Trapping of Cyclopropenyl Radicals by 5,5-Dimethyl-1-pyrroline-*N*-oxide

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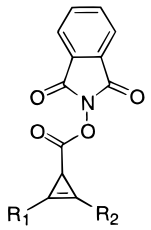
The possible generation of cyclopropenyl radicals by ultraviolet irradiation of different cyclopropenyl derivatives in fluid solution and in the presence of 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) as spin trap has been detected by electron paramagnetic resonance. The spectra consist of doublets of triplets in which the β-hydrogen splitting is larger than that of the nitrogen, in good agreement with data reported in the literature for other DMPO adducts.This methodology is unprecedented in the study of these transient radical species, and these results suggest the participation of cyclopropenyl radicals in the photosensitized decarboxylation of *N*-(2-cyclopropenylcarbonyloxy)-phthalimides.

Introduction

Recently, we reported the unexpected, almost quantitative, formation of *N*-(2-cyclopropenyl)phthalimides **2** in the photosensitized decarboxylation of *N*-(2-cyclopropenylcarbonyloxy)phthalimides **1** in the presence of a radical initiator. This reaction also occurred under thermal conditions with catalytic amounts of AIBN.[1] A



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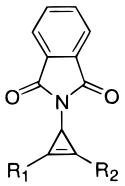


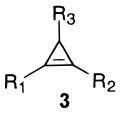
2

plausible rationalization for the formation of **2** would be the cage collapse of the cyclopropenyl and the phthalimidyl radicals prior to the trapping of the cyclopropenyl radical by H-donors. On the other hand, the putative intermediate carboxyl radical should be very short-lived to avoid the escape of the phthalimidyl radical prior to decarboxylation.

To gain some insight into this reaction, we have tried to detect by electron paramagnetic resonance (EPR) the possible occurrence of cyclopropenyl radicals. Very few reports have appeared in the literature concerning EPR investigations of these transient free radicals, and all of them are directed toward obtaining and detecting the radicals by photolysis or γ-irradiation of conveniently substituted cyclopropenes at low temperatures.[2] Only one of these reports deals with the detection by EPR of the parent cyclopropenyl radical, observed by γ-irradiation of 3-chlorocyclopropene in matrix isolation between 20 and 140 K.[2d]

As far as we know, the spin trapping technique has never been used to detect cyclopropenyl intermediates in any chemical experiment hitherto. We anticipated that the use of 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) as spin trap could be advantageous to detect the formation of transient cyclopropenyl radicals. DMPO is a particularly reactive radical scavenger and as a nitrone shows a wide reactivity toward radical additions to give persistent spin adducts with useful information derived from nitrogen and β-hydrogen splittings which appear within a broad range, facilitating the spectral interpretation.

Herein we will describe the EPR results on spin adducts of DMPO and cyclopropenyls, generated in situ starting from *N*-(2-cyclopropenylcarbonyloxy)phthalimides **1** or cyclopropenes **3**.



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a: $R_1 = C_4H_9$, $R_2 = C_5H_{11}$, $R_3 = H$
b: $R_1 = C_6H_{13}$, $R_2 = C_5H_{10}CO_2H$, $R_3 = H$
c: $R_1 = C_6H_{13}$, $R_2 = C_5H_{10}CO_2H$, $R_3 = CO_2H$
d: $R_1 = C_6H_5$, $R_2 = C_6H_5$, $R_3 = CO_2H$
e: $R_1 = C_6H_5$, $R_2 = C_6H_5$, $R_3 = CO_2Et$
f: $R_1 = C_6H_5$, $R_2 = C_6H_5$, $R_3 = H$

Results and Discussion

When benzene solutions of **1a** ($R_1 = C_5H_{11}$, $R_2 = C_4H_9$) and DMPO were irradiated with UV light, in the same cavity of the EPR spectrometer, a weak signal of a doublet of triplets was observed ($a^N = 14.75$ G, $a^{\beta-H} = 21.25$ G, $g = 2.0060$). Likewise, irradiation of **1b**[3] ($R_1 = R_2 = C_6H_5$) under the same conditions also afforded a similar EPR spectrum ($a^N = 14.5$ G, $a^{\beta-H} = 22.0$ G, $g = 2.0062$). Both spectra were consistent with putative cyclopropenyl spin adducts **4a** and **4b**, respectively.

(1) Cano, M.; Fabriàs, G.; Camps, F.; Joglar, J. *Tetrahedron Lett.* **1998**, *39*, 1079−1082.

(2) (a) Schreiner, K.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 698. (b) Closs, G. L.; Evanochko, W. T.; Norris, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 350−352. (c) Sutcliffe, R.; Lindsay, D. A.; Griller, D.; Walton, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1982**, *104*, 4674−4676. (d) Closs, G. L.; Redwine, O. D. *J. Am. Chem. Soc.* **1986**, *108*, 506−507.

(3) Compound **1b** has been prepared as described in Okada, K.; Okamoto, K.; Oda, M. *J. Am. Chem. Soc.* **1988**, *110*, 8736−8738 starting from the corresponding 2,3-diphenyl-2-cyclopropenecarboxylic acid (see Experimental Section).

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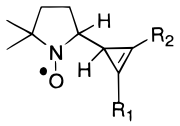


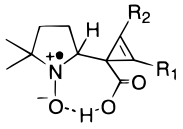
4a: $R_1=C_5H_{11}$; $R_2=C_4H_9$
4b: $R_1=R_2=C_6H_5$

Attempts to increase the formation of these radicals by photolysis in the presence of di-*tert*-butyl peroxide [4] or treatment with nickel peroxide [5] were unsuccessfully investigated.

Encouraged by those previous results and to prove the scope of this trapping reaction, we extended the EPR experiments to other cyclopropene derivatives. Thus, compounds **3a**−**f** were synthesized by well-established procedures,[6] and their photochemical behavior was investigated. Irradiation of benzene solutions of cyclopropenes **3a**−**f** in the presence of DMPO gave also the corresponding radical adducts with the EPR spectral parameters depicted in Table 1.

The spectra consist only of doublets of triplets in which the β-hydrogen splitting is larger than that of the nitrogen, in good agreement with data reported in the literature for other DMPO adducts.[7,8] The spectra of spin adducts corresponding to cyclopropenes **1b**, **3f**, and **3c** are shown in Figures 1 and 2.

Two cases deserve special mention: cyclopropenes **3c** and **3d** give rise to two spin adducts, one of them with larger splitting values especially with the β-hydrogen (see Table). Figure 3 shows the progress of the irradiation of cyclopropene **3d** monitored by EPR. Initially the spectrum of the spin adduct with "normal" splitting values appears and, as irradiation continues, the amount of this radical gradually decreases, while the amount of the radical with larger splitting values increases. The presence of this latter radical is probably due to an increase in the spin density on nitrogen as a consequence of an intramolecular H-bonding from the carboxylic hydrogen to the nitroxide oxygen, as denoted by structures **5c** and **5d**, respectively. Similar behavior has been reported for some hydroxyalkyl spin adducts of DMPO.[7a]



5c: $R_1=C_6H_{13}$; $R_2=C_5H_{10}CO_2H$
5d: $R_1=R_2=C_6H_5$

It is worth noting the concordance between the spectral parameters of the DMPO spin adducts generated from

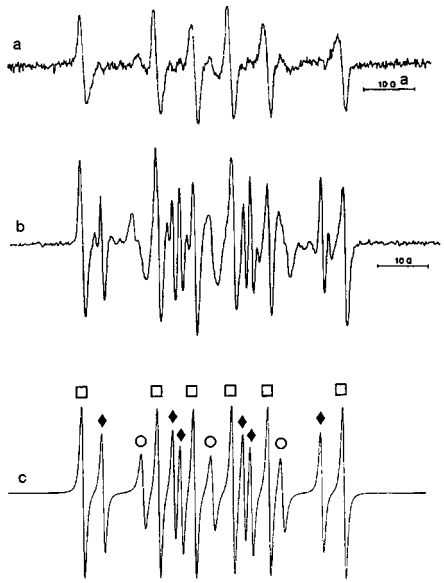


Figure 1. (a) EPR spectrum of DMPO spin adduct formed from photolysis of a benzene solution ($\sim 10^{-2}$ M) of *N*-(2-cyclopropenylcarbonyloxy)phthalimide **1b** at room temperature (microwave power, 5 mW; modulation frequency, 100 kHz; modulation amplitude, 0.5). (b) EPR spectrum of DMPO spin adduct formed from photolysis of a benzene solution ($\sim 10^{-2}$ M) of diphenylcyclopropene **3f** at room temperature.[8] (c) Computer simulation of (b) using the parameters given in the table. The signals were assigned as follows: □ is due to the adduct of cyclopropene **3f**, ♦ is due to a R-C•(=O) radical and ○ corresponds to the residual DMPO decomposition.

Table 1. EPR Spectral Parameters from Cyclopropenyl Spin Adducts Generated from the UV Irradiation of Cyclopropenes 3 with DMPO

	a^N (G)	$a^{\beta-H}$ (G)	*g*
3a	14.7	21.8	2.0062
3b	15.0	22.25	2.0062
3c	14.8	21.0	2.0059
	15.75	25.0	2.0061
3d	14.5	21.5	2.0064
	15.5	24.25	2.0060
3e	14.75	21.62	2.0061
3f	15.0	22.25	2.0060

N-(2-cyclopropenylcarbonyloxy)phthalimides **1a** and **1b** with those formed by irradiation of compounds **3a** and **3f**, respectively. This agreement suggest a common structure in both cases that implies that cyclopropenyl radicals are being trapped.

In regard to the possible mechanism of generation of these cyclopropenyl radicals, the photolytic process starting either from *N*-(2-cyclopropenylcarbonyloxy)phthalimides **1** or cyclopropenes **3** in the EPR experiments must be quite similar. In both cases, the excited states can evolve to homolytic dissociation of the C−H bond in the cyclopropenes and the weak N−O bond in the *N*-(2-cyclopropenylcarbonyloxy)phthalimides, with concomitant decarboxylation in this second case, to give the cyclopropenyls, which are then trapped by DMPO (Figure

(4) Di-*tert*-butyl peroxide is generally used to abstract hydrogen atoms to generate paramagnetic species. However, photolysis of benzene solutions of cyclopropenes and DMPO in the presence of di-*tert*-butyl peroxide gave, predominantly, the *tert*-butoxy spin adduct ($a^N = 13.62$ G, $a^{\beta-H} = 8.37$ G, and $a^{\gamma-H} = 1.87$ G, $g = 2.0061$; lit.[7a] $a^N = 13.11$ G, $a^{\beta-H} = 7.93$ G, and $a^{\gamma-H} = 1.97$ G). Owing to the strong interference of this adduct, it was very difficult to detect any other contribution from cyclopropenyl spin adducts.

(5) We tried to test nickel peroxide to remove hydrogen from cyclopropenes in the presence of either DMPO or 2-methyl-2-nitrosopropane as spin traps. However, the blank experiments gave complex spectra that made this procedure useless.

(6) Compounds **3a**−**e** have been synthesized according to the methodology described in: Quintana, J.; Barrot, M.; Fabriàs, G.; Camps, F. *Tetrahedron* **1998**, *54*, 10187−10198 and references therein. Diphenylcyclopropene **3f** was prepared as reported in: Yoshida, Z.; Miyahara, H. *Chem. Lett.* **1972**, 335−338 (see Experimental Section).

(7) (a) Janzen, E. G.; I-Ping Liu, J. *J. Magn. Reson.*, **1973**, *9*, 510−512. (b) Janzen, E. G.; Anderson Evans, C.; I-Ping Liu, J. *J. Magn. Reson.* **1973**, *9*, 513−516.

(8) In some cases, a new signal of doublets of triplets overlaps with the spectrum of the spin adduct. These new signals show similar N-splitting values and much lower β-hydrogen splittings in agreement with a DMPO spin adduct of a R−C•(=O) type. The presence of this artifact could be due to decomposition of the sample under the EPR experimental conditions.

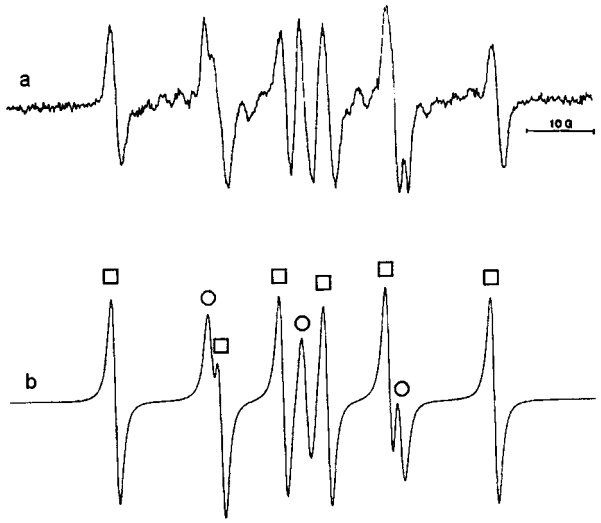


Figure 2. (a) EPR spectrum of DMPO spin adduct formed from photolysis of a benzene solution ($\sim 10^{-2}$ M) of cyclopropene **3c** at room temperature (microwave power, 5 mW; modulation frequency, 100 kHz; modulation amplitude, 0.5). (b) Computer simulation using the parameters given in the table. The signals were assigned as follows: □ is due to the adduct of cyclopropene **3c**, and ○ corresponds to the residual DMPO decomposition.

4). In no case was the spin adduct of the intermediate phthalimidyl radical observed when starting from **1**.

In conclusion, we have shown that cyclopropenyl radicals, generated by UV photolysis in benzene solutions at room temperature, can be trapped by DMPO. This methodology is unprecedented in the study of these transient radical species. These results suggest the participation of cyclopropenyl radicals in the photosensitized decarboxylation of *N*-(2-cyclopropenylcarbonyloxy)phthalimides.

Experimental Section

General Methods. Reactions sensitive to oxygen and moisture were carried out under Ar atmosphere. Unless otherwise stated, commercial grade reagents were used directly without further purification. Solvents were dried by standard methods and distilled prior to use. Purification of products by column chromatography was performed on Merck silica gel 60. TLC was carried out on precoated silica gel Merck 60 F_{254} (0.25 mm) sheets. Elemental analyses were determined on a Carlo Erba model 1106 instrument. IR spectra were recorded on a Michelson Bomem MB-120 with Fourier transform instrument and are reported in cm^{-1}. ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ solutions (unless otherwise indicated) on Varian Gemini XL200 and Varian Unity 300 spectrometers, operating at 200 and 300 MHz for ^1H and 50 and 75 MHz for ^{13}C, respectively. The chemical shifts are reported in δ units, parts per million (ppm) downfield from Me_4Si, or in ppm relative to the singlet at 7.26 ppm of $CDCl_3$ for ^1H and in ppm relative to the center line of a triplet at 77.0 ppm of $CDCl_3$ for ^{13}C.

EPR Experiments. EPR spectra were recorded with a Varian E-109 spectrometer (100 kHz modulation frequency, microwave power 0.5 mW, modulation amplitude 0.5−1 G) at room temperature. Determinations of the *g* values of the radicals were made with DPPH ($g = 2.0037$) as standard. Solutions of the appropriate cyclopropenyl derivatives and DMPO in benzene in a quartz tube were degassed by passing a stream of dry argon through the solution to remove oxygen before introduction into the cavity of the spectrometer. Irradiation of the sample directly into the cavity has been perform with an Oriel high-pressure mercury lamp (500 W),

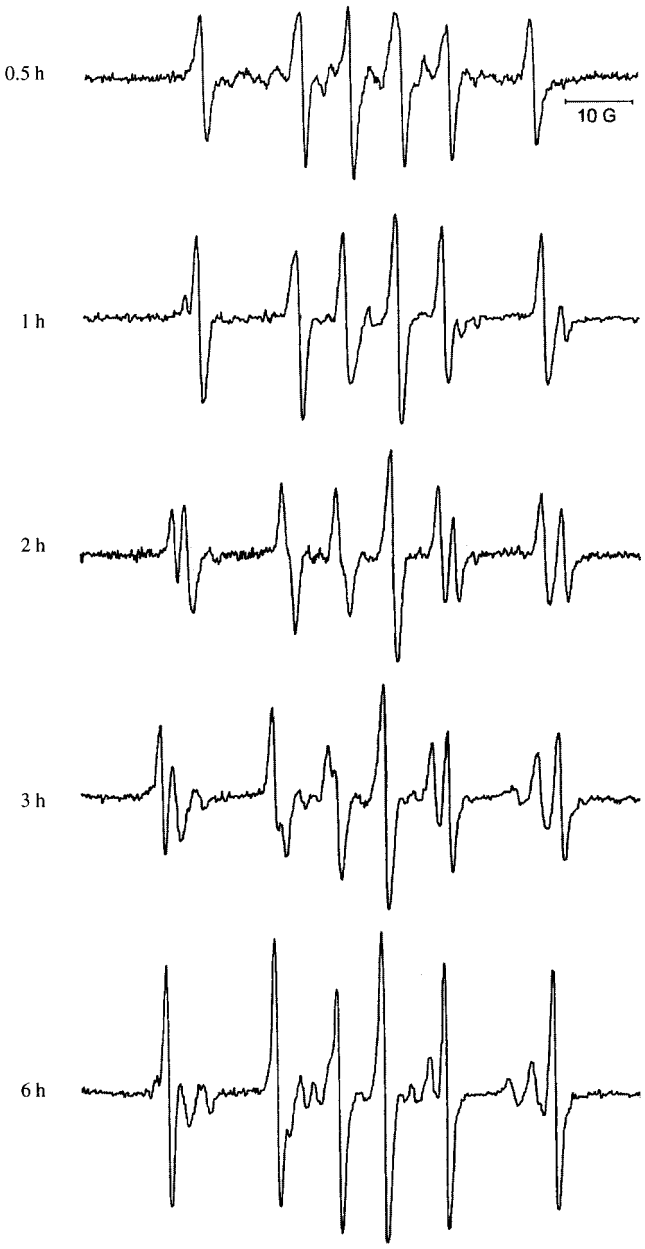


Figure 3. EPR spectra of DMPO spin adduct formed from photolysis of a benzene solution ($\sim 10^{-2}$ M) of cyclopropene **3d** at room temperature as a function of time (microwave power, 5 mW; modulation frequency, 100 kHz; modulation amplitude, 0.5).

model 68810. UV light was filtered through a continuous flux of cold water to avoid sample heating. In all cases, blank experiments with target compounds and with the spin trap in the same solvent and conditions were run to avoid incorrect results. When necessary, EPR simulations were carried out with the WINSIM program.

***N*-(2,3-Diphenyl-2-cyclopropenylcarbonyloxy)phthalimide (1b).** This compound was prepared as previously reported in ref 3 starting from 84 mg (0.36 mmol) of **3d**, 64 mg (0.39 mmol) of *N*-hydroxyphthalimide, 147 mg (0.71 mmol) of *N*,*N*-dicyclohexylcarbodiimide, and 4.3 mg (0.03 mmol) of 4-(dimethylamino)pyridine. Pure phthalimide **1b** (118 mg, 0.31 mmol, 87%) was thus obtained after flash chromatography with pentane/CH_2Cl_2 (1:1). IR (film): 2956, 1770, 1745, 1446, 1363, 1188, 1078, 964, 898, 877, 757, 698. ^1H NMR (300 MHz): 7.86−7.73 (m, 8H), 7.72−7.42 (m, 6H), 3.14 (s, 1H). ^{13}C NMR (75 MHz): 170.71 (C), 162.11 (C), 134.56 (CH), 130.04 (CH), 129.84 (CH), 129.03 (CH), 125.94 (C), 127.76 (CH),

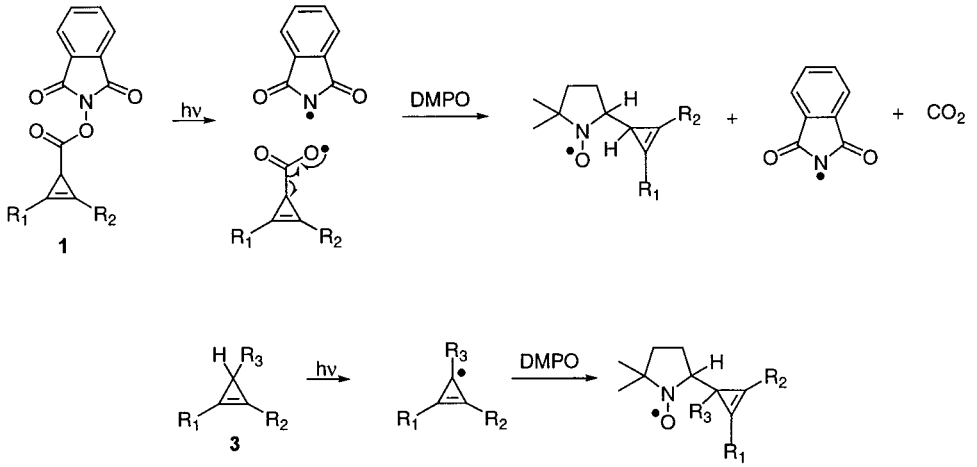


Figure 4. Plausible mechanism for the EPR generation and trapping of cyclopropenyl radicals from *N*-(2-cyclopropenylcarbonyloxy)phthalimides **1** or cyclopropenes **3**, respectively.

105.72 (C), 18.90 (CH). Anal. Calcd for $C_{24}H_{15}NO_4$: C, 75.58; H, 3.96; N, 3.67; O, 16.78. Found: C, 75.65; H, 4.09; N, 3.61.

1-Butyl-2-pentylcyclopropene (3a). This compound was prepared as previously reported in ref 6 starting from 143 mg (0.6 mmol) of ethyl 2-butyl-3-pentyl-2-cyclopropenecarboxylate. Pure cyclopropene **3a** (51,5 mg, 0.31 mmol, 52%) was thus obtained after flash chromatography with hexane/diethyl ether (9:1). IR (film): 2958, 2929, 2860, 1465, 1379, 1010. ^{1}H NMR (300 MHz): 2.38 (t, 4H), 1.60−1.48 (m, 4H), 1.36−1.22 (m, 6H), 0.94−0.82 (m, 6H), 0.77 (s, 2H). ^{13}C NMR (75 MHz): 109.37 (C), 109.32 (C), 31.61 (CH_2), 29.70 (CH_2), 29.54 (CH_2), 27.06 (CH_2), 25.73 (CH_2), 25.61 (CH_2), 22.45 (CH_2), 14.02 (CH_3), 13.84 (CH_3), 7.36 (CH_2). Anal. Calcd for $C_{12}H_{22}$: C, 86.67; H, 13.33. Found: C, 86.63; H, 13.37.

7,8-Methylene-7-tetradecenoic Acid (3b) and 7,8-Carboxymethylene-7-tetradecenoic Acid (3c). These products were prepared as described in ref 6.

2,3-Diphenyl-2-cyclopropenecarboxylic Acid (3d). Treatment of ethyl 2,3-diphenyl-2-cyclopropenecarboxylate **3e** (265 mg, 1 mmol) with a 1 N solution of KOH in THF/MeOH/H_2O (2:1:1) (20 mL) at room temperature for 48 h gave a crude that was purified by flash chromatography on deactivated silica gel to afford pure **3d** (224 mg, 95%). IR (film): 3600−3200, 3060, 3029, 2960, 2927, 1703, 1498, 1446, 1224, 757, 692. ^{1}H NMR (300 MHz): 7.73−7.65 (m, 4H), 7.54−7.35 (m, 6H), 2.81 (s, 1H). ^{13}C NMR (50 MHz): 180.03 (C), 129.96 (CH), 129.50 (CH), 128.92 (CH), 126.66 (C), 107.09 (C), 21.11 (CH). Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12; O, 13.54. Found: C, 81.53; H, 5.36.

Ethyl 2,3-Diphenyl-2-cyclopropenecarboxylate (3e). This compound was prepared as previously reported,[6] starting from 2.34 g (13.1 mmol) of diphenylacetylene, 0.5 g of activated Cu-bronze, and 2.76 mL (26.3 mmol) of ethyl diazoacetate. Pure ester **3e** (1,93 g, 7.3 mmol, 56%) was obtained after flash chromatography with hexane/ethyl acetate (95:5). IR (film): 3083, 3064, 3033, 3026, 2981, 2960, 1728, 1720, 1496, 1446, 1251, 1180, 1172, 1039, 1010, 688. ^{1}H NMR (300 MHz): 7.75−7.64 (m, 4H), 7.53−7.37 (m, 6H), 4.20 (q, 2H), 2.84 (s, 1H), 1.26 (t, 3H). ^{13}C NMR (75 MHz): 174.79 (C), 129.86 (CH), 129.22 (CH), 128.80 (CH), 127.10 (C), 107.58 (C), 60.33 (CH_2), 21.65 (CH), 14.36 (CH_3). Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10; O, 12.11. Found: C, 81.66; H, 6.24.

1,2-Diphenylcyclopropene (3f). This compound was prepared as previously reported in ref 6 starting from 1.55 g (6.77 mmol) of 1-chloro-1,2-diphenylcyclopropane. Pure 1,2-diphenylcyclopropene **3f** (975 mg, 5.07 mmol, 75%) was thus obtained after flash chromatography with hexane. IR (film): 3078, 3058, 3028, 3022, 2952, 2867, 1820, 1596, 1494, 1444, 1020, 752, 686. ^{1}H NMR (300 MHz): 7.73−7.69 (m, 4H), 7.44−7.28 (m, 6H), 1.55 (s, 2H). ^{13}C NMR (75 MHz): 130.06 (C), 129.66 (CH), 128.54 (CH), 128.14 (CH), 111.65 (C), 6.32 (CH_2). Anal. Calcd for $C_{15}H_{12}$: C, 93.71; H, 6.29. Found: C, 93.62; H, 6.38.

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Supporting Information Available: Copies of EPR spectra for the spin adducts of cyclopropene derivatives **1a**, **3a**, **3b**, **3e**, and di-*tert*-butylperoxide with DMPO. This material is available free of charge via the Internet at http://pubs.acs.org.

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