Stereochemistry of the Aryl–Vinyl Version of the Di-π-methane Rearrangement[1,2]

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Of the three known versions of the di-π-methane rearrangement—the divinylmethane case, the aryl–vinylmethane variety, and the oxa–di-π-methane variation—the reaction stereochemistry has been established in only two. The present study deals with stereochemistry at the methane carbon in the aryl–vinylmethane rearrangement. The rearrangement proceeds with inversion of configuration at this center in analogy to the divinylmethane rearrangement but in contrast to the oxa–di-π-methane process where stereochemistry is sometimes lost. Thus, direct irradiation of (−)-3-(*p*-methoxyphenyl)-3-methyl-1,1-diphenyl-1-pentene led to (+)-*trans*-2-ethyl-2-methyl-3,3-diphenyl-1-(*p*-methoxyphenyl)cyclopropane and to the (−)-cis isomer. By correlation of configurations of reactant and products it was shown that the methane carbon was inverted in the reaction. Extrapolation of the photochemistry to zero percent conversion revealed 100.1 ± 1.7% optical purity of photoproduct. The example is one where extrapolation is required, and even runs as low as 6% conversion lead to error. In the ordinary divinylmethane version inversion of configuration is readily predicted using a six-orbital cyclic array of atomic and hybrid orbitals. In the present aryl–vinylmethane case a cyclic array including one molecular orbital allowed theoretical treatment. Again inversion was predicted.

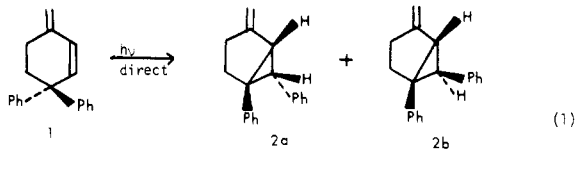
The di-π-methane rearrangement has become one of the most general and useful of photochemical reactions. A thorough understanding of all of its facets has been a goal of our research for some years.[3] Our research has concentrated on two of the three variations of the reaction. Thus, of the divinylmethane version, the aryl–vinylmethane variety and the oxa-di-π-methane type, the first two have been of special interest to us.

While structurally similar, the three versions do differ in a number of respects. The divinylmethane and the aryl–vinylmethane rearrangements utilize both singlets and triplets while the oxa–di-π-methane modification proceeds by the triplet excited state.[4] The aryl–vinylmethane singlets tend to rearrange more slowly than their divinylmethane counterparts.[5-7] Still another difference is that the divinylmethane rearrangement requires central (i.e., methane carbon) substitution while the aryl–vinylmethane[6] and oxa–di-π-methane varieties do not.[4]

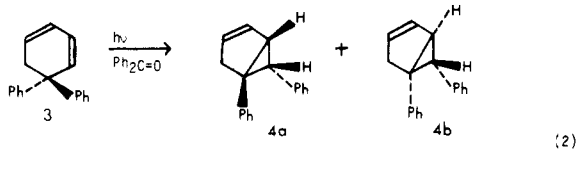
The reaction stereochemistry has been investigated in two of the three rearrangements. Here, again, there is a difference. Thus, our earlier efforts[8] have shown that the methane carbon is inverted in the divinylmethane rearrangement. In contrast, the oxa–di-π-methane rearrangement sometimes proceeds with loss of methane carbon stereochemistry,[9] and sometimes proceeds with inversion.[10]

Our present study was aimed at determining the stereochemistry of the aryl–vinylmethane version of the rearrangement. The most difficult question deals with the nature of the stereochemistry at the methane carbon.

In the cases of 1-methylene-4,4-diphenyl-2-cyclohexene (**1**)[11] and 5,5-diphenyl-1,3-cyclohexadiene (**3**),[12] there is constrained geometry; nevertheless, the di-π-methane rearrangement is of the aryl–vinyl type and is instructive. It is seen that the major products from each of these photolyses is the *trans*- or *endo*-phenyl stereoisomer (i.e., **2a** and **4a**). Reference to structure **5** in Figure 1 reveals that as one phenyl group migrates from the methane carbon, overlap of the anti lobes of the orbitals at carbons 2 and 4 with disrotatory twisting leads to the preferred product. Disrotatory twisting with syn overlap affords the minor product. Accordingly, the major reaction course involves inversion of configuration at the methane carbon (i.e., C-4) and anti overlap with the vinyl p orbital (i.e., at C-2) in this phenyl–vinylmethane system.

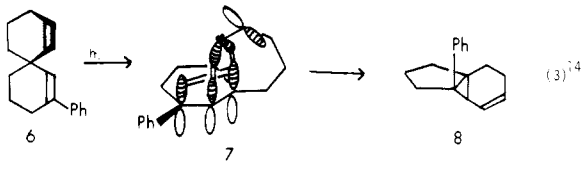


(1)



(2)

This stereochemistry is then the same at the methane carbon as in divinylmethane systems,[8] and the anti preference for bonding with the vinyl moiety also parallels our findings in divinylmethane systems.[13] However, the systems in eq 1 and 2 are constrained, and thus the natural preference in absence of constraints is still uncertain. For example, Mariano and co-workers[14] have presented an unusually elegant example of enforced syn-disrotatory stereochemistry in the divinylmethane example in eq 3.



(3)[14]

With this background, it was clear that a test of the stereochemistry of an unconstrained aryl–vinylmethane needed investigation. The aim of the present investigation was determination of the methane carbon behavior.

For our study we selected the 3-(*p*-methoxyphenyl)-3-methyl-1,1-diphenyl-1-pentene (**9**). Our approach required resolution of the reactant, study of its photolysis, and then correlation of configurations of reactant and products.

Results. Synthesis of Photochemical Reactant. The synthesis employed is outlined in Scheme I and detailed in the Experimental Section. One requisite for the synthesis was that one of the intermediates be resolvable; the synthesis selected utilized anisyl acid **12** for this purpose. A point of interest is the facile fragmentation of the anisyl carbinol **14** to give diphenylethylene and alkene derived from the 2-anisyl-2-butyl cation under acidic dehydration conditions. Thus, the phosphorus oxychloride–pyridine method was required.

Results. Exploratory Photochemistry. In a typical exploratory run irradiation of 430 mg of anisyl–vinylmethane

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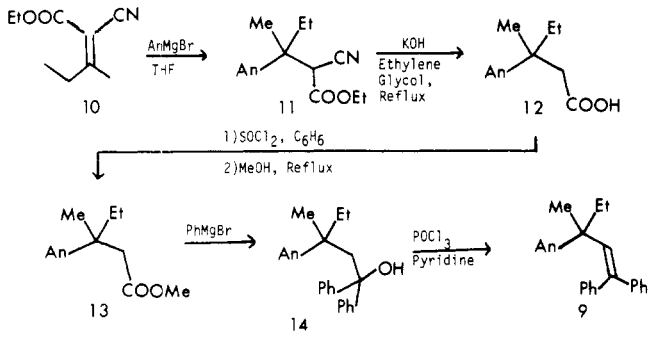
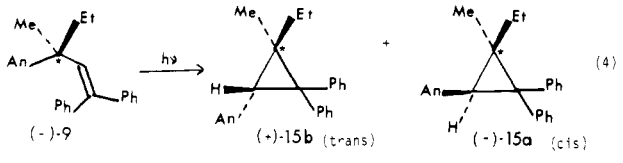
Scheme I. Synthesis of Photochemical Reactant



reactant **9** in a 450 W immersion apparatus for 45 min led to 185 mg of a mixture of *cis*- and *trans*-2-ethyl-2-methyl-3,3-diphenyl-1-(*p*-methoxyphenyl)cyclopropane (**15**), 112 mg of recovered aryl–vinylmethane reactant (**9**), and 54 mg of a fraction consisting of a 10:1 mixture of reactant and cyclopropane product. The product stereoisomers were separable by recycling HPLC and were found to be present in a 3:1 ratio favoring the trans isomer. The product structure derives from a degradation described below in connection with correlation of configurations. The overall reaction is given in eq 4. How-



ever, thus far, the relative configurations of reactant and products remain unknown and are depicted arbitrarily.

Results. Reactant Resolution, Product Degradation, and Correlation of Configurations. In order to elucidate the stereochemical course of the reaction as pertains to the methane carbon, it was necessary to obtain optically active aryl–vinylmethane **9.** It was also necessary to develop a scheme relating the configuration of this photochemical reactant to the cis and trans isomers of photoproduct **15.**

The first objective was achieved by resolution of 3-anisyl-3-methylpentanoic acid (**12**). This was then used as depicted in Scheme II to synthesize optically active aryl–vinylmethane **9.**

The second objective was to correlate the configuration of resolved aryl–vinylmethane **9** to the configurations of *cis*- and *trans*-2-ethyl-2-methyl-3,3-diphenyl-1-anisylcyclopropane (i.e., **15a** and **15b**). Again, this is depicted in Scheme II. It was found that aryl–vinylmethane **9,** cis photoproduct **15a,** and trans photoproduct **15b** with the relative configurations shown in Scheme II have negative, negative, and positive rotations, respectively. Scheme II depicts (*S*)-**9** as having a rotation opposite in sign to **15b** having an (*R*) configuration at the methane carbon but a rotation the same in sign as **15a** with an (*R*) configuration at the methane carbon.

In the above configurational interrelating efforts it seemed particularly important to ascertain that each compound was free of contaminating impurities. Therefore, for each active compound rotations were taken at five wavelengths. This promised that the correlations would be error free and that the relative optical purity of photochemical reactant and products could be determined with maximum accuracy. Table I lists the optically active compounds and their rotations. Finally, we note that to obtain the rotation of optically pure cis and trans anisylcyclopropane photoproducts, active photoproducts of known rotation were ozonized as in Scheme II to diphenyl acids **20a** and **20b** whose activity then could be compared with the optically pure acids.[8]

Results. Irradiation of Optically Active Anisyl–Vinylmethane 9. Photolysis of resolved (−)-**9** (i.e., anisyl–vinylmethane) to a conversion of 14.2% gave optically active *cis*- and *trans*-1-anisyl-2-ethyl-2-methyl-3,3-diphenylcyclopropanes (**15a** and **15b**). The first point to be noted is that trans photoproduct **15b** had a positive rotation at all five wavelengths while cis photoproduct **15a** had a negative rotation at these wavelengths. Reference to Scheme II therefore indicates that anisyl–vinylmethane **9** of the relative configuration depicted in this scheme affords cis and trans photoproducts having configurations which also are as drawn in this scheme. Comparison with eq 4 then reveals that this equation quite properly depicts the stereochemistry of the rearrangement. Of course, only relative and not absolute configurations are connoted by eq 4 and Scheme II.

However, comparison of the rotations of the photoproducts with that of optically pure materials revealed that the trans

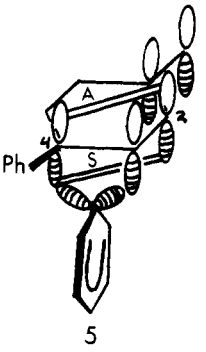
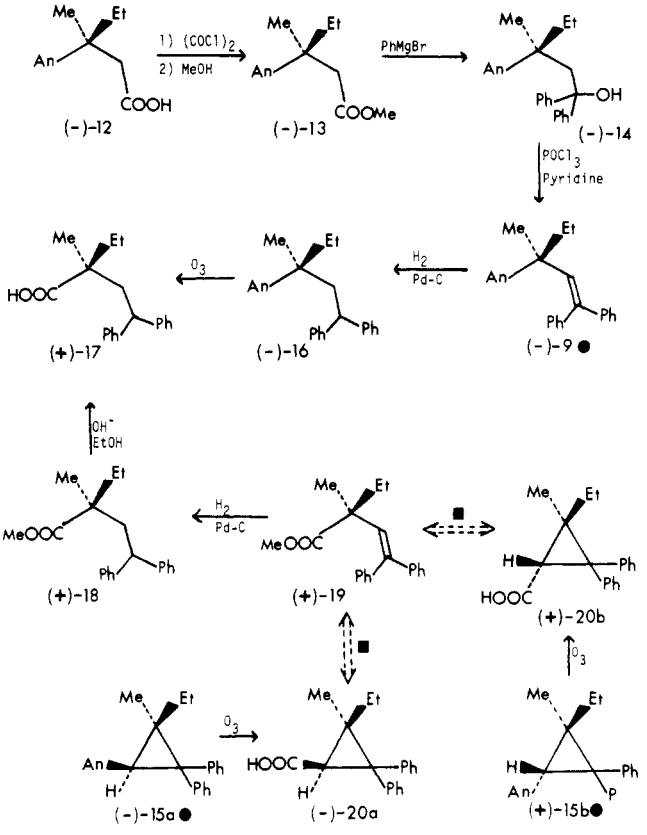


Figure 1. Phenyl-bridged species showing syn (S) and anti (A) disrotatory twisting illustrated for diene **1.**

Scheme II. Interrelation Scheme Correlating Photochemical Reactant 9 and Product 15[a]



[a] Experimentally, (−)-**17,** (−)-**18,** and (−)-**19** were actually interrelated but reverse configurations are depicted for simplicity of presentation. (●) Compounds to be related. (■) Relative configurations known (ref 8).

Table I. Configurationally Related Compounds and Their Rotations

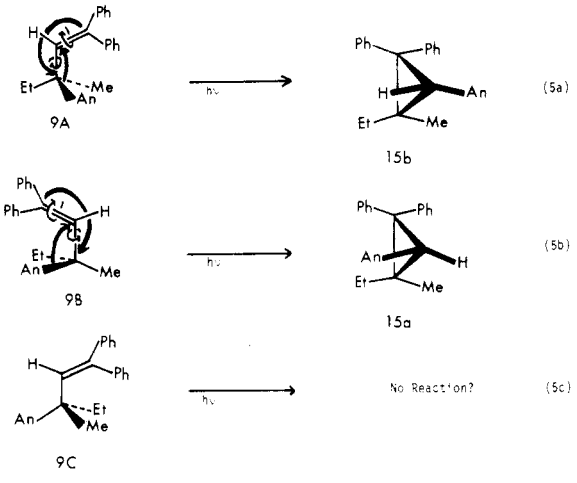
compd[a]	specific rotations[b] at 25 °C, nm 589	578	546	436	365
anisyl–vinylmethane **9**	−93.0	−97.0	−112.0	−205.0	−342.0
saturated acid **17**	21.8	22.7	25.9	46.5	80.4
unsaturated ester **19**[c]	19.6	20.8	24.4	50.4	102.5
photoproduct **15b**[d]	−103.0	−107.0	−125.0	−250.0	−488.0
photoproduct **15a**[d]	72.2	74.7	88.6	184.0	368.0
cyclopropyl acid **20b**[c]	−195.0	−205.0	−238.0	−456.0	−842.0
cyclopropyl acid **20a**[c]	172.0	182.0	208.0	404.0	757.0

[a] These compounds all have the same configuration at the ethyl–methyl carbon. [b] Degrees. [c] See ref 8. [d] Rotations given are for materials of 100% optical purity.

Table II. Effect of Percent Conversion on Photoproduct 15b Optical Purity[a]

% conversion	14.2 ± 0.7	10.1 ± 0.5	5.6 ± 0.4	zero conversion
optical purity of **15b**	87.2 ± 1.5	91.3 ± 1.6	95.0 ± 2.0	100.1 ± 1.7[b]

[a] Measurements at five wavelengths provided evidence for absence of contaminants. Each value is the average of two independent determinations. [b] Extrapolated value.



product was only 87.2% optically pure and the cis photoproduct was only 79.0% pure. Accordingly, the stereochemistry was studied at two lower conversions, 10.1 and 5.6%. Interestingly, the optical purity of the trans photoproduct **15b** rose successively to 91.3 and 95.0%. For each run, rotations at five wavelengths were employed to give optical purity. Additionally, the sample from each run was subjected to a second purification process by recycling HPLC followed by remeasurement of rotations. The optical purities summarized in Table II thus result from a least-squares treatment of data derived from five wavelengths and two successive purifications by HPLC. The scatter proved to be below 2%.

In view of the variation of optical purity with extent conversion it was clear that product racemization during photolysis was a problem. Reactant was found not to racemize during reaction. Product racemization arose due to overlap of absorption peaks of reactant **9** and products **15a** and **15b**. Extrapolation led to a 0% conversion optical purity of 100.1 ± 1.7%, and this is included in Table II. For the cis photoproduct the smaller amounts afforded did not allow a similar extrapolation. The extrapolation for the trans isomer is seen to lead to a prediction of photorearrangement without loss of optical activity.

Results. Quantum Yield Determinations. Quantum yields were determined on the Black Box apparatus[15] using our electronic actinometer.[16] The actinometer was calibrated prior to each run with ferrioxalate actinometry.[17] Product assay was by VPC calibrated with an internal standard. As with the optical purity, the quantum yields determined proved to be a function, albeit weaker, of extent conversion, and these, too, were extrapolated back to zero conversion. For the formation of cis and trans photoproducts the quantum yields were ϕ(cis) = 0.023, ϕ(trans) = 0.070, and ϕ(total) = 0.093.

Interpretative Discussion. The first conclusion to be drawn is that the aryl–vinylmethane version of the di-π-methane reaction proceeds with inversion of configuration at the methane carbon. Thus (note eq 4), as the anisyl group migrates from the methane carbon to the adjacent vinyl position, the benzyhydryl moiety bonds to the methane carbon on the face opposite to the departing anisyl.

A second point of interest is that there is a preference for formation of the trans photoproduct over cis (3.0:1.0). If we consider the stereochemistry of the anisyl migration as in eq 5a and 5b, we note that there are two reactive conformations, **9A** and **9B**. Actually, the most stable conformation **9C** (note eq 5c) is one in which the diphenylvinyl group is skewed between the smallest two groups on the methane carbon, namely methyl and ethyl. However, this conformer does not allow access of the anisyl group to the vinyl π system. In the reactive conformer **9A**, the diphenylvinyl group is skewed between the methyl and anisyl groups, while in the reactive conformer **9B**, the diphenylvinyl moiety is skewed between the ethyl and anisyl groups. It is clear that the population of conformer **9A** is greater than for **9B** due to the smaller diphenylvinyl–methyl interaction compared with diphenylvinyl–ethyl. To the extent that the rearrangement captures only molecules conformationally prepared to react (i.e., in conformations **9A** and **9B**), one would expect more trans product (i.e., **15b**) than cis product (i.e., **15a**). Thus, inspection of eq 5a and 5b reveals that **9A** leads to trans product while **9B** leads to cis product as a consequence of inversion of configuration at the methane carbon.

The above discussion assumes that the rate of excited singlet decay is rapid compared with reactant conformational equilibration in the excited state. To the extent that S_1 molecules formed in unreactive conformation, **9C**, can leak into the reactive conformations **9A** and **9B**, product approach control[18] should also lead to the observed preference for trans product, since formation of trans product **15b** involves buildup of lesser van der Waals repulsions (i.e., vinyl–methyl interactions instead of vinyl–ethyl) in the product.

An intriguing point arises from this stereoselectivity. It has been noted in the divinylmethane version of the di-π-methane rearrangement that methane substitution only by hydrogen and absence of geminal (e.g., methyl) substitution inhibits the reaction.[19,20] In the case of the aryl–vinylmethane version the effect is less severe but, nevertheless, a dramatic S_1 rate inhibition is encountered.[6,21] The present discussion and findings lead us to note that in absence of central (i.e., methane carbon) substitution, the transoid conformer analogous to **9C** should be virtually exclusively populated and this conformer is unreactive. Thus the central methyl effect on reactivity may well stem from stereochemical factors as well as electronic ones arising from the methane carbon becoming[6] electron deficient in the rearrangement.

Finally, it is important to comment that the observed ste-

reochemistry is in accord with the predicted allowed stereochemistry involving a Möbius transition state.[22] The array (note Figure 2) is analogous to one we have postulated[8] for the divinylmethane version of the rearrangement. One novel feature of the present array is that one of the basis orbitals constituting the cycle is a molecular orbital rather than an atomic or hybrid orbital; this is the nonbonding MO (orbital f in Figure 2) of the pentadienyl portion of the bridging aryl group. Thus in Möbius–Hückel reasoning, the cyclic array employed may consist of MO's as well as AO's. With six delocalized electrons in a Möbius system, the reaction is excited state allowed.[22]

It does require comment that a disrotatory twist is assumed in the orbital array depicted, although no test of reaction stereochemistry was possible at the diphenyl carbon. In such acyclic systems the term disrotatory is not meaningful without an assumed initial conformation and is better defined for an aryl bridged species of the type in Figure 1 and species **21** in Figure 2. Until further studies are completed, this assumption rests on (a) the observation of disrotatory twisting without reaction inefficiency[11,12] in the examples shown in eq 1 and 2 and (b) on the analogy to disrotatory twisting in the divinylmethane version of the di-π-methane rearrangement.[13,14,23]

Conclusion. Discussion of our present study is best ended with the comments that the di-π-methane rearrangement has become one of the most common and understood photochemical reactions and that this poses a challenge to determine the factors controlling organic photochemistry more generally.

Experimental Section[24]

Ethyl 2-Cyano-3-(*p*-methoxyphenyl)-3-methylpentanoate. A solution of *p*-anisylmagnesium bromide, prepared from 7.92 g (0.33 mol) of magnesium and 61.0 g (0.33 mol) of *p*-bromoanisole in 150 mL of anhydrous tetrahydrofuran, was cooled to 0 °C, and to it a solution of 54.5 g (0.33 mol) of ethyl 2-cyano-3-methyl-2-pentenoate[25] was slowly added dropwise. After the addition was complete, the mixture was cooled and stirred at room temperature for 12 h and then poured into saturated aqueous ammonium chloride and ether extracted. The extracts were washed with water and saturated aqueous sodium chloride, dried over anhydrous magnesium sulfate, and concentrated in vacuo. The residue was vacuum distilled, and the fraction boiling at 160–205 °C (0.05 to 0.3 torr) was collected to give 48.5 g (54%) of a clear colorless oil which was a mixture of the two diastereomers of ethyl 2-cyano-3-(*p*-methoxyphenyl)-3-methylpentanoate.

The spectral data of the mixture follows: NMR (CCl_4) τ 2.6–3.0 (d of d, 2 H, half of two overlapping AB q, aromatic, J = 8 Hz), 3.0–3.4 (d of d, 2 H, second half of two overlapping AB q, aromatic, J = 8 Hz), 5.95 and 6.12 (q, 2 H, $CO_2C\mathbf{H}_2CH_3$, J = 7 Hz), 6.26 (s, 3 H, OCH_3), 6.35 and 6.40 (s, 1 H, methines), 7.7–8.3 (m, 2 H, $\mathbf{CH}_2CH_3$), 8.43 (br s, 3 H, CH_3), 8.88 and 9.03 (t, 3 H, $CO_2CH_2\mathbf{CH}_3$, J = 7 Hz), 9.30 (br t, 3 H, $CH_2\mathbf{CH}_3$, J = 7 Hz); IR (CCl_4) 3.35, 3.40, 3.42, 3.47, 3.52, 4.45, 4.49, 5.75, 6.20, 6.32, 6.62, 6.85, 6.95 (sh), 7.21, 7.30, 7.55, 7.70, 8.00, 8.45, 8.82, 9.10, 9.67, and 12.10–13.70 μm.

Anal. Calcd for $C_{16}H_{21}O_3N$: C, 69.79; H, 7.68; N, 5.08. Found: C, 69.97; H, 7.56; N, 5.18.

3-(*p*-Methoxyphenyl)-3-methylpentanoic Acid. A mixture of 33.0 g (0.12 mol) of ethyl 2-cyano-3-(*p*-methoxyphenyl)-3-methylpentanoate, 133 g (2.4 mol) of potassium hydroxide, and 360 mL of ethylene glycol was refluxed for 7.5 h. The resulting solution was cooled to room temperature, poured into water, and washed with ether. The aqueous layer was acidified to the methyl orange end point with concentrated hydrochloric acid and ether extracted. The extracts were dried over anhydrous magnesium sulfate and treated with norite; the solvent was removed in vacuo to give an oily brown solid residue. The residue was sublimed twice under reduced pressure (80 °C, 0.05 torr) and recrystallized from chloroform–hexane to give 6.0 g (60%) of 3-(*p*-methoxyphenyl)-3-methylpentanoic acid, mp 90–92 °C. An analytical sample was prepared by recrystallization from chloroform–hexane to give colorless needles, mp 92–93 °C.

The spectral data were: NMR ($CDCl_3$) τ −0.07 (br s, 1 H, COOH), 3.08 (AB q, 4 H, aromatic, J = 9 Hz), 6.27 (s, 3 H, OCH_3), 7.44 (s, 2 H, $\mathbf{CH}_2COOH$), 8.26 (m, 2 H, $\mathbf{CH}_2CH_3$), 8.58 (s, 3 H, CH_3), 9.33 (t, 3 H, $CH_2\mathbf{CH}_3$, J = 7 Hz); IR ($CHCl_3$) 3.0–3.6, 5.88, 6.21, 6.62, 6.85, 7.10, 7.21, 7.72, 8.00, 8.30, 8.50, 8.85, 9.68, and 12.20 μm.

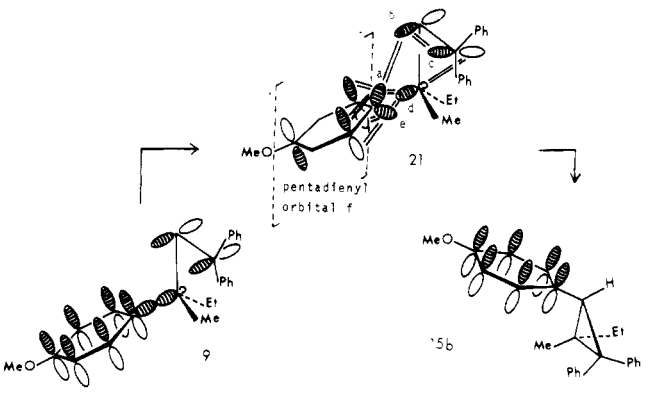


Figure 2. Involvement of a Möbius orbital array in the rearrangement.

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.08; H, 8.26.

Methyl 3-(*p*-Methoxyphenyl)-3-methylpentanoate. To a solution of 2.22 g (10 mmol) of 3-(*p*-methoxyphenyl)-3-methylpentanoic acid in 15 mL of benzene were added 1.7 mL (20.0 mmol) of thionyl chloride and 0.05 mL of dimethylformamide. The resulting mixture was stirred at room temperature for 1.5 h, poured into 50 mL of methanol, refluxed for 30 min, and cooled; the solvent was removed in vacuo. The residue was taken up in ether, washed once with water and once with saturated aqueous sodium bicarbonate, and dried; the solvent was removed in vacuo to give 2.32 g (98%) of the methyl 3-(*p*-methoxyphenyl)-3-methylpentanoate as a light yellow oil. This material was decolorized by passage through a 2.0 × 40 cm slurry packed silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column; elution with 1 L of 3% ether in hexane gave 2.30 g (97%) of the pure ester as a colorless oil.

The spectral data were: NMR (CCl_4) τ 3.08 (AB q, 4 H, aromatic, J = 10 Hz), 3.60 (s, 3 H, OCH_3), 6.58 (s, 3 H, CO_2CH_3), 7.52 (s, 2 H, $\mathbf{CH}_2CO_2CH_3$), 8.10–8.50 (m, 2 H, $\mathbf{CH}_2CH_3$), 8.64 (s, 3 H, CH_3), 9.38 (t, 3 H, $CH_2\mathbf{CH}_3$, J = 8 Hz); IR (CCl_4) 3.31, 3.36, 3.38, 3.39, 3.42, 3.46, 3.51, 5.76, 6.20, 6.31, 6.61, 6.82, 6.96, 7.22, 7.45, 7.80, 7.98, 8.44, 8.85, 9.05, 9.60, 9.90, and 12.00–13.60 μm.

Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 70.95; H, 8.67.

3-(*p*-Methoxyphenyl)-3-methyl-1,1-diphenyl-1-pentanol. To a solution of phenylmagnesium bromide, prepared from 21.98 g (140 mmol) of bromobenzene and 3.40 g (140 mg-atom) of magnesium turnings in 140 mL of anhydrous tetrahydrofuran, was added dropwise under nitrogen a solution of 8.30 g (35 mmol) of methyl 3-(*p*-methoxyphenyl)-3-methylpentanoate in 50 mL of anhydrous tetrahydrofuran. After being stirred for 12 h, the mixture was quenched by addition of 2 mL of saturated aqueous ammonium chloride solution, poured into water, and ether extracted. The extracts were dried, and the solvent was removed in vacuo to give a viscous yellow oil which was chromatographed on a 2.5 × 90 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column. Biphenyl was eluted with hexane and then the 3-(*p*-methoxyphenyl)-3-methyl-1,1-diphenyl-1-pentanol was eluted as the only other UV-active band with 3% ether in hexane to give 10.96 g (87%) of a colorless oil which was essentially pure. An analytical sample was prepared by recrystallization from pentane to give colorless plates, mp 61–62 °C.

The spectral data were: NMR (CCl_4) τ 2.48–3.04 (m, 12 H, aromatic), 3.29 (d, half of AB q, 2 H, aromatic, J = 9 Hz), 6.27 (s, 3 H, OCH_3), 7.21 (br s, 1 H, OH), 8.25 (s, 2 H, $\mathbf{CH}_2C(Ph)_2OH$), 8.40 (q, 2 H, $\mathbf{CH}_2CH_3$, J = 7 Hz), 9.02 (s, 3 H, CH_3), 9.47 (t, 3 H, $CH_2\mathbf{CH}_3$, J = 7 Hz); IR (CCl_4) 2.79, 3.25, 3.29, 3.36, 3.40, 3.45, 3.51, 6.20, 6.32, 6.62, 6.70, 6.90, 7.21, 7.40, 7.70, 8.00, 8.42, 9.40, 9.60, 9.90, 10.18, 11.35, 12.10–13.70, and 14.28 μm.

Anal. Calcd for $C_{25}H_{28}O_2$: C, 83.29; H, 7.83. Found: C, 83.14; H, 7.91.

3-(*p*-Methoxyphenyl)-3-methyl-1,1-diphenyl-1-pentene. To a stirred solution of 2.39 g (6.64 mmol) of 3-(*p*-methoxyphenyl)-3-methyl-1,1-diphenyl-1-pentanol in 60 mL of dry pyridine was added 2.55 g (16.6 mmol) of phosphorus oxychloride. After refluxing for 7 h under nitrogen the solution was poured into a mixture of 65 mL of concentrated hydrochloric acid and 100 g of ice and ether extracted. The extract was washed three times with 2 N hydrochloric acid and once with saturated aqueous sodium bicarbonate and dried; the sol-

vent was removed in vacuo. The resulting clear, slightly yellow oil was decolorized by passage through a 4 × 35 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column. Elution with 5% ether in hexane gave in the only UV-active band 2.10 g (92.5%) of the 3-(*p*-methoxyphenyl)-3-methyl-1,1-diphenyl-1-pentene as a colorless oil. Recrystallization from pentane gave 2.00 g (88%) of the olefin as colorless prisms, mp 35–36 °C.

The spectral data were: NMR (CCl_4) τ 2.8–3.3 (m, 12 H, aromatic), 3.38 (d, half of AB q, 2 H, aromatic, J = 9 Hz), 3.64 (s, 1 H, vinyl), 6.28 (s, 3 H, OCH_3), 8.26 (q, 2 H, $\mathbf{CH_2}CH_3$, J = Hz), 8.88 (s, 3 H, CH_3), 9.20 (t, 3 H, $CH_2\mathbf{CH_3}$, J = 7 Hz); IR (CCl_4) 3.22, 3.23, 3.26, 3.29, 3.32 (sh), 3.36, 3.40, 3.46, 3.49, 3.52, 6.21, 6.32, 6.62, 6.69, 6.74, 6.85, 6.92, 7.23, 7.70, 7.75, 8.00, 8.46, 8.98, 9.32, 9.62, 9.98, 12.10–13.66, 14.25, 14.80, and 14.98 μm; UV (EtOH) λ_{max} 228 (ϵ 17 600), 251 (15 000), 285 (4200).

Anal. Calcd for $C_{25}H_{26}O$: C, 87.67; H, 7.65. Found: C, 87.47; H, 7.61.

Exploratory Photolysis of 3-Methyl-3-(*p*-methoxyphenyl)-1,1-diphenyl-1-pentene. A solution of 430 mg of 3-methyl-3-(*p*-methoxyphenyl)-1,1-diphenyl-1-pentene in 250 mL of *tert*-butyl alcohol was degassed with vanadous purified nitrogen[26] for 45 min and swept with nitrogen while irradiated with a 450-W medium-pressure lamp using a Corex filter for 45 min. The photolysate was concentrated in vacuo to a yellow oil which was chromatographed on a 1.8 × 90 cm, silica gel column, slurry packed in hexane, with UV scanning at 260 nm. Elution was with 5% methylene chloride in hexane; 40-mL fractions were collected. Fractions 44–100 gave 112.4 mg of starting material; 101–114 gave 21.3 mg of a mixture of starting material and *cis*-2-ethyl-2-methyl-3,3-diphenyl-1-(*p*-methoxyphenyl)cyclopropane, approximately 3:1 by NMR; 115–125 gave 32.7 mg of a mixture of starting material, *cis*-cyclopropane and *trans*-cyclopropane approximately 1:1:1 by NMR; 126–145 gave 88.5 mg of a mixture of *cis*- and *trans*-cyclopropanes, approximately 1:2 by NMR; and 145–190 gave 96.9 mg of a mixture of *cis*- and *trans*-cyclopropanes, approximately 1:10 by NMR. See the next section for the spectral and physical data for the two photoproducts. VPC analysis of the various fractions revealed the following retention times on 3% Carbowax at 200 °C: starting material, 30 min, *cis*-cyclopropane, 30 min; and *trans*-cyclopropane, 34 min. A base line separation of the cis and trans photoproducts is readily achieved using these conditions. The two isomers do not interconvert thermally under these conditions to any detectable extent.

Separation of *trans*- and *cis*-2-Ethyl-2-methyl-3,3-diphenyl-1-(*p*-methoxyphenyl)cyclopropane. A mixture of the *trans*- and *cis*-cyclopropanes obtained from the exploratory photolysis of 3-(*p*-methoxyphenyl)-3-methyl-1,1-diphenyl-1-pentene was separated by high-pressure liquid chromatography (HPLC) with recycling on a 0.95 × 50 cm column of 10 μm porous glass spheres[27] using a Waters ALC-100 liquid chromatography instrument. Elution was with 0.5% ether in hexane with 0.05% methanol added as a modifier. All solvents were carefully dried (ether by distillation from lithium aluminum hydride, hexane from calcium hydride, and methanol from magnesium methoxide) to preserve column activity. A flow rate of 5 mL/min was employed.

Portions of 20–25 mg of the mixture of the cyclopropanes were injected in 250 μL of eluent and recycled until two overlapping peaks developed. Recycling was continued while fractions were collected from the head and tail of the overlapping peaks. A total of 500 mg of the mixture was chromatographed in this manner. The fractions collected from the faster eluting peak gave 125 mg of a 60/40 mixture of the *cis*- and *trans*-cyclopropanes, respectively. The slower eluting peak gave 375 mg of a 93/7 mixture of the *trans*- and *cis*-cyclopropanes, respectively.

A portion of the enhanced *trans*-cyclopropane (150 mg) was twice rechromatographed with recycling to give 75 mg of essentially pure material. Recrystallization from pentane gave 63 mg of *trans*-2-ethyl-2-methyl-3,3-diphenyl-1-(*p*-methoxyphenyl)cyclopropane, mp 94.5–95 °C, which was greater than 99% pure (VPC, 0.5% carbowax on Varaport 30, 165 °C). The spectral data were: NMR (270 MHz, $CDCl_3$) τ 2.55–3.00 (m, 10 H, aromatic), 3.23 (AB q, 4 H, aromatic, J = 8.8 Hz), 6.24 (s, 3 H, OCH_3), 7.43 (s, 1 H, cyclopropyl), 8.40 (m, 1 H, one diastereotopic $\mathbf{CH_2}CH_3$ proton), 8.74 (s, 3 H, CH_3), 9.05 (m, 4 H, one diastereotopic $\mathbf{CH_2}CH_3$ proton and $CH_2\mathbf{CH_3}$); IR ($CHCl_3$) 3.24, 3.27, 3.33, 3.38, 3.41, 3.48, 3.52, 6.21, 6.25, 6.33, 6.60, 6.68, 6.84, 6.90, 7.22, 7.70, 7.99, 8.25, 8.45, 9.05, 9.26, 9.68, 12.00, 12.20 μm; UV (EtOH) λ_{max} 231.5 nm (ϵ 25 800), 268.5 (1620), 273 (1650), 282 (1722), 290 (1314); MS *m/e* 342.19782 (Calcd for $C_{25}\mathbf{H}_{26}O$, *m/e* 342.19836).

Anal. Calcd for $C_{25}H_{26}O$: C, 87.68; H, 7.65. Found: C, 87.90; H, 7.70.

The enhanced *cis*-cyclopropane was also rechromatographed with recycling (vide supra) three times to yield 28 mg of a glassy oil which was greater than 98% pure (VPC, 0.5% carbowax on Varaport 30, 165 °C). The spectra data were: NMR (270 MHz, $CDCl_3$) 2.59–2.94 (m, 10 H, aromatic), 3.28 (AB q, 4 H, J = 9.2 Hz), 6.24 (s, 3 H, OCH_3), 7.47 (s, 1 H, cyclopropyl), 8.05–8.19 and 8.22–8.36 (sym m, 2 H, $\mathbf{CH_2}CH_3$), 8.93 (s, 3 H, CH_3), 9.29 (t, 3 H, $CH_2\mathbf{CH_3}$, J = 7.2 Hz); IR ($CHCl_3$) 3.24, 3.27, 3.32, 3.40, 3.48, 3.52, 6.23, 6.33, 6.60, 6.70, 6.84, 6.91, 7.68, 7.99, 8.50, 9.10, 9.25, 9.68, and 12.00 μm; MS *m/e* 342.19845 (Calcd for $C_{25}H_{26}O$, *m/e* 342.19836).

3-(*p*-Methoxyphenyl)-3-methyl-1,1-diphenylpentane. A solution of 332 mg (0.97 mmol) of 3-(*p*-methoxyphenyl)-3-methyl-1,1-diphenyl-1-pentene in 30 mL of ethyl acetate was hydrogenated at atmospheric pressure using 168 mg of 10% palladium on carbon as a catalyst. Filtration of the catalyst and concentration in vacuo afforded 323 mg of an oil which was chromatographed on a 2 × 18 cm slurry packed silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column. A single UV-active band was eluted with hexane which gave 317 mg (95%) of the 3-(*p*-methoxyphenyl)-3-methyl-1,1-diphenylpentane as a colorless oil, pure by NMR. Molecular distillation (150 °C, 0.005 torr) afforded an analytical sample.

The spectral data were: NMR (CCl_4) τ 2.82–3.20 (m, 12 H, aromatic), 3.28 (upfield half of ABq, 2 H, aromatic, J = 8 Hz), 6.25 (s, 3 H, OCH_3), 6.35 (t, 1 H, $Ph_2\mathbf{CH}$, J = 6.5 Hz), 7.69 (d, 2 H, CH_2, J = 6.5 Hz), 8.10–8.60 (m, 2 H, $\mathbf{CH_2}CH_3$), 9.01 (s, 3 H, CH_3), 9.41 (t, 3 H, $CH_2\mathbf{CH_3}$, J = 7 Hz); IR (CCl_4) 3.20, 3.22, 3.27, 3.34, 3.39, 3.44, 3.49, 6.19, 6.59, 6.68, 6.87, 7.20, 7.85, 8.42, 9.59, 12.05–13.60, and 14.24 μm.

Anal. Calcd for $C_{25}H_{28}O$: C, 87.16; H, 8.19. Found: C, 86.95; H, 8.18.

2-Ethyl-2-methyl-4,4-diphenylbutanoic Acid. A solution of 278 mg (0.99 mmol) of 2-ethyl-2-methyl-4,4-diphenyl-3-butenoic acid[8] in 50 mL of ethyl acetate was hydrogenated at atmospheric pressure using 150 mg of 10% palladium on carbon as catalyst. Filtration of catalyst and concentration in vacuo afforded 280 mg (100%) of the 2-ethyl-2-methyl-4,4-diphenylbutanoic acid as a colorless oil. Trituration with pentane and storage at −12 °C for 24 h gave a glassy solid, mp 53–59 °C. Recrystallization from pentane gave mp 61–61.5 °C.

The spectral data were: NMR ($CDCl_3$) τ 0.98 (br s, 1 H, CO_2H), 2.56–3.00 (m, 10 H, aromatic), 5.88 (t, 1 H, Ph_2CH, J = 7 Hz), 7.48 and 7.54 (centers of d of AB q, 2 H, diastereotopic CH_2, J = 7 and 14 Hz), 8.10–8.75 (m, 2 H, diastereotopic $\mathbf{CH_2}CH_3$), 8.96 (s, 3 H, CH_3), 9.09 (t, 3 H, $CH_2\mathbf{CH_3}$, J = 7 Hz); IR ($CHCl_3$) 3.24, 3.29, 3.30, 3.77, 5.90, 6.25, 6.69, 6.88, 7.10, 7.20, 7.50, 7.91, 8.11, 8.42, 8.66, 9.27, 9.70, 9.95, 10.75, 11.03, 13.75, and 14.30 μm.

Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.82; H, 7.85. Found: C, 81.06; H, 7.57.

2-Ethyl-2-methyl-4,4-diphenylbutanoic Acid from Ozonolysis of 3-(*p*-Methoxyphenyl)-3-methyl-1,1-diphenylpentane. Ozone (from a Welsbach ozonator) was passed into a well-stirred solution of 160 mg (0.48 mmol) of 3-(*p*-methoxyphenyl)-3-methyl-1,1-diphenylpentane in 40 mL of carbon tetrachloride at room temperature for 1.5 h. The resulting mixture was poured into a solution of 10 mL of 20% sodium hydroxide, 16 mL of 30% hydrogen peroxide, and 50 mL of water and stirred at room temperature for 20 min. The resulting two-phase mixture was brought to reflux of the carbon tetrachloride and cooled to room temperature, and the layers were separated. The aqueous phase was washed with ether, cooled to 0 °C, acidified to methyl orange end point with concentrated hydrochloric acid, and ether extracted. The extract was dried and the solvent removed in vacuo to afford 139 mg of an oil which was chromatographed on a 10 × 20 cm thick plate of silica gel (Macherey, Nagel, Silica gel G/UV 254) and eluted with 50% ether in hexane. A UV-active band with R_f 0.5 was extracted with ether and concentrated in vacuo to give 42.8 mg (31%) of the 2-ethyl-2-methyl-4,4-diphenylbutanoic acid as an oily solid, identical by NMR and TLC with that material obtained by hydrogenation of 2-ethyl-2-methyl-4,4-diphenyl-3-butenoic acid.[8]

Resolution of 3-(*p*-Methoxyphenyl)-3-methylpentanoic Acid. Racemic 3-(*p*-methoxyphenyl)-3-methylpentanoic acid (2.87 g, 12.9 mmol) was dissolved in 30 mL of hot hexane and a minimum amount of chloroform. To the warm solution was added 1.56 g (12.9 mmol) of (−)-1-phenylethylamine and a crystalline solid precipitated upon cooling. The solid was isolated by suction filtration and gave 1.92 g (8.6 mmol) of long colorless needles. Three successive recrystallizations from the same solvent system yielded 450 mg of this solid. The solid was treated with 3 N sodium hydroxide, and the resulting solution was washed with ether. The aqueous layer was then acidified to methyl orange end point with 6 N hydrocyloric acid and ether extracted. The extract was dried and the solvent removed in vacuo to afford 290 mg (1.29 mmol, 20%) of the (−)-3-(*p*-methoxyphenyl)-

3-methylpentanoic acid, $[\alpha]_D^{25}$ −19.4° (*c* 0.0152, $CHCl_3$), mp 94–95 °C. Recrystallization of the acid from chloroform–hexane changed neither the specific rotation nor the melting point. The specific rotation was also not affected by formation of the amine salt (with (−)-1-phenylethylamine) and recrystallization. The specific rotations were (λ in parentheses): −19.4 ± 0.2° (589), −20.3 ± 0.2° (578), −23.7 ± 0.3° (546), −45.8 ± 0.5° (436), and −86.7 ± 0.9° (365) (*c* 0.0152, $CHCl_3$).

Optically Active Methyl 3-(*p*-Methoxyphenyl)-3-methylpentanoate. The method used was that employed for the racemic compound, except that oxalyl chloride was substituted for thionyl chloride. Reaction of 0.970 g (4.30 mmol) of the optically pure (−)-3-(*p*-methoxyphenyl)-3-methylpentanoic acid with 1.11 g (8.8 mmol) of oxalyl chloride and 0.05 mL of dimethylformamide in 10 mL of benzene at room temperature for 45 min gave the acid chloride, which was, without purification, poured into 20 mL of methanol and refluxed for 20 min. The resulting ester was purified by chromatography on a 3 × 50 cm, slurry packed, silica gel column (Matheson Coleman and Bell, grade 62, 60–200 mesh). Elution with 1500 mL of 2% ether in hexane gave 0.976 g (95%) of the pure (−)-methyl 3-(*p*-methoxyphenyl)-3-methylpentanoate as a colorless liquid, whose spectral data were identical with those previously obtained for the racemic ester. A sample of this ester was dried in vacuo (0.005 torr) to constant weight for specific rotation measurements.

The specific rotations were (λ in parentheses): −17.1 ± 0.2° (589), −18.6 ± 0.2° (578), −21.1 ± 0.2° (546), −40.0 ± 0.4° (436), −75.5 ± 0.8° (365) (*c* 0.0075, $CHCl_3$).

Optically Active 3-(*p*-Methoxyphenyl)-3-methyl-1,1-diphenyl-1-pentanol. The method used for the racemic compound was employed. Reaction of 0.976 g (4.15 mmol) of optically pure methyl 3-(*p*-methoxyphenyl)-3-methylpentanoate with 16.6 mmol of phenylmagnesium bromide in anhydrous ether afforded the crude alcohol which was purified by chromatography on a 3 × 50 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column. Biphenyl was eluted with hexane and elution with 4% ether in hexane gave a single UV-active band which afforded 1.37 g (95%) of the (−)-3-(*p*-methoxyphenyl)-3-methyl-1,1-diphenyl-1-pentanol. The spectral data were identical with racemic material.

The specific rotations were (λ in parentheses): −42.5 ± 0.2° (589), −45.4 ± 0.2° (578), −52.7 ± 0.3° (546), −99.5 ± 0.5° (436), −181.4 ± 0.9° (365) (*c* 0.0063, $CHCl_3$).

Optically Active 3-(*p*-Methoxyphenyl)-3-methyl-1,1-diphenyl-1-pentene. The method used for the racemic compound was employed. Thus, dehydration of 1.37 g (4.10 mmol) of (−)-3-(*p*-methoxyphenyl)-3-methyl-1,1-diphenyl-1-pentanol with 0.56 mL (60 mmol) of phosphorus oxychloride in 15 mL of pyridine gave the crude olefin as a yellow oil which was chromatographed on a 2.5 × 90 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column. Elution with 2.5 L of 1% ether in hexane furnished 1.25 g (97%) of the pure 3-(*p*-methoxyphenyl)-3-methyl-1,1-diphenyl-1-pentene. The spectral data were identical with those obtained for racemic material.

The specific rotations were (λ in parentheses): −93 ± 1° (589), −97 ± 1° (578), −112 ± 1° (546), −205 ± 2° (436), −342 ± 3° (365) (*c* 0.007, $CHCl_3$).

The specific rotations were unchanged upon recrystallization, mp 35–36 °C.

Optically Active 3-(*p*-Methoxyphenyl)-3-methyl-1,1-diphenylpentane. The method used for the racemic material was employed. Atmospheric hydrogenation of 265 mg (0.8 mmol) of (−)-3-(*p*-methoxyphenyl)-3-methyl-1,1-diphenyl-1-pentene, $[\alpha]_D^{25}$ −93 ± 1°, in 30 mL of ethyl acetate using 133 mg of 10% palladium on carbon as catalyst afforded 266 mg (100%) of the 3-(*p*-methoxyphenyl)-3-methyl-1,1-diphenylpentane as a colorless oil, pure by NMR and spectroscopically identical with racemic material.

The specific rotations at 25 ± 0.1° were (λ in parentheses): −5.2 ± 0.1° (589), −5.4 ± 0.1° (578), −6.3 ± 0.1° (546), −12.4 ± 0.2° (436), −23.5 ± 0.4° (365) (*c* 0.0082, $CHCl_3$).

Optically Active Methyl 2-Ethyl-2-methyl-4,4-diphenylbutanoate. A solution of 0.305 g (0.96 mmol) of the known optically pure (−)-methyl-2-ethyl-2-methyl-4,4-diphenyl-3-butenoate, $[\alpha]_D^{25}$ −19.6 ± 0.3°, in 25 mL of ethyl acetate was hydrogenated at atmospheric pressure using 168 mg of 10% palladium on carbon as catalyst. After uptake of hydrogen ceased, the catalyst was filtered and the filtrate concentrated in vacuo to afford 0.305 g (99%) of the methyl 2-ethyl-2-methyl-4,4-diphenylbutanoate as a colorless oil, pure by NMR.

The spectral data were: NMR (CCl_4) τ 2.80 (m, 10 H, aromatic), 6.00 (t, 1 H, Ph_2CH, *J* = 6.5 Hz), 6.88 (s, 3 H, OCH_3), 7.72 (d of AB q, 2 H, diastereotopic $\mathbf{CH_2}CH(Ph)_2$, *J* = 6.5 and 14 Hz), 8.06–8.80 (m, 2 H, diastereotopic $\mathbf{CH_2}CH_3$), 8.92 (s, 3 H, CH_3), 9.25 (t, 3 H, $CH_2\mathbf{CH_3}$, *J* = 7 Hz); IR (CCl_4) 3.21, 3.25, 3.29, 3.34, 3.38, 3.45, 5.78, 6.23, 6.69, 6.89, 7.20, 8.00, 8.30, 8.50, 8.80, 9.20, 9.70, 10.15, 11.60, 13.60, and 14.28 μm.

The specific rotations at 25 ± 0.1° were (λ in parentheses): −34.1 ± 0.3° (589), −35.8 ± 3° (587), −41.0 ± 0.4° (546), −74.4 ± 0.7° (436), −128 ± 1° (365) (*c* 0.0152, $CHCl_3$).

Optically Active 2-Ethyl-2-methyl-4,4-diphenylbutanoic Acid. A solution of 0.510 g (1.72 mmol) of optically pure (−)-methyl 2-ethyl-2-methyl-4,4-diphenylbutanoate, $[\alpha]_D^{25}$ −34.1 ± 0.3°, and 1.68 g (30 mmol) of potassium hydroxide in 35 mL of ethanol was refluxed under nitrogen for 10 h, cooled, and concentrated in vacuo. The residue was taken up in water and washed with ether; the aqueous layer was acidified to methyl orange end point with concentrated hydrochloric acid and ether extracted. The extract was dried and decolorized with norite, and the solvent was removed in vacuo to afford a colorless oil, pure by NMR. Crystallization from pentane yielded 0.310 g (64%) of the 2-ethyl-2-methyl-4,4-butanoic acid, mp 58.5–60 °C. Recrystallization, also from pentane, raised the melting point to 59.5–60.5 °C. The spectral data were identical with racemic material.

The specific rotations were (λ in parentheses); −21.5 ± 0.2° (589), −22.4 ± 0.2° (578), −25.6 ± 0.3° (546), −46.5 ± 0.5° (436), −80.0 ± 0.8° (365) (*c* 0.0104, $CHCl_3$).

Optically Active 2-Ethyl-2-methyl-4,4-diphenylbutanoic Acid from Optically Active 3-(*p*-Methoxyphenyl)-3-methyl-1,1-diphenylpentane. The method used for the racemic compound was employed. Ozonolysis of 250 mg (0.75 mmol) of (−)-3-(*p*-methoxyphenyl)-3-methyl-1,1-diphenylpentane and chromatography as previously described afforded 50 mg of an oil which was crystallized from pentane to give a solid, mp 50–53 °C. Recrystallization from pentane gave 15 mg (7.2%) of the 2-ethyl-2-methyl-4,4-diphenylbutanoic acid, mp 58–59 °C. The spectral data were identical with those previously obtained for the racemic compound.

The specific rotations were (λ in parentheses): 21.8 ± 0.2° (589), 22.7 ± 0.7° (578), 25.9 ± 0.3° (546), 46.5 ± 0.5° (436), 80.4 ± 0.8° (365) (*c* 0.0037, $CHCl_3$).

Photolysis of Optically Active 3-Methyl-3-(*p*-methoxyphenyl)-1,1-diphenyl-1-pentene. All photolyses of the optically active olefin were performed on the "Black Box"[15] apparatus. Several photolyses were carried out at each of three different percent conversions; extent of conversion was determined by isolated yields of the photoproducts.

The wavelength of irradiation was controlled by the use of a triple compartment filter containing (a) (nearest to lamp) 2 M nickel sulfate in 5% sulfuric acid, (b) saturated (approximately 2 M) cobalt sulfate in 5% sulfuric acid, and (c) 2×10^{-4} M bismuth trichloride in 10% hydrochloric acid. The filter gave a transmission maximum at 275 nm (18% transmission) and was opaque above 308 nm and below 245 nm.

All photolyses were carried out in 750 mL of anhydrous *tert*-butyl alcohol. All runs were purged for 0.5 h with purified nitrogen[26] before and during photolysis.

Low Conversion Photolyses. Run 1. After photolysis of 501.5 mg (1.47 mmol) of the optically active olefin, $[\alpha]_D^{25}$ −93 ± 1°, for 27 min, the solvent was removed in vacuo and the residue was chromatographed on a 3 × 147 cm, slurry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column. The column was eluted with 6.5% dichloromethane in hexane and 40-mL fractions were collected: fractions 1–152, nil; 153–232, 449.7 mg of optically active 3-methyl-3-(*p*-methoxyphenyl)-1,1-diphenyl-1-pentene, $[\alpha]_D^{25}$ −93 ± 1°; 233–308, 10% ether in hexane, 46.6 mg of a mixture of the olefin and the *trans*- and *cis*-2-ethyl-2-methyl-3,3-diphenyl-1-(*p*-methoxyphenyl)cyclopropanes. Mass balance: 496.3 mg (1.45 mmol), 99.0%. In fractions 233–308 the photoproduct cyclopropanes were separated from the starting olefin by HPLC with recycling as described previously. Recycling twice was sufficient to effect complete separation of olefin from the cyclopropanes. Total photoproducts isolated: 27.4 mg (0.0801 mmol), 5.5% conversion.

Table III contains the pertinent data for all photolyses run on optically active (−)-3-(*p*-methoxyphenyl)-3-methyl-1,1-diphenyl-1-pentene (**9**). All runs were performed in the same manner as given for low conversion photolysis run 1 in the above Experimental Section.

Separation of the *trans*- and *cis*-2-Ethyl-3-methyl-3,3-diphenyl-1-(*p*-methoxyphenyl)cyclopropanes. In each of the photolysis series from above, the photoproduct mixtures of the *trans*- and *cis*-2-ethyl-2-methyl-3,3-diphenyl-1-(*p*-methoxyphenyl)cyclopropanes were combined and separation of the photoproducts was effected by HPLC with recycling as previously described (vida supra). Fractions containing the *trans*-cyclopropane were collected and the

Table III. Results of the Photolyses of Optically Active Anisyl-Vinylmethane 9

photolysis series	run no.	photolysis time, h	amt of reactant (−)-9 used, mmol	amt of recovered reactant, mmol	amt of photo-products, mmol	mass balance, %
low conversion	1	0.45	1.47	1.37	0.0801	99.0
	2	0.45	1.47	1.34	0.0845	97.6
medium conversion	1	1.50	1.47	1.31	0.153	99.6
	2	3.67	1.47	1.32	0.134	98.9
	3	4.67	1.49	1.31	0.158	98.2
	4	5.33	1.51	1.33	0.134	98.9
high conversion	1	6.00	1.49	1.27	0.214	100.0
	2	5.50	1.51	1.26	0.209	97.6
	3	6.00	1.47	1.23	0.215	98.5
	4	5.75	1.46	1.21	0.201	96.4

solvent was removed in vacuo. Solvent residues were removed by chromatography on a dry packed, 0.5 × 20 cm, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) and Norite (4:1 v/v) column eluting with anhydrous ether. Solvent was removed again in vacuo and the residue dried at 0.05 torr to constant weight. The specific rotations were measured and the sample subjected to further chromatography by HPLC until the specific rotations were maximized.

Specific Rotations of Optically Active *trans*-2-Ethyl-2-methyl-3,3-diphenyl-1-(*p*-methoxyphenyl)cyclopropane from Photolysis of Optically Active 3-Methyl-3-(*p*-methoxyphenyl)-1,1-diphenyl-1-pentene. Low Conversions. The photoproduct mixtures from runs 1 and 2 were combined and separated by HPLC with recycling (vida supra). From this was obtained 27.5 mg of material which was greatly enriched in the *trans*-2-ethyl-2-methyl-3,3-diphenyl-1-(*p*-methoxyphenyl)cyclopropane. The specific rotations of this material were (λ in parentheses): 77 ± 1° (589), 83 ± 1° (578), 98 ± 1° (546), 193 ± 2° (436), 426 ± 4° (365) (*c* 0.0055, $CHCl_3$). Rechromatography yielded 17.5 mg of material whose specific rotations were: 91 ± 2°, 95 ± 2°, 111 ± 2°, 222 ± 4°, 437 ± 6° (*c* 0.0035, $CHCl_3$). After the third chromotography 12.6 mg were obtained which had the following specific rotations: 97 ± 2°, 101 ± 2°, 118 ± 2°, 236 ± 4°, 460 ± 8° (*c* 0.0063, $CHCl_3$). The fourth and final chromotography gave 10.8 mg of the *trans*-cyclopropane whose specific rotations were: 98 ± 2°, 102 ± 2°, 120 ± 3°, 240 ± 5°, 468 ± 10° (*c* 0.0054, $CHCl_3$).

Medium Conversions. The photoproduct mixtures from runs 1–4 were combined and separated by HPLC with recycling (vida supra). After chromatographing twice, 33.0 mg of material enriched in the *trans*-cyclopropane was obtained and it had specific rotations of (λ in parentheses): 91 ± 1° (589), 95 ± 1° (578), 112 ± 1° (546), 223 ± 2° (436), 435 ± 4° (365) (*c* 0.0066, $CHCl_3$). A third chromatography yielded 27.0 mg with rotations of: 93 ± 1°, 98 ± 1°, 114 ± 1°, 229 ± 2°, 445 ± 5° (*c* 0.0054, $CHCl_3$). The last chromatography gave 19.0 mg of the *trans*-cyclopropane whose specific rotations were: 94 ± 2°, 97 ± 2°, 115 ± 2°, 230 ± 3°, 449 ± 6° (*c* 0.0038, $CHCl_3$).

High Conversions. The photoproduct mixtures from runs 1–4 combined and separated by LC with recycling (vida supra). After twice chromatographing the mixture, 54.5 mg of material enhanced in the *trans*-cyclopropane was obtained whose specific rotations were (λ in parentheses): 87 ± 1° (589), 90 ± 1° (578), 106 ± 1° (546), 212 ± 2° (436), 412 ± 4° (356) (*c* 0.0109, $CHCl_3$). Rechromatography gave 40.0 mg of material with specific rotations of: 90 ± 1°, 94 ± 1°, 110 ± 1°, 220 ± 2°, 428 ± 4° (*c* 0.0080, $CHCl_3$). A fourth chromatography gave 38 mg with specific rotations of: 88 ± 1°, 92 ± 1°, 108 ± 1°, 216 ± 2°, 421 ± 4° (*c* 0.0076, $CHCl_3$). A final chromatography gave 31.0 mg of the *trans*-cyclopropane whose specific rotations were: 90 ± 1°, 94 ± 1°, 110 ± 1°, 220 ± 2°, 429 ± 4° (*c* 0.0062, $CHCl_3$).

Optically Active *trans*-2-Ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylic Acid. Ozone (from a Welsbach ozonator) was bubbled through a well-stirred solution of 26.0 mg (0.076 mmol) of optically active *trans*-2-ethyl-2-methyl-3,3-diphenyl-1-(*p*-methoxyphenyl)cyclopropane in 25 mL of carbon tetrachloride at room temperature for 75 min. The slightly cloudy mixture was poured into a solution of 10 mL of 20% sodium hydroxide, 16 mL of 30% hydrogen peroxide, and 50 mL of water. This was heated on a steam bath for 5 min and then removed and stirred as it cooled to room temperature. The layers were separated, and the aqueous layer was washed once with ether, acidified to methyl orange end point with concentrated hydrochloric acid, and ether extracted. The extract was dried over magnesium sulfate, and the solvent was removed in vacuo. The yellow oily residue was chromatographed on a 0.5 × 20 cm, dry packed, silica gel (Matheson Coleman and Bell, grade 62, 60–200 mesh) column and norite (4:1 v/v) column and eluted with 50 mL of dry ether. The solvent was removed in vacuo and the product dried to constant weight at 0.05 torr to yield 11.2 mg (0.037 mmol, 53%) of the optically active *trans*-2-ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylic acid as a clear colorless oil.

The specific rotations of the starting *trans*-cyclopropane were (λ in parentheses): 94 ± 1° (589), 98 ± 1° (578), 115 ± 1° (546), 230 ± 2° (436), 448 ± 5° (365) (*c* 0.0052, $CHCl_3$).

The specific rotations of the product *trans*-cyclopropanecarboxylic acid were (λ in parentheses): 179 ± 4° (589), 188 ± 4° (578), 218 ± 5° (546), 418 ± 9° (436), 771 ± 16° (365) (*c* 0.0056, $CHCl_3$). These specific rotations correspond to a 91.6% optical purity based on previously reported values[8] for the optically pure cyclopropanecarboxylic acid. The spectral data were identical with those previously reported for this compound.[8]

Optically Active Methyl *trans*-2-Ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylate. The method employed by Zimmerman et al.[8] was followed. From 29.5 mg (0.0863 mmol) of (+)-*trans*-2-methyl-2-ethyl-3,3-diphenylcyclopropanecarboxylic acid and 1.0 mmol of diazomethane was prepared 16.7 mg (0.0488 mmol, 55%) of (+)-methyl *trans*-2-methyl-3,3-diphenylcyclopropanecarboxylate.

The starting acid was 81 ± 1% optically pure and its specific rotations were (λ in parentheses): 160 ± 2° (589), 167 ± 2° (578), 195 ± 2° (546), 370 ± 4° (436), 676 ± 6° (365) (*c* 0.0059, $CHCl_3$).

The product ester was 80 ± 2° optically pure based on previously reported[8] values for its specific rotations. The specific rotations of the product at 27.0 ± 0.1° were (λ in parentheses): 159 ± 2° (589), 167 ± 3° (578), 193 ± 3° (546), 355 ± 5° (436), 699 ± 10° (356) (*c* 0.0084, hexane). The spectral data were identical with those reported[8] for methyl *trans*-2-ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylate.

Optically Active (−)-*cis*-2-Ethyl-2-methyl-3,3-diphenyl-1-(*p*-methoxyphenyl)cyclopropane. High-pressure liquid chromatography of the combined photoproduct mixtures of the series 3 photolyses yielded fractions containing 72.5 mg of material enhanced in the *cis*-2-ethyl-2-methyl-3,3-diphenyl-1-(*p*-methoxyphenyl)cyclopropane. After being rechromatographed by HPLC with recycling an additional three times, 26.7 mg of the pure *cis*-cyclopropane was obtained. The specific rotations were (λ in parentheses): −57 ± 1° (589), −59 ± 1° (578), −70 ± 1° (546), −145 ± 2° (436), −291 ± 3° (365) (*c* 0.0053, $CHCl_3$). The spectral data were identical with the racemic compound.

Optically Active (−)-*cis*-2-Ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylic Acid. The cyclopropane from above (26.7 mg, 0.0781 mmol) was ozonized according to the procedure given for the *trans*-cyclopropane. A colorless crystalline product was obtained (12.5 mg, 57%), mp 170–178 °C (sealed capillary, lit.[8] mp 176.5–177 °C), whose spectral data were identical to those reported[8] for *cis*-2-ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylic acid. The specific rotations of the product were (λ in parentheses): −136 ± 3° (589), −144 ± 3° (578), −164 ± 3° (546), −319 ± 6° (436), −598 ± 12° (365) (*c* 0.0056, $CHCl_3$). These rotations correspond to 79 ± 2% optical purity based on previously reported values.[8]

Photolysis Equipment for Quantum Yield Determinations. Quantum yields were performed on the "Black Box".[15] Light output was measured by a digital actinometer[16] calibrated by ferrioxalate actinometry.[17] The same filter was used in the quantum yield runs as was used in the irradiations of the optically active (−)-3-(*p*-methoxyphenyl)-3-methyl-1,1-diphenyl-1-pentene.

Quantum Yield Measurements. 3-(*p*-Methoxyphenyl)-3-methyl-1,1-diphenyl-1-pentene. All runs were performed in 750 mL of anhydrous *tert*-butyl alcohol. After photolysis, the solvent was removed in vacuo, the residue taken up in 145 mL of benzene, and tetraphenylethylene added as an internal standard. All runs were analyzed by VPC and peak areas measured by planimetry. For the analysis of the *trans*-2-ethyl-2-methyl-3,3-diphenyl-1-(*p*-methoxyphenyl)cyclopropane, a 168 × 0.6 cm column of 0.5% carbowax 20M on Varaport 30 (100–200 mesh) at 165 °C was employed. For the *cis*-cyclopropane a 183 × 0.6 cm column of 1.0% Apeizon N on Varaport 30 (100–120 mesh) at 180 °C was used.

Run 1. Starting olefin used, 1.48 mmol; 1.35 mEinsteins absorbed; *trans*-cyclopropane formed, 0.0875 mmol; ϕ(trans) = 0.0648; *cis*-cyclopropane formed, 0.0299 mmol; ϕ(cis) = 0.0221; 8.0% conversion.

Run 2. Starting olefin used, 1.48 mmol; 0.968 mEinsteins absorbed; *trans*-cyclopropane formed, 0.0631 mmol; ϕ(trans) = 0.0652; *cis*-cyclopropane formed, 0.029 mmol; ϕ(cis) = 0.216; 5.8% conversion.

Run 3. Starting olefin used, 1.46 mmol; 0.458 mEinsteins absorbed; *trans*-cyclopropane formed, 0.0306 mmol; ϕ(trans) = 0.0667; *cis*-cyclopropane formed, 0.0105 mmol; ϕ(cis) = 0.0230; 2.8% conversion.

Run 4. Starting olefin used, 1.50 mmol; 1.83 mEinsteins absorbed; *trans*-cyclopropane formed, 0.110 mmol; ϕ(trans) = 0.0600; *cis*-cyclopropane formed, 0.0399 mmol; ϕ(cis) = 0.0218; 10.2% conversion.

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Registry No.—**9,** 69652-87-5; (−)-**9,** 65549-74-8; **10,** 759-51-3; **11** isomer A, 69652-88-6; **11** isomer B, 69652-89-7; **12,** 69652-90-0; (−)-**12,** 69652-91-1; (−)-**12** (−)-1-phenethylamine salt, 69685-62-7; **13,** 69652-92-2; (−)-**13,** 69667-90-9; **14,** 69652-93-3; (−)-**14,** 69652-94-4; **15a,** 69652-95-5; (−)-**15a,** 69652-96-6; **15b,** 69652-97-7; (+)-**15b,** 69652-98-8; **16,** 69652-99-9; (−)-**16,** 69667-91-0; **17,** 69653-00-5; (−)-**17,** 69653-01-6; (+)-**17,** 69653-02-7; (−)-**18,** 69653-03-8; (−)-**19,** 53947-69-6; (−)-**20a,** 53750-37-1; (+)-**20b,** 69653-04-9; (+)-methyl *trans*-2-ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylate, 53750-38-2; *p*-anisylmagnesium bromide, 13139-86-1; 2-ethyl-2-methyl-4,4-diphenyl-3-butenoic acid, 69653-05-0; phenyl bromide, 108-86-1.

References and Notes

(1) This is Paper 118 of our Photochemical Series.
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Stereochemistry of Phenoxathiin *S*-Oxide

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Phenoxathiin sulfoxide has been found to exist in the pseudoaxial conformation in both the solid state and in solution. Single-crystal X-ray analysis reveals that the heterocyclic ring has a dihedral angle of 152°, with S–O 1.489 (4) Å, S–C 1.775 (5) Å, C–O 1.384 (7) Å, and C–S–C 94.8°. Solution conformation was deduced using the aromatic solvent-induced shift (ASIS) NMR procedure and complexation in the IR.

Compounds such as 9,10-dihydroanthracene (**1**), thioxanthene (**2**), phenothiazine (**3**), thianthrene (**4**), and phenoxathiin (**5**) exist in a folded conformation which is undergoing rapid conformational inversion. Alkyl substituents at the meso position(s) (e.g., C9 and C10 of **1**) normally prefer the a′ array, although molecules with e′ alkyl groups are known.[1-3]

Compounds with sulfur in the meso position (**2–5**) can form sulfoxides which, at least in principle, could exist with the sulfinyl oxygen in either the e′ or the a′ array. *cis*-Thianthrene 9,10-dioxide (*cis*-**6**) is more stable then *trans*-thianthrene

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