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Stabilization of Carbinylcarbocation by and Nucleophilic Attack upon Cyclopropyl and *trans*-2, *trans*-3-Diphenylcyclopropyl Rings. Reduction of (*trans*-2, *trans*-3-Diphenylcyclopropyl)methanol and (*trans*-2, *trans*-3-Diphenylcyclopropyl)cyclopropylmethanol

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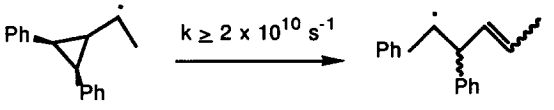
Abstract. (*trans*-2, *trans*-3-Diphenylcyclopropyl)methanol (R^1OH) can be reduced to (*trans*-2, *trans*-3-diphenylcyclopropyl)methane with $NaBH_3CN$ in the presence of $(PhO)_3PMeI$ and (*trans*-2, *trans*-3-diphenylcyclopropyl)cyclopropylmethanol (R^2OH) can be reduced to its hydrocarbon by BH_3-BF_3 without ring opening. Acid catalyzed H_2O elimination from R^2OH by CF_3COOH is accompanied by concerted ring opening of the diphenylcyclopropyl ring with a late transition state, but S_N2 iodiation of R^2OH with $(PhO)_3PMeI$ results in concerted opening of the unsubstituted cyclopropyl ring. The *trans*-2, *trans*-3-diphenylcyclopropyl group is less effective than a simple cyclopropyl group in stabilizing an adjacent positive charge.

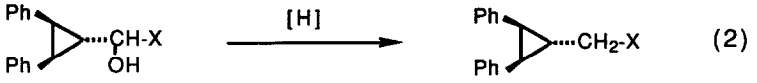
Introduction: The cyclopropylcarbinyl to homoallylcarbinyl radical rearrangement (CPCRR) reaction has been employed effectively in the trapping of radical intermediates in both chemical[1] and enzyme[2] reactions. A number of additions and modification of the cyclopropyl ring have been introduced in order to enhance the rate of the CPCRR and allow the trapping of radical species with increasingly shorter life-times.[3,4] We designed and synthesized the radical trap *(Z)*-1,2-(*trans*-2, *trans*-3-diphenylcyclopropyl)ethene to explore the mechanism of the epoxidation of alkenes by hypervelant metal-oxo porphyrins.[5,6] It has been shown by competitive experiments that the rate constant of CPCRR with the *trans*-2, *trans*-3-diphenylcyclopropyl substituent is $\geq 2 \times 10^{10}$ (eq 1).[5]



(1)

As an extension of the study we should like to trap the putative radical intermediate in non-enzymatic alkane hydroxylation by hypervelant metal-oxo porphyrins. Although a radical intermediate in this hydroxylation is supported by deuterium migration,[7] solvent trapping[8] etc. the use of cyclopropyl traps has not been successful.

In this paper we report the synthesis of the radical trapping alkanes, (*trans*-2, *trans*-3-diphenylcyclopropyl)methane (R^1H) and (*trans*-2, *trans*-3-diphenylcyclopropyl)cyclopropylmethane (R^2H), by direct reduction of (*trans*-2, *trans*-3-diphenylcyclopropyl)methanol (R^1OH) and (*trans*-2, *trans*-3-diphenylcyclopropyl)cyclopropylmethanol (R^2OH), respectively (eq 2).



(2)

R^1OH, X = H; R^2OH, X = cyclopropyl

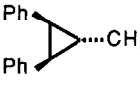
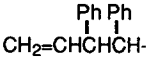
R^1H, X = H; R^2H, X = cyclopropyl

Results and Discussion. Tables 1 and 2 give the conditions and results of the reduction of (*trans*-2, *trans*-3-diphenylcyclopropyl)methanol and (*trans*-2, *trans*-3-diphenylcyclopropyl)cyclopropylmethanol, respectively. The ratio of the isomers in the product mixtures was calculated from ^1H NMR data (detection limit, 1%). No effort has been made for the separation of the Z and E isomers of alkene products.

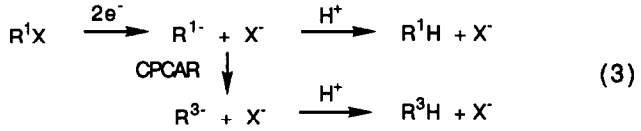
Reduction of (*trans*-2, *trans*-3-diphenylcyclopropyl)methanol (R^1OH). As shown in Table 1, R^1OH can not be reduced by Et_3SiH in the presence of CF_3COOH, and even under relatively rigorous conditions the ester CF_3COOR^1 was the only product. Triethylsilane reduces carbocations varying in stability over a range of greater than 24 pK units by hydrogen transfer.[9,10] One may conclude that the primary alcohol R^1OH does not provide carbocation in the presence of CF_3COOH. Interestingly, the reduction of R^1OH with Me_3SiCl-NaI-Zn system gave a mixture containing the ring-intact product (*trans*-2, *trans*-3-diphenylcyclopropyl)methane (R^1H) and the ring-opened product 3,4-diphenyl-1-butene (R^3H) in a ratio of 2:3. The formation of R^1H from R^1OH is a two step reaction involving substitution of -$OSiMe_3$ by I^- followed, under acidic conditions, by reduction of R^1I by Zn metal.[11] Secondary cyclopropyl alcohols have been reported to undergo ring-opening rearrangement in the first step under similar conditions.[12] A control reaction showed that in the case of R^1OH the first step does not involve opening of the cyclopropyl ring. Thus, R^1OH reacts with Me_3SiCl and NaI in MeCN to give R^1I in 90% yield. Two mechanisms have been proposed for the reduction of alkyl halide with metals.[13] One is the displacement of halogen as anion by a two-electron transfer process leading to the formation of a carbanion, and the other is the one-electron displacement of halogen as an anion leading to a carbon radical which then either adds another electron to form a carbanion intermediate or reacts with solvent to form the reduced product. Both mechanisms are possible for the reduction of (*trans*-2, *trans*-3-diphenylcyclopropyl)methyl iodide. The two-electron transfer process seems to be more reasonable. Once separated from the metal surface, a radical intermediate could return to the metal surface and secure a second e^- at a rate[14] of $< 10^4$ s^{-1} cm which is not competitive with the rate of the CPCRR for *trans*-2, *trans*-3-diphenylcyclopropylcarbinyl radical ($\geq 2 \times 10^{10}$ s^{-1}). Thus, the initial $1e^-$ transfer reaction would lead to completely opening of the cyclopropyl ring. The product ratio can be explained by the two-electron transfer process. We propose that

Table 1. Reduction of (*trans*-2, *trans*-3-Diphenylcyclopropyl)methanol[a]

Reactant	Method	Product	Total Yield
R^1OH	CF_3COOH, Et_3SiH Reflux 5 h in CH_2Cl_2	CF_3COOR^1	90%
R^1OH	Me_3SiCl, NaI, Zn in MeCN, HOAc	R^1H:R^3H (2:3)	92%
R^1OH	$(PhO)_3PMeI$, $NaBH_3CN$ 70 °C, 2 h, in HMPA	R^1H	96%
R^1Br	$NaBH_3CN$, 70 °C, 2 h in HMPA	R^1H	93%

a R^1:  , R^3: 

the (*trans*-2, *trans*-3-diphenylcyclopropyl)carbinyl anion (R^{1-}) undergoes a cyclopropylcarbinyl to homoallylcarbinyl anion rearrangement (CPCAR) which competes with diffusion-controled R^{1-} protonation (eq 3). We



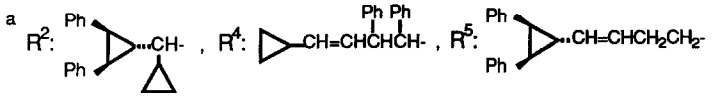
(3)

find that (*trans*-2, *trans*-3-diphenylcyclopropyl)methyl bromide (R^1Br) can be quantitatively reduced to R^1H by $NaBH_3CN$ in HMPA.[15] Similarly, in the presence of $(PhO)_3PMeI$ (*trans*-2, *trans*-3-diphenylcyclopropyl)methanol (R^1OH) can be reduced by $NaBH_3CN$ to provide R^1H in high yield.[16] The mechanism of this alcohol reduction is known to involve the two steps of iodide formation and reduction. Both of the steps are known to occur by S_N2 displacements.[16,17]

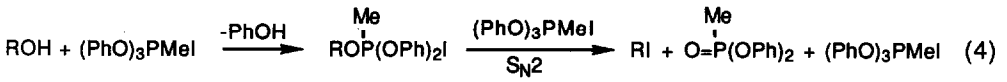
Reduction of (*trans*-2, *trans*-3-diphenylcyclopropyl)cyclopropylmethanol (R^2OH). The reduction of R^2OH (Table 2) differs from that of R^1OH. 1,2-Diphenyl-4-cyclopropyl-3-butenyl trifluoroacetate (CF_3COOR^4, E:Z = 4:1) was the only product of the reaction of R^2OH with CF_3COOH in the presence of Et_3SiH. Since neither cyclobutyl derivatives nor reduced hydrocarbon was found as a product it seems that a carbocation is not an intermediate in the reaction.[18] It should be noted that under similar conditions dicyclopropylmethanol could be reduced to dicyclopropylmethane in high yields.[19] In the reaction of R^2OH with CF_3COOH only the diphenylcyclopropyl unit undergoes rearrangement. This differs from the pure S_N2 process in the reaction of R^2OH with $(PhO)_3PMeI$ which results in the opening of the unsubstituted cyclopropyl ring *(vide infra)*. The reaction of R^2OH with CF_3COOH must involve acid catalyzed elimination of H_2O either concerted with ring opening in a late transition state with considerable benzyl cation character (**I**), or leading to the non-classical carbocation (**II**).[20] Arguments against the intermediary of **II** are the expectations that both (*trans*-2, *trans*-3-diphenylcyclopropyl)cyclopropylmethyl trifluoroacetate (CF_3COOR^1) and 1,2-diphenyl-4-cyclopropyl-3-butenyl trifluoroacetate (CF_3COOR^4) should be products. Concerning **II**, no study has been reported of trapping of non-classical carbocations by Et_3SiH, but it has been reported that several highly delocalized carbocations have been trapped by Et_3SiH.[21]

Table 2. Reduction of (*trans*-2, *trans*-3-Diphenylcyclopropyl)cyclopropylmethanol

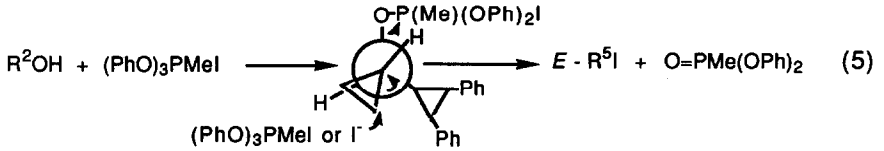
Reactant	Method	Product	Yield
R^2OH	CF_3COOH, Et_3SiH r. t. 2 h in CH_2Cl_2	CF_3COOR^4 (E:Z = 4:1)	80%
R^2OH	$(PhO)_3PMeI$, $NaBH_3CN$ 70 °C, 2 h, in HMPA	R^5H (E:Z > 99:1)	80%
R^2OH	BH_3, BF_3 r. t. 72 h, in THF	R^2H	90%



Unlike the reaction with CF_3COOH, the reaction of R^2OH with $(PhO)_3PMeI$ involves unsubstituted cyclopropyl ring-opening to provide 4-(*trans*-2, *trans*-3-diphenylcyclopropyl)-3-butenyl iodide (R^5I, E:Z > 99:1) as the only product (The results are not shown.). R^2OH can be reduced directly to 1-(*trans*-2, *trans*-3-diphenylcyclopropyl)-1-butene (R^5H, E:Z > 99:1) by $NaBH_3CN$ in the presence of $(PhO)_3PMeI$ (Table 2). It has been well established that the iodide substitution reaction is through the S_N2 mechanism of eq 4.[16,17] The



reaction shows the order of preference R = methyl > ethyl > *iso*-propyl.[17] Therefore, the selectivity in ring opening for the unsubstituted cyclopropyl unit is due to steric hindrance to the approach of the nucleophile $(PhO)_3PMeI$. In comparison with the reaction of R^2OH with CF_3COOH, which involves a good leaving group (H_2O) and a poor nucleophile(CF_3COO^-/CF_3COOH), the reaction with $(PhO)_3PMeI$ (eq 4) involves a rate determining S_N2 nucleophilic displacement by a very good nucleophile which is concerted with ring opening. The stereoselective formation of the *E*-isomer of the alkene product from the reaction also supports the concerted S_N2 mechanism (eq 5). Such a mechanism has been reported for the stereoselective synthesis of *trans*-olefine from the reaction of cyclopropylcarbinol analogues with HBr.[22]



Both reactions of R^2OH with PBr_3 in THF and Me_3SiCl-NaI in MeCN are not selective (The results are not shown.). They provide a mixture of products which stems from both substituted and unsubstituted cyclopropyl ring opening. (*trans*-2, *trans*-3-Diphenylcyclopropyl)cyclopropylmethane (R^2H) was obtained by the reduction of R^2OH with BH_3 catalyzed by BF_3 in high yield and no ring-opened product was found from the reaction. The reaction takes a much longer time and needs excess BH_3 and BF_3 as compared with the reduction of dicyclopropyl ketone under the similar conditions.[23] Combined with the fact that dicyclopropylcarbinol can be reduced to dicyclopropylmethane by Et_3SiH in the presence of CF_3COOH,[19] but (*trans*-2, *trans*-3-diphenylcyclopropyl)cyclopropylmethanol (R^2OH) can only give 1,2-diphenyl-4-cyclopropyl-3-butenyl trifluoroacetate (CF_3COOR^4) under the same conditions, one can conclude that (*trans*-2, *trans*-3-diphenylcyclopropyl)carbinyl cation is less stable than cyclopropylcarbinyl cation.[24] The result may be explained by the fact that the two phenyl rings of the *trans*-2, *trans*-3-diphenylcyclopropyl unit can not act in resonance with the cyclopropyl ring but can only act as electron-withdrawing groups.[5]

Experimental Section

General. Melting points were determined on a Bristoline hot-stage microscope and are uncorrected. Infrared (IR) spectra were obtained on a Perkin-Elmer mono-chromator grating spectrometer (Model 1330). Low-resolution and high-resolution mass spectra (LRMS and HRMS) were recorded on a VG Analytical spectrometer (Model VGII-250) by electron impact (EI) or fast atom bombardment (FAB) in a *m*-nitrobenzyl alcohol matrix. ^{1}H NMR spectra were obtained in $CDCl_3$ with General Electric GN-500 spectrometers. Chemical shifts are reported in δ (ppm) relative to Me_4Si with s, d, t, q, and m signifying singlet, doublet, triplet, quartet, and multiplet; coupling constants J are reported in Hertz. Silica gel column chromatography columns were run with Davisil Grade 633 Type 60A silica gel (200-425 mesh) obtained through Fisher Scientific. Thin-layer chromatography (TLC) was performed on glass-backed plates 0.25-mm silica gel 60-F_{254} (Merck). High-pressure liquid chromatography (HPLC) used two Perkin-Elmer Series 10 Pumps. For analytic HPLC, a Hewlett-Packard variable wavelength detector (Model HP1050) at 254 nm, integrator (Model 3392A), and an Altex column 5 μm Lichrosorb SI-60 (4.6 x 250 mm) were used. For semipreparative HPLC an ISCO variable wavelength absorbance detector (Model V4) at 254 nm, fraction collector (Model Retriever II), and a Whatman column 10 μm Partisil SiO_2 (10 x 500 mm) were used.

Materials. Methylene chloride was purified as described previously.[6] Tetrahydrofuran (THF) was refluxed over sodium metal and distilled before use. *N, N*-Dimethyl formamide (DMF) and hexamethylphosphoramide (HMPA) were distilled over CaH_2 under vacuum and stored over 4A molecular sieves. Trifluoroacetic acid, triethylsilane, trimethylsilily chloride, methyltriphenoxyphosphonium iodide, sodium cyanoborohydride, and cyclopropyl bromide were purchased from Aldrich, and used without further purification. (*trans*-2, *trans*-3-Diphenylcyclopropyl)methanol and (*trans*-2, *trans*-3-diphenylcyclopropyl)methyl bromide were prepared according to the published methods.[5]

Preparation of (*trans*-2, *trans*-3-diphenylcyclopropyl)cyclopropylmethanol (R^2OH). To 0.97 g (8 mmol) cyclopropyl bromide in 20 mL dry ether, 0.24 g (10 mmol) magnesium turnings and 0.1 g iodine were added. The mixture was refluxed for 3 h. After cooling, 0.5 g (2.3 mmol) *trans*-2, *trans*-3-diphenylcyclopropanecarboxaldehyde[5] was added at 0 °C. The resulting mixture was refluxed for 3 h, and then quenched with saturated aq. NH_4Cl. The organic phase was dried over Na_2SO_4 and concentrated to give pale yellow oil as the crude product, which was purified by flash column SiO_2/hexane:EtOAc = 3:1. Final product (0.5 g 82%) was obtained after recrystallization from hexane as a white prism. **R^2OH**: mp: 72-74 °C; TLC (SiO_2/hexane:EtOAc = 3:1): R_f = 0.43; IR(KBr): ν_{OH} = 3420 cm^{-1}; ^{1}H NMR($CDCl_3$): δ 0.40(d, J = 5, 2H), 0.60(m, 2H), 1.18(m, 1H), 1.66(bs, 1H), 1.99(q, J = 6, 1H), 2.50(2dd, J = 6, 10, 2H), 2.99(t, J = 7, 1H), 6.92 - 7.10(m, 10H); LRMS(EI): *m/z* 264 (M^+); Anal. Calcd for $C_{19}H_{20}O$: C, 86.31; H, 7.63. Found: C, 86.02; H, 7.73.

(*trans*-2, *trans*-3-Diphenylcyclopropyl)methanol (R^1OH).

Reaction with Et_3SiH in CF_3COOH. To a 5 mL CH_2Cl_2 solution of 0.22 g (1 mmol) R^1OH and 0.17 g (1.5 mmol) Et_3SiH, 0.22 g (2 mmol) CF_3COOH was added. The solution was refluxed and the reaction was followed by TLC. The reactant was consumed after 5 h refluxing. After cooling 100 mL CH_2Cl_2 was added, and the organic phase was washed with 5% aq. Na_2CO_3 and dried over $MgSO_4$. (*trans*-2, *trans*-3-Diphenylcyclopropyl)methyl trifluoroacetate (CF_3COOR^1) was the only product as a colorless oil (2.8 g, 90%). **CF_3COOR^1**: TLC (SiO_2/hexane:EtOAc = 3:1): R_f = 0.70; IR(Neat): $\nu_{C=O}$ = 1770 cm^{-1}, ν_{C-O} = 1150 cm^{-1}; ^{1}H

NMR($CDCl_3$): δ 2.20(m, 1H), 2.53(d, J = 5.5, 2H), 4.55(d, J = 7, 2H), 6.81 - 7.12(m, 10H); LRMS(EI): *m/z* 320 (M^+).

Reduction with Me_3SiCl-NaI-Zn-HOAc in MeCN. To a mixture of R^1OH (0.22 g, 1 mmol) and NaI (0.38 g, 2.5 mmol) in dry MeCN (20 mL), Me_3SiCl (0.22 g, 2 mmol) was added dropwise over 10 min at r. t. After addition the solution was stirred at 50 °C for 2 h. The solution was diluted with MeCN (10 mL) and HOAc (1 mL). Then zinc dust (0.4 g, 5 mmol) was added with stirring. The resulting dark-yellow mixture was stirred vigorously at 80 °C for 10 h. After cooling the mixture was filtered and washed with ether. The filtrate was washed with 5% aq. $NaHCO_3$ and $NaHSO_3$, and dried over Na_2SO_4. Removal of the solvent gave the crude product as a pale yellow oil, which was purified by a flash column (SiO_2/hexane). colorless oil, 0.2 g 96%. IR(Neat) shows that there is no OH group in the crude product. ^1H NMR and HPLC indicates that the product is a mixture of (*trans*-2, *trans*-3-diphenylcyclopropyl)methane (R^1H) and 3,4-diphenyl-1-butene (R^3H), (R^1H:R^3H = 2:3). LRMS(EI): *m/z* 208 (M^+). **R^1H**: HPLC(SiO_2/hexane:CH_2Cl_2 = 49:1 at 1 mL/min): t_R = 15.5 min; ^1H NMR($CDCl_3$): δ 1.37(d, J = 6, 3H), 1.70(m, 1H), 2.18(d, J = 6, 2H), 6.87 - 7.07(m, 10H). **R^3H**: HPLC (SiO_2/hexane:CH_2Cl_2 = 49:1 at 1 mL/min): t_R = 16.4 min; ^1H NMR($CDCl_3$): δ 2.99(dd, J = 7.5, J_{gem} = 13.5, 1H), 3.03(dd, J = 7.5, J_{gem} = 13.5, 1H), 3.56(q, J = 7.5, 1H), 4.93(d, J = 17, 1H), 5.00(d, J = 10, 1H), 6.01(ddd, J = 7.5, 10, 17, 1H), 7.09 - 7.28(m, 10H).

Reduction with $(PhO)_3PMeI$-$NaBH_3CN$ in HMPA. Methyltriphenoxyphosphonium iodide (0.9 g, 2 mmol) was added to a solution of R^1OH (0.22 g, 1mmol) in HMPA (10 mL) at r. t. and the solution was stirred for 1 h. Then $NaBH_3CN$ (0.25 g, 4 mmol) was added and the resulting mixture was stirred at 70 °C for additional 2 h. After cooling the solution was poured into 200 mL sat. NaCl aq. and aqueous solution was extracted with ether (2 x 100 mL). Ether phase was washed with sat. NaCl aq. and dried over Na_2SO_4. Evaporation of the solvent gave a pale yellow oil which was purified by a flash column (SiO_2/hexane) to give (*trans*-2, *trans*-3-diphenylcyclopropyl)methane (R^1H) as colorless oil (0.2 g, 96%). **R^1H**: TLC (SiO_2/hexane): R_f = 0.41; ^1H NMR($CDCl_3$): δ 1.37(d, J = 6, 3H), 1.70(m, 1H), 2.18(d, J = 6, 2H), 6.87 - 7.07(m, 10H); LRMS(EI): *m/z* 208 (M^+); Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.10; H, 7.54.

Reduction of (*trans*-2, *trans*-3-diphenylcyclopropyl)methyl bromide (R^1Br) with $NaBH_3CN$ in HMPA. $NaBH_3CN$ (0.35 g, 5.6 mmol) was added to a solution of R^1Br (0.4 g, 1.4 mmol) in HMPA (10 mL) at r. t. and the resulting mixture was stirred at 70 °C for 2 h. After cooling the solution was poured into 200 mL sat. NaCl aq. and the aqueous solution was extracted with ether (2 x 100 mL). The ether phase was washed with sat. NaCl aq. and dried over Na_2SO_4. Evaporation of the solvent gave a pale yellow oil which was purified by a flash column (SiO_2/hexane) to give R^1H as colorless oil (0.27 g, 93%). The spectra of the product are identical with those as shown above.

(*trans*-2, *trans*-3-Diphenylcyclopropyl)cyclopropylmethanol (R^2OH).

Reaction with Et_3SiH and CF_3COOH. To a 5 mL CH_2Cl_2 solution of 0.1 g (0.38 mmol) R^2OH and 0.06 g (0.5 mmol) Et_3SiH, 0.09 g (0.8 mmol) CF_3COOH was added at r. t. The solution was stirred at r t. and the reaction was followed by TLC (SiO_2/hexane: EtOAc = 10:1). The reactant was consumed within 30 min. Then 100 mL CH_2Cl_2 was added, and the organic phase was washed by 5% aq. Na_2CO_3 and dried over $MgSO_4$. Concentration of the solution gave a pale yellow oil which contains 1,2-diphenyl-4-cyclopropyl-3-

butenyl trifluoroacetate (CF_3COOR^4, E:Z = 4:1) as major product (>95%) as shown by ^1H NMR (Yield: 0.12 g, 88%). The crude product was purified with flash column (SiO_2/hexane: EtOAc = 3:1) and pure 1,2-diphenyl-4-cyclopropyl-3-butenol (R^4OH, E:Z = 4:1) was isolated as a colorless oil which solidified on standing. **Z-** and ***E*-CF_3COOR^4**: TLC (SiO_2/hexane:EtOAc = 10:1): R_f = 0.44; IR(Neat): $\nu_{C=O}$ = 1780 cm^{-1}, ν_{C-O} = 1150 cm^{-1}; ^1H NMR($CDCl_3$): δ 0.25 - 0.34(m, 2H), 0.62 -0.73(m, 2H), 1.33-1.39 (m, 1H), 3.71_E, 4.29_Z(dd, J = 9_E, 9_E, 9_Z, 9_Z, H), 4.96_Z, 5.11_E(dd, J = 10_Z, 10_Z, 9_E, 15_E, 1H), 5.63_Z, 5.76_E(dd, J = 10_Z, 10_Z, 9_E, 15_E, 1H), 6.03_E, 6.09_Z(d, J = 9_E, 8_Z, 1H), 7.00 - 7.23(m, 10H); LRMS(EI): *m/z* 360 (M^+). **Z-** and ***E*-R^4OH**: TLC (SiO_2/hexane:EtOAc = 3:1): R_f = 0.6; IR(Neat): ν_{O-H} = 3420 cm^{-1}, ν_{C-O} = 1050 cm^{-1}; ^1H NMR($CDCl_3$): δ 0.31 - 0.39(m, 2H), 0.66 -0.72(m, 2H), 1.41-1.44 (m, 1H), 3.40_E, 4.00_Z(dd, J = 8.5_E, 8.5_E, 10_Z, 8.5_Z, H), 4.73_E, 4.80_Z(d, J = 8_E, 7.5_Z, 1H), 5.05_Z, 5.17_E(dd, J = 10.5_Z, 10.5_Z, 9_E, 15_E, 1H), 5.76_Z, 5.89_E(dd, J = 10.5_Z, 10.5_Z, 9_E, 15_E, 1H), 7.00 - 7.23(m, 10H); LRMS(FAB): *m/z* 247 (M^+-OH); Anal. Calcd for $C_{19}H_{20}O$: C, 86.31; H, 7.63. Found: C, 86.36; H, 7.61.

Reduction with $(PhO)_3PMeI$-$NaBH_3CN$ in HMPA. Methyltriphenoxyphosphonium iodide (0.36 g, 0.8 mmol) was added to a solution of R^2OH (0.1 g, 0.38 mmol) in HMPA (10 mL) at r. t. and the solution was stirred for 1 h. Next $NaBH_3CN$ (0.1 g, 1.6 mmol) was added and the resulting mixture was stirred at 70 °C for additional 2 h. After cooling the solution was poured into 200 mL sat. NaCl aq. and aqueous solution was extracted with ether (2 x 100 mL). The ether phase was washed with sat. NaCl aq. and dried over Na_2SO_4. Evaporation of the solvent gave a pale yellow oil which was purified by a flash column (SiO_2/hexane) to give 1-(*trans*-2, *trans*-3-diphenylcyclopropyl)-1-butene (R^5H, E:Z > 99:1, 0.08 g, 80%), which was purified further by semipreparative HPLC. **R^5H**: HPLC (SiO_2/hexane:CH_2Cl_2 = 49:1, 1 mL/min): t_R = 19.3 min; ^1H NMR($CDCl_3$): δ 1.00(t, J = 7.5, 3H), 2.04 - 2.09(m, 2H), 2.23 - 2.28(m, 1H); 2.45(d, J = 5.5, 2H), 5.36(dd, J = 7.5, 15, 1H), 5.72(dt, J = 6.5, 15, 1H), 6.85 - 7.15(m, 10H); HRMS(EI): calcd for $C_{19}H_{20}$: 248.1565, Found: 248.1559.

Reduction with BH_3-BF_3 in THF. To a solution of 0.06 g (0.23 mmol) of R^2OH in 10 mL THF at 0 °C was added 2 mL of 1 M THF solution of BH_3·THF (2 mmol). After reaching r. t. the reaction mixture was stirred for 1 h and then 0.02 g (0.14 mmol) of BF_3·Et_2O was added. The solution was stirred at r. t. and the reaction was followed by TLC (SiO_2/hexane:EtOAc = 10:1). After the reactant disappeared on TLC the solution was quenched with a small amount of water. The resulting mixture was concentrated and the residue was dissolved in 200 mL ether. The organic phase was washed by 10% HCl aq., 5% Na_2CO_3 aq., sat. NaCl aq., and dried over Na_2SO_4. Removal of the solvent gave a crude product as a pale yellow oil. Further purification with flash column SiO_2/hexane gave the product as a colorless oil (0.05 g, 90%). **R^2H**: TLC (SiO_2/hexane): R_f = 0.35; ^1H NMR($CDCl_3$): δ 0.14 - 0.17(m, 2H), 0.48 - 0.52(m, 2H), 0.90 - 0.98(m, 1H), 1.52(t, J = 6.5, 2H), 1.74 - 1.78(m, 1H), 6.90 - 7.10(m, 10H); HRMS(EI): calcd for $C_{19}H_{20}$: 248.1565, Found: 248.1567.

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Reference

1. (a) Adam, W.; Heil, M. *J. Am. Chem. Soc.* **1991**, 113, 1730. (b) Clive, D. L. J.; Daibneault, S. *J. Org. Chem.* **1991**, 56, 3801. (c) Gozdz, A. S.; Maslak, P. *Ibid.* **1991**, 56, 2179. (d) Bullock, R. M.; Samsel, E. G. *J. Am. Chem. Soc.* **1990**, 112, 6886.

2. (a) Fu, H.; Newcomb, M.; Wong, C.-H. *J. Am. Chem. Soc.* **1991**, 113, 5878. (b) Ruzicka, F.; Huang, D.-S.; Donnelly, M. I.; Frey, P. A. *Biochemistry* **1990**, 29, 1696. (c) Ortiz de Montellano, P. R.; Stearns, R. A. *J. Am. Chem. Soc.* **1987**, 109, 3415.
3. (a) Bowry, V. W.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, 113, 5687. (b) Engel, P. S.; Gulotta, A. M. *Ibid.* **1991**, 113, 2686. (c) Newcomb, M.; Manek, M. B. Glenn, A. G. *Ibid.* **1991**, 113, 949. (d) Lemieux, R. R.; Beak, P. *J. Org. Chem.* **1990**, 55, 5454.
4. Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, 113, 5699.
5. Castellino, A. J.; Bruice, T. C. *J. Am. Chem. Soc.* **1988**, 110, 7512.
6. (a) He, G.-X.; Bruice, T. C. *J. Am. Chem. Soc.* **1991**, 113, 2747.
(b) He, G.-X; Arasasingham, R. D.; Zhang, G.-H.; Bruice, T. C. *Ibid.* **1991**, 113, 9828.
7. Groves, J. T.; Subramanian, D. V. *J. Am. Chem. Soc.* **1984**, 106, 2177.
8. (a) Groves, J. T.; Nemo, T. E. *J. Am. Chem. Soc.* **1983**, 105, 6243. (b) Groves, J. T.; Kruper, W. J. Jr.; Haushalter R. C. *Ibid.* **1980**, 102, 6375. (c) Hill, C. L.; Schardt, B. C. *Ibid.* **1980**, 102, 6374.
9. Carey, F. A.; Tremper, H. S. *J. Am. Chem. Soc.* **1968**, 90, 2578.
10. Kursanov, D. N.; Parnes, Z. N.; Loim, N. M. *Synthesis* **1974**, 633.
11. (a) Morita, T.; Okamoto, Y.; Sakurai, H.; *Synthesis* **1981**, 32. (b) Olah, G. A.; Narang, S. C.; Balaram Gupta, B. G.; Malhotra, R. *J. Org. Chem.* **1979**, 44, 1247.
12. Balme, G.; Fournet et Jacques Gore, G. *Tetrahedran Lett.* **1986**, 27, 1907.
13. (a) Erickson, R. E.; Annino, R.; Scanlon, M. D.; Zon, G. *J. Am. Chem. Soc.* **1969**, 91, 1767.
(b) Yamanaka, H.; Oshima, R.; Teramura, K. *J. Org. Chem.* **1972**, 37, 1734.
14. The upper limit for the heterogeneous $1e^-$ transfer rate constant is 10^4 cm s^{-1}. Cauquis, G. In *Organic Electrochemistry*; Baizer, M. M.; Lund, H. Ed.; Marcel Dekker, Inc.: New York, 1983; pp 11 - 76.
15. Hutchins, R. O.; Kandasamy, D.; Maryanoff, C. A.; Masilamani, D.; Maryanoff, B. E. *J. Org. Chem.* **1977**, 42, 82.
16. Hutchins, R. O.; Kandasamy, D.; Dux, F. III; Maryanoff, C. A.; Rotstein, D.; Goldsmith, B.; Burgoyne, W.; Cistone, F.; Dalessandro, J.; Puglis, J. *J. Org. Chem.* **1978**, 43, 2259.
17. Verheyden, J. P. H.; Moffatt, J. G. *J. Org. Chem.* **1970**, 35, 2319 and references therein cited..
18. H. Richey In *Carbonium Ions*; Olah, G., Schleyer, P. v. R., Eds.; Wiley: New York, 1972; Vol. 3, pp 1201-1294.
19. Carey, F. A.; Tremper, H. S. *J. Am. Chem. Soc.* **1969**, 91, 2967.
20. Sarel, S.; Yovell, J.; Sarel-Imber, M. *Angew. Chem., Internat. Edit.* **1968**, 7, 577.
21. Badejo, I. T.; Karaman, R.; Pinkerton, A. A.; Fry, J. L. *J. Org. Chem.* **1990**, 55, 4327.
22. Brady, S. F.; Ilton, M. A.; Johnson, W. S. *J. Am. Chem. Soc.* **1968**, 90, 2882.
23. Breuer, E. *Tetrahedran Lett.* **1967**, 1849.
24. For the unusual stability of cyclopropylcarbinyl cation, see Scheyer, P. R.; Van Dine, G. W. *J. Am. Chem. Soc.* **1966**, 88, 2321 and references therein cited.