A Study of the Intramolecular Diels–Alder Reaction[1]

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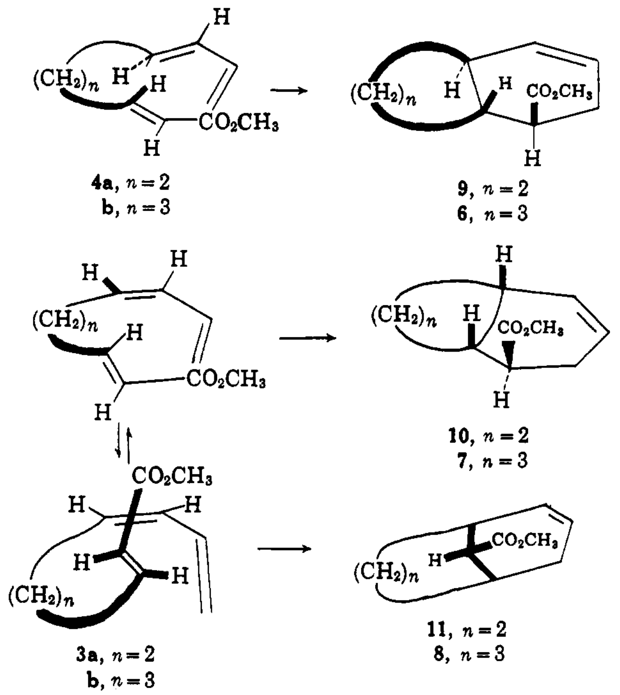
The *trans,trans* and *cis,trans* isomers of methyl 2,6,8-nonatrienoate (**3a** and **4b**) and of methyl 2,7,9-decatrienoate (**3b** and **4b**) have been prepared. Although thermal cyclization failed with the nonatriene derivatives, each of the decatrienes underwent a stereospecific cyclization of the Diels–Alder type to form one of the stereoisomers (**6** from **4b**, **7** from **3b**) of 4-carbomethoxy-4,4a,5,7a-tetrahydroindane. Evidence is presented indicating that 9-carbomethoxybicyclo[3.3.1]non-2-ene (**11**) was not formed in these cyclizations of the decatriene derivatives. These intramolecular Diels–Alder reactions were slower than the intermolecular Diels–Alder reaction of the *trans,trans*-trienes **4a** and **4b** with maleic anhydride. Synthesis of various stereoisomers of 4-carbomethoxyperhydroindane and 2-carbomethoxybicyclo[4.2.0]octane are described.

Our interest in intramolecular Diels–Alder reactions was stimulated by the possibilities (1) that the favorable entropy factor offered by intramolecular processes might facilitate reaction,[2] and (2) that suitable choice of the number and type of atoms bridging the diene and dienophile moieties might offer a method for obtaining only one of the structural isomers and stereoisomers normally possible from reaction of an unsymmetrical diene with an unsymmetrical dienophile.[3] Prior to and during the course of this study several publications have appeared which described either examples of intramolecular Diels–Alder reactions[4] or the formation of products most readily explained by invoking an intramolecular Diels–Alder reaction.[5] In the present study, we were interested in the behavior of the triene esters **3** and **4**. From an examination of Dreiding models of these materials, it appeared that the only conformations of the *trans,trans* isomers **4** which would permit the dienophile and the diene to approach one another sufficiently closely for bond formation are those conformations indicated in Chart I leading to the bicyclic esters **6** and **9**. The model studies further suggested that the formation of ester **9** from the triene **4a** could occur only with extreme deformation of certain of the normal carbon–carbon bond angles. On the other hand both *cis,trans* isomers **3** offered the possibility of two reasonable conformations (see Chart I) leading to structurally isomeric bicyclic esters **7** or **8** and **10** or **11**. Although consideration of the bond deformation required for these ring closures suggested that triene **3a** might close to the ester **10** more readily than to the ester **11**, no obvious difference was noted for the closure of triene **3b** to either bicyclic ester **7** or **8**.

CHART I



The preparative routes employed for the triene esters **3** and **4** are summarized in Chart II. The reactions of dialdehydes **1** with carbomethoxymethylenetriphenylphosphorane in a nonhydroxylic solvent led to the unsaturated esters **2** having the expected[6] *trans* stereochemistry accompanied by higher molecular weight products believed to be the doubly unsaturated diesters.[7] Samples of the acid and ester **12** were also examined as potential precursors for the aldehyde ester **2a**; however, none of the transformation products, such as the lactone **13** from reaction of **12a** with hydrobromic acid, proved useful. Each pure alde-

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[1] This research has been supported by Grant No. GM-08761 from the National Institutes of Health.

[2] The low activation entropy values observed for Diels–Alder reactions argue for a transition state in which the diene and dienophile are rather rigidly oriented with respect to one another: (a) R. B. Woodward and T. J. Katz, *Tetrahedron*, **6**, 70 (1959); (b) J. A. Berson and A. Remanick, *J. Am. Chem. Soc.*, **83**, 4947 (1961); (c) C. Walling and H. J. Schugar, *ibid.*, **85**, 607 (1963).

[3] For general reviews of the Diels–Alder reaction, see (a) M. C. Kloetzel, *Org. Reactions*, **4**, 1 (1948); (b) H. L. Holmes, *ibid.*, **4**, 60 (1948); (c) L. W. Butz and A. W. Rytina, *ibid.*, **5**, 136 (1949); (d) K. Alder in "Newer Methods of Preparative Organic Chemistry," Interscience Puulishers, Inc., New York, N. Y., 1948, pp. 381–511; (e) O. Diels in "Progress in the Chemistry of Organic Natural Products," Vol. 3, Julius Springer, Wien, Germany, 1939, pp. 1–29; (f) K. Alder and M. Schumacher, *ibid.*, Vol. 10, 1953, pp. 1–118; (g) for a review of the stereochemical orientation in this reaction, see J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961); (h) for a review of the structural orientation in this reaction, see Yu. A. Titov, *Russ. Chem. Rev.*, **31**, 267 (1962).

[4] (a) G. Brieger, *J. Am. Chem. Soc.*, **85**, 3783 (1963); (b) L. H. Klemm and K. W. Gopinath, *Tetrahedron Letters*, **No. 19**, 1243 (1963); (c) D. Bilović, Z. Stojanac, and V. Hahn, *ibid.*, **No. 31**, 2071 (1964); (d) K. E. Lewis and H. Steiner, *J. Chem. Soc.*, 3080 (1964).

[5] (a) See ref. 3f, p. 66; (b) K. Alder and K. Heimback, *Chem. Ber.*, **86**, 1312 (1953); (c) E. T. McBee, J. O. Stoffer, and H. P. Braendlin, *J. Am. Chem. Soc.*, **84**, 4540 (1962); (d) H. H. Wasserman and A. R. Doumaux, Jr., *ibid.*, **84**, 4611 (1962); (e) W. von E. Doering and W. R. Roth, *Angew. Chem., Intern. Ed. Engl.*, **2**, 115 (1963); (f) G. Eglinton, R. A. Raphael, R. G. Willis, and J. A. Zabkiewicz, *J. Chem. Soc.*, 2597 (1964); (g) D. Devaprabhakara, C. G. Cardenas, and P. D. Gardner, *J. Am. Chem. Soc.*, **85**, 1553 (1963); (h) R. Srinivasan, *ibid.*, **83**, 2806 (1961); (i) W. R. Roth and B. Peltzer, *Angew. Chem.*, **76**, 378 (1964); (j) J. Zirner and S. Winstein, *Proc. Chem. Soc.*, 235 (1964).

[6] (a) H. O. House and G. H. Rasmusson, *J. Org. Chem.*, **26**, 4278 (1961); (b) A. J. Speziale and D. E. Bissing, *J. Am. Chem. Soc.*, **85**, 3878 (1963); (c) H. O. House, V. K. Jones, and G. A. Frank, *J. Org. Chem.*, **29**, 3327 (1964).

[7] K. Eiter [*Angew. Chem.*, **73**, 619 (1961); *Ann.*, **658**, 91 (1962)] has reported the preparation of unsaturated ester **2b**.

CHART II

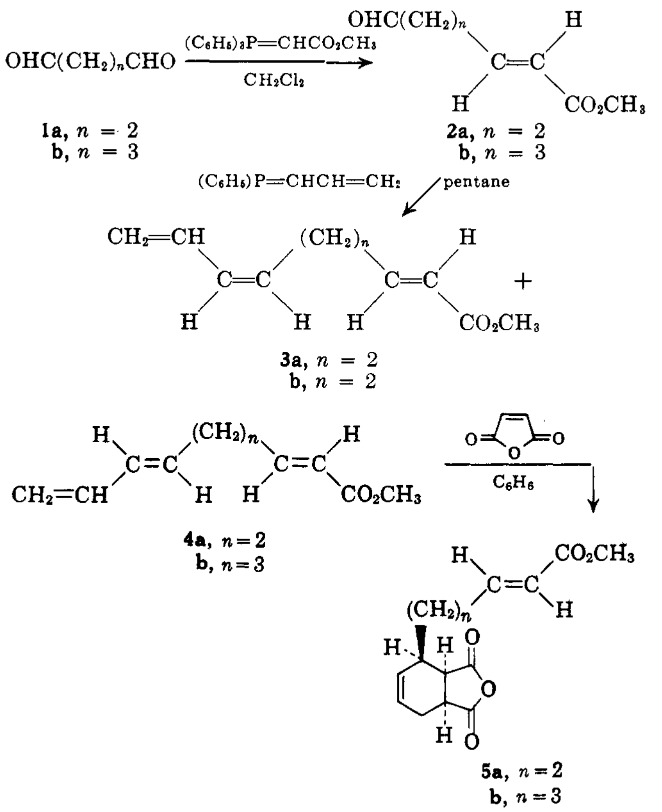
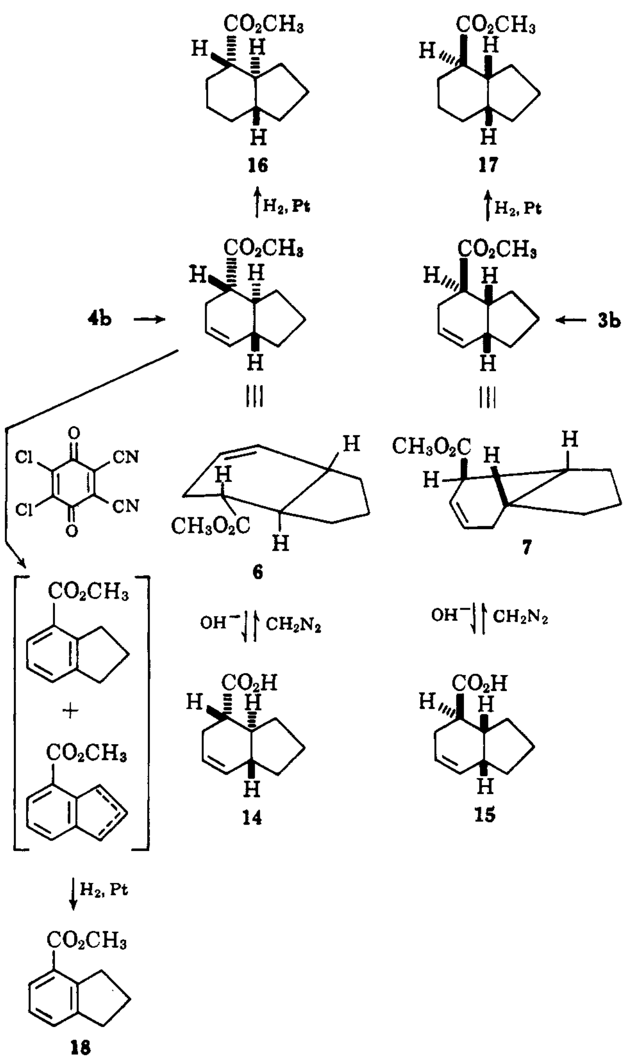
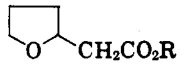
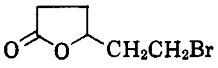


CHART III





12a, R = H
b, R = CH3



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hyde ester **2** reacted with the Wittig reagent from allyltriphenylphosphonium bromide under carefully controlled conditions.[8] Again as expected,[9] this latter Wittig reaction led to mixtures of the geometrical isomers **3** and **4**. After devoting a good deal of unproductive effort to attempts to separate these mixtures (which cyclized at the temperatures required for gas chromatography), we resorted to reaction of the mixtures of *cis* (**3**) and *trans* (**4**) isomers with maleic anhydride in benzene at 80°. This procedure resulted in reaction of only the *trans* isomers (**4**) of the dienes to form adducts **5**. The failure of the *cis* 1-substituted dienes **3** to undergo ready intermolecular Diels–Alder reactions has ample precedent.[3g,10] By use of this procedure we had samples containing both geometrical isomers **3** and **4** as well as samples of the *cis,trans*-trienes **3** available for study. It should be noted in passing that the separation procedure used, conversion of the trienes **4** to the adducts **5**, constitutes a competitive reaction in which an *intermolecular* Diels–Alder reaction with a reactive dienophile (maleic anhydride) has occurred in preference to an *intramolecular* reaction involving a less reactive dienophile.

Either distillation of the mixture of trienes **3b** and **4b** (b.p. *ca.* 245° at 760 mm.) or heating a benzene solution of the mixture to 180° in the presence of 2,5-di-*t*-butyl-1,4-hydroquinone (a free-radical inhibitor) served to produce a mixture of the tetrahydroindane esters **6** and **7** as well as higher molecular weight material which may either have resulted from radical polymerization or from intermolecular Diels–Alder reactions. The comparable cyclization of the *cis,-trans*-triene **3b** produced the ester **7** leading us to believe that ester **6** is derived from the *trans,trans*-triene **4b** (*cf.* Chart I). Furthermore, there was no large difference in the relative rates of cyclization of the trienes **3b** and **4b**. The further transformations of the esters **6** and **7** are summarized in Chart III. Partial saponification of the mixture **6** and **7** selectively converted the ester **6** to the corresponding acid **14** and provided a useful separation method. This selectivity presumably reflects the fact that the ester **6** exists largely in the indicated conformation with an unhindered, equatorial carbomethoxy group, whereas several conformations are probable for the ester **7** including the conformation indicated with a hindered, axial carbomethoxy group.

In order to explore the possibility that the bicyclo-[3.3.1]nonane derivative **8** might have formed from the cyclization of triene **3b**, an authentic sample of the cor-

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[8] C. F. Hauser, T. W. Brooks, M. L. Miles, M. A. Raymond, and G. B. Butler [*J. Org. Chem.*, **28**, 372 (1963)] have reported that reactions of aliphatic aldehydes with this Wittig reagent are normally not satisfactory preparative reactions because of competing aldol condensation. The reaction conditions we have employed appear to overcome this difficulty.

[9] S. Trippett, *Quart. Rev.* (London), **17**, 406 (1963).

[10] (a) D. Craig, J. J. Shipman, and R. B. Fowler, *J. Am. Chem. Soc.*, **83**, 2885 (1961); (b) L. K. Montgomery, K. Schueller, and P. D. Bartlett, *ibid.*, **86**, 622 (1964); (c) C. A. Stewart, Jr., *J. Org. Chem.*, **28**, 3320 (1963).

Chart IV

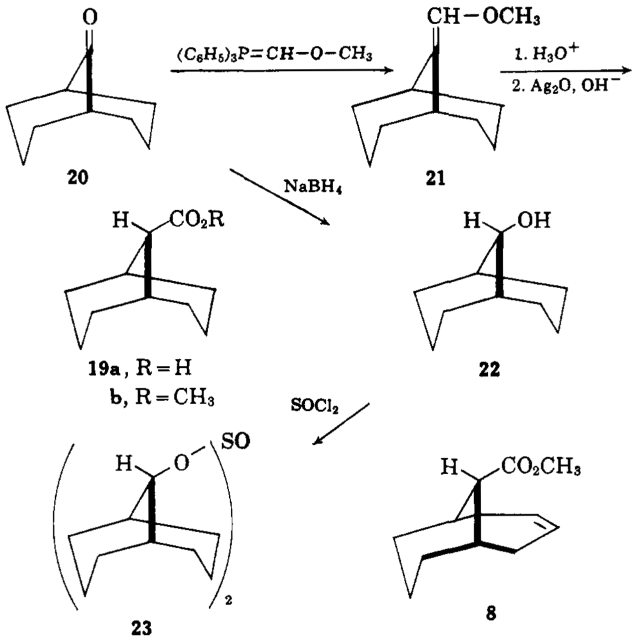
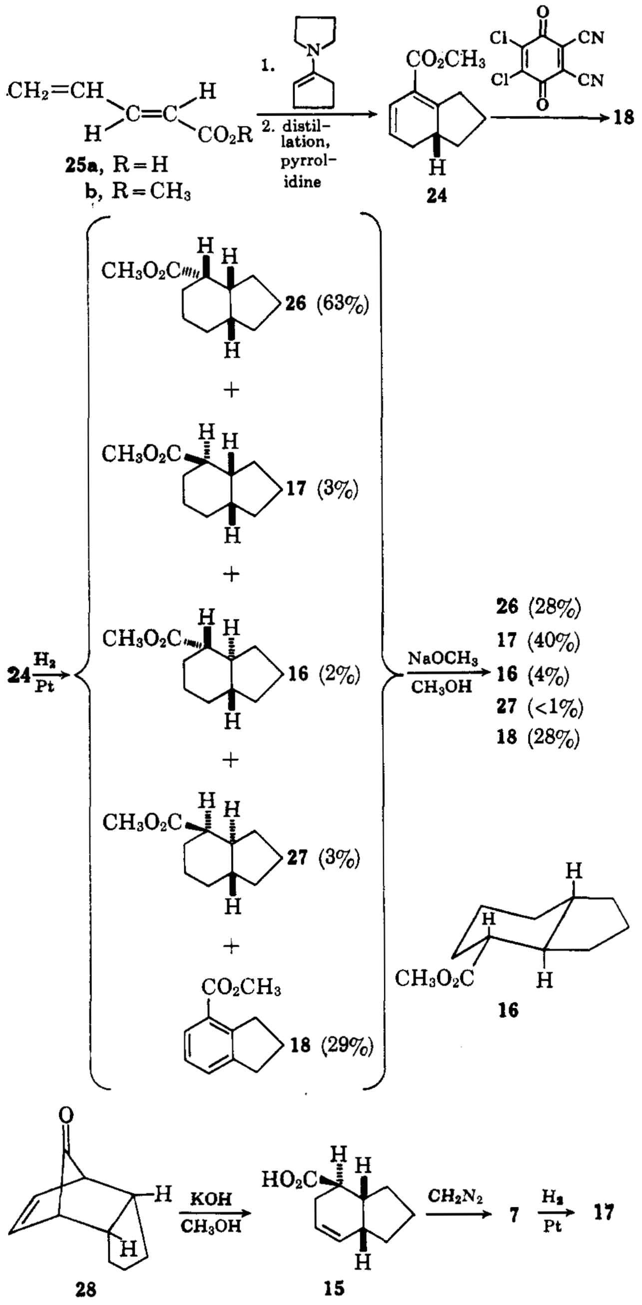


Chart V



responding saturated ester was prepared (Chart IV). After hydrogenation of the crude reaction mixture obtained from trienes **3b** and **4b**, gas chromatographic analysis demonstrated the presence of saturated esters **16** and **17** but not ester **19b**. Therefore, if the cyclization **3b** → **8** is occurring, the product **8** is not stable under the reaction conditions; it seems more probable to us that no significant amount of ester **8** is being formed.

In order to obtain authentic samples of the saturated esters **16** and **17**, we studied the hydrogenation of the diene ester **24**, a material readily available from reaction of the unsaturated ester **25b** with the pyrrolidine enamine of cyclopentanone.[11] As illustrated in Chart V, hydrogenation of the diene **24** over platinum produced a mixture of four saturated products (**16**, **17**, **26**, and a compound believed to be **27**) as well as the known[12] indan ester **18** from concurrent dehydrogenation. Application of the usual concept of the *cis* addition of hydrogen from the less hindered side of the diene leads to the conclusion that the hydrogenated major product has the structure **26**. Treatment of this mixture with methanolic sodium methoxide effected partial epimerization of **26** to **17** and essentially complete epimerization of the component thought to be **27** to ester **16**. Samples of **16**, **17**, **18**, and **26** were collected from these mixtures to permit rigorous identification and comparison with the samples from the Diels–Alder reaction; however, we were unable to obtain a sufficient quantity of the component thought to be **27** to permit characterization. It will be noted that the epimerization **27** → **16** corresponds to the conversion of an axial to an equatorial carbomethoxyl group as illustrated in the conformational formula for **16** in Chart V.

Although the foregoing data are all consistent with the stereochemistry assigned structures **16**, **17**, and **26**, we were pleased to learn of an alternative synthesis for the acid **15** by cleavage of the ketone **28**[13] which unambiguously confirms our stereochemical assignments. Cleavage of the ketone **28** produced a mixture of acids containing predominantly the acid **15**. A purified sample of this acid was shown to be identical with the sample we obtained from the Diels–Alder reaction. The acid **15** from **28** was converted to esters **7** and **17** which were also identified with previously described samples.

Our efforts to obtain a monomeric product from the thermal cyclization of the nonatriene derivatives **3a** and **4a** were unsuccessful. Under a variety of experimental conditions these trienes were slowly converted

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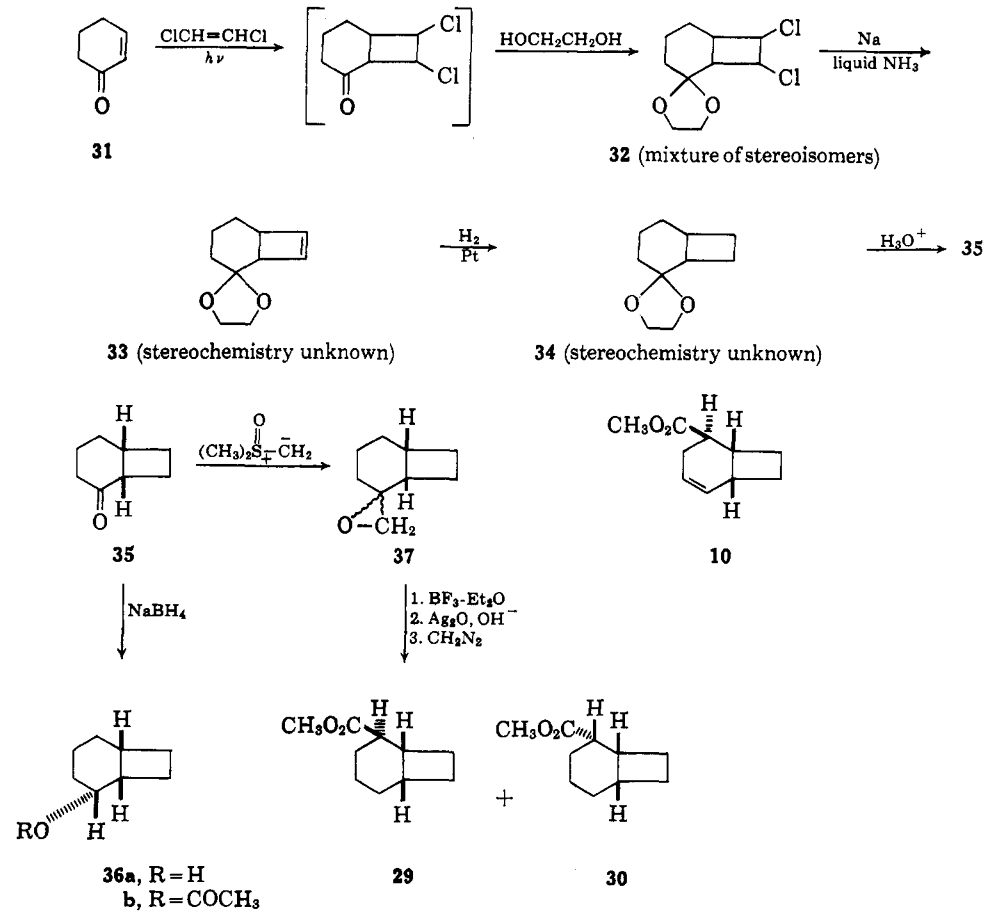
(11) This reaction has been studied by Professor G. A. Berchtold and Mr. J. Ciabattoni, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass. These studies will be published in the *Journal of Organic Chemistry*.

(12) I. M. Hunsberger, D. Lednicer, H. S. Gutowsky, D. L. Bunker, and P. Taussig, *J. Am. Chem. Soc.*, **77**, 2466 (1955).

(13) The reaction **28** → **15** was discovered by Dr. Kirby V. Scherer, Jr., Ph.D. Dissertation, Harvard University, 1962. This work is to be published by Dr. Scherer of the Department of Chemistry, University of California at Berkeley, Berkeley, Calif.

CHART VI

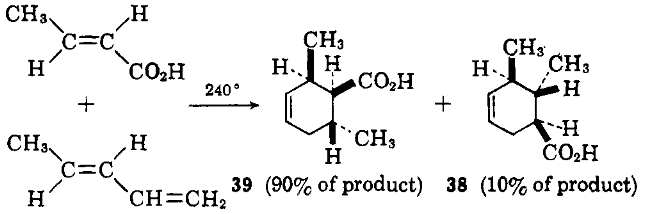


to higher molecular weight materials. Since both examination of molecular models and our aforementioned results with the decatriene derivatives **3b** and **4b** suggested that the unsaturated ester **10** would be the most probable product from thermal cyclization of the nonatriene derivatives, we synthesized the saturated analog **29** as illustrated in Chart VI.

Although the initial photochemical reaction would be expected[14] to form a mixture of stereoisomers including isomers with a *trans* fusion of the 4- and 6-membered rings, equilibration during hydrolysis of the ketal **34** was expected[14a,15] to produce only the more stable *cis* ketone **35**. This expectation was verified by conversion of the ketone **35** to the acetate **36b** which was compared with an authentic sample.[15] The crude oxirane **37** was rearranged, the resulting aldehyde was oxidized, and the crude acid was esterified without purification of intermediates to form a mixture of the stereoisomeric methyl esters **29** and **30**. The crude product obtained from heating the trienes **3a** and **4a** was hydrogenated and then compared with the esters **29** and **30**. From this comparison, we conclude that less than 3% of these esters could have been present. Photochemical cyclization of the nonatriene derivatives **3a** and **4a** was also examined briefly. A mixture of at least four new compounds, whose structures have not yet been determined, was produced However, none of the products obtained by hydrogenation of this mixture was one of the esters **29** or **30**.

Thus, our data obtained with the triene esters **3** and **4** suggest that when the diene and dienophile are separated by three (or presumably more, *cf.* ref. 4a) carbon atoms (as in **3b** and **4b**) intramolecular Diels–Alder reactions may be effected in useful yields even with *cis*-1-substituted dienes (*e.g.*, **3b**) which frequently fail to react in intermolecular Diels–Alder reactions.[10] It seems likely that use of starting trienes containing more reactive diene and/or dienophile components than are present in **3** and **4** would permit the preparation of more strained systems of the types for which trienes **3a** and **4a** are potential precursors.

It is of interest that cyclizations of trienes **3b** and **4b** yield single structural and stereoisomers. Furthermore, the structural orientation observed in our *intramolecular* reactions corresponds to the minor product (*e.g.*, **38**) produced in an analogous *intermolecular* reaction.[16] We have examined briefly the possi-



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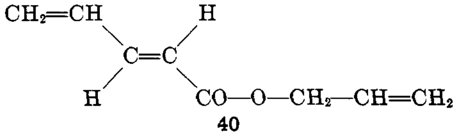
[14] (a) E. J. Corey, R. B. Mitra, and H. Uda, *J. Am. Chem. Soc.*, **86**, 485 (1964); (b) P. de Mayo, R. W. Yip, and S. T. Reid, *Proc. Chem. Soc.*, 54 (1963); (c) R. Robson, P. W. Grubb, and J. A. Barltrop, *J. Chem. Soc.*, 2153 (1964).

[15] (a) A. C. Cope and R. W. Gleason, *J. Am. Chem. Soc.*, **84**, 1928 (1962); (b) G. Büchi and E. M. Burgess, *ibid.*, **84**, 3104 (1962); (c) A. C. Cope, S. Moon, C. H. Park, and G. L. Wood, *ibid.*, **84**, 4865 (1962).

[16] (a) I. N. Nazarov, A. I. Kuznetsova, and N. V. Kuznetsov, *J. Gen. Chem. USSR*, **25**, 75 (1955); (b) see also ref. 3h and K. Alder and W. Vogt, *Ann.*, **564**, 120 (1949).

bility of preparing and cyclizing the triene esters **40** and **41** since these molecules possess an array of atoms bridging the diene and dienophile components which could be cleaved after an intramolecular Diels–Alder reaction has been effected. However, the extreme ease with which these materials polymerized discouraged us from studying them further.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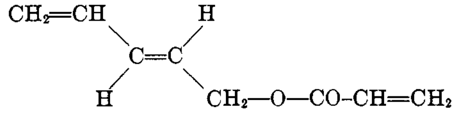
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Experimental[17]

Preparation of Aldehydes 1.—The following procedures were employed to obtain pure, anhydrous succinaldehyde and glutaraldehyde; each material was used immediately after distillation since it rapidly polymerized on standing. A mixture of 200 g. (1.25 moles) of 2,5-diethoxytetrahydrofuran[18] and 1 l. of 0.6 *N* aqueous hydrochloric acid[19] was stirred at room temperature for 0.75 hr. and then neutralized (pH 7 to 8) with sodium carbonate and extracted with three 250-ml. portions of methylene chloride. The aqueous phase was reacidified with 51 ml. of concentrated hydrochloric acid, again stirred at room temperature for 0.75 hr., neutralized, and extracted. This process was performed a total of five times[20] after which the combined methylene chloride extracts were dried and concentrated. Distillation of the residual yellow liquid (129.2 g.) separated 74.89 g. (70%) of succinaldehyde, b.p. 55–60° (12 mm.), $n^{25}\mathrm{D}$ 1.4258–1.4260 [lit.[19] b.p. 62° (14 mm.)]. After a 300-ml. sample of 25% aqueous glutaraldehyde[18] had been extracted with four 100-ml. portions of methylene chloride, the organic extract was dried and concentrated. Distillation of the residual yellow oil (60.55 g.) afforded 36.98 g. of glutaraldehyde, b.p. 68–69° (25 mm.). Redistillation gave 30.48 g. of fractions, b.p. 68–69° (25 mm.), $n^{25.5}\mathrm{D}$ 1.4312–1.4376 [lit. b.p. 64–65° (12 mm.),[21a] 75–80° (18 mm.)[21b]]. One fraction, $n^{25.5}\mathrm{D}$ 1.4312, gave a single peak on gas chromatography[22] and had infrared absorption[23] at 2700 and 2800 (aldehyde C–H), at 1725 (C=O), and at 1415 cm.$^{-1}$ (CH_2 adjacent to C=O).

Preparation of the Aldehyde Esters 2.—A solution of 103 g. (0.30 mole) of carbomethoxymethylenetriphenylphosphorane[6,24] in 1 l. of methylene chloride was added, dropwise and with stirring over a 75-hr. period, to a solution of 160 g. (1.6 moles) of glutaraldehyde in 2 l. of methylene chloride. The resulting solution was distilled, first at atmospheric pressure to remove the solvent and then under reduced pressure, to separate 87 g. of unchanged glutaraldehyde, b.p. 89–94° (10 mm.), $n^{27}\mathrm{D}$ 1.4295. The residue was triturated with several portions of ether to separate the bulk of the crystalline triphenylphosphine oxide. The resulting ether solution was concentrated and distilled to separate an additional 36.35 g. of unchanged glutaraldehyde and 35.76 g. (76.5%) of the aldehyde ester **2b**, a colorless, liquid, b.p. 66–86° (0.7 mm.), $n^{25}\mathrm{D}$ 1.4605. The aldehyde ester **2b** could be shown to be free of the starting dialdehyde by gas chromatographic analysis.[22] Redistillation afforded an analytical sample, $n^{26}\mathrm{D}$ 1.4592 [lit.[7] b.p. 60–75° (0.09 mm.), $n^{20}\mathrm{D}$ 1.4590], with infrared absorption[23] at 2700 and 2800 (aldehyde C–H), at 1720 with a shoulder at 1735 (C=O of aldehyde and ester), at 1660 (C=C), and at 977 cm.$^{-1}$ (*trans* CH=CH). The sample has complex n.m.r. absorption[23] in the region δ 1.5–2.7 (6H, methylene) as well as a singlet at 3.69 (3H, O–CH_3), a triplet (J = 1 c.p.s.) at 9.77 (1H, aldehyde C–H), and two sets of doublets of triplets, one centered at 6.88 (1H, J = 15.5 and 6.5 c.p.s., β-vinyl C–H) and the other at 5.79 (1H, J = 15.5 and 1 c.p.s., α-vinyl C–H), indicative of the grouping *trans* CH=CH.

Anal. Calcd. for $C_8H_{12}O_3$: C, 61.52; H, 7.75. Found: C, 61.55; H, 7.81.

In a run where a shorter time (60 hr.) for the addition of glutaraldehyde was employed, the yield of ester **2b** was 66%. In runs where a smaller excess of glutaraldehyde was employed, the yield of the aldehyde ester **2b** was lower (44–48%) and a second component, b.p. 105–110° (0.15 mm.), $n^{24.5}\mathrm{D}$ 1.4716, believed to be the diaddition product, became a significant by-product. Presumably the higher boiling fraction, b.p. 75–100° (0.08 mm.), $n^{20}\mathrm{D}$ 1.4664, reported by Eiter[7] is partially composed of this same by-product.

Following the reaction and isolation procedures described above, a solution of 21.50 g. (0.25 mole) of succinaldehyde in 50 ml. of methylene chloride was added over a 4-hr. period to a solution of 19.15 g. (0.05 mole) of carbomethoxymethylenetriphenylphosphorane in 50 ml. of methylene chloride. After separation of the unchanged succinaldehyde, b.p. 31–35° (0.15 mm.), $n^{24}\mathrm{D}$ 1.4260, the aldehyde ester **2a** was collected as a colorless liquid, b.p. 67–110° (0.15 mm.), $n^{24}\mathrm{D}$ 1.4590–1.4612, yield 5.571 g. (78.3%). Redistillation afforded an analytical sample, b.p. 58° (0.12 mm.), $n^{25}\mathrm{D}$ 1.4608, with infrared absorption[23] at 2725 and 2825 (aldehyde C–H), at 1730 (aldehyde and ester C=O), at 1655 (C=C), and at 980 cm.$^{-1}$ (*trans* CH=CH) and an ultraviolet maximum[25] at 204 mμ (ϵ 14,600). The sample has complex n.m.r. absorption[23] in the region δ 2.2–2.8 (4H, methylene) with a singlet at 3.65 (3H, O–CH_3), a partially resolved multiplet at 9.72 (1H, aldehyde C–H), and two sets of doublets (J = 16 c.p.s.) centered at 5.77 and 6.87 attributable to the α- and β-vinyl protons of the *trans* olefin. Each of the vinyl proton doublets exhibits further complex splitting apparently the result of virtual coupling[26] with each of the two methylene groups present.

Anal. Calcd. for $C_7H_{10}O_3$: C, 59.14; H, 7.09; mol. wt., 142. Found: C, 58.99; H, 6.99; mol. wt., 142 (mass spectrum).

As in the previous reaction, the use of a smaller excess of succinaldehyde led to mixtures of the desired aldehyde ester **2a** (46% yield) and a higher boiling component, b.p. 110–115° (0.5 mm.), $n^{24}\mathrm{D}$ 1.4769. This latter material, with infrared absorption[23] at 1735 (ester C=O), 1660 (C=C), and 975 cm.$^{-1}$ (*trans* CH=CH) but no absorption in the 2700–2800-cm.$^{-1}$ region attributable to an aldehyde, is presumably the diaddition product.

Preparation and Transformations of 2-Tetrahydrofurylacetic Acid (12a).—Reaction of the tetrahydrofurfuryl ester[27] of methanesulfonic acid with a refluxing solution of potassium cyanide in aqueous ethanol produced tetrahydrofurfurylnitrile (55.6% yield), b.p. 105–112° (22 mm.), $n^{25}\mathrm{D}$ 1.4456 [lit.[27] b.p. 45° (2 mm.), $n^{15}\mathrm{D}$ 1.4490], which was hydrolyzed with potassium hydroxide in ethanol to form the acid **12a** (75.5% yield), a colorless viscous liquid, b.p. 112–118° (1.3 mm.), $n^{26}\mathrm{D}$ 1.4580 [lit.[28] b.p. 144–146° (16 mm.)].

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[17] All melting points are corrected and all boiling points are uncorrected. Unless otherwise stated magnesium sulfate was employed as a drying agent. The infrared spectra were determined with a Perkin-Elmer, Model 237, infrared recording spectrophotometer fitted with a grating. The ultraviolet spectra were determined with a Cary recording spectrophotometer, Model 14. The n.m.r. spectra were determined at 60 Mc. with a Varian, Model A-60, n.m.r. spectrometer. The mass spectra were obtained with a CEC, Model 21-130, mass spectrometer. The microanalyses were performed by Dr. S. M. Nagy and his associates and by the Scandinavian Microanalytical Laboratory.

[18] We are indebted to Dr. Herbert E. Johnson of the Union Carbide Chemicals Co. for a generous supply of this material.

[19] *Cf.* J. Fakstorp, D. Raleigh, and L. E. Schniepp, *J. Am. Chem. Soc.*, **72**, 869 (1950).

[20] Apparently the equilibrium between succinaldehyde and other water-soluble components in this reaction mixture does not favor succinaldehyde since we uniformly obtained only 30% yields of succinaldehyde when a single acid treatment, neutralization, and subsequent extraction were employed (*cf.* ref. 19). In cases where the reaction mixture was not neutralized prior to extraction, the acid and ethanol present in the extract converted part of the succinaldehyde back to the starting material.

[21] (a) S. Hattori, *Yûki Gôsei Kagaku Kyôkai Shi*, **19**, 453 (1961); *Chem. Abstr.*, **55**, 20928 (1961); (b) H. Schildknecht and W. Föttinger, *Ann.*, **659**, 20 (1962).

[22] A column packed with silicone fluid, no. 550, suspended on ground firebrick was employed.

[23] Determined as a solution in carbon tetrachloride.

[24] O. Isler, *et al.*, *Helv. Chim. Acta*, **40**, 1242 (1957).

[25] Determined as a solution in *n*-heptane.

[26] J. I. Musher and E. J. Corey, *Tetrahedron*, **18**, 791 (1962).

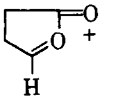
[27] M. Zief, H. G. Fletcher, Jr., and H. R. Kirshen, *J. Am. Chem. Soc.*, **68**, 2743 (1946).

[28] G. Barger, R. Robinson, and L. H. Smith, *J. Chem. Soc.*, 718 (1937).

A 13.02-g. (0.10 mole) sample of the acid **12a** was esterified with excess ethereal diazomethane to yield 7.42 g. (51%) of **methyl 2-tetrahydrofurylacetate** (**12b**), b.p. 91–93° (13 mm.), $n^{25.5}D$ 1.4363. Redistillation gave a pure[22] sample of the ester **12b**, b.p. 87.5° (15 mm.), $n^{24}D$ 1.4375, with infrared absorption[23] at 1737 cm.$^{-1}$ (ester C=O) and an ultraviolet maximum[29] at 259.5 mμ (ϵ 116).

Anal. Calcd. for $C_7H_{12}O_3$: C, 58.31; H, 8.39; mol. wt., 144. Found: C, 58.25; H, 8.44; mol. wt., 144 (mass spectrum).

A solution of 13.0 g. (0.10 mole) of the acid **12a** in 36 ml. (0.34 mole) of 48% aqueous hydrobromic acid was refluxed for 15 hr. and then neutralized with aqueous sodium bicarbonate and extracted with ether. Only the starting acid was recovered from the acidic fractions. The ethereal solution of the neutral product was dried, concentrated, and distilled to separate 3.19 g. (16.5%) of the crude bromo lactone **13** as a yellow liquid, b.p. 100–108° (0.1 mm.), $n^{24}D$ 1.4999. Redistillation afforded the pure[22] **bromo lactone 13** as a colorless liquid, b.p. 121–122° (0.9 mm.), $n^{25}D$ 1.4999, with infrared absorption[23] at 1780 cm.$^{-1}$ (γ-lactone C=O) and an ultraviolet maximum[29] at 268 mμ (ϵ 80). The material has complex n.m.r. absorption[23] in the region δ 1.7–2.7 (6H, methylene), a complex of 5 peaks with further splitting evident centered at 4.63 (1H, >CH–O), and a series of 4 distinguishable peaks centered at 3.52 (2H, CH_2–Br) which are apparently part of an A_2B_2 pattern.[30] The mass spectrum of the sample has molecular ion peaks at *m/e* 192 and 194 as well as a pair of peaks at 166 and 164 (M − 28, loss of CO_2, CH_2=CH_2, or both) and abundant bromine-free peaks at *m/e* 113 (M − Br) and 85 as well as peaks at lower masses. The peak at *m/e* 85 is presumbably attributable to the following ion.



Anal. Calcd. for $C_6H_9BrO_2$: C, 37.33; H, 4.69; Br, 41.39. Found: C, 37.52; H, 4.71; Br, 41.48.

Allyltriphenylphosphonium Bromide.—This salt, prepared in 95% yield as previously described,[31] separated from the benzene solution as white crystals; after washing with ether and drying, the material melted at 224–226° (lit.[31] m.p. 209–214°). The product has complex n.m.r. absorption[32] in the region δ 7.5–8.1, (15H, aryl C–H) with a doublet of doublets (J_{PH} = 15 c.p.s., J_{HH} = 5 c.p.s.) centered at 4.79 (2H, $>P^{+}$—CH_2—) and partially resolved absorption attributable to 3 vinyl protons in the region 5.3–5.9.

Preparation of the Trienes 3 and 4.—A suspension of 18.88 g. (0.0493 mole) of allyltriphenylphosphonium bromide in 300 ml. of pentane was treated with 51.9 ml. of an ethereal solution containing 0.0493 mole of methyllithium, and the resulting solution was stirred at room temperature for 6 hr. at which time the deep red supernatant liquid gave a negative Gilman color test for methyllithium. To this mixture was added, dropwise and with stirring over a 15-min. period, a solution of 7.0 g. (0.049 mole) of the aldehyde ester **2a** in 200 ml. of ether. The resulting solution was filtered and the residue was washed with 200 ml. of a 2:1 pentane–ether mixture. The combined filtrates were washed with aqueous sodium bisulfite, dried, and concentrated. After 50 mg. of inhibitor[33] had been added to the residual yellow liquid (8.22 g.), it was distilled to separate 3.664 g. (44.5%) of a pale yellow liquid, b.p. 60–100° (0.05 mm.), containing[22] more than 95% of a mixture of trienes **3a** and **4a**. A collected sample of this triene mixture **3a** and **4a**, which was not resolved by our gas chromatography column, has infrared absorption[23] at 1735 (ester C=O), at 1660 and 1610 (C=C), at 910 (—CH=CH_2), and at 955 and 980 cm.$^{-1}$ (*trans* —CH=CH). The n.m.r. spectrum[23] of the mixture has a complex pattern of lines in the region δ 4.8–7.1 (7H, vinyl C—H) with a singlet at 3.70 (3H, O—CH_3) and absorption in the region 2.2–2.6 (4H, methylene), and the mass spectrum has a molecular ion peak at *m/e* 166 with an intense peak at *m/e* 67 (CH_2=CH—CH=CH—CH_2^+).

A solution of 1.5685 g. (9.45 mmoles) of the mixture of trienes **3a** and **4a**, 909.4 mg. (9.17 mmoles) of maleic anhydride, and a few milligrams of inhibitor[33] in 10 ml. of benzene was refluxed for 3 hr. and then concentrated and diluted with pentane. A total of 985 mg. (39.5%) of the crude adduct **5a**, m.p. 82–85°, was collected. Recrystallization from ether–pentane mixtures afforded the pure **Diels–Alder adduct 5a** as white needles, m.p. 86–87°. The product has infrared absorption[34] at 1840 and 1770 (anhydride C=O), at 1710 (C=O of conjugated ester), at 1655 (conjugated C=C), and at 970 cm.$^{-1}$ (*trans* CH=CH) with an ultraviolet maximum[25] at 204 mμ (ϵ 1570). The n.m.r. spectrum[32] of the adduct **5a** has a pair of triplets (J = 6 and 16 c.p.s.) centered at δ 7.08 (1H, β-vinyl C–H of *trans* olefin), complex absorption in the region 5.7–6.2 (3H, α-vinyl C–H of *trans* olefin superimposed on vinyl C–H of cyclic olefin), a singlet at 3.77 (3H, O–CH_3), a multiplet centered at 3.47 (2H, tertiary C–H groups at ring juncture), and complex absorption in the region 1.6–3.0 (7H, aliphatic C–H).

Anal. Calcd. for $C_{14}H_{16}O_5$: C, 63.62; H, 6.10. Found: C, 63.56; H, 6.12.

The unchanged triene (611.3 mg., presumably **3a**) recovered from the mother liquor still exhibited a single peak on gas chromatography.[22]

Following the procedures outlined above, 22.6 g. (0.058 mole) of allyltriphenylphosphonium bromide, suspended in 400 ml. of pentane, was treated with 71 ml. of an ether solution containing 0.575 mole of phenyllithium. To the resulting mixture containing the ylid was added, dropwise and with stirring over a 30-min. period, a solution of 8.97 g. (0.0575 mole) of the aldehyde ester **2b** in 200 ml. of ether. The crude triene mixture, 9.574 g. of a pale yellow liquid, was mixed with a few milligrams of inhibitor[33] and distilled to separate 5.793 g. (56%) of a mixture of the trienes **3b** and **4b** as well as a small amount of biphenyl (from the phenyllithium preparation). Although the trienes **3b** (second eluted) and **4b** (first eluted) were separated by gas chromatography,[22] the analysis was complicated by the fact that the trienes were partially converted to the cyclized products **6** (first eluted) and **7** (second eluted) on the column, and these cyclized products **6** and **7** weren't separated from the triene **4b**. When a solution of the trienes in xylene was refluxed and aliquots were removed and analyzed at various time intervals, cyclization of the trienes **3b** and **4b** to an approximately equal mixture of esters **6** and **7** was found to be complete after 83.5 hr. The relative rates of formation of the two cyclized products **6** and **7** were approximately equal. The mixture of trienes **3b** and **4b** has infrared absorption[23] at 1710 (conjugated ester C=O), at 1645 (conjugated C=C), at 970 and 945 (*trans* CH=CH), and at 895 cm.$^{-1}$ (CH=CH_2) with complex n.m.r. absorption[23] in the region δ 4.7–7.2 (7H, vinyl C—H), as well as a singlet at 3.65 (3H, O–CH_3), and absorption attributable to aliphatic protons in the region 1.3–2.5 (6H).

After reaction of 858.1 mg. (4.76 mmoles) of the mixture of trienes **3b** and **4b** with 476.6 mg. (4.85 mmoles) of maleic anhydride in 10 ml. of refluxing benzene containing 5 mg. of inhibitor[33] for 3 hr., the previously described isolation procedure separated 713.9 mg. (54%) of the crude adduct **5b**, m.p. 90–94°. Recrystallization from an ether–pentane mixture afforded the pure **Diels–Alder adduct 5b** as white needles, m.p. 96–97°. The material has infrared absorption[34] at 1840 and 1770 (anhydride C=O), at 1710 (conjugated ester C=O), at 1655 (conjugated C=C), and at 980 cm.$^{-1}$ (*trans* CH=CH) with an ultraviolet maximum[25] at 200 mμ (ϵ 885). The n.m.r. spectrum[32] of the sample has a pair of triplets (J = 6.5 and 16 c.p.s.) centered at δ 7.08 (1H, β-vinyl C–H of *trans* olefin) with complex absorption in the region 5.7–6.3 (3H, α-vinyl C–H of *trans* olefin superimposed on the signal for the vinyl protons of the cyclic olefin), as well as a singlet at 3.77 (3H, O–CH_3), a multiplet centered at 3.45 (2H, tertiary C–H groups at ring junction), and absorption attributable to aliphatic protons in the region 1.5–3.0 (9H).

Anal. Calcd. for $C_{15}H_{18}O_5$: C, 64.73; H, 6.52. Found: C, 64.77; H, 6.53.

Concentration of the mother liquors remaining after separation of the adduct **5b** left 317 mg. of the *cis*-triene **3b** which gave gas chromatographic peaks[22] for the triene **3b** and the cyclized product **7**. A collected[22] sample of this *cis,trans*-triene **3b** (containing about 30% of the cyclization product **7** formed on the column) had n.m.r. absorption comparable with that previously described

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

[30] (a) R. C. Hirst and D. M. Grant, *J. Chem. Phys.*, **40**, 1909 (1964); (b) R. J. Abraham and K. G. R. Pachler, *Mol. Phys.*, **7**, 165 (1964).

[31] G. Wittig and U. Schöllkopf, *Chem. Ber.*, **87**, 1318 (1954).

[32] Determined as a solution in deuteriochloroform.

[33] Throughout this study, 2,5-di-*t*-butyl-1,4-hydroquinone was employed as a free-radical inhibitor.

[34] Determined as a solution in chloroform.

for the mixture of trienes **3b** and **4b**. After a solution of 100 mg. of the triene **3b** in 2 ml. of xylene had been refluxed for 92 hr., the only product found[22] was the ester **7** identified with the subsequently described sample by comparison of retention times and the n.m.r. spectrum of a collected sample.

Cyclization of the Trienes 3b and 4b.—A 3.411-g. (18.9 mmole) sample of the previously described mixture of trienes **3b** and **4b** was distilled in portions in a short path still at atmospheric pressure. The product, collected at 245°, was 2.026 g. (65.4%) of a pale yellow liquid containing[22] an approximately equal mixture of esters **6** and **7** as well as about 10% of unchanged triene. Redistillation of this sample at atmospheric pressure afforded 1.675 g. (47% over-all) of a mixture of esters **6** and **7**.

A 4.033-g. (22.4 mmole) sample of a mixture of esters **6** and **7** from a comparable cyclization was stirred with a mixture of 75 ml. of ether and a solution of 7.54 g. (0.13 mole) of potassium hydroxide in 75 ml. of water at room temperature for 42 hr. The aqueous phase from this reaction was acidified and extracted with ether; 1.735 g. of the crude acid **14**, containing a small amount of acid **15**,[35] was recovered from the ether extract. Repeated sublimation (50–70° at 0.1 mm.) of a 332-mg. portion of the crude acid afforded 101 mg. of the acid **14**, m.p. 80–90°; recrystallization from nitromethane separated the pure **acid 14** as white needles, m.p. 90–91.5°. This product has broad infrared absorption in the 3-μ region (associated OH) as well as peaks at 1710 (carboxyl C=O) and 1645 cm.$^{-1}$ (weak, C=C). The n.m.r. spectrum[32] of the product has a peak δ 11.76 (1H, carboxyl O–H), with complex absorption in the regions 5.4–6.2 (2H, vinyl C–H) and 1.1–2.9 (11H, aliphatic C–H).

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49; mol. wt., 166. Found: C, 71.91; H, 8.47; mol. wt., 166 (mass spectrum).

The neutral, ethereal layer from the above saponification which contained[22] the esters **7** (major component) and **6** (minor component) was stirred at room temperature with a solution of 2.02 g. (0.012 mole) of potassium hydroxide in 75 ml. of water for 11 days at which time the neutral ether layer contained only the ester **7**. The crude acid, 647 mg. of waxy yellow solid, m.p. 55–67°, recovered from the aqueous phase contained[35] a mixture of both acids **14** and **15**. The neutral, ethereal layer (containing **7**) was concentrated, and a solution of the residue in a mixture of 100 ml. of methanol and 50 ml. of water containing 3.94 g. (0.07 mole) of potassium hydroxide was stirred at room temperature for 24 hr. After the resulting mixture had been diluted with water and extracted with ether, the aqueous phase was acidified and extracted with ether to separate 778 mg. of the crude acid **15**[35] as a yellow, waxy solid. A 43.8-mg. portion of this crude acid, when distilled in a short-path still, afforded 30 mg. of the acid **15** as white crystals, m.p. 46–58°. Recrystallization from a formic acid–water mixture gave the pure **acid 15**, m.p. 58.5–60°, which was shown to be identical with a subsequently described sample by a mixture melting point determination.

Transformations of the Acid 14.—A 160-mg. (0.963 mmole) sample of the partially purified acid **14**, m.p. 84.5–89°, was esterified with excess diazomethane in ether solution. The crude neutral product, 170 mg. of a pale yellow liquid, contained[22] primarily the ester **6** contaminated with a small amount of the isomer **7**. A collected[22] sample of the pure **ester 6** has infrared absorption[23] at 1735 (ester C=O) and 1635 cm.$^{-1}$ (weak, C=C) with n.m.r. absorption[23] in the regions δ 5.4–6.1 (2H, vinyl C–H) and 1.1–2.7 (11H, aliphatic C–H) as well as a singlet at 3.67 (3H, OCH_3) and a molecular ion peak in the mass spectrum at *m/e* 180. On standing the sample was converted in part to a different substance with a slightly longer retention time; a collected sample of this new material has infrared absorption[23] at 1735 cm.$^{-1}$ (ester C=O) with a molecular ion peak in the mass spectrum at *m/e* 178. Thus, it appears that the ester **6** is undergoing rapid air oxidation to an allylic alcohol which is dehydrated on the gas chromatography column to form one or more diene esters. Because of this instability of the unsaturated ester, it was converted to other products for further characterization.

A solution of 170 mg. (0.94 mmole) of the crude ester **6** and 440 mg. (1.94 mmoles) of 2,3-dichloro-5,6-dicyanobenzoquinone in 15 ml. of benzene was refluxed for 14 hr. and then chromatographed on 10 g. of Woelm alumina (activity IV). The crude product, 122 mg. of yellow liquid eluted with benzene, contained[22] both the starting ester **6** and a new peak in the gas chromatogram. The mass spectrum of a collected sample of the new component had peaks in its mass spectrum attributable to molecular ions at both *m/e* 176 (expected for indane ester **18**) and 174 indicating that further dehydrogenation of **6** to an indene had also occurred. Consequently, a solution of 40 mg. of the above product in ethanol was hydrogenated over platinum oxide at room temperature and atmospheric pressure for 90 min. at which time absorption of hydrogen ceased. The resulting product was collected and shown to be identical with the subsequently described sample of **methyl indan-4-carboxylate** (**18**) by comparison of retention times, infrared spectra, and mass spectra.

A solution of 170 mg. (0.94 mole) of the crude ester **6** (contaminated with a small amount of the isomeric ester **7**) in 1.5 ml. of ethanol was hydrogenated at 27° and atmospheric pressure over the catalyst from 37.5 mg. of platinum oxide. After 1.7 hr. when the hydrogen uptake (24.6 ml. or 1.0 equiv.) ceased, this solution was filtered and concentrated to leave 163 mg. of a yellow liquid which contained[22] the saturated ester **16** accompanied by a small amount of the stereoisomer **17**. A collected[22] sample of the **saturated ester 16** has infrared absorption[23] at 1735 cm.$^{-1}$ (ester C=O) with an n.m.r. peak[23] at δ 3.60 (3H, O–CH_3) as well as complex absorption in the region 0.9–2.1 (15H, aliphatic C–H).

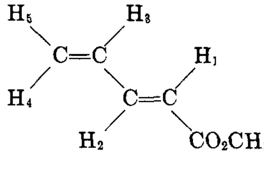
Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96; mol. wt., 182. Found: C, 72.32; H, 9.94; mol. wt., 182 (mass spectrum).

Transformations of the Acid 15.—The crude acid **15** (350 mg. or 2.1 mmoles) was esterified with excess diazomethane in ethereal solution. The crude, neutral product 360 mg. of yellow liquid, contained[22] primarily the ester **7** accompanied by several minor components. A collected[22] sample of the **unsaturated ester 7** has infrared absorption[23] at 1735 (ester C=O) and 1650 cm.$^{-1}$ (weak, C=C), a molecular ion peak in the mass spectrum at *m/e* 180, and n.m.r. absorption in the regions δ 5.5–5.9 (2H, vinyl C—H) and 1.1–2.6 (11H, aliphatic C–H), as well as a singlet at 3.65 (3H, OCH_3).

A solution of 160 mg. (0.989 mmole) of the unsaturated ester **7** in 3.5 ml. of acetic acid was reduced at 25° and atmospheric pressure over the catalyst from 31.6 mg. of platinum oxide. A total of 21.4 ml. (0.89 equiv.) of hydrogen was absorbed over a period of 2.75 hr. After the resulting mixture had been filtered and concentrated, the major component was collected[22] to separate the **saturated ester 17**. The product has infrared absorption at 1740 cm.$^{-1}$ (ester C=O) with n.m.r. absorption[23] in the region δ 1.2–2.4 (15H, aliphatic CH), as well as a singlet at 3.58 (3H, OCH_3).

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96; mol. wt., 182. Found: C, 72.26; H, 9.71; mol. wt., 182 (mass spectrum).

Preparation and Transformations of the Diene 24.—Samples of 1-(1-pyrrolidino)cyclopentene, b.p. 101° (20 mm.) [lit.[36] b.p. 97–98° (20 mm.)], and methyl *trans*-2,4-pentadienoate (**25b**),[37] b.p. 50–51° (18 mm.), $n^{23}D$ 1.4822 [lit.[37d] b.p. 57–58° (25 mm.), $n^{25}D$ 1.4797], were prepared as previously described. The n.m.r. spectrum[23] of the ester **25b** has a singlet at δ 3.66 (3H, O–CH_3) with absorption attributable to five vinyl protons which can be assigned as follows



H_2 at δ 7.23, H_3 at 6.45, H_1 at 5.85, H_4 at 5.57, and H_5 at 5.43; $J_{1,2}$ = 15.5 c.p.s., $J_{2,3}$ = 10 c.p.s., $J_{3,4}$ = 17.5 c.p.s., $J_{5,5}$ = 9 c.p.s., and $J_{4,5}$ = 2 c.p.s.

A solution of 24.79 g. (0.22 mole) of the ester **25b** and 33.28 g. (0.25 mole) of 1-(1-pyrrolidino)cyclopentene in 100 ml. of benzene was refluxed for 5 hr. and then concentrated and treated with dilute, aqueous hydrochloric acid. The neutral product

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[35] The composition of the crude acid was determined by esterification of a portion of the acid with ethereal diazomethane followed by analysis[22] of the resulting ester **6** and/or **7**.

[36] G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).

[37] (a) I. E. Muskat, B. C. Becker, and J. S. Lowenstein, *ibid.*, **52**, 326 (1930); (b) E. Adlerova, *et al.*, *Collection Czech. Chem. Commun.*, **25**, 221 (1960); (c) H. O. House and G. H. Rasmusson, *J. Org. Chem.*, **26**, 4278 (1961); (d) R. B. Woodward, F. E. Bader, H. Bickel, A. J. Frey, and R. W. Kierstead, *Tetrahedron*, **2**, 1 (1958).

was extracted with ether. After the ethereal extract had been washed with water, dried, and concentrated, distillation of the residue (9.25 g.) afforded 7.0 g. (17%) of the **diene ester 24**, b.p. 64–71° (0.05 mm.) [lit.[11] b.p. 95–108° (0.4 mm.)] which was shown to be identical with an authentic sample[11] by comparison of infrared spectra.

A solution of 0.30 g. (1.7 mmoles) of the diene **24** in 2 ml. of acetic acid was hydrogenated at 25° and atmospheric pressure over the catalyst from 40 mg. of platinum oxide. The hydrogen uptake (76.8 ml. or 1.87 equiv.) ceased after 9 hr. and the solution was filtered and concentrated. The residue contained, in order of increasing retention time,[22] a component believed to be **27** (3%), **16** (2%), **17** (3%), **26** (63%), and **18** (29%). The major component, the **ester 26**, was collected[22] and redistilled to afford a colorless liquid, b.p. 80–90° (0.25 mm.), $n^{19}\mathrm{D}$ 1.4792. This product has infrared absorption[23] at 1740 cm.$^{-1}$ (ester C=O), with n.m.r. absorption[23] in the region δ 1.0–2.8 (15H, aliphatic C=H) as well as a singlet at 3.62 (3H, O-CH_3).

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96; mol. wt., 182. Found: C, 72.60; H, 9.99; mol. wt., 182 (mass spectrum).

Solutions of 91 mg. (0.5 mmole) of the above mixture from hydrogenation of the diene **24** in 0.5 ml. of methanol containing 2.5 mmoles of sodium methoxide were prepared and sealed in tubes under nitrogen. The tubes were heated to 55° for 22 and 48 hr. after which time the contents were added to mixtures of ether and aqueous acid. The recovered neutral fractions contained[22] **16** (4%), **17** (40%), **26** (28%), and **18** (28%). Samples of the esters **16** and **17** were collected[22] from the mixture and shown to be identical with the previously described samples by comparison of retention times and infrared and mass spectra. In both runs, the composition of the epimeric esters was 60% **17** and 40% **26**.

To establish that these reaction conditions were adequate to epimerize the *trans*-fused ester **16** at the position α to the carbomethoxyl group, 87.7 mg. (0.48 mmole) of a mixture of the esters **16** and **17** (from cyclization of the trienes **3b** and **4b** and subsequent hydrogenation) was heated to 55–60° for 50 hr. with 0.5 ml. of methanol-d_1 containing 2.5 mmoles of sodium methoxide. The resulting mixture was quenched in a deuterium oxide–acetic acid-d_1 mixture and the neutral product containing[22] esters **16**, **17**, and **26** was separated. A collected[22] sample of the *trans*-fused ester **16** was analyzed by mass spectrometry and found to contain 92% d_1 species and 8% d_0 species.

A solution of 561 mg. (3.15 mmoles) of the diene **24** and 693 mg. (3.09 mmoles) of 2,3-dichloro-5,6-dicyanobenzoquinone in 20 ml. of benzene was refluxed for 17 hr. and then filtered and chromatographed on 25 g. of Woelm alumina (activity IV). The crude indan ester **18**, 0.49 g. (87%) of pale yellow liquid, was eluted with benzene. A collected[22] sample of pure **methyl indan-4-carboxylate (18)**[38] had infrared absorption[23] at 1725 cm.$^{-1}$ (conjugated ester C=O) and a molecular ion peak in the mass spectrum at *m/e* 176.

Cleavage of the Ketone 28.—A solution of 880 mg. (5.94 mmoles) of the ketone **28**[13] and 2.5 g. (44.5 mmoles) of potassium hydroxide in 30 ml. of methanol was refluxed for 50 hr. after which time the mixture was concentrated and diluted with water. The neutral product (168 mg.) and acidic product (695 mg. of brown, partially crystalline material) were separated in the usual way. A 480-mg. portion of the crude acid was recrystallized from pentane to separate 50 mg. of the acid as white crystals, m.p. 51–54°. Sublimation under reduced pressure afforded the pure acid **15** as white needles, m.p. 58–59.5°. This acid has broad infrared absorption[23] in the 3-μ region (associated carboxyl O-H) with a peak at 1715 (carboxyl C=O) and a shoulder at 1660 cm.$^{-1}$ (weak, C=C).

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49; mol. wt., 166. Found: C, 72.16; H, 8.49; mol. wt., 166 (mass spectrum).

A 215-mg. sample of the above crude acid was esterified with ethereal diazomethane. The neutral product, 215 mg. of pale yellow liquid, contained[22] one major component (>90%) which was collected and shown to be identical with ester **7** by comparison of retention times and infrared and mass spectra. A solution of 140 mg. (0.77 mmole) of this neutral product in 2 ml. of ethanol was hydrogenated at room temperature and atmospheric pressure over the catalyst from 80 mg. of platinum oxide. The hydrogen uptake (19.0 ml. or 1.0 equiv.) was complete after 2.3 hr. and the neutral product, 120 mg. of colorless liquid, was recovered. This sample contained[22] primarily the saturated ester **17** (>90%) accompanied by four other minor components. A collected[22] sample of the ester **17** was shown to be identical with the previously described sample by comparison of retention times and infrared and mass spectra.

Transformations of the Ketone 20.—The ketone **20**[39] was prepared and reduced to the alcohol **22**, m.p. 203–205° (lit.[39] m.p. 207–208.2°), which was further converted to its tosylate, m.p. 89–91° (lit.[39] m.p. 92–93°), as previously described. Attempts to displace the tosyloxy function with cyanide ion were unsuccessful. A solution of 1.20 g. (10.1 mmoles) of thionyl chloride in 10 ml. of petroleum ether was added, dropwise and with stirring over a 1.5-hr. period, to a solution of 1.135 g. (8.1 mmoles) of the alcohol **22** in 20 ml. of a 1:1 ether–petroleum ether mixture, the reaction mixture being maintained at −5 to −10° throughout the addition. The resulting solution was concentrated and the residual solid (m.p. 85–91°) was recrystallized from hexane to separate 1.073 g. (80.7%) of the dialkyl sulfite **23**, m.p. 94–96°. Additional recrystallizations afforded the pure **sulfite 23** as white needles, m.p. 99–99.5°. The sample has infrared absorption[23] at 1190 and 1205 cm.$^{-1}$ (S=O) with weak end absorption in the ultraviolet[25] and n.m.r. absorption[23] in the region δ 1.1–2.5 (28H, aliphatic C-H) as well as a partially resolved multiplet at 4.60 (2H, >CH-O).

Anal. Calcd. for $C_{18}H_{30}SO_3$: C, 66.22; H, 9.26; S, 9.82; mol. wt., 326. Found: C, 66.26; H, 9.28; S, 9.85; mol. wt., 329 (vapor pressure in benzene).

A solution of 6.883 g. (20 mmoles) of methoxymethyltriphenylphosphonium chloride, m.p. 199–201° dec. (lit.[40] m.p. 201–202° dec.), n.m.r. absorption δ 7.5–8.3 (15H, aryl C—H), 6.03 (2H doublet, J = 4 c.p.s., $\geqslant P^+—CH_2O—$), and 3.80 (3H singlet, O-CH_3), in 25 ml. of dimethyl sulfoxide was added with cooling to 16 ml. of a solution containing 20 mmoles of the dimethylsulfinyl carbanion[41] in dimethyl sulfoxide and the resulting deep red solution was stirred for 15 min. Then a solution of 2.7285 g. (19.8 mmoles) of the ketone **20** in 20 ml. of dimethyl sulfoxide was added with stirring and cooling. After the resulting solution had been stirred for 11 hr., it was poured into water and the insoluble material which separated was collected and extracted with boiling pentane. The material from the pentane extract was distilled in a short-path still to separate 1.1351 g. (34.5%) of the crude **enol ether 21** as a colorless liquid, b.p. 65° (0.05 mm.). This material had infrared absorption[23] at 1685 (C=C of enol ether) and at 1715 cm.$^{-1}$ (weak, C=O of starting ketone or aldehyde from hydrolysis) with a molecular ion peak in the mass spectrum at *m/e* 166 and n.m.r. absorption[23] in the region δ 1.2–2.5 (aliphatic C—H), as well as a singlet at 3.61 (O—CH_3), and a partially resolved multiplet at 5.83 (vinyl C-H). A solution of this crude enol ether **21** (1.135 g. or 6.84 mmoles) in 10 ml. of ether was stirred with dilute (*ca.* 2 *N*) aqueous hydrochloric acid for 92 hr. under a nitrogen atmosphere. The crude organic product, 1.12 g. of white semisolid material, has infrared absorption[23] at 1720 (C=O) and 2750 cm.$^{-1}$ (aldehyde C-H). The mass spectrum of this material has peaks at *m/e* 168 and 152 corresponding to the molecular ion peaks of the **19a** and the corresponding aldehyde. To a solution of 1.0 g. (*ca.* 6 mmoles) of this aldehyde–acid mixture and 3.774 g. (22 mmoles) of silver nitrate in a mixture of 15 ml. of water and 11 ml. of absolute ethanol was added, dropwise and with stirring over a 2-hr. period, a solution of 1.402 g. (35 mmoles) of sodium hydroxide in 25 ml. of water.[42] The resulting mixture was stirred overnight, filtered, extracted with ether, acidified, and again extracted with ether. Drying and concentration of the latter extract afforded 649 mg. of the acid **19a** as white crystals, m.p. 107–115°. Recrystallization from petroleum ether (b.p. 30–60°) separated the pure **acid 19a** as white plates, m.p. 128–129.5°, with broad infrared absorption[23] in the 3-μ region (associated carboxyl O-H) and a peak at 1700 cm.$^{-1}$ (carboxyl C=O). The material has

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[38] A sample of this ester **18** [lit.[12] b.p. 130–131° (7 mm.)] was saponified with sodium hydroxide in aqueous methanol to give the crude acid, m.p. 146.5–149.5°, in 83% yield. Recrystallization from aqueous methanol afforded the pure indan-4-carboxylic acid as pale beige needles, m.p. 151.5–152.5°. L. F. Fieser and E. B. Hershberg [*J. Am. Chem. Soc.*, **59**, 396 (1937)] reported 152.5–153.5°.

[39] C. S. Foote and R. B. Woodward, *Tetrahedron*, **20**, 687 (1964).

[40] G. Wittig and M. Schlosser, *Chem. Ber.*, **94**, 1373 (1961).

[41] E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962).

[42] This procedure has been described by K. J. Clark, G. I. Fray, R. H. Jaeger, and R. Robinson, *Tetrahedron*, **6**, 217 (1959).

n.m.r. absorption in the region δ 1.2–2.8 (15H, aliphatic C–H) as well as a broad peak at 12.37 (1H, COOH).

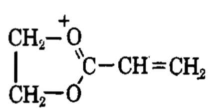
Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59; mol. wt., 168. Found: C, 71.17; H, 9.60; mol. wt., 168 (mass spectrum).

A sample of the acid **19a** was esterified with ethereal diazomethane and the neutral product, the crude methyl ester **19b**, was separated. A collected[22] sample of this **methyl ester 19b** has infrared absorption[23] at 1735 cm.$^{-1}$ (ester C═O) with a molecular ion peak in the mass spectrum at *m/e* 182. A solution of 2.075 g. (11.5 mmoles) of the previously described mixture of trienes **3b** and **4b** in 75 ml. of benzene containing a few milligrams of inhibitor[33] was heated to 190° in an autoclave for 12 hr. Concentration of this solution left 2.00 g. of a brown liquid residue which no longer contained[22] the trienes **3b** and **4b**. A 545.2-mg. portion of this residue in 2 ml. of ethanol was hydrogenated at room temperature and atmospheric pressure over the catalyst from 36 mg. of platinum oxide. After 20.5 hr. the hydrogen absorption (3.1 mmoles) ceased; the reaction mixture was filtered, concentrated and distilled in a short-path still to separate 259.1 mg. (47% based on the triene mixture) of a colorless liquid which contained[22] approximately equal quantities of the saturated esters **16** and **17** accompanied by a few per cent of biphenyl (a contaminant in the original triene). However, the ester **19b** was not present in this product.

Preparation of the Ketal 32.—A solution of 10.0 g. (0.104 mole) of 2-cyclohexen-1-one (**31**) and 45 g. (0.47 mole) of *cis*-1,2-dichloroethylene in 300 ml. of pentane was irradiated at room temperature for 19 hr. with a Hanovia 450-w., high-pressure lamp surrounded by a Corex filter.[43] The reaction was followed by observing the disappearance of the infrared band at 1690 cm.$^{-1}$ (conjugated C═O) and the appearance of a new peak at 1715 cm.$^{-1}$ (nonconjugated C═O). After the above reaction period, evaporation of the solvent under reduced pressure left 17.6 g. of the crude bicyclic ketone as a brown liquid. Since our attempts to isolate this intermediate uniformly lead to decomposition, a mixture of the crude ketone (17.6 g. or 0.092 mole), 6.2 g. (0.10 mole) of ethylene glycol, and a few milligrams of *p*-toluenesulfonic acid in 150 ml. of benzene was refluxed overnight with continuous separation of water (1.8 ml. of water separated). The resulting solution was concentrated under reduced pressure with the final volatile components being removed at room temperature and 0.1-mm. pressure. The residual orange oil (14.8 g.) was chromatographed on 350 g. of Merck neutral alumina, the desired product (8.37 g. of light yellow liquid) being eluted with 3:7 ether–pentane mixtures. A solution of the liquid in pentane deposited 4.9 g. (20% based on cyclohexenone) of one stereoisomer of the **ketal 32** as white needles, m.p. 64–67°. Additional recrystallizations from pentane and from hexane raised the melting point to 69.5–71°. In subsequent runs, the crude ketal was dehalogenated directly without purification by chromatography and subsequent recrystallization. The product, m.p. 69.5–71°, has no infrared absorption[23] in the 3- or 6-μ region attributable to carbonyl or hydroxyl functions; it has n.m.r. absorption[23] in the regions δ 1.2–2.0 (6H, aliphatic CH_2) and 2.0–3.0 (2H, aliphatic C–H at ring juncture), with a singlet at 3.92 (4H, —CH_2—O—) and a complex multiplet in the region 4.1–4.4 (2H, ⋗CH—Cl). The mass spectrum has very weak molecular ion peaks at *m/e* 236, 238, and 240 with abundant fragment peaks at *m/e* 201 and 203 (M–Cl).

Anal. Calcd. for $C_{10}H_{14}Cl_2O_2$: C, 50.60; H, 5.95; Cl, 30.10. Found: C, 50.65; H, 5.95; Cl, 29.90.

Preparation of the Unsaturated Ketal 33.—To a solution of 31.6 g. (0.133 mole) of the crude mixture of stereoisomeric ketals **32** in 250 ml. of ether and 600 ml. of liquid ammonia was added, portionwise and with stirring, 7.3 g. (0.32 g.-atom) of sodium. The resulting mixture was stirred for 1.75 hr. at the end of which time the solution was still blue indicating the presence of sodium. Excess ammonium chloride was added, and the ammonia was allowed to evaporate. Then water was added and the organic products were extracted with ether. After this extract had been dried and concentrated, distillation of the residue (19.177 g. of red-brown liquid) separated 10.399 g. (46.2%) of the **unsaturated ketal 33**, as a colorless liquid, b.p. 38–47° (0.15 mm.), n^{25}D 1.4883. The product exhibits a single peak on gas chromatography,[22] has no infrared absorption[23] in the 3- or 6-μ region attributable to hydroxyl or carbonyl functions, and has a weak molecular ion peak in its mass spectrum at *m/e* 166 with a very abundant one at *m/e* 99 presumably attributable to this fragment. A comparable reaction with 4.30 g. (18.2 mmoles) of the previously described crystalline dichloro ketal **32** gave 2.874 g. (95%) of the unsaturated ketal **33** which was identified with the previous sample by comparison of retention times and infrared spectra. Consequently, it appears that a single stereoisomer (probably the *cis* isomer) of the unsaturated ketal **33** was obtained in each case. The n.m.r. spectrum of this product has two doublets (*J* = 3 c.p.s.,[44] further coupling apparent but not resolved) at δ 6.02 and 6.17 (2H, vinyl C–H), a partially resolved multiplet at 3.83 (4H, —CH_2—O), a broad multiplet at 3.01 (1H, C–H at ring juncture), a doublet (*J* = 4.5 c.p.s., further coupling apparent but not resolved) at 2.77 (1H, C–H at ring juncture), and absorption in the region 1.3–1.9 (6H, aliphatic CH_2).



Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.94; H, 8.51.

Preparation of the Ketone 35.—A solution of 10.39 g. (0.0616 mole) of the unsaturated ketal **33** in 40 ml. of ethanol was hydrogenated at room temperature and atmospheric pressure over the catalyst from 1.0 g. of platinum oxide. The hydrogen uptake (1400 ml. or 0.934 equiv.) ceased after 21.3 hr. at which point the solution was filtered and concentrated to leave 10.1 g. of the crude ketal **34** as a colorless liquid. A portion of this product was distilled to give the **ketal 34**, b.p. 44.5–52° (0.2–0.4 mm.), having no infrared bands in the 3- or 6-μ region attributable to hydroxyl or carbonyl functions and exhibiting a molecular ion peak in its mass spectrum at *m/e* 168. The sample has complex n.m.r. absorption[23] in the region δ 1.0–2.8 (12H, aliphatic C–H) with a singlet at 3.78 (4H, —CH_2—O). A solution of 10.1 g. (0.060 mole) of the saturated ketal **34** in 40 ml. of ether was stirred at room temperature with 20 ml. of 3 *N* hydrochloric acid for 4 hr. After the organic product had been extracted with ether, the extract was dried and concentrated. Distillation of the residue (7.5 g.) afforded 6.09 g. (80% based on the unsaturated ketal) of the **bicyclic ketone 35** as a colorless liquid, b.p. 87–97° (18 mm.) [lit.[15a] b.p. 89–91° (18 mm.)]. The product has infrared absorption[23] at 1715 cm.$^{-1}$ (C═O) with a molecular ion peak in the mass spectrum at *m/e* 124 and complex n.m.r. absorption in the regions δ 2.5–3.2 (2H) and 1.2–2.5 (10H).

A 354-mg. (2.86 mmole) sample of the ketone **35** was reduced with 1.0 g. of sodium borohydride in aqueous methanol at room temperature for 2 hr. The organic product, the crude ***endo* alcohol 36a**, was recovered as 350 mg. (97%) of colorless liquid which exhibited a single peak on gas chromatography[22] with infrared absorption[23] at 3620 and 3400 cm.$^{-1}$ (unassoc. and assoc. O–H). This alcohol **36a** (207 mg. or 1.64 mmoles) was acetylated with excess acetic anhydride in pyridine. The recovered neutral organic product (235 mg. or 87%) had a single peak on gas chromatography[22] with infrared absorption[23] at 1740 cm.$^{-1}$ (ester). A collected[22] sample of this material was shown to be identical with a sample of the previously reported[15c] **acetate 36b** by comparison of retention times and infrared spectra.

Preparation of the Esters 29 and 30.—To a solution of dimethylsulfoxonium methylide,[45] prepared from 2.20 g. (10 mmoles) of trimethylsulfoxonium iodide, 240 mg. (10 mmoles) of sodium hydride, and 50 ml. of dimethyl sulfoxide, was added, dropwise and with stirring over a 30-min. period, a solution of 1.00 g. (8.06 mmoles) of the bicyclic ketone **35**. The resulting red solution was heated to 100° for 0.75 hr. and then cooled and poured into water. After extraction with pentane, drying, and concentration of the extract left 1.05 g. of the crude **epoxide 37** as a pale yellow oil which exhibited two peaks on gas chromatography.[22] A collected[22] sample of each peak has only weak infrared absorption[23] attributable to a carbonyl function in the 6-μ region.

A cold (−15°) solution of 1.05 g. (*ca.* 7.5 mmoles) of this crude epoxide **37** in 30 ml. of ether was treated with 1.26 g. (8.1 mmoles) of boron trifluoride etherate, and the resulting solution was allowed to warm to room temperature over a 20-min. period.

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(43) *Cf.* H. Hikino and P. de Mayo, *J. Am. Chem. Soc.*, **86**, 3582 (1964).

(44) *Cf.* (a) O. L. Chapman, *ibid.*, **85**, 2014 (1963); (b) P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2017 (1962).

(45) E. J. Corey and M. Chaykovsky, *ibid.*, **84**, 867 (1962).

The resulting solution was diluted with water, and the ether layer was separated, dried, and concentrated. The residue, 945 mg. of colorless liquid with infrared absorption[23] at 2750 (aldehyde C–H) and 1720 cm.$^{-1}$ (C=O), was dissolved in 30 ml. of ethanol containing 15 ml. of water and 3.789 g. (22.3 mmoles) of silver nitrate. To this solution was added, dropwise over a 45-min. period, a solution of 1.442 g. (36 mmoles) of sodium hydroxide in 25 ml. of water.[42] The resulting suspension was stirred at room temperature for 10 hr. and then filtered, extracted with ether, acidified, and again extracted with ether. The latter extract was dried and concentrated to leave 365 mg. of crude acid as a yellow oil with infrared bands[23] at 3000 (broad, assoc. carboxyl O—H) and 1710 cm.$^{-1}$ (C=O). Esterification of this acid with excess ethereal diazomethane afforded 370 mg. of a mixture[46] of esters **29** and **30**. This mixture contained[46] 32% of component A (first eluted) and 68% of component B (second eluted). Infrared spectra[23] of collected[46] samples of each component A and B have absorption at 1740 cm.$^{-1}$ (ester C=O) and differ only in details in the fingerprint region. The mass spectrum of each component has a molecular ion peak at *m/e* 168 with abundant fragment peaks at *m/e* 140 (M − CH_2=CH_2), 109 (M − CO_2CH_3), and 81 (M − $^+CH_2$—CH=C(OH)OCH_3). By comparison of the n.m.r. spectra of the mixture and of a collected[46] sample of component B, it was apparent that each component A and B has broad absorption in the region δ 1.0–2.8 (13H, aliphatic C–H). In addition component A has a singlet at δ 3.65 (3H, OCH_3) and component B has a singlet at δ 3.62 (3H, OCH_3). A sample of the mixture of esters **29** and **30** was collected[46] for analysis.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.22; H, 9.60.

A solution of 65.2 mg. (0.39 mmole) of this ester mixture in 0.75 ml. of methanol containing 3.7 mmoles of sodium methoxide was refluxed for 65 hr. The crude neutral product (73 mg.) recovered from this reaction mixture contained the two esters in the proportions 59% of component A and 41% of component B. Although we favor assignment of the stereochemistry **29** to the more stable isomer (component A) and stereochemistry **30** to component B, we have no evidence permitting firm stereochemical assignments.

Transformations of the Nonatriene Derivatives 3a and 4a.—In one of a number of experiments, 744 mg. of the mixture of trienes **3a** and **4a** containing a few milligrams of inhibitor[33] was heated to 210° in a sealed tube for 4.5 hr. Distillation of the resulting material in a short-path still separated 39.7 mg. of volatile material as a pale yellow liquid containing[22] primarily the starting trienes **3a** and **4a** (first eluted) plus a new component (second eluted) and biphenyl (third eluted, a minor contaminant in the original triene mixture). A sufficient quantity of the new component was obtained by collection from the gas chromatograph[22] to learn that it has infrared absorption at 1730 (ester C=O) and 1655 cm.$^{-1}$ (C=C) with a molecular ion peak in the mass spectrum at *m/e* 166. The mass spectrum of this sample did not have an abundant fragment peak at *m/e* 138 (M − CH_2=CH_2) as had been characteristic of bicyclo[4.2.0]octane derivatives described previously. Repeated efforts to obtain more of this product in order to permit further characterization led either to recovery of the unchanged trienes **3a** and **4a** or to formation of higher molecular weight materials.

After 387.4 mg. of a mixture of trienes **3a** and **4a** had been distilled at 235–250° over a 15-min. period, an ethanol solution of the distillate (122.3 mg.) was hydrogenated at room temperature and atmospheric pressure over the catalyst from 114 mg. of platinum oxide until the hydrogen absorption (73.6 ml. or 3.0 mmoles) ceased. After the reduction product (119.4 mg.) had been recovered in the usual way, comparison of its gas chromatogram[22] with the chromatogram of the esters **29** and **30** established that the reduction product could not contain more than 3% of the esters **29** or **30**. The major product in the reduction mixture was **methyl nonanoate**, a collected sample of which was identified with an authentic sample by comparison of retention times and infrared spectra.

A solution of 1.0978 g. (6.63 mmoles) of the mixture of trienes **3a** and **4a** in 250 ml. of hexane was irradiated for 34 hr. with a 450-w. Hanovia high-pressure mercury lamp surrounded by a Corex filter. Evaporation of the solvent left 1.0 g. of a colorless liquid which contained[22] at least four new components. A solution of 244 mg. (*ca.* 1.5 mmoles) of this mixture in 2 ml. of ethanol was hydrogenated at room temperature and atmospheric pressure over the catalyst from 69 mg. of platinum oxide until the hydrogen absorption (62 ml. of 1.7 equiv.) ceased. The crude product, 207 mg. of colorless liquid, exhibited two peaks on gas chromatography[22] neither of which corresponded to the esters **29** and **30**. A collected sample of the peak eluted first was identified with an authentic sample of **methyl nonanoate** by comparison of retention times and mass spectra. The nature of the component(s) under the second peak remains to be established.

Preparation of the Unsaturated Ester 40.—A mixture of 34 g. (0.348 mole) of *trans*-2,4-pentadienoic acid (**25a**),[37] 80 ml. of allyl alcohol, and 1 ml. of concentrated sulfuric acid was stirred for 16.5 hr. at room temperature and then heated to reflux for 2 hr. The resulting solution was concentrated, diluted with ice-water, and extracted with ether. After the ethereal extracts had been washed with aqueous sodium bicarbonate, dried, and concentrated, distillation of the residue (26.88 g. of yellow-orange liquid) separated 11.31 g. (23%) of the **allyl ester 40** as a colorless liquid, b.p. 76–83° (15 mm.), n^{22}D 1.4912; on redistillation the sample boiled at 74–74.5° (17 mm.), $n^{22.5}$D 1.4913. The product had infrared absorption[23] at 1720 (conjugated ester C=O), at 1640 and 1600 (conjugated C=C), at 985 (*trans* CH=CH—), and at 920 cm.$^{-1}$ (—CH=CH_2) with an ultraviolet maximum[25] at 244 mμ (ϵ 32,100). The n.m.r. spectrum[23] of the material has a doublet of triplets (J = 1 and 5 c.p.s.) centered at δ 4.52 (2H, —O—CH_2—) with a doublet (J = 16 c.p.s.) at 5.79 (vinyl C-H α to ester) superimposed on complex absorption in the region δ 4.9–7.5 attributable to the remaining vinyl protons in the molecule.

Anal. Calcd. for $C_8H_{10}O_2$: C, 69.54; H, 7.30; mol. wt., 138. Found: C, 69.22; H, 7.30; mol. wt., 138 (mass spectrum).

Samples of the allyl ester **40** containing a few milligrams of inhibitor[33] were heated to temperatures ranging from 100–230° for varying periods of time. The crude products were analyzed by gas chromatography and infrared spectrometry. In all cases only high molecular weight products and/or starting material were found.

In an attempt to prepare the unsaturated ester **41**, *trans*-2,4-pentadienoic acid (**25a**) was reduced with excess ethereal aluminum hydride to form *trans*-2,4-pentadien-1-ol, b.p. 49–51° (6 mm.), $n^{28.5}$D 1.4792, $\lambda_{\max}^{\mathrm{EtOH}}$ 223.5 mμ (ϵ 22,000) [lit.[47] b.p. 70–72.5° (31 mm.), n^{22}D 1.4808, $\lambda_{\max}^{\mathrm{EtOH}}$ 223.7 mμ (ϵ 23,700)], in low (6%) yield. The crude ester **41** ($\bar{\nu}_{\max}^{\mathrm{CCl_4}}$ 1725 cm.$^{-1}$) prepared by reaction of this dienol with acryloyl chloride underwent very rapid polymerization discouraging us from studying its intramolecular cyclization.

Acknowledgment.—We are indebted to Professor Kirby V. Scherer, Jr., Department of Chemistry, University of California at Berkeley, for providing us with a sample of the ketone **28** and to our colleagues, Professor Glenn A. Berchtold and Mr. Joseph Ciabattoni, who provided information about the diene ester **24**.

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(46) A gas chromatography column packed with Carbowax 20M suspended on ground firebrick was employed.

(47) A. D. Mebane, *J. Am. Chem. Soc.*, **74**, 5227 (1952).