Perhydroindanone Derivatives. I. Applicability of the Diels–Alder Reaction[1a]

Herbert O. House and Gary H. Rasmusson[1b]

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts

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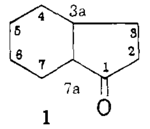
The reactions summarized in Charts I and II have been carried out to explore the use of the Diels–Alder reaction for the preparation of variously substituted perhydroindanones.

In anticipation of synthetic work directed toward the synthesis of the gibberellins,[2] we have investigated both the syntheses and chemical properties of a number of perhydroindanone systems **1**. Since we envision these systems, **1**, to be models of the A-B ring system in the gibberellins, we have been particularly concerned with those derivatives which bear methyl and/or carboxyl substituents at position 7.



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In this and the subsequent paper of this series, we have explored the possible utility of various cyclopentenones as dienophiles in the Diels–Alder reaction as well as the possible use of a 3-vinyl-2-cyclopenten-1-one as a diene. This latter approach is summarized by the reactions outlined in Chart I which start with the reactive 4-cyclopentene-1,3-dione (**2**).[3]

Because of the instability of intermediates **9** and **10**, these materials were handled as partially purified intermediates. Since very mild reaction conditions were employed for the various Diels–Alder reactions summarized in Chart I, we have assumed that the adducts obtained are the result of kinetically controlled processes. Accordingly, the reactions are expected to proceed by *cis, endo* addition of the dieneophile to the diene and reaction of the diene **10** with dieneophiles may be expected to occur from the less hindered side.[4] These considerations lead to the indicated stereochemical assignments. The stereochemistry of the diketone **7** has been established by degradation.[3e] The question of the relative stabilities of *cis* and *trans* ring fusions in 3a,4,7,7a-tetrahydro-1-indanone systems is examined in a subsequent paper of this series. The structure tentatively assigned the adduct **11a** is based on the observation[5] that terminally substituted dienes and monosubstituted dieneophiles afford predominantly the product with the substituents vicinal to one another. The general synthetic approach to perhydroindanones represented by the reaction sequence **8** → **9** → **10** → **11a** was considered unattractive because of the instability of intermediates **9** and **10** and, particularly, the low yield (4.9% of **11a**) obtained in the last step of the sequence.

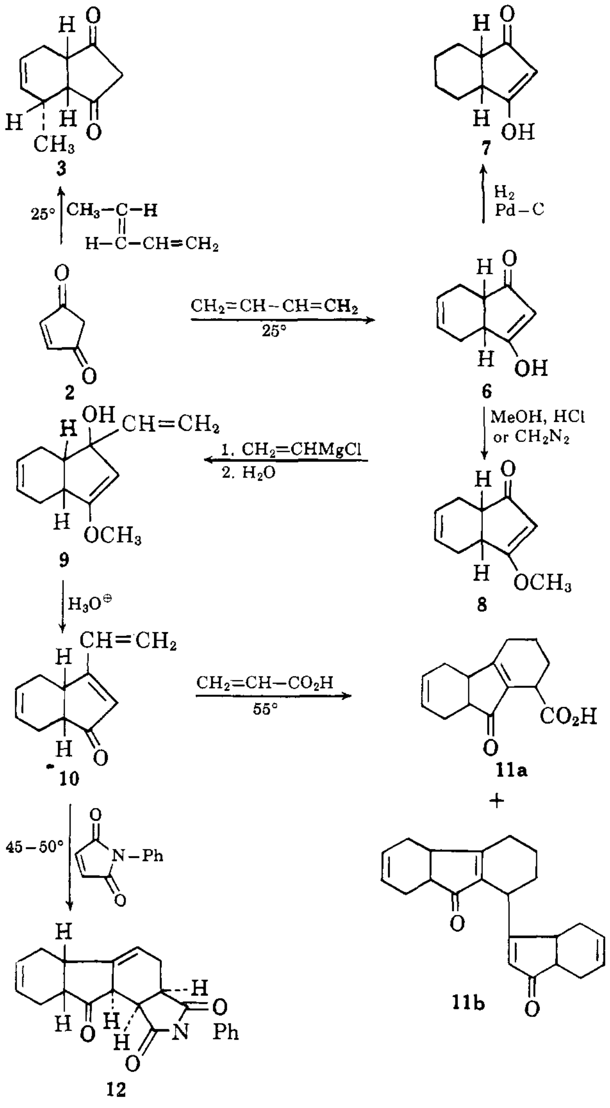

Chart I

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[1] (a) Supported in part by National Science Foundation Grant No. G-9486. (b) National Science Foundation Predoctoral Fellow, 1958–1962.

[2] For a recent review see J. F. Grove, *Quart. Rev.*, **15**, 56 (1961).

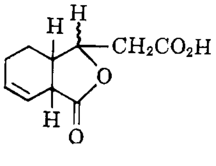
[3] (a) C. H. DePuy and E. F. Zaweski, *J. Am. Chem. Soc.*, **81**, 4920 (1959). (b) C. H. DePuy and C. E. Lyons, *ibid.*, **82**, 631 (1960). (c) C. H. DePuy and P. R. Wells, *ibid.*, **82**, 2909 (1960). (d) C. H. DePuy, R. D. Thurn, and M. Isaks, *J. Org. Chem.*, **27**, 744 (1962). (e) V. F. Kucherov and L. I. Ivanova, *Dokl. Akad. Nauk, SSSR*, **131**, 1077 (1960); *Chem. Abstr.*, **54**, 21021 (1960).

[4] J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961).

[5] (a) I. N. Nazarov, A. I. Kuznetsova, and N. V. Kuznetsov, *J. Gen. Chem., USSR*, **25**, 75 (1955). (b) I. N. Nazarov, Y. A. Titov, and A. I. Fuznetsova, *Acad. Sci. USSR, Chem. Sci. Bull.*, 1224 (1959). (c) Although the diene system in structure **10** has substituents at both the 1 and 2 positions of the diene, the carbonyl function at position 1, being capable of resonance interaction with the diene system, may be expected to determine the product orientation. For example, reaction of 1-phenyl-2-methyl-1,3-butadiene with acrylic acid produced 2-methyl-3-phenyl-4-carboxycyclohexene [K. Alder, J. Hayden, K. Hemibach, and K. Neufang, *Ann.*, **586**, 110 (1954)].

[6] H. O. House and G. H. Rasmusson, *J. Org. Chem.*, **26**, 4278 (1961).

[7] K. Alder and W. Vogt, *Ann.*, **570**, 190 (1950). From dimerization of the acid **13a**, the lactone pictured below was isolated.



We next investigated the use of pentadienoic acid derivatives **13** and **14**[6] as dienes in Diels–Alder reactions. These investigations, outlined in Chart II, indicated that the dienes **13** could be employed with reactive dieneophiles (4-cyclopentene-1,3-dione, N-phenylmaleimide), but not with the less reactive dieneophile, cyclopentenone (**18**). We were unable to isolate an adduct from the diene **14** with any of the dieneophiles studied; this lack of reactivity is presumably attributable to steric interference with the existence of the diene **14** in the required cisoid conformation.[4] The stereochemistry assigned adducts **15** and **17** is based on the previously discussed considerations. The diene dimer **19** obtained either in the presence or absence of cyclopentenone is analogous to the previously reported dimerization of the acid **13a.**[7] Although the *trans* stereochemistry of the carbon–carbon double bond in the side chain was apparent from the infrared spectrum of **19** we did not establish the stereochemistry of the two substituents on the cyclohexene ring. An attempt to utilize the tetrahydroindenone **20** as a dienophile resulted in the isolation of the isomer **21**; no Diels–Alder adduct was isolated.

Experimental[8]

***cis*-3a,4,7,7a-Tetrahydroindane-1,3-dione** (6).—A solution of 75.0 g. (0.78 mole) of 4-cyclopentene-1,3-dione, 90 ml. (58 g. or 1.1 moles) of butadiene and 0.3 g. of 2,5-di-*t*-butylhydroquinone in 220 ml. of benzene was allowed to stand in an autoclave at room temperature for 12 days. An additional 40 ml. (26 g. or 0.48 mole) of butadiene was added and the mixture was allowed to stand for an additional 5 days. After the reaction mixture had been filtered to separate 94.4 g. (80.6%) of the crude product, m.p. 157.5–161°, concentration of the mother liquor followed by crystallization from ether afforded 6.02 g. (8% recovery) of the unchanged starting material, m.p. 33–34.5°. Recrystallization from a methanol–ethyl acetate mixture afforded the pure adduct 6 as white prisms, m.p. 160–161.5° (lit.[3e] 157.5–158.5°), with infrared absorption[9] at 1635 and 1585 cm.$^{-1}$ (enolic β-diketone) and a ultraviolet maximum[10] at 244.5 mμ (ϵ 15,400)

Anal. Calcd. for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 72.01; H, 6.72.

A suspension of 25.7 g. (0.17 mole) of the enolic diketone 6 in 70 ml. of methanol which had been saturated with hydrogen chloride was stirred at room temperature for 8 hr. The resulting solution was added, dropwise and with stirring, to an excess of cold (10°), aqueous potassium carbonate. After the resulting mixture had been extracted with ether, the ethereal solution was washed with water, dried, and concentrated. Distillation of the residue afforded 23.31 g. (83%) of the **enol ether 8**, b.p. 91–96° (0.07 mm.), which solidified on standing, m.p. 40.3–41.7°. Recrystallization from ether afforded the pure enol ether as white prisms, m.p. 42.5–42.6°, with infrared absorption[11] at 1685 cm.$^{-1}$ (C=O) and 1595 cm.$^{-1}$ (C=C) and an ultraviolet maximum at 239 mμ (ϵ 15,700). Acidification of the aqueous potassium carbonate layer from this preparation followed by appropriate manipulations separated 1.16 g. (4.5%) of the starting material.

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 73.11; H, 7.41.

Reaction of 2.00 g. (13 mmoles) of the enolic diketone 6 with excess diazomethane in an ether–methanol mixture followed by concentration and distillation afforded 1.90 g. (87%) of the same enol ether **8**, b.p. 105° (0.9 mm.), m.p. 37.5–39.0°, identified by comparison of the infrared spectra of the two samples.

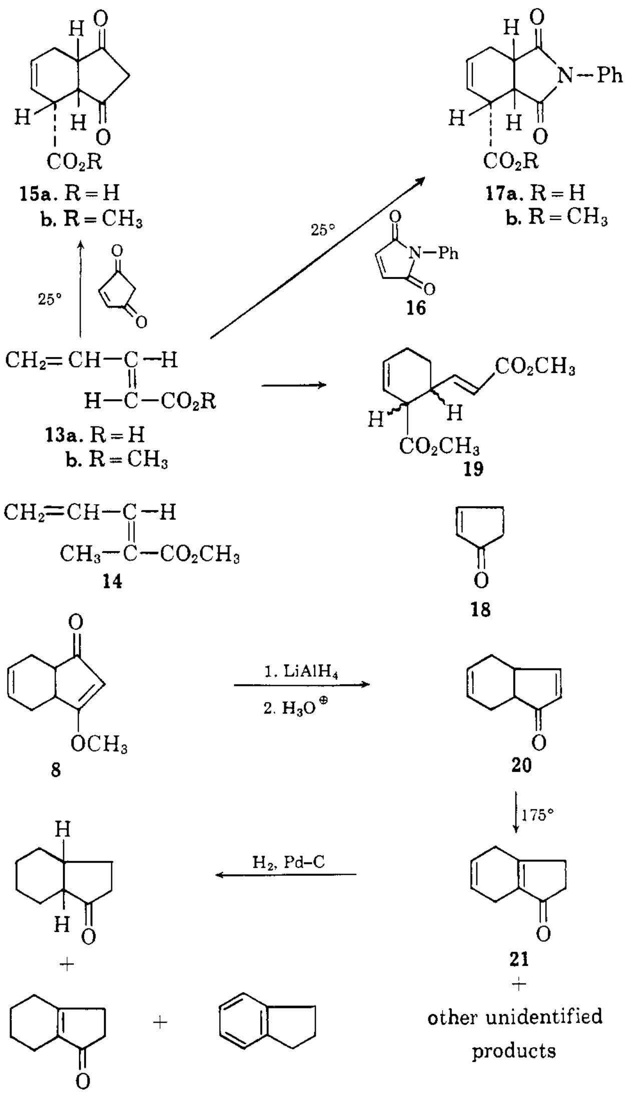


CHART II

7-Methyl-*cis*-3a,4,7,7a-tetrahydroindane-1,3-dione (3).—A solution of 242 mg. (2.5 mmoles) of the enedione 2, 430 mg. (6.3 mmoles) of *trans*-1-methylbutadiene (b.p. 39–41°, $n^{21.5}\mathrm{D}$ 1.4298, lit.,[12] 41.5–41.9°, $n^{20}\mathrm{D}$ 1.4292–1.4306) and a few crystals of 2.5-di-*t*-butylhydroquinone in 1 ml. of benzene was allowed to stand at room temperature for 2 days. Filtration separated 368 mg. (89%) of the crude adduct, m.p. 145–146.5°. The pure enolic diketone **3** crystallized from a methanol–ethyl acetate mixture as white microprisms, m.p. 149.5–150.5°, whose melting point was raised to 150.7–151° by sublimation under reduced pressure. The product has broad infrared absorption[9] at 1590 and 1630 (shoulder) cm.$^{-1}$ (enolic β-diketone) with an ultraviolet maximum at 245 mμ (ϵ 15,000).

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 72.91; H, 7.15.

***cis*-Hexahydroindane-1,3-dione** (7).—A solution of 1.28 g. (8.6 mmoles) of the enolic diketone 6 in 25 ml. of methanol was hydrogenated at room temperature and atmospheric pressure over 130 mg. of a 30% palladium-on-carbon catalyst. After the absorption of 239 ml. (9.7 mmoles) of hydrogen, the reaction was stopped and the mixture was filtered and then concentrated. Crystallization of the residue from an ether–ethyl acetate mixture afforded 0.86 g. (67%) of the enolic diketone **7** as white plates, m.p. 86.6–88°. The pure diketone **7**, obtained after recrystal-

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[8] All melting points are corrected and all boiling points are uncorrected. The infrared spectra were determined with either a Baird, Model B, or a Perkin–Elmer, Model 21, infrared recording spectrophotometer fitted with a sodium chloride prism. The ultraviolet spectra were determined with a Cary recording spectrophotometer, Model 11 MS. The microanalyses were performed by Dr. S. M. Nagy and his associates and by the Scandinavian Microanalytical Laboratory. Unless otherwise stated magnesium sulfate was employed as a drying agent. The n.m.r. spectra were determined with a Varian, Model A-60, n.m.r. spectrometer.

[9] Determined as a suspension in a potassium bromide pellet.

[10] Determined as a solution in 95% ethanol.

[11] Determined in chloroform solution.

[12] J. F. Bussert, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Am. Chem. Soc.*, **78**, 6076 (1956). Our diene sample, prepared by the dehydration of *trans*-2-penten-4-ol in the presence of potassium acid sulfate at 130–170°, contained more than 95% of the *trans* isomer as judged from its gas chromatograph and infrared spectrum.

lization, melted at 87.9–89.3° (lit.,[3e] 86–86.5°) and exhibits infrared absorption[11] at 1725, 1635, and 1590 (broad) cm.$^{-1}$ (partially enolized β-diketone) with an ultraviolet maximum[10] at 243 mμ (ε 17,000).

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.90; H, 8.10.

Preparation and Reactions of the Trienone 10.—A cold (0°) ethereal solution of 12.76 g. (0.078 mole) of the enol ether **8** was added, dropwise and with stirring in a nitrogen atmosphere, to 100 ml. (0.107 mole) of a 1.07 *N* solution of vinylmagnesium chloride in tetrahydrofuran. After the addition was complete, the mixture was stirred at 0° for 2 hr. and then treated with saturated, aqueous ammonium chloride (adjusted to pH 7 by the addition of aqueous ammonia). After the organic layer had been separated and the aqueous phase had been extracted with ether, the combined organic solutions were dried and concentrated to leave 15.2 g. of the crude alcohol **9** as a yellow oil with infrared absorption[13] at 1705 cm.$^{-1}$ (weak, C═O impurity), 1645 and 1620 cm.$^{-1}$ (C═C) and 925 cm.$^{-1}$ (CH═CH$_2$). To a cold (0°) solution of 14.4 g. of the crude alcohol **9** and 10 mg. of 2,5-di-*t*-butylhydroquinone in 120 ml. of tetrahydrofuran was added 45 ml. of a cold (0°), very dilute, aqueous solution of sulfuric acid (1 drop of sulfuric acid in 100 ml. of water). After the addition was complete, the mixture was stirred at 0° for 30 min. and then diluted with 500 ml. of ice–water and extracted with petroleum ether. This extract was dried and concentrated under reduced pressure at room temperature. Distillation of the residue in a short-path still afforded 3.10 g. of the crude trienone **10** as a yellow oil, b.p. 92–98° (0.2 mm.) with infrared absorption[13] at 1710 cm.$^{-1}$ (cyclopentenone C═O), 1640 and 1605 cm.$^{-1}$ (C═C) and 990 and 930 cm.$^{-1}$ (CH═CH$_2$), and an ultraviolet maximum[10] at 262 mμ (ε 14,400).

A solution of 415 mg. (2.6 mmoles) of the crude trienone **10**, 28.5 mg. of 2,5-di-*t*-butylhydroquinone and 477 mg. (2.7 mmoles) of N-phenylmaleimide in 1.5 ml. of benzene was heated to 45–50° under a nitrogen atmosphere for 40 hr. Chromatography of the crude product on Merck acid-washed alumina separated 185 mg. (39% recovery) of N-phenylmaleimide (eluted with benzene) and 414 mg. (48%) of the crude adduct **12**, m.p. 186–194° (eluted with methanol). Several recrystallizations from methanol and from ethyl acetate afforded the pure adduct **12** as white crystals, m.p. 203.5–205.5°, with infrared absorption[11] at 1780 (weak) and 1715 (broad, intense) cm.$^{-1}$ (C═O of 5-membered imide and cyclopentanone) and an ultraviolet maximum[10] at 221 mμ (ε 16,000).[14]

Anal. Calcd. for $C_{21}H_{19}NO_3$: C, 75.65; H, 5.74; N, 4.20. Found: C, 75.48; H, 5.95; N, 4.01.

A mixture of 1.134 g. (7.1 mmoles) of the crude trienone **10**, 0.512 g. (7.1 mmoles) of acrylic acid, and 2 mg. of 2,5-di-*t*-butylhydroquinone was heated to 55° in a sealed tube for 5 days. The partially polymeric reaction mixture was then extracted with methylene chloride and the organic layer was extracted with aqueous sodium bicarbonate solution. After this aqueous extract had been acidified and extracted with chloroform, the chloroform solution was dried and concentrated to leave a white solid. Recrystallization from ethyl acetate afforded 80.1 mg. (4.9%) of the adduct **11a** as white prisms, m.p. 187–188°, with broad infrared absorption[11] in the 3μ region (associated O—H) as well as peaks at 1750 and 1700 cm.$^{-1}$ (carboxyl and cyclopentenone C═O) and 1660, 1645, and 1630 cm.$^{-1}$ (C═C). The product has an ultraviolet maximum[10] at 236 mμ (ε 10,800). The n.m.r. spectrum[15] (60 Mc.) has a triplet (*J* = 4 c.p.s.) centered at 4.22 τ (2H, vinyl C—H), a series of broad, poorly resolved peaks in the region 6.8–8.0 τ (10H, allylic C—H and carboxyl OH) and a broad peak centered at 8.2 τ (4*H*, nonallylic CH$_2$).

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.36; H, 6.86.

After the methylene chloride solution containing neutral material from the reaction had been dried and concentrated, trituration of the residue with ether separated a solid. Recrystallization of this solid from an ether–ethyl acetate mixture afforded 0.138 g. (12%) of the dimer **11b** as white prisms, m.p. 130–133°. This material was shown to be identical with a subsequently described sample by a mixed melting-point determination and comparison of infrared spectra.

After a mixture of 1.31 g. (8.2 mmoles) of the crude trienone **10** and 890 mg. (11.8 mmoles) of α-methylacrolein had been heated to 55° for 5 days, chromatography of the crude product on 40 g. of neutral alumina separated 0.5425 g. (41%) of the dimer **11b**, m.p. 129–133°. Recrystallization from an ether–ethyl acetate mixture afforded the pure dimer **11b** as white prisms, m.p. 135.8–136.7°, with infrared absorption[11] at 1690 cm.$^{-1}$ (cyclopentenone C═O), 1640, and 1615 cm.$^{-1}$ (C═C), an ultraviolet maximum[10] at 235 mμ (ε 20,000) and n.m.r.[16] peaks (60 Mc.) at 4.19 τ (5*H*, broad, vinyl C—H), a series of broad unresolved peaks in the region 6.4–8.0 τ (15*H*, allylic C—H) and a broad, partially resolved peak centered at 8.22 τ (4*H*, nonallylic CH$_2$).

Anal. Calcd. for $C_{22}H_{24}O_2$: C, 82.46; H, 7.55. Found: C, 82.29; H, 7.60.

3a,4,7,7a-Tetrahydroindenone (20).—To a cold (0°) solution of 68.0 g. (0.414 mole) of the enol ether **8** in 200 ml. of ether was added gradually with stirring, a solution of 6.5 g. (0.17 mole) of lithium aluminum hydride in 250 ml. of ether. The resulting mixture was refluxed, with stirring, for 1 hr. and then cooled and 25 ml. of water was added. The mixture was poured into excess cold, 10% aqueous sulfuric acid, and the ether layer was separated. After the aqueous phase had been extracted with ether, the combined organic extracts were washed successively with aqueous sodium bicarbonate and water and then dried and concentrated. After short-path distillation of the residue to separate 48.0 g. of colorless liquid containing[17] 75–80% of the desired product **20**, fractional distillation through a 40-cm. spinning-band column afforded 17.51 g. (32.4%) of fractions, b.p. 118–119° (20 mm.), $n^{25}D$ 1.5250–1.5256, containing[17] more than 95% of the desired ketone **20** as well as 23.56 g. of intermediate fractions, b.p. 104–118° (20 mm.), $n^{25}D$ 1.5044–1.5243, containing mixtures of the desired ketone **20** and lower boiling impurities. The pure ketone **20** has infrared absorption[13] at 1710 cm.$^{-1}$ cyclopentenone C═O) and at 1595 cm.$^{-1}$ (C═C) with ultraviolet maxima at 221 mμ (ε 8500) and 315 mμ (ε 40). The n.m.r. spectrum[13] (60 Mc.) of the material has two quadruplets centered at 2.52 τ (1*H*, *J* = 6 and 3 c.p.s., vinyl proton *beta* to C═O) and 3.91 τ (1*H*, *J* = 6 and 2 c.p.s., vinyl proton *alpha* to C═O), a partially resolved multiplet centered at 4.23 τ (2*H*, vinyl protons of cyclohexene ring), a broad multiplet centered at 6.74 τ (1*H*, tertiary proton alpha to C═O), and a complex multiplet in the region 7.4 to 8.0 τ attributable to the remaining 5 allylic protons in the molecule.

Anal. Calcd. for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.47; H, 7.76.

A solution of 4.8 g. (0.028 mole) of the unsaturated ketone **20**, 4.7 g. (0.028 mole) of dicyclopentadiene and 0.2 g. of 2,5-di-*t*-butylhydroquinone in 7 ml. of benzene was heated to 175° for 2 days in a sealed tube. Distillation of the reaction mixture in a short-path still separated 6.24 g. of volatile material, b.p. 90–140° (0.3 mm.). A solution of this material in an ether–petroleum ether mixture deposited 2.85 g. (60%) of the crude dienone **21**, m.p. 61–74°. This product was sublimed under reduced pressure and then recrystallized from an ether–petroleum ether mixture to separate the pure **dienone 21** as white prisms, m.p. 76.5–77°, yield 1.68 g. (35%). The product has infrared absorption[13] at 1700 cm.$^{-1}$ (cyclopentenone C═O) and 1675 and 1635 cm.$^{-1}$ (C═C) with an ultraviolet maxima[10] at 220 mμ (ε 6,000) and 244 mμ (ε 6,400).[18] The n.m.r. spectrum[13] (60 Mc.) of the product has a partially resolved multiplet centered at 4.24 τ attributable to two vinyl protons and a complex series of peaks in the region 7 to 8 τ attributable to eight allylic protons.

Anal. Calcd. for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.38; H, 7.40.

The product **21** formed a semicarbazone which crystallized from methanol as a white solid, m.p. 235° dec., yield 60%.

Anal. Calcd. for $C_{10}H_{13}N_3O$: C, 62.80; H, 6.85; N, 21.98. Found: C, 62.61; H, 6.83; N, 21.88.

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(13) Determined in carbon tetrachloride solution.

(14) The absence of an ultraviolet maximum in the region 235–240 mμ indicates that the adduct has structure **12** rather than the alternative structure in which the ketone and double bond functions are conjugated.

(15) Determined as a solution in perdeuteriodimethylformamide.

(16) Determined as a solution in deuteriochloroform.

(17) A gas chromatography column packed with Dow Corning silicone fluid no. 710 on 60–80-mesh firebrick was employed for this analysis.

(18) The appearance of the maximum at abnormally long wave length is comparable to the spectra of 2,5-dihydroacetophenone [245 mμ (ε 5000)] and 6-methyl-2,5-dihydroacetophenone [245 mμ (ε 5000)]. See (a) K. Bowden and E. R. H. Jones, *J. Chem. Soc.*, 52 (1946); (b) E. A. Braude, E. R. H. Jones, F. Sondheimer, and J. B. Toogood, *ibid.*, 607 (1949); (c) D. J. Cram and H. Steinberg, *J. Am. Chem. Soc.*, **73**, 5691 (1951).

The gas chromatograph[17] of the mother liquors remaining after removal of the ketone **21** indicated a complex mixture of products which was not further investigated.

A solution of the dienone **21** (50 mg. 0.37 mmole) in 15 ml. of ether was hydrogenated at atmospheric pressure and room temperature over 10 mg. of 5% palladium-on-charcoal catalyst. When hydrogen uptake had ceased (6.6 ml. of 0.80 equiv.), the solution was filtered and concentrated. The gas chromatogram[17] of the crude product indicated the presence of three major components identified by comparison of retention times and infrared spectra of collected samples with the data for authentic samples.[19] The three products (in order of elution) were indane (*ca.* 20% of the mixture), *cis*-hexahydro-1-indanone (*ca.* 20% of the mixture), and 4,5,6,7-tetrahydro-1-indanone (*ca.* 45% of the mixture.)

Cyclopentane-1,3-dione (4) and Its Methyl Enol Ether 5.—Reduction of 4-cyclopentene-1,3-dione (2.00 g., 0.028 mole) with zinc in acetic acid as previously described[3a] afforded the enolic cyclopentane-1,3-dione (**4**) (1.75 g., 49%) as white prisms from a methanol–ethyl acetate mixture, m.p. 151–152° (lit.[3a] 149–150°), with an ultraviolet maximum[10] at 243 mμ (ε 17,500) and infrared absorption (Nujol mull) comparable to that reported[20] (only broad, general absorption with no distinguishing peaks).

Reaction of the diketone **4** (0.924 g., 9.4 mmoles) with an excess of diazomethane in an ether–methanol mixture followed by concentration left an oil which on sublimation gave 0.8155 g. (77%) of 3-methoxy-2-cyclopenten-1-one (**5**) as white prisms, m.p. 49–50°. Recrystallization from an ether–cyclohexane mixture followed by sublimation gave the pure enol ether, m.p. 51.3–52.1°, with infrared absorption[13] at 1705 (C═O), 1680 (C═C—OC), and 1600 cm.$^{-1}$ (C═C) and an ultraviolet maximum[10] at 237 mμ (ε 20,000). The n.m.r. spectrum[13] (60 mc.) of this material has a triplet (J = 1 c.p.s.) at 4.75 τ (1*H*, vinyl C—H), a singlet at 6.16 τ (3H, OCH_3) and a series of peaks corresponding to an A_2B_2 pattern centered at 7.58 τ (4*H*, CH_2).

Anal. Calcd. for $C_6H_8O_2$: C, 64.27; H, 7.19; m.w., 112. Found: C, 64.02; H, 7.29; mol. wt., 112 (mass spectrum).

Attempted Reaction of Methyl *trans*-2,4-Pentadienoate (13b) with Cyclopentenone (18).—A solution of 22.4 g. (0.27 mole) of cyclopentenone,[21] 18.75 g. (0.167 mole) of the diene **13b** and 4.7 g. of 2,5-di-*t*-butylhydroquinone in 50 ml. of benzene was heated to 115–125° in an autoclave for 13 days. The resulting mixture was chromatographed on 370 g. of neutral alumina. The nonpolymeric product, eluted with benzene, was distilled in a short-path still to separate 5.994 g. of yellow liquid, b.p. 110–112° (0.25 mm.), containing[17] one major component. Fractional distillation through a Holtzmann column separated 2.0195 g. of colorless liquid, b.p. 104° (0.04 mm.), n^{25}D 1.4942, containing[17] only the previously mentioned major component, namely the diester **19**. This material has infrared absorption[13] at 1740 (shoulder) and 1730 cm.$^{-1}$ (unconj. and conj. ester C═O) and 1655 cm.$^{-1}$ (C═C) with ultraviolet maxima[10] at 207 mμ (ε 11,800) and 302 mμ (ε 83). The n.m.r. spectrum[13] (60 Mc.) exhibits a quadruplet centered at 3.11 τ (1H, J = 16 and 8 c.p.s. vinyl proton beta to ester function) a multiplet at approximately 4.2 τ (3*H*, vinyl proton alpha to ester function and two vinyl protons of the cyclohexene moiety), a singlet at 6.33 τ (6H, $COOCH_3$) and broad unresolved absorption in the region 6.7–8.5 τ.

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.55; H, 7.23.

Methyl 2,4-pentadienoate **13b** (81 mg., 0.72 mmole) was dissolved in five times its volume of benzene and the mixture was saturated with 2,5-di-*t*-butylhydroquinone. This mixture was sealed in an ampule and was heated to 120° for 12 days. The mixture was concentrated to a heavy oil which was distilled (b.p. ~110° at 0.06 mm.) to give 37 mg. of a liquid which had infrared absorption[13] identical to that of the material characterized above.

Diels–Alder Reactions with Pentadienoic Acid (13a) and Its Ester (13b).—A mixture of 5.16 g. (0.046 mole) of the ester **13b**, 5.23 g. (0.054 mole) of the enedione **2**, and 380 mg. of 2,5-di-*t*-butylhydroquinone was allowed to stand at room temperature under nitrogen for 23 days. A solution of the resulting mixture in a methanol–ethyl acetate mixture deposited 4.55 g. of the adduct **15b**, m.p. 181–182.5°. Extraction of the mother liquor with aqueous potassium carbonate followed by acidification of the aqueous extract and appropriate manipulations afforded an additional 0.491 g. (total yield 5.04 g. of 53%) of the adduct. Recrystallization gave the pure enolic diketo ester **15b** as white prisms, m.p. 182.9–183.9°, with infrared absorption[9] at 1735 cm.$^{-1}$ (ester C═O) and 1630 (shoulder) and 1580 cm.$^{-1}$ (enolic β-diketone) with an ultraviolet maximum at 244 mμ (ε 13,800).

Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.45; H, 5.84. Found: C, 63.17; H, 5.75.

After a solution of 0.75 g. (7.7 moles) of the acid **13a**, 0.75 g. (7.8 mmoles) of the enedione **2**, and 3 mg. of 2,5-di-*t*-butylhydroquinone in 3 ml. of benzene had been allowed to stand at room temperature for 10 days, the solid which separated was filtered and washed with ether to leave 175 mg. (11%) of the crude adduct, m.p. 184.7–185° dec. Recrystallization from a methanol-ethyl acetate mixture gave the pure adduct **15a** as white solid, m.p. 191.3° dec., with infrared absorption[9] at 1695 cm.$^{-1}$ (carboxyl C═O) and 1655 and 1595 cm.$^{-1}$ (enolic β-diketone) and an ultraviolet maximum at 245 mμ (ε 15,200).

Anal. Calcd. for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19. Found: C, 61.89; H, 5.38.

A solution of 100 mg. (5.8 mmoles) of N-phenylmaleimide **16** and 65 mg. (5.8 mmoles) of the ester **13b** in 0.5 ml. of benzene saturated with 2,5-di-*t*-butylhydroquinone, was allowed to stand at room temperature for 18 days and then concentrated under reduced pressure. Trituration of the residue with ether left 147 mg. (87%) of the crude adduct, m.p. 120–123°. Recrystallization from an ether–ethyl acetate mixture followed by sublimation under reduced pressure afforded the pure adduct **17b** as white prisms, m.p. 123–124°. The product has infrared absorption[11] at 1710 (broad) cm.$^{-1}$ with shoulders at 1740 and 1780 cm.$^{-1}$ (C═O of ester and five-membered imide) with end absorption in the ultraviolet[10] and a point of inflection at 215 mμ (ε 2,600).

Anal. Calcd. for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30. Found: C, 67.23; H, 5.27.

After solution of 165 mg. (9.5 mmoles) of the imide **16** had 118 mg. (8.3 mmoles) of the acid **13a** in 1 ml. of benzene had been allowed to stand at room temperature for 40 hr., the solid which separated was recrystallized from methanol to give 165 mg. (50%) of the adduct **17a** as white prisms, m.p. 225–226.5° dec. Recrystallization raised the decomposition point to 230–231°. The material has infrared absorption[9] at 1775 and 1730 cm.$^{-1}$ (C═O of inside in a five-membered ring) and 1690 cm.$^{-1}$ (carboxyl C═O) with end absorption in the ultraviolet[10] (at 214 mμ, ε 11,000).

Anal. Calcd. for $C_{15}H_{13}NO_4$: C, 66.41; H, 4.83; N, 5.16. Found: C, 66.33; H, 4.66; N, 5.22.

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(19) See H. O. House and G. H. Rasmusson, *J. Org. Chem.*, **28**, 31 (1963).

(20) J. H. Boothe, R. G. Wilkinson, S. Kushner, and J. H. Williams, *J. Am. Chem. Soc.*, **75**, 1732 (1953).

(21) Prepared by the procedure of C. H. DePuy and E. L. Eilers, *J. Org. Chem.*, **24**, 1380 (1958).