Reactions and Reactivity of Acyloxycarbenes

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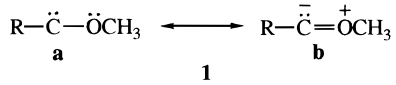
Abstract: Phenylacetoxycarbene, phenyl(pivaloyloxy)carbene, and phenyl(benzoyloxy)carbene, photolytically generated from diazirine precursors in pentane at 25 °C, efficiently rearranged by 1,2-acyl migrations to give high yields of the appropriate 1,2-diketones. The kinetics of these rearrangements were determined by laser flash photolysis. Substituent effects on the acyl migrations and ab initio electronic structure calculations on ground state carbenes and transition states were employed to analyze the rearrangement mechanism. Additions of phenylacetoxycarbene to alkenes proceeded in good yields, in lieu of the 1,2-acyl shift; absolute rate constants were obtained for these reactions of the ambiphilic carbene. (Phenoxymethyl)acetoxycarbene gave only a 1,2-H shift; the potentially competitive 1,2-acetyl migration was suppressed.

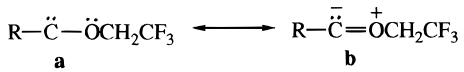
Oxa substituents profoundly affect the stability and reactivity of carbenes.[1,2] For example, the ground state of methylene is a triplet,[3] whereas that of dimethoxycarbene is a singlet, calculated to lie 76 kcal/mol below the triplet.[4] Moreover, dimethoxycarbene[2,4] and such monooxacarbenes as methylmethoxycarbene[5] or phenylmethoxycarbene[6] are strongly nucleophilic; the electrophilic character apparent in the reactions of methylene and (e.g.) the halocarbenes is suppressed.[7,8]

In theoretical terms, a strongly electron-donating substituent like MeO ($\sigma_R^+ = -0.66$)[9] raises both the LUMO and HOMO energies of a singlet carbene, making the vacant LUMO less accessible and the electrons of the HOMO more accessible, thus accentuating the nucleophilic properties of the carbene.[1,4,7] A simple resonance representation of a methoxycarbene (**1**) makes the same point through the contribution of form **1b**.[8]



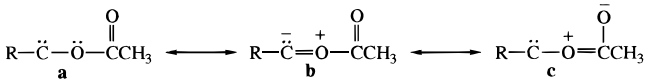
1

It should be possible to modulate the properties of oxacarbenes by "fine-tuning" the donor potential of the oxa substituent. For example, due to its inductively withdrawing trifluoromethyl moiety, the trifluoroethoxy substituent is a weaker resonance donor ($\sigma_R^+ = -0.56$),[9] so that (trifluoroethoxy)carbenes are somewhat more reactive and less nucleophilic than the corresponding methoxycarbenes.[10−12] In resonance terms, form **2b** makes a smaller contribution to the electronic distribution of (trifluoroethoxy)carbene **2** than does the analogous form **1b** to methoxycarbene **1**.



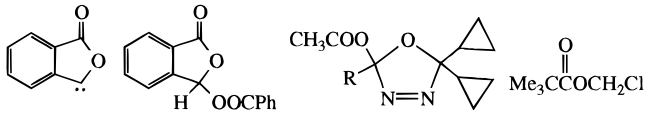
2

In this light, the acetoxy substituent assumes importance because it is a still weaker electron donor ($\sigma_R^+ = -0.26$)[13] than trifluoroethoxy, as suggested by resonance hybrid **3**, where the oxa lone pair can be delocalized over the carbonyl group (**3c**) as well as the carbene center (**3b**). Indeed, on the basis of substituent constants alone, acetoxycarbenes should be closer in reactivity to the corresponding chlorocarbenes [σ_R^+ (Cl) = -0.21][9] than to the methoxycarbenes.[14]



3

Acetoxycarbenes or, more generally, acyloxycarbenes are relatively unexplored species. The cyclic example **4** was generated in solution by photolysis of benzocyclobutene-3,4-dione[15] or in the gas phase by pyrolysis (560 °C) of benzoate **5**.[16] Flash vacuum pyrolysis of 5-acyloxy-4,6-dioxo-1,3-dioxanes gave acyloxycarbenes [eq 1; R = Me, Ph], which



4 **5** **6** **7**

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1996.

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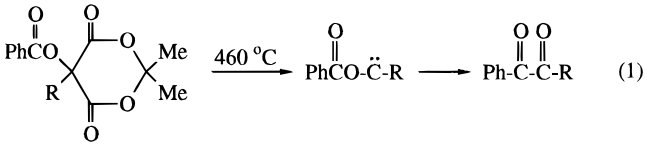
afforded diones by an apparent 1,2-acyl shift.[16−18] Analogous generation of methyl(benzoyloxy)carbene [eq 1; R = Me, 560 °C] labeled with ^{18}O at its carbonyl oxygen gave a benzoyl-labeled dione product, excluding significant oxygen scrambling during the lifetime of the carbene.[18]



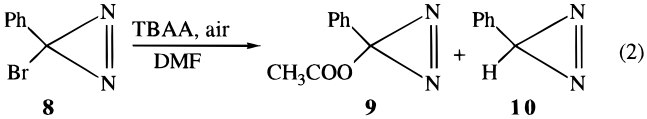
Mild thermolysis of the oxadiazolines **6** (R = Me, Et) gave methyl- and ethylacetoxycarbenes, as well as dicyclopropylcarbene.[19] Among the products were the diones expected from acetyl shifts of the acetoxycarbenes. Finally, treatment of (e.g.) the chloromethylpivalate **7** with lithium tetramethylpiperidide in refluxing alkene−ether afforded modest yields of cyclopropanes derived from pivaloylcarbene or pivaloylcarbenoid.[20]

The foregoing methods for the generation of acyclic acyloxycarbenes require high temperature, proceed in low yield, or may not involve free carbenes. Moreover, they are not suitable for the generation of acyloxycarbenes under kinetically accessible conditions. In 1994, we communicated the preparation of 3-phenyl-3-acetoxydiazirine and the generation, reactions, and associated absolute kinetics of the phenylacetoxycarbene (PhCOAc) that was photolytically derived from this precursor.[21] Now we present full details of the chemistry of PhCOAc and several related acyloxycarbenes.

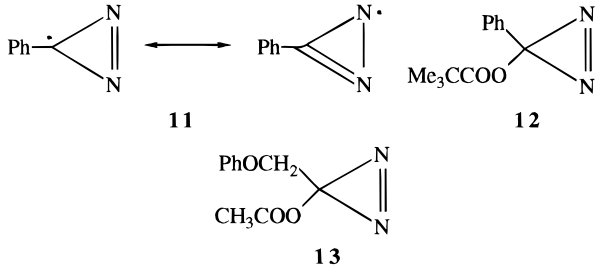
The defining intramolecular reaction of the acyloxycarbenes is the 1,2-acyl shift that affords a 1,2-dione; see, for example, eq 1.[16−19] Here we will consider the absolute rate constants and activation parameters that characterize this transformation, its structural dependence, an appropriate mechanistic formulation, and the efficiency of competitive intramolecular reactions (e.g., the 1,2-H shift). We will also describe the intermolecular reactivity and philicity toward alkenes of PhCOAc.

Results

Diazirines. The halodiazirines that are readily obtained by the hypohalite oxidation of amidines[22] can often be converted to other functionalized diazirines by a nucleophilic exchange reaction.[7,23] Indeed, stirring phenylbromodiazirine (**8**)[22] with excess tetra-*n*-butylammonium acetate (TBAA) under air in dry DMF for 20 min at 25−30 °C afforded 45% of phenylacetoxydiazirine (**9**), as well as 15% of phenyldiazirine (**10**) (eq 2),[21,24]

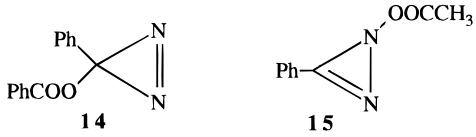


presumably via a $S_{RN}1$ mechanism of the type proposed by Creary,[25] in which the phenyldiazirinyl radical **11** is a presumptive intermediate.[24,25]



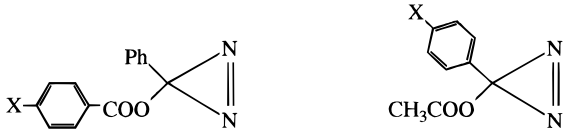
In parallel applications of eq 2, reactions of **8** with TBA (tetra-*n*-butylammonium) pivalate and of 3-(phenoxymethyl)-3-bromodiazirine[26] with TBAA gave 3-phenyl-3-(trimethylacetoxy)-diazirine (**12**, 60%) and 3-(phenoxymethyl)-3-acetoxydiazirine (**13**, 42%),[21] respectively.

The reaction of diazirine **8** with TBA *benzoate* in DMF did not give 3-phenyl-3-(benzoyloxy)diazirine (**14**); benzonitrile (presumably derived from the dimer of **11**)[27] was formed instead. Apparently, benzoate anion was not reactive enough to capture diazirinyl radical **11**, but with *both* TBA acetate and benzoate present, **8** gave 32% of acetoxydiazirine **9**, 28% of (benzoyloxy)-diazirine **14**, and 5% of phenyldiazirine **10**.[24] A similar outcome



accompanied the reaction of **8** with KOAc and potassium benzoate solubilized in DMF with 18-crown-6.[24] The requirement for acetate ion in the formation of **14** is attributed to the necessity of prior *N*-capture of radical **11** by acetate ion, with the formation of *N*-acetoxyisodiazirine (**15**), from which **14** arises by S_N2' reaction with benzoate.[25,28] (Competitive S_N2' reactions of **15** with acetate afford **9**.)

Similar "synergistic" diazirine exchange reactions of diazirine **8**, with acetate and either *p*-methyl- or *p*-methoxybenzoate ions as nucleophiles, gave 43% of 3-(*p*-methyl(benzoyloxy))-3-phenyldiazirine (**16**) or 80% of 3-(*p*-methoxy(benzoyloxy))-3-phenyldiazirine (**17**), accompanied by 25 or 7%, respectively, of acetoxydiazirine **9**. Unfortunately, electron-withdrawing group substituted benzoates (e.g., *p*-chlorobenzoate) were unable to compete with acetate ion for **15** (nor for **11**), so that only **14**, **16**, and **17** were prepared in the (benzoyloxy)phenyldiazirine series.



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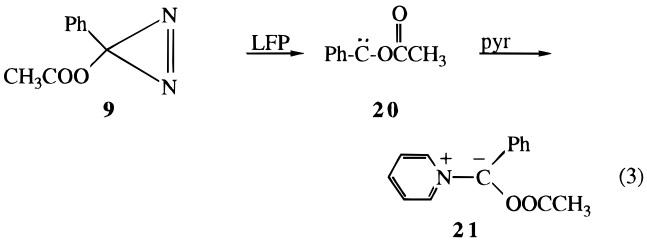
We also prepared the *p*-chloro and *p*-trifluoromethyl analogues of **9**, diazirines **18** (69%) and **19** (54%), by reactions of the appropriate arylbromodiazirine[29] with TBAA in DMF. Because these acetate−diazirine exchange reactions are initiated by electron transfer to the initial arylbromodiazirine,[24,25] electron-withdrawing groups on the aryl moiety accelerate the reaction.[24] Conversely, electron-donating substituents inhibit the process, and we could not obtain the *p*-methoxy analogue of **18** using (*p*-methoxyphenyl)bromodiazirine as the substrate. Thus, **9**, **18**, and **19** are the available representatives in the arylacetoxydiazirine series.

All of the diazirines were purified by silica gel chromatography and characterized by UV and NMR spectroscopy; details appear in the Experimental Section.

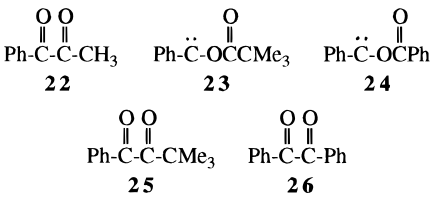
Carbene Kinetics; Ylide Formation. Laser flash photolysis (LFP)[6] at 351 nm of diazirine **9** ($A_{366} = 0.4$) at 25 °C in pentane revealed a weak absorbance at ∼310 nm for PhCOAc that was not suitable for precise kinetic study. We therefore made use of the pyridine ylide methodology:[30] LFP of **9** in pentane containing 0.0122−0.0589 M pyridine gave PhCOAc (**20**) and then ylide **21** (eq 3).[21,30]



9 **20** **21** (3)

The ylide featured a strong absorption, λ_{max} 470−480 nm, similar to the signal observed for the analogous ylide of phenylchlorocarbene at 480 nm.[30,31] From the slope of the observed linear dependence of the pseudo-first-order rate constants for the formation of **21** vs the concentration of pyridine, we obtain $k_{ylide} = (3.5 \pm 0.1) \times 10^7$ M^{-1} s^{-1} for the second order reaction between PhCOAc and pyridine.[21,31] As we indicated previously, this is a "middling" value for carbene−pyridine ylide formation, indicative of an oxacarbene of modified reactivity in accord with structure **3**.[21,31] We return to this point below.

Kinetics of Dione Formation. Photolysis of a pentane solution of diazirine **9** ($A_{366} = 0.4$) for 1 h at λ >320 nm destroyed the diazirine and afforded >90% of dione **22**, identified by NMR and GC-MS comparisons to an authentic sample.[21] A similar yield of **22** was obtained from thermolysis of **9** in pentane at 60 °C for 30 h (sealed tube).



Extrapolation of the correlation between the observed LFP rate constant of ylide formation and [pyridine] to [pyridine] = 0 gives the aggregate rate constant for all processes that destroy PhCOAc in the absence of pyridine.[30] The yield of dione exceeded 90%, and no azine formation was observed (from reaction of **9** and PhCOAc), so that we can equate the extrapolated rate constant $k_{re} = (1.3 \pm 0.2) \times 10^5$ s^{-1} (r > 0.999) with the rate constant for the rearrangement of carbene **20** to dione **22**.[32]

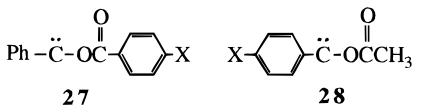
Similarly, we examined analogous reactions of phenyl(pivaloyloxy)carbene (**23**) and phenyl(benzoyloxy)carbene (**24**) with pyridine. Photolysis for 1−1.5 h of diazirines **12** ($A_{366} = 0.4$) or **14** at 25 °C ($A_{368} = 0.4$) with λ > 320 nm in pentane solutions caused the disappearance of the diazirines and the formation of diones **25** or **26**, respectively, in >90% conversion. The products were identified by NMR spectroscopy and either elemental analysis (**25**) or comparison with an authentic sample (**26**). Thermolysis of **14** in pentane (60 °C, 30 h, sealed tube) afforded >98% of benzil.

The kinetics of these rearrangements were determined by LFP using the pyridine ylide method as outlined above. For diazirine **12** and carbene **23**, [pyridine] was varied from 1.22 to 5.89 × 10^{-2} M in isooctane at 20 °C, affording the appropriate ylide which was monitored at 470 nm. From the correlation (r > 0.999), the slope $k_{ylide} = (7.4 \pm 0.1) \times 10^7$ M^{-1} s^{-1} and the intercept at [pyridine] = 0 $k_{re} = (4.9 \pm 0.5) \times 10^5$ s^{-1}. The latter can be taken as the rate constant for the 1,2-pivaloyl shift.

For diazirine **14** and PhCOOCPh (**24**), [pyridine] was varied from 0.61 to 3.01 × 10^{-2} M in isooctane at 20 °C, affording the appropriate ylide upon LFP. The correlation of k_{obsd} for ylide formation vs [pyridine] (r > 0.999) gives $k_{ylide} = (2.1 \pm 0.1) \times 10^8$ M^{-1} s^{-1} and $k_{re} = (6.7 \pm 0.7) \times 10^5$ s^{-1}, which we take as representative of the 1,2-benzoyl shift of PhCOOCPh to benzil.

Arrhenius Study of Phenyl(benzoyloxy)carbene. In precisely the same manner, k_{re} was determined for the rearrangement of carbene **24** at 253, 268, 283, and 303 K. Reaction temperatures were measured with an indwelling thermocouple connected to a digital voltmeter. The correlations of k_{obsd} for ylide formation vs [pyridine] were all good (r > 0.998) and afforded k_{ylide} values ranging from 1.6 to 2.2 × 10^8 M^{-1} s^{-1}. The rate constants for the 1,2-benzoyl shifts were 7.18 × 10^4 (253 K), 1.59 × 10^5 (263 K), 4.24 × 10^5 (283 K), 6.69 × 10^5 (293 K), and 1.14 × 10^6 s^{-1} (303 K). Errors of ∼15% are estimated for these rate constants. The corresponding Arrhenius correlation (r = 0.999) afforded the parameters $E_a = 8.4 \pm 0.2$ kcal/mol and log $A = 12.1 \pm 0.1$ s^{-1} (corresponding to $\Delta S^* = -5.0$ eu at 298 K). The "high" activation energy and small negative entropy of activation are noteworthy and will be discussed below.

Substituent Effects. In order to probe the electronic character of representative acyl shift transition states, we determined k_{re} values (in isooctane) for several substituted phenyl(benzoyloxy)carbenes and phenylacetoxycarbenes. From diazirines **14**, **16**, and **17**, using the pyridine ylide methodology, we obtained k_{re} for carbenes **27a**−**c**, whereas, from diazirines **9**, **18**, and **19**, we obtained k_{re} for carbenes **28a**−**c**.



27 **28**

a, X = H
b, X = Me
c, X = MeO

a, X = H
b, X = Cl
c, X = CF_3

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(32) For a review of the kinetics of 1,2-carbenic rearrangements, see: Moss, R. A. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; JAI Press: Greenwich, CT, 1994; Vol. 1, pp 59ff.

Table 1. Rate Constants for Acyl Shifts[a]

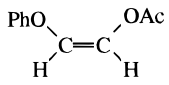
carbene	substituent	σ_p[b]	$10^5\ k_{re}\ (s^{-1})$[c]
27a[d]	H	0.00	6.69
27b	Me	−0.14	9.24
27c	MeO	−0.28	12.4
28a[e]	H	0.00	1.33
28b	Cl	0.24	2.44
28c	CF_3	0.53	2.56

[a] At 20 °C in isooctane; see text. [b] Reference 33. [c] Estimated error, ±15%. [d] Identical with **24**. [e] Identical with **20**.

Ylide signals were monitored at 470 nm at 20 °C. In each case, preparative photolysis of the diazirine in pentane gave ≥90% of the expected dione which was isolated and characterized (see Experimental Section). Each kinetic determination employed six or more pyridine concentrations, and the resulting k_{obsd} vs [pyridine] correlations had $r \geq 0.998$. The kinetic data appear in Table 1.

The k_{re} data for the substituted (benzoyloxy)carbenes **27a**−**c** correlate nicely with $\sigma_p(X)$[33] affording a Hammett $\rho = -0.96$ ($r = 0.99$). Donating substituents on the migrant benzoyl groups of **24** (**27a**) therefore mildly accelerate these benzoyl shifts. On the other hand, the data show that electron-withdrawing groups at the migration termini of the carbenes accelerate the acetyl shifts of the substituted phenylacetoxycarbenes **28a**−**c**. A satisfactory Hammett correlation is not observed, however, and the CF_3-substituted carbene **28c** rearranges more slowly than anticipated from its σ value, relative to carbenes **28a** (**20**) and **28b**. The substituent effects will be discussed below.

A Competitive 1,2-H Shift. Photolysis of diazirine **13** in pentane solution ($\lambda > 320$ nm, $A_{328} = 1.0$, 25 °C, 36 h) gave only the 1,2-H shift product alkene *cis*-**29**, expected from (phenoxymethyl)acetoxycarbene (**30**); there was no evidence for a 1,2-acetyl shift.[21] The structure of **29** was secured by NMR



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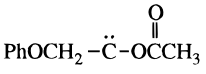

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spectroscopy, GC-MS, and elemental analysis. Its cis configuration follows from the small (3.7 Hz) vinyl H-coupling constant; a similar preference for *Z*-alkene products from the 1,2-H shifts of $PhOCH_2CX$ has been observed with X = Cl or F.[26]

LFP of diazirine **13** ($A_{328} = 0.8$) in pentane containing (1.87−6.24) × 10^{-3} M pyridine gave a strong ylide signal at 470 nm. From the slope and intercept of the correlation ($r = 0.997$, 8 points) between the rate constants for ylide growth and [pyridine], we obtained $k_{ylide} = (1.03 \pm 0.06) \times 10^9\ M^{-1}\ s^{-1}$ and $k_H = (4.1 \pm 0.3) \times 10^6\ s^{-1}$ for the 1,2-H shift of carbene **30** to alkene **29**.[21]

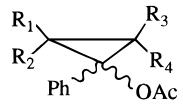
When diazirine **13** was photolyzed in acrylonitrile ($A_{328} = 1.0$, $\lambda > 320$ nm, 2 h), GC-MS showed that <1% of alkene **29** had been formed; >99% of the product mixture consisted of the isomeric 1-acetoxy-1-(phenoxymethyl)-2-cyanocyclopropanes expected from the addition of carbene **30** to acrylonitrile. The near absence of H-shift product **29**, under conditions where **30** is scavenged by an alkene, indicates that **29** stems almost exclusively from carbene **30** and not from H-shift in an excited state of the diazirine.[32]

Intermolecular Additions. Photolysis of diazirine **9** ($\lambda >$ 320 nm, 2 h, 25 °C) in trimethylethylene, isobutene, *trans*-butene, methyl acrylate, acrylonitrile, or α-chloroacrylonitrile afforded cyclopropanes **31a**−**f**, adducts of PhCOAc, in yields of 60−90%; *syn*-*anti*-cyclopropane isomers were not separated. In some cases, the cyclopropanes were further purified by preparative GC. The adducts were characterized by NMR spectroscopy, GC-MS, and either high-resolution MS or elemental analysis. Details appear in the Experimental Section.

Table 2. Experimental Relative Reactivities of PhCOAc at 25 °C[a]

case	olefin a	olefin b	k_a/k_b[b,c]
1	CH_2=CHCN	*trans*-MeCH=CHMe	15.7 ± 0.7
2	CH_2=CHCN	Me_2CH=CH_2	2.44 ± 0.03
3	CH_2=CHCN	Me_2CH=CHMe	3.56 ± 0.19
4	Me_2C=CH_2	Me_2CH=CHMe	1.44[d]

[a] See text for details. [b] Where appropriate, relative reactivities are based on composites of syn and anti isomeric cyclopropane adducts. [c] Errors are average deviations from the means of two determinations. [d] Single experiment.



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a, R_1=R_2=R_3=Me, R_4=H
b, R_1=R_2=Me, R_3=R_4=H
c, R_1=R_4=Me, R_2=R_3=H
d, R_1=COOMe, R_2=R_3=R_4=H
e, R_1=CN, R_2=R_3=R_4=H
f, R_1=CN, R_2=Cl, R_3=R_4=H

Note that the high yields of olefin adducts and the absence of dione **22** in these product mixtures signify that the dione is a product of carbene **20**; it is not formed by an acyl shift of excited diazirine **9**. The kinetics of the PhCOAc alkene addition reactions were determined by a combination of absolute and relative rate measurements. For acrylonitrile, chloroacrylonitrile, and methyl acrylate, absolute rate constants were determined by the pyridine ylide method:[21,30] diazirine **9** ($A_{366} = 0.8-1.0$) was subjected to LFP, generating PhCOAc in pentane or isooctane solutions containing a fixed concentration of pyridine (0.0247 M) and variable concentrations of acrylonitrile (0.0234−0.642 M), chloroacrylonitrile (0.0250−0.125 M), or methyl acrylate (0.214−0.808 M). Correlations of the apparent rate constants for the formation of ylide **21** as a function of alkene concentration were linear ($r > 0.998$ for 5−7 points), with slopes that were equivalent to k_{addn} for the carbene−alkene reactions. We thus obtained $k_{addn}\ (M^{-1}\ s^{-1}) = (1.20 \pm 0.09) \times 10^6$ (methyl acrylate), $(3.54 \pm 0.04) \times 10^6$ (acrylonitrile), and $(5.1 \pm 0.1) \times 10^7$ (chloroacrylonitrile) for these PhCOAc additions.

Rate constants for trimethylethylene, isobutene, and *trans*-butene were initially determined relative to acrylonitrile by standard competitive methods[34] and then converted to absolute rate constants using the k_{abs} value for acrylonitrile (determined above).

Diazirine **9** was photolytically decomposed ($\lambda > 320$ nm, 25 °C) in binary mixtures of at least 10-fold excess of alkenes. The product cyclopropanes (**31a**−**c**,**e**), which were stable to the reaction conditions, were quantitated by capillary GC using a flame ionization detector and an electronic integrator. The relative reactivity of alkene a vs alkene b was calculated from $(k_a/k_b) = (P_a/P_b)\ (O_b/O_a)$, where P_i is the mole fraction of product cyclopropane and O_i is the initial alkene mole fraction.[34] The experimentally determined relative reactivities appear in Table 2.

(33) March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992; p 280.

(34) For a review, see: Moss, R. A. In *Carbenes*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1973; Vol. 1, pp 153ff.

Reproducibilities are good; the highest uncertainty, associated with trimethylethylene, is <5.5%. A satisfactory cross check experiment[34] was performed: from cases 2 and 3 of Table 2, we calculate k_{rel} ($Me_2C{=}CH_2/Me_2C{=}CHMe$) = 1.46, and the experimentally determined value (case 4) is 1.44.

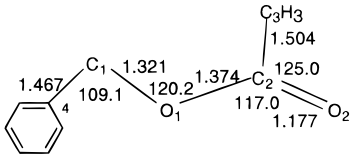
Recalling that k_{abs} for addition of PhCOAc to acrylonitrile is 3.54×10^6 M^{-1} s^{-1} (see above), the k_{rel} data of Table 2 affords k_{abs} for PhCOAc additions to trimethylethylene, isobutene, and *trans*-butene of 0.99×10^6, 1.45×10^6, and 0.23×10^6 M^{-1} s^{-1}, respectively. We estimate errors of ~10% in these values. These data will be considered further below.

Ab Initio Electronic Structure Calculations. A computational study of acyloxycarbenes was undertaken using standard ab initio electronic structure methods[35] implemented in the Gaussian 94 series of programs.[36] The calculations were made at the levels of Hartree−Fock (HF) and second order Møller−Plesset perturbation theory (MP2)[37] with STO-3G, 4-31G, and 6-31G* basis sets.[38,39]

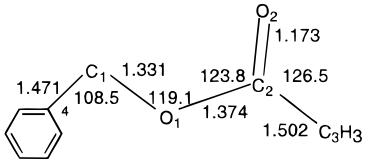
Minima on the ground state potential energy surfaces of **22**, **27a**−**c**, and **28a**−**c** and the transition states for 1,2-acyl shifts (**27aTS**−**cTS**, **28aTS**−**cTS**) or internal rotation were located[40] at the HF level with the 6-31G* split-valence plus polarization function basis set (HF/6-31G*//6-31G*). Harmonic normal mode analysis on the parent systems (**22**; **27a** and **27aTS**; **28a** and **28aTS**) characterized the located stationary points as minima or transition states and provided thermodynamic data for zero-point vibrational energy and finite temperature corrections.[35] Improved relative energies were obtained from single point MP2/6-31G* calculations at the optimized HF geometries (MP2/6-31G*//HF/6-31G*). Molecular charge distributions were partitioned into orbital and atomic charges using the techniques developed by Weinhold et al. (NBO analysis).[41]

Ground State Geometries of Acyloxycarbenes. Most structural features observed in the ground state of PhCOAc (**28a**) are representative of all carbenes considered in this computational study. Minima are found for two orientations of the COOCMe unit, corresponding to dihedral angles $C_1O_1C_2O_2 \sim 0°$ (**28a**-*Z*) or ~180° (**28a**-*E*), as illustrated by the HF/6-31G*-optimized structures shown below. Conformer **28a**-*Z* optimizes to a fully planar structure (ignoring the two H's on C_3). In **28a**-*E*, however, a small rotation occurs around the O_1-C_2 bond ($\angle C_1O_1C_2O_2 = 21.5°$), and the phenyl group is also rotated a few degrees away from coplanarity with the skeleton ($\angle C_4$-(phenyl)$C_1O_1C_2 = 176.2°$).

Conformer **28a**-*E* is lower in energy than conformer **28a**-*Z* by 2.9 kcal/mol at the MP2/6-31G*//HF/6-31G* level. The



28a-*E*



28a-*Z*

transition state separating the two conformers is located at dihedral angle $C_1O_1C_2O_2 \approx 75°$, and the barrier height is 3.0 kcal/mol above **28a**-*E* (but only 0.1 kcal/mol above **28a**-*Z*) at the MP2/6-31G*//HF/6-31G* level. At thermal equilibrium at ambient temperatures, the population ratio of *Z*/*E* conformers should thus not only be less than 1% but also, considering the small barrier separating the *Z* from the *E* minimum, it appears possible that **28a**-*Z* might not survive as a minimum at high levels of theory.[42]

Replacing Me by Ph on the acetoxy carbon (**28a** → **27a**) leads, as expected, to only very small structural changes in the C,O backbone, that is, bond lengths and bond angles in **27a**-*Z* are superimposable onto those of **28a**-*Z* to better than 0.01 Å and 1° accuracy. Both phenyl groups are oriented for optimal conjugation with the skeletal framework in **27a**-*Z* which, in addition, shows a slightly larger rotation around the O_1-C_2 bond ($\angle C_1O_1C_2O_2 = 34.4°$) than does **28a**-*Z* (21.5°). There is no minimum corresponding to a **27a**-*E* conformer, however, only a transition state for internal rotation around the O_1-C_2 bond could be located in the dihedral angle region expected for an *E* conformer ($\angle C_1O_1C_2O_2 \approx 180°$). The energy difference between **27a**-*Z* and this transition state for internal rotation is 3.3 kcal/mol (MP2/6-31G*//HF/6-31G*). The phenyl group on C_2 must rotate away from coplanarity with the carbonyl and the skeletal C,O atoms in this dihedral angle region and the loss of electronic stabilization, combined with the steric bulk of the phenyl group, presumably are the factors responsible for the absence of an *E* conformer for **27a**.

Introduction of the various substituents on the phenyls of the parent acyloxycarbenes (**27a** → **27b,c**; **28a** → **28b,c**) affects only the local phenyl geometries and does not change the ground state *E* vs *Z* conformational preference exhibited by the parent species. Thus, for **28b** and **28c** the *Z* conformers are preferred by 2.7 and 2.5 kcal/mol, respectively.

A large vertical singlet−triplet splitting was computed in **28a** ($\Delta E_{ST} \approx 100-105$ kcal/mol), and the carbenes considered here clearly all possess singlet ground states and react accordingly. The delocalization of O_1 and Ph π electrons into the formally empty carbenic p orbital leads to a destabilized, high lying carbene LUMO, whereas the σ electron-withdrawing character of O_1 stabilizes the carbene HOMO, viz., $\epsilon_{HOMO(\sigma)} = -10.13$ (9.82) eV and $\epsilon_{LUMO(p)} = 1.61(1.77)$ eV in **28a**-*E*(*Z*), −9.90 and 1.62 eV, respectively, in **27a**-*Z* (HF/4-31G//STO-3G orbital energies quoted to conform with previous usage).[1,7] On the basis of these orbital energies, we predict that **27a** and **28a** (and the related carbenes) should behave as ambiphiles in reactions

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(42) Structures **28a**−**c** and **28aTS**−**cTS** were reoptimized with electron correlation included at the MP2/6-31G* level. The MP2/6-31G*//6-31G*-optimized structures are not dramatically different from those obtained at the HF/6-31G*//6-31G* level, in particular conformer **28a**-*Z* does persist as minimum at this computational level.

with alkenes,[7,8] a prediction verified for **28a** by the experimental data (see below).

Discussion

Reactivity. Alkoxycarbenes such as RCOMe are strongly stabilized (cf., **1**) and therefore considerably less reactive and more nucleophilic than (e.g.) halocarbenes.[1−8] Moreover, the electronic and stabilizing effects of an oxa substituent can be modulated by "fine-tuning" the electronic character of the substituent. The trifluoroethoxy group, for instance, is less donating than methoxy, so that $RCOCH_2CF_3$ (cf., **2**) is a more reactive, less nucleophilic carbene than $RCOCH_3$.[10−12] Additional weakening of electron donation, coupled with decreased carbene stabilization and increased reactivity, is anticipated for acyloxy-substituted carbenes (cf., **3**),[13] and our results support this expectation.

Thus, k_{ylide} for the reaction of PhCOAc with pyridine (eq 3) is 3.5×10^7 M^{-1} s^{-1}, representing rate constant increases of 19 and 292 relative to comparable reactions of $PhCOCH_2CF_3$ (1.8×10^6 M^{-1} s^{-1}) and $PhCOCH_3$ (1.2×10^5 M^{-1} s^{-1}), respectively.[31] Note, however, that the reactivity of PhCOAc toward pyridine remains 43 times lower than that of PhCCl (1.5×10^9 M^{-1} s^{-1}), so that the deactivating properties of the resonance-donating oxa substituent persist in the acetoxy substituent, even though they are mitigated.

The reactivities of phenyl(pivaloyloxy)carbene (**23**) and phenyl(benzoyloxy)carbene (**24**) are slightly greater than that of PhCOAc, with k_{ylide} values of 7.4×10^7 and 2.1×10^8 M^{-1} s^{-1}, respectively.

The signature *intramolecular* reaction of an acyloxycarbene is its 1,2-acyl migration to afford a dione; by such rearrangements, diones **22**, **25**, and **26** arise from carbenes **20**, **23**, and **24**, respectively. The attendant rate constant (s^{-1}) are 1.3×10^5 (**20**), 4.9×10^5 (**23**), and 6.7×10^5 (**24**). Compared to many 1,2-H shifts, these acyl migrations are relatively "slow";[32] the lifetime of PhCOAc in pentane, for example, is ~8 μs. Note that steric effects do not retard the rearrangement of the pivaloyl group of **23**, which occurs 3.8 times more rapidly than the acetyl shift of PhCOAc. The rearrangement of **24** to benzil by a benzoyl shift is even faster, 5.2 times more rapid than that of PhCOAc. The acetyl shift of the latter is comparable in rate to the 1,2-C shift ring expansion of cyclopropylchlorocarbene.[32,43]

The rearrangement of PhCOOCPh (**24**) to benzil was subjected to an Arrhenius study that afforded $E_a = 8.43$ kcal/mol, log $A = 12.1$ s^{-1}, and $\Delta S^* = -5.0$ eu. The activation energy is the highest experimental value yet reported for a 1,2-carbenic rearrangement of any type;[32] 1,2-carbon shifts of cyclopropylfluorocarbene[26] and cyclopropylchlorocarbene,[43] for example, occur with $E_a = 4.2$ or 3.0 kcal/mol, respectively.[44]

Noteworthy is the near-neutral ΔS^* (−5.0 eu) determined for the PhCOOPh rearrangement. The mildly negative activation entropy is consistent with a moderate degree of ordering in the transition state and stands in contrast to the strongly negative ΔS^* values reported for other carbenic rearrangements.[32] For example, these parameters for the 1,2-H shift of methylchlorocarbene[45] and the 1,2-C shift of cyclopropylchlorocarbene[43] are −16 and −20 to −24 eu, respectively. Activation entropies this negative have been associated with H or even C tunneling, an attribution supported by calculations and (in the case of MeCCl) by a curved Arrhenius correlation of k_H vs $1/T$.[46] In this light, the mildly negative ΔS^* and linear Arrhenius behavior of PhCOOCPh (at least to −20 °C) would suggest that tunneling is unimportant in this 1,2-acyl shift near ambient temperature. Additionally, as suggested by a referee, the negative contributions to ΔS^* arising from restrictions on internal rotations that operate in 1,2-H or 1,2-C shifts would be mitigated in 1,2-acyl migrations where the migration origin is an oxygen atom, and rearrangement creates a carbonyl group rather than an alkene.

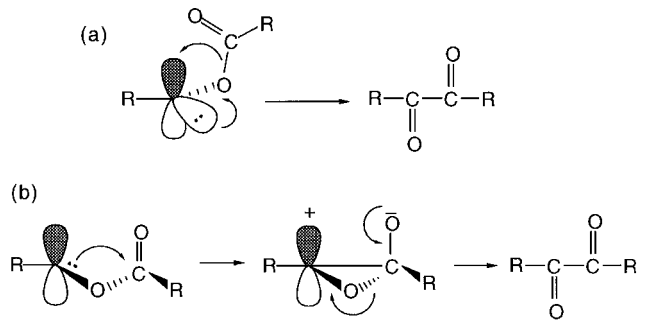

Figure 1. (a) Acylanion-like pathway for the acyloxycarbene to dione rearrangement; the "terminus" is the carbene LUMO. (b) Carbanion-like attack on the carbonyl group as an alternative pathway for the same rearrangement. The principal interaction is carbene-HOMO/carbonyl-LUMO, and the carbonyl group acquires negative charge in the transition state.

Combining relative energies (MP2/6-31G*//HF/6-31G*) with thermal and zero-point vibrational energy corrections (HF/6-31G*//6-31G*), we obtain a calculated E_a value for the 1,2-acyl shift of PhCOOCPh (**27a**-*Z*) of 5.1 kcal/mol and $\Delta S^* = -3.3$ eu, in (fortuitously?) rather good agreement with the experimental values determined above as 8.4 kcal/mol and −5.0 eu, respectively. Similarly, for the rearrangement of PhCOAc (**28a**-*E*), we obtain $E_a = 7.0$ kcal/mol and $\Delta S^* = -3.0$ eu. Viewed differently, the calculated $\Delta G^* = 6.1$ kcal/mol for PhCOOCPh, whereas the experimental data lead to $\Delta G^* \approx 9.9$ kcal/mol; for PhCoAc, the calculated $\Delta G^* = 7.8$ kcal/mol. Note that even the small difference in acyl shift rate constants between PhCOOCPh and PhCOAc (the former reacts ~5 times faster than the latter, Table 1) is qualitatively born out by the calculated ΔG^* values (6.1 vs 7.8 kcal/mol). We note also that the 1,2-acyl shift to form the dione is accompanied by a substantial release of energy. For example, the reaction **28a**-*E* → **22** is computed to be exothermic by 54.5 kcal/mol (MP2/6-31G*//HF/6-31G*).

The Transition State. A priori, we might imagine two "extreme" transition states for the 1,2-acyl rearrangement of the acyloxycarbenes. One pathway, Figure 1a, traverses an *acyl anion-like* transition state, in which the C−O bond that breaks is eclipsed with the vacant carbene p orbital or LUMO. In the transition state, analogous to that of a 1,2-hydride migration, the carbene LUMO is the migration terminus, the C−O σ-bonding pair migrates with the acyl moiety, and the carbene center should acquire negative charge. The second pathway, Figure 1b, features a *carbanion-like* attack of the carbene σ pair (HOMO) on the carbonyl LUMO (π^*). In this case, the carbonyl group would assume negative charge in the transition state.

Experimental probes of these ideas were carried out by the Hammett-type substituent variations that are summarized in Table 1. For the substituted (benzoyloxy)carbenes PhCOOCAr (**27a**−**c**), electron-donating groups modestly accelerate the acyl

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(44) However, see: Liu, M.TH.; Bonneau, R. *J. Am. Chem. Soc*. **1989**, *93*, 7298. The cyclopropylchlorocarbene 1,2-C shift is assigned $E_a = 7.4$ kcal/mol.

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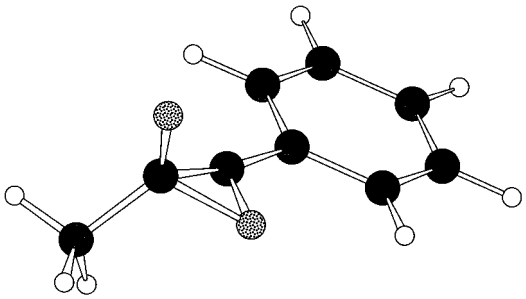
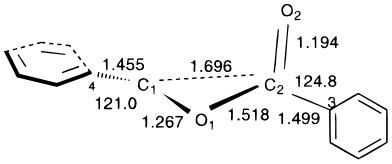


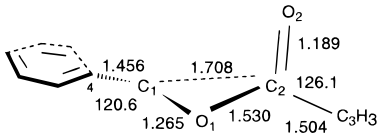
Figure 2. Perspective drawing of transition state **28aTS**; see structure for bond lengths and angles. Note that the perspective drawing is in mirror image orientation to **28aTS**.

shift ($\rho \approx -1$), which seems consistent with an acyl anion-like pathway (Figure 1a). With the arylacetoxycarbenes ArCOAc (**28a-c**), electron-withdrawing groups on the aryl moiety bonded to the migration terminus mildly accelerate the acetyl shift. These results, too, are in accord with an acyl anion-like transition state. Alternatively, it is known that electron-withdrawing groups destabilize carbenes and enhance their reactivity.[47]

Substituent effects in carbenes **27** and **28** support the acyl carbanion-like character of the 1,2-acyl migration transition state, but the picture that emerges from the computational studies seems at variance with this conclusion. Extensive searches were made to identify "rearrangement pathways A and B" (see Figure 1), but only a single transition state could be found for the 1,2-acyl shift in **27a** or in **28a**. Specifically, the transition state for 1,2-acyl shift (**27aTS**), illustrated below, is reached starting from **27a**-*Z*; both **28a**-*E*,*Z* rearrange via **28aTS** to **22**.



27aTS



28aTS

The calculated geometry for transition state **28aTS** seems more in keeping with a carbanion-like attack of the carbene s electron pair on the carbonyl LUMO (Figure 1b). The breaking C_2-O_1 bond has lengthened from 1.37 Å in the ground state of the carbene to 1.53 Å in the transition state, and the carbonyl oxygen is almost perpendicular to the central $C_1-O_1-C_2$ unit as evidenced by dihedral angle $\angle O_2C_2O_1C_1 = 104.5°$. The dissociating C_2-O_1 bond is almost orthogonal to the carbene p orbital; it is the carbonyl group which appears to eclipse the carbene LUMO in **28aTS**. These geometric features resemble our expectations for the carbanion attack pathway (Figure 1b). In the acyl anion-like pathway (Figure 1a), the dissociating C_2-O_1 bond should eclipse the carbene LUMO. Furthermore, the carbene−acyl carbon distance (C_1C_2) has decreased from 2.34 Å in **28a**-*E* (2.33 Å in **28a**-*Z*) to 1.71 Å in **28aTS**. The overall structure of **28aTS** is well-represented in the perspective drawing shown in Figure 2. Transition state **27aTS** is virtually identical to **28aTS** in all major features.

Table 3. Atomic Natural Charges (NBO Analysis, HF/6-31G*//6-31G* Level) on Essential Atoms in **27a−c** (*Z* Conformers), **27aTS−cTS**, **28a−c** (*E* Conformers), and **28aTS−cTS**

species	substituent	q (C_1)	q (O_1)	q (C_2)	q (O_2)
27a	H	0.383	−0.687	0.993	−0.628
27b	CH_3	0.383	−0.687	0.993	−0.630
27c	OCH_3	0.381	−0.686	0.995	−0.638
27aTS	H	0.500	−0.614	0.833	−0.748
27bTS	CH_3	0.500	−0.616	0.835	−0.747
27cTS	OCH_3	0.497	−0.616	0.837	−0.751
28a	H	0.336	−0.660	0.989	−0.632
28b	Cl	0.339	−0.660	0.988	−0.628
28c	CF_3	0.346	−0.659	0.988	−0.624
28aTS	H	0.478	−0.621	0.830	−0.740
28bTS	Cl	0.474	−0.622	0.834	−0.732
28cTS	CF_3	0.475	−0.620	0.835	−0.727

A population analysis shows modest negative charge buildup on the carbonyl group (C_2,O_2) and charge depletion on the carbene carbon (C_1) and O_1 occurring in the transition state relative to the ground state (Table 3). For example, there are losses of 0.14 e on C_1 and 0.04 e on O_1 between **28a** and **28aTS** and concomitant gains of 0.16 e on C_2 and 0.11 e on O_2. The changes are similar for **27a** → **27aTS** ($\Delta q(C_1) = -0.12$ e; $\Delta q(O_1) = -0.07$ e; $\Delta q(C_2) = 0.16$ e; $\Delta q(O_2) = 0.12$ e).

The modest changes in charge computed between the ground and the transition states imply that rate effects due to substituents far away from the reaction center are likely to be small. Indeed, as shown in Table 1, substituting a *p*-Cl or *p*-CF_3 group on **28a** essentially doubles the rate of the 1,2-acyl shift. The computed activation energies (MP2/6-31G*//HF/6-31G*, not corrected for zero-point and thermal energies) are 8.2_4 kcal/mol for **28a** → **28aTS**, 8.2_8 kcal/mol for **28b** → **28bTS** and 8.0_8 kcal/mol for **28c** → **28cT**. The calculations thus fail to pick up the rate increase induced by the *p*-Cl substituent.

The computed activation energies are 6.4 kcal/mol for **27a**, 6.7 kcal/mol for **27b**, and 3.9 kcal/mol for **27c**. The experimental rate data (Table 1) show an approximately 50% increase in acyl shift rate going from **27a** to **27b** and roughly a doubling of the rate going from **27a** to **27c**. Thus, the calculations again fail to properly reflect the influence of the weak substituent (Me) and perhaps overestimate the rate-enhancing effect of the OMe group. It appears that reliable prediction of relatively small energetic (rate) effects in large molecular systems like **27** and **28** may be slightly beyond the capability of the ab initio methods presently applicable to the problem.

We are troubled, but unable to explain, the apparent discrepancy between the experimental substituent effects, which seem more in keeping with expectations for an acyl anion-like rearrangement pathway, and the calculated transition states (and associated atomic charges), which appear more consonant with a carbanion-like attack on the carbonyl group.

Competitive 1,2-H Shift. Due to the strong electron donation by the methoxy substituent that mitigates the electrophilicity of the "vacant" carbene 2p orbital or LUMO (cf., **1**), typical 1,2-rearrangements involving the R group of **1** and the carbenic center are suppressed. For example, at ambient temperatures, cyclopropylmethoxycarbene does not offer ring expansion via a 1,2-C shift ($k_c < 3 \times 10^3$ s^{-1}),[48] and neither neopentylmethoxycarbene nor (phenoxymethyl)methoxycarbene afford alkenes by 1,2-H shifts ($k_{1,2\text{-H}} < 10^4$ s^{-1}).[10] However, because the acetoxy substituent is a considerably poorer electron donor than methoxy (cf., **3**), we may expect the restoration of other

(47) For example, the additions of ArCCl to various alkenes are accelerated by electron-withdrawing groups, with $\rho \approx 1.4-1.6$: Moss, R. A.; Perez, L. A.; Turro, N. J.; Gould, I. R.; Hacker, N. P. *Tetrahedron Lett.* **1983**, *24*, 685.

(48) Moss, R. A.; Jang, E. G.; Fan, H.; Wlostowski, M.; Krogh-Jespersen, K. *J. Phys. Org. Chem.* **1992**, *5*, 104.

Table 4. Absolute (and Relative) Rate Constants for Carbene Addition Reactions[a]

alkene	10^{-6} k_{abs}, M^{-1} s^{-1} (k_{rel})		
	PhCOAc[b]	PhCOMe[c]	PhCCl[d]
$Me_2C{=}CHMe$	0.99 (4.3)	0.013 (3.4)	130. (16.0)
$Me_2C{=}CH_2$	1.45 (6.3)	0.040 (10.6)	40. (5.0)
$MeCH{=}CHMe$[e]	0.23 (1.00)	0.0038 (1.00)	8.1 (1.00)
$CH_2{=}CHCOOMe$	1.20 (5.2)	0.66 (172)	5.1 (0.50)
$CH_2{=}CHCN$	3.54 (15)	1.7 (445)	5.4 (0.55)
$CH_2{=}CClCN$	51. (220)	34. (8950)[f]	210. (26)[f]

[a] At 25 °C. Relative reactivities refer to *trans*-butene. [b] This work and ref 21. [c] Data from refs 6, 7, and 50. [d] Data from refs 7 and 51. [e] *trans*-Butene is assigned $k_{rel} = 1.00$. [f] Calculated from the k_{abs} values in this table.

1,2-shifts competitive with 1,2-acyl shifts in appropriate alkylacyloxycarbenes.

(Phenoxymethyl)acetoxycarbene (**30**) provides an apposite case. As described above, it undergoes a 1,2-H shift to alkene **29** with $k_H = 4.1 \times 10^6$ s^{-1} and no evidence of a competitive acetyl shift to a dione. In contrast, the strongly donating ($\sigma_R^+ < -0.5$) methoxy and trifluoroethoxy substituents "shut off" 1,2-H shifts at ambient temperature ($k_H < 10^4$ s^{-1}), although thermal activation at 95 °C can partly restore these reactions.[10] Thus, the acetoxy substituent ($\sigma_R^+ = -0.26$)[13] permits a highly competitive 1,2-H shift at 25 °C, behavior closely resembling that of the chloro substituent ($\sigma_R^+ = -0.21$).[13]

The 1,2-acetyl shift does not successfully compete with the 1,2-H shift in $PhOCH_2COAc$ (**30**), so that here k_{acetyl} must be $<10^5$ s^{-1}. We note, however, that the phenoxymethyl substituent is particularly prone to H shifts because the phenoxy unit augments k_H by stabilizing the partial positive charge that develops at the migration origin as the hydride shift proceeds.[26] With other examples of RCOAc, the acetyl shift can compete more effectively with the H shift.[49]

Intermolecular Addition. From the absolute rate constants determined for the additions of PhCOAc to acrylonitrile, chloroacrylonitrile, and methyl acrylate, together with the relative reactivities for trimethylethylene, isobutene, and *trans*-butene (Table 2), we derived absolute rate constants for additions of PhCOAc to the latter three alkenes (see above). The k_{abs} values are collected in Table 4, together with comparable data for PhCOMe[6,50] and PhCCl.[51] For convenience, the data in Table 4 are also presented as relative rate constants, normalized to *trans*-butene.

Table 4 indicates that PhCCl can behave as an ambiphile, displaying latent nucleophilic reactivity when challenged with the very electrophilic alkene, chloroacrylonitrile.[50] However, its pronounced reactivity toward methyl-substituted alkenes such as isobutene and trimethylethylene, together with its comparatively low reactivity toward methyl acrylate and acrylonitrile, indicates that the expressed philicity of PhCCl is primarily electrophilic.[52]

Phenylmethoxycarbene presents quite a different picture. Its absolute reactivity toward alkylethylenes is 3−4 orders of magnitude less than that of PhCCl, but the reactivity increases steadily as the alkene substrates become more electron deficient. PhCOMe is therefore an ambiphile of pronounced nucleophilic character.[6,7]

Phenylacetoxycarbene, in keeping with its oxacarbene identity, more closely resembles PhCOMe than PhCCl. The acetoxycarbene is a predominantly nucleophilic ambiphile with a reactivity toward alkenes that parallels PhCOMe. However, it is clear from the absolute rate constants that PhCOAc is more reactive than PhCOMe, particularly toward the alkylethylenes. Accordingly, PhCOAc is a somewhat more "central" (less nucleophilic) ambiphile than PhCOMe. The greater intermolecular reactivity and decreased nucleophilicity of PhCOAc, relative to PhCOMe, are in keeping with the simple resonance arguments offered above and summarized in structures **1** and **3**.

The experimentally expressed ambiphilicity of PhCOAc is also in harmony with expectations based on the differential orbital energies calculated for PhCOAc−alkene frontier molecular orbital interactions.[1,7] Thus, for PhCOAc additions to trimethylethylene, isobutene, or *trans*-butene the (p−π) orbital interactions are dominant, whereas with methyl acrylate or the acrylonitriles, the (σ−π*) orbital interactions dominate.[53] The "crossover" as the substrates change from electron rich to electron poor is characteristic of ambiphilic carbenes.[1,7]

Finally, the carbene selectivity index m_{cxy} that can be calculated[8] for PhCOAc from the σ_1 and σ_R^+ constants of its substituents[9,13,21] is 0.76, similar to that of PhCCl (0.71).[8] However, as we have seen, the alkene selectivity of PhCOAc more closely resembles that of PhCOMe ($m_{cxy} = 1.34$)[6] than that of PhCCl. This agrees with our earlier observation:[7] the m_{cxy} index, which is calibrated with the selectivities of "electrophilic" carbenes, may be useful in guiding the search for ambiphilic carbenes but cannot be expected to quantitatively correlate their selectivities. For this purpose, the frontier molecular orbital approach[1,7] is much more effective.

Conclusions

Arylacyloxycarbenes undergo efficient 1,2-acyl migrations to afford 1,2-diketones with rate constants in the 10^5−10^6 s^{-1} regime (pentane, 25 °C). The rearrangement of phenyl(benzoyloxy)carbene (**24**) to benzil exhibits $E_a = 8.4$ kcal/mol, log $A = 12.1$ s^{-1}, and $\Delta S^* = -5.0$ eu (25 °C). The ab initio computed activation parameters are $E_a = 5.1$ kcal/mol and $\Delta S^* = -3.3$ eu.

Electron-withdrawing substituents in phenylacetoxycarbenes (**28**) and electron-donating substituents in phenyl(benzoyloxy)carbenes (**27**) mildly accelerate the 1,2-acyl migrations, in keeping with an acyl anion-like rearrangement pathway (Figure 1a). However, high-level ab initio calculations of ground and transition state geometries and charge distributions support a carbanion-like attack of the lone pair of the carbene on the carbonyl carbon (Figure 1b).

A 1,2-hydride shift ($k = 4.1 \times 10^6$ s^{-1}), rather than a 1,2-acyl shift, is the kinetically dominant reaction exhibited by (phenoxymethyl)acetoxycarbene (**30**).

Phenylacetoxycarbene (**20**) undergoes efficient intermolecular addition to a variety of alkenes, with rate constants ranging from 2.3×10^5 M^{-1} s^{-1} (*trans*-butene) to 5.1×10^7 M^{-1} s^{-1} (α-chloroacrylonitrile). Carbene **20** exhibits ambiphilic selectivity with a moderate nucleophilic bias, but, in line with the weaker electron-donating properties of the acetoxy vs the methoxy group, phenylacetoxycarbene is both more reactive and less nucleophilic than phenylmethoxycarbene.

(49) Moss, R. A.; Xue, S.; Ma, H. Unpublished work.

(50) Moss, R. A.; Fan, H.; Hadel, L. M.; Shen, S.; Wlostowska, J.; Wlostowski, M.; Krogh-Jespersen, K. *Tetrahedron Lett.* **1987**, *28*, 4779.

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(52) Moss, R. A.; Lawrynowicz, W.; Hadel, L. M. *Tetrahedron Lett.* **1986**, *27*, 4125.

(53) The HOMO (σ) and LUMO (p) orbital energies of PhCOAc are calculated at −10.13 and 1.61 eV, respectively (see above). The HOMO (π) and LUMO (π*) orbital energies of the alkenes can be found in ref 1 and 8. The π and π* energies of $CH_2{=}CClCN$ are −10.98 and −0.34 eV, respectively.[50]

Experimental Section

General. NMR spectra were recorded with a Varian VXR-200 spectrometer; chemical shifts for ^{1}H and ^{13}C are reported in δ units relative to TMS. For ^{19}F NMR, the chemical shifts are reported in δ units relative to $CFCl_3$. UV spectra were determined with a Hewlett-Packard Model 8451A diode array spectrometer. GC-MS spectra were recorded on an HP 5971 MSD instrument interfaced with an HP 5890 II GC spectrometer (column HP-1), and the data are reported as *m/e* (relative intensity). Capillary GC analyses employed a Varian Model 3700 flame ionization instrument, fitted with a Cp-sil 5 CB or HP-1 capillary column, and connected to a Varian Model 4270 integrator. Preparative GC employed a Varian Model 90-P unit with a 4 ft × 0.25 in. 12% SF-96 Teflon column on 60/70 Anakrom ABS. Photolyses of diazirines were carried out with a Corning 3-94 uranium glass filter (λ > 320 nm) using a focused Osram 200 W Xe mercury lamp.

Isobutene and *trans*-butene were obtained from Matheson and used as received. All other alkenes were purchased from Aldrich Chemical Co. and purified before use. Benzamidine hydrochloride was obtained from Aldrich. The preparation and properties of *p*-chloro- and (*p*-trifluoromethyl)benzamidine hydrochlorides have been described.[29]

All bromodiazirines were prepared by hypobromite oxidation (Graham's reaction[22]) of the appropriate amidine. These procedures have been described for phenylbromodiazirine (**8**) and its *p*-Cl and *p*-CF_3 derivatives.[29]

The tetrabutylammonium (TBA) salts of *p*-methylbenzoate, *p*-methoxybenzoate, and trimethylacetate were prepared from the corresponding acid by the "ion pair extraction" method.[54] A solution of 0.1 mol of the carboxylic acid in 30 mL of water was added to 26 g (0.10 mol) of 40% aqueous TBAOH (Aldrich). Then 150 mL of CH_2Cl_2 was added, and after shaking, the organic layer was separated and retained. The aqueous phase was extracted with 3 × 50 mL of CH_2Cl_2, and the combined CH_2Cl_2 solutions were dried (MgSO4), filtered, and stripped at 25 °C. The TBA salt thus obtained was dissolved in 50 mL of MeCN, and the solvent was stripped on the rotary evaporator. This drying process was repeated, and the TBA salt was dissolved in 80 mL of anhydrous DMF. The DMF volume was reduced to about 50 mL by rotary evaporation. The DMF TBA salt solution was retained for the syntheses described below.

Elemental analyses were performed by Quantitative Technologies, Inc., Whitehouse, NJ.

3-Acetoxy-3-phenyldiazirine (9). A solution of 10 g (0.033 mol) of TBA acetate in 50 mL of DMF was combined with a solution of phenylbromodiazirine (**8**) prepared from 6.0 g (0.038 mol) of benzamidine hydrochloride[22,29] and contained in 50 mL of dry DMF. The combined DMF solution was stirred under air at 25−30 °C for 20 min and then poured into a large separatory funnel that contained 1000 mL of ice cold brine and 150 mL of pentane. The pentane extract was separated, washed with 3 × 600 mL of water, and then dried over $CaCl_2$. The pentane extract was reduced to ∼2 mL, and the desired diazirine **9** was purified from accompanying phenyldiazirine (**10**) by chromatography over silica gel, using pentane−CH_2Cl_2 (4:1) as the eluent. The yield[55] of 3-acetoxy-3-phenyldiazirine was variable (∼45%) based on the bromodiazirine consumed and the reaction time. UV (pentane): 345 (sh), 364, 378 nm.[56] NMR ($CDCl_3$): 2.18 (s, 3H, Me), 6.90−7.00 (m, 2H, Ph), 7.36−7.40 (m, 3H, Ph).

3-Phenyl-3-(trimethylacetoxy)diazirine (12). In a similar manner, 50 mL of a DMF solution of phenylbromodiazirine (from 3 g, 0.019 mol, of benzamidine hydrochloride) was combined with 50 mL of DMF containing 12 g (0.035 mol) of TBA trimethylacetate and stirred at 25 °C for 1 h. A workup as for **9**, followed by analogous chromatography, afforded a pentane−CH_2Cl_2 solution of **12** in about a 60% yield, based on consumed bromodiazirine. UV (pentane): λ_{max} 366, 378 nm. NMR ($CDCl_3$): 1.27 (s, 9H, CMe_3), 6.90−6.96 (m, 2H, Ph), 7.35−7.39 (m, 3H, Ph).

3-Acetoxy-3-(phenoxymethyl)diazirine (13). Similarly, 50 mL of a DMF solution of (phenoxymethyl)bromodiazirine[26] (from 5.0 g, 0.027 mol of (phenoxymethyl)amidine hydrochloride[26]) was combined with 50 mL of DMF containing 15 g (0.050 mL) of TBA acetate and stirred under air at 21 °C for 10 min. The usual workup, followed by chromatography, gave 42% of **13**. UV (pentane): λ_{max} 328, 340 (sh) nm. The NMR is described in ref 21, note 27.

3-(Benzoyloxy)-3-phenyldiazirine (14). Potassium benzoate (1.36 g, 8.5 mmol) was dissolved in 60 mL of anhydrous DMF with the aid of 1.4 g (5.3 mmol) of 18-crown-6. This solution was combined with 40 mL of DMF containing phenylbromodiazirine[22,29] prepared from 2.5 g (1.6 mmol) of benzamidine hydrochloride. Then 0.30 g (3.1 mmol) of potassium acetate was added, and the mixture was stirred under air at 25 °C for 8 h. The usual workup afforded a pentane concentrate that contained 32% of acetoxydiazirine **9**, 28% of the desired (benzoyloxy)diazirine **14**, and 5% of phenyldiazirine **10**.[24] Diazirine **14** was purified by chromatography on silica gel (4:1 pentane−CH_2Cl_2). UV (pentane): λ_{max} 368, 380 (sh) nm. ^{1}H NMR ($CDCl_3$): 6.96−7.01 (m, 2H, Ph), 7.34−7.38 (m, 3H, Ph), 7.44−7.52 (t, 2H, J = 7.9 Hz, PhCOO), 7.60−7.68 (t, J = 7.0 Hz, 1 H, PhCOO), 8.05−8.10 (d, J = 7.9 Hz, 2H, PhCOO). ^{13}C NMR ($CDCl_3$): 55.41, 124.87, 127.99, 128.65, 128.75, 129.08, 130.22, 133.73, 134.29, 164.02.

3-(*p*-Methyl(benzoyloxy))-3-phenyldiazirine (16). Phenylbromodiazirine (**8**), prepared from 3.0 g (19 mmol) of benzamidine hydrochloride,[22,29] in 50 mL of DMF was added to 50 mL of a DMF solution of 7.9 g (21 mmol) of TBA *p*-methylbenzoate. Then 0.50 g (5.6 mmol) of KOAc was added, and the mixture was stirred under air for 5 h at 25 °C. The usual workup and chromatography gave 43% of diazirine **16**, accompanied by ∼25% of phenylacetoxydiazirine (**9**).[55] UV (pentane): λ_{max} 366, 378 nm. NMR ($CDCl_3$): 2.45 (s, 3H, Me), 6.97−7.03 (m, 2H, Ph), 7.30 (d, J = 8 Hz, 2H, ArCOO), 7.35−7.40 (m, 3H, Ph), 7.99 (d, J = 8 Hz, 2H, ArCOO).

3-(*p*-Methoxy(benzoyloxy))-3-phenyldiazirine (17). Similarly, from phenylbromodiazirine prepared from 3.0 g (19 mmol) of benzamidine hydrochloride, 11.8 g (30 mmol) of TBA *p*-methoxybenzoate and 0.50 g (5.6 mmol) of KOAc stirred in 100 mL of DMF for 2 h at 25 °C, we obtained 80% of diazirine **17**, accompanied by ∼7% of diazirine **9**. The desired **17** was purified by chromatography on silica gel (3.5:1 pentane−CH_2Cl_2). UV (pentane): λ_{max} 368, 380 (sh) nm. NMR ($CDCl_3$): 3.89 (s, 3H, MeO), 6.94−7.03 (m, 4H, ArCOO + Ph), 7.36−7.39 (m, 3H, Ph), 8.05 (d, J = 8.8 Hz, 2H, ArCOO).

3-Acetoxy-3-(*p*-chlorophenyl)diazirine (18). (*p*-Chlorophenyl)-bromodiazirine,[29] prepared from 3.0 g (16 mmol) of *p*-chlorobenzamidine hydrochloride[29] in 50 mL of DMF was added to 6.2 g (21 mmol) of TBA acetate in 50 mL of DMF. The mixture was stired for 10 min at 25 °C and then worked up as usual. Chromatography on silica gel (1:1 pentane−CH_2Cl_2) afforded 69% of diazirine **18** as well as 10% of (*p*-chlorophenyl)diazirine. UV: 347 (sh), 366 (λ_{max}), 375, 386 nm. NMR ($CDCl_3$): 1.98 (s, 3H, MeCOO), 6.78 (d, J = 8.6 Hz, 2H, Ar), 7.23 (d, J = 8.6 Hz, 2H, Ar).

3-Acetoxy-3-(*p*-(trifluoromethyl)phenyl)diazirine (19). *p*-(Trifluoromethyl)phenylbromodiazirine,[29] prepared from 3 g (13 mmol) of *p*-trifluoromethylbenzamidine hydrochloride[29] and 6.2 g (21 mmol) of TBA acetate in 100 mL of DMF were stirred for 5 min at 25 °C and then worked up as usual. The desired diazirine (**19**) was formed in 54% yield and purified by silica gel chromatography (1:1 pentane−CH_2Cl_2). *p*-(Trifluoromethyl)phenyldiazirine was also formed in 2% yield. UV (pentane): λ_{max} 358, 370 nm. NMR ($CDCl_3$): 2.17 (s, 3H, MeCOO), 7.04 (d, J = 8.3 Hz, 2H, Ar), 7.57 (d, J = 8.3 Hz, Ar).

Diones. Photolyses of the various diazirines (except for **13**) afforded dione products by 1,2-acyl migration. *General procedure:* A pentane solution (30 mL) of the diazirine, A = 0.4 at λ_{max}, was photolyzed for 1.5 − 2 h with λ > 320 nm at 25 °C. The UV spectrum showed that no diazirine remained. Removal of pentane gave the dione, which was identified either by comparison with literature data or an authentic sample or characterized by standard methods.

1-Phenyl-1,2-propanedione (**22**) was obtained in >90% yield by photolysis of diazirine **9**.[21]

1-Phenyl-3,3-dimethyl-1,2-propanedione (**25**) was obtained in >90% yield by photolysis of diazirine **12**. NMR ($CDCl_3$): 1.30 (s, 9H, CMe_3), 7.49 (t, J = 7.3 Hz, 2H, Ph), 7.64 (t, J = 7.3 Hz, 1H, Ph), 7.82 (t, J

(54) Brandstrom, A.; Berntsson, P.; Carlsson, S.; Djurhuus, A.; Gustavii, K.; Junggren, U.; Lamm, B.; Samuelsson, B. *Acta Chem. Scand.* **1969**, *23*, 2202.

(55) All diazirine yields were determined by NMR and are based on consumed bromodiazirine.

(56) In ref 21, note 18, λ_{max} of **9** is erroneously given as 336 instead of 364 nm.

= 7.3 Hz, 2H, Ph). Anal. Calcd for C, 75.7; H, 7.42. Found: C, 75.5; H, 7.06.

Benzil (**26**) was obtained in >90% yield by photolysis of diazirine **14**. It was identified by comparison with an authentic sample. Thermolysis of **14** in pentane (60 °C, 30 h, sealed tube) gave >98% of benzil.

p-Methylbenzil[57] (lit. mp 29−30 °C) was obtained in >92% yield by photolysis of diazirine **16**. GC-MS *m*/*e*: M^+ 224. NMR ($CDCl_3$): 2.48 (s, 3H, Me), 7.36 (d, J = 8.3 Hz, 2H, Ar), 7.55 (t, J = 7.1 Hz, 2H, Ph), 7.70 (t, J = 7.1 Hz, 1H, Ph), 7.92 (d, J = 8.3 Hz, 2H, Ar), 8.02 (d, J = 7.1 Hz, 2H, Ph).

p-Methoxybenzil[57] (lit. mp 64 °C) was obtained in >93% yield by photolysis of diazirine **17**. GC-MS *m*/*e*: M^+ 240. NMR ($CDCl_3$): 3.89 (s, 3H, Me), 6.98 (d, J = 9 Hz, 2H, Ar), 7.50 (t, J = 7.3 Hz, 2H, Ph). 7.65 (t, J = 7.3 Hz, 1H, Ph), 7.92−7.99 (m, 4H, 2Ar + 2Ph).

1-(p-Chlorophenyl)-1,2-propanedione[58] (lit.[57] mp 72−73 °C) was obtained in >90% yield by photolysis of diazirine **18**. GC-MS *m*/*e*: M^+ 182, 184. NMR ($CDCl_3$): 2.51 (s, 3H, Me), 7.45 (d, J = 8.6 Hz, 2H, Ar), 7.96 (d, J = 8.6 Hz, 2H, Ar).

1-(p-(Trifluoromethyl)phenyl)-1,2-propanedione[59] (mp 42−44 °C) was obtained in >90% yield by photolysis of diazirine **19**. GC-MS *m*/*e*: M^+ 216. ^{1}H NMR ($CDCl_3$): 2.57 (s, 3H, Me), 7.76 (d, J = 8.1 Hz, 2H, Ar), 8.14 (d, J = 8.1 Hz, 2H, Ar). ^{19}F NMR ($CDCl_3$): −63.78.

The photolysis of diazirine **13** afforded >90% of alkene **29**, which has been described previously.[21]

Cyclopropanes 31. General Procedure. A 30 mL pentane solution of phenylacetoxydiazirine **9** (A_{366} = 10, ∼1.6 mmol) was added to ∼100 mmol of alkene (condensed at −20 °C in the cases of isobutene and *trans*-butene). The resulting solution was photolyzed (λ > 320 nm) for 2 h at 25 °C (using a screw-top Carius tube for gaseous alkenes). Solvent and excess alkene were removed by preparative GC on a 4 ft 12% SF-96 on 60/70 Anakrom ABS column at 150 °C with 60 mL/min of He carrier gas.

1-Acetoxy-1-phenyl-2,2,3-trimethylcyclopropane (31a). Photolysis of **9** in the presence of 2-methyl-2-butene gave 81% of a 11:1 mixture of syn and anti **31a**; isomer identities are unassigned.[60] GC-MS *m*/*e*: M^+ 218 (each isomer). NMR ($CDCl_3$): major isomer, 0.95 (s, 3H, Me), 1.01 (d, J = 6 Hz, 3H, Me), 1.29 (s, 3H, Me), 0.96−1.13 (m, 1H, CH), 1.90 (s, 3H, OOCMe), 7.25−7.37 (m 3H, Ph), 7.46−7.51 (m, 2H, Ph); minor isomer, 0.75 (s, 3H, Me), 1.07 (d, $J \approx$ 6 Hz, 3H, Me), 1.16 (s, 3H, Me), 1.98 (s, 3H, Me) (Ph protons as for major isomer). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.0; H, 8.32. Found: C, 76.8; H, 8.06.

1-Acetoxy-1-phenyl-2,2-dimethylcyclopropane (31b). Photolysis of **9** in isobutene led to 86% of **31b**. GC-MS *m*/*e*: M^+ 204. NMR ($CDCl_3$): 0.80 (s, 3H, Me), 0.90 (d, J = 6.7 Hz, 1H, CH), 1.33 (s, 3H, Me), 1.34 (d, J = 6.7 Hz, 1H, CH), 1.96 (s, 3H, OOCMe), 7.23−7.36 (m, 3H, Ph), 7.41−7.46 (m, 2H, Ph). Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.4; H, 7.90. Found: C, 76.4; H, 7.66.

1-Acetoxy-1-phenyl-trans-2,3-dimethylcyclopropane (31c). Photolysis of **9** in *trans*-butene gave 60% (NMR yield) of **31c**. GC-MS *m*/*e*: M^+ 204. NMR ($CDCl_3$): 0.79 (d, J = 6.5 Hz, 3H, Me), 1.06 (q, J = 6.5 Hz, 1H, CH), 1.21 (d, J = 6.2 Hz, 1H, Me), 1.35 (q, J = 6.2 Hz, 1H, CH), 2.00 (s, 3H, OOCMe), 7.25−7.37 (m, 3H, Ph), 7.40−7.45 (m, 2H, Ph). Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.4, H, 7.90. Found: C, 76.0, H, 7.71.

1-Acetoxy-1-phenyl-2-(carbomethoxy)cyclopropane (31d). Photolysis of **9** in the presence of methyl acrylate afforded >90% of **31d** as a 2.7:1 mixture of syn and anti isomers. NMR ($CDCl_3$): major isomer, 1.63−1.72 (m, 2H, CH_2), 2.04 (s, 3H, OOCMe), 2.42 (dd, J = 7.5, 7.7 Hz, 1 H, *H*CCOOMe), 3.74 (s, 3H, COOMe), 7.2−7.6 (m, 5H, Ph); minor isomer, 1.63−1.72 (m, 2H, CH_2), 1.96 (s, 3H, OOCMe), 2.17 ("t", J = 7.5 Hz, *H*CCOOMe), 3.46 (s, 3H, COOMe), 7.2−7.6 (m, 5H, Ph). On the basis of the shielding effect of Ph relative to OAc, the major isomer is provisionally assigned the *syn*-OAc/COOMe configuration. Exact mass: calcd for $C_{13}H_{14}O_4$ 234.0891, found 234.0892.

1-Acetoxy-1-phenyl-2-cyanocyclopropane (31e). Photolysis of diazirine **9** in acetonitrile afforded ∼90% of **31e** as a 1.2:1 mixture of syn and anti isomers. NMR ($CDCl_3$, both isomers): 1.82−2.22 (m, 2H, CH_2), 2.03 (s, 3H, OOCMe, minor isomer), 2.16 (s, 3H, OOCMe, major isomer), 2.62−2.78 (m, HCCN, both isomers), 7.3−7.7 (m, 5H, Ph). Exact mass: calcd for $C_{12}H_{12}NO_2$ 202.0868, found 202.0868.

1-Acetoxy-1-phenyl-2-chloro-2-cyanocyclopropane (31f). Photolysis of diazirine **9** in α-chloroacrylonitrile afforded ∼90% of **31f** as a 1.3:1 mixture of isomers. NMR ($CDCl_3$): isomer a, 2.01 (d, J = 9.1 Hz, 1H, CH), 2.11 (s, 3H, OOCMe), 2.70 (d, J = 9.1 Hz, 1H, CH), 7.3−7.6 (m, 5H, Ph); isomer b, 2.10 (s, 3H, OOCMe), 2.32, 2.36, 2.39, 2.44 (AB, J = 8 Hz, 2H, CH_2), 7.3−7.6 (m, 5H, Ph). Exact mass: calcd for $C_{12}H_{11}ClNO_2$ ($M^+ + H^+$) 236.0478, found 236.0480.

Kinetics. Relative reactivities were determined by standard methods[34] as described in the results; experimental relative reactivities of PhCOAc toward various alkenes appear in Table 2.

Absolute rate constants for the various acyloxycarbenes were determined on our LFP installation which has been described previously.[6] The installation has been upgraded by the addition of a Tektronix TDS 520A programmable digitizer which generates a 512-point trace with a minimum resolution of 0.5 ns/point. Data were analyzed with the program Igor Pro 2.0 (WaveMatrices, Inc.). Kinetic methodology and results are extensively described above.

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