

Oxidation of Aryl- and Diarylcyclopropanes in a Pentasil Zeolite: Ring Opening with Deprotonation or Net Hydrogen Migration

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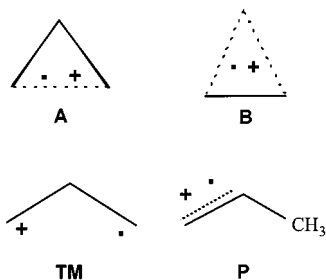
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Incorporation of *trans*-1,2-diphenylcyclopropane (**1**) and its 3,3-D2-isotopomer into the channels of a redox-active pentasil zeolite (Na-ZSM-5) resulted in the formation of *exo,exo*-1,3-diphenylallyl radical (**2**[•]) and its 2-D1 isotopomer, respectively. This conversion requires oxidation, ring opening, and deprotonation, in an unspecified sequence. The allyl radical **2**[•] is also formed upon incorporation of *trans*-1,3-diphenylpropene (**3**). A

comparison with the solution photochemistry, in the presence or absence of added base, shows the conversion of **1** into **2**[•] to be a zeolite-specific reaction. Incorporation of arylcyclopropanes **9** (R = H, OCH₃) into ZSM-5 generated *trans*-propenylbenzene radical cations **10**^{•+} (R = H, OCH₃); the 2,2-D2 isotopomer of **9** (R = OCH₃) gave rise to three different isotopomers of **10**^{•+} (R = OCH₃).

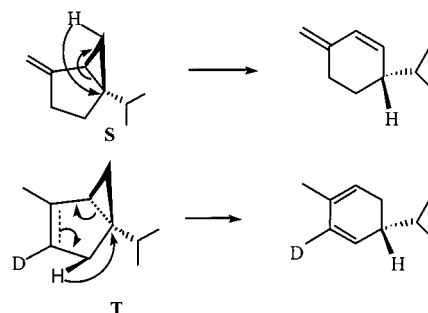
Introduction

The structure and reactivity of cyclopropane radical cations have attracted much attention;^{[1][2]} the spin density distributions of many derivatives have been delineated, and many intra- and intermolecular reactions have been studied in gas phase,^[3] solution,^[1e,2] or solid matrices. Vertical ionization of the parent cyclopropane from a degenerate pair of in-plane e' orbitals (s and a) generates a doubly degenerate ²E' state, which undergoes first-order Jahn–Teller distortion to two nondegenerate electronic states, ²A₁ and ²B₂ (C_{2v} symmetry).^[4] These components relax to structures with one ("trimethylene"; type **A**) or two lengthened C–C bonds ("π-complex"; type **B**).^[1e,5] Structures of type **A** are established for many cyclopropane radical cations;^[1e,5,6] structure type **B** is less common.^[5c,7]



Some radical cations of type **A** are known to rearrange to propene radical cations (**P**); bifunctional trimethylene radical cations (**TM**) are potential intermediates in this conversion. Detailed theoretical calculations have, so far, re-

vealed no evidence for their existence (as unsolvated species).^[4f] However, species of this type have been reported in solid matrices.^[6b,6c] In at least two cases, the conversion of type **A** to type **P** radical cations proceeds as a sigmatropic shift, clearly eliminating **TM** type intermediates in solution.^{[8][9]} Thus, sabinene radical cation (**S**^{•+}) undergoes a [1,3]-sigmatropic shift whereas α-thujene radical cation (**T**^{•+}) rearranges by competing [1,3]- and homo[1,5]-sigmatropic shifts.

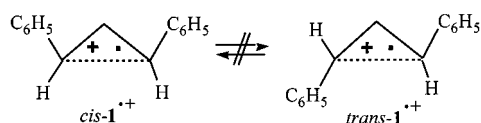


In this paper, we report results pertinent to the structure and reactivity of *cis*- and *trans*-1,2-diphenylcyclopropane, *cis*-, *trans*-**1**. CIDNP studies have shown that *cis*- and *trans*-**1**^{•+} have significant spin density on the benzylic carbon atoms and sizeable hyperfine coupling constants (hfc) for benzylic and geminal ¹H nuclei.^[5] The doubly benzylic C₁–C₂ bond retains a significant degree of bonding interaction, as documented by the failure of either radical cation to undergo geometric isomerization. The observation that no polarized isomerization products are observed with chloranil as acceptor/sensitizer, requires that the lifetimes of *cis*- and *trans*-**1**^{•+} with respect to isomerization must be greater than their spin lattice relaxation times (*T*₁ values of doublet species typically fall into the microsecond range).^[10] This assignment was recently confirmed by fast, time-resolved optical spectroscopy.^[11] On the other hand,

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the ESR spectra of the radical cations, *cis*- or *trans*-**1**^{•+}, have so far been elusive.



In an attempt to characterize *trans*-**1**^{•+} by its EPR spectrum, we incorporated *trans*-**1** into the channels of pentasil zeolite (Na-ZSM-5). This attempt is based on the fact that radical cations can be generated by incorporating appropriate precursors with redox potentials, $E_{\text{ox}} = 1.65$ V, at ambient temperatures into the zeolite.^{[12][13]} In some cases (formation of iminoxyls from oximes), the zeolite played the dual role of one-electron oxidant and proton acceptor.^[14] In others, it promoted more complex conversions (*p*-propylanisole to *p*-propenylanisole radical cation).^[15] Model considerations indicate that *trans*-**1** might fit into the zeolite channels ($ID \approx 5.5$ Å), whereas the *cis* isomer appears too bulky. The oxidation potential of *trans*-**1** ($E_{\text{ox}} = 1.17$ V vs. Ag/Ag^+ , ca. 1.5 V vs. SCE)^[16] is sufficiently low for oxidation by the zeolite.

Results and Discussion

Zeolite-Induced Conversions of *trans*-**1**

Incorporation of *trans*-**1** into Na-ZSM-5 produced a strong, long-lived EPR spectrum (Figure 1). The observed evenly spaced multiplet indicates the presence of two strongly coupled nuclei ($A = 11.5$ G) and six more weakly coupled nuclei ($A = 3.0$ G); the spectrum can be simulated satisfactorily with these data (Figure 1, bottom). A spectrum with only one pair of strongly coupled nuclei is incompatible with the structure established for *trans*-**1**^{•+} by the CIDNP results; it rules out a simple one-electron oxidation of *trans*-**1** and suggests a significant chemical conversion on the internal surfaces of the zeolite. The identity of the two strongly coupled nuclei hold the key to the nature of the paramagnetic intermediate formed.

In order to establish the identity of the strongly coupled nuclei, an isotopomer, *trans*-**1**-3- D_2 , was studied; incorporation of this material into Na-ZSM-5 gave rise to an EPR spectrum essentially identical to that obtained from *trans*-**1**^{•+}. Accordingly, the rearrangement must place the secondary cyclopropane carbon atom (with the geminal deuterium label) into a position without appreciable hyperfine coupling. This finding identifies the benzylic protons as the strongly coupled nuclei. The range of structures to be considered for the intermediate is significantly limited by the presence of six ^1H nuclei with intermediate coupling. This finding requires a fully delocalized species in which both phenyl groups (2 *ortho*- plus 1 *para*- ^1H each) participate in delocalizing the unpaired spin. Intermediates, in which the electron spin is delocalized onto only one phenyl group, formed, e.g., by hydrogen shift (**3**^{•+}) or hydrogen abstraction (**4**[•]), are excluded also because their EPR spectra must

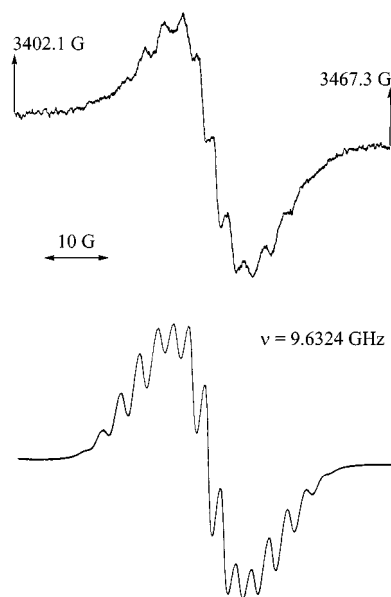


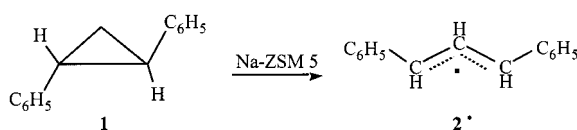
Figure 1. Top: X-band EPR spectrum generated by incorporation of *trans*-1,2-diphenyl-cyclopropane (*trans*-**1**) into the channels of pentasil zeolite (Na-ZSM-5); the spectrum is identified as that of *exo,exo*-1,3-diphenylallyl radical (**2**[•]); (bottom): second-order simulated spectrum, an envelope of two Gaussian simulations, 1) a triplet of septets with $A_{2\text{H}} = 11.5$ G and $A_{6\text{H}} = 3.0$ G, and a line-width, FWHH = 2.3 G, and 2) a broad line, FWHH = 17 G; the two spectra are simulated with relative intensities of 1:2; the two components of the experimental spectrum have slightly different centers (*g* factors); the simulation program^[17] only allows for the addition of isocentric spectra, resulting in a slight mismatch between simulation and experiment.

show pronounced changes upon deuterium incorporation. In analogy to *p*-propenylanisole radical cation,^[14] species **3**^{•+} should have three strongly coupled ^1H nuclei ($A \approx 10$ G) when generated from perprotio-*trans*-**1**, but only one such nucleus when generated from *trans*-**1**-3- D_2 . Given the hfc pattern of typical cyclopropyl radicals ($A_{\alpha} \approx 7$ G, $A_{\beta} \approx 24$ G),^[18] deuterium incorporation would produce **4**[•] with greatly diminished α -coupling.

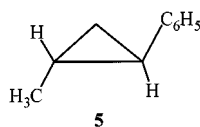
One species compatible with all features of the EPR spectrum is a 1,3-diphenylallyl radical (**2**[•]). This intermediate could be formed by ring opening of the cyclopropane radical cation, *trans*-**1**^{•+}, with deprotonation. Structure **2**[•] readily explains why the ^1H nuclei originating at the secondary cyclopropane carbons fail to show hyperfine coupling; one ^1H nucleus is lost by deprotonation, the other ends up in the nodal plane of the singly occupied molecular orbital (SOMO).

Additional support for the identity of the intermediate as a ring-opened species is derived from incorporation of *trans*-1,3-diphenylpropene (**3**) into the zeolite; *trans*-**3** produced a spectrum identical to that obtained from *trans*-**1**; clearly, the same species is generated from *trans*-**1** and *trans*-**3**. Since ring-opening of *trans*-**1**^{•+} is much more plausible than ring-closure of *trans*-**3**^{•+}, the free radical **2**[•] (and not **4**[•]) is the logical species formed from the two precursors. Only the stereochemistry of this species remains to be assigned.

The key to structure and stereochemistry of $2^\bullet$ lies in the known spectra of *endo,exo*- ($A_{\text{endo}} = 9.4$ G; $A_{\text{exo}} = 14$ G; $A_{\text{o,p}} = 2.3$ G) and *exo,exo*-diarylallyl radicals ($A_{\text{endo}} = 10.2$ G; $A_{\text{o,p}} = 2.9$ G).^[19] The hyperfine coupling of the species observed in the zeolite ($A = 11.5$ G) are closer to those of the *exo,exo*-diarylallyl species; particularly, the hyperfine coupling is closer to the 10.2 G measured for the *endo*- ^1H nuclei and quite different from the 14.0 G assigned to the *exo*- ^1H nuclei.^[19] Accordingly, we identify the spectrum (Figure 1) as that of the *exo,exo*-1,3-diphenylallyl radical, *exo,exo*- $2^\bullet$, and the major splitting as that of 2 *endo*- ^1H atoms. As *trans*- $1^{\bullet+}$ is converted into $2^\bullet$ the secondary cyclopropane carbon atom is rehybridized with deprotonation and becomes the nodal center of the allyl SOMO; the remaining ^1H nucleus lies in the nodal plane; no significant hyperfine coupling can be expected.



Under conditions similar to those used for the oxidative conversion of *trans*- 1 , we also incorporated *cis*- 1 and *trans*-1-methyl-2-phenylcyclopropane (**5**), into ZSM-5. Incorporation of *cis*- 1 failed to generate an EPR spectrum; this result is likely caused by the failure of the bulky substrate to be incorporated into the zeolite. Incorporation of *trans*-**5** generated a broad EPR spectrum ($g = 2.0027$) showing that *trans*-**5** is oxidized on ZSM-5. However, the spectrum showed no features that would reveal the identity of the resulting species.

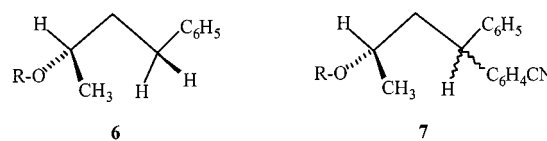


Solution Photochemistry of *trans*- 1

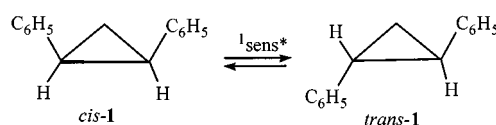
The solution photochemistry of cyclopropane derivatives, including *trans*- 1 , has been studied in detail;^[5a,5b,11,16,22] we have carried out additional reactions to probe pathways relevant to the zeolite-induced conversions under consideration. The electron-transfer photochemistry of *trans*- 1 provided little evidence for the deprotonation at C-2 with ring opening observed in the zeolite. The salient results of these experiments are described below.

Perhaps the best known photochemical reaction of cyclopropane derivatives, including **5**, occurs upon irradiation of (singlet) photo-sensitizers (*p*-dicyanobenzene) in the presence of alcoholic nucleophiles (methanol). This reaction typically results in ring-opened products bearing either an alkoxy group (e.g., **6**, $\text{R} = \text{CH}_3$) or an alkoxy and a *p*-cyanophenyl group (e.g., **7**); these products are formed by the well-established nucleophilic capture of the corresponding radical cation by the alcohol with ring-opening.^[8,9,22,23] In the reaction of *trans*- 1 , no isomerization products were

observed; apparently nucleophilic capture is faster than isomerization.



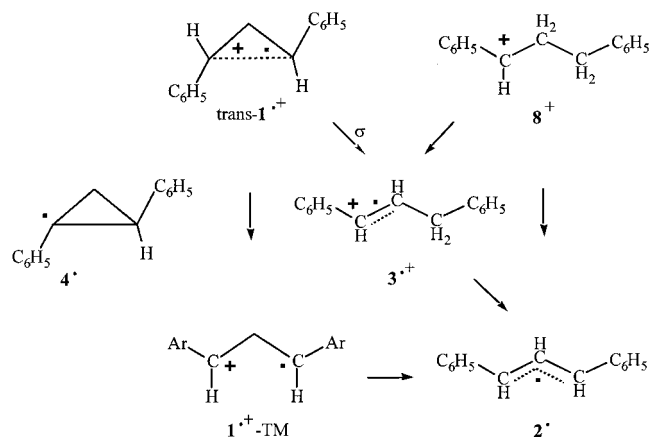
Irradiation of singlet-excited acceptors, 1,4-dicyanonaphthalene, 9-cyanophenanthrene (9-CNP), or 9,10-dicyanoanthracene in the presence of *cis*- or *trans*- 1 resulted in the slow conversion into the geometric isomers. CIDNP effects observed during these reactions were ascribed to the formation of a ring-opened triplet (biradical) species, formed by recombination of triplet radical ion pairs.^[5a,5b,16] This assignment was confirmed recently on the basis of fast time-resolved optical spectroscopy.^[11]



The 9-CNP-sensitized reaction of *trans*- 1 in the presence of 2-propanol as nucleophile formed a 2-propanol adduct [$\text{R} = \text{CH}(\text{CH}_3)_2$] and resulted in slow geometric isomerization. In addition, this reaction produced minor quantities of *trans*- and *cis*-1,3-diphenylpropenes, *trans*- and *cis*-**3**, formally generated by a sigmatropic shift. Addition of a strong base (2,6-di-*tert*-butylpyridine) likewise produced the *cis* isomer, but failed to give rise to deprotonation with ring opening. Overall, the electron-transfer photochemistry of *trans*- 1 in solution fails to produce any evidence for the ring-opened, deprotonated free radical $2^\bullet$.

Mechanistic Considerations

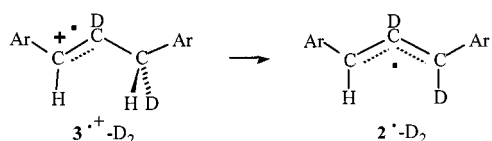
The overall transformation of *trans*- 1 to $2^\bullet$ on the zeolite requires three net changes: electron transfer, deprotonation, and ring opening. In view of the demonstrated redox reactivity of Na-ZSM-5^{[12][13]} and the oxidation potential of *trans*- 1 ($E_{\text{ox}} \approx 1.5$ V vs. SCE),^[16] one-electron oxidation might appear to be a reasonable first step. However, the recent realization that Na-ZSM-5 contains Lewis and Brønsted acid site^[24] suggests that protonation, yielding a 1,3-diphenylpropyl carbenium ion, 8^+ , must also be considered; this species should be readily deprotonated. As for the oxidation product, the significant electrostatic fields inside the zeolite channels may favor the ring-opened bifunctional species, $1^{\bullet+}$ -TM, even though it has been eliminated specifically in solution.^[5,11,16] The mechanism for the conversion of *trans*- 1 to $2^\bullet$ has to accommodate the key fact that the benzylic protons of **1** remain adjacent to the phenyl groups; there does not appear to be any random D vs. H exchange. Some reactions of the potential primary intermediates (Scheme 1) have precedent, others can be excluded unambiguously. The enforced close contact between zeolite and substrate must play a major role in the conversion, par-



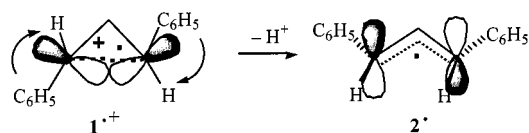
Scheme 1. Potential intermediates in the conversion of *trans*-1^{•+} to 2[•].

ticularly the strong electrostatic fields in the zeolite interior.

Although a [1,3]-hydride shift generating 3^{•+} has precedent in some vinylcyclopropane radical cations^[8,9,20] and in the solution reaction of *trans*-1^{•+} (formation of *trans*- and *cis*-3 in the 9-CNP sensitized reaction), the involvement of 3^{•+} is incompatible with the EPR data obtained from *trans*-1-3-D₂. A [1,3]-D shift in *trans*-1^{•+}-3-D₂ would form 3^{•+}-2,3-D₂, which is expected to lose H⁺ (not D⁺). The spectrum of the resulting 2[•]-2,3-D₂ should have only one strongly coupled ¹H, not two as the EPR spectrum obtained from *trans*-1-3-D₂ (cf. Figure 1, top).



Since the starting material and the allyl radical, *exo,exo*-2[•], are formally related by a conrotatory distortion of *trans*-1^{•+} towards *exo,exo*-2[•], we have considered this process with simultaneous transfer of a proton to the zeolite matrix. However, this mechanism is rendered unlikely in the light of results observed upon incorporation of phenyl (9a, R = H) or anisylcyclopropane (9b, R = OCH₃).



ZSM-5-Induced Conversion of 9

Sequestering 9a or 9b into ZSM-5 resulted in strong EPR spectra, showing quintets ($g = 2.0032 \pm 0.0002$; $A = 11.2$ G, 4 H; e.g., Figure 2, top; R = OCH₃). These spectra were identified, by analogy with the known spectra of anethol radical cation, 10b^{•+}, as those of 1-arylpropene radical cations 10a,b^{•+} in which the allylic methyl protons and the olefinic β -proton are the strongly coupled nuclei.^[15] An iso-

topomer of 9b (9b-2,2-D₂) gave rise to a particularly interesting spectrum (Figure 2, bottom).

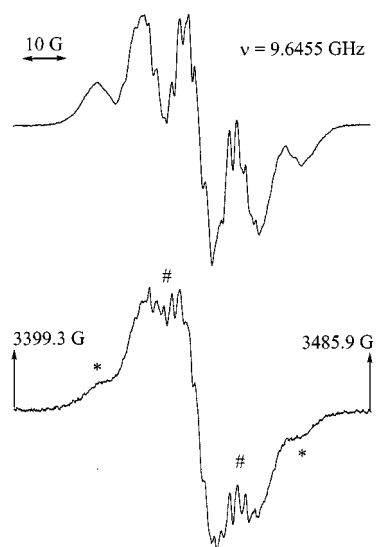
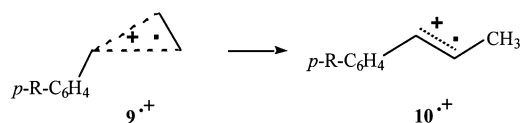
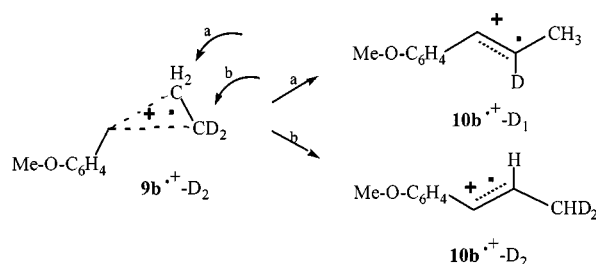


Figure 2. X-band EPR spectrum generated upon incorporation of anisylcyclopropane (9b, top) and anisylcyclopropane-D₂ (9b-D₂, bottom) into pentasil zeolite (Na ZSM-5); the top spectrum is identified as that of anethole radical cation (10b^{•+}) whereas the bottom one is a superposition of three isotopomers, 10b^{•+}-D₂, -D₁, and -D₀; the “wings” of the -D₀ isotopomer are marked by asterisks (*), the two central lines of the -D₁ isotopomer are denoted by pound signs (#)

This spectrum has the same overall width as the per-protio species; however, two changes are obvious: The upfield and downfield wings are less intense and the “valleys” between the five lines are “filled in”. Changes of this nature can be accommodated by the presence of two isotopomers, 10b^{•+}-D₂ (represented by the three central lines) and 10b^{•+}-D₁ (represented by four lines in the “valleys”), in addition to the -D₀ isotopomer (represented by the five principal lines). The presence of three isotopomers of 10b^{•+} unambiguously rules out any specific reaction, such as a sigma-tropic shift.



Two of the isotopomers, 10b^{•+}-D₂ and 10b^{•+}-D₁, are readily explained by protonation with ring opening followed by deprotonation and oxidation. The third species requires an additional (random) H vs. D exchange. In the light of



these results, the formation of *exo,exo*-diphenylallyl radical **2**[•] upon incorporation of *trans*-**1** in Na-ZSM-5 clearly is a zeolite-specific reaction.

Conclusion

The “spontaneous” ring opening with deprotonation of *trans*-**1** on Na-ZSM-5 zeolite is a novel conversion without precedent or analog in solution. The structure assigned to **2**[•] rests firmly on the generation of identical EPR spectra from two different precursors (the cyclic *trans*-**1** and its isotope, and the acyclic *trans*-**3**) and on the satisfactory simulation, using the hyperfine coupling constants corresponding to a known *exo,exo*-bisaryl radical. Radical cations often are generated in zeolites; the restrictive environment increases their stability because it protects them from external reagents and prevents dimerization; these features facilitate the study of otherwise unstable intermediates by conventional spectroscopic techniques at ambient temperatures.

The results reported here provide further evidence that the interaction of organic substrates with redox- as well as acid-base-active zeolites may result in interesting, complex, and occasionally specific conversions. We are pursuing the oxidation/dehydrogenation of a range of targets containing strained-ring as well as unsaturated functions. Although the incorporation of *trans*-**5** failed to yield evidence for a specific radical or radical cation, the oxidation/rearrangement of cyclopropane compounds upon incorporation into ZSM-5 is not limited to *trans*-**1**. Related reactions have been observed for several mono-arylcyclopropanes as well as for 1-benzyl-2-phenylcyclopropane.

Experimental Section

General Remarks, Materials, and Solvents: The electron acceptor/sensitizer, 9-cyanophenanthrene (Aldrich, 97%), the nucleophile, 2-propanol (Fisher), and the hindered base, 2,6-di-*tert*-butylpyridine (Aldrich, 97%) were used as received. For the preparation of EPR samples, hexane (Aldrich, anhydrous, 95%) and 2,2,4-trimethylpentane (Aldrich, anhydrous, 99.8%), were used, from SureSeal bottles, as received. Acetonitrile (Fisher, A.C.S. certified) was distilled under nitrogen from calcium hydride immediately prior to the photo-reaction. The donor/substrates were synthesized by adapted literature procedures. — Na-ZSM-5 was synthesized by hydrothermal crystallization of silica and alumina gels in aqueous basic medium (NaOH) without a template according to a literature procedure.^[25] Although the chemical analysis of the resulting zeolite was consistent with the Na⁺ form, the pyridine adsorption-desorption method showed the presence of Brønsted acid sites (pyridinium ion, 1550 cm^{−1}) and Lewis acid sites (coordinated Lewis adduct, 1450 cm^{−1}).^[26–29]

Preparation of EPR Samples: Pentasil zeolite (Na-ZSM-5; Si/Al 15) was thermally activated by calcination at 500 °C for 12 h and stored under argon. EPR samples were prepared by stirring ca. 1.5 mg of appropriate substrates with 70 mg of the zeolite in 10 mL of 2,2,4-trimethylpentane for 2 h. The incorporation of the substrates was essentially complete judging by their depletion in the supernatant liquid. Upon mixing the reagents the zeolite developed light color-

ation, due likely to free radicals or radical ions on its external surface. The loaded zeolite was collected by filtration, washed with hexane, and dried under vacuum (0.001 Torr). Some of the coloration was removed by washing, suggesting that the corresponding radicals were removed from the external surface of the zeolite. The dried zeolite samples were transferred to an EPR tube and their spectra recorded with a Bruker ESP 300 EPR spectrometer.

Photo Reactions: Acetonitrile solutions, containing 0.2 M donor and 0.2 M acceptor, in the presence or absence of base and/or nucleophile in 5-mm NMR tubes, were irradiated in a Rayonet RPR-100 photoreactor equipped with 16 RPR-3000 lamps. The reaction progress was monitored by gas chromatography with a GC/MS system (HP 5890 series II Plus GC interfaced with a HP 5972 mass-selective detector), using a 30 m × 0.25 mm × 0.25 μm HP-5 capillary column (crosslinked methyl silicone on fused silica). The identity of the products was established by comparison of retention times and MS spectral features with those of independently synthesized samples.

***trans*-1,2-Diphenylcyclopropane (*trans*-**1**):** *trans*-**1** was prepared by a modified Simmons-Smith^[30] addition of methylene (from CH₂I₂) to *trans*-stilbene in 1,4-dioxane. Similarly, addition of methylene-D₂ (from CD₂I₂) to *trans*-stilbene furnished *trans*-1,2-diphenylcyclopropane-3-D₂ (*trans*-**1**-3-D₂); ¹H-NMR analysis of *trans*-**1**-3-D₂ indicated > 95% of deuterium incorporation. CD₂I₂ was prepared from CH₂I₂ by base-catalyzed deuterium exchange (D₂O, NaOMe, NaI)^[31] in 1,4-dioxane. — The following modified Simmons–Smith^[30] procedure is intended for the conversion of 0.1 mol of olefin: 19.6 g (0.3 mol) of zinc dust, 1.0 g (0.01 mol) of Cu^ICl and 0.1 mol of olefin were suspended in 150 mL of 1,4-dioxane, freshly distilled from potassium. A reflux condenser was capped with a balloon, the suspension was magnetically stirred and heated to the boiling point of the solvent. After the addition of ca. 5 mL of CH₂I₂, an induction period of 15–30 min was required before the reaction became self-sustaining. The color changed from a dull gray to dark purple. The progress of the reaction was frequently checked by GC/MS. Additional CH₂I₂ and zinc dust were added until complete conversion of the olefin. After complete conversion, the mixture was cooled to room temperature and filtered through silica gel to remove the sludge-like zinc residue. The filter cake was then washed with ca. 100 mL of pentane and/or ethyl ether, and the filtrate is washed repeatedly with water and dried with anhydrous potassium carbonate. The combined pentane/ether layers were concentrated by evaporation or distillation; further purification by column chromatography with pentane on silica gel leads to moderate yields (ca. 50%) of pure cyclopropanation products.

***cis*-1,2-Diphenylcyclopropane (*cis*-**1**):** *cis*-**1** was isolated from a commercially available mixture of *cis*- and *trans*-**1** (Wiley Organics, Coshocton, Ohio, USA) by column chromatography on silica gel (200–400 mesh, doped with AgNO₃), eluted with petroleum ether (bp < 65 °C).

***cis*- and *trans*-1,3-Diphenylpropene (**3**):** A mixture of these compounds was prepared by dehydration of 1,3-diphenylpropan-2-ol^[32] or, in better yields, by base-catalyzed aldol condensation of phenylacetaldehyde.^[33]

***trans*-1-Methyl-2-phenylcyclopropane (*trans*-**5**):** *trans*-**5** was prepared by a modified Simmons-Smith^[25] addition of methylene (from CH₂I₂) to *trans*-1-phenylpropene in 1,4-dioxane.

Anisylcyclopropane (9b** and **9b**-D₂):** **9b** and **9b**-D₂ were prepared by a modified Simmons-Smith^[30] addition of methylene (from CH₂I₂) to *p*-methoxystyrene in 1,4-dioxane. Similarly, addition of methyl-

ene-D₂ (from CD₂I₂) to *p*-methoxystyrene furnished anisylcyclopropane-2-D₂; ¹H-NMR analysis of **9b**-2-D₂ indicated > 95% of deuterium incorporation.

Photo Reaction of *trans*-1,2-Diphenylcyclopropane (*trans*-1): Irradiation of acetonitrile solutions containing 0.2 M 9-cyanophenanthrene (**9-CNP**) and 0.2 M of *trans*-**1** produced *cis*-**1** as the sole product (*cis-trans* isomerization of the donor); ca. 10% conversion after 9.0 h.

Photo Reaction of *trans*-1,2-Diphenylcyclopropane (*trans*-1) in the Presence of 2-Propanol: Irradiation of acetonitrile/2-propanol (3:1 by volume) solutions containing 0.2 M **9-CNP** and 0.2 M of *trans*-**1** resulted in the formation of various 2-propanol adducts (ca. 75%), moderate geometric isomerization (*cis*-**1**; ca. 20%), and minor amounts of 1,3-diphenylpropene (ca. 1% *cis*-**3**, ca. 4% *trans*-**3**); ca. 40% conversion after 9.0 h.

Photoreaction of *trans*-1,2-Diphenylcyclopropane (*trans*-1) in the Presence of 2,6-Di-*tert*-butylpyridine: Irradiation of acetonitrile solutions containing 0.2 M **9-CNP**, 0.2 M of *trans*-**1** and 0.2 M 2,6-di-*tert*-butylpyridine resulted in efficient geometric isomerization to *cis*-**1** ca. 90% and minor rearrangement to 1,3-diphenylpropene (ca. 2% *cis*-**3**, ca. 8% *trans*-**3**); ca. 10% conversion after 9.0 h.

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