the corresponding amino acids in quantitative yield (98%) (Table IX).

***tert*-Butyl *o*-Benzoylbenzoate.** To a solution of potassium *tert*-butoxide in *tert*-butyl alcohol (obtained by dissolving 1.17 g of potassium in 250 mL of *tert*-butyl alcohol) was added dropwise phenyl pseudo *o*-benzoylbenzoate (9.06 g) in 200 mL of dry ether. The reaction mixture was refluxed on a water bath for 3 h, and the solvents were removed under reduced pressure (water pump). Water was added to the solid residue, and then it was extracted with ether. The ether layer was washed with ice-cold 0.5 M sodium hydroxide solution in order to remove the phenol and then with distilled water. The organic layer was dried over anhydrous sodium sulfate and filtered, and the solvent was distilled. The residue, which was homogeneous on TLC, was crystallized from petroleum ether, which afforded a sample melting at 72–74 °C (7.96 g, 83%): IR max (Nujol) 1708 (ester C=O), 1670 (aromatic C=O) cm^{-1}.

Anal. Found: C, 76.57; H, 6.73. $C_{21}H_{18}O_3$ requires: C, 76.25; H, 6.75.

pK_a Measurements. Ethyl alcohol was purified by standard methods[25] and subsequently further distilled over zinc and sodium hydroxide twice. Double-distilled water was used to make 50% aqueous ethanol (v/v), and the solvents were stored under nitrogen. Sodium hydroxide (0.05 M) solution was prepared 1 h before use and was kept under nitrogen. The acid whose pK_a was to be determined was accurately weighed and dissolved in 50% aqueous ethanol (0.001 M).

The pH meter was standardized by measuring the pH value of 0.05 M potassium hydrogen phthalate (pH 4.01).[26] The acid solution (25 mL) was pipetted out into a double-walled beaker provided with outlets for water circulation from a thermostat in order to keep the contents of the beaker at constant temperature (30.0 ± 0.1 °C). Nitrogen was gently bubbled through the acid solution in the beaker. After 1 h, the calomel electrode of the Photovolt Digicord pH meter was immersed in the acid solution and the pH was noted. The pH reading was recorded after every 0.1 mL of 0.05 M sodium hydroxide solution was added. The process was continued until the neutralization point was reached. The pK_a value was read from the plot of the titer value against pH by measuring the half-neutralization point.[27]

Kinetic Procedure. The kinetic procedure was the same as that described for the alkaline hydrolysis of pseudo esters.[1]

Registry No.—Phenyl pseudo *o*-benzoylbenzoate, 5471-75-0; *tert*-butyl alcohol, 75-65-0.

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Effect of Strain on Singlet Oxygen ($^1O_2$) Reactions. 2.[1] Photooxidation of Methylenecyclopropanes

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In contradistinction to methylenecyclopropanes **2–4** which are inert to $^1O_2$, 2,2-diphenylmethylenecyclopropane (**1**) reacts sluggishly, producing benzophenone as the only isolable product. On the other hand 1,1-dimethyl- and 1,1-dicyclopropylmethylenecyclopropanes **5** and **6** yield a variety of products (depending on the reaction conditions) whose formation is explicable in terms of secondary rearrangements of an initially formed allylic hydroperoxide.

While the reactions of singlet oxygen have been well studied,[2] the effect of strain on the rate, mode, and direction of reaction has been almost totally neglected. Until recently there was only a handful of reports[3] in which three- and four-membered alicyclic olefins were photooxidized. In each instance, however, the double bond was flanked by at least one phenyl group. The expected formation of endoperoxides[4] explains the high yield of polymeric material, and the well-documented secondary rearrangements[2d,4,5] of endoperoxides to dioxetanes and allylic hydroperoxides may well explain the formation of what might otherwise be mistaken as "ene" or 2 + 2 cycloaddition products.[6] Hence, an unambiguous study of small ring systems was clearly warranted. The recent publication of two related reports[10,11] prompts us to communicate the results of our study on the photooxidation of methylenecyclopropanes.

For the purpose of this study we synthesized olefins **1–6**. Methylenecyclopropane **1** is the photochemical rearrangement

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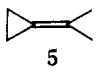
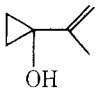
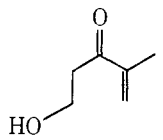
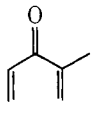
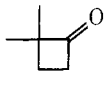
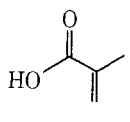
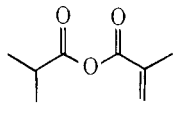
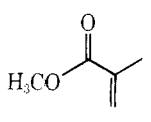
Table I. Product Distribution of the $^1O_2$ Reaction of Methylenecyclopropane 5

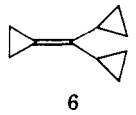


5 $\xrightarrow{^1O_2}$ products (k_{rel}[a] = 0.0056)

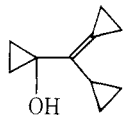
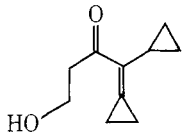
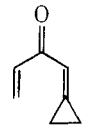
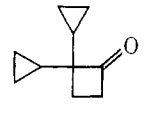
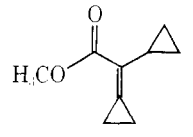
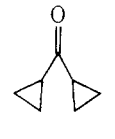
solvent	reaction conditions[b,c]	 7A	 8A	 9A	 10A	 11A	 12A	 13A	 14A
acetone	−78 °C/Ph_3P	62%	25%	13%					
	−78 °C		75%	25%					
	20 °C		57%	15%	28%				*d*
$CHCl_3$	−78 °C/Ph_3P	40%				40%	20%		
	−78 °C					67%	33%		
	20 °C					67%	33%		
CH_3OH	20 °C		20%	10%	10%			45%	15%

[a] Rate of reaction with $^1O_2$ as compared to that of tetramethylethylene (k_{rel} = 1.0[2a]). [b] Ph_3P was added upon completion of the photooxidation at the temperature of the photooxidation; yields were determined by NMR at 20 °C. At 20 °C the product yields were unaffected by the addition of Ph_3P. [c] Ph_2S[25] did not affect the product yields under all conditions. [d] Using acetone-d_6 as solvent, a sharp singlet corresponding to acetone-d_6 was observed in the 20 °C runs but not in the −78 °C runs. It represents, however, only a few percent.

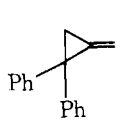
Table II.[a] Product Distribution of the $^1O_2$ Reaction of Methelenecyclopropane 6



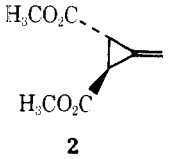
6 $\xrightarrow{^1O_2}$ products (k_{rel} = 0.0021)

solvent	reaction conditions	 7B	 8B	 9B	 10B	 13B	 14B
acetone	−78 °C/Ph_3P[c]	60%	10%		20%		10%
	−78 °C		50%		20%		30%
	20 °C		22%	12%	33%		33%
$CHCl_3$	−50 °C/Ph_3P[b,c]	65%			15%		20%
	−50 °C				15%		85%
	20 °C[b,c]		21%	14%	21%		44%
CH_2Cl_2	−78 °C		10%		35%		55%
	20 °C		20%	20%	20%		40%
CH_3OH	20 °C		10%		20%	20%	50%
CH_3CN	20 °C		15%		25%		60%
C_6H_6	20 °C		20%		30%		50%
C_2H_6O + 5% C_5H_5N	20 °C		20%	25%	20%		35%

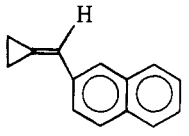
[a] See footnotes to Table I. [b] NMR reveals peaks probably corresponding to the acid analogue of ester **13B**, **11B**, or the corresponding anhydride **12B**. [c] See the discussion in the Eperimental Section.



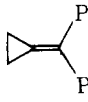
1



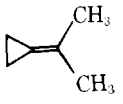
2



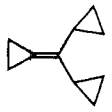
3



4



5

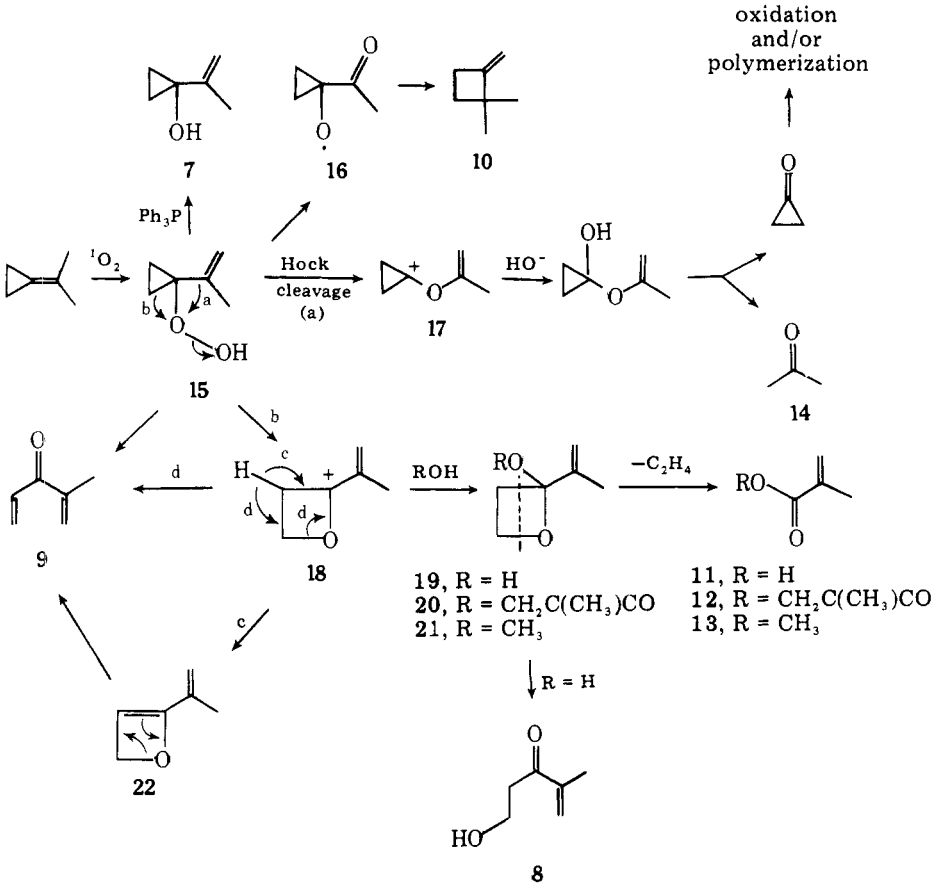


6

product of compound **4**.[12] Feist ester **2**[13] was synthesized by literature procedures. Compounds **3–6** were prepared according to the one-step procedure of Utimoto.[14]

Compound **1** reacted extremely sluggishly with $^1O_2$, producing benzophenone as the only isolable product. Olefins **2–4** proved completely inert[15] to $^1O_2$, while **5** and **6** yielded a variety of products depending on the reaction conditions (see Tables I and II). The products were isolated by preparative GLC in most cases and identified by their spectral data. Cyclobutanones **10A** and **10B** were independently synthesized via the acid-catalyzed rearrangement[16] of the epoxides of **5** and **6**, respectively. Dienone **9A** was obtained from the pyrolysis of the adduct resulting from the Mannich reaction of formalin and dimethylamine hydrochloride with either ethyl methyl ketone or ethyl vinyl ketone.[17] Relative yields of products **7–14** were determined by integration of GLC peak areas and from the ^1H NMR data of the reaction mixture. Relative rates for olefins **5** and **6** as compared to tetramethylethylene (TME; k_{rel} = 1.0[2a]) were determined in competition studies with 1-methylcyclohexene (k_{rel} = 0.0041[2a]) in CH_3CN.

Scheme I. Proposed Mechanism for the Formation of Products 7-14



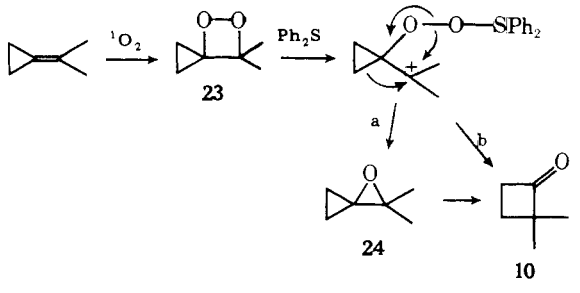
A priori, it might have been inviting to suggest that the inertness of methylenecyclopropanes **2**–**4** to $^1O_2$ results from strain factors. After all, for compounds **2**–**4** the only available allylic hydrogens are ring hydrogens; hence, an "ene" reaction would result in the formation of cyclopropene with an 8–10 kcal/mol increase in strain energy over the starting olefin.[19] We have previously suggested,[1] however, that $^1O_2$ is insensitive to any strain that might result in the final product. The lack of reactivity of the allylic ring hydrogens would seem to stem then from another source.

Based on the values determined by Laurie and co-workers for the atomic coordinates in methylenecyclopropane[20] and isobutylene,[21] we have calculated the interatomic distances between the α-olefinic carbon and the γ-allylic hydrogen, the latter lying in a plane perpendicular to the plane of the double bond.[22] For methylenecyclopropane this distance is 3.269 Å, while for isobutylene the value[22] is somewhere between 3.017 and 3.031 Å. In other words, the C_α–$H_{allylic}$ interatomic distance is larger in the former olefin by 0.24–0.25 Å. We suggest that as a result of this increment the ring allylic hydrogens are essentially "out of reach" for the abstracting oxygen atom which must span this gap. This should be true irrespective of the exact mechanism of the ene reaction,[2] particularly since Dewar[23a] has argued that the second transition state in the perepoxide mechanism leading to allylic hydroperoxide has the same chair-type geometry expected for the concerted ene mechanism.

It is not surprising, therefore, that in the case of the alkylated analogues **5** and **6** abstraction of the other allylic hydrogens now available will occur. Indeed, no trace of cycloprop-1-enylcarbinols[23b] could be found and the plethora of products observed may all be rationalized as secondary rearrangement products of the initially formed hydroperoxide **15** (Scheme I). This hydroperoxide is moderately stable at low temperatures and can be reduced to give the corresponding alcohol **7**. The hydroperoxide may also cleave homolytically, a process favored at higher temperatures, with the resulting alkoxy radical (**16**) rearranging to cyclobutanone **10**. This last step is reminiscent of the acid-catalyzed rearrangement of the corresponding alcohol **7**,[24] but since this alcohol is stable under the reaction conditions it is unlikely that it is the source of the cyclobutanone. Similarly the suggestion[10] that cyclobutanone **10** is formed from the corresponding epoxide is untenable, as the epoxide is also stable under the reaction conditions; yet, none of its characteristic absorption peaks were visible in the ^1H NMR spectrum of the reaction mixture.

With respect to the formation of acetone and dicyclopropyl ketone in the photooxidations of **5** and **6**, respectively, it has been argued[10] that they stem from a dioxetane intermediate **23**. That this is indeed not the case is attested to by the fact that diphenyl sulfide[25] has absolutely no affect whatsoever on the product distribution, irrespective of the reaction conditions. Were a dioxetane present, we would have expected formation of epoxide **24** or increased yields of cyclobutanone **10** formed as shown in Scheme II. It is far more likely that

Scheme II. Expected Reaction Pathway of Dioxetane 23 with Ph_2S

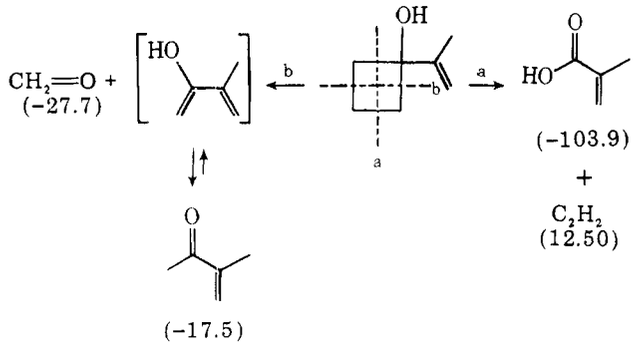


Hock cleavage[2c,d,11,26] is at play. The exact fate of the cyclopropanone[27] fragment formed in such a cleavage is unknown, and attempts to trap it in methanol were unsuccessful. It may well undergo polymerization[28] or more likely autoxidation analogous to that reported for tetramethylcyclopropanone.[29]

The initially puzzling formation of the remaining products can be readily explained (see Scheme I) if we postulate the rearrangement of vinylcyclopropyl hydroperoxide **15** to oxetane intermediate **18**. Note that the formation of **18** and the Hock cleavage intermediate **17** differs only in which σ bond migrates. Both rearrangements, however, are analogous to the classic cumene hydroperoxide rearrangement.[30] In particular, the migration of the strained σ bond in **15** finds precedent in the facile ring expansion of 1-phenylcyclobutyl hydroperoxide via the corresponding tetrahydrofuranyl intermediate.[31]

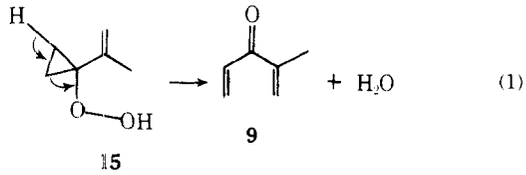
Once formed, **18** can react with available nucleophiles, yielding oxetanes **19–21**. While **20** and **21** are acetals, 2-hydroxyoxetane **19** is a hemiacetal and as such it is not surprising that it would open to hydroxy ketone **8**. The possibility that **8** might be formed as an autoxidation product of cyclopropanol **7** (or hydroperoxy analogue **15**) as has been observed for other hydroxycyclopropanes[32] may be ruled out by the following observations. Firstly, **8** is formed even at −78 °C, at which temperature such autoxidative processes are inhibited. Furthermore, **8** is obviously a secondary rearrangement product since the addition of Ph_3P at −78 °C, subsequent to oxidation, supresses its formation drastically.

In an alternate pathway, oxetanes **19–21** may cleave via a retro-Paterno–Buchi reaction[33,34] to give enones **11–13**, respectively. Predictions regarding the cracking modes of simple 2-substituted oxetanes have been made based either on relative diradical stabilities[33] or on the weakest C–O bond.[34] In our case, two modes (a and b) are available, but it is not totally



clear which approach is applicable. If we assume, however, that for calculations using heats of formation[35] [$\Delta H_f°$ (kcal/mol)] the $\Delta H_f°$ of 3-penten-2-one is a good approximation for that of 3-methyl-3-buten-2-one and that the latter has an energy lower than its enol form, then it is clear that mode a, the observed pathway, is thermodynamically favored over b by approximately 43.5 kcal.

Dienone **9** may be formed directly[36] from **18** or via oxetane **22**[37] as shown in Scheme I or directly from hydroperoxide **15** by a Kornblum–DeLaMare type process[38] as outlined in eq 1. This latter process is well known[38b] to be base catalyzed;



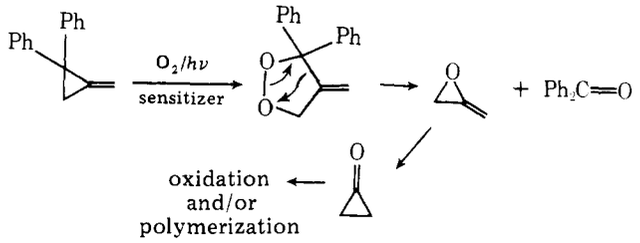
(1)

hence, the observation that the addition of 5% pyridine to acetone increases the yield of **9** in the photooxidation of **6** (see Table II) tends to favor this latter mechanism. The evidence, however, is far from conclusive.

The relative rates for the reaction of **5** and **6** are surprisingly low. They indicate that despite a 35 kcal/mol decrease in strain energy[19] in going from methylenecyclopropane **5** to cyclopropyl hydroperoxide **14**, **5** nevertheless reacts 180 times slower than TME. This confirms our previous suggestion[1] that $^1O_2$ is totally insensitive in the transition state to the relative thermodynamic stability of the final product and is consistent with the proposal of a variety of researchers, be they concerted ene mechanism proponents[39] or perepoxide supporters,[23a] that the rate-determining transition state occurs early and essentially resembles the starting material. Indeed, there is only a factor of 2.5 between k_{rel} of **5** and **6** despite the fact that for the latter there is no relief of strain in going to the corresponding hydroperoxide.[40]

The low k_{rel} of methylenecyclopropanes **5** and **6** may be correlated with the higher ionization potential[41] of these olefins as compared to TME. Aue[16a] reports that epoxidation of methylenecyclopropanes is also surprisingly slow. The rates of both epoxidation[16a] and photooxygenation[2b,c] decrease with increasing ionization potential.

Let us close with a brief discussion of the photooxidation of olefin **1**. The formation of benzophenone suggests the probable intermediacy of the corresponding methylenedioxolane,[42] which subsequently cleaves.[43] Attempts to trap cyclopropanone, the expected side product, as its hemiacetal, by carrying out the photooxidation in methanol, were unsuccessful, and its probable fate has been discussed above. This case would represent the fifth reported instance[44] of a reaction between singlet oxygen and a strained σ bond.



Further studies on the reaction of $^1O_2$ with small ring olefins such as bicyclopropylidene, cyclopropenes, methylenecyclobutanes, and cyclobutenes are presently under investigation and will be reported shortly.

Experimental Section

^1H NMR spectra were obtained on a Varian HA-100 spectrometer. IR spectra were taken with a Perkin-Elmer Model 257 spectrometer. Mass spectra were run on a single-focusing Hitachi Perkin-Elmer RMU-6 spectrometer. A Perkin-Elmer Model 402 ultraviolet–visible spectrophotometer was used for recording the UV spectra. When gas chromatograms were obtained using a Varian Aerograph Model 920 preparative GLC, peak areas were determined by triangulation. When, however, the Packard Model 824 analytical GLC was used, peak areas were determined by digital integration. The photooxidation apparatus has been previously described.[45] For low temperature photoxidations, a serum-capped Pyrex test tube containing the sample was placed flush against the inside wall of a glass Dewar filled with dry ice and acetone.

Cyclopropylidenediphenylmethane (4). This compound was synthesized according to the one-step procedure of Utimoto.[14] The crude product was distilled (140 °C (10 mm)) but was found to be contaminated with benzophenone. The latter was removed by column chromatography on neutral alumina using a 1:1 solvent mixture of hexane–chloroform as eluant. Recrystallization from hexane gave white crystals: mp 65–66 °C; ^1H NMR ($CDCl_3$) δ 1.36 (s, 4 H, methylene), 7.14–7.50 (m, 10 H, phenyl); IR (KBr) 3050 (m), 1590 (m), 1490 (s), 1440 (s), 1080 (s), 1060 (s), 1030 (s), 1010 (s), 900 (m), 770 (s), 755 (s), 700 (s) cm^{-1}; UV (ethanol) λ_{max} nm (ϵ) 232 (55 000), 256 shoulder, 277 (61 000); MS (70 eV) *m/e* 206 (M^+), 192 ($M^+ - CH_2$), 179 ($M^+ - C_2H_4$), 129 ($M^+ - C_6H_6$).

1-Methylene-2,2-diphenylcyclopropane (1).[12] A solution of 3 g of olefin **4** dissolved in 1.2 L of dry acetonitrile was purged with N_2 and irradiated with a 450-W mercury lamp for 6.5 h. The reaction was followed by GLC using a 3.5 ft × ¼ in. copper column packed with 2%

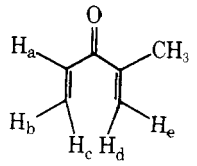
Carbowax 20M on Chromosorb WAWDMCS. When the column temperature was 120 °C and the flow rate 75 mL/min, the retention times of 1 and 4 were 0.5 and 1 h, respectively. When no further change occurred, the solvent was evaporated and the resulting mixture of olefins was chromatographed on neutral alumina using a 1:1 mixture of chloroform–hexane as eluant. This process assured the removal of all traces of benzophenone, which had the same retention time on the Carbowax column as the product (1). Pure 1 was isolated by preparative GLC: ^{1}H NMR ($CDCl_3$) δ 7.23 (m, 10 H, phenyl), 5.75 (m, 1 H, vinyl), 5.57 (m, 1 H, vinyl), 1.86 (m, 2 H, cyclopropyl); IR (neat) 3050, 1600, 1500, 1450 cm^{-1}; MS (70 eV) *m/e* 206 (M^+), 191 ($M^+ - CH_3$), 165 ($M^+ - PhCH_2$), 91 ($M^+ - CPh_2$).

Cyclopropylidenenaphthylmethane (3). The title compound was prepared according to the one-step procedure of Utimoto[14] as modified by Goldschmidt and Finkel.[46]

Isopropylidenecyclopropane (5). To a suspension of sodium hydride (49.3 g, 1.1 mol)[47] in 1.2 L of rigorously dried (CaH_2) diglyme was added 232.1 g (0.5 mol) of (3-bromopropyl)triphenylphosphonium bromide[14] and 10 mL of dry ethanol. The reaction was carried out under a nitrogen cloud, and the mixture was mechanically stirred for 6 h at 75–80 °C. The reaction flask was cooled to room temperature and 24 g (0.5 mol) of acetone was added. Stirring was then continued for an additional 84 h at room temperature, during which time the color of the reaction mixture turned from deep red to brown. The reaction mixture was distilled (25–35 °C (10 mm)), and the distilling vapor was passed through a series of two collection vessels, the first at 0 °C and the second at −78 °C. Gas chromatography (13 ft × ¼ in. glass column packed with 20% Carbowax 20M on Chromosorb WAWDMC; column temperature 50 °C; carrier gas flow rate 150 mL/min) of the distillate (47 g) indicated that nearly 25% (13 g, 30% yield) was the desired product **5**. Compound **5** was obtained pure by preparative GLC (retention time 3 min): ^{1}H NMR[48] ($CDCl_3$) δ 1.79 (br s, 6 H, methyl), 0.97 (br s, 4 H, cyclopropyl); MS (70 eV) *m/e* 82 (M^+), 67 ($M^+ - CH_3$) 54 ($M^+ - CH_2CH_2$), 39 ($M^+ - CH(CH_3)_2$).

Cyclopropylidenedicyclopropylmethane (6).[49] To a suspension of sodium hydride[47] in 200 mL of rigorously dried glyme was added, under N_2, 46.4 g (0.1 mol) of (3-bromopropyl)triphenylphosphonium bromide[14] and a few drops of ethanol. The reaction mixture was stirred at 60–70 °C for 6 h and then cooled back down to room temperature, at which time 10.2 g (0.09 mol) of dicyclopropyl ketone (Aldrich)[52] was added. The reaction was stirred for an additional 12 h at 60 °C and then refluxed for an additional hour. Ice water was added, and the organic layer was extracted with hexane, dried over $MgSO_4$, and vacuum distilled (31 mm). The fraction distilling at 78–82 °C proved to be dicyclopropyl ketone (2.9 g). A second fraction distilling at 86–94 °C (6.27 g) was identified by ^{1}H NMR as olefin **6** contaminated with ~10% of the ketone (yield 45%). Pure olefin was obtained by preparative GLC on a 6.5 ft × ¼ in. copper column packed with 7% SE-52 on Chromosorb WAWDMCS. With the column temperature at 90 °C and a carrier gas flow rate of 80 mL/min, the retention time of **6** was 15 min. The pure olefin should be stored in a freezer under argon since it slowly undergoes autoxidation, yielding cyclobutanone **10B**: ^{1}H NMR (CCl_4) δ 1.32 (quintet, J = 7 Hz, 2 H, allylic methyne), 0.92 (s, 4 H, allylic methylene), 0.62–0.46 (m, 8 H, methylene); ^{1}H NMR ($CDCl_3$) δ 1.37, 0.97, 0.68–0.51; IR (neat) 3090, 3000, 1760, 1425, 1020, 980, 820 cm^{-1}; MS (70 eV) *m/e* 134 (M^+), 105 ($M^+ - CH_2CH_2$), 93 ($M^+ - (CH_2)_3$).

Reaction of 5 with $^1O_2$. Photooxidation in Acetone at 20 °C. Olefin **5** (500 μL) was dissolved in 1 mL of acetone containing 10^{-3} M Rose Bengal. (RB). The solution was photolyzed at 20 °C until 98 mL of oxygen was absorbed, by which time the O_2 uptake had slowed appreciably. The reaction mixture was analyzed by GLC[53] (oven temperature 60 °C) before and after the addition of Ph_3P, and there was no observable difference in the chromatograms. Two peaks eluted (retention times 14 and 29.5 min) in a ratio of 2:1.[54] The first peak was identified as compound **10A** by comparison of its spectral data with those reported in the literature[16b,55,56] and with the data of an independently synthesized sample (vide infra). The second peak proved to be dienone **9A**, and its spectral data were analogous to those of similar compounds prepared by Conia et al.[10] Its spectral data were identical with those of an independently synthesized sample (vide infra). NMR analysis (acetone-d_6) also revealed no difference between those samples which had Ph_3P added to them following photooxidation and those which did not. However, a third compound was observed whose spectral data were consistent with **8A** and similar to the data described for analogous compounds by Conia and Rousseau.[10] Based on the GLC and ^{1}H NMR data, relative yields could be determined and are listed in Table I. **10A**: ^{1}H NMR ($CDCl_3$) δ 3.00 (t, J = 9 Hz, 2 H, methylene), 1.8 (t, J = 9 Hz, 2 H, methylene), 1.2 (s, 6 H, methyl); IR (neat) 1750 cm^{-1}; MS (70 eV) *m/e* 98 (M^+), 70 ($M^+ - CO$), 56 ($M^+ - CH_2CO$), 55 ($M^+ - CH_3CO$), 41 ($M^+ - CH_2CH_2CO$). **9A**: ^{1}H NMR (acetone-d_6) δ 7.05 (dd, H_a, J_{ac} = 17 Hz,



9A

J_{ab} = 10 Hz), 6.19 (dd, H_c, J_{bc} = 3 Hz), 6.05 (s, H_e), 5.9 (m, H_d), 5.73 (dd, H_b), 1.98 (m, CH_3); IR (neat) 2930, 1670, 1430, 1365, 1320, 1140, 935 cm^{-1}; UV (95% EtOH) λ_{max} nm (ϵ) 277 (50); MS (70 eV) *m/e* 96 (M^+), 95 ($M^+ - H$), 81 ($M^+ - CH_3$), 69 ($M^+ - CH_2CH$), 55 ($M^+ - CH_2CCH_3$). **8A**: ^{1}H NMR (acetone-d_6) δ 6.04 (m, 1 H, vinyl), 5.8 (m, 1 H, vinyl), 3.8 (t, 2 H, methylene, J = 3 Hz), 2.87 (t, 2 H, methylene, J = 3 Hz), 1.85 (m, 3 H, methyl).

Photooxidation in Methanol at 20 °C. GLC analysis[53] of a sample of **5** (250 μL) photooxidized in 1 mL of methanol containing 10^{-3} M RB revealed, in addition to **9A** and **10A**, a third peak with a retention time of 8.5 min. This compound was identified as methyl methacrylate (**13A**) by comparison of its spectral data with that of an authentic sample. A ^{1}H NMR spectrum of the reaction mixture (CD_3OD) revealed the presence of a fourth component, compound **8A**.

Photooxidation in Chloroform at 20 °C. When the photooxidation of **5** (100 μL) was carried out in $CDCl_3$ (10^{-3} M Methylene Blue [MB]), the following ^{1}H NMR absorptions ($CDCl_3$) were observed (relative areas in parentheses): δ 8.2 (br s, 1), 6.23 (br s, 2 H), 5.8 (br s, 1 H), 5.67 (m, 1 H), 2.01 (s, 3 H), 1.95 (s, 3 H). The mass spectrum (70 eV) of the mixture showed peaks at *m/e* 98, 69, and 41, while the IR ($CHCl_3$) revealed three carbonyl absorptions[57] at 1697, 1720, and 1785 cm^{-1}. These data are consistent with a 2:1 mixture of methacrylic acid (**11A**) and methacrylic anhydride (**12A**) as is clear from a comparison of these spectral data with those of authentic commercially available samples of methacrylic acid (Aldrich) and methacrylic anhydride (K and K). **11A**: ^{1}H NMR ($CDCl_3$) δ 8.2 (br s, 1 H, carboxylic), 6.23 (br s, 1 H, vinyl), 5.67 (m, 1 H, vinyl), 1.95 (m, 3 H, methyl). **12A**: ^{1}H NMR ($CDCl_3$) δ 6.23 (br s, 2 H, vinyl), 5.8 (br s, 2 H, vinyl), 2.01 (s, 6 H, methyl).

Photoxidation in Acetone and Chloroform at −78 °C. Photooxidation of 100 μL of **5** at −78 °C was carried out in 1 mL of either acetone-d_6 (10^{-3} M RB) or $CDCl_3$ (10^{-3} M MB). Following the photolysis, the reaction sample was halved with one portion treated with Ph_3P and the other not. The two portions were then allowed to warm to room temperature, and a ^{1}H NMR spectrum was taken. The results are listed in Table I.

Synthesis of Isopropylidenecyclopropane Epoxide (24, R = CH_3) and 2,2-Dimethylcyclobutanone (10A). Olefin **5** (50 mg, 0.6 mmol) was dissolved in 1 mL of $CDCl_3$ and cooled to 0 °C. To this solution was added a solution of 0.09 g (1 mmol) of *m*-chloroperoxybenzoic acid dissolved in 1 mL of $CDCl_3$ slowly. The addition was continued until a test with KI–starch paper proved positive. Immediate ^{1}H NMR analysis revealed the presence of epoxide **24** (R = CH_3) and cyclobutanone **10A** in a ratio of 3:2. After 24 h at 20 °C, the ratio dropped to 1:4. The spectral data for **10A** were identical with those for the sample obtained from the photooxidation of **5**. **24** (R = CH_3): ^{1}H NMR ($CDCl_3$) δ 1.48 (s, 6 H), 1.4 (m, 2 H), 0.94 (m, 2 H).

Synthesis of Vinyl Isopropenyl Ketone (9). A mixture of 50 mL (0.5 mol) of ethyl vinyl ketone, 42 g (0.5 mol) of dimethylammonium chloride,[17] 50 mL (0.5 mol) of 35% aqueous formaldehyde, 1 mL of concentrated HCl, and a trace of hydroquinone was heated in a sealed Pyrex carius tube for 7 h at 100 °C. The water was distilled off under vacuum at 70 °C/44 mmHg. The resulting salt was decomposed in vacuo (70–80 mmHg) at an oil bath temperature of 150–210 °C. The distillate was passed through two traps, one cooled to 10 °C and the other to −78 °C. The contents of the latter were dissolved in ether and dried over $MgSO_4$. Upon evaporation of the ether, 5 g (10% yield) of crude product was obtained. The latter was purified by preparative GLC,[53] and the spectral data of this compound proved to be identical with those of compound **9** obtained from the photooxidation of **5**. **9** in lower yields was also obtained when the Mannich reaction was repeated as above using 18 g (0.25 mol) of ethyl methyl ketone instead of ethyl vinyl ketone.

Reaction of 6 with $^1O_2$. The photooxidations were carried out as described above for olefin **5**. The relative product yields were determined by ^{1}H NMR, when the reaction was carried out in $CDCl_3$ or acetone-d_6. It should be noted that when the reaction was carried out at −78 °C and followed by reduction with Ph_3P, peaks were observed in the NMR spectrum which are attributable to alcohol **7B**.[10b] How-

ever, because of the complexity of the NMR spectrum, it is difficult to assign yield values directly. The isolated yield for **7B** reported by Rousseau[10b] was assumed to be valid with the relative yields of the remaining products determined by a combination of ^{1}H NMR and GLC data. Furthermore, the ^{1}H NMR spectrum of the chloroform system at room temperature revealed the presence of several peaks, including a large singlet at δ 2.36 (4 H, allylic) probably corresponding to acid **11B** or the corresponding anhydride **12B.** Hence, the yield assignments are tentative. When CH_3CN, CH_3OH, CH_2Cl_2, or C_6H_6 served as the solvent, they were stripped off and replaced by $CDCl_3$. The chloroform system was also analyzed by GLC (10 ft × 1/4 in. glass column packed with 20% SE-30 on Chromosorb W; oven temperature 120 °C; flow rate 80 mL/min), and four products were eluted: dicyclopropyl ketone **14B** (retention time 3 min), 2,2-dicyclopropylcyclobutanone **10B** (12 min), divinyl ketone **9B** (27 min), and hydroxy ketone **8B** (51 min). When the reaction was performed in methanol, a new product was obtained and identified as ester **13B** (retention time 20 min). The spectral data were consistent with that reported by Conia et al.[10] **8B:** ^{1}H NMR ($CDCl_3$) δ 3.92 (t, J = 8 Hz, methylene), 3.00 (t, J = 8 Hz, methylene), 1.92 (m, 1 H, allyl), 1.38 (s, 4 H, allyl), 0.7 (m, 4 H, cyclopropyl); MS (70 eV) m/e 121 ($M^+ - CH_2CH_2OH$), 93 ($M^+ - C(=O)CH_2CH_2OH$), 91, 85, 83. **9B:** ^{1}H NMR ($CDCl_3$) δ 7.2 (dd, H_a,[59] J_{ab} = 11 Hz, J_{ac} = 18 Hz), 6.33 (dd, H_c, J_{bc} = 3 Hz), 5.68 (dd, H_b), 2.00 (m, 1 H, allylic), 1.37 (s, 4 H, allylic), 0.73 (m, 4 H, cyclopropyl); MS (70 eV) m/e 122 ($M^+ - CH_2C$), 108 ($M^+ - C_3H_5$), 94, 93 ($M^+ - CH_2CHCO$), 89, 53 (M^+ – cyclopropylcyclopropylidenemethane), 52. **10B:** ^{1}H NMR ($CDCl_3$) δ 2.76 (t, J = 9 Hz, 2 H, methylene), 1.58 (t, J = 9 Hz, 2 H, methylene), 1.05–0.5 (m, 10 H, cyclopropyl); MS (70 eV) m/e 122 ($M^+ - CO$), 109 ($M^+ - C_3H_5$), 79 ($M^+ - CH_3CH_2C_3H_5$), 68 ($M^+ - 2C_3H_5$); IR (neat) 3080, 3000, 1765 cm^{-1}. **13B:** ^{1}H NMR ($CDCl_3$) δ 3.77 (s, 3 H, methoxy),[60] 1.9 (m, 1 H, allylic), 1.23 (s, 4 H, allylic), 0.7 (m, 4 H, cyclopropyl); IR (neat) 1750, 1700 cm^{-1}; UV (95% ethanol) λ_{max} nm (ϵ) 230 (5 × 10^5); MS (70 eV) m/e 152 (M^+), 151 ($M^+ - H$), 121 ($M^+ - OCH_3$), 93 ($M^+ - CO_2CH_3$).

Preparation of 2,2-Dicyclopropylcyclobutanone (10B). Olefin **6** was epoxidized as described in the preparation of **10A.** The NMR spectrum revealed the presence of cyclobutanone **10B** contaminated with about 15% of another compound whose absorptions correspond to epoxide **24** (R = cyclopropyl). After 24 h at 10 °C, only **10B** remained.

Attempted Photooxidation of Olefins 2–4. A solution of 1 mmol of olefin in 2 mL of methanol containing 10^{-3} M RB was irradiated for 10–15 h. No oxygen was absorbed by the system, and the starting material remained unchanged as determined by GLC, TLC, and ^{1}H NMR.

Photooxidation of Olefin 1. Pure olefin **1** (200 mg) dissolved in 3 mL of methanol (10^{-3} M RB) was irradiated for 27 h, at which time the reaction had proceeded approximately 70% the way to completion and the uptake of oxygen had essentially ceased. GLC analysis of the product mixture under a variety of conditions revealed only three products. The retention times of these products on a 2.5 ft × 1/8 in. glass column packed with 10% Carbowax 20 M on Chromosorb P (flow rate = 40 mL/min) at 150 °C were 15, 50, and 100 min. The corresponding peak area ratios were 30:1:1. Only the former product could be isolated and was identified by its spectral data as benzophenone. Essentially the same GLC trace was obtained for reactions carried out in benzene or acetone.

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Registry No.—**1,** 25152-47-0; **3,** 68854-50-2; **4,** 7632-57-7; **5,** 4741-86-0; **6,** 37559-52-7; **7,** 40791-85-3; **7B,** 68843-93-6; **8A,** 68843-92-5; **8B,** 68843-94-7; **9A,** 25461-87-4; **9B,** 68843-95-8; **10A,** 1192-14-9; **10B,** 68843-96-9; **11A,** 79-41-4; **12A,** 760-93-0; **13A,** 80-62-6; **13B,** 66051-16-9; **14A,** 67-64-1; **14B,** 1121-37-5; **24,** 68843-97-0; (3-bromopropyl)triphenylphosphonium bromide, 3607-17-8; ethyl vinyl ketone, 1629-58-9; oxygen, 7782-44-7.

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(60) When the reaction was carried out in CD_3OD, this absorption was absent.

Asymmetric Induction in Cholesteric Media Revisited

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The photocyclization of α-(*N*-methylanilino)styrene (**1**) to indoline **2** proceeded in a cholesteric liquid crystal medium with no detectable asymmetric induction. Similarly, the photochemical interconversion of methyl α-naphthyl sulfoxide (**11**) in a cholesteric phase afforded a negligible (<1–2%) enantiomeric excess. On the basis of these results and after reinvestigating several of the reported cases of asymmetric inductions in cholesteric media, we conclude that asymmetric transformation in cholesteric phases, as in ordinary chiral solvents, can generally result in only low optical yields although exceptions may be found in special cases where strong and specific interactions between solute and solvent exist.

There is a great current interest[1-11a] in the possibility of influencing or controlling chemical reactivity by an organized medium such as a liquid crystal. Part of this interest is due to the analogies between liquid crystal and some biological media.

Nematic mesophases were used as reaction solvent in xanthogenate pyrolysis[2] and Claisen rearrangements of *O*-allyl aryl ethers.[3] Although initial kinetic measurements indicated a definite effect when compared to isotropic solvents, further work[4,5] failed to substantiate any specific effect of the nematic solvent on Claisen rearrangement. Dewar[5] hypothesized that bimolecular reactions would be more sensitive to the nematic environment, but for several years there was no evidence for any positive result in this area.[6] One of the few chemical reactions strongly influenced by the organization of a liquid crystal was the polymerization of nematic or cholesteric phases which retains in the solid polymer the features of the liquid crystal structure.[7] It is only recently that a large rate enhancement was described in the photodimerization of acenaphthylene to *syn*- and *anti*-cyclobutane dimers;[8] it was concluded that solvent order exerts a dramatic influence on the efficiency of dimerization but plays little role in determining the stereochemical course of the reaction.

In contrast to the lack of evidence for control over reactivity of nonphotochemical reactions in nematic solvents, asymmetric inductions were recently reported to occur in cholesteric media.[9-11a] In view of the successful asymmetric photocyclizations of various substrates with circularly polarized light,[12] we repeated these reactions with natural light in various cholesteric systems[13] in an attempt to observe asymmetric synthesis. However, photocyclization of α-(*N*-methylanilino)styrene (**1**) into *N*-methyl-2-phenylindoline (**2**) gave a racemic material.

We turned then to another simple cyclization reaction, the transformation **3** → **4.** We were encouraged to investigate this photosynthesis of chiral oxaziridines because photocyclization of nitrones to optically active oxaziridines in a chiral solvent has been described.[14] We indeed obtained good chemical yields (75%) but the irradiation in the cholesteric J mixture[13] at 28–30 °C gave **4** having a very low specific rotation ($(\alpha)_D$ = +0.18 ± 0.04°). When cholesteryl 2-(2-ethoxyethoxy)ethylcarbonate (ChEC) was used as a cholesteric phase (mesomorphic range, −5 to +32 °C) we obtained a completely racemic oxaziridine **4** after photocyclization at 0 °C.

Due to the negative results in asymmetric photocyclization of **3,** even at low temperature, we decided to reinvestigate some of the asymmetric reactions previously described.[9-11] First we reproduced the Claisen rearrangement of **5** to **6** in cholesteryl *p*-nitrobenzoate (ChNB) at 200 °C (in the mesomorphic region) as indicated in ref 9. Phenol **6** was isolated by two different procedures and had no significant specific rotation. The CD curve of **6** showed a very weak positive Cotton effect ($\Delta\epsilon/\epsilon$ 4 ± 2 × 10^{-5} at 275 nm). Since the chiroptical properties of **6** are not known the optical purity of **6**[9a] cannot be calculated

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