Opening of a Cyclopropyl Ring in (Diphenylcyclopropyl)alkenes Promoted by Electron Transfer from Potassium 4,4'-Di-*tert*-butylbiphenyl Radical Anion and X-ray and Theoretical Calculations of the Structure of (*Z*)-1,2-Bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene

Rafik Karaman, Gong-Xin He, Felice Chu, Andrei Blaskó, and Thomas C. Bruice*

Department of Chemistry, University of California at Santa Barbara, Santa Barbara, California 93106

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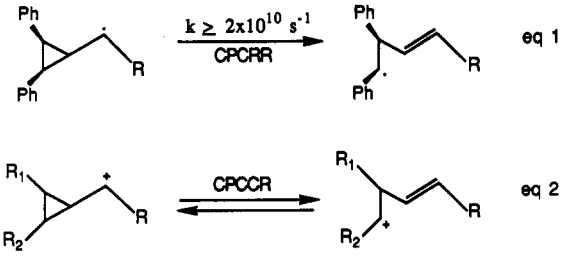
We have prepared the (diphenylcyclopropyl)alkenes 1a–c and studied their reductions, using potassium 4,4'-di-*tert*-butylbiphenyl radical anion (DBB$^{\bullet-}$) as an electron source. Spectra analyses of the reaction products reveal that the double bond of the alkene stayed intact, whereas the cyclopropyl moiety was cleaved to provide alkenes 2a–c. When the reaction was carried out with a simple cyclopropylalkene without phenyl substituents (1e), the starting material was fully recovered. This indicates that the opening of the cyclopropyl ring in the alkenes is promoted by electron transfer from potassium DDB$^{\bullet-}$ onto the phenyl rings attached to the cyclopropyl moiety. Two mechanisms were considered: (1) opening of the cyclopropyl via a cyclopropylcarbinyl to homoallylcarbinyl radical rearrangement (CPCRR) with potassium DBB$^{\bullet-}$ as the $1e^-$ reductant, with electron transfer to the phenyl rings attached to the cyclopropyl moiety, and (2) $2e^-$ transfer to the phenyl rings and opening of the cyclopropyl moiety via an anionic rearrangement (CPCAR). (*Z*)-1-(*trans*-2,*trans*-3-Diphenylcyclopropyl)butene (1c) was used as a model for AM1 calculations which establish that the isomeric form of the radical anion product with opened cyclopropyl ring (1c$^{\bullet-}$ form 1) is about 7 kcal/mol lower in energy than an isomeric form in which the cyclopropyl ring is closed (1c$^{\bullet-}$ form 2). This suggests that the opening of the cyclopropyl ring is likely to happen through CPCRR rather than CPCAR. The X-ray crystal structure of (*Z*)-1,2-bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene (1a) shows the two phenyl rings to be completely out of the cyclopropyl ring plane. The average C–C bond distance for the cyclopropyl moiety in the *trans*-2,*trans*-3-diphenylcyclopropyl rings is 1.562 Å, which is longer than the average bond distance in unsubstituted cyclopropyl rings. The gas-phase structures as calculated by AM1, PM3, and MNDO molecular orbital methods are all quite similar and agree closely with the X-ray structure. However, MNDO gave more satisfactory results than AM1 and PM3 for bond distances and bond angles and deviated more for torsion angles. The latter is reflected by the relatively large difference in the heat of formations (7 kcal/mol) of the gas-phase fully optimized structure and the X-ray structure.

Introduction

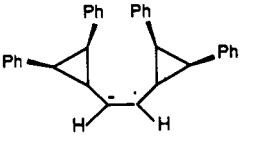
(*Z*)-1,2-Bis(*trans*-2,*trans*-3-diphenylcyclopropyl)-ethene (1a) has proved useful as a radical trap for investigating the mechanisms of epoxidation of alkenes taking place in the presence of hypervalent metal–oxo porphyrins.[1,2] We have shown that the radical cation of 1a decomposes via the opening of one of the cyclopropyl rings by a cyclopropylcarbinyl to homoallylcarbinyl radical rearrangement (CPCRR) (eq 1) while the other ring rearranges by way of cyclopropylcarbinyl to homoallyl-carbinyl cation (CPCCR) (eq 2).[2] It has been shown[1] that the rate constant of CPCRR with 1a is larger than 2×10^{10} s^{-1}, whereas the opening of the cyclopropylcarbinyl to homoallylcarbinyl cation provides a stable carbocation and the CPCCR is reversible.[3] During the course of our studies



eq 1

eq 2

on 1a, we became intrigued with the fact that one-electron transfer from a reducing agent to 1a will provide a system such as 1a$^{\bullet-}$, where the two cyclopropyl rings can open in



1a$^{\bullet-}$

two different ways, as in the case of 1a$^{\bullet+}$. Thus, one ring may rearrange by way of cyclopropylcarbinyl to homoallylcarbinyl radical (CPCRR) (eq 1) and the other could then open by a way of cyclopropylcarbinyl to homoallylcarbinyl anion (CPCAR) (eq 3). System 1a$^{\bullet-}$ would allow

(1) (a) Castellino, A. J.; Bruice, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 1313. (b) Castellino, A. J.; Bruice, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 7512.

(2) (a) He, G.-X.; Mei, H.-Y.; Bruice, T. C. *J. Am. Chem. Soc.* **1991**, *113*, 5644. (b) He, G.-X.; Arasasingham, R. D.; Zhang, G.-H.; Bruice, T. C. *J. Am. Chem. Soc.* **1991**, *113*, 9828.

(3) (a) Richey, H. In *Carbonium Ions*; Olah, G., Schleyer, P. v. R., Eds.; Wiley: New York, 1972; Vol. 3, pp 1201–1294. (b) Sarel, S.; Yovell, J.; Sarel-Imber, M. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 577. (c) Childs, R. F.; Kostyk, M. D.; Lock, C. J. L.; Mahendran, M. *J. Am. Chem. Soc.* **1990**, *112*, 8912. (d) Hehre, W. J.; Hiberty, P. C. *J. Am. Chem. Soc.* **1972**, *94*, 5917. (e) Falkenberg-Andersen, C.; Ranganayakulu, K.; Schmitz, L. R.; Sorensen, T. S. *J. Am. Chem. Soc.* **1984**, *106*, 178.

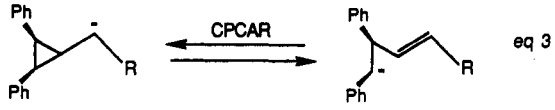
0022-3263/93/1958-0438$04.00/0

Table I. Reactions of System 1 with Potassium DBB Radical Anion in Dry THF under an Argon Atmosphere[a]

compd	mmol	THF, mL	time, h	product	yield, %
1a	0.1	20	5	**2a**	85
1a[b]	0.1	20	5	**2a**	23
1a[c]	0.025	20	3	**2a-d_4**	75
1b	0.05	30	0.5	**2b**	78
1c	0.2	40	1	**2c**	84
1d[d]	0.4	25	2.5	**2d**	42

[a] For experimental details, see the Experimental Section. [b] Lithium DBB radical anion was used instead of $K^+DBB^{\bullet-}$. [c] In this case, the reaction mixture was quenched with D_2O (2 mL) before the dilution with chloroform. [d] Upon the addition of **1d** to the THF solution of $K^+DBB^{\bullet-}$ the reaction mixture turned red.

a comparison of the cyclopropylcarbinyl anion stability[4] with that of cyclopropylcarbinyl radicals.[5]

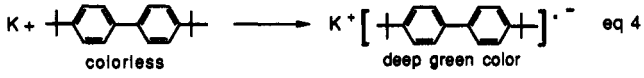


eq 3

Herein, we report the electron transfer reactions of **1a** and similar compounds using potassium 4,4′-di-*tert*-butylbiphenyl (DBB) radical anion as the electron source. Further, we present the X-ray structure and the gas-phase calculated structure of **1a**.

Results and Discussion

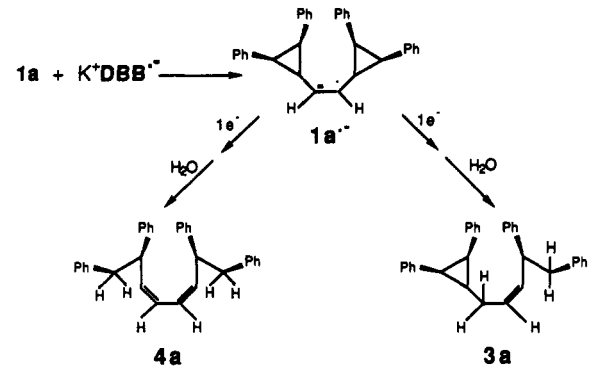
Generation of the Electron Transfer Reagent Potassium 4,4′-Di-*tert*-butylbiphenyl Radical Anion. It has been shown that lithium DBB radical anion has unique reducing properties toward a variety of compounds such as aromatic ketones, esters, amides, acids, alkenes, halides, and others.[6] The presence of the *tert*-butyl groups on the para positions of the two phenyls prevents attack by electrophiles on the DBB moiety. This makes this reagent more useful, as an electron source, than sodium naphthalene which is destroyed upon exposure to electrophiles or moisture.[6a,7] We have chosen to use $K^+DBB^{\bullet-}$ instead of $Li^+DBB^{\bullet-}$ because it is observed that the yields of the reduction reactions using the former are higher[6b] (see Table I). Potassium DBB radical anion is formed through a single-electron transfer from potassium metal onto DBB (eq 4).



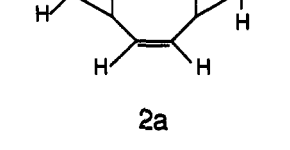
eq 4

The reaction procedure involves the addition of dry DBB to excess potassium in dry THF and sonication at 50 °C for 5 min under an argon atmosphere. The rate of the formation of $K^+DBB^{\bullet-}$ was found to be greatly dependent on the temperature and the power of the ultrasonic bath.[8] When the reaction vessel was immersed in a laboratory ultrasonic bath at 50 °C, the deep green colored solution of $K^+DBB^{\bullet-}$ appeared immediately, whereas if the temperature was kept at 0 °C, it took 30 min for the THF solution to turn deep green. If magnetic stirring was used instead of sonication, 5 h was required for the DBB to react with the potassium to give the deep green color.

Scheme I



Reactions of Potassium DBB Radical Anion with (*Z*)-1,2-Bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene (1a). We have explored the reaction of alkene **1a** with potassium DBB radical anion in THF. It was anticipated that the reaction would proceed through a one-electron transfer from $K^+DBB^{\bullet-}$ onto the double bond of **1a** to provide intermediate **1a**$^{\bullet-}$. Opening of one cyclopropyl ring in **1a**$^{\bullet-}$ will result upon electron transfer and quenching with water in the formation of **3a**. The final product upon quenching would be **4a** (Scheme I) if both cyclopropyl rings open. In the first case, the C–C bond of the cyclopropyl ring, α to the radical in **1a**$^{\bullet-}$, is cleaved, and in the second case both C–C bonds of both cyclopropyl moieties, α to the radical and to the anion, are cleaved.[9] Surprisingly, IR, MS, ^{1}H-NMR, ^{13}C-NMR, and ^{1}H–^{1}H COSY analyses indicate that the olefin **2a** is the exclusive product. **2a** could be isolated in 85% yield.



2a

The reduction was repeated with cyclopropyl systems **1b** and **1c**, and it was found that the products were the alkenes *trans*-1,6-diphenyl-2,5-dibenzyl-3-hexene (**2b**) and *cis*-1-phenyl-2-benzyl-3-hexene (**2c**), respectively (see Table I). When the reaction of **1a** was repeated and the workup was accomplished by quenching with D_2O, the deuterated alkene *cis*-1,6-diphenyl-2,5-dibenzyl-d_4-3-hexene (**2a-d_4**; one hydrogen of each of the four benzyl groups of **2a** represents deuterium) was formed in 75% yield.

In the above reduction reactions the double bond stays intact and both cyclopropyl rings open. In order to evaluate the role of the phenyl rings attached to the

(4) Stable (cyclopropylcarbinyl)lithium systems have been successfully prepared. See: (a) Lansbury, P. T.; Pattison, V. A.; Clement, W. A.; Sidler, J. D. *J. Am. Chem. Soc.* **1964**, *86*, 2247. (b) Lansbury, P. T.; Pattison, V. A. *J. Am. Chem. Soc.* **1963**, *85*, 1886. Landgrebe, J. A.; Shoemaker, J. D. *J. Am. Chem. Soc.* **1967**, *89*, 4465.

(5) It has been shown that cyclopropylcarbinyl type rearrangement of ketyl anions (radical anions) are not similar to that of free radicals. See: Tanko, J. M.; Drumright, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 5362.

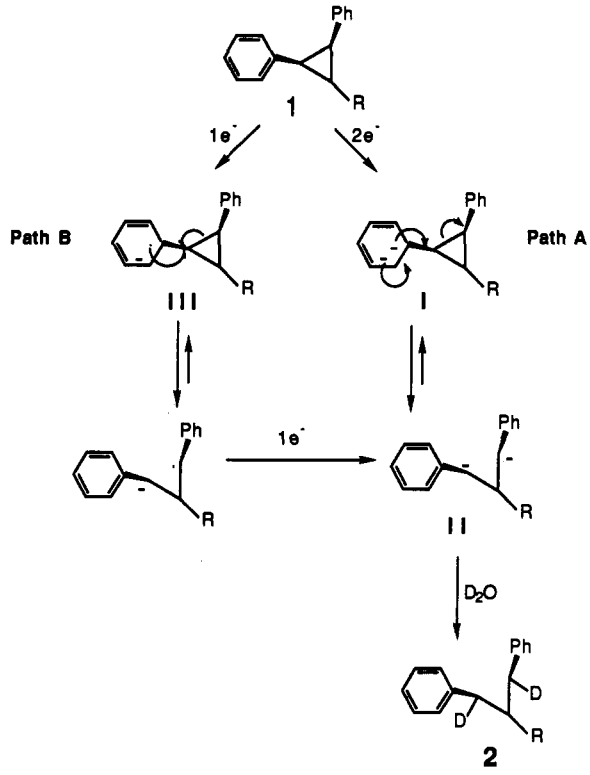
(6) (a) Freeman, P. K.; Hutchinson, L. H. *Tetrahedron Lett.* **1976**, 1849; *J. Org. Chem.* **1980**, *45*, 1924. (b) Karaman, R.; Kohlman, D. T.; Fry, J. L. *Tetrahedron Lett.* **1990**, *31*, 6155. (c) Karaman, R.; Fry, J. L. *Tetrahedron Lett.* **1989**, *30*, 4931, 4935, 6267; **1990**, *31*, 941. (d) Badejo, I. T.; Karaman, R.; Lee, N. W. I.; Lutz, E. C.; Mamanta, M. T.; Fry, J. L. *J. Chem. Soc., Chem. Commun.* **1989**, 566. (e) Badejo, I. T.; Karaman, R.; Fry, J. L. *J. Org. Chem.* **1989**, *54*, 4591.

(7) Holy, N. L. *Chem. Rev.* **1974**, *74*, 243.

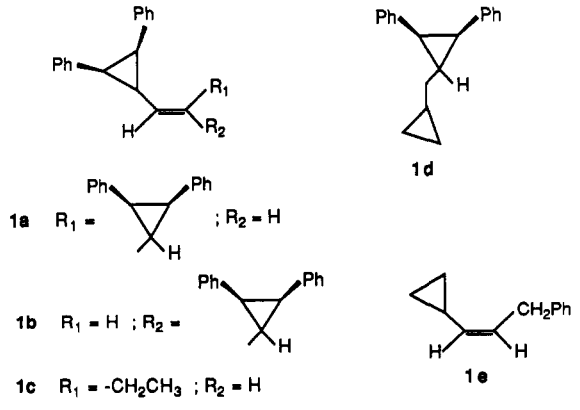
(8) (a) de Souza-Barboza, J. C.; Petrier, C.; Luche, J. L. *J. Org. Chem.* **1988**, *53*, 1212. (b) Abdulla, R. F. *Aldrichimica Acta* **1988**, *21*, 31.

(9) In the presence of excess potassium, **3a** and **4a** might undergo further reduction to the corresponding hydrocarbons (reduction of the double bonds).

Scheme II

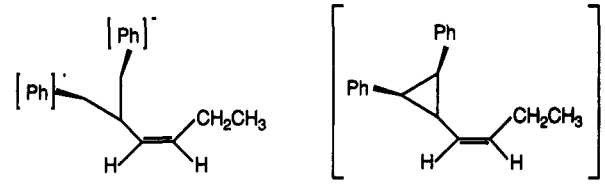


cyclopropyl moiety, compounds **1d** and **1e** were subjected to the same reaction conditions. It was found by analysis of the products that **1d** undergoes reduction to provide 1-cyclopropyl-2-benzyl-3-phenylpropane (**2d**) in 42% yield (Table I), whereas **1e** was recovered after prolonged exposure to the same conditions. Comparison of the results with **1d** and **1e** to those with **1a**, **1b**, and **1c** shows that the unsubstituted cyclopropyl ring is not opened upon electron transfer, whereas the cyclopropyl rings with phenyl substituents undergo reduction to furnish a product with opened cyclopropyl rings. This indicates that the opening of the cyclopropyl moiety occurs through electron transfer from $K^+DBB^{\bullet-}$ onto the phenyl substituents.



At least two mechanisms can be considered to explain these results. One is a $2e^-$ transfer process to provide I followed by opening of the cyclopropyl ring to form dianion II (path A, Scheme II), and the other involves a $1e^-$ transfer leading to the formation of anion radical intermediate III. The latter promotes a cleavage of the cyclopropyl ring which in the next step adds another electron from potassium DBB radical anion to form dianion II (path B, Scheme II). In both pathways, the last step is quenching of dianion II with H_2O or D_2O to provide products. In both mechanisms the reduction process proceeds as a result of electron transfer from potassium DBB radical anion to the phenyl rings. While both mechanisms are possible, the stepwise electron-transfer process (path B) seems to be more likely since the rate constant for the cyclopropyl ring opening via radical anion is estimated to be around $10^{10}\ s^{-1}$; however the rate constant for reaction of potassium metal with DBB is not likely to exceed $10^4\ s^{-1}$.[10]

In order to add further credibility to these mechanistic explanations, AM1 calculations[11] for a model compound **1c** and its radical anion, $\mathbf{1c}^{\bullet-}$, were carried out using the restricted Hartree–Fock (RHF) method for **1c** and the unrestricted Hartree–Fock (UHF) method for $\mathbf{1c}^{\bullet-}$. The results of the calculation indicate that the global minimum for $\mathbf{1c}^{\bullet-}$ dictates an opened cyclopropyl ring (form 1). When the bond between the two benzylic carbons in $\mathbf{1c}^{\bullet-}$ was forced to be intact (form 2) and all other parameters were optimized, the energy obtained for the ring closed radical anion (form 2) was found to be 7 kcal/mol above that of the opened one (form 1). Inspection of the AM1 atomic



$\mathbf{1c}^{\bullet-}$ Form 1 $\mathbf{1c}^{\bullet-}$ Form 2

charge population of form 1 reveals high negative charges densities in the ortho and para positions of the phenyl rings, as well as on the benzylic carbons. The combined AM1 calculation results support the idea that the cyclopropyl ring opening in the system studied is the one described in path B (Scheme II).

Relatively stable 1,3-dianions are known.[12] Boche and co-workers[13] have studied the reduction of *cis*- and *trans*-1,2-diphenylcyclopropane employing a potassium and sodium alloy (Na/K) and found that the cyclopropyl ring opens through a radical anion intermediate. This is in accord with the results of the present study which indicate that product **2** is derived from a stable 1,3-dianion (path B, Scheme II) which could be trapped by D_2O to furnish the deuterated product **2** as is the case with **2a-*d*₄**.

X-ray Structure and Gas-Phase Calculations of (*Z*)-1,2-Bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene (1a). The X-ray crystal structure for (*Z*)-1,2-bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene (**1a**) along with the atom numbering is shown in Figure 1 in full PLUTO view. The two phenyl rings in **1a** are completely out of the cyclopropyl ring plane. The average C–C bond distance of the cyclopropyl moiety in the *trans*-2,*trans*-3-diphenylcyclopropyl ring is 1.562 Å (Table II) which is longer than that in unsubstituted cyclopropyl rings. For the unsubstituted cyclopropyl ring the average C–C bond

(10) Canquis, G. In *Organic Electrochemistry*; Baizer, M. M., Lund, H., Eds.; Marcel Dekker, Inc.; New York, 1983; pp 11-76.
(11) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.
(12) Schleyer, P. v. P.; Kos, A. J.; Kaufmann, E. *J. Am. Chem. Soc.* **1983**, *105*, 7617.
(13) (a) Boche, G.; Schneider, D. R.; Wernicke, K. *Tetrahedron Lett.* **1984**, *25*, 2961. (b) Boche, G.; Wintermayr, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 874. (c) Boche, G.; Schneider, D. R.; Wintermayr, H. *J. Am. Chem. Soc.* **1980**, *102*, 5697. (d) Walborsky, H. M.; Powers, E. J. *Isr. J. Chem.* **1981**, *21*, 210.

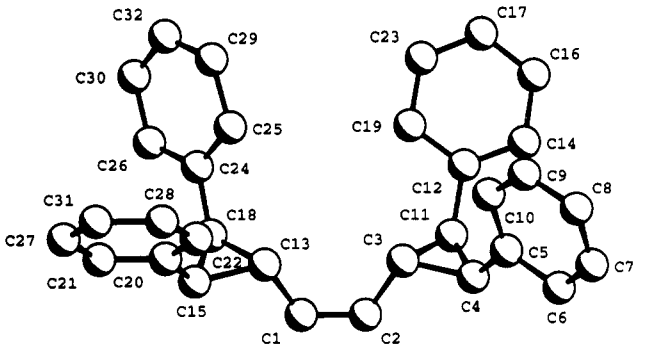


Figure 1. Full PLUTO view of (*Z*)-1,2-bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene (**1a**).

Table II. Bond Distances Determined by X-ray and Calculated

atoms		bond distances, Å			
1	2	X-ray	AM1	PM3	MNDO
C2	C1	1.378	1.338	1.336	1.349
C3	C2	1.513	1.464	1.472	1.487
C4	C3	1.562	1.516	1.514	1.546
C11	C3	1.534	1.511	1.510	1.541
C11	C4	1.558	1.516	1.515	1.542
C13	C1	1.502	1.464	1.471	1.488
C15	C13	1.564	1.511	1.508	1.544
C18	C13	1.595	1.513	1.512	1.544
C18	C15	1.556	1.517	1.514	1.543

distances were reported as 1.513 Å in 1-(cyclopropylmethyl)-4-phenyl-6-methoxy-2(1*H*)-quinazolinone[14] and 1.496 Å in bis(cyclopropylmethyl)-1,4-piperazine bischlorhydrate.[15] The very rapid ring opening of the *trans*-2,*trans*-3-diphenylcyclopropyl rings of **1a** is due to the inherent stability of the immediate products which are benzylic (radical, carbocation, anion). The reactivity is apparent in the long bond distances of the cyclopropyl moiety in **1a**.

Selected observed and calculated (AM1,[11] PM3,[16] and MNDO[17]) bond distances, bond angles, and torsion angles are listed in Tables II–IV. The gas-phase structures as calculated by the various semiempirical molecular orbital methods (AM1, PM3, and MNDO) are all quite similar and agree closely with the X-ray structure. Although the discrepancies between the observed and the calculated parameters are greater than the experimental error, they are small enough to give confidence in the semiempirical methods. The deviations from the X-ray structure are quite similar for all the semiempirical methods. However, MNDO gave more satisfactory agreement for the bond distances and bond angles and less for the torsion angles, especially for the angle $C_4C_3C_2C_1$. The heat of formations (ΔH_f) for the X-ray structure and the gas-phase calculated structures by AM1, PM3, and MNDO methods are listed in Table V. The differences in the heats of formation for the X-ray structure and the AM1 and PM3 fully optimized gas-phase structures are 2–3 kcal/mol, whereas for MNDO it is about 7 kcal/mol. The relatively large difference with MNDO might be attributed to the quite large deviation between the experimentally and calculated $C_4C_3C_2C_1$ torsion angle (the difference is 61°). The small deviations between the X-ray structure and the semiempirical gas-phase calculated structures might be due to the packing forces existing in the solid state.

Summary

We have studied the electron transfer reactions of cyclopropyl alkenes **1a-c** and **1e** with potassium 4,4′-di-*tert*-butylbiphenyl radical anion (DBB$^{\bullet-}$) as an electron-transfer agent. It was found that (*trans*-2,*trans*-3-diphenylcyclopropyl)alkenes (**1a–c**) undergo reduction to furnish the corresponding opened cyclopropylalkenes (**2a-c**), whereas those with cyclopropyl rings without phenyl substituents (**1e**) do not react. The stability of the cyclopropyl systems lacking an aromatic ring might be related to the fact that in these systems the reduction potential is not less than the oxidation potential of potassium DBB$^{\bullet-}$. Two mechanisms can be drawn for 1e$^-$ reduction of the diphenylcyclopropyl ring. One is a 2e$^-$ transfer from potassium DBB$^{\bullet-}$ onto the phenyl ring followed by opening of the cyclopropyl ring via CPCAR, and the other is a stepwise 2e$^-$ transfer which promotes opening the cyclopropyl rings via a CPCRR process. The latter mechanism is supported by the AM1 calculation of the structure and potential energy of **1c** and its radical anion (**1c**$^{\bullet-}$) which indicate that **1c**$^{\bullet-}$ exists in open form, and the energy difference between this form and the closed one is 7 kcal/mol. This indicates that upon 1e$^-$ transfer the cyclopropyl ring opens before securing the second 1e$^-$ transfer. The X-ray crystal structure of (*Z*)-1,2-bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene (**1a**) reveals that the two phenyl rings and the olefinic double bond are out of the cyclopropyl ring plane. The average bond length of the cyclopropyl moiety in **1a** (1.562 Å) is longer than that in unsubstituted cyclopropyl rings. The gas-phase structures as calculated by AM1, PM3 and MNDO methods are all quite similar and in good agreement with the X-ray structure.

Experimental Section

General. General nuclear magnetic resonance spectra were obtained on Nicolet NT-300 and General Electric GN-500 spectrophotometers at 25 °C. Chemical shifts (ppm) were referenced to $CHCl_3$ (7.240 ppm) or DMSO (2.49 ppm). Phase-sensitive double quantum filtered COSY spectra were recorded using a pulse sequence[18] 90°–*t*1–90°$_{\phi 1}$–Δ–90°$_{\phi 2}$–acquisition$_{\phi R}$ with 90° pulse of 22.5 μs calibrated before the experiment Δ = 8 μs, and an eight-step phase cycling has been applied.[19,20] Spectra were collected into 4K daba blocks for 256 t_1 increments with a relaxation delay of 1.5 s. The data matrix was zero filled to 2K and apodized with exponential function to give a line broadening of 1 Hz in both dimensions. Infrared spectra were determined on a Perkin-Elmer 1330 spectrophotometer. Absorption spectra were recorded on a Cary-14 spectrophotometer interfaced to a Zenith computer equipped with OLIS (On-Line Instrument System Inc.) data acquisition and processing software. Low-resolution and high-resolution mass spectra (LRMS and HRMS) were recorded on a VG analytical spectrometer (Model VGII-250) by electron impact (EI) and chemical ionization (CI) with CH_4. Melting points were taken on Laboratory Devices MEL-TEMP apparatus and are uncorrected. Elemental analyses were carried out by Galbraith Laboratories, Inc.

Materials. (*Z*)- and (*E*)-1,2-bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene, **1a** and **1b**, respectively, were synthesized according to the published methods.[1,21] (*trans*-2,*trans*-3-Diphe-

(14) Kimura, M.; Hirohashi, T.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2696.
(15) Dung, N. H.; Viossat, B.; De Sevricourt, M. C.; Robba, M. *Chem. Pharm. Bull.* **1987**, *35*, 1093.
(16) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209, 221.
(17) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.
(18) Martin, G. E.; Zekter, A. S. In *Two Dimensional NMR Methods for Establishing Molecular Connectivity*; VCH Publishers; New York, 1988; p 100.
(19) Wokaun, A.; Ernst, R. R. *Chem. Phys. Lett.* **1977**, *52*, 407.
(20) Morris, G. A. *Magn. Reson. Chem.* **1980**, *24*, 371.
(21) He, G.-X.; Bruice, T. C. *J. Am. Chem. Soc.* **1991**, *113*, 2747.

Table III. Bond Angles Determined by X-ray and Calculated

atoms			bond angles, deg			
1	2	3	X-ray	AM1	PM3	MNDO
C3	C2	C1	120.6	125.7	123.4	128.3
C3	C11	C4	60.7	60.1	60.1	60.2
C4	C3	C2	113.5	119.0	120.0	121.6
C4	C3	C11	60.5	60.1	60.1	59.9
C11	C4	C3	58.9	59.8	59.8	59.9
C13	C1	C2	123.2	125.6	123.5	128.5
C13	C18	C15	59.5	59.8	59.8	60.0
C15	C13	C1	113.9	119.5	120.2	120.9
C15	C13	C18	59.0	60.2	60.2	59.9
C18	C13	C1	112.8	118.7	118.7	120.8
C18	C15	C13	61.5	60.0	60.1	60.0

Table IV. Torsion Angles Determined by X-ray and Calculated

atoms				torsion angles, deg			
1	2	3	4	X-ray	AM1	PM3	MNDO
C4	C3	C2	C1	162.0	125.3	160.4	100.9
C5	C4	C3	C2	-142.8	-137.9	-137.0	-133.1
C6	C5	C4	C3	153.5	150.7	158.3	156.4
C7	C6	C5	C4	179.6	179.7	-177.7	-179.2
C8	C7	C6	C5	1.1	0.3	-0.8	0.4
C9	C8	C7	C6	-2.3	0.7	1.6	-0.8
C10	C9	C8	C7	4.2	-1.4	-0.8	0.8
C11	C4	C5	C6	-136.5	-136.8	-130.7	-127.6
C12	C11	C4	C5	0.7	1.1	3.2	0.4
C13	C1	C2	C3	-2.8	-2.0	1.6	-1.8
C14	C12	C11	C4	65.9	79.6	65.2	62.9
C15	C13	C1	C2	-167.3	-164.9	-162.1	179.8
C16	C14	C12	C11	171.7	179.3	178.3	176.5
C17	C16	C14	C12	2.2	-1.0	0.4	-0.4
C18	C13	C1	C2	127.7	125.0	127.6	108.6
C19	C12	C11	C4	-117.4	-102.5	-115.8	-121.6
C20	C15	C13	C1	143.5	139.4	140.6	135.2
C21	C20	C15	C13	162.3	162.4	161.4	147.0
C22	C20	C15	C13	-17.8	-19.6	-20.1	-37.1
C23	C19	C12	C11	-171.9	-178.8	-178.7	-176.4
C24	C18	C13	C1	-144.2	-138.0	-137.0	-136.3
C25	C24	C18	C13	1.1	1.3	2.5	4.8
C26	C24	C18	C13	179.0	-179.3	-178.9	-176.9
C27	C21	C20	C15	179.2	178.6	178.8	178.1
C28	C22	C20	C15	-176.5	-178.3	-178.4	-177.1
C29	C25	C24	C18	179.3	178.8	177.6	178.6
C30	C26	C24	C25	-2.2	0.5	0.2	-0.3
C31	C27	C21	C20	-1.5	-0.3	-0.3	-1.6
C32	C29	C25	C24	-1.4	0.4	1.2	-0.1

Table V. Heats of Formation for the X-ray Structure of 1a and Semiempirical Gas-Phase Calculated Structures

structure	AM1	PM3	MNDO
gas phase optimized ΔH_f (kcal/mol)	165	159	158
X-ray optimized[a] ΔH_f (kcal/mol)	167	162	165

[a] Optimization of the X-ray structure was done by forcing the torsion angles while optimizing other parameters.

nylcyclopropyl)cyclopropylmethane (1d) was available from a previous study.[22] 4,4'-Di-*tert*-butylbiphenyl (DBB) was obtained as a gift from Prof. James L. Fry, Department of Chemistry, the University of Toledo. All other reagents were commercially obtained in high purity. All reactions were carried out with purified reagents in dry, purified solvents under argon unless noted otherwise. Column chromatography was performed with Fischer type 60Å (200–425-mesh) silica gel. Preparative thin-layer chromatography (TLC) was performed using E.M. Sciences Kieselgel 60 F_{254}.

Theoretical Calculations. The AM1, PM3, and MNDO calculations were done using the MOPAC 6.0 package[23] running on a Silicon Graphics 4D/340GTX workstation. The starting geometries were obtained from the program Quanta (Polygen Corp.). The calculations were carried out by the standard AM1,[11] PM3,[16] and MNDO[17] programs based on the restricted Hartree–Fock (RHF) method, unless otherwise indicated. Geometries were optimized in internal coordinates and were terminated when Herberts test was satisfied in the Broyden–Fletcher–Goldfarb–Shanno method (BFGS). All optimizations were terminated when the change in energy on successive iterations was less than 0.000 01 kcal/mol and the change in density matrix elements on two successive iterations was less than 0.001. All the calculations have been performed with full optimization of all geometrical variables (bond lengths, bond angles, and dihedral angels) without any symmetry constraint.

X-ray Crystallography. A single crystal of (*Z*)-1,2-bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene (1a) of approximate dimensions 0.35 × 0.33 × 0.10 mm was mounted on a glass fiber with epoxy prior to data collection on an automated Huber four-circle X-ray diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.710 73 Å), interfaced to a DEC Micro VAX-II computer with Crystal Logic stepping motor controllers. The orthorhombic unit cell constants were determined to final values of a = 9.949 (4) Å, b = 23.282 (7) Å, and c = 20.753 (7) Å. Intensity data were collected by using the θ–2θ scan method, with a scan rate of 4.5°/min from 1.3° below Kα1 to 1.6° above Kα2. Measurements were made out to 45° in 2θ, giving a total of 3573 collected reflections. Systematic absences indicated one unique space group, *Pbca*, with 8 formula units in the unit cell. Only unique data sets were collected, and 753 independent observed reflections were considered, on the basis of the criterion $I > 3\sigma(I)$. The final isotropic refinement of F converged to give

(22) He, G.-X.; Almarsson, Ö.; Bruice, T. C. *Tetrahedron* **1992**, *48*, 3275.

(23) Dewar, M. J. S. *QCPE* 506.

agreement values of R = 10.9% and R_w = 11.8% for 129 parameters. The relatively large R values are due to the small size and relatively poor quality of the crystal, resulting in an inadequate number of observable reflections for anisotropic refinement and location of hydrogen atoms. The largest residual peak on the final difference Fourier map is 0.66 e/Å^3. All least-squares and subsidiary calculations were performed by using the UCLA Crystallographic Computing Package. The crystallographic data are available as supplementary material.

(*Z*)-1-(*trans*-2,*trans*-3-Diphenylcyclopropyl)butene (1c). A 18% sodium acetylide slurry (0.48 g, 1.8 mmol) was washed with dry hexane (2 × 5 mL), and the remaining solid was dried over an argon stream. To the solid were added [(*trans*-2,*trans*-3-diphenylcyclopropyl)methyl]triphenylphosphonium bromide[1] (0.9 g, 1.6 mmol) and dry DMF (5 mL) at 0 °C. After the mixture was stirred at 0 °C for 0.5 h, propionaldehyde (0.12 g, 2.0 mmol) was added. The temperature was allowed to rise gradually to room temperature, and the color of the solution changed from orange to pale yellow. After being stirred for 2 h at room temperature, the reaction mixture was poured into cold water (100 mL) and extracted with Et_2O (4 × 50 mL). The combined organic solution was dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness. The residue was subjected to silica gel column chromatography eluting with hexane to give (*Z*)-1-(*trans*-2,*trans*-3-diphenycyclopropyl)butene as a colorless oil (0.3 g, 76%) along with its trans isomer which was obtained in 5% yield as it is judged by ^{1}H NMR; TLC (SiO_2/hexane) R_f = 0.39; ^{1}H NMR ($CDCl_3$) δ 1.05 (t, J = 7.5 Hz, 3 H), 2.25–2.32 (m, 2 H), 2.44 (d, J = 2.5 Hz, 3 H), 5.12–5.18 (m, 1 H), 5.47 (dt, J = 7, 10.5 Hz, 1 H), 6.89–7.10 (m, 10 H); LRMS (EI) m/z (rel abund) 248 (M^+, 15), 219 ($M^+ - CH_2CH_3$, 58), 91 ($C_7H_7^+$, 100). Anal. Calcd for $C_{19}H_{20}$: C, 91.88; H 8.12. Found: C, 91.76; H, 8.14.

(*Z*)-1-Cyclopropyl-4-phenylbutene (1e). 1e was prepared by a similar method to that of 1c. A benzene solution of (bromomethyl)cyclopropane (2 g, 14.8 mmol) and triphenylphosphine (5.8 g, 22 mmol) was refluxed for 24 h. After cooling, a white precipitate was collected, washed with ether, and dried over P_2O_5 under vacuum to yield (cyclopropylmethyl)triphenylphosphonium bromide (1 g, 17%): mp 178–180 °C; ^{1}H NMR (DMSO-d_6) δ 0.14–0.17 (m, 2 H), 0.45–0.52 (m, 2 H), 0.88–0.95 (m, 1 H), 3.62 (dd, J = 7, 13 Hz, 2 H), 7.72–7.95 (m, 15 H); LRMS (FAB) m/z (rel abund) 317 (M^+ – Br, 100). Wittig condensation of (cyclopropylmethyl)triphenylphosphonium bromide (1 g, 2.5 mmol) and 3-phenylpropionaldehyde (0.4 g, 3 mmol) after purification with silica column chromatography (hexane as an eluent) afforded (*Z*)-1-cyclopropyl-4-phenylbutene (1e) as a colorless oil in 70% yield along with its trans isomer which was obtained in 10% yield as it is judged by ^{1}H NMR: TLC (SiO_2/hexane) R_f = 0.57; ^{1}H NMR ($CDCl_3$) δ 0.26–0.31 (m, 2 H), 0.66–0.70 (m, 2 H), 1.45–1.53 (m, 1 H), 2.48 (q, J = 7.5 Hz, 2 H), 2.70 (t, J = 7.5 1 H), 4.75 (t, J = 10.5 Hz, 1 H), 5.34 (dt, J = 7, 10.5 Hz, 1 H), 7.16–7.29 (m, 5 H); LRMS (EI) m/z (rel abund) 172 (M^+, 10), 91 ($C_7H_7^+$, 84), 81 ($M^+ - C_7H_7$, 100). Anal. Calcd for $C_{13}H_{16}$: C, 90.63; H, 9.37. Found: C, 90.41; H, 9.42.

General Reaction of a Cyclopropyl System 1 with Potassium DBB Radical Anion. Into a dried flash containing 10 equiv of potassium, cut into small pieces and washed with dry hexane, was added a solution of 1 equiv of DBB in dry THF. The reaction mixture was sonicated for 5 min at 50 °C under argon atmosphere. Into the dark green solution of the potassium DBB radical anion was added a solution of 1 equiv of 1 in THF, and the reaction mixture was sonicated at room temperature for a certain time (see Table I). The blue solution was carefully diluted with wet chloroform and quenched with 10% HCl (2 mL). The reaction mixture was washed with 10% potassium carbonate, brine, and water. The organic layer was dried over anhydrous magnesium sulfate, filtered, and evaporated to dryness. The residue was subjected to preparative TLC plates eluting with hexane to provide pure 2 (see Table I).

***cis*-1,6-Diphenyl-2,5-dibenzyl-3-hexene (2a):** white solid; mp 95–96 °C; IR (Nujol) 1580, 1595 (C=C and C=C aromatic, m); ^{1}H NMR ($CDCl_3$) δ 2.06 (dd, J = 13.0, 7.0 Hz, 4 H, benzylic H), 2.30 (dd, J = 13.0, 6.5 Hz, 4 H, benzylic H), 2.53 (m, 2 H, allylic H), 5.07 (dd, J = 7, 2 Hz, 2 H, vinylic H), 6.96 (d, J = 7 Hz, 8 H, aromatic H), 7.12 (t, J = 7.5 Hz, aromatic H), 7.22 (t, J = 7.5 Hz, 8 H, aromatic H); ^{13}C NMR ($CDCl_3$) δ 40.6 (benzylic), 41.9 (methine), 125.7 (para), 128.0 (ortho), 129.4 (meta), 132.9 (olefinic), 140.5 (ipso); HRMS calcd for $C_{32}H_{32}$ 416.2504, found 416.2531.

***cis*-1,6-Diphenyl-2,5-dibenzyl-d_4-3-hexene (2a-d_4):** white solid; mp 90–92 °C; IR (Nujol) 1580, 1595 (C=C and C=C aromatic, m); ^{1}H NMR ($CDCl_3$) δ 2.02 (d, J = 7 Hz, 2 H, benzylic H), 2.27 (d, J = 7 Hz, 2 H, benzylic H), 2.50 (dd, J = 7, 6 Hz, 2 H, allylic H), 5.06 (dd, J = 7, 1.5 Hz, 2 H, vinylic H), 6.94 (d, J = 7.5 Hz, 8 H, aromatic H), 7.11 (t, J = 7.5 Hz, 4 H, aromatic H), 7.21 (t, J = 7.5 Hz, 8 H, aromatic H); ^{13}C NMR ($CDCl_3$) δ 40.7 (benzylic), 41.8 (methine), 125.7 (para), 128.0 (ortho), 129.4 (meta), 132.9 (olefinic), 140.5 (ipso); HRMS calcd for $C_{32}H_{28}D_4$ 420.2755, found 420.2800.

***trans*-1,6-Diphenyl-2,5-dibenzyl-3-hexene (2b):** white solid; mp 72–74 °C; IR (Nujol) 1580, 1595 (C=C and C=C aromatic, m); ^{1}H NMR ($CDCl_3$) δ 2.42 (m, 8 H, benzylic H), 2.56 (m, 2 H, allylic H), 5.02 (dd, J = 4.5, 2 Hz, 2 H, vinylic H), 6.95 (d, J = 7.5 Hz, 8 H, aromatic H), 7.14 (t, J = 7 Hz, 4 H, aromatic H), 7.20 (t, J = 7.5 Hz, 8 H, aromatic H); ^{13}C NMR ($CDCl_3$) δ 41.2 (benzylic), 45.8 (methine), 125.7 (para), 128.0 (ortho), 129.3 (meta), 133.4 (olefinic), 140.5 (ipso); HRMS calcd for $C_{32}H_{32}$ 416.2504, found 416.2529.

***cis*-1-Phenyl-2-benzyl-3-hexene (2c):** colorless oil; IR (neat) 1580, 1600 (C=C and C=C aromatic, m); ^{1}H NMR ($CDCl_3$) δ 0.51 (t, J = 7 Hz, 3 H), 1.60 (m, 2 H), 2.51 (m, 2 H, benzylic H), 2.74 (m, 2 H, benzylic H), 2.93 (m, 1 H, allylic H), 5.13 (t, J = 7 Hz, 1 H, vinylic H), 5.24 (dt, J = 10.5, 7 Hz, 1 H, vinylic H), 7.04–7.25 (m, 10 H, aromatic H); ^{13}C NMR ($CDCl_3$) δ 13.8 (methyl), 20.6 (methylene), 41.3 (methine), 41.8 (benzylic), 125.7 (para), 128.0 (ortho), 129.2 (meta), 131.8 (olefinic), 132.3 (olefinic) 140.7 (ipso); HRMS calcd for $C_{19}H_{22}$ 250.1722, found 250.1730.

1-Cyclopropyl-2-benzyl-3-phenylpropane (2d): colorless oil; IR (neat) 1600 (C=C aromatic, m); ^{1}H NMR ($CDCl_3$) δ –0.01 (m, 2 H), 0.47 (m, 2 H), 0.78 (m, 1 H), 1.23 (t, J = 6.5 Hz, 2 H), 2.17 (septet, J = 7 Hz, 1 H), 2.55 (m, 2 H, benzylic H), 2.64 (m, 2 H, benzylic H), 7.20–7.25 (m, 10 H, aromatic H); ^{13}C NMR ($CDCl_3$) δ 4.8 (cyclopropyl methylene), 8.7 (cyclopropyl methine), 38.1 (methylene), 40.3 (benzylic), 42.7 (methine), 125.6 (para), 128.1 (ortho), 129.1 (meta), 141.4 (ipso); HRMS calcd for $C_{19}H_{22}$ 250.1722, found 250.1698.

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Supplementary Material Available: ^{1}H–^{1}H-NMR spectra of 2a and ^{1}H-NMR spectra for 2a, 2a-d_4, 2b, and 2c (7 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.