being that the reaction cannot be monitored by ir. The stainless steel cell has a 22-ml capacity and has been constructed using quartz end plates rather than sodium chloride as is used for the smaller apparatus.

Infrared Monitored Photolysis of 4,4-Diphenylcyclopentenone at Low Temperature. Irradiations were carried out using the microbench[11] and the small scale low-temperature photolysis apparatus described above. Solutions of 4,4-diphenylcyclopentenone or 4-methyl-4-phenylcyclopentenone in 1:1 ether–tetrahydrofuran were irradiated at $-140 \pm 5°$. Typically, a 0.4 *M* solution of enone dissolved in 1:1 ether–tetrahydrofuran was added to the reaction cell and after evacuation of the surrounding chamber the cell was cooled to $-140°$ and photolysis was initiated. Photolysis of the diphenylenone (0.4 *M*) at $-140°$ using 366-nm light was monitored over 930 min. During this time a new band appeared at 5.67 μ and increased in intensity until the housone comprised *ca.* 80% of the photomixture at the expense of the enone carbonyl absorption at 5.86 μ. There was no sign of ketene absorption at 4.74 μ. The irradiation wavelength was then changed from 366 to 315 nm and photolysis was continued at $-140°$. The band at 5.67 μ (housone) was converted to a band at 4.74 μ (ketene) over a period of 5 hr of irradiation. The light flux was 0.119 mEinsteins/hr.

Low-Temperature Photolysis of 4-Methyl-4-phenylcyclopentenone. Irradiation of 4-methyl-4-phenylcyclopentenone (0.40 *M*) in 1:1 ether–tetrahydrofuran for 100 min at $-140°$ using 366-nm light afforded a new absorption at 5.71 μ (housone) at the expense of the enone absorption at 5.87 μ. There was no sign of ketene absorption at 4.74 μ. When the wavelength was changed to 315 nm and the photolysis continued for 200 min at $-140°$, the 5.71-μ band was converted to a band at 4.74 μ (ketene). The light flux was 0.121 mEinstein/hr. This behavior closely parallels that of diphenylenone (*vide supra*).

Infrared Monitored Photolysis of 4,4-Diphenylcyclopentenone. Photolysis at Low Temperature and Warming to Room Temperature. A 0.4 *M* solution of 4,4-diphenylcyclopentenone in 1:1 ether–tetrahydrofuran was irradiated at 366 nm and $-140°$ using the apparatus described above. After 8.0 hr, ir spectroscopy indicated that the housone absorption at 5.67 μ had increased to *ca.* 70% of the photomixture at the expense of the enone absorption at 5.86 μ. Irradiation was terminated and the reaction mixture was allowed to warm to room temperature while being monitored by ir. As the warming proceeded, the housone absorption at 5.67 μ disappeared in a thermal process which converted it to the ketene band at 4.74 μ.

Preparative Photolysis of 4,4-Diphenylcyclopentenone at Low Temperature. Isolation of Methyl 3,4-Diphenyl-4-pentenoate and 3,4-Diphenyl-4-pentenoic Acid upon Warming to Room Temperature. A solution of 4,4-diphenylcyclopentenone (109.1 mg, 0.466 mmol) in 22 ml of 1:1 ether–tetrahydrofuran was irradiated using the large scale photolysis apparatus described above. Potassium ferrioxalate actinometry[12] was used to determine that the light flux was 0.133 mEinstein/hr.

After cooling to $-120°$, photolysis was initiated. On termination of photolysis (24 hr), the solution was warmed to room temperature, removed from the photolysis cell, quenched with methanol, ether extracted, dried, and concentrated *in vacuo* to afford 98.7 mg of material. Preparative thick layer chromatography on a 20 × 20 cm silica gel plate eluted three times using 10% ether in hexane afforded 15.6 mg of 3,4-diphenyl-4-pentenoic acid, mp 161.5–162.5°, 38.1 mg of methyl 3,4-diphenyl-4-pentenoate, identical with the compounds previously obtained, and 36.1 mg of 4,4-diphenylcyclopentenone, mp 62–63°.

Acknowledgment. Appreciation is expressed by R. D. L. for an NSF Traineeship and to the Graduate School for a WARF Fellowship. Also, support of this research by National Institutes of Health Grant GMO7487 is gratefully acknowledged.

Stereochemistry at the Methane Carbon in the Di-π-methane Rearrangement. Mechanistic and Exploratory Organic Photochemistry[1,2]

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Contribution from the Chemistry Department of the University of Wisconsin, Madison, Wisconsin 53706. *Received February 8, 1974*

Abstract: 3-Ethyl-3,5-dimethyl-1,1-diphenyl-1,4-hexadiene was shown to undergo the di-π-methane rearrangement. Both cis and trans stereoisomers of 3-ethyl-3-methyl-2-(2′-methylpropenyl)-1,1-diphenylcyclopropane were obtained as photoproducts. This system was used to investigate the stereochemistry of the di-π-methane rearrangement, since the methane carbon is asymmetric. The starting 1,4 diene was synthesized optically active. Also both *cis*- and *trans*-vinylcyclopropane photoproducts were independently synthesized optically active. Then a synthetic route was devised wherein both vinylcyclopropanes and the 1,4 diene were configurationally interrelated. Negatively rotating (365 nm) diene was shown to have the same methane carbon configuration as negatively rotating *cis*-vinylcyclopropane and positively rotating *trans*-vinylcyclopropane. ORD was used throughout to ensure that rotations had no contribution from impurities. After photolysis of the methylethyl diene *cis*- and *trans*-vinylcyclopropanes were separated using recycling high-pressure liquid chromatography and the rotations determined. It was found that in both cases the di-π-methane rearrangement proceeded with inversion of configuration at the methane carbon. The quantum yield for total vinylcyclopropane formation was determined as 0.11. Finally the overall stereochemistry of the di-π-methane rearrangement is discussed.

In our investigations on the di-π-methane rearrangement[3-13] we have elucidated the reaction stereochemistry at two of the three centers of interest. Thus we showed that the stereochemistry at both C-1 and at

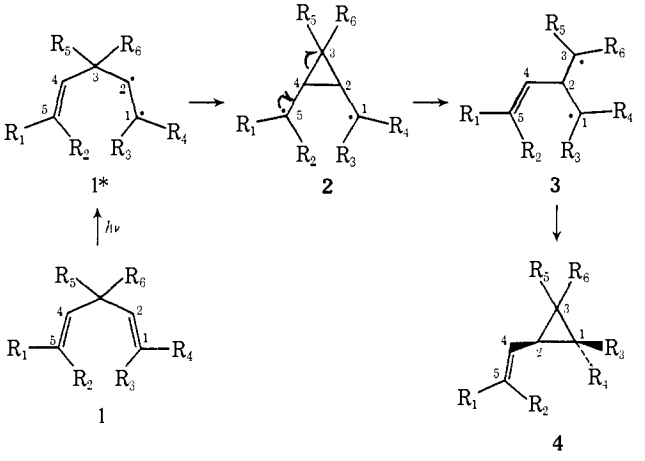
(1) This is Paper LXXXVIII on Mechanistic and Exploratory Organic Photochemistry. For the previous paper of the series see ref 2.

(2) (a) For a preliminary communication describing a portion of the present results, see H. E. Zimmerman, J. D. Robbins, R. D. McKelvey, C. J. Samuel, and L. R. Sousa, *J. Amer. Chem. Soc.*, **96**, 1974 (1974). (b) For the last paper of the series note: H. E. Zimmerman and R. D. Little, *J. Amer. Chem.* **96**, 4623 (1974).

(3) (a) H. E. Zimmerman and G. L. Grunewald, *J. Amer. Chem. Soc.*, **88**, 183 (1966); (b) H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. S. Sherwin, *ibid.*, **89**, 3932 (1967).

(4) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *J. Amer. Chem. Soc.*, **90**, 6096 (1968).

Chart I. Qualitative Valence Bond Representation of the Di-π-methane Rearrangement



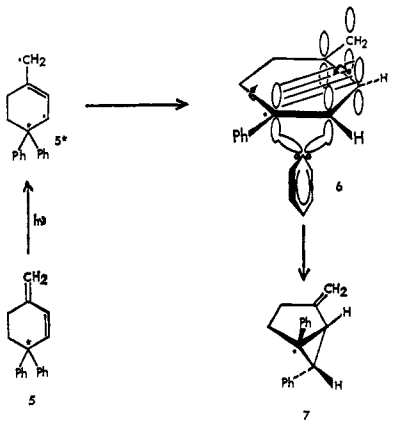
C-5 was retained in the product. However, very little information was available about the preferred reaction stereochemistry at the central, methane carbon (*i.e.*, C-3) (note the reactant in Chart I for numbering of the skeleton).

One way of picturing the reaction is in qualitative valence bond terms as outlined in Chart I. As we have commented earlier these structures are convenient in emphasizing the different structural and electronic changes proceeding during the reaction. Thus, the valence bond structures shown allow us to predict the effect of substituents and reaction regiospecificity which is often observed. Yet, as we have also noted, the structures are not necessarily intermediates and may merely correspond to points on an energy hypersurface leading from the excited state of reactant to product.

Specifically, if species **3** were a true intermediate of long lifetime, one would expect loss of stereochemistry at carbons 1 and 3. Similarly, if biradical **2** were long lived and subject to single bond free rotation, one would lose stereochemistry at carbons 1 and 5, and this is known[6b,9,13] not to be the case. Rather, the reaction appeared either to be concerted or to have rotation about single bonds much slower than the sequential steps in Chart I.

Some tentative information was available regarding the stereochemistry at C-3. Thus, in a variety of phenylvinylmethane systems, the phenyl migration reaction is an example of the di-π-methane rearrangement, and the preferred stereochemistry has been shown[10-14] to lead to the endo-phenyl stereoisomer of the bicyclo[3.1.0]hexane system formed. This is depicted in Chart II for one example[10] and can be seen to involve inversion of stereochemistry at the methane carbon (note asterisk marking this carbon in Chart II).

Chart II. Stereochemistry of Phenyl Migration



However, the factors controlling this inversion of configuration are not certain. While a demand for this stereochemistry by electronic control (note a later discussion) may account for inversion, an alternative, nonconcerted mechanism has already been noted as being capable of accounting for the reaction stereochemistry.[10,14e]

Mariano[15] in his elegant studies has attacked the problem from another perspective and demonstrated that in constrained di-π-methane systems it is possible to enforce either retention or inversion of configuration.[15]

The present research had as its objective the problem of determining the preferred stereochemistry of the di-π-methane rearrangement at the methane carbon in a nonconstrained, acyclic example where the molecule would be equally free, *a priori*, to give one of (a) retention of configuration, (b) inversion of configuration, or (c) loss of methane carbon stereochemistry.

The molecule chosen for this study was 3-ethyl-3,5-dimethyl-1,1-diphenyl-1,4-hexadiene (**8**). This is closely analogous to molecules previously studied but the methane carbon is asymmetric. A determination of the reaction stereochemistry in this instance thus promised to provide the desired mechanistic answer.

Synthesis of Reactant Di-π-methane and Its Potential Vinylcyclopropane Photoproducts. Chart III outlines the synthesis of the desired ethylmethyldiene **8**. This synthesis began with the Reformatsky reaction of diphenylacetaldehyde with ethyl 2-bromo-2-methylbutanoate (**9**) to give a mixture of the diastereoisomers of ethyl 2-ethyl-3-hydroxy-2-methyl-4,4-diphenylbutanoate (**10**). This secondary carbinol was dehydrated with thionyl chloride in pyridine to give β,γ-unsaturated ester **11**. That simple elimination had occurred without sketetal rearrangement was demonstrated by the nmr spectrum (note the Experimental Section) and interconversions with compounds of independently established structures (*vide infra*). Lith-

(5) H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969).

(6) (a) H. E. Zimmerman and A. C. Pratt, *J. Amer. Chem. Soc.*, **92**, 6259 (1970); (b) *ibid.*, **92**, 6267 (1970).

(7) H. E. Zimmerman and A. A. Baum, *J. Amer. Chem. Soc.*, **93**, 3646 (1971).

(8) H. E. Zimmerman, R. J. Boettcher, and W. Braig, *J. Amer. Chem. Soc.*, **95**, 2155 (1973).

(9) H. E. Zimmerman, P. Baeckstrom, T. Johnson, and D. Kurtz, *J. Amer. Chem. Soc.*, **96**, 1459 (1974).

(10) H. E. Zimmerman and Gary E. Samuelson, *J. Amer. Chem. Soc.*, **89**, 5971 (1967); *ibid.*, **91**, 5307 (1969).

(11) (a) H. E. Zimmerman and G. A. Epling, *J. Amer. Chem. Soc.*, **94**, 3647, 8749 (1972); (b) see also J. S. Swenton, *J. Amer. Chem. Soc.*, **92**, 1406 (1970).

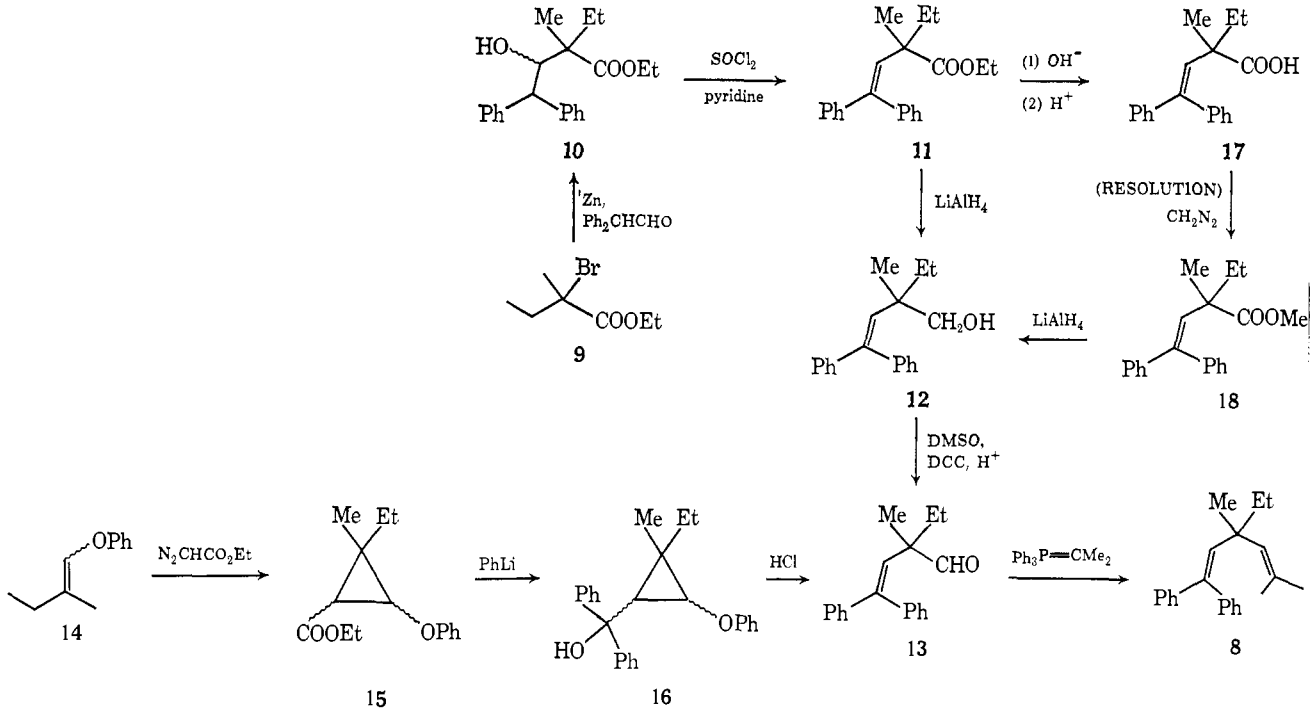
(12) H. E. Zimmerman, P. Hackett, D. F. Juers, J. M. McCall, and B.Schröder, *J. Amer. Chem. Soc.*, **93**, 3653 (1971).

(13) For a review of much of the di-π-methane rearrangement literature, see S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).

(14) The same stereochemistry is preferred in formally similar phenyl migrations of 4,4-diarylcyclohexenones: (a) H. E. Zimmerman and J. W. Wilson, *J. Amer. Chem. Soc.*, **86**, 4036 (1964); (b) H. E. Zimmerman and D. J. Sam, *ibid.*, **88**, 4114, 4905 (1966); (c) H. E. Zimmerman, R. D. Rieke, and J. R. Scheffer, *ibid.*, **89**, 2033 (1967); (d) H. E. Zimmerman and R. L. Morse, *ibid.*, **90**, 954 (1968); (e) H. E. Zimmerman and K. G. Hancock, *ibid.*, **90**, 3749 (1968).

(15) (a) P. S. Mariano and J. Ko, *J. Amer. Chem. Soc.*, **94**, 1766 (1972); (b) P. S. Mariano and R. B. Steitle, *ibid.*, **95**, 6114 (1973).

Chart III. Synthesis of Ethylmethyldiene **8**



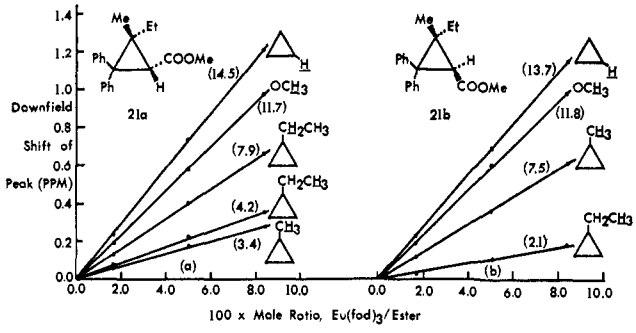


Figure 1. Plots of downfield shifts of nmr signals as functions of added $Eu(fod)_3$ for (a) *cis*- and (b) *trans*-cyclopropyl methyl esters (**21a** and **21b**). Numbers in parentheses are slopes in parts per million per mole ratio. Note Experimental Section for additional details.

ium aluminum hydride reduction of unsaturated ester **11** led to carbinol **12**. This was oxidized to the corresponding aldehyde **13** using Moffatt conditions.[16] Finally the desired ethylmethyldiene **8** was obtained by treatment of this aldehyde with isopropylidenetriphenylphosphorane.

This synthesis proved particularly useful when optically active diene was needed as discussed below. However, an alternative and more direct route began with reaction of 2-methyl-1-phenoxy-1-butene (**14**) with ethyl diazoacetate to give ethyl 2-ethyl-2-methyl-3-phenoxycyclopropanecarboxylate (**15**) followed by reaction of this compound with phenyllithium to afford tertiary carbinol **16**. Treatment of this with acid in the Julia variation[17a] of the 1,3-diol cleavage[17b] led nicely to aldehyde **13**. This aldehyde was identical with that obtained by the previously described route. The present synthesis can be seen to be shorter, but subsequent requirements for optically active material demanded use of the longer synthesis. Details of both syntheses are given in the Experimental Section.

Also needed were the potential photochemical products, namely *cis*- and *trans*-3-ethyl-3-methyl-2-(2′-methylpropenyl)-1,1-diphenylcyclopropane (**19a** and **19b**). These are expected on the basis of the reaction course and regiospecificity.[5,13,6a] This synthesis is outlined in Chart IV. It began with the reaction of diphenyldiazomethane with methyl 3-methyl-2-pentenoate which gave rise, after saponification, to the cis and trans isomers of 2-ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylic acid (**20a** and **20b**). Lithium aluminum hydride reduction of the methyl esters (**21a** and **21b**) led to the corresponding carbinols **22a** and **22b**. Sarett oxidation[18] gave the desired aldehydes **23a** and **23b** in excellent yield. Finally, reaction of each of these with isopropylidenetriphenylphosphorane gave the desired *cis*- and *trans*-vinylcyclopropanes **19a** and **19b**.

Assignment of cis and trans configurations to the two diastereomers was made on the basis of the nmr spectra. For the cyclopropyl acids (**20a** and **20b**), the corresponding aldehydes (**23a** and **23b**), and the methyl esters (**21a** and **21b**) the methyl group cis to the functional group was deshielded selectively and shifted downfield. Similarly the ethyl methylene was deshielded by the same groups. This interpretation was substantiated by use of a europium shift reagent ($Eu(fod)_3$).[19] A plot of the nmr absorptions *vs.* concentration of shift reagent is given in Figure 1 for the *cis*- and *trans*-methyl esters (**21a** and **21b**). It is seen that the nmr absorptions of the ring methyl of each isomer and of the methyl of the ethyl group are shifted downfield linearly with europium concentration. In each case the methyl group cis to the

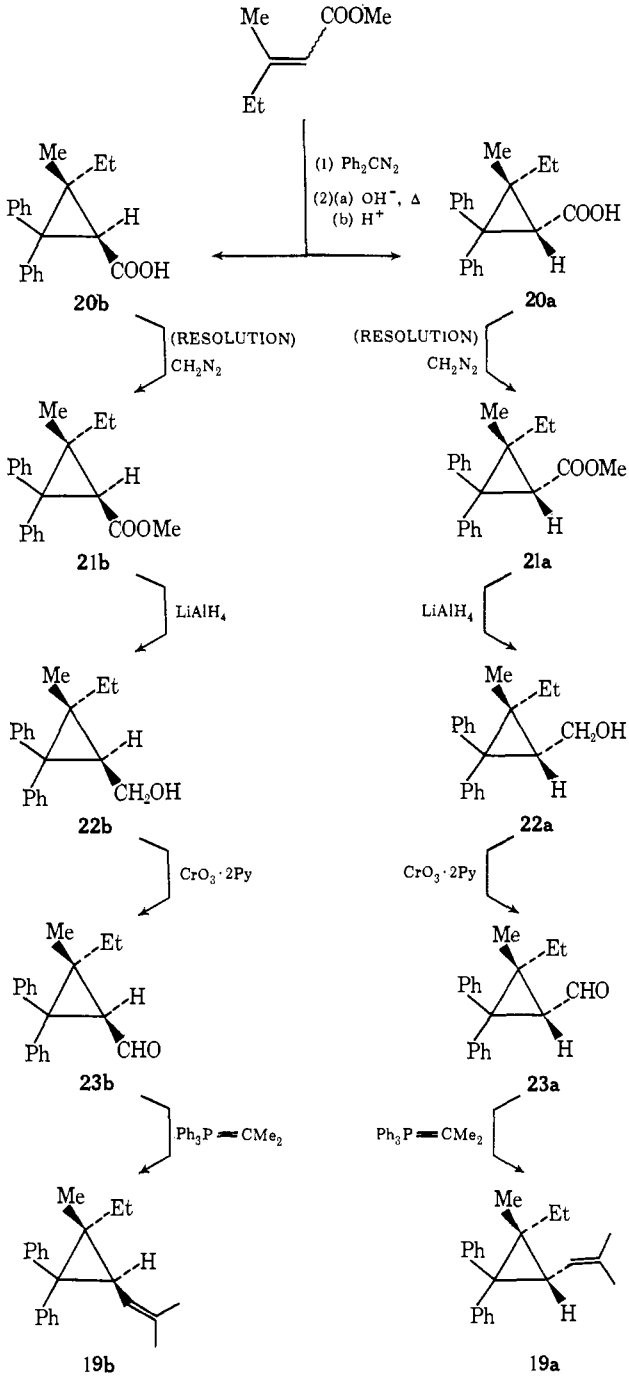
(16) K. E. Pfitzner and J. G. Moffatt, *J. Amer. Chem. Soc.*, 87, 5661, 5670 (1965).

(17) (a) M. Julia and M. Baillarge, *Bull. Soc. Chim. Fr.*, 734 (1966); (b) J. English, Jr., and F. V. Brutcher, *J. Amer. Chem. Soc.*, 74, 4279 (1952); H. E. Zimmerman and J. English, Jr., *J. Amer. Chem. Soc.*, 76, 2285, 2291, 2294 (1954).

(18) (a) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Amer. Chem. Soc.*, 75, 422 (1953); (b) K. E. Stensiö and C. A. Wachtmeister, *Acta Chem. Scand.*, 18, 1013 (1964).

(19) R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, 93, 1522 (1971).

Chart IV. Synthesis of Ethylmethylvinylcyclopropanes **19a** and **19b**[a]



[a] Only relative configurations are connoted.

carbonyl group is shifted much more strongly than the trans one.

Resolution of Di-π-methane Reactant and Vinylcyclopropane Products and Interrelation of Reactant and Product Configurations. With the photochemical reactant, *i.e.*, the ethylmethyldiene **8**, synthesized and the two potential photoproducts **19a** and **19b** prepared, attention was turned toward preparing each of these three compounds optically active and then interrelating their configurations at the ethylmethyl center (*i.e.*, the "methane carbon").

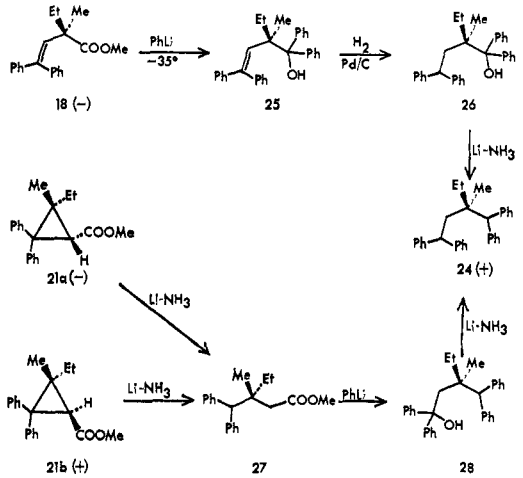
In the case of ethylmethyldiene **8**, resolution of carboxylic acid **17** was accomplished with cinchonidine. This acid was then employed in the synthetic scheme of Chart III.

For the trans isomer of photoproduct **19** (*i.e.*, **19b**), quinine resolution of acid **20b** was utilized. For the cis isomer of photoproduct (*i.e.*, **19a**), cinchonidine resolution of acid **20a** proved effective. The synthetic approaches to the optically active vinylcyclopropanes **19a** and **19b** were then identical with those discussed above except for the additional resolution steps (note Chart IV).

The ethylmethyldiene **8** enantiomer obtained had a negative rotation at 365 nm (67.5°). The *cis*-vinylcyclopropane **19a** had a negative rotation (286°) at the same wavelength. The *trans*-vinylcyclopropane **19b** had a positive rotation of +490° at 365 nm. The question was how the absolute configurations at the methane carbon (*i.e.*, the ethylmethyl center) in these three compounds were related, that is, whether they were all the same or instead one was enantiomeric with the other two.

To solve this question the relating scheme in Chart V

Chart V. Scheme Used for Interrelating Configurations at the Ethylmethyl Center[a]



[a] Configurations shown are relative.

was devised. The approach used converted one optically active synthetic intermediate from each of the three synthetic routes to a common compound. The reactions were designed to leave the ethylmethyl center undisturbed.

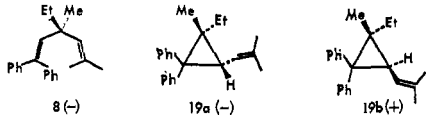
Thus, β,γ-unsaturated ester **18** (note Chart III) was the compound selected from the synthesis of ethylmethyldiene **8**. *cis*-Cyclopropyl methyl ester **21a** (note Chart IV) was the compound chosen from the synthetic route leading to *cis*-vinylcyclopropane **19a**. Finally, *trans*-cyclopropyl methyl ester **21b** (note Chart IV) was selected from the synthesis of *trans*-vinylcyclopropane. The correlation of each one of the three synthetic compounds with a single compound then allows one to determine relative configurations.

The scheme selected is given in Chart V. The correlation compound selected was 3-[diphenylmethyl]-3-methyl-1,1-diphenylpentane (**24**). Optically active (−)-**18** was converted to this relating compound (*i.e.*, **24**) by reaction with phenyllithium to give the unsaturated tertiary carbinol **25**, catalytic reduction of this to give saturated carbinol **26**, and then lithium–liquid ammonia conversion to the relating compound **24** which had a positive rotation of +16.5° at 365 nm. In similar fashion both the (−)-*cis*- and (+)-*trans*-cyclopropyl esters (*i.e.*, **21a** and **21b**, respectively) were converted to

relating compound with the same positive rotation of +16.5 ± 0.2°. Also, ethylmethyldiene **8** of rotation −67.5° was known to be derived synthetically from β,γ-unsaturated methyl ester **18** of rotation −102.5°, and similarly (−)-**21a** was a synthetic intermediate leading to (−)-*cis*-vinylcyclopropane of rotation −286° and (+)-**21b** led synthetically to (+)-*trans*-vinylcyclopropane of rotation +490°. In each case ORD curves and polarimetric rotations at five different wavelengths (note Experimental Section) confirmed the correlations and the absence of optically active impurities.

From this it could be concluded that (−)-ethylmethyldiene **8** has the same configuration at the methane carbon as (−)-*cis*-vinylcyclopropane **19a** and as (+)-*trans*-vinylcyclopropane **19b**; note Chart VI. All of

Chart VI



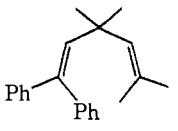
the configurational relationships are summarized in Table I.

Table I. Configurationally Related Compounds and Their Rotations (degrees)

Compd[a]	Specific rotations at 27° (λ, nm) 589	578	546	436	365
Ethylmethyldiene **8**	−8.1	−8.4	−10.4	−26.3	−67.5
β,γ-Unsaturated ester **18**	−19.6	−20.8	−24.4	−50.4	−102.5
cis-Vinylcyclopropane **19a**	−66.4	−69.8	−81.0	−155	−286
trans-Vinylcyclopropane **19b**	122	128	147	274	490
cis-Cyclopropyl methyl ester **21a**	−180	−188	−219	−423	−793
trans-Cyclopropyl methyl ester **21b**	200	210	243	456	827
Relating compound **24**	3.6	3.9	4.5	8.7	16.5

[a] These compounds all have the same configuration at the ethylmethyl center (see Charts III–V).

Photochemical Reaction Course and Quantum Yield Determinations. The photochemical reaction proved very similar to that of the dimethyl analog, 3,3,5-trimethyl-1,1-diphenyl-1,4-hexadiene (**29**), studied



29

previously.[6a] However, in the present case, two diastereomeric vinylcyclopropanes were observed as photoproducts. The ratio of cis to trans isomers was determined by nmr analysis as 4:5. The diastereomers were separated by recycling high-speed liquid chromatography (note Experimental Section). Their structures were consistent with the nmr spectra and were firmly established by comparison with authentic material synthesized as described above.

The quantum yields were determined using the Black Box apparatus described by us previously[20] and with ferrioxalate actinometry.[21] The total quantum yield was 0.11, and details are given in the Experimental Section.

Photolysis of Optically Active Ethylmethyldiene 8. Results. Ethylmethyl diene **8** was photolyzed in the Black Box apparatus under conditions similar to those described above for exploratory runs. Photolyses were made to 11 and 18% conversions in two runs. Under these conditions vinylcyclopropane products were absorbing less than 1% of the incident light. The mixture of vinylcyclopropanes, **19a** and **19b**, was isolated by silicic acid chromatography and then the cis and trans isomers were separated by repetitive recycling high-pressure liquid chromatography (note Experimental Section for details). After each set of cycles the separate fractions were subjected to monitoring of the optical rotation at five different wavelengths. When no further change was found, final rotations were taken and also ORD curves were measured to ascertain that only the desired vinylcyclopropane (*i.e.*, **19a** or **19b**) was present and contributing to the rotation.

The direction of rotations obtained in both cases corresponded to inversion of configuration at the ethylmethyl center (*i.e.*, the methane carbon) in formation of both *cis*- and *trans*-vinylcyclopropane products (**19a** and **19b**, respectively). The rotations after repeated recycling corresponded to 97.5% inversion in the case of the cis product (**19a**) and 98.0% in the case of trans product (**19b**). Experimentally, this corresponds to an apparent 5% racemization in the case of cis product and 4% for trans product. This proved to be somewhat beyond the experimental error of the polarimeter used (note Experimental Section). However, in a control experiment, recycling of optically active photoproduct on the same silicic acid column was found to lead to loss of optical activity increasingly with increased recycling, and the apparent racemization observed on the photoproduct appears to derive from such column decomposition. The net result then is inversion of configuration in the photochemical formation of both *cis*- and *trans*-vinylcyclopropanes **19a** and **19b**.

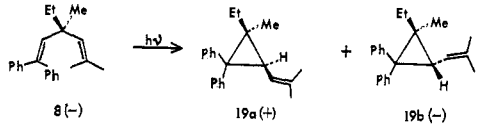
Interpretative Discussion. The first point to be made is that the present rearrangement is typical of the acyclic di-π-methane rearrangements. Thus the reaction is very similar to that observed earlier[6a] in the very close analog **29** having two central methyls in place of the present central ethyl and methyl substitution in diene **8**. The reaction efficiency is also typical; compare the present $\phi = 0.11$ and $\phi = 0.10$ in the case of the dimethyl analog **29**. Hence, the stereochemistry presently under study is generally relevant.

As noted above (see Chart **1**) the di-π-methane reaction stereochemistry at carbons 1 and 5 has been elucidated in our earlier studies. In the case of carbon-5 it was observed[6b] that cis substitution on the vinyl group remained cis on the π bond of the vinylcyclopropane product and that trans reactant similarly afforded *trans*-vinylcyclopropane. While it superficially

(20) H. E. Zimmerman, *Mol. Photochem.*, 3, 281 (1971).
(21) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., London*, 235, 518 (1956).

appears that the π bond of the reactant merely survives the rearrangement, the esoteric point has been made[13] that the double bond of product only appears to be the double bond of reactant (note Chart VII). In the case of carbon-1, again cis reactant gives cis product and trans reactant gives trans product in a stereospecific process. In this case, the stereochemistry of the double bond of reactant determines the configuration of a three-ring substituent of product. Relevant to C-1 stereochemistry,[9] it has been noted that the reaction course is not least motion controlled and that electronic factors are operating.

As discussed above in the introductory section, the one uncertainty in the stereochemistry of the di-π-methane rearrangement was the stereochemical course at carbon-3 (*i.e.*, the methane carbon). The reaction is now seen to proceed *via* inversion of configuration at this center as shown in eq 1.



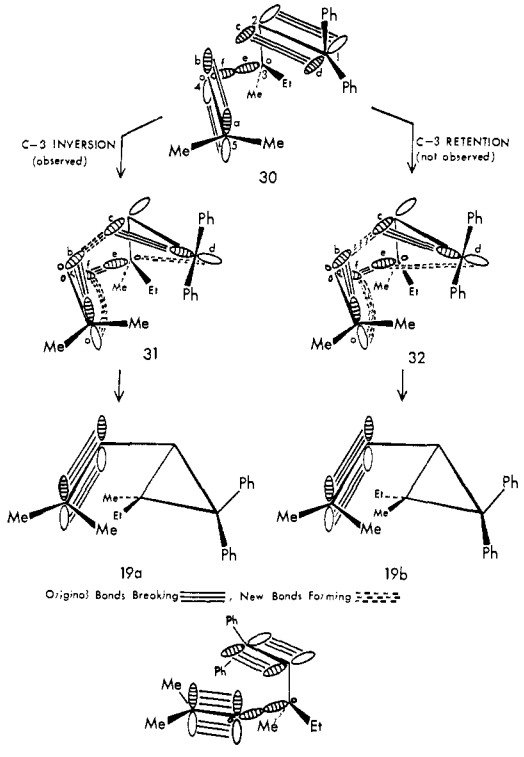
(1)

In our earlier discussions of the di-π-methane rearrangement, we have commented that valence bond type mechanisms as outlined in Chart I are especially useful in depicting the molecular structure at various points along the reaction coordinate. Also, the structures are useful in prediction of substituent effects and regiospecificity. Nevertheless, these resonance species are not to be taken as intermediates since it is not known that they correspond to energy minima. Instead they may merely represent points along the reaction hypersurface. The reaction stereospecificity suggests concertedness, and it is probable in most cases that the valence bond species represent slight depressions, at most, in the energy surface.

An equivalent picture of the reaction is given by following the change in basis orbitals as the reaction proceeds. It has been noted[5–7,9,13] that the reaction does involve a cyclic array of six local orbitals and that this array is of the type shown in Chart VII. Hitherto, it was necessary to assume the reaction stereochemistry at carbon-3. Presently, Chart VII shows the two alternative reaction stereochemistries at this center. The stereochemistry at C-1 and at C-5 depicted is that established by our earlier studies.[6b,9,13] The C-3 inversion process in this chart is seen to involve a Möbius cyclic array of orbitals, since there is an odd number of sign inversions between pairs of orbitals (between orbitals a and f in the arbitrary choice of basis set orbitals in Chart VII). With six delocalized electrons, a Möbius array affords a ground state forbidden but excited state allowed transition state. Conversely, the C-3 retention mechanism is seen to have a Hückel array since there is an even number of sign inversions (one between a and f and one between d and e); we note that one could choose a different set of basis orbitals oriented with plus and minus signs so that zero inversions would result, but the conclusion is invariant to the choice. Hückel arrays with six electrons are excited state forbidden.

It should be noted that the conformer (**30**) of ethylmethyldiene shown in Chart VII as the reactant is really just one of two U-shaped geometries. The

Chart VII. Basis Orbital Array and Reaction Stereochemistry



alternative conformer for ethylmethyldiene

alternative one is labeled **30′** in Chart VII. Given one enantiomer of ethylmethyldiene (*e.g.*, the one shown in Chart VII) one will obtain the *cis*-vinylcyclopropane **19a** starting from conformer **30** and using the inversion route while one obtains the *trans*-vinylcyclopropane **19b** from conformer **30′** and the same inversion mechanism. But the configuration at C-3 (the ethylmethyl center) is the same in the vinylcyclopropane product obtained from the two routes. Additionally, one can envisage s-transoid conformations of ethylmethyldiene **8** as the species leading to vinyl–vinyl bridging, but again this does not change the configurational result at C-3.

We therefore have found that the observed inversion stereochemistry is that which the Möbius–Hückel analysis[22] would predict. Alternatively, we could term the reaction as ${}_{\sigma}2_a + {}_{\pi}2_a + {}_{\pi}2_a$ which is more favorable[23] than the alternative ${}_{\sigma}2_s + {}_{\pi}2_a + {}_{\pi}2_a$. However, this treatment is identical with ours since a system with an odd number of antarafacial components will also have an odd number of sign inversions and be Möbius and conversely systems with an even (or zero) number of antarafacial components will be Hückel.

In conclusion, we note that the di-π-methane rearrangement is not only one of the most general of photochemical reactions but also is one where mechanistic understanding has proven quite attainable in the 8 years following our first description of the reaction.

Experimental Section[24]

***cis*- and *trans*-2-Methyl-1-phenoxy-1-butene.** Phenyllithium

(22) (a) H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1564 (1966); (b) *Accounts Chem. Res.*, **4**, 272 (1971).

(23) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(24) Except where otherwise indicated melting points were taken on a hot-stage apparatus calibrated with known compounds. Capillary melting points were determined on a calibrated oil bath apparatus.

(100 ml, 1.08 *M* in ether) was added over 20 min to a stirred suspension of 38.5 g (0.095 mol) of phenoxymethyltriphenylphosphonium chloride[25] in 200 ml of anhydrous ether under nitrogen. After 20 min more stirring 11.4 ml (9.15 g, 0.127 mol) of ethyl methyl ketone was added over 30 min, and the mixture was stirred for 16 hr. The ether was distilled and 200 ml of hexane was added. The suspension was filtered through Celite, water washed, dried, concentrated, and distilled to give 7.84 g (51%) of *cis*- and *trans*-2-methyl-1-phenoxy-1-butene, bp 81–84° (6 Torr). The spectral data were: ir (neat) 3.29, 3.37, 3.42, 3.48, 5.96, 6.29, 6.72, 6.88, 7.26, 7.78, 8.15, 8.59, 8.92, 9.34, 10.04, 11.32, 12.30, 13.34, 14.52 μ; nmr (neat) τ 2.60–3.30 (m, 5 H, arom), 3.75–3.99 (m, 1 H, vinyl), 7.56–8.36 (sextet from two overlapping q, 2 H, J = 8 Hz, *cis*- and *trans*-CH_2), 8.31 and 8.43 (two d, 3 H, J = 1.5 Hz, *cis*- and *trans*-CH_3), 9.03 (t, 3 H, J = 8 Hz, CH_2CH_3). Equal intensities of the methyl doublets indicated the cis : trans ratio to be *ca.* 1.

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.33; H, 8.76.

Ethyl 2-Ethyl-2-methyl-3-phenoxycyclopropanecarboxylate. To a stirred 150° suspension of 400 mg of copper–bronze (99.9%) copper) in 30.15 g (0.075 mol) of *cis*- and *trans*-2-methyl-1-phenoxy-1-butene under nitrogen was added, over 6 hr, 23.0 ml (21.2 g, 0.186 mol) of ethyl diazoacetate. Heating was continued for 1.5 hr. The mixture was diluted with ether, filtered, concentrated, and distilled to give 21.2 g (65.1%) of ethyl 2-ethyl-2-methyl-3-phenoxycyclopropanecarboxylate (mixture of isomers), bp 103–110° (0.4 Torr). The spectral data were: ir (neat) 3.39, 3.44, 3.50, 5.85 (C=O), 6.28, 6.33, 6.72, 6.90, 7.05, 7.34, 7.52, 7.75, 8.13, 8.62, 9.14, 9.60, 9.82, 10.70, 11.36, 12.05, 12.35, 13.33, 14.52 μ; nmr (neat) τ 2.60–3.33 (m, 5 H, arom), 5.67–6.45 (m, 3 H, ester CH_2 and $PhOCH$), 8.00–9.33 (complex m, 12 H, aliphatic).

Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.76; H, 8.19.

2-Ethyl-2-methyl-4,4-diphenyl-3-butenal from Ethyl 2-Ethyl-2-methyl-3-phenoxycyclopropanecarboxylate. The following is an application of Julia's method[17a] for the preparation of α,α-disubstituted-β,γ-unsaturated aldehydes. A solution of 5.86 g (0.024 mol) of ethyl 2-ethyl-2-methyl-3-phenoxycyclopropanecarboxylate in 20 ml of ether was added dropwise to a stirred solution of phenyllithium (100 ml, *ca.* 1.3 *M* in ether) under nitrogen during 10 min. The mixture was then stirred for 15 hr at room temperature. Ethanol was added followed by water. The solution was diluted with ether and the ether layer was water washed, dried, and concentrated. The crude tertiary alcohol was dissolved in 25 ml of acetone and a mixture of 6 ml of water, 12 ml of concentrated hydrochloric acid, and 36 ml of acetone was added. The mixture was stirred for 1.5 hr at room temperature, then diluted with 100 ml of ether, and washed with saturated sodium chloride solution, 5% sodium hydroxide solution, and water. The concentrated solution was chromatographed on a 5 × 67 cm silicic acid (Mallinckrodt cc-7, 100–200 mesh) column slurry packed in 1.25% ether in hexane; 500 ml fractions were taken: fraction 1, 1.25% ether in hexane, nil; fractions 2 and 3, 1.25% ether in hexane, 1.57 g of biphenyl; fractions 4–6, 1.25% ether in hexane, nil; fractions 7 and 8, 2.5% ether in hexane, nil; fractions 9–11, 2.5% ether in hexane, 4.37 g (69.0%) of 2-ethyl-2-methyl-4,4-diphenyl-3-butenal. The spectral data were: ir (neat) 3.28, 3.32, 3.37, 3.42, 3.49, 3.72, 5.82 (C=O), 6.29, 6.72, 6.94, 7.26, 9.34, 9.73, 10.04, 11.70, 13.25, 13.85, 14.40 μ; nmr (CCl_4) τ 0.92 (s, 1 H, CHO), 2.69–3.10 (m, 10 H, arom), 4.03 (s, 1 H, vinyl), 8.57 (br q, 2 H, J = 7.5 Hz, CH_2), 8.98 (s, 3 H, CH_3), 9.15 (t, 3 H, J = 7.5 Hz, CH_2CH_3).

Anal. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.19; H, 7.80.

2-Methylbutanoic Acid. The procedure described[26a] for 2-methyldodecanoic acid was followed. From 414 g (2.20 mol) of diethyl ethylmalonate, 48.3 g (2.08 g-atom) of sodium, 1.4 l. of ethanol, and 283.8 g (2.0 mol) of methyl iodide was obtained 149.9 g (73%) of the desired acid as a colorless oil, bp 94° (34 Torr) (lit.[26b] 173° (760 Torr)).

Ethyl 2-Bromo-2-methylbutanoate. The Hell–Volhard–Zelinsky bromination alluded to by Ray[27] was initiated by slowly adding 293 g (1.84 mol) of anhydrous bromine to a stirred solution of 99.8 g (0.975 mol) of 2-methylbutanoic acid and 251 g (0.926 mol) of phosphorus tribromide. After half the bromine was added, the solution became dark and gas evolution slowed; the remaining bromine was added more rapidly. After 1 hr at 75° an additional 44 g (0.276 mol) of bromine was added and the temperature maintained as the red solution was stirred overnight. Absolute ethanol (300 ml, 236 g, 5.13 mol) was added slowly and the solution refluxed for 1 hr, cooled, and poured into 600 ml of ice–water containing 6.0 g of sodium sulfite. The mixture was hexane extracted and the extracts were washed with dilute aqueous sodium sulfite, water washed, dried, concentrated *in vacuo*, and distilled to give 184 g (90%) of the desired bromo ester as a colorless liquid, bp 83° (26 Torr) (lit.[27] 75–80° (25 Torr)). Nmr and ir spectral data confirmed the product identity.

Ethyl 2-Ethyl-3-hydroxy-2-methyl-4,4-diphenylbutanoate. Zinc dust (35 g) was activated by stirring for 15 min with 10% hydrochloric acid, washing with absolute ethanol and benzene, and drying by benzene distillation. To the zinc and 50 ml of anhydrous benzene was added, dropwise under nitrogen, a solution of 75.0 g (0.357 mol) of ethyl 2-bromo-2-methylbutanoate, 67.1 g (0.342 mol) of diphenylacetaldehyde, and 50 ml of anhydrous benzene. Addition was stopped at 10 ml and the reaction mixture was heated to gentle reflux with vigorous stirring; an exothermic reaction began after *ca.* 10 min. The remainder of the reactants were then added dropwise at a rate to maintain very rapid refluxing. Refluxing was continued for 3 hr after the exothermic reaction had subsided. To the resulting green slurry, kept at 0°, was added, over 1 hr with stirring, 200 ml of 10% sulfuric acid. Then 100 ml of ether was added, stirring was continued for 3 hr at 0°, the phases were separated, and the organic phase was washed with 100-ml portions of 10% sulfuric acid until 5% aqueous sodium carbonate wash produced no gray precipitate. The organic layer was dried, concentrated *in vacuo*, and carefully distilled through a 6-cm Vigreaux column to give a 69.5-g (62%) fraction of colorless oil, bp 147.5–149.5° (0.07 Torr), that was the desired hydroxy ester by nmr.

The spectral data were: ir (neat) 2.8 (OH), 3.23–3.47 (CH), 5.82 (C=O), 6.25, 6.69, 6.88, 7.22, 8.10, 8.7, 9.2, 9.7, 11.63 (w), 13.47, 14.25 μ; nmr ($CDCl_3$) τ 2.48–2.94 (m, 10 H, arom), τ_{A_1} 5.41, τ_{A_2} 5.65, τ_{B_2} 5.84, τ_{B_1} 5.92 (two AB q, 2 H, $J_{A_1B_1}$ = 7 Hz, $J_{A_2B_2}$ = 4 Hz, $Ph_2CHCHOH$), 6.2–6.62 (m, 2 H, OCH_2CH_3), 7.18 (br s, 1 H, OH), 8.0–8.5 (m, 2 H, CCH_2CH_3), 8.83 and 8.85 (two s, 3 H, CH_3), 8.99 (t, 3 H, J = 7 Hz, OCH_2CH_3), 9.22 and 9.24 (two t, 3 H, J = 7 Hz for both, CCH_2CH_3). The complexity of the nmr indicated that the product was composed of diastereomers.

Anal. Calcd for $C_{21}H_{22}O_3$: C, 77.27; H, 8.03. Found: C, 77.22; H, 8.17.

Ethyl 2-Ethyl-2-methyl-4,4-diphenyl-3-butenoate. To a stirred, room temperature solution of 31.18 g (0.0955 mol) of ethyl 2-ethyl-3-hydroxy-2-methyl-4,4-diphenylbutanoate in 175 ml of dry pyridine was added, dropwise, 18.2 g (0.153 mol) of thionyl chloride. The reaction mixture was then stirred under nitrogen for 2.5 hr at 65°. The resulting brown-black solution was poured into 500 ml of ice–water, 250 ml of hexane added, and the aqueous layer ether extracted. The combined organic phase was washed with 2 *N* hydrochloric acid, water washed, dried, and concentrated *in vacuo* to give 32.2 g of light orange oil (*ca.* 30% desired unsaturated ester by nmr). The crude product was vacuum distilled through a 6-cm Vigreaux column to give: 6.28 g of green oil (*ca.* 70% desired ester by nmr), bp 134–150.5° (0.17 Torr); 6.59 g of light yellow oil (*ca.* 70% desired ester by nmr), bp 150.5–160° (0.15–0.20 Torr); and 11.23 g of yellow oil (*ca.* 25% desired ester by nmr), bp 160–167° (0.20–0.31 Torr). The first two fractions were combined and crystallized from 95% ethanol to give 8.324 g (27.4%) of colorless needles, mp 60.5–78°. Recrystallization did not improve the melting point range. Similar unusual melting point behavior was found for methyl *cis*-2-ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylate (see below).

The spectral data were: ir (CCl_4) 3.24, 3.27, 3.31, 3.36, 3.41, 3.48, 5.80 (C=O), 6.27, 6.71, 6.88, 6.92, 7.24, 7.51, 7.69, 8.15, 8.32, 8.77, 8.86, 9.32, 9.50, 9.71, 11.17, 14.38 μ; nmr (CCl_4) τ 2.67–3.10 (m, 10 H, arom), 3.97 (s, 1 H, vinyl), 6.27 (q, 2 H, J = 7 Hz, OCH_2CH_3), 8.02–8.55 (m, 2 H, CCH_2CH_3), 8.88 (s, 3 H, CH_3), 8.90 (t, 3 H, J = 7 Hz, OCH_2CH_3), and 9.15 (t, 3 H, J = 7 Hz, CCH_2CH_3).

Anal. Calcd for $C_{21}H_{24}O_2$: C, 81.78; H, 7.84. Found: C, 81.55; H, 7.95.

2-Ethyl-2-methyl-4,4-diphenyl-3-butenoic Acid. A solution of 2.050 g (6.65 mmol) of ethyl 2-ethyl-2-methyl-4,4-diphenyl-3-butenoate and 8.70 g (155 mmol) of potassium hydroxide in 60 ml of 95% ethanol was refluxed for 6.0 hr. The reaction mixture was then concentrated *in vacuo* to *ca.* 30 ml and poured into a mixture of 25 ml of hexane, 25 ml of ether, and 50 ml of 5% potassium hy-

(25) G. Wittig, W. Boll, and K. Krück, *Chem. Ber.*, **95**, 2514 (1962).

(26) (a) C. F. Allen and M. J. Kalm, "Organic Syntheses," Collect. Vol. 4, Wiley, New York, N. Y., 1963, p 618; (b) M. Conrad and C. A. Bischoff, *Chem. Ber.*, **13**, 595 (1880).

(27) F. E. Ray, *J. Amer. Chem. Soc.*, **50**, 561 (1928).

droxide. The combined aqueous extracts were acidified to Congo Red with concentrated sulfuric acid and ether extracted. These extracts were water washed, dried, and concentrated *in vacuo* to give 1.93 g (100%) of the desired acid as a clear colorless oil that crystallized after long standing. Recrystallization from pentane gave 1.50 g of colorless crystals, mp 63.5–65.5°.

The spectral data were: ir (neat) 2.90–4.40 (COOH), 5.90 (C=O), 6.26, 6.71, 6.92, 7.12, 7.22, 7.65, 7.98, 8.75, 9.32, 9.72, 12.79, 13.24, 13.80, 14.34 μ; nmr (CCl_4) τ −1.83 (s, 1 H, COOH), 2.72 (m, 10 H, arom), 3.69 (s, 1 H, vinyl), 8.24 (br q, 2 H, J = 7 Hz, CH_2), 8.85 (s, 3 H, CH_3), 9.06 (t, 3 H, J = 7 Hz, CH_2CH_3).

Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.15; H, 7.12.

Methyl 2-Ethyl-2-methyl-4,4-diphenyl-3-butenoate. A solution of 1.93 g (6.79 mmol) of 2-ethyl-2-methyl-4,4-diphenyl-3-butenoic acid in 25 ml of ether was added dropwise to 100 ml of stirred, ice-cold ethereal diazomethane (*ca.* 13 mmol). After 15 min at 0°, excess diazomethane was removed in a nitrogen stream, and the reaction mixture was concentrated *in vacuo* to give 1.945 g of colorless oil. This was chromatographed on a 4.0 × 63 cm column of silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) slurry packed in 0.25% ether in hexane. Elution was with 2 l. of 0.25% ether in hexane, 9 l. of 0.5% ether in hexane, and 2 l. of 1.0% ether in hexane; 500 ml fractions were collected. The product, 1.78 g (89%) of colorless oil that crystallized, mp 44–46.5°, when taken up in a little hexane and chilled to Dry Ice temperature, was found in fractions 13 to 23. Recrystallization from methanol gave 1.14 g of white needles, mp 45–47°.

The spectral data were: nmr (CCl_4) τ 2.59–3.01 (m, 10 H, arom), 3.97 (s, 1 H, vinyl), 6.72 (s, 3 H, OCH_3), 8.29 (m, 2 H, CH_2), 8.83 (s, 3 H, CH_3), 9.15 (t, 3 H, J = 7 Hz, CH_2CH_3); ir (CCl_4) 3.25, 3.28, 3.31, 3.37, 3.40, 3.48, 3.52, 5.78 (C=O), 6.25, 6.71, 6.87, 6.94, 6.97, 7.14, 7.53, 7.67, 8.13, 8.19, 8.74, 8.83, 9.33, 9.50, 9.73, 10.17, 11.43, 14.4 μ.

Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.84; H, 7.36.

2-Ethyl-2-methyl-4,4-diphenyl-3-buten-1-ol from Methyl 2-Ethyl-2-methyl-4,4-diphenyl-3-butenoate. A 0.44 *M* clarified solution of lithium aluminum hydride was prepared and standardized according to Brown,[28] and 14.1 ml (6.2 mmol) of it was cooled to 0° under nitrogen.[29] To it was added, with stirring, a solution of 1.525 g (5.17 mmol) of methyl 2-ethyl-2-methyl-4,4-diphenyl-3-butenoate in 15 ml of anhydrous ether. After 10 min excess lithium aluminum hydride was destroyed by dropwise addition of 20% ethanol in ether. The reaction mixture was then diluted with 50 ml of ether and extracted with 6 *N* HCl, water, 5% aqueous sodium bicarbonate, and water again. Drying the organic phase and concentrating it *in vacuo* gave 1.427 g of oil.

The crude product was chromatographed on a 4.6 × 76 cm silica gel column (Grace, grade 950) slurry packed in 20% ether in hexane. Elution was with 500 ml of 20% ether in hexane and 9 l. of 30% ether in hexane; 500-ml fractions were collected. The 1.355 g (98%) of clear colorless oil found in fractions 8–19 was the desired alcohol.

The spectral data were: ir (neat) 2.96 (OH), 3.26, 3.30, 3.36, 3.41, 3.47, 6.27, 6.71, 6.94, 7.28, 9.35 (sh), 9.75, 10.00, 13.18, 13.85, 14.40 μ; nmr (CCl_4) τ 2.65 (s, 5 H, phenyl), 2.91 (s, 5 H, phenyl), 4.17 (s, 1 H, vinyl), 6.80 (s, 2 H, CH_2O), 8.32 (br s, 1 H, OH), 8.48–9.33 (A_2B_3, 5 H, τ_A 8.75, τ_B 9.15, J_{AB} = 8 Hz, CH_2CH_3), 9.26 (s, 3 H, CH_3).

Anal. Calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.33. Found: C, 85.75; H, 8.61.

2-Ethyl-2-methyl-4,4-diphenyl-3-buten-1-ol from Ethyl 2-Ethyl-2-methyl-4,4-diphenyl-3-butenoate. A solution of 424 mg (1.38 mmol) of ethyl 2-ethyl-2-methyl-4,4-diphenyl-3-butenoate in 15 ml of anhydrous ether was added dropwise to a refluxing suspension of 235 mg (6.19 mmol) of lithium aluminum hydride in 18 ml of anhydrous ether, and the mixture was refluxed for 1.5 hr more. After addition of water and ether, the organic phase was extracted with 6 *N* hydrochloric acid, washed with 5% aqueous sodium carbonate, water washed, dried, and concentrated *in vacuo* to give 345 mg (94%) of 2-ethyl-2-methyl-4,4-diphenyl-3-buten-1-ol. The product had ir and nmr spectra identical with those of the alcohol prepared from the methyl ester.

2-Ethyl-2-methyl-4,4-diphenyl-3-butenal from 2-Ethyl-2-methyl-4,4-diphenyl-3-buten-1-ol. To a stirred solution of 250.1 mg (0.941 mmol) of 2-ethyl-2-methyl-4,4-diphenyl-3-buten-1-ol in 5.0 ml of benzene under nitrogen were added 2.20 g (28 mmol) of anhydrous dimethyl sulfoxide, 995 mg (4.83 mmol) of dicyclohexylcarbodiimide, 74.5 mg (0.941 mmol) of pyridine, and, finally, 53.6 mg (0.471 mmol) of trifluoroacetic acid.[16] The progress of the reaction was followed by tlc on silical gel; the alcohol was completely consumed after 5.5 hr at room temperature. After dilution of the reaction mixture with 15 ml of ether, excess DCC was destroyed by adding, dropwise, 836 mg (6.64 mmol) of oxalic acid dihydrate in 5.0 ml of methanol, and stirring was continued for 0.5 hr. The insoluble dicyclohexylurea by-product was filtered and the filtrate washed with 5% aqueous sodium bicarbonate, water washed, dried, and concentrated *in vacuo* to give 296 mg of oil.

The crude product mixture was chromatographed on a 2.5 × 70 cm silicic acid (Mallinckrodt SilicAR cc-7, 100–200 mesh) column slurry packed and eluted with 1% ether in hexane; 250-ml fractions were collected. The 214.3 mg (86%) of colorless oil found in fractions 10–15 was the desired product; it had ir and nmr spectral properties identical with those of the independently synthesized material. The aldehyde appeared to be quite light sensitive.

3-Ethyl-3,5-dimethyl-1,1-diphenyl-1,4-hexadiene. To a suspension of 8.20 g (19 mmol) of isopropyltriphenylphosphonium iodide[30] in 100 ml of hexane under nitrogen was added 8.00 ml of 2.0 *M* *n*-butyllithium in hexane (16.0 mmol), and the mixture was refluxed for 2 hr. After cooling 4.43 g (16.8 mmol) of 2-ethyl-2-methyl-4,4-diphenyl-3-butenal in 5.0 ml of dry hexane was added dropwise, then the mixture was refluxed for 50 min and stirred at room temperature for 16 hr. The mixture was filtered through Celite and the filtrate was concentrated and passed through a 4.5 × 30 cm alumina column (Fisher Scientific, A-540, 80–200 mesh) slurry packed in hexane. Elution with 1000 ml of 5% ether in hexane gave 1.60 g (33%) of 3-ethyl-3,5-dimethyl-1,1-diphenyl-1,4-hexadiene as a colorless oil. The spectral data were: ir (neat) 3.27, 3.32, 3.38, 3.43, 6.28, 6.72, 6.95, 7.30, 9.35, 9.75, 13.25, 14.35 μ; nmr (CCl_4) τ 2.67–3.10 (m, 10 H, arom), 3.90 (s, 1 H, $Ph_2C=CH$), 4.97–5.16 (m, 1 H, $Me_2C=CH$), 8.33 (d, 3 H, J = 1 Hz, vinyl-CH_3), 8.48 (d, 3 H, J = 1.5 Hz, vinyl-CH_3), 8.40–8.75 (m, 2 H, CH_2), 9.00 (s, 3 H, CH_3), 9.13 (t, 3 H, J = 7.5 Hz, CH_2CH_3); uv λ_{max} (95% ethanol) 249 (ϵ 13,000).

Anal. Calcd for $C_{22}H_{26}$: C, 90.98; H, 9.02. Found: C, 91.13; H, 8.89.

2-Ethyl-2-methyl-1,1,4,4-tetraphenyl-3-buten-1-ol. Ethyl 2-ethyl-2-methyl-4,4-diphenyl-3-butenoate (0.9888 g, 3.73 mmol) in 10 ml of ether was added over 10 min to 9.34 mmol of phenyllithium in 23.0 ml of stirred anhydrous ether at −40° under nitrogen. After 10 min at −35°, 17 ml of 10% aqueous ammonium chloride was added quickly, and the resulting slurry was poured into 120 ml of ether and 80 ml of 10% aqueous ammonium chloride. The ether layer was water washed, dried, and concentrated *in vacuo* to give 1.239 g of viscous oil. This material was chromatographed on a 2.8 × 42 cm alumina column (Fisher Scientific, A-540, 80–200 mesh) slurry packed in 10% ether in hexane. Elution in 250-ml fractions gave: fractions 1 and 2, 10% ether in hexane, 0.0277 g, biphenyl; fraction 3, 10% ether in hexane, nil; fractions 4–6, 10% ether in hexane, 0.0708 g, starting material; fractions 7–9, 10% ether in hexane, nil; fractions 10–12, 20% ether in hexane, nil; fractions 13–24, 20% ether in hexane, 0.8886 g (57%), desired product; fractions 25 and 26, 20% ether in hexane, nil. Crystallization from hexane–ether gave 0.6487 g of colorless crystals, mp 111–112°. The spectral data were: ir (CCl_4) 2.74 (OH), 3.23–3.46 (CH), 5.12 (w), 5.30 (w), 5.52 (w), 6.01 (w), 6.25, 6.71, 6.92, 7.25, 7.55, 7.68, 7.82, 8.4 (w), 8.68, 8.95, 9.3, 9.7, 9.9, 10.65 (w), 11.17, 14.4, 15.25, 15.78 μ; nmr (CCl_4) τ 2.22–3.1 (m, 20 H, arom), 3.79 (s, 1 H, vinyl), 7.83 (s, 1 H, OH), 8.35 (br q, 2 H, J = 7 Hz, CH_2), 9.17 (t, 3 H, J = 7 Hz, CH_2CH_3), 9.29 (s, 3 H, CH_3).

Anal. Calcd for $C_{31}H_{30}O$: C, 88.95; H, 7.22. Found: C, 89.07; H, 7.10.

2-Ethyl-2-methyl-1,1,4,4-tetraphenyl-1-butanol. A stirred suspension of 123 mg of 10% Pd-C in 30 ml of absolute ethanol was equilibrated with hydrogen in a standard atmospheric hydrogenation apparatus. To it was added a solution of 201.3 mg (0.481 mmol) of 2-ethyl-2-methyl-1,1,4,4-tetraphenyl-3-buten-1-ol in 14 ml of absolute ethanol. When hydrogen uptake ceased 9.2 hr later, the reaction mixture was filtered through Celite and concentrated *in vacuo* to give 192.6 mg of nearly colorless oil. This was chro-

(28) W. G. Brown, *Org. React.*, **6**, 649 (1951).

(29) It was found that appreciable double bond reduction can occur under harsher conditions.

(30) G. Wittig and D. Wittenberg, *Justus Liebigs Ann. Chem.*, **606**, 1 (1957).

matographed on a 2.2 × 78 cm alumina column (Fisher Scientific, A-540, 80–200 mesh) slurry packed in 8% ether in hexane. Elution in 250 ml fractions gave: fractions 1–14, 10% ether in hexane, 13.8 mg of oil, uncharacterized; fractions 15–22, 15% ether in hexane, 180.3 mg (89%) of the desired alcohol as a colorless oil (pure by nmr) that began to crystallize after long standing. Recrystallization from hexane gave a sample, mp 79–81°, of analytical purity. The spectral data were: nmr (CCl_4) τ 2.4–3.2 (m, 20 H, arom), 5.97 (t, 1 H, J = 6 Hz, Ph_2CHCH_2), 7.48 (d, 2 H, J = 6 Hz, Ph_2CHCH_2), 7.94 (br s, 1 H, OH), 8.35 (m, 2 H, CH_2CH_3), 9.00 (s, 3 H, CH_3), 9.22 (t, 3 H, J = 7.5 Hz, CH_2CH_3); ir (CCl_4) 2.77, 2.82, 3.25, 3.27, 3.31, 3.37, 3.40, 3.48, 5.14 (w), 5.35 (w), 5.56 (w), 5.81 (w), 6.25, 6.71, 6.92, 7.25, 7.57, 7.73, 8.68, 9.29, 9.71, 10.02, 10.6 (w), 11.1, 14.3, 15.8 μ.

Anal. Calcd for $C_{31}H_{32}O$: C, 88.53; H, 7.67. Found: C, 88.50; H, 7.74.

3-Diphenylmethyl-3-methyl-1,1-diphenylpentane from 2-Ethyl-2-methyl-1,1,4,4-tetraphenyl-1-butanol. A solution of 122.7 mg (0.292 mmol) of 2-ethyl-2-methyl-1,1,4,4-tetraphenyl-1-butanol in 7.0 ml of anhydrous ether was added dropwise to a stirred, refluxing solution of 13.9 mg (2.00 mg-atoms) of lithium in 50 ml of anhydrous liquid ammonia. The mixture was stirred at reflux, under nitrogen, for 0.8 hr. Then the reaction was quenched with *ca.* 200 mg of ammonium chloride, the ammonia was allowed to distill, and the residue was taken up in ether and water. The organic layer was water washed, dried, and concentrated *in vacuo* to give 108.9 mg of colorless oil.

The crude product mixture was chromatographed on a 2.0 × 84 cm silica gel column (Matheson Coleman and Bell, SX144-5 L1194, 60–200 mesh) slurry packed in hexane. Elution in 250-ml fractions gave: fractions 1–8, hexane, nil; fractions 9–12, 1% benzene in hexane, nil; fractions 13–14, 2% benzene in hexane, nil; fractions 15 and 16, 4% benzene in hexane, nil; fractions 17 and 18, 8% benzene in hexane, nil; fractions 19–24, 10% benzene in hexane, nil; fractions 25–28, 15% benzene in hexane, 6.5 mg of oil, uncharacterized; fractions 29–33, 30% benzene in hexane, 89.8 mg (76%) of the desired tetraphenylalkane (pure by nmr) as a colorless oil. Crystallization of the product was induced by taking it up in methanol–benzene and chilling. Recrystallization from 95% ethanol to a constant melting point afforded 24.4 mg of colorless needles, mp 79.5–81.5°. The physical properties of the product were identical with those of the compound prepared by an independent synthetic route (*vide infra*).

Methyl 3-Methyl-2-pentenoate.[31a] The following is an application of the general procedure of Wadsworth and Emmons.[31b] To 1500 ml of anhydrous dimethylformamide was added 39.2 g of a dispersion of 56.8% sodium hydride in mineral oil (0.926 mol), and the mixture was stirred under nitrogen. Dropwise addition of 173.4 g (0.951 mol) of trimethyl phosphonoacetate followed; occasional cooling kept the temperature below 40° during the addition. Upon cessation of hydrogen evolution and cooling to room temperature, 66.8 g (0.926 mmol) of anhydrous ethyl methyl ketone was added dropwise. The reaction mixture was stirred at room temperature for 24, hr then poured into 8 l. of water and pentane extracted. The extracts were water washed, dried, and concentrated to *ca.* 200 ml with a 30-cm Vigreaux column. Distillation of the concentrate afforded 100.8 g (85%) of colorless liquid, bp 75–78° (45 Torr) (lit.[32] 74–79° (50 Torr)), which was shown by nmr to be a *ca.* 3:1 mixture of the trans and cis isomers.

Distillation of the product on a 100-cm helipak column provided samples of the pure cis, bp 148–150° (lit.[32] 151°), and trans, bp 155–156° (lit.[32] 160°), isomers. The nmr spectra agreed with the literature.[32]

***cis*- and *trans*-2-Ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylic Acids.** In a round-bottomed flask washed with dichromate cleaning solution, rinsed with distilled water, and dried[33] was prepared a (deep reddish-purple) solution of 46.2 g (0.238 mol) of diphenyldiazomethane[34] in 183.1 g (1.43 mol) of methyl 3-methyl-2-pentenoate. The mixture was protected from light and heated at 68° for 274 hr, becoming yellow orange, and then heated at 165° for 50 min with vigorous gas evolution. Most of the excess methyl 3-methyl-2-pentenoate was then distilled at 39 Torr; 20 g of benzophenone azine separated. After removal of the remaining methyl 3-methyl-2-pentenoate by addition and Vigreaux distillation at 6 Torr of four 20-ml portions of decane, the residual yellow oil in 105 ml of absolute ethanol and a solution of 12.5 g (0.222 mol) of potassium hydroxide in 18 ml of water were combined and refluxed for 3.2 hr. The mixture was concentrated, diluted with water, and extracted with benzene and ether. The aqueous phase was carefully acidified to methyl orange at 0°, then ether extracted, and the extracts were water washed, dried, and concentrated *in vacuo* to give 28.8 g of residue (*ca.* 65% desired *cis*- and *trans*-cyclopropyl acids by nmr). Crystallization from ether–hexane gave 8.80 g of essentially pure cyclopropyl acids. Repetitive silica gel chromatography of the concentrated mother liquors, in *ca.* 6-g portions, on 5.0 × 185 cm columns using increasing amounts of ether in hexane gave a total of 9.9 g of less pure *cis*- and *trans*-cyclopropyl acids.

A phosphate buffer solution of pH 11.48 was prepared from 1 l. of 0.50 *M* aqueous disodium hydrogen phosphate and 400 ml of 1.00 *M* aqueous sodium hydroxide. A 300-ml portion of the buffer solution was then equilibrated at 28.5° with 1300 ml of ether. A mixture of 259 g of the ether saturated buffer and 646.7 g of diatomaceous earth (Eagle Picher FW80 "Celatom") was dry packed into a thermostated (28.5°) 4.0 × 145 cm column and eluted with buffer-saturated ether. Then 1.0-g portions of the acids were chromatographed. In one run using essentially pure acids, 40-ml fractions were collected with uv scanning at 262 nm to give: fractions 76–90, 129 mg, a *ca.* 90:10 mixture of *cis*- and *trans*-cyclopropyl acids; fractions 91–100, 179 mg, a *ca.* 75:25 cis–trans mixture; fractions 101–110, 187 mg, a *ca.* 60:40 cis–trans mixture; fractions 111–120, 183 mg, a *ca.* 70:30 trans–cis mixture; fractions 121–145, 247 mg, a *ca.* 90:10 trans–cis mixture. The buffered column proved to be reusable; five or six runs could be made on one column before it became ineffective.

Repetitive crystallization from ether–hexane completed the purification of cyclopropyl acid mixtures enriched in either the cis or trans isomer.

The yield of pure *trans*-2-ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylic acid was 9.06 g (13.6%). It crystallized either as colorless thick needles, mp 176.5–178.5° (sealed capillary), or prisms, mp 184–185.5° (sealed capillary). The spectral data were: nmr ($CDCl_3$) τ −0.60 (br s, 1 H, COOH), 2.79 (m, 10 H, arom), 7.72 (s, 1 H, cyclopropyl), 8.4–9.2 (m with sharp s at 8.59, 8 H, CH_3 and CH_2CH_3); ir ($CHCl_3$) 2.8–4.15 (COOH), 5.88 (C=O), 6.26, 6.70, 6.91, 6.99, 7.21, 7.25 (sh), 7.50, 7.70, 7.96, 8.11, 8.24 (sh), 8.48, 9.07, 9.15, 9.51, 9.76, 10.02, 10.83, 11.0, 11.66, 14.40 μ.

Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.57; H, 7.21.

The yield of *cis*-2-ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylic acid was 2.87 g (4.3%) of white prisms, mp 189–190° (sealed capillary). The spectral data were: nmr ($CDCl_3$) τ −0.38 (br s, 1 H, COOH), 2.73 (m, 10 H, arom), 7.73 (s, 1 H, cyclopropyl), 7.86–8.42 (complex m, 2 H, CH_2), 8.95 (s, 3 H, CH_3), 9.02 (br t, 3 H, J = 7 Hz, CH_2CH_3); ir (KBr) 2.8–4.7 (COOH), 5.57, 5.88 (C=O), 6.25, 6.33, 6.68, 6.90 (sh), 6.96, 7.22, 7.27 (sh), 7.45, 7.64, 7.78, 8.13, 8.35, 8.46, 8.53 (sh), 8.65 (sh), 9.07, 9.27, 9.54, 9.73, 9.96, 10.09, 10.19, 10.6, 10.86, 11.29, 11.58, 12.81, 13.06, 13.36, 13.44 (sh), 14.19, 14.40 μ.

Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.59; H, 7.17.

Methyl *trans*-2-Ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylate. A solution of 727.9 mg (2.60 mmol) of *trans*-2-ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylic acid in 25 ml of ether was added dropwise to 40 ml of stirred, 0°, ethereal diazomethane (*ca.* 6 mmol). After 2.0 hr of stirring at 0°, removal of excess diazomethane in a nitrogen stream and concentration gave 763.6 mg of colorless crystalline solid, mp 79–86°, which was then passed through a 1.6 × 14 cm silica gel column (Matheson Coleman and Bell, grade 62, 60–200 mesh) slurry packed in 0.5% ether in hexane. Elution with 275 ml of 0.5% ether in hexane and 100 ml of 2.0% ether in hexane gave 713.0 mg (93%) of essentially pure trans ester as a colorless crystalline solid, mp 85–89°. Recrystallization from hexane gave 341 mg of analytically pure crystals, mp 88.5–89.5°. The spectral data were: nmr (CCl_4) τ 2.87 (m, 10 H, arom), 6.40 (s, 3 H, OCH_3), 7.80 (s, 1 H, cyclopropyl), 8.4–9.2 (m with sharp s at 8.62, 8 H, CH_3 and CH_2CH_3); ir (CCl_4) 3.26 (sh), 3.28, 3.31, 3.38, 3.39, 3.49, 5.77 (C=O), 5.87, 6.28, 6.71, 6.94 (sh), 6.98, 7.17, 7.22, 7.27 (sh), 7.80, 7.88, 7.99, 8.27, 8.40, 8.70, 9.08, 9.21, 9.79, 9.95 (sh), 10.68 (sh), 10.89, 11.05, 11.61, 14.20, 14.40 μ.

Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.64; H, 7.57.

(31) (a) The details of the procedure were communicated to us privately by Professor B. M. Trost; (b) W. S. Wadsworth and W. D. Emmons, *J. Amer. Chem. Soc.*, **83**, 1733 (1961).

(32) D. E. McGreer, *et al.*, *Can. J. Chem.*, 41, 726 (1963).

(33) *Cf.* W. M. Jones, T. H. Glenn, and D. G. Baarda, *J. Org. Chem.*, **28**, 2887 (1963).

(34) J. B. Miller, *J. Org. Chem.*, 24, 560 (1959).

Methyl *cis*-2-Ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylate. A procedure identical with that used for the trans ester was employed. The reaction of 235.0 mg (0.840 mmol) of *cis*-2-ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylic acid with *ca.* 10 mmol of diazomethane yielded 234.6 mg (95%) of the cis ester. The product crystallized, mp 95–115°, when a hexane solution of it was chilled to Dry Ice temperature. Recrystallization from hexane to constant melting point gave 117.4 mg of analytically pure ester, mp 99–121° (open capillary). When the recrystallized product was divided into two portions, one displayed a small positive optical rotation ($[\alpha]^{27}_{365}$ 11°), the other a small negative one. Thus spontaneous partial resolution was encountered. The spectral data were: nmr (CCl_4) τ 2.89 (m, 10 H, arom), 6.40 (s, 3 H, OCH_3), 7.82 (s, 1 H, cyclopropyl), 8.12 (symmetrical m, 2 H, CH_2CH_3), 9.00 (s, 3 H, CH_3), 9.09 (br t, 3 H, J = 7 Hz, CH_2CH_3); ir (CCl_4) 3.23, 3.27, 3.30, 3.39, 3.43 (sh), 3.48, 3.52 (sh), 5.76 (C=O), 5.87, 6.26, 6.31, 6.70, 6.91 (sh), 6.98, 7.11, 7.21, 7.26 (sh), 7.41, 7.63, 7.79, 7.89 (sh), 8.28, 8.39, 8.69, 9.07, 9.21, 9.52, 9.76, 9.93, 10.0, 10.60, 10.93, 11.05, 11.37, 11.60, 14.22, 14.40 μ.

Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.53; H, 7.51.

Assignment of the Stereochemistry of Methyl *cis*- and *trans*-2-Ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylates. A 0.6 *M* solution of methyl *cis*-2-ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylates in carbon tetrachloride (containing 1% TMS) and a similar solution of the trans isomer were prepared, and the nmr spectrum of 0.5 ml of each was taken. Then, in each case, a 10- or 20-μl portion of a 0.5 *M* solution of $Eu(fod)_3$[19] in CCl_4 was added and the spectrum was redetermined. This procedure was repeated until a total of 50 μl of shift reagent solution had been added to each sample. In the cis case the downfield shifts for the various mole ratios ($Eu(fod)_3$/ester) were: cyclopropyl-CH_3 (0.06 ppm, 0.017 mol of $Eu(fod)_3$/mol of ester; 0.18 ppm, 0.050; 0.28 ppm, 0.083), CH_2CH_3 (0.07 ppm, 0.017; 0.22 ppm, 0.050; 0.35 ppm, 0.083), average for the diastereotopic methylene H (0.13 ppm, 0.017; 0.40 ppm, 0.050; 0.66 ppm, 0.083), OCH_3 (0.19 ppm, 0.017; 0.58 ppm, 0.050; 0.97 ppm, 0.083), cyclopropyl H (0.23 ppm, 0.017; 0.73 ppm, 0.050; 1.20 ppm, 0.083). In the trans case these values were: CH_2CH_3 (0.03 ppm, 0.017 mol of $Eu(fod)_3$/mol of ester; 0.11 ppm, 0.050; 0.18 ppm, 0.083), cyclopropyl-CH_3 (0.12 ppm, 0.017; 0.36 ppm, 0.050; 0.61 ppm, 0.083), OCH_3 (0.19 ppm, 0.017; 0.60 ppm, 0.050; 0.98 ppm, 0.083), cyclopropyl H (0.23 ppm, 0.017; 0.69 ppm, 0.050; 1.15 ppm, 0.083).

***trans*-(2-Ethyl-2-methyl-3,3-diphenylcyclopropyl)carbinol.** A solution of 351.3 mg (1.20 mmol) of methyl *trans*-2-ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylate in 5.0 ml of anhydrous ether was added to a stirred, ice-cold suspension of 69.4 mg (1.83 mmol) of lithium aluminum hydride in 5.0 ml of anhydrous tetrahydrofuran. Stirring at room temperature for 12 hr was followed by refluxing for 30 min. After cooling excess 1:1 (v/v) sodium sulfate decahydrate–Celite was added, the mixture was stirred until the gray solid turned white, and the granular precipitate was filtered. Removal of the solvent gave 330 mg of oil, which was purified by chromatography on a 2.2 × 34 cm silica gel column (Matheson Coleman and Bell, grade 62, 60–200 mesh) slurry packed in 5% ether in hexane. Elution with 5% ether in hexane in 250-ml fractions gave, in fractions 6–14, 320.6 mg (100%) of the desired alcohol as a colorless oil. The spectral data were: nmr (CCl_4) τ 2.9 (m, 10 H, arom), τ_A 6.26, τ_B 6.53 (symmetrical seven line m, AB portion of ABX, 2 H, J_{AB} = 11 Hz, J_{AX} = J_{BX} = 7 Hz, CH_2O), 7.50 (s, 1 H, removed by shaking with D_2O, OH), 8.2–9.2 (m with sharp s at 8.90, 9 H, cyclopropyl H, CH_3, and CH_2CH_3); ir (CCl_4) 2.75, 2.95, 3.22 (sh), 3.24, 3.27, 3.30, 3.34, 3.38, 3.41, 3.48, 6.26, 6.70, 6.87, 6.91, 7.23 (sh), 7.28, 8.84, 9.06, 9.26, 9.72, 9.91, 14.18, 14.38 μ.

Anal. Calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.33. Found: C, 85.84; H, 8.30.

***cis*-(2-Ethyl-2-methyl-3,3-diphenylcyclopropyl)carbinol.** A procedure identical with that used for the trans alcohol was employed. The reaction of 195.1 mg (0.662 mmol) of methyl *cis*-2-ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylate with 45.9 mg (1.21 mmol) of lithium aluminum hydride yielded 169.3 mg (96%) of the cis alcohol. Recrystallization from hexane gave 145.2 mg of colorless needles, mp 109.5–111°. The spectral data were: nmr ($CDCl_3$) τ 2.5–3.0 (m, 10 H, arom), 6.23 (d, 2 H, J = 7.5 Hz, CH_2O), 8.2–8.8 (series of peaks, 4 H, cyclopropyl, CH_2CH_3, and OH), 8.9–9.2 (m with sharp s at 9.05, 6 H, CH_3 and CH_2CH_3); ir ($CHCl_3$) 2.77, 2.90, 3.22 (sh), 3.24, 3.28, 3.30, 3.32, 3.37, 3.42, 3.48, 6.25, 6.32, 6.68, 6.85 (sh), 6.90, 7.21 (sh), 7.25, 7.61, 8.2, 8.26, 8.54, 8.89, 9.07, 9.25, 9.75, 9.99, 10.32 (sh), 14.39, 15.1, 15.7 μ.

Anal. Calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.33. Found: C, 85.84; H, 8.27.

***trans*-2-Ethyl-2-methyl-3,3-diphenylcyclopropanecarboxaldehyde.** A solution of chromium trioxide–pyridine complex (13.95 mmol) in 10 ml of acetic acid was prepared by the method of Stensiö and Wachtmeister,[18b] cooled to 10°, and stirred. A solution of 285.4 mg (1.07 mmol) of *trans*-(2-ethyl-2-methyl-3,3-diphenylcyclopropyl)carbinol in 5.0 ml of ether was then added to it over 7 min. After 10 min more at 10°, the reaction mixture was poured into 75 ml of ice–water and ether extracted. The combined organic extracts were washed with water, saturated sodium bicarbonate, and water again, then dried and concentrated *in vacuo* to give 278 mg of colorless oil. This was chromatographed on a 2.2 × 114 cm silica gel column (Matheson Coleman and Bell, grade 62, 60–200 mesh) slurry packed in 1.0% ether in hexane. Elution with 1.0% ether in hexane in 250-ml fractions gave, in fractions 11–15, 238.1 mg (84%) of the desired trans aldehyde as a colorless oil. The spectral data were: nmr (CCl_4) τ 0.92 (d, 1 H, J = 7 Hz, CHO), 2.79 (m, 10 H, arom), 7.82 (d, 1 H, J = 7 Hz, cyclopropyl), 8.3–9.3 (m with sharp s at 8.54, 8 H, CH_3 and CH_2CH_3); ir (CCl_4) 3.22 (sh), 3.24, 3.27, 3.30, 3.34 (sh), 3.37, 3.40, 3.48, 3.50, 3.57, 3.62, 3.69 (sh), 5.90 (C=O), 6.26, 6.69, 6.90, 7.09, 7.21, 7.26, 7.55, 7.60, 8.71, 9.08, 9.25, 9.33, 9.72, 9.88, 9.97, 10.80, 11.0, 14.18, 14.39 μ.

Anal. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.45; H, 7.85.

***cis*-2-Ethyl-2-methyl-3,3-diphenylcyclopropanecarboxaldehyde.** A procedure identical with that used for the trans aldehyde was employed. The reaction of 7.89 mmol of chromium trioxide–pyridine complex with 155.6 mg (0.585 mmol) of *cis*-(2-ethyl-2-methyl-3,3-diphenylcyclopropyl)carbinol yielded 136.7 mg of the desired aldehyde. Recrystallization from hexane gave 107.1 mg (69%) of colorless crystals, mp 118.5–121° (sealed capillary). The spectral data were: nmr (CCl_4) τ 0.90 (d, 1 H, J = 7.3 Hz, CHO), 2.7 (m, 10 H, arom), 7.75 (d, 1 H, J = 7.3 Hz, cyclopropyl), 8.13 (m, 2 H, CH_2), 8.95 (s, 3 H, CH_3), 8.99 (br, t, 3 H, J = 7 Hz, CH_2CH_3); ir (CCl_4) 3.24, 3.28, 3.31 (sh), 3.33, 3.38, 3.42, 3.49, 3.58, 3.62, 5.95 (C=O), 6.25, 6.68, 6.89, 7.20, 7.50, 7.59, 8.78, 9.07, 9.24, 9.36, 9.74, 9.96, 10.17, 10.82, 11.07, 11.29, 14.38, 15.1 μ.

Anal. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.45; H, 7.72.

***trans*-3-Ethyl-3-methyl-2-(2′-methylpropenyl)-1,1-diphenylcyclopropane.** To a rapidly stirred suspension of 363.3 mg (0.839 mmol) of isopropyltriphenylphosphonium iodide[39] in 5.0 ml of dry ether was added 0.720 ml of 1.08 *M* ethereal phenyllithium (0.78 mmol). The mixture became dark red immediately. After 2.5 hr of stirring under nitrogen, a solution of 173.1 mg (0.655 mmol) of *trans*-2-ethyl-2-methyl-3,3-diphenylcyclopropanecarboxaldehyde in 3.0 ml of dry ether was added dropwise. After an additional 9 hr, solvent was removed. The residue was stirred with 20 ml of methylene chloride to give a slurry, which was filtered through Celite and concentrated to give *ca.* 2 ml of a clear yellow solution. This was chromatographed on a 2.2 × 82 cm silica gel column (Matheson Coleman and Bell, grade 62, 60–200 mesh) slurry packed in hexane. Elution with hexane in 50-ml fractions gave, in fractions 8–21, 97.0 mg of a mixture of the desired vinylcyclopropane and biphenyl. The material of fractions 8–21 was rechromatographed on a 1.0 × 41-cm Vycor column of silicic acid (Mallinckrodt SilicAR cc-7, 200–325 mesh)–Celatom (3:1) that contained *ca.* 2% Sylvania No. 290 red phosphor. This was slurry packed with hexane. Bands were monitored with a short wavelength uv handlamp during elution with hexane, which gave: fraction 1, 50 ml, nil; fraction 2, 20 ml, first band, 0.6 mg of biphenyl; fraction 3, 90 ml, second band, 84.9 mg (45%) of the desired *trans*-vinylcyclopropane as a colorless oil. The spectral data were: nmr (CCl_4) τ 2.85 (m, 10 H, arom), 5.30 (d of m, 1 H, J = 9.5 Hz, vinyl), 7.91 (d, 1 H, J = 9.5 Hz, cyclopropyl), 8.11 (d, 3 H, J = 1 Hz, vinyl-CH_3), 8.26 (d, 3 H, J = 1 Hz, vinyl-CH_3), 8.4–9.4 (m with sharp s at 8.92, 8 H, cyclopropyl-CH_3 and CH_2CH_3); ir (CCl_4) 3.24, 3.27, 3.30, 3.38, 3.42, 3.49, 3.50, 5.18, 6.28, 6.70, 6.91, 7.22, 7.28, 7.57 (sh), 7.63, 8.59, 9.09, 9.28, 9.38 (sh), 9.79, 10.80, 10.99, 11.07 (sh), 11.41, 11.83, 11.9 (sh), 14.21, 14.40 μ; λ_{max} (95% ethanol) 225 nm (ϵ 19,400).

Anal. Calcd for $C_{22}H_{26}$: C, 90.98; H, 9.02. Found: C, 90.82; H, 9.13.

***cis*-3-Ethyl-3-methyl-2-(2′-methylpropenyl)-1,1-diphenylcyclopropane.** This compound was prepared from 127.0 mg (0.481 mmol) of *cis*-2-ethyl-2-methyl-3,3-diphenylcyclopropanecarboxaldehyde and 0.57 mmol of isopropylidinetriphenylphosphorane by the method described above for the trans isomer. The yield of colorless oily *cis*-vinylcyclopropane was 39.7 mg (28%). The spectral data were: nmr (CCl_4) τ 2.87 (m, 10 H, arom), 5.27 (d of m, 1 H, J = 10

Hz, vinyl), 7.95 (d, 1 H, J = 10 Hz, cyclopropyl), 8.12 (d, 3 H, J = 1 Hz, vinyl-CH_3), 8.27 (d, 3 H, J = 1 Hz, vinyl-CH_3), 8.3–8.8 (complex m, 2 H, CH_2), 9.03 (overlapping s and m, 6 H, cyclopropyl-CH_3 and CH_2CH_3); ir (CCl_4) 3.23 (sh), 3.25, 3.28, 3.31, 3.38, 3.42, 3.49, 3.68 (w), 6.25, 6.32 (sh), 6.68, 6.90, 7.23 (sh), 7.26, 8.67, 9.06, 9.26, 9.52, 9.74, 10.03 (w), 10.16, 10.82, 11.34, 11.85, 14.21, 14.38 μ; uv λ_{max} (95% ethanol) 226 nm (ϵ 18,200).

Anal. Calcd for $C_{22}H_{26}$: C, 90.98; H, 9.02. Found: C, 91.02; H, 8.97.

Methyl 3-Diphenylmethyl-3-methylpentanoate. A solution of 197.7 mg (0.669 mmol) of methyl *trans*-2-ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylate in 13 ml of dry ether was added dropwise under nitrogen to a stirred, refluxed solution of 15.1 mg (2.18 mg-atom) of lithium in 50 ml of sodium-dried ammonia. The deep blue solution quickly became dark blue-green, then pale orange. After 12 min the reaction was quenched with excess solid ammonium chloride (*ca.* 90 mg), and the ammonia was distilled off. Solvent was then removed and the residue taken up in ether and water. The ether layer was water washed, dried, and concentrated *in vacuo* to 193.5 mg of slightly yellow oil. The crude product mixture was chromatographed on a 1.8 × 116 cm silica gel column (Matheson Coleman and Bell, grade 62, 60–200 mesh) slurry packed in 1% ether in hexane. Elution with the same solvent in 40-ml fractions, with uv scanning of the eluate at 260 nm, gave, in fractions 40–58, 148.0 mg (75%) of the desired ester as a colorless oil. The spectral data were: nmr (CCl_4) τ 2.5–3.0 (m, 10 H, arom), 5.73 (br s, 1 H, Ph_2CH), 6.52 (s, 3 H, OCH_3), 7.88 (br s, 2 H, CH_2COOMe), 8.3–8.8 (m, 2 H, CH_2CH_3), 8.85 (s, 3 H, CH_3), 9.18 (br t, 3 H, J = 7 Hz, CH_2CH_3); ir (CCl_4) 3.24, 3.26, 3.30, 3.37, 3.39 (sh), 3.46, 5.50 (w), 5.78 (C=O), 6.26, 6.70, 6.84, 6.90, 6.98, 7.23, 7.39, 7.53, 8.38, 8.52, 8.77, 9.0, 9.12, 9.69, 9.88, 14.23 μ.

Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 80.89; H, 8.11.

3-Diphenylmethyl-3-methyl-1,1-diphenyl-1-pentanol. To a stirred solution of 1.8 mmol of phenyllithium in 2.0 ml of ether was added a solution of 213.4 mg (0.720 mmol) of methyl 3-diphenylmethyl-3-methylpentanoate in 6.0 ml of ether. The reaction mixture was refluxed under nitrogen for 1.0 hr and ethanol added. Addition of water and ether extraction, followed by water washing of the extracts, drying, and concentration *in vacuo*, gave 327.7 mg of yellow-brown oil.

The crude product was chromatographed on a 1.8 × 114 cm silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column slurry packed in 1% ether in hexane. Elution was with 2 l. of 1.0% ether in hexane and 1 l. of 2.0% ether in hexane; 250-ml fractions were collected. Fractions 9–12 contained 295.5 mg (98%) of the desired tetraphenyl alcohol as a colorless oil. The spectral data were: nmr ($CDCl_3$) τ 2.74 (m, 20 H, arom), 5.87 (br s, 1 H, Ph_2CH), τ_A 7.27, τ_B 7.40 (AB q, 2 H, J = 15 Hz, $Ph_2C(OH)CH_2$), 8.03 (s, 1 H, removed by shaking with D_2O, OH), 8.52 (m, 2 H, CH_2CH_3), 9.0–9.4 (m with sharp s at 9.17, 6 H, CH_3 and CH_2CH_3); ir (CCl_4) 2.79, 2.80, 3.24, 3.27, 3.31, 3.37, 3.41 (sh), 3.48, 6.27, 6.32, 6.70, 6.85 (sh), 6.92, 7.26, 8.78, 9.25, 9.45, 9.56 (sh), 9.70, 11.06, 14.31, 15.06, 15.54 μ.

Anal. Calcd for $C_{31}H_{32}O$: C, 88.53; H, 7.67. Found: C, 88.65; H, 7.75.

3-Diphenylmethyl-3-methyl-1,1-diphenylpentane from 3-Diphenylmethyl-3-methyl-1,1-diphenylpentanol. The method used was identical with that employed starting with 2-ethyl-2-methyl-1,1,4,4-tetraphenyl-1-butanol. Here reduction of 176.1 mg (0.419 mmol) of 3-diphenylmethyl-3-methyl-1,1-diphenyl-1-pentanol by a solution of 8.4 mg (1.21 mg-atom) of lithium in 60 ml of sodium-dried ammonia gave 114.8 mg of the desired hydrocarbon as a colorless oil. Recrystallization from 95% ethanol gave 90.0 mg (53%) of 3-diphenylmethyl-3-methyl-1,1-diphenylpentane as colorless needles, mp 79–82°. The spectral data were: nmr ($CDCl_3$) τ 2.82 (m, 20 H, arom), 6.00 (br t, 1 H, J = 6.5 Hz, Ph_2CHCH_2), 6.03 (s, 1 H, other Ph_2CH), 7.70 (br d, 2 H, J = 6.5 Hz, Ph_2CHCH_2), 8.54 (br q, 2 H, J = ~7 Hz, CH_2CH_3), 9.05–9.42 (m with sharp s at 9.12, 6 H, CH_3 and CH_2CH_3); ir (KBr) 3.25, 3.27, 3.31, 3.33, 3.37, 3.41 (sh), 3.42, 3.48, 5.17 (w), 6.28, 6.32 (sh), 6.71, 6.88 (sh), 6.90, 6.96 (sh), 7.28, 7.38, 7.51 (w), 7.80 (w), 8.51 (w), 8.70, 9.25 (sh), 9.32, 9.71, 10.00, 10.93 (w), 11.14 (w), 13.43, 14.22, 14.45, 15.10, 15.89 μ; ir ($CHCl_3$) 3.24, 3.27, 3.33, 3.38, 3.41, 3.47 (sh), 6.26, 6.31 (sh), 6.70, 6.84 (sh), 7.25, 9.26, 9.72, 10.0 (w), 14.35, 15.0 μ.

Anal. Calcd for $C_{31}H_{32}$: C, 92.03; H, 7.97. Found: C, 91.95; H, 7.88.

The above spectral data are identical with those obtained from the sample of this hydrocarbon prepared from the other tetraphenyl alcohol (*vide supra*), mmp 77.5–80°.

Resolution of 2-Ethyl-2-methyl-4,4-diphenyl-3-butenoic Acid. Cinchonidine (3.59 g, 12.2 mmol) was dissolved in a solution of 3.43 g (12.3 mmol) of 2-ethyl-2-methyl-4,4-diphenyl-3-butenoic acid in 20 ml of chloroform. The solution was warmed and 25 ml of hexane was added. Upon standing overnight at room temperature, the solution deposited 132 mg of crystalline salt. Reducing the volume of the solution and adding more hexane gave two additional crops of salt, increasing the total amount to 3.60 g. Four successive crystallizations of this gave 1.34 g of cinchonidine salt as colorless crystals, mp 174–174.5°, which on hydrolysis (6 N HCl) afforded 0.650 g (38%) of 2-ethyl-2-methyl-4,4-diphenyl-3-butenoic acid, $[\alpha]^{27}_{365}$ 115 ± 1° (c 0.010, methanol),[35,37] as a colorless oil. The specific rotations were unchanged from those of a sample obtained from the previous recrystallization. The specific rotations at 27° were (λ in parentheses): 25.0 ± 0.6° (589), 26.4 ± 0.4° (578), 30.9 ± 0.4° (546), 60.6 ± 0.5° (436), 115 ± 1° (365) (c 0.010, methanol). The optically active acid had ir and nmr spectra identical with those of the racemic compound.

Optically Active Methyl 2-Ethyl-2-methyl-4,4-diphenyl-3-butenoate. The method used for the racemic compound was employed. The reaction of 5.38 g (19.2 mmol) of 2-ethyl-2-methyl-4,4-diphenyl-3-butenoic acid, with *ca.* 34 mmol of diazomethane, gave 4.89 g (87%) of the ester as a colorless solid, mp 60.5–63°, with $[\alpha]^{27}_{365}$ −95.5 ± 0.5° (c 0.008, hexane). Crystallization from methanol gave 3.031 g of methyl 2-ethyl-2-methyl-4,4-diphenyl-3-butenoate, $[\alpha]^{27}_{365}$ −102.5 ± 0.5° (c 0.008, hexane), as colorless needles, mp 63–65°. Further crystallization changed neither the melting point nor the specific rotations. The specific rotations at 27° were (λ in parentheses): −19.6 ± 0.3° (589), −20.8 ± 0.2° (578), −24.4 ± 0.2° (546), −50.4 ± 0.3° (436), −102.5 ± 0.5° (365) (c 0.008, hexane). The optically pure ester had ir and nmr spectra identical with those of the racemic compound.

Optically Active 2-Ethyl-2-methyl-4,4-diphenyl-3-buten-1-ol. The method employed was that used for the racemic compound. Reaction of 1.96 g (6.67 mmol) of methyl 2-ethyl-2-methyl-4,4-diphenyl-3-butenoate, $[\alpha]^{27}_{365}$ −102.5 ± 0.5°, with 8.0 mmol of lithium aluminum hydride gave 1.74 g (98%) of 2-ethyl-2-methyl-4,4-diphenyl-3-buten-1-ol as a colorless oil. The specific rotations at 27° were (λ in parentheses): 26.3 ± 0.1° (589), 27.7 ± 0.1° (578), 32.5 ± 0.1° (546), 62.9 ± 0.2° (436), 119.5 ± 0.5° (365) (c 0.008, hexane). The alcohol had ir and nmr spectra identical with those of the racemic compound.

Optically Active 2-Ethyl-2-methyl-4,4-diphenyl-3-butenal. The method employed was that used to prepare the racemic compound, except that during the reaction, work-up, and purification, the aldehyde was protected from light (*vide supra*). Oxidation of 1.74 g (6.54 mmol) of 2-ethyl-2-methyl-4,4-diphenyl-3-buten-1-ol, $[\alpha]^{27}_{365}$ 119.5 ± 0.5°, with 6.913 g (33.5 mmol) of dicyclohexylcarbodiimide, 15.4 g (197 mmol) of dimethyl sulfoxide, and 3.27 mmol of pyridinium trifluoroacetate yielded 1.66 g (95%) of the desired aldehyde as a colorless oil. The specific rotations at 27° were (λ in parentheses): −29.0 ± 0.2° (589), −30.2 ± 0.3° (578), −35.4 ± 0.3° (546), −74.7 ± 0.8° (436), −165 ± 2° (365) (c 0.0061, hexane). The optically active aldehyde had ir and nmr spectra identical with those of the racemic compound.

Optically Active 3-Ethyl-3,5-dimethyl-1,1-diphenyl-1,4-hexadiene. A slurry of 3.394 g (7.83 mmol) of powdered isopropyltriphenylphosphonium iodide[30] in 50 ml of dry hexane was prepared under nitrogen, and 2.1 ml of 2.97 M n-butyllithium in hexane (6.3 mmol) was added. The mixture was then refluxed for 2.5 hr. The dark red solution of the ylide was cooled to room temperature, and a solution of 1.662 g (6.30 mmol) of 2-ethyl-2-methyl-4,4-diphenyl-3-butenal, $[\alpha]^{27}_{365}$ −165 ± 2°, in 5.0 ml of dry hexane was added. The reaction mixture was then refluxed for 1 hr and stirred at room temperature overnight. Throughout the period of reaction, the mixture was protected from light (*vide supra*).

Solids were filtered and washed with methylene chloride. The

(35) All quantitative work was done on a Perkin-Elmer Model 141 polarimeter with thermostated 1-dm cells. The $[\alpha]$'s of purified (+)-10-camphorsulfonic acid were measured on this instrument and found to agree to within 1.5% or less with the values published by DeTar.[36] We are grateful to Professor Harlan Goering for use of the polarimeter.

(36) D. F. DeTar, *Anal. Chem.*, 41, 1406 (1969).

(37) All optically active compounds that were purified by recrystallization were recrystallized to constant rotation at all five wavelengths available on the Perkin-Elmer 141. And all chromatographically purified optically active compounds were checked to be sure that the earliest and latest product-containing fractions had the same $[\alpha]$'s at all five wavelengths.

combined organic phase was concentrated, taken up in *ca.* 10 ml of methylene chloride, and applied to a 4.0 × 42 cm column of 3:1 (v/v) silicic acid (Mallinckrodt SilicAR cc-7, 200–325 mesh)–diatomaceous earth (Eagle Picher FW 80 "Celatom") slurry packed in hexane. Elution with hexane in 250-ml fractions gave, in fractions 2-4, 1.362 g of impure desired ethylmethyldiene as a colorless oil.

This was rechromatographed on a 3.0 × 84 cm silicic acid Celatom column slurry packed in hexane. Elution with this solvent in 100-ml fractions gave, in fraction 8, 399.3 mg of the desired ethylmethyldiene, $[\alpha]^{27}_{365}$ −66.6° (*c* 0.0117, hexane), as a colorless oil; fraction 9 gave 470.3 mg of colorless oil, ethylmethyldiene, $[\alpha]^{27}_{365}$ −67.0° (*c* 0.00905, hexane); fraction 10 gave 260.1 mg of colorless oil, ethylmethyldiene, $[\alpha]^{27}_{365}$ −64.4° (*c* 0.00752, hexane); fractions 11 and 12 gave 126.2 mg of colorless oil, ethylmethyldiene. The material of fractions 8 and 9 had ir and nmr spectra identical with those of the racemic compound. Fractions 10–12 were rechromatographed on a similar column to afford an additional 241.7 mg of product, $[\alpha]^{27}_{365}$ −66.1° (*c* 0.01072, hexane), which brought the total yield of optically active 3-ethyl-3,5-dimethyl-1,4-hexadiene to 1.161 g (64%).

It was found that optically active diphenyldiene prepared in this manner required still further purification by chromatography. Application of 3.063 g of such material to a 4.0 × 132 cm silicic acid–Celatom column slurry packed in hexane, followed by elution with hexane in 100-ml fractions, gave, in fractions 19–24, 2.951 g of pure ethylmethyldiene as a colorless oil. Its specific rotations at 27° were (λ in parentheses): −8.1 ± 0.1° (589), −8.4 ± 0.1° (578), −10.4 ± 0.1° (546), −26.3 ± 0.2° (436), −67.5 ± 0.5° (365) (*c* 0.013, hexane).

Optically Active 3-Diphenylmethyl-3-methyl-1,1-diphenylpentane from Optically Active 2-Ethyl-2-methyl-1,1,4,4-tetraphenyl-1-butanol. The method employed was that used to prepare the racemic compound. The tetraphenyl alcohol starting material was prepared from methyl 2-ethyl-2-methyl-4,4-diphenyl-3-butenoate, $[\alpha]^{27}_{365}$ −102.5°, by the two-step synthesis described above. Reduction of 415 mg (0.984 mmol) of optically active 2-ethyl-2-methyl-1,1,4,4-tetraphenyl-1-butanol with 20 mg (2.9 mg-atom) of lithium in 125 ml of anhydrous liquid ammonia gave 147.7 mg of impure desired tetraphenylalkane as a colorless oil, $[\alpha]^{27}_{365}$ 14.7° (*c* 0.0738, hexane). This material was crystallized from 95% ethanol plus benzene (20:1). The tetraphenylalkane crystallized, mp 44–73°, along with an equimolar amount of benzene. Dissolving the crystals in hexane followed by concentration *in vacuo* to constant weight gave 130.0 mg of oil, $[\alpha]^{27}_{365}$ 15.8° (*c* 0.065, hexane). One more crystallization gave 120.4 mg of 3-diphenylmethyl-3-methyl-1,1-diphenylpentane, $[\alpha]^{27}_{365}$ 16.5 ± 0.2° (*c* 0.060, hexane), as a colorless oil. Further crystallization did not change the specific rotations. At 27° these were (λ in parentheses): 3.6 ± 0.1° (589), 3.9 ± 0.1° (578), 4.5 ± 0.1° (546), 8.7 ± 0.1° (436), 16.5 ± 0.2° (365) (*c* 0.04 to 0.06, hexane). The ir and nmr spectra of the optically pure tetraphenylalkane were identical with those of the racemic compound. The ORD curve[38] had maxima at 260, 266, and 273 nm, minima at 256, 262, and 269 nm, and an intercept at 257 nm: $[\alpha]^{27}_{256}$ −10 ± 3°, $[\alpha]^{27}_{260}$ 29 ± 3°, $[\alpha]^{27}_{262}$ 14 ± 3°, $[\alpha]^{27}_{268}$ 112 ± 5°, $[\alpha]^{27}_{269}$ 60 ± 4°, $[\alpha]^{27}_{275}$ 166 ± 5° (*c* 4.69 × 10^{-4}, hexane).

Resolution of *trans*-2-Ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylic Acid. A mixture of 7.76 g (2.40 mmol) of (−)-quinine and 6.59 g (23.5 mmol) of *trans*-2-ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylic acid was dissolved in 50 ml of chloroform. The solution was diluted with 50 ml of hexane and concentrated to 75 ml. Addition of 25 ml of hexane, cooling, and seeding gave 5.31 g of the salt as colorless needles, mp 127–129°. A portion of the salt on hydrolysis (3 *N* HCl) gave acid of $[\alpha]^{27}_{365}$ 701° (*c* 0.0113, $CHCl_3$). Three additional crystallizations gave 3.91 g of salt, mp 129–130°, which was hydrolyzed to 1.51 g of partly crystalline acid with $[\alpha]^{27}_{365}$ 778 ± 12° (*c* 0.006, $CHCl_3$), unchanged from the previous crystallization. Crystallization from hexane gave 1.410 g (43%) of *trans*-2-ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylic acid, $[\alpha]^{27}_{365}$ 840 ± 4° (*c* 0.004, $CHCl_3$), as colorless prisms, mp 148.5–149° (sealed capillary). Further crystallization from hexane did not change the melting point or rotations. The specific rotations at 27° were (λ in parentheses): 196 ± 2° (589), 206 ± 2° (578), 238 ± 2° (546), 455 ± 4° (436), 840 ± 6° (365) (*c* 0.004, $CHCl_3$). The ir and nmr spectra of the optically pure trans acid were identical with those of the racemic compound.

Resolution of *cis*-2-Ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylic Acid. A mixture of 2.48 g (8.71 mmol) of *cis*-2-ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylic acid and 2.60 g (8.71 mmol) of purified[39] (−)-cinchonidine was heated with 120 ml of ethyl acetate until solution occurred. The hot solution was concentrated to *ca.* 85 ml, then cooled, and addition of seeds (obtained by trituration with ethyl acetate at Dry Ice temperature) initiated crystallization. Three crops of the salt, 1.90 g in all, were obtained as colorless needles, mp 108–112°. Hydrolysis (3 *N* HCl) of a small portion of the salt gave acid with $[\alpha]^{27}_{365}$ −625° (*c* 0.004, $CHCl_3$). Crystallization of the salt gave 1.60 g of white needles, mp 110–112°, a little of which was hydrolyzed to acid of $[\alpha]^{27}_{365}$ −743° (*c* 0.004, $CHCl_3$). Further crystallization of the salt followed by hydrolysis gave acid of unchanged specific rotation. Consequently, the salt of the second crystallization was hydrolyzed to 650 mg of acid, which on crystallization from hexane afforded 355 mg of *cis*-2-ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylic acid as colorless needles, mp 176.5–177° (sealed capillary). The specific rotations at 27° were (λ in parentheses): −171 ± 1° (589), −179 ± 1° (578), −208 ± 1° (546), −406 ± 2° (436), −765 ± 5° (365) (*c* 0.004, $CHCl_3$). The optically pure compound had nmr spectral data identical with those of the racemic acid and was not changed in any way by further crystallization.

By recrystallization of various acid and salt mother liquors, it was possible to improve the yield of optically pure cis acid to 812 mg (66%).

Optically Active Methyl *trans*-2-Ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylate. The method used was that employed in preparing the racemic compound. Reaction of 812.5 mg (2.90 mmol) of *trans*-2-ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylic acid, $[\alpha]^{27}_{365}$ 840 ± 4°, with *ca.* 22 mmol of diazomethane gave 814.2 mg (95%) of the desired trans ester as a colorless oil that crystallized on standing, mp 48–50°. Its specific rotations at 27° were (λ in parentheses): 200 ± 1° (589), 210 ± 1° (578), 243 ± 1° (546), 456 ± 2° (436), 827 ± 4° (365) (*c* 0.013, hexane). The optically pure ester had ir and nmr spectra identical with those of the racemic compound.

Optically Active Methyl *cis*-2-Ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylate. This was prepared by the method used for the racemic compound. Reaction of 312 mg (1.11 mmol) of *cis*-2-ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylic acid, $[\alpha]^{27}_{365}$ −765 ± 5°, with *ca.* 11 mmol of diazomethane gave 267.5 mg (82%) of the desired ester, $[\alpha]^{27}_{365}$ −778° (*c* 0.0128, CCl_4), as a colorless solid, mp 130–131° (hot stage). Recrystallization from hexane to constant melting point and specific rotation afforded 228.0 mg of pure methyl *cis*-2-ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylate as colorless crystals, mp 128.5–129.5° (sealed capillary). Its specific rotations at 27° were (λ in parentheses): −180 ± 1° (589), −188 ± 1° (578), −219 ± 1° (546), −423 ± 2° (436), −793 ± 4° (365) (*c* 0.011, CCl_4). The cis ester had ir and nmr spectra identical with those of the racemic material.

Optically Active *trans*-(2-Ethyl-2-methyl-3,3-diphenylcyclopropyl)carbinol. The method employed was that used for the racemic compound. Reduction of 389.7 mg (1.32 mmol) of methyl *trans*-2-ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylate, $[\alpha]^{27}_{365}$ 827 ± 4°, with 76.2 mg (2.01 mmol) of lithium aluminum hydride yielded 354.2 mg (100%) of the desired trans alcohol as a colorless oil. Its specific rotations at 27° were (λ in parentheses): 157 ± 2° (589), 164 ± 3° (578), 190 ± 3° (546), 360 ± 5° (436), 661 ± 9° (365) (*c* 0.012, hexane). The optically pure trans alcohol had ir and nmr spectra identical with those of the racemic compound.

Optically Active *cis*-(2-Ethyl-2-methyl-3,3-diphenylcyclopropyl)carbinol. The method used was that employed for the racemic compound. Reduction of 260 mg (0.883 mmol) of methyl *cis*-2-ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylate, $[\alpha]^{27}_{365}$ −793 ± 3°, with 52 mg (1.37 mmol) of lithium aluminum hydride afforded 238 mg (100%) of the desired cis alcohol as a colorless solid. The specific rotations at 27° were (λ in parentheses): −129 ± 4° (589), −134 ± 4° (578), −156 ± 5° (546), −300 ± 10° (436), −566 ± 20° (365) (0.0043, $CHCl_3$). The ir and nmr spectra of the optically active cis alcohol were identical with those of the racemic material.

Optically Active *trans*-2-Ethyl-2-methyl-3,3-diphenylcyclopropanecarboxaldehyde. This compound was prepared by the method used for the racemic material. Oxidation of 354.2 mg

(38) ORD curves were measured on a Durrum-Jasco Model J-20 spectropolarimeter. The wavelength scale was calibrated against the known[36] λ_{min} at 270 nm of (+)-10-camphorsulfonic acid.

(39) T. A. Henry, "The Plant Alkaloids," 4th ed, Blakiston Co., Philadelphia, Pa., 1949, pp 427 and 428.

(1.33 mmol) of *trans*-(2-ethyl-2-methyl-3,3-diphenylcyclopropyl)-carbinol, $[\alpha]^{27}_{365}$ 661 ± 9°, with 17.5 mmol of chromium trioxide–pyridine complex gave 310.9 mg (89%) of the trans aldehyde as a colorless solid, mp 87–89.5°. Its specific rotations at 27° were (λ in parentheses): 241 ± 1° (589), 253 ± 1° (578), 295 ± 1° (546), 605 ± 2° (436), 1298 ± 5° (365) (*c* 0.007, CCl_4). The ir and nmr spectra of the optically pure trans aldehyde were identical with those of the racemic material.

Optically Active *cis*-2-Ethyl-2-methyl-3,3-diphenylcyclopropanecarboxaldehyde. The method used was that employed for the racemic compound. Oxidation of 238 mg (0.895 mmol) of *cis*-(2-ethyl-2-methyl-3,3-diphenylcyclopropyl)carbinol, $[\alpha]^{27}_{365}$ −566 ± 20°, with 11.6 mmol of chromium trioxide–pyridine complex afforded 187.6 mg (79%) of the desired cis aldehyde as a colorless oil. The specific rotations at 27° were (λ in parentheses): −151 ± 2° (589), −158 ± 2° (578), −186 ± 2° (546), −387 ± 4° (436), −837 ± 8° (365) (*c* 0.0029, hexane). The optically pure cis aldehyde had ir and nmr spectra identical with those of the racemic compound.

Optically Active *trans*-3-Ethyl-3-methyl-2-(2′-methylpropenyl)-1,1-diphenylcyclopropane. This was prepared by the method used for the racemic compound. Reaction of 304.2 mg (1.15 mmol) of *trans*-2-ethyl-2-methyl-3,3-diphenylcyclopropanecarboxaldehyde, $[\alpha]^{27}_{365}$ 1298 ± 5°, with the ylide generated from 1.47 mmol of *n*-butyllithium and 806.2 mg (1.87 mmol) of isopropyltriphenylphosphonium iodide gave 172.4 mg (52%) of *trans*-3-ethyl-3-methyl-2-(2′-methylpropenyl)-1,1-diphenylcyclopropane as a colorless oil. Its specific rotations at 27° were (λ in parentheses): 122 ± 1° (589), 128 ± 1° (578), 147 ± 1° (546), 274 ± 2° (436), 490 ± 4° (365) (*c* 0.005, hexane). Rechromatography did not affect these values, nor did recrystallization from 95% ethanol to a constant melting point, which afforded 59.5 mg of colorless prisms, mp 55–56°. The ir and nmr spectra of the optically pure vinylcyclopropane were identical with those of the racemic compound. The ORD curve had maxima at 261, 268, and 275 nm, minima at 257, 263, and 271 nm, and intercepts at 250, 260, 262, and 265 nm; $[\alpha]^{27}_{257}$ -9.0×10^{2}°, $[\alpha]^{27}_{261}$ 4×10^{1}°, $[\alpha]^{27}_{263}$ -3×10^{2}°, $[\alpha]^{27}_{269}$ 2.2×10^{3}°, $[\alpha]^{27}_{271}$ 1.2×10^{3}°, $[\alpha]^{27}_{275}$ 3.9×10^{3}° (*c* 2.55×10^{-4}, hexane).

Optically Active *cis*-3-Ethyl-3-methyl-2-(2′-methylpropenyl)-1,1-diphenylcyclopropane. The method employed was that used for the racemic compound. Reaction of 177.0 mg (0.665 mmol) of *cis*-2-ethyl-2-methyl-3,3-diphenylcyclopropanecarboxaldehyde, $[\alpha]^{27}_{365}$ −837 ± 5°, with 1.22 mmol of isopropylidenetriphenylphosphorane gave 103 mg (53%) of the desired *cis*-vinylcyclopropane as a colorless oil. The specific rotations at 27° were (λ in parentheses): −66.4 ± 0.3° (589), −69.8 ± 0.3° (578), −81.0 ± 0.4° (546), −155 ± 1° (436), −286 ± 1° (365) (*c* 0.01, hexane). Crystallization and recrystallization from ethanol–water to constant melting point gave 51.1 mg of colorless crystals, mp 34–36°, with unchanged specific rotations. The ir and nmr spectra were identical with those of the racemic compound. The ORD curve had maxima at 256, 263, and 271 nm, minima at 261, 268, and 275 nm, and an intercept at 266; $[\alpha]^{27}_{256}$ 2.6×10^{3}°, $[\alpha]^{27}_{261}$ 1.2×10^{3}°, $[\alpha]^{27}_{263}$ 1.6×10^{3}°, $[\alpha]^{27}_{268}$ -1.1×10^{3}°, $[\alpha]^{27}_{271}$ 0 ± 40°, $[\alpha]^{27}_{275}$ -3.1×10^{3}° (*c* 4.5×10^{-4}, hexane).

Optically Active Methyl 3-Diphenylmethyl-3-methylpentanoate from Optically Active Methyl *trans*-2-Ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylate. The method employed was that used for the racemic compound. Reduction of 425.7 mg (1.45 mmol) of methyl *trans*-2-ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylate, $[\alpha]^{27}_{365}$ 827 ± 4°, with 27.2 mg (3.92 mg-atom) of lithium in 100 ml of anhydrous liquid ammonia afforded 285.3 mg (66%) of methyl 3-diphenylmethyl-3-methylpentanoate as a colorless oil. Its specific rotations at 27° were (λ in parentheses): −16.1 ± 0.2° (589), −17.1 ± 0.2° (578), −19.6 ± 0.2° (546), −35.0 ± 0.4° (436), −58.5 ± 0.7°) (365) (*c* 0.011, hexane). The ir and nmr spectra of the optically active ester were identical with those of the racemic material.

Optically Active Methyl 3-Diphenylmethyl-3-methylpentanoate from Optically Active Methyl *cis*-2-Ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylate. The method employed was the one used for the racemic compound. Reduction of 125.9 mg (0.427 mmol) of methyl *cis*-2-ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylate, $[\alpha]^{27}_{365}$ −793 ± 4°, with 8.9 mg (1.28 mg-atom) of lithium in 40 ml of anhydrous liquid ammonia gave 98.6 mg (78%) of the desired ester as a colorless oil. The ir and nmr spectra of this compound were identical with those of the racemic material, and its specific rotations were identical, in sign as well as in absolute value, with those of the (−)-methyl 3-diphenylmethyl-3-methylpentanoate prepared from (+)-methyl *trans*-2-ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylate.

Optically Active 3-Diphenylmethyl-3-methyl-1,1-diphenyl-1-pentanol. The method used was that employed for the racemic compound. Reaction of 281.6 mg (0.948 mmol) of methyl 3-diphenylmethyl-3-methylpentanoate, $[\alpha]^{27}_{365}$ −58.5 ± 0.7°, and 2.7 mmol of phenyllithium afforded 359 mg (90%) of the desired alcohol as a colorless oil. Its specific rotations at 27° were (λ in parentheses): 10.5 ± 0.2° (578), 12.2 ± 0.2° (546), 21.9 ± 0.3° (436), 37.3 ± 0.3° (365) (*c* 0.01, hexane). The optically active alcohol had ir and nmr spectra identical with those of the racemic compound. The product dehydrated to a small extent (*ca.* 2% or less) during the usual purification by chromatography. However, the dehydration product was effectively removed by discarding the first 10% of the eluted alcohol.

Optically Active 3-Diphenylmethyl-3-methyl-1,1-diphenylpentane from Optically Active 3-Diphenylmethyl-3-methyl-1,1-diphenyl-1-phenol. The method used was the one employed for the racemic compound. Reduction of 246.6 mg (0.586 mmol) of 3-diphenylmethyl-3-methyl-1,1-diphenyl-1-pentanol, $[\alpha]^{27}_{365}$ 37.3 ± 0.3°, with 12.2 mg (1.76 mg-atom) of lithium in 90 ml of anhydrous liquid ammonia gave 172.6 mg of colorless oil, $[\alpha]^{27}_{365}$ 20.6° (*c* 0.0140, hexane). The product was further purified by preparative tlc on a 20 × 20 cm plate coated with 40 g of silica gel (Brinkman GF-254). After elution with increasing amounts of benzene in hexane, two cleanly separated zones were observed by uv. The slower moving one was extracted with ether and concentrated *in vacuo* to give 151.8 mg (64%) of the desired tetraphenylalkane, $[\alpha]^{27}_{365}$ 16.7 ± 0.3° (*c* 0.035, hexane), as a colorless oil.

Final purification of the compound, as its benzene solvate, was effected by recrystallization as described earlier. This afforded 137.5 mg of 3-diphenylmethyl-3-methyl-1,1-diphenylpentane as a colorless oil. Its specific rotations and ir, nmr, and ORD data were identical with the values obtained from the (+)-tetraphenylalkane that was prepared from the other optically active tetraphenyl alcohol.

Quantum Yield Apparatus and Equipment. Quantum yield irradiations were carried out in the previously described "Black Box" apparatus.[20] Potassium ferrioxalate actinometry was used.[21]

Filter Solutions. Cell 1 of a triple compartment filter was filled with 2 *M* nickel sulfate in 5% sulfuric acid, cell 2 with 5% sulfuric acid saturated with cobalt sulfate at 25° and diluted with 25% of its volume of 5% sulfuric acid, and cell 3 with 2×10^{-4} *M* bismuth trichloride in 10% hydrochloric acid. This filter was opaque below 248 nm and above 313 nm; it showed a maximum transmission of 41% of 283 nm.

Quantum Yield Irradiations. *tert*-Butyl alcohol was distilled from calcium hydride. Solutions of 3-ethyl-3,5-dimethyl-1,1-diphenyl-1,4-hexadiene, $[\alpha]^{27}_{365}$ −67.5 ± 0.5°, in 750 ml of *tert*-butyl alcohol were irradiated to 11–18% conversion. For 1 hr before and during irradiation vanadous purified nitrogen[40] was bubbled through the solutions.

Run 1. The optically active ethylmethyldiene (966.9 mg, 3.33 mmol) captured 5.61 mEinsteins of light. After removal of the solvent *in vacuo* at less than 40°, 976.2 mg of slightly yellow oil remained; it was chromatographed on a 3.5 × 100 cm column of silicic acid–Celatom (*vide supra*) slurry packed in hexane. Elution with this solvent in 40-ml fractions, with uv scanning of the eluate at 260 nm, gave: fractions 22–31, 775.7 mg (2.67 mmol) of starting diphenyldiene, $[\alpha]^{27}_{365}$ −68.0 ± 0.2 (*c* 0.01, hexane); fractions 32–35, 4.3 mg of oil, starting diene and some uncharacterized material; fractions 36–51, 174.2 mg of a colorless oil that was, by nmr, a *ca.* 5:4 mixture of *trans*- and *cis*-3-ethyl-3-methyl-2-(2′-methylpropenyl)-1,1-diphenylcyclopropanes (0.600 mmol, ϕ = 0.107 ± 0.007).

Run 2. The ethylmethyldiene (994 mg, 3.42 mmol) absorbed 3.37 mEinsteins of light. Chromatography of the concentrated photolysate afforded 795.7 mg (2.74 mmol) of starting diene and 107.5 mg (0.404 mmol) of the photovinylcyclopropane isomer mixture, ϕ = 0.110 ± 0.007.

Separation of the Photovinylcyclopropanes. The vinylcyclopropane isomer mixtures obtained from the quantum yield runs were separated by high-pressure liquid chromatography (hplc), with recycling, on three 4 ft × 3/8 in. columns of silicic acid (Mallinckrodt SilicAR cc-7, 200–325 mesh) installed in series in a liquid chromatograph similar in design to Waters Associates' Model

(40) L. Meites and T. Meites, *Anal. Chem.*, 20, 984 (1948).

ALC-100. Elution was with hexane at a flow rate of 3 ml/min. In order to preserve the activity of the columns, a drying column of activated silica gel was included in the line connecting the solvent reservoir and the pump.

Portions of *ca.* 50 mg of photovinylcyclopropanes were injected as solutions in *ca.* 250 μl of hexane and eluted until a total of five to eight cycles had been completed. In each case a partial separation had been effected by this time; the uv scan showed two overlapping peaks, the faster moving of which was later seen to contain the cis isomer. The eluate was collected at this point and fractions were concentrated. In each case all but *ca.* 50 ml of the solvent was distilled off at reduced pressure through a short column of glass beads; the rest was removed *in vacuo*. Then, after elimination of solvent residue *via* chromatography on a short (1.0 × 25 cm) silica gel column, specific rotations were measured. From the photovinylcyclopropanes of quantum yield No. 2 were obtained 25.1 mg of material highly enriched (*ca.* 90%) in the cis isomer and 32.6 mg similarly enriched in the trans isomer. Both of these fractions were subjected to further recycling hplc, and the material obtained was, in each case, combined with parallel product from quantum yield No. 1 and chromatographed again. The rate at which the separation progressed was indicated by the improvement with repeated chromatography of the $[\alpha]^{27}_{365}$ of the cis- and trans-enriched fractions. In the cis case these values changed as follows: after the first chromatography, 267 ± 6°; after the second, 273 ± 3°; and after the last, 274 ± 1°. In the trans case these rotations were: after the first chromatography, −442 ± 13°; after the second, −460 ± 8°; after the third, −472 ± 5°; and after the last, −470 ± 2°.

The specific rotations (at 27°) of the cis vinylcyclopropane that had been chromatographed to constant rotation were (λ in parentheses): 64.0 ± 0.4° (589), 67.2 ± 0.4° (578), 78.5 ± 0.5° (546), 148.5 ± 1.5° (436), 273 ± 3° (365) (*c* 0.005, hexane). Those of the similarly purified trans isomer were: −117 ± 1° (589), −123 ± 1° (578), −141 ± 1° (546), −263 ± 2° (436), −472 ± 5° (365) (*c* 0.005, hexane). The purified *cis*- and *trans*-3-ethyl-3-methyl-2-(2′-methylpropenyl)1,1-diphenylcyclopropanes had ir and nmr spectra identical with those of the independently synthesized compounds, and their ORD curves were perfect mirror images of those of the independently synthesized compounds.

Control Experiment. The Effect of Hplc on Optically Active *trans*-3-Ethyl-3-methyl-2-(2′-methylpropenyl)-1,1-diphenylcyclopropane. A 50.5-mg sample of *trans*-3-ethyl-3-methyl-2-(2′-methylpropenyl)-1,1-diphenylcyclopropane, $[\alpha]^{27}_{365}$ 490 ± 4°, was subjected to hplc under conditions identical with those described above. After five cycles the eluate was collected. Approximately the first 10% of the vinylcyclopropane to elute was removed. The rest amounted to 35 mg of clear colorless oil, $[\alpha]^{27}_{365}$ 494° (*c* 0.009, hexane), after removal of solvent residue on a short silica gel column. This material was rechromatographed under the same conditions, and this time all the eluate was combined to give 19 mg of clear slightly yellow oil, $[\alpha]^{27}_{365}$ 479 ± 1° (*c* 0.009, hexane). This oil was subjected to hplc once again, with separation of the first 10% or so of the collected vinylcyclopropane from the rest. The larger fraction amounted to 11.2 mg of clear yellow oil, $[\alpha]^{27}_{365}$ 487 ± 3° (*c* 0.0056, hexane). Nmr and ir spectral properties of the three-times chromatographed *trans*-vinylcyclopropane were unchanged.

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Kinetics of the Electron Transfer Reactions of Azaviolene Radical Ions. I

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Abstract: Azaviolenes are part of a two-step redox system in which three forms can be reversibly interconverted by one-electron transfers, $Ox^{2+} + e^- \rightleftharpoons Sem^+ + e^- \rightleftharpoons Red$. The comproportionation–disproportionation kinetics of two such systems have been studied by the temperature-jump and stopped-flow methods in 50% 2-methoxyethanol–water. It is shown that, depending on the pH, there are up to three electron transfer pathways of importance, *viz.*, (1) $Red + Ox^{2+} \rightleftharpoons 2Sem^+$, (2) $RedH^+ + Ox^{2+} \rightleftharpoons Sem^+ + SemH^{2+}$, and (3) $RedH_2^{2+} + Ox^{2+} \rightleftharpoons 2SemH^{2+}$. Furthermore, there is a general acid–base catalyzed pathway, *viz.*, $RedH^+ + Ox^{2+} + B^- \rightleftharpoons 2Sem^+ + BH$. This study focuses on the relationship between rate and equilibrium constants in organic redox systems and in particular on the question of how strongly must an electron transfer reaction be favored thermodynamically for its rate to become diffusion controlled. Our results correlate reasonably well with the Marcus theory of electron transfer reactions.

Because of the fundamental importance of electron transfer reactions in organic redox systems, it is desirable to seek a better understanding of the factors determining the rates of these elementary processes. We now focus attention on the relationship between the kinetics and the thermodynamics of systems for which both the equilibrium constant and the rate of equilibration can be determined.

With reference to the redox equilibrium

$$A^m + D^n: \underset{k_r}{\overset{k_f}{\rightleftharpoons}} A\cdot^{m-1} + D\cdot^{n+1} \qquad (1)$$

a relevant question is: how large must the equilibrium constant $K_f = k_f/k_r$ be in order for the k_f step to be diffusion controlled?

For another important class of elementary processes, *viz.*, proton transfer reactions, there exists a large body of data correlating rates with equilibrium constants; the data give a satisfactory answer to the same kind of question.[2a] Unfortunately, relatively few such data exist for reversible organic redox reactions.

A class of compounds, known as azaviolenes,[2b] ap-

(1) Alfred P. Sloan Fellow, 1971–1973.

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