Figure 1. Reaction of (+)-1-phenylethylamine with a (+)-(upper) and a (−)-(lower) crystal of 2,2-diphenylcyclopropane-1-carboxylic acid: top left, before reaction, transmitted light; top right, before reaction, crossed polarizing filters; middle left, 5 min; middle right, 20 min; bottom left, 1 hr; bottom right, 24 hr.

employed to sort the crystals of such a conglomerate and so to effect a resolution.

In this communication is described a method which is certainly simpler to apply and hopefully more general than many of those listed above. It depends on the selectivity of reaction of a chiral gas exposed to a mixture of dextro and levo crystals. Previous studies of related solid–gas reactions have been reviewed elsewhere.[12-14]

(+)- and (−)-Enantiomeric single crystals of an optically active carboxylic acid were placed side-by-side in a cell formed from two microscope slides separated by a metal ring 5 mm thick with an inside diameter of 7.5 mm. Three drops of one of the enantiomeric 1-phenylethylamines were placed next to the crystals with a barrier formed from a small amount of stopcock grease to prevent the liquid amine from coming into contact with the crystals. Although the amine has bp 188°, its vapor pressure at room temperature is sufficiently high to permit a relatively rapid gas–solid reaction. The assembly, placed on a microscope stage between crossed polarizing filters was photographed at regular intervals. In Figure 1 are shown a series of photographs of crystals of (+)- and (−)-2,2-diphenyl-cyclopropane-1-carboxylic acid[15,16] with (S)-(+)-1-phenylethylamine vapor. It is apparent that the top surface of the (−)-acid crystal has become opaque after only 5 min due to the formation of microcrystallites of the product salt. However, at the same time the (+)-acid crystal has remained essentially unchanged. This difference in reactivity is evident throughout the entire 24-hr period the reaction was followed. A similar experiment in which (−)-amine was used showed the same selectivity, except that the (+)-crystal was attacked preferentially. Similar enantiomer specificity was shown in competitions of (+)- and (−)-crystals of

(12) R. S. Miller, D. Y. Curtin, and I. C. Paul, J. Amer. Chem. Soc., in press, and references cited therein.

(13) C.-T. Lin, I. C. Paul, and D. Y. Curtin, J. Amer. Chem. Soc., 96, 3699 (1974).

(14) I. C. Paul and D. Y. Curtin, Science, in press.

(15) This acid was prepared and resolved by the method of Walborsky and his collaborators.[16] In addition we are indebted to Dr. Walborsky for providing samples of those acids.

(16) H. M. Walborsky, L. Barash, A. E. Young, and F. J. Impastato, J. Amer. Chem. Soc., 83, 2517 (1961); H. M. Walborsky and A. E. Young, ibid., 86, 3288 (1964).

Table I. Relative Reactivities of (+) and (−) Optically Active Carboxylic Acids with (+)- or (−)-1-Phenylethylamine

	Sign of rotation Acid	Base	Relative rate obsd[a]	Composition and mp (°C) of product
2,2-Diphenyl-	(+)	(+)	Slow[b]	1:1, 201–203
cyclopropane-	(−)	(+)	Fast[b]	1:1, 190–192
1-carboxylic	(+)	(−)	Fast	
acid	(−)	(−)	Slow	
Mandelic acid	(+)	(+)	Fast	1:1, 109–111
	(−)	(+)	Slow	1:1, 176–178
	(+)	(−)	Slow	
	(−)	(−)	Fast	
Tartaric acid	(+)	(+)	Slow	1:2, 179–182
	(−)	(+)	Fast	1:2, 175–178
	(+)	(−)	Fast	
	(−)	(−)	Slow	

[a] Based on the rate of development of opacity observed microscopically. [b] The results of visual observation were confirmed by interrupting the reaction of a pair of crystals each weighing 0.3 g (after 3.5 hr of reaction with the amine) and submitting each entire crystal for microanalysis. The calculated % reaction was 18 for the (+) crystal and 51 for the (−) or a ratio of (−)/(+) of 2.8.

mandelic acid and tartaric acid for (+)- or (−)-1-phenylethylamine. The results are summarized in Table I.[17]

The limited information available at present[12,13,18] makes it impossible to predict or even to explain the preference shown by a particular enantiomer of the amine for one enantiomer of a crystalline acid. However, our work suggests that such solid–gas reactions may provide a general method for readily sorting a conglomerate of (+)- and (−)-crystals obtained from crystallization of a racemic substance and so providing an additional means of resolving optically active compounds.

(17) It should be observed that the selective attack of the top (major) face of the crystals reported here is different from the behavior reported previously for a number of reactions of ammonia gas with other acids. The nature of the anisotropic behavior has not yet been seriously examined with the compounds studied here.

(18) R. S. Miller, D. Y. Curtin, and I. C. Paul, J. Amer. Chem. Soc., in press.

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Received June 10, 1974

Application of Chemically Induced Dynamic Nuclear Polarization to a Study of Acylsilane Photolysis

Sir:

The stereochemistry and chemical reactivity of silyl radicals has been the focus of several recent investigations.[1-5] It has been suggested, for example, that the

(1) A. G. Brook and J. M. Duff, J. Amer. Chem. Soc., 91, 2118 (1969).

(2) H. Sakurai, M. Murakami, and M. Kumada, J. Amer. Chem. Soc., 91, 519 (1969).

(3) L. H. Sommer and L. Ulland, J. Org. Chem., 37, 3878 (1972).

(4) (a) R. A. Jackson, Advan. Free-Radical Chem., 3, 231 (1969); (b) S. W. Bennett, C. Eaborn, A. Hudson, R. A. Jackson, and K. D. J. Root, J. Chem. Soc. A, 348 (1970).

(5) A. G. Brook, P. J. Dillon, and R. Pearce, Can. J. Chem., 49, 133 (1971).

photolysis of acylsilanes in CCl_4 proceeds by a Norrish type I cleavage[1,5] to yield an acyl–silyl radical pair as shown below in Scheme I. Products isolated from the

Scheme I

$$Ph_3Si\overset{O}{\overset{\parallel}{C}}CH_3 \longrightarrow [Ph_3Si\cdot\cdot\overset{O}{\overset{\parallel}{C}}CH_3]$$

$$Ph_3Si\cdot + ClCCl_3 \longrightarrow Ph_3SiCl + \cdot CCl_3$$

$$CH_3\overset{O}{\overset{\parallel}{C}}\cdot + ClCCl_3 \longrightarrow CH_3\overset{O}{\overset{\parallel}{C}}Cl + \cdot CCl_3$$

$$CH_3\overset{O}{\overset{\parallel}{C}}\cdot + \cdot CCl_3 \longrightarrow CH_3\overset{O}{\overset{\parallel}{C}}CCl_3$$

$$2CCl_3\cdot \longrightarrow Cl_3CCCl_3$$
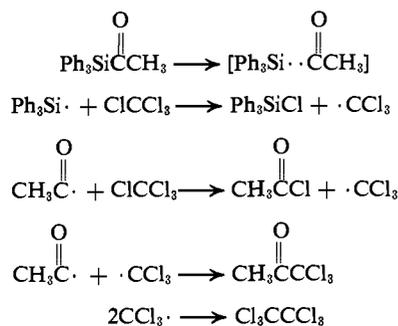
photolysis of acetyltriphenylsilane in carbon tetrachloride include triphenylsilyl chloride, acetyl chloride, trichloroacetone, and hexachloroethane. In other elegant studies, Brook[6,7] has shown that the photolysis of acylsilanes in solvents such as alcohol takes a quite different course. In the alcohol solvents carbenoid, rather than free radical intermediates, are proposed.

We report here the results of a CIDNP study of the photolysis of acylsilanes in CCl_4. These results call into question the accepted mechanism for acylsilane photolysis in CCl_4 and suggest caution in interpreting the chemical and stereochemical behavior of silyl radicals generated from acylsilane photolysis.

A 0.33 M solution of 1 in CCl_4 was irradiated with ultraviolet light inside an nmr spectrometer probe.[8] The resulting CIDNP spectrum (see Figure 1) showed strong emission (E) from acetyl chloride (2) and also strong enhanced absorption (A) from trichloroacetone (3). The methyl signals of phenyl dimethylsilyl chloride (4), a product of the photolysis, grew in a normal

$$CH_3\overset{O}{\overset{\parallel}{C}}\overset{CH_3}{\underset{|}{\underset{CH_3}{\overset{|}{Si}}}}Ph$$

1
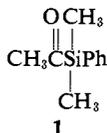
fashion during photolysis and were neither enhanced absorption nor emission.

Product distributions from photolysis of 1 in CCl_4 were temperature dependent. Thus, the ratio of acetyl chloride to trichloroacetone increased from 1.0 at $-19°$ to nearly 2.0 at 50° (Table I). This behavior is ap-

Table I. Product Yield (%) from Photolysis of 0.33 M 1 in CCl_4

T, °C	Acetyl chloride (2)	1,1,1-Trichloroacetone (3)	2/3	Phenyldimethylsilyl chloride (4)
−19	47	47	1.0	~100
0	56	35	1.6	95
50	61	31	1.95	98

(6) A. G. Brook, *Accounts Chem. Res.*, 7, 77 (1974).

(7) A. G. Brook and J. M. Duff, *J. Amer. Chem. Soc.*, 89, 454 (1967).

(8) 1 was synthesized by the method of Brook and Corey. See, for example, A. G. Brook, J. M. Duff, P. F. Jones, and N. R. Davis, *J. Amer. Chem. Soc.*, 89, 431 (1967). 1 synthesized in this way had a satisfactory elemental analysis.
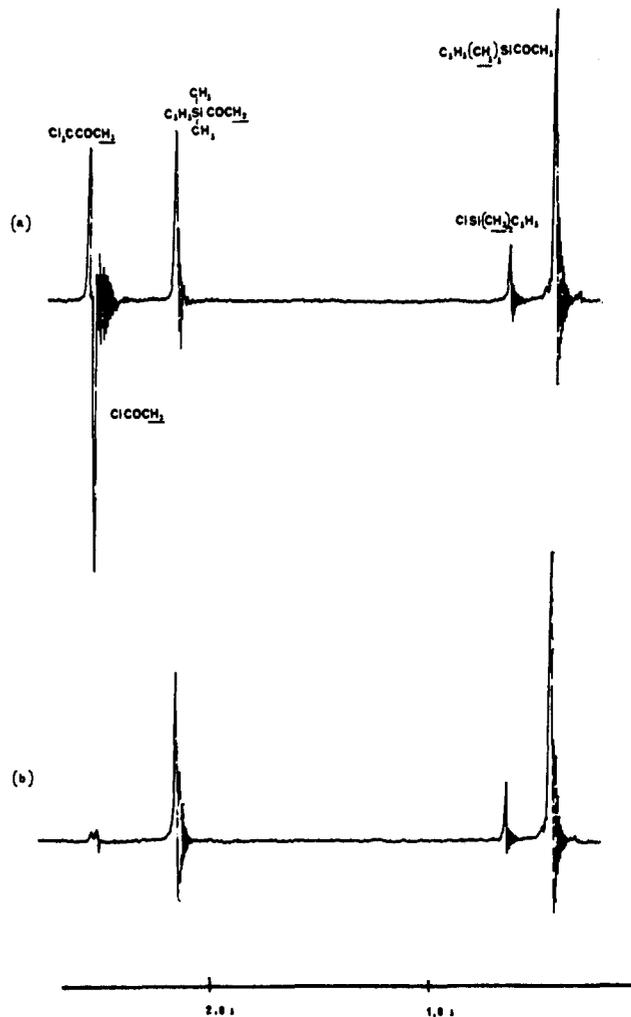
Figure 1. (a) CIDNP spectrum obtained during photolysis of 0.33 M 1 in CCl_4. (b) Pmr spectrum of same solution after photolysis.

parently general in acylsilane–CCl_4 photolyses since Brook earlier reported a similar observation.[5]

The CIDNP spectrum is difficult to interpret with the mechanism shown in Scheme I as a format. If Scheme I applied, the silyl chloride should be polarized since it is an escape product from the initial radical pair.[9-11] Also, trichloroacetone, formed by encounter of free radicals in Scheme I, should show emission rather than the observed enhanced absorption.

A mechanism which is consistent with the CIDNP spectrum and product distribution–temperature data is outlined in Scheme II.

We suggest initial formation of 5, an acylsilane–CCl_4 exciplex, followed by a selective collapse to 6, an acetyl-trichloromethyl singlet radical pair, and the silyl chloride. An alternative to the exciplex mechanism is a Norrish type I cleavage of 1 from an excited singlet followed by an extremely rapid transfer reaction with CCl_4 (pair substitution). This alternative seems less attractive than the exciplex mechanism because of its requirement for a highly selective pair substitution

(9) A. R. Lepley and G. L. Closs, Ed., "Chemically Induced Magnetic Resonance," Wiley, New York, N. Y., 1973.

(10) H. D. Roth, *Mol. Photochem.*, 5, 91 (1973).

(11) The following magnetic parameters were assumed: $\cdot CCl_3$, $g = 2.0091$; $\cdot C(=O)CH_3$, $g = 2.000$, $a_H > 0$; $Ph(CH_3)_2Si\cdot$, $g = 2.003$, $a_{H(CH_3)} > 0$. See ref 4b and 12. See also H. Fisher, *et al.*, *Helv. Chim. Acta.*, 57, 920 (1974).

Scheme II

$$
\begin{array}{c}
\overset{O}{\underset{\|}{}} \overset{CH_3}{\underset{|}{}} \\
CH_3CSiPh \\
\underset{|}{} \\
CH_3 \\
\mathbf{1}
\end{array}
\xrightarrow[CCl_4]{h\nu}
\begin{bmatrix}
\overset{O}{\underset{\|}{}} \overset{CH_3}{\underset{|}{}} \\
CH_3CSiPh\cdot CCl_4 \\
\underset{|}{} \\
CH_3
\end{bmatrix}^*
\longrightarrow
$$

5

$$
\begin{bmatrix}
\overset{O}{\underset{\|}{}} \\
CH_3C\cdot\cdot CCl_3
\end{bmatrix}
+
\begin{array}{c}
CH_3 \\
\underset{|}{} \\
ClSiPh \\
\underset{|}{} \\
CH_3
\end{array}
$$

6   **4**

$$
\overset{O}{\underset{\|}{CH_3CCCl_3}}
$$

$$
\begin{bmatrix}
\overset{O}{\underset{\|}{}} \\
CH_3C\cdot\cdot CCl_3
\end{bmatrix}
$$

diffusion and formation of CH_3CCl by CCl_4 trapping

$$
\overset{O}{\underset{\|}{}} \\
CH_3CCl
$$
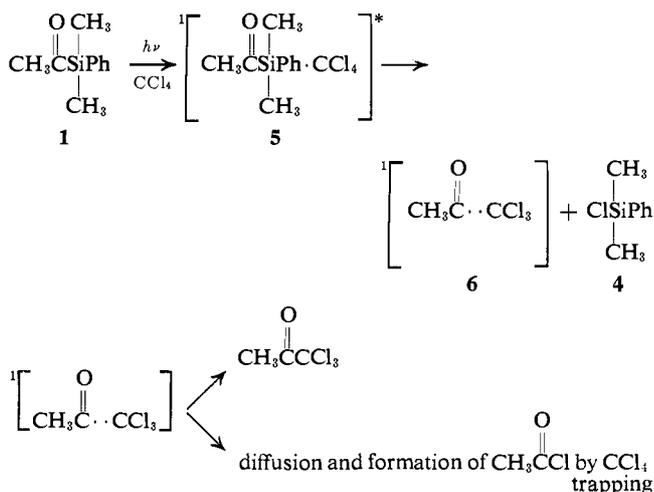
leading only to the acetyl–trichloromethyl pair at the expense of any silyl–trichloromethyl pair.[11a]

The mechanism proposed in Scheme II for acylsilane photolysis is analogous to one proposed earlier for the photolysis of diisopropyl ketone (DIK) in CCl_4.[12,13] The favored mechanism in the DIK studies involves nonradiative decay of a complex from DIK (S_1) and CCl_4 (exciplex). The DIK$\cdot CCl_4$ exciplex selectively collapses to form acetyl chloride and an isopropyl–trichloromethyl singlet radical pair.

Regardless of the mechanism for its formation, the key intermediate in Scheme II is the singlet acetyl–trichloromethyl radical pair **6**. Cage recombination of **6** should yield trichloroacetone which exhibits enhanced absorption (as is observed). The cage escaped product, acetyl chloride, is observed in the CIDNP spectrum in emission, as predicted by application of the CKO rules.[9,10] The product distribution temperature dependence is also accommodated by this scheme. At low temperatures, the cage recombination product of **6**, trichloroacetone, is favored. At higher temperatures, cage escape is favored, as expected,[14] and the relative proportion of escape product, acetyl chloride, increases accordingly.

The photolysis of **1** in solvents other than CCl_4 takes an entirely different course. Photolysis of **1** in benzyl chloride, for example, results in a complex product mixture as well as a complex CIDNP spectrum. However, the signals from the methyl groups of the silyl compound **4**, which were observed unpolarized during the photolysis of **1** in CCl_4, clearly exhibit emission during the photolysis of **1** in benzyl chloride. This observation is consistent with a mechanism involving formation of an authentic silyl–acyl triplet pair, from which the silyl chloride is an escape product.

Our observations force the conclusion that CCl_4 plays an active role in the photochemistry of acylsilanes. In fact, it seems likely that the type I cleavage to radicals is

avoided when CCl_4 is used as a solvent for these photolyses.

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Some Unusually Long-Lived α-Aminoalkyl Radicals[1]

Sir:

We have recently shown that long-lived alkyl radicals can be prepared by addition of a wide variety of simple radicals to 1,1-di-*tert*-butylethylene.[2] The resulting 2-substituted 1,1-di-*tert*-butylethyl radicals have provided important insights into problems of alkyl radical conformation[3] and kinetics.[4] As a logical outgrowth of this work, we have generated a number of long-lived α-aminoalkyls by radical additions to di-*tert*-butylimine, t-Bu_2C=NH, and pivalonitrile, t-BuC≡N. Some of the radicals produced had quite unexpected structures and some have epr hyperfine couplings that are quite different from those expected from earlier epr studies of simple α-aminoalkyl radicals.[5-9]

A number of radicals that add readily to t-Bu_2C=CH_2 gave no epr signals attributable to addition to the imine (*e.g.*, $C_6H_5\cdot$, $C_6F_5\cdot$, and $\dot{C}Cl_3$) or nitrile (*e.g.*, $C_6H_5\cdot$, $\dot{C}F_3$, $CF_3O\cdot$, and $\dot{S}iCl_3$).[10,11] However, both trimethylsilyl, $Me_3Si\cdot$, and diethoxyphosphonyl, $(EtO)_2$-$\dot{P}O$,[12] added readily to yield the radicals listed in Table I. Addition to the imine gives initially a monoadduct, as expected. What were not expected, were the diadducts produced after a few minutes of photolysis.

$$t\text{-}Bu_2C\text{=}NH + R\cdot \longrightarrow t\text{-}Bu_2\dot{C}NHR \xrightarrow{(-H\cdot)}$$

$$t\text{-}Bu_2C\text{=}NR \xrightarrow{R\cdot} t\text{-}Bu_2\dot{C}NR_2$$
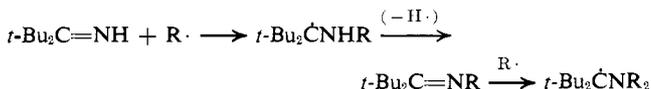
The diadduct structure is certain for R = $(EtO)_2PO$ but with Me_3Si a number of long-lived radicals were formed that so complicated the spectra that structural assignment was impossible. However, with R = n-Bu_3Si a radical containing nitrogen that we believe was the diadduct was identified.

Although the phosphonyl radical adds to t-BuC≡N

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(1) Issued as N.R.C.C. No. 14249.

(2) D. Griller and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 6459 (1973).

(3) D. Griller and K. U. Ingold, *J. Amer. Chem. Soc.*, in press.

(4) G. D. Mendenhall, D. Griller, D. Lindsay, T. T. Tidwell, and K. U. Ingold, *J. Amer. Chem. Soc.*, **96**, 2441 (1974).

(5) D. E. Wood and R. V. Lloyd, *J. Chem. Phys.*, **52**, 3840 (1970); *ibid.*, **53**, 3932 (1970).

(6) P. Neta and R. W. Fessenden, *J. Phys. Chem.*, **75**, 738 (1971).

(7) R. O. C. Norman and N. H. Anderson, *J. Chem. Soc. B*, 993 (1971).

(8) A. R. Lyons and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 2*, **68**, 502 (1972).

(9) For epr spectra of radicals from amino acids and amides see, *e.g.*, H. Paul and H. Fischer, *Ber. Bunsenges. Phys. Chem.*, **73**, 972 (1969); R. Poupko, A. Lowenstein, and B. L. Silver, *J. Amer. Chem. Soc.*, **93**, 580 (1971).

(10) A referee has pointed out that addition may occur but remain unobserved by epr because the adduct radical is unstable. Such processes might be probed by chemical analysis.

(11) We were also unsuccessful in attempts to add $(CH_3)_3C\cdot$ and $(CH_3)_3Sn\cdot$ to these compounds.

(12) Generated by photolysis of di-*tert*-butyl peroxide solutions containing Me_3SiH or $(EtO)_2POH$.

(11a) NOTE ADDED IN PROOF. Professor A. G. Brook has informed us that fluorescence quenching of acyl silanes by CCl_4 has recently been observed in his laboratories. This is further support of the exciplex mechanism.

(12) (a) J. A. denHollander, R. Kaptein, and P. A. T. M. Brand, *Chem. Phys. Lett.*, **10**, 430 (1971); (b) J. A. denHollander, *Chem. Ind. (Belge)*, **36**, 1083 (1971).

(13) See also T. DoMinh, *Chem. Ind. (Belge)*, **36**, 1080 (1971).

(14) For a comprehensive review of the chemistry of "caged" radicals, see J. P. Lorand, *Prog. Inorg. Chem.*, **17**, 207 (1972).