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Phenoxychlorocarbene, a Second Ambiphile

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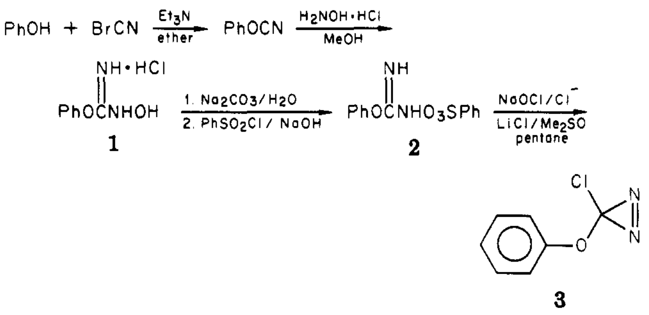
Phenoxychlorocarbene (PhOCCl) was generated by thermolysis (25 °C) of 3-chloro-3-phenoxydiazirine and added to six alkenes, affording the corresponding cyclopropanes. The substrates and (relative) reactivities were tetramethylethylene (3.0), isobutene (7.3), *trans*-2-pentene (1.00), 1-hexene (0.36), methyl acrylate (3.7), and acrylonitrile (5.5). The ambiphilic reactivity pattern of PhOCCl resembles that of MeOCCl but stands in contrast to the electrophilic reactivity patterns of MeCCl and CCl_2.

The olefinic selectivity of a carbene can often be experimentally described by a selectivity index, m_{CXY}, defined as the least-squares slope of the correlation between $\log (k_i/k_0)_{CXY}$ vs. $\log (k_i/k_0)_{CCl_2}$, where the relative reactivities (k_i/k_0) refer to additions of the carbenes to a standard set of alkenes at 25 °C.[1,2] We have also shown that m_{CXY} can be calculated from eq 1, where $\sum_{X,Y}$ represents the sum of the appropriate substituent constants for X and Y.[1,2] Using measured and calculated m_{CXY}'s, we constructed a "carbene selectivity spectrum", along which various carbenes were positioned in order of increasing m_{CXY}.[2] Examination of this spectrum revealed that experimentally nucleophilic carbenes [$(MeO)_2C$[3] and $MeOCNMe_2$[4]] had $m_{CXY} \gtrsim 2.2$, whereas typical electrophiles (CCl_2[5] and CF_2[5]) had $m_{CXY} \lesssim 1.5$.[2]

$$m_{CXY} = -1.10\textstyle\sum_{X,Y}\sigma_R^+ + 0.53\sum_{X,Y}\sigma_I - 0.31 \qquad (1)$$

An *ambiphilic* carbene can be operationally defined as one which exhibits electrophilic selectivity toward electron-rich alkenes but nucleophilic selectivity toward electron-poor alkenes. Intuitively, such species would be expected to reside in the "transitional region" of the carbene selectivity spectrum, $1.5 \lesssim m_{CXY} \lesssim 2.2$. In 1979, we showed that methoxychlorocarbene, $m_{MeOCl}^{calcd} = 1.59$, was indeed an ambiphile according to the operational definition.[6,7] More recently, the ambiphilicity of MeOCCl has been demonstrated in experiments with 6,6-dimethylfulvene and ring-substituted styrene substrates.[8,9]

Scheme I



The known electrophilic[5] carbene of highest m_{CXY} is CF_2: $m_{CXY}^{calcd} = 1.47$, $m_{CXY}^{obsd} = 1.48$.[2] It was therefore of interest that m_{CXY} for phenoxychlorocarbene, *calculated* from eq 1, was 1.49.[10] This value was essentially equal to that of CF_2 and significantly less than that of MeOCCl ($m_{CXY}^{calcd} = 1.59$).[6] We therefore wished to determine the experimental behavior of PhOCCl. Would it behave as an

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[2] Moss, R. A. *Acc. Chem. Res.* **1980**, *13*, 58.

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[4] Hoffmann, R. W.; Reiffen, M. *Chem. Ber.* **1977**, *110*, 37.

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[7] Moss, R. A.; Munjal, R. C. *Tetrahedron Lett.* **1979**, 4721. See also: Smith, N. P.; Stevens, I. D. R. *J. Chem. Soc., Perkin Trans. 2*, **1979**, 1298.

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[10] We used σ_R^+ (PhO) = -0.87, σ_R^+ (Cl) = -0.36, σ_I (PhO) = 0.38, and σ_I(Cl) = 0.46. These values come from the compilation[11] which was employed for the linear free energy analysis of the nine "basis carbenes" upon which equation 1 rests.[1] At this point, we do not feel that it is necessary to renormalize all of our data to newer σ compilations, especially as the most encyclopedic of these[12] does not contain a value for σ_R^+(PhO).

[11] Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 1.

[12] Charton, M. *Prog. Phys. Org. Chem.* **1981**, *13*, 119.

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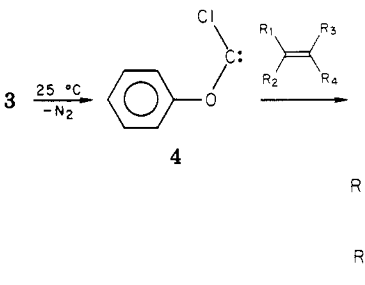
Scheme II



5a, $R_1 = R_2 = R_3 = R_4 = CH_3$
b, $R_1 = R_2 = CH_3$; $R_3 = R_4 = H$
c, $R_1 = CH_3$; $R_4 = C_2H_5$, $R_2 = R_3 = H$
d, $R_1 = n\text{-}C_4H_9$; $R_2 = R_3 = R_4 = H$
e, $R_1 = COOMe$; $R_2 = R_3 = R_4 = H$
f, $R_1 = CN$; $R_2 = R_3 = R_4 = H$

electrophile or an ambiphile? The answer would help define the "border" between electrophilic and ambiphilic carbenes and would be important to the operational differentiation of these species. In the event, phenoxychlorocarbene has proven to be the second established ambiphilic carbene.

Results

Phenoxychlorocarbene was generated from the corresponding diazirine, which was synthesized as shown in Scheme I. Phenol was converted to phenyl cyanate (86%) with cyanogen bromide. Treatment of the cyanate with methanolic hydroxylamine hydrochloride gave the *N*-hydroxyl-*O*-phenylisourea salt, **1** (84%), which was neutralized (58%) and converted to the *N*-benzenesulfonyloxy derivative **2** (47%). Subjection of **2** to Graham's oxidation[13,14] (aqueous NaOCl–Me_2SO/pentane) afforded a pentane solution of phenoxychlorodiazirine (**3**) which was chromatographed on silica gel to afford 37% of the pure, thermally unstable, pale green liquid. (The overall yield of **3** was 7.6% from phenol). Diazirine **3** exhibited λ_{max} 342 and 356 nm (ϵ ~50, both absorptions, pentane) and ν_{max} 1545 cm^{-1} (neat); these spectral properties are similar to those of representative halodiazirines.[13]

Cyclopropanes **5** were prepared by permitting **3** to thermally decompose in darkened alkene solutions over 72 h. The PhOCCl (**4**) thus generated was trapped by addition to excess tetramethylethylene, isobutene, *trans*-2-pentene, 1-hexene, methyl acrylate, or acrylonitrile (Scheme II). The cyclopropanes were isolated and purified by Kugelrohr distillations (reduced pressure) after removal of the alkenes. No attempt was made to separate the mixtures of *syn*- and *anti*-cyclopropane isomers which were present in products **5c**–**f**. The isolated yields, based on **3**, ranged from 10% (**5d**) to 40% (**5b**), and the assigned structures were substantiated by NMR spectroscopy and elemental analyses (see Experimental Section)

The relative reactivity of PhOCCl toward the several alkenes was determined by the competitive addition method.[15] Diazirine **3** was thermally decomposed (25 °C, 72 h) in binary mixtures of excess alkenes, and the product cyclopropanes were quantitatively determined by NMR or HPLC on a C-18 reverse-phase column with CH_3CN as the eluent and with UV detection at 254 nm. The products were stable to the HPLC conditions, and the detector was calibrated with known mixtures of pure products. The relative reactivity of olefin **a** vs. olefin **b** was calculated from eq 2, where P_i is the mole fraction of product cyclopropane and O_i is the initial mole fraction of an olefin.[15]

Table I. Experimentally Observed Relative Reactivities of PhOCCl (25 °C)

case	olefin a	olefin b	k_a/k_b[a, b]
1	$Me_2C{=}CH_2$	$CH_2{=}CHCOOMe$	$1.98 \pm 0.01_2$[c]
2	$Me_2C{=}CMe_2$	$CH_2{=}CHCOOMe$	$0.82 \pm 0.04_4$
3	$t\text{-}MeCH{=}CHEt$	$CH_2{=}CHCOOMe$	$0.27 \pm 0.02_6$
4	$CH_2{=}CH\text{-}n\text{-}C_4H_9$	$CH_2{=}CHCOOMe$	$0.0975 \pm 0.001_4$
5	$CH_2{=}CHCN$	$CH_2{=}CHCOOMe$	$1.50 \pm 0.06_4$
6	$CH_2{=}CH\text{-}n\text{-}C_4H_9$	$t\text{-}MeCH{=}CHEt$	0.34[d]
7	$Me_2C{=}CMe_2$	$CH_2{=}CHCN$	0.55[d]
8	$Me_2C{=}CH_2$	$Me_2C{=}CMe_2$	2.2[c,d]

[a] Where applicable, relative reactivities are based on composites of syn plus anti isomeric cyclopropane products. Products were analyzed by HPLC unless otherwise indicated. [b] Errors are average deviations from the means of *n* (subscript) experiments. [c] Analysis by quantitative NMR. [d] Single experiment.

Table II. Relative Reactivities of XCCl toward Olefins

	X in XCCl			
olefin	PhO[a]	MeO[b]	Me[c]	Cl[d]
$Me_2C{=}CMe_2$	3.0	12.6	7.44	78.4
$Me_2C{=}CH_2$	7.3	5.43	1.92	4.89
$t\text{-}MeCH{=}CHEt$[e]	1.00	1.00[f]	1.00[f]	1.00[f]
$CH_2{=}CH\text{-}n\text{-}C_4H_9$[e]	0.36			
$CH_2{=}CHCOOMe$[e]	3.7	29.7	0.078	0.060
$CH_2{=}CHCN$[e]	5.5	54.6	0.074	0.047

[a] This work, 25 °C. [b] From ref 6, 25 °C. [c] From ref 7 and 16, 25 °C. [d] From ref 7, 80 °C. [e] The overall k_{rel} is the sum of both *syn*-Cl and *anti*-Cl additions of XCCl (except for X = Cl) to this olefin. [f] The standard olefin is *trans*-butene instead of *trans*-pentene.

$$(k_a/k_b) = (P_a/P_b)(O_b/O_a) \qquad (2)$$

The experimentally determined relative reactivities of PhOCCl are collected in Table I. Reproducibility (% average deviation) is generally better than ±5%, except for case 3, where it is ±7.4%. Three cross-check experiments[15] were done to demonstrate the internal consistency of the data. From cases 4 and 3, we calculate k_{rel} (hexene-1/*trans*-2-pentene) = 0.36; the direct competition (case 6) gave 0.34. From cases 2 and 5, we calculate k_{rel} (tetramethylethylene/acrylonitrile) = 0.59; the direct competition gave 0.55 (case 7). Finally, from cases 1 and 2, we calculate k_{rel} (isobutene/tetramethylethylene) = 2.4; the direct competition gave 2.2 (case 8).

Discussion

In Table II, the experimental relative reactivities of PhOCCl (cf., Table I) are normalized to a *trans*-2-pentene standard and compared to analogous data for MeOCCl, CCl_2, and MeCCl.

It is readily apparent that PhOCCl is an ambiphile; its relative reactivities follow the trend established by ambiphilic MeOCCl, rather than the pattern of the electrophiles MeCCl and CCl_2.[2,6,7,15] PhOCCl displays a "parabolic" dependence on alkene ionization potential (approximately the energy of the alkene HOMO), reacting rapidly with electron-rich isobutene and tetramethylethylene, as well as with electron-poor methyl acrylate and acrylonitrile; its reactivity is at a minimum with the

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(15) Review: Moss, R. A. In "Carbenes"; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1973; Vol. 1, p 153 ff.

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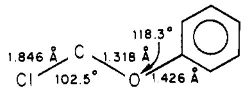
electronically "intermediate" 1-hexene. In contrast, the electrophilic carbenes display steadily decreasing reactivities as the π-electron-donating abilities of the substrates decrease; indeed, logarithms of the CCl_2 and MeCCl relative reactivities are inversely related to the ionization potentials of the substrate alkenes, indicating control by the LUMO–carbene/HOMO–alkene orbital interactions.

There are two details in which the reactivity of PhOCCl differs from that of MeOCCl. First, a plot (not shown) of log k_{rel} vs. substrate ionization potential generates a "flatter" parabola in the case of PhOCCl. This effect is also visible upon inspection of the data in Table II. Second, PhOCCl reacts less rapidly with $Me_2C{=}CMe_2$ than with $Me_2C{=}CH_2$. In this it differs from the other carbenes of Table II and, indeed, from most common carbenes, including those forming the basis set of eq 1[1,2] and the closely related PhCCl.[17] We attribute this behavior to a differential steric effect. The stabilized[18] PhOCCl adds to alkenes via a relatively tight, product-like transition state, in which repulsive PhO/Me interactions are significant. These cannot be avoided when the substrate is $Me_2C{=}CMe_2$ but are mitigated in additions to di- or monosubstituted alkenes, where the carbene selects trajectories which oppose PhO to alkenic protons. We note that similar steric problems attend the additions of lithium phenoxycarbenoid[20] and phenylsulfinylcarbene[21] to $Me_2C{=}CMe_2$. A particularly detailed steric analysis was offered in the latter case.[21]

Although the relative reactivities of CF_2 toward methyl acrylate and acrylonitrile have yet to be determined, in all alkenic additions of which we are aware, CF_2 behaves as an electrophile.[1,2,5,15] This includes additions to substituted styrenes,[5] where MeOCCl behaves as an ambiphile.[9] Thus the "border" of electrophilicity and ambiphilicity now appears to be experimentally located at $m_{CXY} \approx 1.48$–1.49, with CF_2 and the electrophiles on the lower side and PhOCCl and MeOCCl on the higher.

Frontier molecular orbital (FMO) theory has proven useful in rationalizing the "philicity" of carbenic cycloadditions.[2,6,8,9,19] This led us to make a brief FMO study of PhOCCl. The carbene's geometry was optimized at the STO-3G level,[22a] with fixed bond lengths and angles for the phenyl moiety.[22b] We obtained the geometry shown in **6**.[23] Next, using the 4-31G basis set,[24] we calculated orbital energies of −10.78 (HOMO or σ) and 2.02 eV (LUMO or p) for PhOCCl. These values are very similar to the HOMO and LUMO energies calculated for MeOCCl (−10.82 and 2.46 eV, respectively[19]), so that the ambiphilicity of PhOCCl is understandable.



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Thus, an important component defining the philicity of a carbene/alkene cycloaddition is the identity of the *smaller* of the differential orbital energies [$(E_{CXY}{}^{LU} - E_{alk}{}^{HO})$, the "electrophilic term", and $(E_{alk}{}^{LU} - E_{CXY}{}^{HO})$, the "nucleophilic term"].[2,15,19] Just as in the MeOCCl case,[6] the prescribed differential energies show that the electrophilic term is smaller and dominant for reactions of PhOCCl with $Me_2C{=}CMe_2$ or $Me_2C{=}CH_2$, whereas it is the nucleophilic term which is smaller and dominant in additions of PhOCCl to $CH_2{=}CHCOOMe$ or $CH_2{=}CHCN$.[26,27] An analogous FMO treatment applied to CCl_2 or CF_2 indicated that the carbenes added to these four alkenes in an electrophilic ($LUMO_{CXY}/HOMO_{alk}$) sense.[2]

In summary, PhOCCl ($m_{CXY}{}^{calcd} = 1.49$) behaves as an ambiphile in additions to alkenes. This result is intuitively reasonable, on the basis of an empirical correlation of carbenic selectivity[2] and is also in accord with FMO considerations.

Experimental Section

General Methods. Proton NMR spectra were normally recorded with a Varian T-60 spectrometer; chemical shifts are given in δ units, relative to internal Me_4Si and were determined in CCl_4 solution. All liquid alkenes were purchased from Aldrich Chemical Co. and distilled before use, except for *trans*-pentene (99%, Aldrich) which was used as received. Isobutene was obtained from Matheson Co. and used as furnished. Melting points are uncorrected. Microanalyses were performed by Robertson Laboratory, Florham Park, NJ.

3-Chloro-3-phenoxydiazirine (3). Phenyl cyanate was prepared in 86% yield from cyanogen bromide and phenol by the method of Vowinkel and Baese.[30] Without purification, the isocyanate was then converted to *N*-hydroxyl-*O*-phenylisourea hydrochloride (1).[31]

Hydroxylamine hydrochloride (18.5 g, 0.27 mol) was added to 200 mL of methanol in a three-necked, 1-L, round-bottomed flask equipped with a mechanical stirrer and a dropping funnel. After 5 min of stirring at 15–20 °C, 32 g (0.27 mol) of phenyl cyanate was added dropwise; the temperature was maintained at 15–20 °C. Stirring was continued for 30 min after the addition at a temperature of 30–35 °C. Then methanol was removed under reduced pressure and the resulting solid was washed twice with ether to yield 42.8 g (0.227 mmol, 91%) of 1, mp 136–137 °C (lit.[31] mp 140 °C).

Without further purification, the above hydrochloride was stirred in 50 mL of water while a solution of 1 equiv of sodium carbonate in 50 mL of water was slowly added. After the cessation of CO_2 evolution, the solid product was filtered, washed with water, and air-dried to afford 20 g (0.132 mol, 58%) of the free base corresponding to 1, mp 95–96 °C (lit.[31] mp 100 °C).

The free base (20 g, 0.132 mol) was stirred with 50 mL of water in a three-necked, 1-L, round-bottomed flask equipped with a mechanical stirrer and an addition funnel. A solution of 5.7 g (0.143 mol) of NaOH in 100 mL of water was added and stirred

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(17) Moss, R. A.; Whittle, J. R.; Freidenreich, P. *J. Org. Chem.* **1969**, *34*, 2220.

(18) Using eq 5 of ref 19, we calculate a "carbene stabilization energy" of 53.6 kcal/mol for PhOCCl on a scale where the stabilization energies of MeCCl, PhCCl, CCl_2, MeOCCl, and CF_2 are 29.3, 37.0, 26.5, 60.3, and 62.8 kcal/mol, respectively.[19]

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(23) The Cl–C–O–C dihedral angle was fixed at 180°. The rotation of the Ph group around the C(Ph)–O bond was examined between 0° and 90°. The 0° conformation was a shallow (<1 kcal/mol) minimum.

(24) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.

(25) For a more thorough discussion, including the problem of overlap, see ref 19.

(26) (a) The PhOCCl differential orbital energies (eV) for "electrophilic" and "nucleophilic" terms, respectively, are as follows: $Me_2C{=}CMe_2$, 10.29 vs. 13.05; $Me_2C{=}CH_2$, 11.26 vs. 12.97; $CH_2{=}CHCOOMe$, 12.74 vs. 11.58; $CH_2{=}CHCN$, 12.94 vs. 10.99. See ref 2, Table IV, for references and values of alkene orbital energies. (b) Note that it is arbitrary to mix experimental alkene orbital energies with calculated carbene orbital energies. In view, however, of the unavailability of experimental carbene orbital energies, the present FMO rationalization is offered for whatever didactic value it may possess.

(27) Using the HOMO and LUMO values of *trans*-butene[2] as approximations for those of *trans*-pentene and the HOMO of 1-pentene[28] and LUMO of propene[29] as approximations for the corresponding orbital energies of 1-hexene, one finds the additions of PhOCCl to *trans*-pentene and 1-hexene to be best interpreted as electrophilic (in the FMO sense).

(28) Bieri, G.; Burger, F. Heilbronner, E.; Maier, J. P. *Helv. Chim. Acta* **1977**, *60*, 2213.

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for 5 min. Then, 23.4 g (0.133 mol) of benzenesulfonyl chloride was added dropwise, with stirring, while the temperature was maintained below 20 °C. A precipitate formed during the addition. After addition, the yellow mixture was stirred for 30 min at ~13 °C and then for 45 min at 25 °C. The color changed to green. The solid was filtered, washed with water, and recrystallized from absolute ethanol to yield 18 g (62 mmol, 47%) of *N*-(benzenesulfonyloxy)-*O*-phenylisourea (**2**), mp 113–115 °C (lit.[31] mp 107–108 °C).

Oxidation of **2** was carried out by Graham's procedure.[13] A three-necked, 1-L, round-bottom flask was equipped with a mechanical stirrer, addition funnel, and thermometer. Then, 4.8 g (16.4 mmol) of **2**, 6.0 g (0.14 mol) of LiCl, 70 mL of pentane, and 70 mL of Me_2SO were added. The mixture was cooled to -5 °C and stirred for 5–10 min. A saturated solution of NaCl in 175 mL of 11% (weight) sodium hypochorite ("pool chlorine") was precooled to -10 °C and slowly added via the funnel to the stirred slurry. The temperature was maintained at -2 to -7 °C during the addition. The reaction mixture became yellow-green and was stirred for an additional 50 min at -5 °C. The mixture was poured into 200 mL of ice–water, and the pentane layer was separated. The aqueous layer was extracted twice with 50 mL of pentane, and the combined organic phases were back-washed with 100 mL of cold brine and dried over $MgSO_4$. Filtration and removal of pentane under reduced pressure gave a residual oil which was dissolved in 5–10 mL of spectrograde pentane and chromatographed on 50 g of silica gel with pure pentane as the eluent. Removal of pentane under reduced pressure gave 1.0 g (5.9 mmol, 37%) of 3-chloro-3-phenoxydiazirine (**3**) as a pale green liquid. The UV and IR properties of **3** appear above.

Synthesis of Cyclopropanes. General Procedure. Diazirine **3** (2.4–14 mmol) in pentane was placed in a screw-top Pyrex Carius tube containing a magnetic stirring bar and a large excess of the desired alkene (60–120 mmol, cooled to -78 °C in the case of isobutene). The tube was sealed, and the contents were stirred in the dark for 72 h at 25 °C. The tube was then cooled to -78 °C and opened. Excess olefin was removed under reduced pressure, and the residue was distilled on a Kugelrohr apparatus to afford the product. Yields refer to isolated products and are based upon diazirine **3**.

1-Chloro-1-phenoxy-2,2,3,3-tetramethylcyclopropane (5a). This product was formed from PhOCCl and $Me_2C{=}CMe_2$ in 32% yield and distilled at a Kugelrohr temperature of 30–32 °C (0.050 mmHg): NMR δ 1.07, 1.28 (2 s, 6 H each, Me's), 6.80–7.50 (m, 5 H, Ph). The HPLC retention time of **5a** was 7.30 min.[32] Anal. ($C_{13}H_{17}ClO$) C, H, Cl.

1-Chloro-1-phenoxy-2,2-dimethylcyclopropane (5b). This product was formed from PhOCCl and $Me_2C{=}CH_2$ in 40% yield and distilled at a Kugelrohr temperature of 32 °C (0.025 mmHg): NMR δ 1.12 (s, 2 H, CH_2), 1.18, 1.42 (2 s, 3 H each, Me's), 6.80–7.45 (m, 5 H, Ph). The HPLC retention time of **5a** was 5.70 min.[32] Anal. ($C_{11}H_{13}ClO$) C, H, Cl.

1-Chloro-1-phenoxy-*trans*-2-ethyl-3-methylcyclopropanes (5c).[33] These compounds were formed from PhOCCl and *t*-MeCH=CHEt in 20% yield and distilled at a Kugelrohr temperature of 46–47 °C (0.050 mmHg); NMR δ 0.80–1.80 (m, 10 H, alkyl and cyclopropyl H), 6.70–7.40 (m, 5 H, Ph). The HPLC retention time of **5c** was 6.86 min.[32] Anal. ($C_{12}H_{15}ClO$) C, H.

1-Chloro-1-phenoxy-2-*n*-butylcyclopropanes (5d).[33] These compounds were formed from PhOCCl and 1-hexene in 10% yield and distilled at a Kugelrohr temperature of 40 °C (0.020 mmHg); NMR δ 0.70–1.17, 1.17–1.97 (m, 12 H, alkyl and cyclopropyl H), 6.82–7.55 (m, 5 H, Ph). The HPLC retention time of **5d** was 7.60 min.[32] Anal. ($C_{13}H_{17}ClO$) C, H, Cl.

1-Chloro-1-phenoxy-2-(carbomethoxy)cyclopropanes (5e).[33] These compounds were formed from PhOCCl and methyl acrylate in 28% yield and distilled at a Kugelrohr temperature of 32 °C (0.050 mmHg): NMR δ 1.62–2.70 (m, 3 H, cyclopropyl), 3.55, 3.77 (2 s, total 3 H, *syn*- and *anti*-OCH_3's), 6.90–7.60 (m, 5 H, Ph). The HPLC retention time of **5e** was 5.00 min.[32] Anal. ($C_{11}H_{11}ClO_3$) C, H.

1-Chloro-1-phenoxy-2-cyanocyclopropanes (5f).[33] These compounds were formed from PhOCCl and acrylonitrile in 30% yield and distilled at a Kugelrohr temperature of 40 °C (0.10 mmHg): NMR δ 1.75–2.35 (m, 3 H, cyclopropyl), 6.90–7.55 (m, 5 H, Ph). The HPLC retention time of **5f** was 4.61 min.[32] Anal. ($C_{10}H_8ClON$) C, H, N.

Competition Experiments. Diazirine **3** (2–3 mmol) was added to a Carius tube containing a carefully weighed binary mixture of olefins (each present in at least a 10-fold excess). The tube was sealed, and its contents were stirred magnetically in the dark for 72 h. The tube was cooled to -78 °C and opened, and the excess olefins were removed under reduced pressure. The residue was dissolved in CH_3CN for HPLC analysis. The results are summarized in Table I. Note that in cases 1 and 8 (Table I), NMR analyses were carried out in C_6D_6 (80 MHz) and CCl_4 (60 MHz), respectively.

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Registry No. 1, 3174-89-8; **2**, 3170-96-5; **3**, 82849-43-2; **4**, 82849-44-3; **5a**, 19809-76-8; **5b**, 19809-73-5; **5c**, 82849-45-4; 5d, 82849-46-5; **5e**, 82849-47-6; **5f**, 82849-48-7; PhOCN, 1122-85-6; $H_2NOH\cdot HCl$, 5470-11-1; $PhSO_2Cl$, 98-09-9; $Me_2C{=}CMe_2$, 563-79-1; $Me_2C{=}CH_2$, 115-11-7; *t*-MeCH=CHEt, 646-04-8; 1-hexene, 592-41-6; methyl acrylate, 96-33-3; acrylonitrile, 107-13-1.

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(32) All HPLC citations refer to a Waters Associates instrument equipped with a C-18 reversed-phase, radial compression column. The eluent was CH_3CN at a flow rate of 0.7 mL/min.

(33) A *syn*-Cl/*anti*-Cl isomer mixture was present, but did not separate on reversed-phase HPLC.[32]