the desired anthraquinone derivative containing a 1,2-dihydroquinone moiety. However, compound 8 can be fully oxidized to the orange anthraquinone 9 by using either DDQ (benzene, reflux) or CrO_3 (AcOH/acetone, rt). A crystal structure of anthraquinone 9 (Figure 2B) showed clearly a bowed angular anthraquinone system similar to that observed in the crystal structure of triacetyl dynemicin A.[1b,14] The amount of ring bowing in this instance is similar to that seen in 8: 22.7° between the right- and left-hand aromatic rings of the anthraquinone. The average deviation of the carbonyls from the plane of the middle ring in 9 is 30.4°, which is similar to that observed in 8. Such an orientation of the carbonyls is likely derived from steric interactions of the carbonyls with *peri*-substituted groups. The difficulty in the selective oxidation of 8 may also be rationalized by the severe buttressing effects in a dihydroquinoline–anthraquinone structure. The prior removal of the carbamoyl group from 8 (structure 2A) may be necessary to achieve complete oxidation to an anthraquinone moiety.

In summary, the applicability of methods for linear anthraquinone synthesis[9,12] to the construction of the angular anthraquinone subunit of dynemicin A has been demonstrated. The DNA binding behavior of novel angular anthraquinone–quinoline systems such as 9 and the application of this chemistry to enediyne-containing molecules will be the subject of future reports from these laboratories.

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Supplementary Material Available: Complete spectral data for compounds 3–9 and crystallographic data for compound 8 and 9 (including experimental details, atomic coordinates and thermal parameters, bond distances and angles, and torsional angles) (28 pages). Ordering information is given on any current masthead page.

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(14) Anthraquinone 9 was crystallized from $CHCl_3$/isooctane as clear, orange triangular plates. An appropriately sized (~0.40 × 0.25 × 0.15 mm) single crystal was mounted with epoxy in a cold N_2 (g) stream (−30 °C) and analyzed by X-ray diffraction. Preliminary rotation and axial photos indicated only triclinic symmetry, while least-squares refinement of 20 centered diffraction maxima with $20° \le 2\theta \le 45°$ gave refined unit cell parameters: a = 7.236 (2) Å, b = 13.293 (3) Å, c = 13.868 (0) Å, α = 62.87 (2)°, β = 87.48 (2)°, and γ = 87.99 (2)°; 3234 unique reflections were collected with $0° \le 2\theta \le 115°$, of which 2874 (88.9%) were judged observed ($|F_o| \le 4.0\sigma(|F_o|)$). Examination of the complete data set showed the space group to be $P\bar{1}$ (Z = 2), a choice that was verified by successful structure solution and refinement. The structure was solved by using direct methods and the SHELX-86 package of programs. The asymmetric unit was shown to consist of a 1:1 ratio of 9 and chloroform. Refinement utilized full-matrix least squares and converged to a standard residual of 0.0793. Large, unaccounted-for electron density peaks were observed in the final difference maps at ~1 Å from the bromine and are thought to be experimentally observed lone pairs.

Solvent and Substituent Effects on the Reaction of Phenylchlorocarbene with Pyridine

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Summary: The absolute rate of reaction of phenylchlorocarbene with pyridine is not a function of solvent polarity but does respond to placement of polar substituents para to the carbene center.

We recently reported that carbenes react very rapidly with pyridine to form ylides whose long lifetimes and intense absorptions in the visible region of the electromagnetic spectrum make them ideal probes of carbene dynamics in laser flash photolysis (LFP) studies.[1] The technique has rapidly found use in the study of arylhalo-,[2] alkylhalo-,[3] alkylalkoxy-,[4] and dialkylcarbenes.[5] A probe method is used to determine rate constants for a carbene reaction with substrates when neither the carbene nor the substrate is capable of generating a useful signal. A probe that is insensitive to solvents and substituent effects is particularly useful because it allows study of the substrate of interest rather than the probe itself. For this reason we felt it necessary to systematically study the effect of solvent polarity and substituent on the absolute rate of ylide formation with a representative carbene.

Table I. The Effect of Solvent upon the Absolute Rate Constant for Reaction of Phenylchlorocarbene with Pyridine at 293 K

solvent	ϵ[9]	k (M^{-1} s^{-1})
hexane	1.89	(7.56 ± 0.93) × 10^8
toluene	2.38	(3.74 ± 0.38) × 10^8
ethyl acetate	6.02	(2.94 ± 0.36) × 10^8
α,α,α-trifluorotoluene	9.18	(4.20 ± 0.32) × 10^8
o-dichlorobenzene	9.93	(5.37 ± 0.64) × 10^8
2-butanone	18.5	(4.73 ± 1.06) × 10^8
propionitrile	27	(3.58 ± 0.35) × 10^8
acetonitrile	36.2	(3.94 ± 0.40) × 10^8
sulfolane	44	(2.90 ± 0.30) × 10^8

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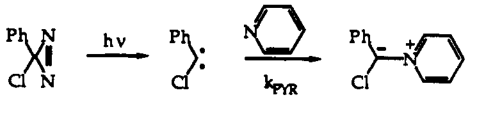
Table II. Substituent Effect on Rate of Reaction of Phenylchlorocarbenes with Pyridine in Toluene at 293 K

para substituent	k (M^{-1} s^{-1})	k_{rel}	k (M^{-1} s^{-1}) TME[6,10]
MeO	$(2.92 \pm 0.36) \times 10^7$	0.08	1.4×10^7
H	$(3.74 \pm 0.38) \times 10^8$	1.0	2.8×10^8
NO_2[a]	$(2.26 \pm 0.37) \times 10^9$	6.04	2.9×10^9

[a] A value of the rate constant of the pyridine reaction of 7.5×10^9 M^{-1} s^{-1} has been reported previously, see ref 10.

LFP of diazirine 1 produces phenylchlorocarbene 2 (λ = 318 nm).[6] LFP of diazirine 1 in toluene, in the presence of pyridine, produces ylide 3 with λ_{max} = 480 nm.[1]

(1)



1 2 3

The ylide is formed in an exponential process following the laser flash, which can be analyzed to yield a pseudo-first-order rate constant k_{obsd}. The observed rate constant is related to k_{PYR} as

$$k_{obsd} = k_o + k_{PYR}[PYR]$$

where k_0 is the sum of all pseudo-first-order and first-order rate constants of reactions which consume the carbene in the absence of pyridine.[7,8] Typically these processes include reaction of the carbene with traces of water and the diazirine precursor. The value of k_{PYR} is obtained from the slope of a plot of k_{obsd} versus [pyridine].[7,8] Values of k_{PYR} as a function of solvent polarity are given in Table I. It can be seen that k_{PYR} is rather insensitive to solvent polarity, and in fact the largest rate constant was found in hexane. These results are very similar to the small solvent effects observed in the reaction of PCC with alkenes.[6] Substitution of the aromatic moiety of the carbene

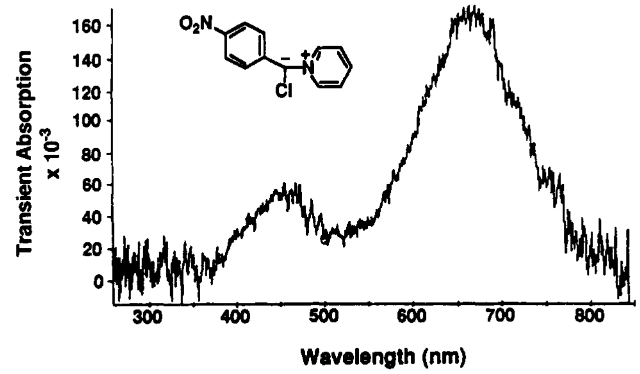
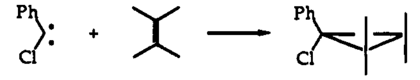


Figure 1. Transient optical density spectrum of the pyridinium ylid of *p*-nitrophenylchlorocarbene in acetonitrile at ambient temperature, taken 400 ns after the laser pulse. The band at 440 nm has been attributed to ylide formation between p-nitrophenylchlorocarbene and acetonitrile.

(2)



influences the absolute rates of reactions 1 and 2 in a similar manner (Table II). Thus, the data indicates that the rate of reaction of PCC with pyridine to form an ylide is probably governed by the same types of HOMO-LUMO interactions which Moss and Houk have demonstrated control the rates of cyclopropanation reactions of arylhalocarbenes.[6]

Finally it is interesting to note that *p*-methoxy substitution has only a modest effect on the UV spectrum of the arylhalopyridinium ylid (λ_{max} = 460 nm), but λ_{max} of the *p*-nitro derivative is shifted to a very long wavelength (λ_{max} = 665, Figure 1), longer in fact than has been reported previously.[10]

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Registry No. Phenylchlorocarbene, 19807-41-1; pyridine, 110-86-1; 4-methoxypyridine, 620-08-6; 4-nitropyridine, 1122-61-8; 4-methoxyphenylchloropyridinium ylid, 122277-66-1; 4-nitrophenylchloropyridinium ylid, 125208-12-0.

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