Anal. Calcd for $C_{10}H_{14}O_2S$: C, 60.57; H, 7.12. Found: C, 60.73; H, 7.15.

Ethyl 3,4-Dimethyl-5,6-dihydro-2*H*-thiine-6-carboxylate (7).[3] A slurry of 11.5 g (0.140 mol) of 2,3-dimethyl-1,3-butadiene and 4.5 g (0.010 mol) of 4 was stirred at reflux under N_2 for 16 h. The reaction mixture was cooled to room temperature and filtered. The filtrate was concentrated, and the residue was flash distilled at 0.25 torr to give 0.95 g (48%) of a colorless liquid: bp 86–88 °C [lit.[3] bp 110–120 °C (3 torr)]; ^{1}H NMR δ 4.17 (q, J = 7, 2 H), 3.59 (t, J = 7, 1 H), 3.06 (m, 2 H), 2.43 (m, 2 H), 1.70 (s, 6 H), 1.26 (t, J = 7, 3 H).

Anal. Calcd for $C_{10}H_{16}O_2S$: C, 59.97; H, 8.05. Found: C, 59.46; H, 8.03.

Registry No. **1**, 41404-93-7; **2**, 97171-53-4; **3**, 97171-54-5; **4**, 97171-55-6; **6**, 87258-39-7; **7**, 87258-36-4; SCl_2, 10545-99-0; $CH_2{=}C(CH_3)C(CH_3){=}CH_2$, 513-81-5; 1,3-cyclohexadiene, 592-57-4.

Supplementary Material Available: Additional X-ray crystallographic data for compound 4 and tables of positional and thermal parameters and bond distances and angles (9 pages). Ordering information is given on any current masthead page.

Reaction of Benzylchlorocarbene with Hydrogen Chloride

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The reaction of benzylchlorocarbene generated from 0.02 M solutions of 3-benzyl-3-chlorodiazirine in benzene with methanol has been found to be termolecular and gives rise to three products, (*E*)- and (*Z*)-chlorostyrene, HCl, and phenylacetaldehyde dimethyl acetal.[1] However, when the diazirine concentration is increased to 0.08 M, a fourth product is formed in a significant amount. Product analysis reveals that this product is 1-phenyl-2,2-dichloroethane. As diazirine concentration is increased, the amount of HCl in the reaction mixtures builds up. Since the reactions of benzylchlorocarbene toward HCl and methanol are competitive processes,[2] the formation of the dichloroethane suppresses the formation of the acetal. This observation led us to examine the reaction of HCl with the chlorocarbene since very little is known about the reaction of acid with carbene despite the wealth of information available on the carbene reaction with alcohols and olefins.[3] We report herein our findings on the kinetics and mechanism of the chlorocarbene–HCl reaction in ether solution.

Solutions of 3-chloro-3-benzyldiazirine (1) (0.01 M) in dried ether were photolyzed in the presence of various concentrations of HCl from 1 to 22 °C such that the concentrations of HCl were always in excess. The products were (*E*)- and (*Z*)-chlorostyrene (2) and 1-phenyl-2,2-dichloroethane (3).

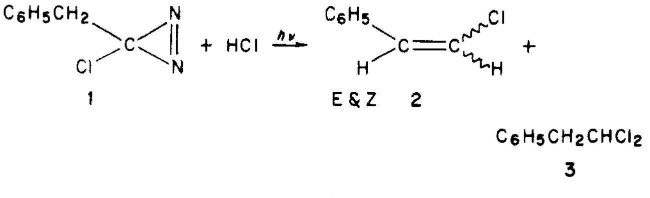
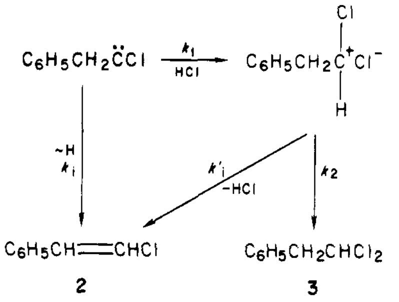


Table I. Distribution of Products from the Photolysis of 1 as a Function of [HCl] and Temperature

[HCl], M	1.0 °C		14.4 °C		22.0 °C	
	3/2	(*Z*)-/(*E*)-2	3/2	(*Z*)-/(*E*)-2	3/2	(*Z*)-/(*E*)-2
0.10	0.614	0.29	0.616	0.31	0.666	0.31
0.21	0.963	0.36	0.995	0.38	0.964	0.39
0.31	1.21	0.41	1.21	0.43	1.24	0.44
0.42	1.29	0.45	1.40	0.47	1.49	0.48
0.62	1.69	0.51	1.66	0.53	1.91	0.52
1.20	1.93	0.60	1.85	0.62	1.95	0.62
1.30	2.03	0.61	2.06	0.64	2.08	0.63

Scheme I



The product 2 could result from an intramolecular 1,2-H shift in the photochemically generated benzylchlorocarbene, and product 3 could arise from its reaction with HCl. Temperature does not appear to have an effect on the product distribution as can be seen in Table I. Control experiments confirm that 2 and 3 maintain their identity under reaction conditions and that 3 does not revert to 2.

A plot of **3**/**2** vs. [HCl] shows pronounced curvature (Figure 1); this could be due to the formation of an intermediate prior to product formation.

The kinetic results can be accommodated by Scheme I in which the carbene can rearrange to 2 by a 1,2-H shift to react with HCl giving an intermediate which subsequently collapses to 3. This intermediate is likely an ion pair since the solvent used is of low polarity.[4] As well, the ion pair can undergo elimination of HCl leading to 2. The possible rearrangement of this ion pair to a phenonium ion can be excluded since no product other than 2 and 3 was detected.

Since the formation of the ion pair is a bimolecular reaction, an increase in HCl concentration leads to a higher concentration of 3. However, the high concentration of HCl has two effects on the formation of 2. The yields of chlorostyrene increase in the k_i' step and decrease in the k_i step. It is possible that the trend toward higher Z/E ratio of 2 with higher HCl concentration may be accounted

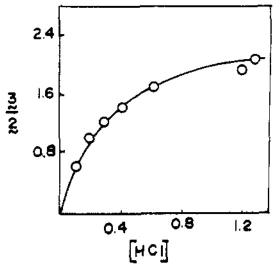


Figure 1. Plot of **3**/**2** vs. [HCl] at 14.4 °C.

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0022-3263/85/1950-3218$01.50/0

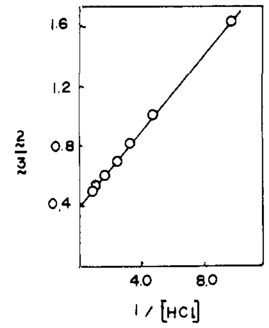
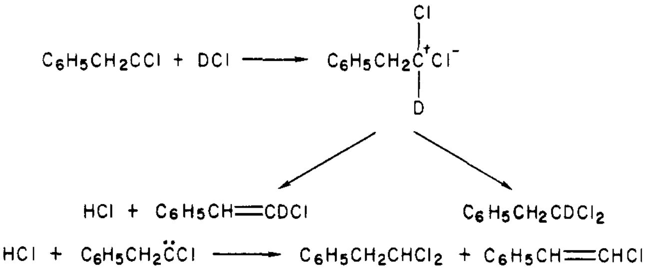


Figure 2. Plot of **2**/**3** vs. 1/[HCl] at 14.4 °C.

Scheme II



for by the interplay of the two routes to chlorostyrene.

Application of the steady-state treatment to Scheme I leads to the following:

$$\frac{2}{3} = \frac{k_i(k_i' + k_2)}{k_1 k_2[\mathrm{HCl}]} + \frac{k_i'}{k_2}$$

Linear regression analysis of **2**/**3** vs. 1/[HCl] gave correlation coefficient >0.99. The dependence of **2**/**3** on HCl is inverse first order (Figure 2). Since the intercept, k_i'/k_2, in Figure 2 is equal to 0.4, the ratio $k_i(k_i' + k_2)/k_1k_2$ can, therefore, be reduced to $\sim k_i/k_1$. The data in Table I show that the product ratios are insensitive to temperature, and it follows that $E_i - E_1 \sim 0$.

Further evidence for the proposed intermediacy of an ionic intermediate is obtained from the product distribution of the photolysis of **1** with DCl. The reaction path involving an ion pair can be expected to lead to a mixture of deuterated **3**, deuterated **2**, and undeuterated **2**. However, analysis of the product mixture by NMR and mass spectroscopy reveals that considerable amounts of undeuterated **3** is also formed. The relative distribution of the four products is as follows: deuterated and undeuterated **2**, 5.3% and 30.2%; deuterated and undeuterated **3**, 43.9% and 20.6%. Formation of the deuterated **2** suggests the presence of the ion pair. This intermediate gives rise to $C_6H_5CH{=}CDCl$ and HCl by *β-elimination* reaction. The HCl so produced can react with the carbene to give undeuterated **3** as shown in Scheme II.

To test the existence of the carbene intermediate in acid medium, experiments on the reaction of chlorocarbene with mixed substrates were conducted (Table II). When **1** was photolyzed in 1.0 M HCl, the product ratio **3**/**2** was 1.85. However, when **1** was photolyzed in the presence of 1.0 M HCl and 1.0 M tetramethylethylene, the ratio of **3**/**2** was decreased to 1.55. Since the insertion and cyclopropanation are competitive reactions, the cyclopropane **5** is formed at the expense of **3**. Although the cyclopropanation does not compete as well as the insertion reaction, the formation of **5** is still significant (10.6%). This demonstrates the existence of carbene intermediate even in the presence of HCl. Moreover, HCl appears to be 3 times as efficient as acetic acid in the trapping of benzylchlorocarbene.

Table II. Product Distribution in Mole Percent in the Photolysis of 0.01 M Benzylchlorodiazirine (1) with Mixed Substrates at 15.0 °C

substrate[a]	2	3	4[b]	5[c]
HCl	35.1	64.9		
TME[d]	27.0			73.0
HCl + HOAc[e]	34.3	49.1	16.7	
HCl + TME	35.0	54.4		10.6

[a] [Substrate] = 1.0 M in ether. [b] 4 is 2-phenyl-1-chloroethyl acetate. [c] 5 is 1-benzyl-1-chloro-2,2,3,3-tetramethylcyclopropane. [d] Photolysis of 1 in 1.0 M tetramethylethylene at 10 °C. [e] Control experiment indicates acetic acid does not react with 3 under the experimental conditions.

It is interesting to note that, although there is considerable chlorostyrene formation (35%) in the reaction of **1** with a mixture of HCl and TME, only about 4% could arise from 1,2-hydrogen migration since the ratio of **5**/**2** has been found to be 2.7 in the photolysis of **1** with TME at 10.0 °C. Thus, the majority of chlorostyrene comes from the elimination of HCl in the ion pair. By combining kinetic measurements with the analysis of reaction products, it is shown that chlorostyrene can be produced from the different intermediates.

Since diazirines are known to give rise to diazo intermediates[5] upon decomposition, the observed hydrogen chloride effects on product ratio could be argued to arise from reactions of benzylchlorodiazomethane rather than the corresponding carbene. In the photolysis of phenyl-*n*-butyldiazirine in acetic acid,[6] it was found that the reaction proceeded without any participation of the carbene intermediate. However, further work on the photochemical decomposition of 3-chloro-3-benzyldiazirine in acetic acid supports a carbenic mechanism.[7] Although some diazirine decompositions are believed to proceed through a diazo species, the participation of this intermediate in the product-forming steps depends on its stability. Since halodiazomethanes[8] are known to decompose at −60 °C, it is unlikely that any diazo chemistry is involved in the present reaction.

Experimental Section

Materials. Diethyl ether was dried by distillation over lithium aluminum hydride. A saturated solution of hydrogen chloride was obtained by bubbling HCl gas into dry ether. The conductance of a 1.3 M HCl solution in ether was measured, and this value corresponds to a pK_a value of ~5 which suggests that most of the HCl is in the molecular form. 3-benzyl-3-chlorodiazirine was synthesized from benzylamidine hydrochloride by Graham's method.[9] DCl was generated by the reaction of D_2O and benzoyl chloride.[10] Reaction solutions were prepared by appropriate dilution of concentrated stock solutions.

Photolysis. Irradiation was carried out with a 275-W GE sunlamp until all of the diazirine was destroyed. Temperature control during photolysis was within ±0.1 °C. A CS-052 filter was used to allow transmission of wavelength >350 nm to avoid product isomerization.

Products. The products were separated by column chromatography using silica gel and eluting with 95:5 pentane–diethyl ether. The identity of the products was established by NMR spectroscopic analysis and by comparison with spectra of authentic samples. Relative yields of products were obtained by gas chromatographic analysis on a Varian VISTA 6000 instrument

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using a 6 ft × 2 mm (i.d.) glass column packed with CSP-20M. Peak areas were integrated by a HP 3390A recorder.

Photolysis of 1 in HCl. **1**, 0.4 g (2.4×10^{-3} mol), was added to 20 mL of 1.3 M solution of HCl in ether and the mixture was irradiated for 16 h. The reaction mixture was diluted with water and the products were extracted twice with ether. The combined extracts were washed with sodium bicarbonate solution and water and dried over magnesium sulfate. The solvent was removed, and the crude product mixture was chromatographed on silica gel. Two fractions were collected. The first (120 mg) was a mixture of (*Z*)- and (*E*)-**2**: NMR ($CDCl_3$) δ 7.38 (phenyl), AB quartet with the outer pairs centered at 6.63 and 6.78 (*E* olefinic H) and AB quartet with the outer pairs centered at 6.08 and 6.63 (*Z* olefinic H). The second fraction contained 240 mg of the dichloride **3**: NMR ($CDCl_3$) δ 7.37 (s, 5 H), 5.87 (t, 1 H), 3.47 (d, 2 H). The overall product yield is found to be 93%.

Photolysis of 1 in DCl. A solution of 0.3 g of **1** (1.8×10^{-3} mol) and 15 mL of 1.5 M DCl in ether was irradiated for 16 h. The products were isolated as described before. Two components were obtained by column chromatography. One was a mixture of deuterated and undeuterated **2** (85 mg): MS, m/e 141 (2), 140 (11), 139 (5.5), 138 (33), 104 (14), 103 (100). The other component was a mixture of deuterated and undeuterated **3** (195 mg): MS, m/z 175 (7.02), 174 (3.2), 104 (12), 103 (15), 92 (8.4), 91 (100). The overall product yield is 95%.

Photolysis of 1 with Substrates. Products of reaction of 1 in HCl–TME and HCl–HOAC were isolated as described above and identified by comparison of their spectra with those of authentic samples.

Control Experiment. It has been observed that 1 does not react with HCl in the dark.

Photolysis of 1 in benzene without HCl yields the two isomeric β-chlorostyrenes in the ratio of 0.20 ((*Z*)-/(*E*)-**2**) which is independent of reaction time (0.3–3 h) and temperature (1–25 °C).

A mixture of **2** (5.0×10^{-3} M) and **3** (5.0×10^{-3} M) with excess HCl (1.2 M) in ether was irradiated under our experimental conditions for 10 h. Analysis of this mixture by GLC indicated that the composition remained unchanged.

A solution of **2** (5.0×10^{-2} M) and HCl (1.3 M) in ether was photolyzed for 10 h and analyzed by GLC. No addition or isomerization was found to occur.

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Registry No. **1**, 88211-05-6; **2**, 622-25-3; (*E*)-**2**, 4110-77-4; (*Z*)-**2**, 4604-28-8; **3**, 4412-39-9; **4**, 39773-55-2; **5**, 97073-41-1; HCl, 7647-01-0; $C_6H_5CH_2CDCl_2$, 97073-40-0; $C_6H_5CH{=}CDCl$, 3947-94-2; benzylchlorocarbene, 88211-07-8.

Di-*tert*-butyl Hyponitrite as a Source of Alkoxyl Radicals for Dimerization

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The use of reactive radicals to couple organic molecules is an old approach that has been carried out extensively with di-*tert*-butyl peroxide[1–19] and also with benzoyl peroxide,[3,10,15] acetyl peroxide,[20–23] and Fenton's reagent.[24–26] The desired sequence (1)–(3) is usually accompanied to various extents by cage recombination and cross-coupling

$$\text{initiator} \rightarrow 2\text{In}\cdot \tag{1}$$

$$\text{In}\cdot + \text{RH} \rightarrow \text{In–H} + \text{R}\cdot \tag{2}$$

$$2\text{R}\cdot \rightarrow \text{R}_2 \tag{3}$$

of initiating radicals, induced decomposition of the initiator, scission of alkoxy radicals, disproportionation of substrate radicals and multiple sites for their recombination, and termination reactions of the radicals produced in secondary steps.

A part of a general study of alkyl hyponitrites, we have investigated the use of di-*tert*-butyl hyponitrite as a potentially more convenient source of reactive radicals via reaction 4:

$$t\text{-BuON}{=}\text{NOBu-}t \rightarrow \text{N}_2 + 2t\text{-BuO}\cdot \tag{4}$$

The results of our study are summarized in Table I along with previous approaches with other initiators. Except for the cases with Fenton's reagent, the use of the hyponitrite results in a substantial reduction of reaction time. The yields with hyponitrite were improved over literature procedures in four cases, although we did not make extensive attempts at optimization. Substitution of *tert*-amyl for *tert*-butyl hyponitrite led to a lower yield of dimer from diphenylmethane.

Rather surprisingly, benzaldehyde gave no detectable benzil with di-*tert*-butyl hyponitrite. With a twofold excess of aldehyde a complicated mixture was formed, while with excess aldehyde an interesting tetramer, derived from addition of benzoyl radical to benzaldehyde, crystallized from the reaction mixture. This compound had been isolated previously[10,15] from a high-temperature reaction

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