Three-Electron S_N2 Reactions of Arylcyclopropane Cation Radicals. 1. Mechanism[1]

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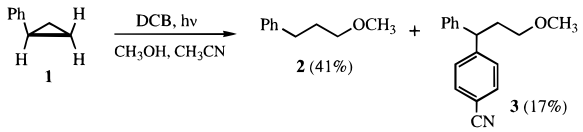
Abstract: The mechanism of photosensitized nucleophilic substitution reactions on arylcyclopropanes was investigated. Stereochemical experiments with methanol, water, and cyanide as nucleophiles showed that the reactions occurred stereospecifically with complete inversion of configuration at the carbon atom undergoing substitution. Independent generation of the arylcyclopropane cation radicals by nanosecond transient methods showed that they reacted rapidly with nucleophiles with kinetics that were first-order in both the cation radical and the nucleophiles. Through a combination of transient kinetics and steady-state Stern−Volmer quenching experiments, the reaction of the phenylcyclopropane cation radical with methanol was kinetically correlated with the formation of the substitution product. The reaction of phenylcyclopropane cation radical with a series of alcohols as nucleophiles showed small steric effects.

Introduction

The activation of carbon−carbon bonds toward reactions that occur both stereospecifically and in high yield is a major challenge in organic chemistry. A particularly well-documented case is formed by the class of S_N2 reactions, which constitute an essential part of organic synthesis[2] as well as a testing ground for theoretical models.[3] Classic four-electron S_N2 reactions suffer, however, from several limitations with respect to the nature of both the substrate and the nucleophile. For example, loss of stereospecificity often occurs with increasing steric demands of either the substrate or the nucleophile by transition to reactions occurring by an S_N1 mechanism. This motivates research into analogous reactions that do not suffer from this drawback. One possibility is provided by three-electron S_N2 reactions between open-shell substrates $(LG^{\bullet}R)^+$ and closed-shell nucleophiles (:Nu), schematically represented by eq 1. As we show in this and the accompanying paper in *J. Am. Chem. Soc*. **1997**, *119*, 994, the reactions of arylcyclopropane cation radicals with nucleophiles are examples of such reactions. They proceed with a complete inversion of configuration in the substitution step and have greatly diminished steric effects—two features that make them attractive for synthetic applications.

$$(LG^{\bullet}R)^+ + :Nu \longrightarrow LG^{\bullet} + R{-}Nu^{\oplus} \qquad (1)$$

The pioneering work of Rao and Hixson[4] on the photosensitized addition of nucleophiles to arylcyclopropanes lead us to explore whether the reactions involved examples of three-electron S_N2 reactions. They discovered that the 1,4-dicyanobenzene-photosensitized addition of methanol to phenylcyclopropane (**1**) gave two major products, **2** and **3**.



Rao and Hixson proposed that methanol-addition product **2** is formed by the mechanism shown in Figure 1. The mechanism starts with photoinduced electron transfer from **1** to the singlet excited state of 1,4-dicyanobenzene (DCB) to give $\mathbf{1}^{\bullet+}$ and $DCB^{\bullet-}$. Methanol is then proposed to react with $\mathbf{1}^{\bullet+}$ by nucleophilic substitution. Following proton loss from oxygen, the benzylic radical intermediate is reduced by $DCB^{\bullet-}$ to give a benzyl anion, which is protonated by methanol to give **2**. The mechanism for formation of **3** will be discussed later.

In a subsequent study of the photooxidation of **1**, Mizuno and co-workers[5] observed formation of methanol-adduct **2** (40%) as well as 1,6-dimethoxy-3,4-diphenylhexane (45%) with 1-cyanonaphthalene (1-CN) as the electron acceptor. The latter product is thought to be formed by coupling of intermediate benzyl radicals. Mizuno *et al.* also demonstrated that cyanide, water, and several other alcohols could be used as nucleophiles. The observation that $PhCHD(CH_2)_2OCH_3$ is formed in the reaction of **1** with CH_3OD provided evidence that the mechanism for formation of **2** involves donation of a proton rather than a hydrogen atom from methanol.

From the standpoint of this work, the most important step in Figure 1 is the reaction of methanol with $\mathbf{1}^{\bullet+}$. Rao and Hixson[4] proposed that the reaction occurs from a ring-closed cation radical intermediate because *trans*-1-methyl-2-phenylcyclopropane did not trans → cis isomerize under the reaction conditions. While this observation is consistent with the proposed mechanism, the unimolecular ring-opening of the cyclopropane cation radicals followed by rapid nucleophilic capture of methanol (i.e., an S_N1 mechanism) could not be entirely excluded. In later work on the photooxidation of bridged bicyclobutanes, Gassman and co-workers observed products formed from nucleophilic substitution with inversion of configuration.[6a−d] Similar results were reported by Arnold and Du for the photooxidation of

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(1) Taken in part from the doctoral thesis of T.R.S., University of Rochester, 1995.

(2) See, e.g.: (a) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*; Plenum Press: New York, 1990; Part B, Chapter 3. (b) March, J. *Advanced Organic Chemistry* Wiley-Interscience: New York, 1992; Chapter 10.

(3) Shaik, S. S.; Schlegel, H. B.; Wolfe, S. *Theoretical Aspects of Physical Organic Chemistry. The S_N2 Mechanism*; Wiley-Interscience: New York, 1992.

(4) Rao, V. R.; Hixson, S. S. *J. Am. Chem. Soc.* **1979**, *101*, 6458.

(5) Mizuno, K.; Ogawa, J.; Otsuji, Y. *Chem. Lett.* **1981**, 741.

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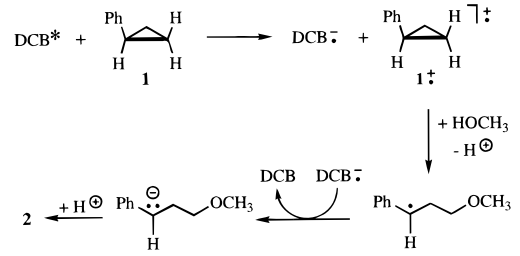
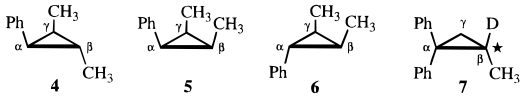


Figure 1. Rao−Hixson mechanism for the photooxidation of **1**.

tricyclene[6e] and by Weng and Roth for the photooxidation of quadricyclane.[6f] Most recently, the stereochemical outcome of methanol addition to (1*R*,5*R*)-(+)-sabinene under photooxidation conditions has been reported by Roth and co-workers.[7] The products of reaction with methanol with sabinene were found to be optically active, although the stereochemical configurations and optical purities were not determined. Nonetheless, the results show that the reaction is partly, if not completely, stereospecific.

In this report, we present results on the mechanism of the photooxidation of **1** and several alkyl-substituted analogues (**4**−**7**).[8] By a combination of transient pulsed laser and steady-state experiments, direct evidence is provided that free, ring-closed cyclopropane cation radical are generated as reaction intermediates and that they rapidly react with added nucleophiles to give substitution products in high yields. In addition, stereochemical experiments with **4**−**7** show that the cation radicals react with nucleophiles in a completely stereospecific manner with inversion of configuration at the atom undergoing nucleophilic substitution.



Results

A. Synthesis of 4−7. Compounds **4**−**6** were prepared by the cyclopropanation method of Olofson and Dougherty[9] using benzyl chloride/lithium tetramethylpiperidide and either *trans*-2-butene or *cis*-2-butene, yielding *r*-1,*t*-2-dimethyl-*t*-3-phenylcyclopropane (**4**) and a mixture of *r*-1,*c*-2-dimethyl-*c*-3-phenylcyclopropane (**5**) and *r*-1,*c*-2-dimethyl-*t*-3-phenylcyclopropane (**6**), respectively. The mixture of **5** and **6** was used in some of the experiments, while pure samples of pure **5** and **6** were obtained by preparative gas chromatography for other experiments. Optically active (*S*)-1-methyl-2,2-diphenyl-[1-^{2}H]cyclopropane (**7**) was received as a gift from Prof. H. M. Walborsky.[10]

B. Photooxidations of 4−7. Stereochemical Outcome of Substitutions. Preparative photooxidations of cyclopropanes **4**−**7** with several nucleophiles were performed in degassed acetonitrile using 1-CN as sensitizer. Compounds **4**−**6** were reacted with methanol, water, and cyanide, while only methanol was used with **7**. The adducts of methanol are designated as **8a**−**10a**, those of water as **8b** and **9b**, and those of (formally) hydrogen cyanide as **8c** and **9c**. As shown in Figure 2, cyclopropane **4** gave the *anti* isomers **8a**−**c** as the sole detectable substitution products. In contrast, cyclopropanes **5** and **6** gave only the corresponding *syn* products **9a**−**c**. These results require stereospecific nucleophilic substitutions with inversion of configuration. Taking into account the detection limits of the GC methods used, all of the reactions were found to be >99.7% stereospecific. Similarly, photooxidation of **7** (22.8 ± 0.3% optically pure) in the presence of methanol gave (*R*)-ether **10a**[10] (22.4 ± 0.7% optically pure). This result requires addition of methanol with 98 ± 4% inversion in the substitution step.

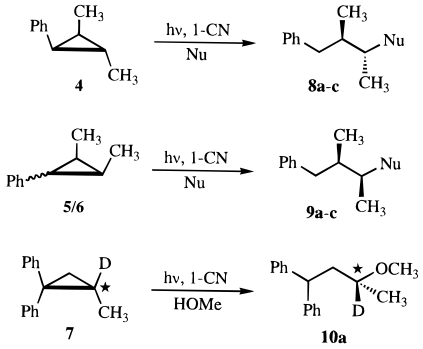


Figure 2. Stereochemical results for the photooxidations of **4**−**7**.

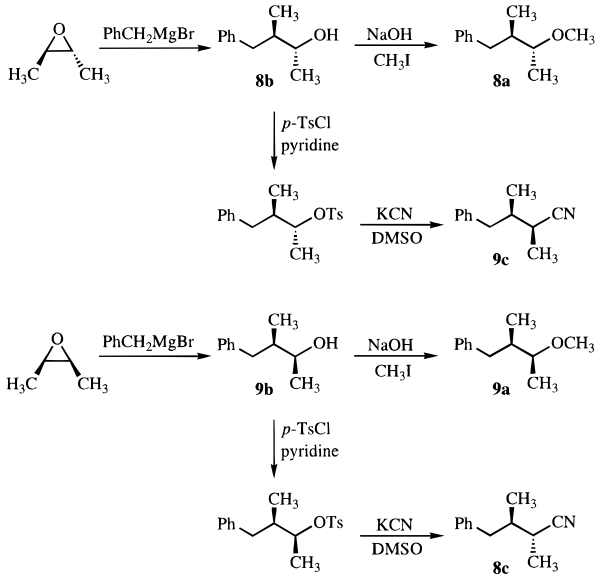


Figure 3. Synthetic scheme for the preparation of **8a**−**c** and **9a**−**c**.

C. Independent Synthesis of the Photoproducts. The absolute configuration and optical purity of ether **10a** derived from photooxidation of cyclopropane **7** was established by comparison with literature data.[10] The stereochemical configurations of the products derived from photooxidation of cyclopropanes **4**−**6** were determined by independent synthesis as shown in Figure 3. The syntheses start with the reaction of benzylmagnesium bromide with either *trans*- or *cis*-2-epoxybutane[11] which gave *anti* and *syn* alcohols **8b** and **9b**, respectively. These alcohols were transformed into the corresponding *anti* and *syn* methoxy ethers **8a** and **9a** by alkylation with methyl iodide. Butyronitriles **8c** and **9c** were prepared from alcohols **8b** and **9b** by tosylation followed by an S_N2 reaction with cyanide. Due to inversion of configuration in the second step, **8b** gives **9c**, and **9b** gives **8c**.

(6) (a) Gassman, P. G.; Olson, K. D.; Walter, L.; Yamaguchi, R. *J. Am. Chem. Soc.* **1981**, *103*, 4977. (b) Gassman, P. G.; Olson, K. D. *J. Am. Chem. Soc.* **1981**, *103*, 4977. (c) Gassman, P. G.; Hay, B. A. *J. Am. Chem. Soc.* **1986**, *108*, 4227. (d) Gassman, P. G. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part C, Chapter 4.2, p 70. (e) Arnold, D. R.; Du, X. *Can. J. Chem.* **1994**, *72*, 403. (f) Weng, H.; Roth, H. D. *J. Org. Chem.* **1995**, *60*, 4136.

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(8) Preliminary results have been previously reported: Dinnocenzo, J. P.; Todd, W. P.; Simpson, T. R.; Gould, I. R. *J. Am. Chem. Soc.* **1990**, *112*, 2464.

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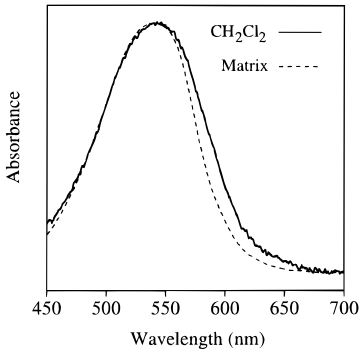

Figure 4. UV-vis spectra from the photosensitized (solid line) and γ-radiolysis (dotted line) oxidation of **1**.

D. Direct Spectroscopic Evidence for Involvement of Cation Radicals. Transient absorption spectroscopy was used to measure the UV-vis spectrum of the species obtained from the photooxidation of phenylcyclopropane (**1**). The transient was generated by irradiation of a dioxygen-saturated, acetonitrile solution containing **1** (0.08 M), *N*-methylquinolinium hexafluorophosphate (NMQ^+, 10^{-4} M), and toluene (2.0 M) with a laser pulse (355 nm, 25 ps, 800 μJ). In this experiment, the first singlet excited state of NMQ^+ (E^*_{red} = 2.7 V vs SCE)[12] is quenched by toluene (E_{ox} = 2.3 V)[13] to produce the *N*-methylquinolyl radical ($NMQ^\bullet$) and free toluene cation radical with a high quantum yield.[14] The toluene cation radical subsequently reacts with **1** (E_{ox} = 1.9 V)[15] by electron transfer. This co-sensitization method with the positively charged sensitizer NMQ^+ produces a much higher yield of cation radicals than by directly using **1** in high concentration.[16] The photolysis solution is saturated with dioxygen to remove $NMQ^\bullet$. Dioxygen reacts with $NMQ^\bullet$ to give products that are optically transparent in the spectral window of interest (400−700 nm). The transient UV-vis spectrum obtained from **1** under these conditions has a maximum at 540 nm and is shown in Figure 4 (solid line). The lifetime of the transient is unaffected by dioxygen and, in the absence of added quenchers, decays mainly by second-order kinetics, presumably due to return electron transfer.

Ionization of **1** by γ-radiolysis in a glass matrix of $CFCl_3$ and $BrCF_2CF_2Br$ at 77 K gave a species with a UV-vis spectrum that is virtually identical to that obtained by transient absorption spectroscopy (Figure 4, dotted line).[17] We assign these spectra to the phenylcyclopropane cation radical. Support for this assignment is provided by the chemical trapping experiments described below.

Time-resolved nanosecond transient absorption spectroscopy was used to measure the rate of decay of the transient species in acetonitrile in the presence of different concentrations of good electron donors, such as 1,2,4,5-tetramethoxybenzene (TMB). The cation radical was generated in the same manner as described above except the excitation source was a nanosecond laser (ca. 15 ns, 340 nm, 4−6 mJ). A plot of the first-order decay rate constants for the transient vs [TMB] yielded a straight line with a slope (k_q) of 1.9×10^{10} M^{-1} s^{-1}. The transient species also reacted rapidly with tris-*p*-tolylamine. Disappearance of the transient was accompanied by appearance of a new species with λ_{max} = 670 nm, which agreed well with that reported for the tris-*p*-tolyl amine cation radical.[18] Finally, kinetic measurements showed that the transient reacted with methanol in a reaction that was first-order in each; the second-order rate constant (k_m) was 1.6×10^7 M^{-1} s^{-1}.

Table 1. Rate Constants ($\times 10^{-7}$ M^{-1} s^{-1}) for the Reaction of Phenylcyclopropane Cation Radical ($\mathbf{1}^{\bullet+}$) with Alcohols in Acetonitrile (ACN), 1,2-Dichloroethane (DCE), and Dichloromethane (DCM) at 23 °C

alcohol	k(alcohol)$_{ACN}$	k(alcohol)$_{DCE}$	k(alcohol)$_{DCM}$
methanol	1.6 ± 0.1[a]	1.52 ± 0.09	1.99 ± 0.08
ethanol	1.4 ± 0.1[a]	1.46 ± 0.09	
isopropyl alcohol	1.10 ± 0.08	1.19 ± 0.06	
butanol	1.43 ± 0.09	1.56 ± 0.08	
tert-butyl alcohol	0.73 ± 0.05	0.95 ± 0.04	1.10 ± 0.06

[a] Data collected up to 0.15 M of the alcohol.

E. Kinetics for Reaction of $\mathbf{1}^{\bullet+}$ and $\mathbf{4-6}^{\bullet+}$ with Alcohols. The kinetics for the reaction of $\mathbf{1}^{\bullet+}$ with a series of alcohols were studied at 23 °C in acetonitrile (ACN), 1,2-dichloroethane (DCE), and dichloromethane (DCM). Plots of the decay rate constants vs [alcohol] were linear, and the second-order reaction rate constants were obtained from the slopes of the plots. The results are given in Table 1. The cation radicals of **4**−**6** were similarly generated and have broad, visible absorption spectra similar to $\mathbf{1}^{\bullet+}$ with maxima at 563, 560, and 551 nm, respectively. The rate constants for reaction of $\mathbf{4-6}^{\bullet+}$ with methanol in DCM are 3.7, 1.9, and 4.4×10^7 M^{-1} s^{-1}, respectively.

Although the bimolecular kinetics for the reactions of $\mathbf{4-6}^{\bullet+}$ with methanol are consistent with an S_N2 mechanism, they do not exclude the possibility that the cation radicals undergo rapid, reversible ring-opening followed by relatively slow capture of methanol. To test this hypothesis, the photooxidations were performed in the absence of nucleophile to determine if isomerization of the cyclopropanes was competitive with formation of the methanol adducts. In practice, photooxidation of a mixture of **5** and **6** in CH_3CN showed < 2% isomerization to **4** after 60 h of irradiation. For comparison, preparative experiments in the presence of 2 M methanol were complete within 2 h.

F. Stern−Volmer Quenching Experiment. Although the transient kinetic experiments described above show that phenylcyclopropane cation radical reacts with methanol, they do not rigorously prove that this reaction is related to the formation of methanol-adduct **2** in the steady-state photolysis experiment. A Stern−Volmer quenching experiment was performed to determine if these two reactions are mechanistically linked. Addition of increasing amounts of TMB to an acetonitrile solution containing **1**, 1-CN, and 0.45 M MeOH decreased the quantum yield for formation of **2**. A plot of ϕ_0/ϕ vs [TMB] was linear and provided a Stern−Volmer slope (k_q/k_m[MeOH]) of 2.2×10^3 M^{-1}. Multiplying the slope by the methanol concentration gives an estimate for k_q/k_m of 1.0×10^3, which is in good agreement with the value obtained from transient kinetics, 1.2×10^3.

Discussion

Reaction Mechanism. We start by discussing the transient kinetics experiments described above in the context of the mechanism originally proposed by Rao and Hixson for the photooxidation of phenylcyclopropane in the presence of

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(15) Lingenfelter, T. G.; Simpson, T. R., Dinnocenzo, J. P. Manuscript in preparation.

(16) Todd, W. P.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R. *J. Am. Chem. Soc.* **1991**, *113*, 3601.

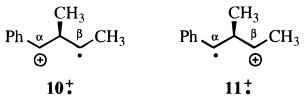
(17) The radiolytic oxidation of **1** at 77 K in a Freon matrix was performed according to previously published procedures (Bally, T. In *Radical Ionic Systems, Properties of Condensed Phase*; Lund, A., Shiotani, M., Eds.; Kluwer Academic Publishers: Dordrecht, 1991).

(18) Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290.

methanol (Figure 1).[4] Regarding the nature of the reactive cyclopropane intermediate, the strong similarity of the UV-vis spectra obtained from oxidation of **1** by photoinduced electron transfer and by γ-radiolysis (Figure 4) demonstrates that the same species is produced in both experiments. The transient kinetics experiments show that this species reacts with the good electron donors TMB and tris-*p*-tolyl amine with diffusion-controlled rate constants. Furthermore, the reaction with tris-*p*-tolyl amine leads to the formation of the tris-*p*-tolyl aminium cation radical. These facts are all consistent with assignment of the transient species to $\mathbf{1}^{\bullet+}$. Finally, the agreement between the rate constant ratios determined for reaction of the species with TMB vs methanol by time-resolved and steady-state experiments provides a direct experimental link between the reaction of $\mathbf{1}^{\bullet+}$ with methanol and the formation of **2** in the preparative photolysis experiment.

The stereochemical probes of the photosensitized reactions of arylcyclopropanes **4**−**7** with nucleophiles show that the reactions are stereospecific and proceed with inversion of configuration at the site of nucleophilic substitution. These data are consistent with ring-closed arylcyclopropane cation radical intermediates undergoing nucleophilic displacement. An alternative hypothesis that might explain the stereochemical and kinetic results would be reversible opening of the cyclopropane ring in the cation radicals followed by rapid nucleophilic capture before bond rotation, i.e., an S_N1-like mechanism. If this were occurring, then one would expect to see rapid isomerization of the starting cyclopropane in the absence of nucleophile. This was not observed and consequently a mechanism involving nucleophilic capture of ring-opened cation radical intermediates is ruled out. The fact that the cation radicals do not rapidly isomerize in the absence of nucleophiles is consistent with thermodynamic cycle and quantum chemical calculations.[19] These calculations show that the $C_\alpha-C_{\beta/\gamma}$ cyclopropane bonds in the cation radicals are substantially weakened upon one-electron oxidation, but still have significant bond strengths (ca. 10 kcal/mol for phenylcyclopropane cation radical).

The regiochemistries of substitution provide a second argument against reaction via ring-opened intermediates. For example, ring-opening of $\mathbf{4}^{\bullet+}$, $\mathbf{5}^{\bullet+}$, or $\mathbf{6}^{\bullet+}$ would be expected to give distonic cation radical $\mathbf{10}^{\bullet+}$ rather than $\mathbf{11}^{\bullet+}$.[20] If $\mathbf{10}^{\bullet+}$ were formed then one would expect nucleophilic addition to C_α, which is not observed. The same argument also applies to the regiochemistry of substitution on $\mathbf{1}^{\bullet+}$; here the argument is even more persuasive since formation of a primary carbocation would be required to explain the observed regioselectivity.



10‡ **11**‡

The regiochemistry of reaction of $\mathbf{7}^{\bullet+}$ with methanol is interesting because nucleophilic substitution occurs at C_β rather than C_γ, i.e., at the more hindered carbon atom. The stereochemical outcome of the reaction shows that the substitution is best rationalized by an S_N2 mechanism. The substitution regiochemistry is, therefore, clearly not determined by steric effects. We instead propose that it is governed by the ability

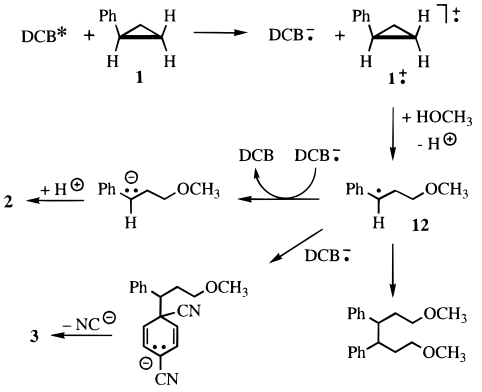
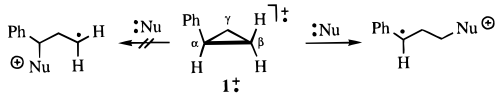


Figure 5. Proposed mechanism for the formation of products from the photosensitized oxidation of **1** in the presence of methanol.

of the methyl group at C_β to stabilize positive charge in the substitution transition state. This explanation is consistent with the regiochemistry of related arylcyclopropane cation radical substitutions and quantum chemical calculations.[19]

The lack of benzylic substitution on the ring-closed phenylcyclopropane cation radical can be rationalized by the relative stabilities of the expected primary substitution products, shown below. Nucleophiles presumably attack $\mathbf{1}^{\bullet+}$ at $C_{\beta/\gamma}$ rather than C_α, because the former pathway provides the more stable distonic cation radical, which benefits from benzylic stabilization of the radical center.



Following nucleophilic substitution, the reaction products can be explained by the three-way partitioning of benzyl radical **12** as shown in Figure 5. This leads to a matter of synthetic interest. All of the preparative experiments described here differ from previous experiments[4,5] in that dioxygen was removed by rigorous freeze−pump−thaw degassing and that 1-cyanonaphthalene (1-CN) was uniformly employed as photosensitizer. These modifications significantly improve the reaction yields by suppressing radical-coupling products. In addition to being synthetically useful, the observations are mechanistically revealing. Removal of dioxygen by degassing most likely alters the partitioning of **12** in the following way. At low conversion of starting material, the sensitizer anion radical ($S^{\bullet-}$) and **12** are formed in equal amounts. To the extent that **12** dimerizes, however, the steady-state concentration of $S^{\bullet-}$ will increase. After a brief reaction time, the steady state concentration of $S^{\bullet-}$ will be much greater than of **12**. As a result, reaction of **12** with $S^{\bullet-}$ will subsequently dominate.[21] If dioxygen is present, however, $S^{\bullet-}$ will react with dioxygen by electron transfer which will prevent the condition $[S^{\bullet-}] \gg [\mathbf{12}]$ from being achieved.

The use of 1-CN as a sensitizer instead of DCB is thought to favor reduction of **12** by the sensitizer anion radical rather than coupling. Since the reduction potential of 1-CN is −1.98 V[22] and the reduction potential of DCB is −1.60 V,[22] it is likely that the $1\text{-CN}^{\bullet-}$ is more efficient at reducing **12** than $DCB^{\bullet-}$. Assuming that the reduction potential of **12** is similar to that of 1-phenylethyl radical (−1.60 V),[20] then the electron transfer reaction from $DCB^{\bullet-}$ to **12** is thermoneutral, while the electron

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(20) This can be deduced from the relative oxidation potentials of the 1-phenylethyl radical and the 2-propyl radical, which are 0.37 and 0.47 V, respectively: Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132.

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(22) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401.

transfer from 1-$CN^{\bullet-}$ to **12** has a driving force of ca. 0.38 V or 8.8 kcal/mol.

Spectroscopy and Kinetics. It is interesting to compare the observed spectrum of $\mathbf{1}^{\bullet+}$ (λ_{max} = 540 nm) with the cation radical of cumene, which has an absorption maximum at 440 nm.[23] The remarkable red-shift of the spectrum of $\mathbf{1}^{\bullet+}$ suggests extensive delocalization of spin and charge into the cyclopropane ring. This is in accordance with expectations for a ring-closed structure and is difficult to rationalize by a ring-opened cation radical. In the latter case, the UV-vis spectrum might be expected to resemble that of either benzyl radical (λ_{max} = 316 nm)[24] or benzyl cation (λ_{max} = 305 and 445 nm).[25] Extensive delocalization in $\mathbf{1}^{\bullet+}$ is also consistent with CIDNP effects observed in the photooxidation of a variety of arylcyclopropanes[26] as well as with quantum chemical calculations.[19]

The rate constants for reaction of the cation radicals of **1** and **4**−**6** with alcohols are very high for S_N2 reactions, but all significantly below that expected for a diffusion-controlled reaction. The linearity of the plots of the first-order decay rate constants vs. [MeOH] indicate a 1:1 stoichiometry of the quenching process, in line with the observed products and postulated mechanism. Since the pseudo-first-order rate constants for nucleophilic capture at the nucleophile concentrations used in the preparative experiments are substantially lower than the rate constants for separation of ion radical pairs,[27] it follows that the cation radicals undergo nucleophilic substitution after diffusional separation of the geminate ion radical pairs, i.e., they react as "free" cation radicals.

Schepp and Johnston have recently determined rate constants for the reaction of methanol with substituted styrene cation radicals to be in the range of 10^4-10^8 M^{-1} s^{-1}, depending on substituent pattern.[28] It is interesting to note that methanol reacts with the *trans*-β-methylstyrene cation radical ca. 20 times slower than with styrene cation radical. In contrast, the methyl-substituted phenylcyclopropane cation radicals $\mathbf{4}-\mathbf{6}^{\bullet+}$ react as fast or faster than $\mathbf{1}^{\bullet+}$, pointing to a different nature of substituent effects on the S_N2 reactions.[19,29]

The data in Table 1 show that the rate constants of nucleophilic substitution are rather insensitive to both the solvent polarity and the steric bulk of the nucleophile. The small solvent polarity effects are consistent with that expected for reaction between a charged species and a neutral one.[30] The reactivity differences between methanol and *tert*-butyl alcohol (k_{HOMe}/k_{HOBu^t} = 1.5−2.1) are smaller than analogous rate data reported for four-electron S_N2 reactions. For example, the relative rate constants for reaction of 1-bromobutane with methoxide and *tert*-butoxide are ≈20:1.[31] It is also worth noting that the relative rate constants for reaction of methanol and *tert*-butyl alcohol with α-aryl vinyl carbocations[32] (k_{HOMe}/k_{HOBu^t} = 9−21) and benzhydryl carbocations[33] (k_{HOMe}/k_{HOBu^t} = 8−21) are larger than the three-electron S_N2 reactions described here. Similarly, the selective nucleophilic attack of methanol on $\mathbf{7}^{\bullet+}$ at C_β rather than C_γ suggests that steric effects are diminished for these three-electron S_N2 reactions. This conclusion is also consistent with the small steric effects observed for alkyl-substituted phenylcyclopropane cation radicals discussed in the accompanying paper in *J. Am. Chem. Soc.* **1997**, *119*, 994.[19]

Conclusions

Direct evidence is provided that photooxidation of arylcyclopropanes in the presence of nucleophiles proceeds via a *bona fide* three-electron S_N2 mechanism. This mechanism is supported by transient absorption experiments which demonstrate the intermediacy of arylcyclopropane cation radicals and by transient kinetic methods which show that the cation radicals rapidly react with nucleophiles with second-order kinetics. Furthermore, the reactions show complete stereospecificity and proceed with inversion of configuration at the atom undergoing substitution.

Experimental Section

General Techniques. All ^{1}H-NMR spectra were recorded at 300.1 MHz, using a General Electric/Nicolet QE-300 spectrometer. ^{13}C-NMR spectra were recorded at 75.5 MHz using a General Electric/Nicolet QE-300 spectrometer and calibrated using internal chloroform. Ultraviolet and visible absorption spectra were recorded using a Hewlett Packard 8452A diode array spectrophotometer. Low-resolution electron impact mass spectra were obtained using a Hewlett-Packard 5890A gas chromatograph equipped with a J&W Scientific Durawax 3, 30 m × 0.32 mm column with a 0.25 μm film thickness, and a Hewlett-Packard 5970 mass selective detector. High-resolution mass spectra were obtained using a VG-7035 mass spectrometer with perfluorokerosene as a standard. Elemental analyses were performed by Quantitative Technologies Inc., P.O. Box 470, Salem Industrial Park, Bldg. 5, Rt. 22E, Whitehouse, NJ 08888. Analytical gas chromatography was performed on a Hewlett Packard 5890 Series II chromatograph equipped with a J&W Scientific Durawax 3, 30 m × 0.32 mm column with a 0.25 μm film thickness, a flame ionization detector, a Hewlett Packard 7673A Controller, and a personal computer. Preparative gas chromatographic separations were performed on a Varian-Aerograph 1720-1 using helium as the carrier gas and a thermal conductivity detector. Inert atmosphere manipulations were conducted under nitrogen in a Vacuum Atmospheres HE-43-2 DRI-LAB glovebox equipped with a Vacuum Atmospheres HE-493 DRI-TRAIN. Degassed samples were prepared using three or more freeze−pump−thaw cycles on a manifold connected to a mercury diffusion pump (1×10^{-6} mmHg) in conjunction with a Sargent Welch Model No. 1405 oil vacuum pump. Transient kinetic and absorption experiments were performed on nanosecond and picosecond apparatuses described previously.[34]

Materials. Reagents were from commercial sources except when noted otherwise. Phenylcyclopropane was vacuum-distilled before use. 1-Cyanonaphthalene was sublimed before use. All syntheses were performed under a nitrogen atmosphere except when noted otherwise. Column chromatography was performed using silica gel (230−400 mesh; EM Science) and several different eluents (*vide infra*) and invariably followed by concentration by rotary evaporation under reduced pressure. Whenever intermediary drying of organic layers was necessary, anhydrous sodium sulfate or magnesium sulfate were used, except when noted otherwise. Reagent grade solvents were used for

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all extractions and workup procedures. Anhydrous benzene, diethyl ether, and tetrahydrofuran were obtained by distillation from sodium benzophenone ketyl under nitrogen. Acetonitrile was distilled under nitrogen successively from aluminum trichloride, potassium permanganate/lithium carbonate, potassium bisulfite, calcium hydride, phosphorous pentoxide and then stored under nitrogen over molecular sieves (3 Å) prior to use. Deionized water was used for the preparation of all aqueous solutions. Dichloromethane was refluxed with aluminum trichloride under nitrogen for 2 h, cooled, and allowed to settle overnight. After decanting, the dichloromethane was washed with water, dried over calcium chloride, distilled from phosphorus pentoxide and stored under nitrogen. Anhydrous dimethylsulfoxide was distilled from calcium hydride *in vacuo*. 2,2,2-Trifluoroethanol was dried over anhydrous calcium sulfate and sodium bicarbonate and distilled at atmospheric pressure. Pyridine was distilled from barium oxide.

***r*-1,*t*-2-Dimethyl-*t*-3-phenylcyclopropane (4).** Preparation of this material was adapted from the method of Olofson and Dougherty.[9] A flask equipped with a Dewar condenser was successively charged with dry ether (20 mL), *trans*-2-butene (18.5 g, 330 mmol), benzyl chloride (2.80 mL, 24.33 mmol), and tetramethylpiperidine (800 μL, 4.74 mmol). The flask was immersed in a −10 °C bath, and methyllithium (1.4 M in ether, 17.4 mL, 24.36 mmol) was added over 2 h by means of a syringe pump. The solution was warmed to room temperature for 3 h, and then 5% HCl (50 mL) was carefully added. The resulting mixture was transferred into a separatory funnel and extracted with 2 × 30 mL ether. The combined ethereal extracts were washed successively with portions of brine, saturated sodium bicarbonate, brine, and dried. Concentration gave a light yellow oil (2.8 g) which after column chromatography (hexane) gave a colorless oil (1.23 g, 35%). ^{1}H NMR ($CDCl_3$): δ 7.33−7.18 (m, 5.17 H), 1.80 (dd, J = 7.2, 5.9, 0.98 H), 1.24 (d, J = 5.8, 3.01 H), 1.04−0.86 (m, 4.94 H).

***r*-1,*c*-2-Dimethyl-*c*-3-phenylcyclopropane (5) and *r*-1,*c*-2-Dimethyl-*t*-3-phenylcyclopropane (6).** This mixture of diastereomers was prepared using the same procedure[9] as above except *cis*-2-butene was used. Column chromatography (hexane) gave a colorless oil (0.80 g, 25%). ^{1}H NMR ($CDCl_3$): δ 7.34−7.20 (m, 5.07 H), 2.04 (t, J = 8.9, 0.93 H), 1.26−1.15 (m, 2.32 H), 1.00−0.93 (m, 5.68 H).

(2*R,3*R**)-3-Methyl-4-phenyl-2-butanol (8b).** This material was prepared following the procedure of Closs.[11] Benzylmagnesium chloride (18.25 mL, 0.90 M in ether, 16.43 mmol) was added dropwise to a solution of *trans*-2,3-epoxybutane (1.30 mL, 14.9 mmol) and 20 mL ether. Extractive workup followed by concentration gave 2.12 g of a yellow oil which after column chromatography (90:10 hexane:ethyl acetate) gave a colorless oil (1.03 g, 42%). ^{1}H NMR ($CDCl_3$): δ 7.34−7.19 (m, 5.18 H), 3.85−3.76 (m, 0.94 H), 2.85 (dd, J = 13.3, 5.9, 0.99 H) 2.43 (dd, J = 13.3, 9.0, 0.96 H), 1.88−1.75 (m, 0.94 H), 1.34 (bs, 0.99 H), 1.23 (d, J = 6.3, 3.00 H), 0.89 (d, J = 6.9, 3.00 H).

(2*S,3*R**)-3-Methyl-4-phenyl-2-butanol (9b).** This material was prepared as described above except *cis*-2,3-epoxybutane was used. Column chromatography (90:10 hexane:ethyl acetate) gave a colorless oil (1.07 g, 44%). ^{1}H NMR ($CDCl_3$): δ 7.33−7.18 (m, 4.85 H), 3.78−3.68 (m, 0.97 H), 2.91 (dd, J = 13.4, 4.9, 1.00 H) 2.37 (dd, J = 13.4, 9.4, 1.01 H), 1.92−1.78 (m, 0.99 H), 1.37 (bs, 1.01 H), 1.24 (d, J = 6.3, 3.15 H), 0.86 (d, J = 6.8, 3.03 H).

(2*R,3*R**)-2-Methoxy-3-methyl-4-phenylbutane (8a).** A solution of 0.9 mL of water, sodium hydroxide (0.90 g, 22 mmol), tetra-*n*-butylammonium iodide (0.206 g, 0.56 mmol), methyl iodide (1.40 mL, 22.5 mmol), and (2*R**,3*R**)-3-methyl-4-phenyl-2-butanol (0.370 g, 2.25 mmol) was refluxed for 95 h. Extractive workup followed by column chromatography (90:10 hexane:ethyl acetate) gave a colorless oil (0.33 g, 82%). ^{1}H NMR ($CDCl_3$): δ 7.32−7.17 (m, 4.86 H), 3.36 (s, 2.96 H), 3.24 (dq, J = 6.2, 3.7, 1.02 H) 2.86 (dd, J = 13.2, 5.6, 1.06 H), 2.35 (dd, J = 13.2, 9.2, 1.10 H), 1.89 (m, 0.97 H), 1.14 (d, J = 6.3, 2.96 H), 0.86 (d, J = 6.8, 3.05 H). HRMS (EI): Calcd for $C_{12}H_{18}O_1$ (M^+): 178.1358. Found: 178.1320.

(2*S,3*R**)-2-Methoxy-3-methyl-4-phenylbutane (9a).** This material was prepared in 72% yield using the same procedure as above except (2*S**,3*R**)-3-methyl-4-phenyl-2-butanol was used. ^{1}H NMR ($CDCl_3$): δ 7.32−7.17 (m, 5.48 H), 3.34 (s, 2.74 H), 3.17 (dq, J = 6.1, 5.6, 0.95 H) 2.83 (dd, J = 13.4, 5.0, 1.04 H), 2.35 (dd, J = 13.4, 9.3, 1.04 H), 1.97 (m, 0.95 H), 1.14 (d, J = 6.3, 2.88 H), 0.82 (d, J = 6.8, 2.93 H). HRMS (EI): Calcd for $C_{12}H_{18}O_1$ (M^+): 178.1358. Found: 178.1346.

(2*R,3*R**)-2-Methyl-1-phenyl-3-(*p*-toluenesulfonyloxy)butane.** *p*-Toluenesulfonyl chloride (73.39 mg, 0.385 mmol) was added to a solution of (2*R**,3*R**)-3-methyl-4-phenyl-2-butanol (48.46 mg, 0.295 mmol) and pyridine (740 μL) at 0 °C. After 26 h, the reaction mixture was subjected to an extractive workup followed by column chromatography (90:10 hexane:ethyl acetate) to give a white solid (0.033 g, 35%). ^{1}H NMR ($CDCl_3$): δ 7.85 (d, J = 7.4, 1.71 H), 7.40−7.17 (m, 4.96 H), 7.08 (d, J = 7.4, 1.86 H), 4.74−4.67 (m, 1.02 H), 2.79 (dd, J = 12.9, 4.3, 1.05 H), 2.48 (s, 3.00 H), 2.28 (dd, J = 12.9, 9.2, 1.07 H), 1.99−1.86 (m, 1.02 H), 1.30 (d, J = 6.8, 3.19 H), 0.83 (d, J = 7.4, 3.12 H). The material was immediately used to prepare **9c**.

(2*R,3*S**)-2-Methyl-1-phenyl-3-(*p*-toluenesulfonyloxy)butane**. This material was prepared in 44% yield using the same procedure as above except (2*S**,3*R**)-3-methyl-4-phenyl-2-butanol (0.049 g, 0.30 mmol) was used. ^{1}H NMR ($CDCl_3$): δ 7.75 (d, J = 7.4, 1.79 H), 7.33−7.18 (m, 4.88 H), 7.04 (d, J = 7.4, 1.90 H), 4.58−4.49 (m, 1.04 H), 2.67 (dd, J = 12.6, 4.9, 1.02 H), 2.46 (s, 3.00 H), 2.27 (dd, J = 12.6, 8.6, 1.04 H), 2.05−1.94 (m, 1.02 H), 1.28 (d, J = 6.5, 3.22 H), 0.84 (d, J = 6.8, 3.08 H). The material was immediately used to prepare **8c**.

(2*R,3*R**)-2,3-Dimethyl-4-phenylbutanecarbonitrile (8c).** A solution of (2*R**,3*S**)-2-methyl-1-phenyl-3-(*p*-toluenesulfonyloxy)butane (32.9 mg, 0.103 mmol), potassium cyanide (26.8 mg, 0.412 mmol), and dimethylsulfoxide (2.5 mL) was stirred at room temperature for 1.7 h followed by heating to 90 °C for 18 h. Extractive workup followed by column chromatography (95:5 hexane:ethyl acetate) gave a colorless oil (0.016 g, 89%). ^{1}H NMR ($CDCl_3$): δ 7.38−7.16 (m, 5.65 H), 2.78−2.58 (m, 2.77 H), 1.94−1.83 (m, 0.87 H), 1.31 (d, J = 7.2, 2.93 H), 1.11 (d, J = 6.7, 2.78 H). HRMS (EI): Calcd for $C_{12}H_{15}N_1$ (M^+): 173.1204. Found: 173.1179.

(2*S,3*R**)-2,3-Dimethyl-4-phenylbutanecarbonitrile (9c)**. This material was prepared in 67% yield using the same procedure as above except (2*R**,3*R**)-2-methyl-1-phenyl-3-(*p*-toluenesulfonyloxy)butane was used. ^{1}H NMR ($CDCl_3$): δ 7.34−7.16 (m, 4.94 H), 2.89 (dd, J = 13.5, 5.5, 0.96 H), 2.63−2.48 (m, 1.84 H), 2.11−2.00 (m, 1.00 H), 1.34 (d, J = 7.2, 3.17 H), 1.01 (d, J = 6.8, 3.10 H). HRMS (EI): Calcd for $C_{12}H_{15}N_1$ (M^+): 173.1204. Found: 173.1173.

Photooxidations. General Procedure. A Pyrex photolysis vessel was typically charged with a solution containing the cyclopropane, 1-cyanonaphthalene, *n*-pentyl ether (internal standard), and the nucleophile in 600 μL of acetonitrile. The solution was degassed by three freeze−pump−thaw cycles and then sealed with a hand torch. The sealed tube was placed in a Rayonet photoreactor containing nominal 300 nm light bulbs and irradiated for 1−3 h. The mixture was subsequently analyzed by GC, in which the retention times were compared with those of independently synthesized materials. All reported yields are based on GC analysis and corrected for differences in response factors. A portion (typically 3−6 mg) of the major product(s) was isolated by preparative GC (column: 6' × $^3/_8$" 17% XF-1150 on Anachrom Q, except when noted otherwise) and analyzed by ^{1}H NMR, GC, and other techniques as described.

***r*-1,*t*-2-Dimethyl-*t*-3-phenylcyclopropane (4) in the Presence of Methanol.** A degassed solution of **4** (23.9 mg, 163.4 μmol), 1-cyanonaphthalene (4.3 mg, 28.1 μmol), *n*-pentyl ether (25.3 mg, 159.8 μmol), methanol (50 μL), and acetonitrile (600 μL) was irradiated for 1.25 h. GC analysis showed the major product (95.7%) to have retention time identical to that of independently synthesized (2*R**,3*R**)-2-methoxy-3-methyl-4-phenylbutane (**8a**) and the absence of ≥0.1% of the (2*S**,3*R**)-2-methoxy-3-methyl-4-phenylbutane (**9a**). A portion of the product was isolated by preparative GC; its ^{1}H NMR spectrum was identical to that of the independently synthesized **8a**.

***r*-1,*c*-2-Dimethyl-*c*-3-phenylcyclopropane (5) and *r*-1,*c*-2-Dimethyl-*t*-3-phenylcyclopropane (6) in the Presence and Absence of Methanol.** The same procedure was followed as for **4** except a mixture of **5** and **6** was used. GC analysis showed the major product (83.2%) to have a retention time identical to that of independently synthesized (2*S**,3*R**)-2-methoxy-3-methyl-4-phenylbutane (**9a**) and the absence of ≥0.1% (2*R**,3*R**)-2-methoxy-3-methyl-4-phenylbutane (**8a**). A portion of the product was isolated by preparative GC; its ^{1}H NMR spectrum was identical to that of independently synthesized **9a**. In a

similar experiment run without added methanol, GC analysis after 61 h of photolysis showed formation of 1.2% of **4**.

***r*-1,*t*-2-Dimethyl-*t*-3-phenylcyclopropane (4) in the Presence of Water.** A degassed solution of **4** (16.8 mg, 115 μmol), 1-cyanonaphthalene (4.9 mg, 31.9 μmol), *n*-pentyl ether (15.6 mg, 98.3 μmol), water (40 μL), and acetonitrile (600 μL) was irradiated for 2 h. GC analysis showed the major product (81.6%) to have a retention time identical to that of independently synthesized (2*R**,3*R**)-3-methyl-4-phenyl-2-butanol (**8b**) and the absence of $\geq$0.2% of (2*S**,3*R**)-3-methyl-4-phenyl-2-butanol (**9b**). A portion of the product was isolated by preparative GC; its ^{1}H NMR spectrum was identical to that of the independently synthesized **8b**.

***r*-1,*c*-2-Dimethyl-*c*-3-phenylcyclopropane (5) and *r*-1,*c*-2-Dimethyl-*t*-3-phenylcyclopropane (6) in the Presence of Water.** The same procedure as above was followed except a mixture of **5** and **6** was used. GC analysis showed the major product (74.3%) to have a retention time the same as that of independently synthesized (2*S**,3*R**)-3-methyl-4-phenyl-2-butanol **9b** and the absence of $\geq$0.2% of (2*R**,3*R**)-3-methyl-4-phenyl-2-butanol **8b**. A portion of the product was isolated by preparative GC; its ^{1}H NMR spectrum was found to be identical to that of the independently synthesized **9b**.

***r*-1,*t*-2-Dimethyl-*t*-3-phenylcyclopropane (4) in the Presence of Cyanide.** A degassed solution of **4** (17.04 mg, 116.5 μmol), 1-cyanonaphthalene (5.1 mg, 33.2 μmol), *n*-pentyl ether (14.4 mg, 91.1 μmol), potassium cyanide (46.8 mg, 719 μmol), water (100 μL), and acetonitrile (600 μL) was irradiated for 3 h. GC analysis showed the formation of two major products with retention times identical to those of (2*R**,3*R**)-2,3-dimethyl-4-phenylbutanecarbonitrile (**8c**, 26.5%) and (2*R**,3*R**)-3-methyl-4-phenyl-2-butanol (**8b**, 37.7%), and the absence of $\geq$0.3% of (2*S**,3*R**)-2,3-dimethyl-4-phenylbutanecarbonitrile (**9c**). A portion of the first product was isolated by preparative GC, and its ^{1}H NMR spectrum was identical to that of the independently synthesized **8c**.

***r*-1,*c*-2-Dimethyl-*c*-3-phenylcyclopropane (5) and *r*-1,*c*-2-Dimethyl-*t*-3-phenylcyclopropane (6) in the Presence of Cyanide.** The same procedure as above was followed except a mixture of **5** and **6** was used. GC analysis showed the formation of two major products with retention times identical to those of (2*S**,3*R**)-2,3-dimethyl-4-phenylbutanecarbonitrile (**9c**, 21.8%) and (2*S**,3*R**)-3-methyl-4-phenyl-2-butanol (**9b**, 23.0%) and the absence of $\geq$0.3% of (2*R**,3*R**)-2,3-dimethyl-4-phenylbutanecarbonitrile (**8c**). A portion of the first product was isolated by preparative GC; its ^{1}H NMR spectrum was identical to the independently synthesized **9c**.

(*S*)-(+)-1-Methyl-2,2-diphenyl[1-^{2}H]cyclopropane (7) in the Presence of Methanol. A degassed solution of **7** (80.73 mg, 386 μmol), 1-cyanonaphthalene (19.36 mg, 126 μmol), *n*-pentyl ether (63.83 mg, 403 μmol), methanol (170 μL), and acetonitrile (2.0 mL) was irradiated for 3 h. Concentration gave 129.0 mg of a light yellow oil from which a portion of the product (77.6%) was isolated by preparative GC (6' $\times$ $^3/_8$" 20% SE-30). The product was analyzed by ^{1}H-NMR, and its spectrum was found to be identical to that reported for 3-deuterio-3-methoxy-1,1-diphenylbutane.[10] ^{1}H NMR ($CDCl_3$): δ 7.18−7.34 (m, 9.83 H), 4.21 (dd, J = 9.8, 6.2, 1.00 H), 3.26 (s, 3.02 H), 2.28 (dd, J = 13.8, 6.1, 1.05 H), 2.13 (dd, J = 13.8, 9.9, 1.04 H), 1.15 (s, 3.06 H). The optical rotation of the starting material $[\alpha]_{Hg}^{25}$ +34.3 (4)° (*c* 2.46, $CHCl_3$) and product $[\alpha]_{Hg}^{25}$ −4.3 (2)° (*c* 4.34, $CHCl_3$) were measured using a polarimeter. The optical purities of the starting material and the product were compared to literature values[10] for (*R*)-(−)-1-methyl-2,2-diphenylcyclopropane ($[\alpha]_{Hg}^{25}$ −150.6° (*c* 1.18, $CHCl_3$)) and (*S*)-(+)-2-methoxy-4,4-diphenylbutane ($[\alpha]_{Hg}^{25}$ +19.2° (*c* 2.10, $CHCl_3$)). The optical purities were thus determined to be 22.8 (3)% and 22.4 (7)%, respectively.

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