem. Soc.*, **81**, 4273 (1959).

(2) S. B. Soloway, *ibid.*, **74**, 1027 (1952).

(3) O. Diels and K. Alder, *Ann. Chem.*, **490**, 236 (1931).

(4) We thank Dr. T. Fukunaga for drawing this procedure to our attention. G. Eglinton, E. R. H. Jones, B. L. Shaw, and M. C. Whiting, *J. Chem. Soc.*, 1860 (1954).

(5) We are indebted to Professor J. R. Johnson for first suggesting this structure. As a referee has pointed out, two isomers are possible. There is no basis on which to favor **4** over the one with the methylene bridges *anti*. A melting point range of 1° does not favor a mixture while the broad pmr lines are consistent with a mixture.