crease in rate of the reaction in cases where there is an electron-donating substituent on the phenyl ring or an alkyl substituent α to the hydroxyl group, as described earlier, also suggests a carbocation character.

The formation of sulfides using this procedure is not restricted to the use of alcohols α to a phenyl ring. As can be seen in Table III, allylic alcohols reacted just as well, leading to the corresponding sulfides. As one can see (entries 2 and 3, Table III), the reaction proceeds smoothly, in high yields, but the rate of reaction is significantly lower than in the cases of alcohols activated by an aromatic group.

It is interesting to note that the regioselectivity of the displacement involved when 1-buten-3-ol is treated with thiophenol (entry 3, Table III) to give [(2-butenyl)thio]benzene involves formally a $S_N 2'$ process in that case. No reaction was noted when aliphatic alcohol was used (entry 5).

In conclusion, the reaction of thiols with activated alcohols in the presence of zinc iodide represents a general, simple, efficient, and useful approach to the synthesis of thioethers, particularly when sensitive substrates preclude the use of bases or basic anions.

Experimental Section

In a typical procedure, dried zinc iodide (0.5 mmol) was added to a solution of 1-phenyl-1-pentanol (1 mmol) in dry 1,2-dichloroethane (2 mL). To the obtained suspension was added thiophenol (1.2 mmol), and the mixture was stirred at room temperature for 40 min during which the reaction was completed. The reaction was quenched with water (10 mL), and the reaction products worked up by extraction with dichloromethane (2×10) mL). The combined organic extracts were washed with brine and dried over Na_2SO_4 from which solvent was evaporated at reduced pressure. The residue was chromatographed in a column of silica gel (70-230 mesh), eluting with 1:100 ethyl acetate-hexane to afford [1-(phenylthio)pentyl]benzene (91%).

Excess thiol can be washed out during the workup by treatment with 1 N NaOH if desired.

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Registry No. Benzyl alcohol, 100-51-6; 1-phenyl-1-pentanol, 583-03-9; (S)- α -phenethyl alcohol, 1445-91-6; 2-phenyl-2-propanol, 617-94-7; p-methoxybenzyl alcohol, 105-13-5; 1-(p-methoxyphenyl)-1-pentanol, 19523-03-6; methyl p-(1-hydroxyethyl)benzoate, 84851-56-9; 1-butanethiol, 109-79-5; methyl 3mercaptopropionate, 2935-90-2; 3-mercaptopropanamide, 763-35-9; thiophenol, 108-98-5; methyl p-mercaptobenzoate, 6302-65-4; p-bromothiophenol, 106-53-6; p-mercaptophenol, 637-89-8; pthiophenol, 1193-02-8; 3-phenylallyl alcohol, 104-54-1; crotyl alcohol, 6117-91-5; 1-buten-3-ol, 598-32-3; 2-thiophenemethanol, 636-72-6; 1-pentadecanol, 629-76-5; benzyl phenyl sulfide, 831-91-4; [(1-phenylpentyl)thio]benzene, 68602-14-2; (R)- α -methylbenzyl phenyl sulfide, 40390-78-1; α, α -dimethylbenzyl phenyl sulfide, 4148-93-0; 1-methoxy-4-[(phenylthio)methyl]benzene, 5023-67-6; 1-methoxy-4-[1-(phenylthio)pentyl]benzene, 60702-18-3; methyl 4-[1-(phenylthio)ethyl]benzoate, 84851-57-0; [(1-phenylpentyl)thio]butane, 84851-58-1; methyl 3-[(1-phenylpentyl)thio]propionate, 84851-59-2; 3-[(phenylpentyl)thio]propanamide, 84851-60-5; methyl 4-[(1-phenylpentyl)thio]benzoate, 84851-61-6; 1-bromo-4-[(1-phenylpentyl)thio]benzene, 84851-62-7; 1-hydroxy-4-[(1-phenylpentyl)thio]benzene, 84851-63-8; 1phenyl-3-(phenylthio)-1-propene, 10276-14-9; 2-butenyl phenyl sulfide, 702-04-5; 2-[(phenylthio)methyl]thiophene, 69639-48-1; zinc iodide, 10139-47-6.

Supplementary Material Available: Full NMR data, chemical analyses, and melting points for compounds listed in Tables I-III are available (4 pages). Ordering information is given on any current masthead page.

Absolute Rate Constants for the Reactions of Some Arylchlorocarbenes with Acetic Acid^{1a}

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Carbene chemistry has traditionally been investigated by using product studies,² which have frequently been combined with assumptions about the multiplicity of the reacting carbene.³ Consequently, the vast majority of kinetic measurements have yielded only relative rate constants.

Absolute rate constants have been measured for a few reactions of carbenes by using flash photolysis techniques.⁴⁻¹² These studies have so far centered on the reactions of carbenes with aromatic substituents, which facilitate optical detection, i.e., diphenylcarbene,^{4,5} fluorenylidene, \hat{b}^{-11} phenylchlorocarbene, 12 and 1-naphthyl-carbene. The substrates of these studies have been mostly olefins, alcohols, or ketones. No absolute rate constants have been reported for the reactions of any carbenes with acids. In this paper we report the first measurements of this type. In particular, we have examined the reaction of singlet phenylchlorocarbene (Ia) and *p*-anysilchlorocarbene (Ib) with acetic acid.



The carbenes were generated by laser excitation of solutions of the corresponding diazirines^{14,15} (which in contrast with diazo compounds are not acid sensitive) by using the pulses (337.1 nm, \sim 8 ns, up to 10 mJ) from a nitrogen laser. The resulting transient absorptions were monitored by using an instrument which has been described elsewhere.¹⁶ All experiments were carried out in deaerated solutions at 300 K.

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Figure 1. Quenching of Ib by acetic acid in acetonitrile at 300 K and (insert) a typical decay trace illustrating the decay of the carbene and bleaching of its precursor.

Photolysis ($\lambda > 300$ nm) of phenylchlorodiazirine (0.35 M) and trifluoroacetic acid (0.32 M) in isooctane solvent gave IIa as the major product with some benzaldehyde (eq 1; yields of 85% and 15%, respectively, by GC/MS



 $C_{6}H_{5}CHO + CX_{3}COCI$ (1)

analysis). A similar experiment with acetic acid gave a product which decomposed thermally to give benzaldehyde and was presumed to be IIb. Similar experiments with (p-methoxyphenyl)chlorodiazirine did not lead to significant product formation since highly colored material was quickly formed which screened the samples from further photolysis. From the above results we conclude that Ia reacts with acetic and trifluoroacetic acids to give the expected insertion products, and we presume that Ib behaves in a similar way (eq 1).

Carbenes Ia and Ib could be easily monitored at 326 and 355 nm, respectively. The unsubstituted carbene, Ia, has been established to have a singlet ground state,¹² which is responsible for the signals observed in the laser flash experiments. Carbene Ib was investigated by using the same experimental criteria, and since it showed essentially the same pattern of behavior, it is therefore also believed to have a singlet ground state.¹⁷

The transient absorptions due to Ia and Ib were quenched when acetic acid was added to the samples used in the laser flash photolysis experiments. When the observed pseudo-first-order rate constants, k_{obsd} , for the decay of transients Ia and Ib were plotted against acetic acid concentration, linear plots of high quality (r > 0.985) were obtained (eq 2 and Figure 1), where k_q are the rate con-

$$k_{\text{obsd}} = k_0 + k_0 [\text{CH}_3 \text{COOH}]$$
(2)

stants for reaction of the carbenes with acetic acid. It was found that k_0 , the rate constant for carbene decay in the absence of acid, was negligible compared to k_q -[CH₃COOH].¹⁸

 Table I.
 Rate Constants for Some Reactions of Singlet Arylchlorocarbenes at 300 K

car- bene	quencher	solvent	$k_{q}, M^{-1} s^{-1}$
Ia Ia Ib Ib Ia Ia Ia Ia	acetic acid acetic acid acetic acid acetic acid trifluoroacetic acid ethyl acetate dimethylbut-2-ene dimethylbut-2.ene	acetonitrile isooctane acetonitrile acetonitrile acetonitrile acetonitrile	$\begin{array}{c} (1.78\pm0.36)\times10^9\\ (3.1\pm0.6)\times10^9\\ (2.16\pm0.10)\times10^9\\ (5.1\pm1.2)\times10^9\\ (2.40\pm0.12)\times10^9\\ <2\times10^6\\ (1.95\pm0.28)\times10^8\\ 1.2\times10^8\end{array}$
Ib	dimethylbut-2-ene	acetonitrile	$(2.04 \pm 0.10) \times 10^8$

^a From ref 12.

Similar studies were carried out with trifluoroacetic acid; the rate constants for all these reactions are summarized in Table I. In all cases plots using eq 2 gave straight lines. This contrasts with experiments in which *tert*-butyl alcohol or methanol was used as a quencher, where similar plots showed pronounced curvature due to changes in hydrogen bonding equilibria.¹⁹ Indeed, at the concentrations of acetic acid used in these experiments, the ratio of monomer to dimer in solution was >10.^{20,21}

The rate constants for the reactions of Ia and Ib with acids are among the fastest known carbene-molecule reactions. They are similar to those for the O-H insertion reactions of Ia and Ib into methanol oligomers for which $k_q \approx 3 \times 10^9 \, M^{-1} \, s^{-1}$ (isooctane solvent) and are much faster than that for insertion of Ib into methanol monomer for which $k_g \approx 2 \times 10^7 \, M^{-1} \, s^{-1}$.

In order to set the results obtained for quenching by acids into the context of other reactions of carbenes Ia and Ib, we have measured rate constants for the reactions of these carbenes with dimethylbut-2-ene and ethyl acetate. The results are given in Table I. Clearly, the reactions with acids are more facile than those with olefins, the insensitivity toward acid strength probably reflecting an early transition state. Moreover, this high reactivity must be associated with the lability of the O-H bonds since ethyl acetate was not effective as a quencher.

Registry No. Ia, 19807-41-1; Ib, 82849-42-1; trifluoroacetic acid, 76-05-1; acetic acid, 64-19-7; ethyl acetate, 141-78-6; dimethylbut-2-ene, 563-79-1; phenylchlorodiazirine, 4660-46-2; (*p*-methoxyphenyl)chlorodiazirine, 4222-26-8.

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Aqueous Polar Aprotic Solvents. Efficient Sources of Nucleophilic Oxygen

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The replacement of various functional groups with oxygenated moieties is of considerable importance in synthetic endeavors and has led, over the years, to the development of several reagents that serve as nucleophilic sources of oxygen, including hydroxide,¹ peracids,² su-

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⁽¹⁸⁾ In the absence of quenchers both carbenes underwent predominantly second-order decay and gave rise to highly colored products. These products were strongly absorbing in the UV region, such that only a few decay traces could be obtained from a single sample.

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