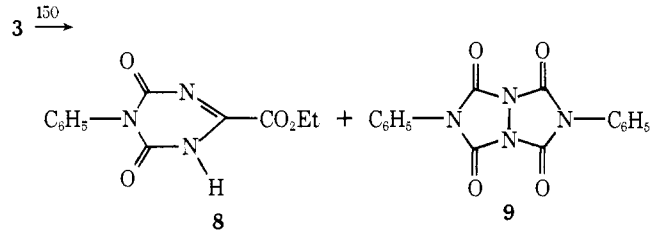
ing at 150° and 0.1 mm gave a mixture containing 76% of the ring-opened product **8**, *m/e* 261, and 17% of the triazolo[1,2-*a*]-*s*-triazole derivative **9**, *m/e* 322.



8 **9**

The presence of **9** which is a primary decomposition product of **2**[13] suggests that **3** can lose carbethoxy carbene. However, the formation of **3** from **1** and **2** most likely proceeded via a 1,3-dipolar cycloaddition pathway rather than through an addition involving a free carbene intermediate. The latter type of addition generally requires a reaction temperature above 100°.[14] In contrast 1,3-dipolar cycloaddition of diazoacetic esters to carbon to carbon double bonds conjugated with carbonyl groups can readily occur below room temperature to give pyrazolines.[14,15]

Further investigations of this new type of addition reaction are in progress.

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(4) Ir (Nujol) 1745 cm^{-1} (C=O); uv_{max} (dioxane) 260 (ϵ 1260) and 265 nm (ϵ 1050); NMR ($CDCl_3$) δ 7.60 (m, 6, C_6H_5 and C–H), 4.36 (broad m, 2, OCH_2), and 1.35 (broad m, 3, CH_3). Calcd for $C_{12}H_{11}N_3O_4$: C, 55.17; H, 4.21; N, 16.09. Found: C, 55.26; H, 4.09; N, 16.01.
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(8) Mp 169–169.5°; ir (Nujol) 1750 cm^{-1} (C=O); NMR ($CDCl_3$) δ 7.70 (s, 5, C_6H_5), and 2.55 (s, 6, OAc).
(9) Compound **7** which is a likely intermediate in the reaction was not isolated.
(10) Ir (neat) 1750 cm^{-1} (C=O); *m/e* 363; NMR ($CDCl_3$) δ 7.40 (s, 5, C_6H_5), 6.90 (s, 1, methine C–H), 4.31 (q, 2, OCH_2), 2.57 (s, 3, N=COAc), 2.15 (s, 3, C–OAc), 1.28 (t, 3, CH_3).
(11) The spectrum was recorded on a Bruker HFX-10.
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Mercury-Sensitized Photolysis of Trichlorosilane. Synthesis and Silicon Nuclear Magnetic Resonance Characterization of Dodecachloroneopentasilane

Sir:

Knowledge of the chemistry of the trichlorosilyl radical is to a great extent localized in the exhaustively studied hydrosilation reaction,[1-4] wherein trichlorosilane adds to olefinic or acetylenic bonds. Systems in which the trichlorosilyl radical is generated via abstraction of hydrogen from trichlorosilane by CH_3[5,6] or CF_3[6,7] radicals have been investigated; however, these efforts have been directed toward determination of Arrhenius parameters for the abstraction reaction without consideration of the fate of the trichlorosilyl radicals. Surprisingly little is known about recombination reactions between silicon radical centers. Trimethylsilyl radicals dimerize at ordinary temperatures,[8] but the fate of the related methyldichloro radical must be considered uncertain in view of the diametrically opposed reports of Urry and Reedy[9] and Davidson[10] regarding the dimerization of the species. We wish to report here the highly novel chemical behavior which results from the mercury-sensitized photodecomposition of trichlorosilane and the ^{29}Si NMR characterization of one of the reaction products as neo-Si_5Cl_{12}.

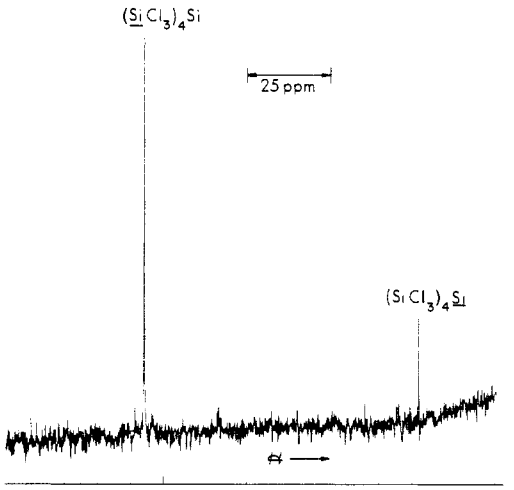

Figure 1. Silicon-29 NMR spectrum of neo-Si_5Cl_{12}, 0.42 *M* in $CDCl_3$, with added $Cr(acac)_3$ (0.03 *M*).

Mercury-sensitized photolyses (at 2537 Å) have been successfully employed by Gunning and coworkers[8] to effect dissocation of the Si–H bond in various alkylsilanes. When trichlorosilane is irradiated under these conditions at 55° and pressures in the range 50–450 Torr, white dendritic crystals are formed on the sides on the reaction vessel (a 20 cm length of 30 mm quartz tubing fitted with a high vacuum stopcock). The other products of complete photolytic destruction of $SiCl_3H$ include H_2, the perchloropolysilanes $SiCl_4$, Si_2Cl_6, Si_3Cl_8, and Si_4Cl_{10} (given in order of decreasing abundance), and a viscous yellow oil—as yet uncharacterized—which may contain polymeric silicon subchlorides.[11-13]

Characterization of the liquid perchloropolysilanes was afforded by mass spectral analysis and, for $SiCl_4$ and Si_2Cl_6, comparison with authentic infrared spectra. The crystals may be removed mechanically and purified by sublimation in vacuo (5×10^{-5} Torr). Mass spectral analysis of the crystals indicates their molecular formula to be Si_5Cl_{12}.

Dodecachloropentasilane is a molecule with a rather curious history. Species with a formula of Si_5Cl_{12} were first isolated as low volatility liquids in minute yields from reactions of $SiCl_4$ or Cl_2 with silicon or various silicides.[14-16] More recently, Urry and coworkers[17-19] have described a specific, high-yield synthetic route to Si_5Cl_{12} involving the base-catalyzed disproportionation of Si_2Cl_6. The pentasilane generated in this manner, unlike others previously reported, is a high-melting crystalline solid. These workers postulated[20] a neopentyl structure for the compound based on the simplicity and tentative assignments of the bands in the infrared spectrum of the molecule. However, no direct evidence for such a structure was presented.[21]

Silicon NMR spectra appeared to us to be the most appropriate means for determining the molecular structure of the crystalline product of the $SiCl_3H$ photolysis. The appli-

cation of Fourier transform techniques to NMR spectrometry has made the direct observation of silicon-29 spectra—at the 4.7% natural abundance of the isotope—practicable. Since no values of spin-lattice relaxation times have been reported for perhalosilanes, and T_1 can be quite long for organosilanes not containing hydrogen directly bonded to silicon,[22] we felt it advisable to include the shiftless paramagnetic "relaxation reagent" tris(acetylacetonato)chromium-(III)[23] in our NMR samples.

The ^{29}Si NMR spectrum[24] of a $CDCl_3$ solution of the photolytically generated crystals along with added $Cr(acac)_3$ is displayed in Figure 1. The spectrum consists of two single lines at chemical shifts (relative to external TMS) of 3.7 and −80.0 ppm, respectively.[25] The relative integrated intensities of the two lines, averaged over several spectra, is very close to 4.0 to 1, with the more intense line appearing at lower field. Crystals of Si_5Cl_{12} were also prepared as described in ref 17 and silicon spectra taken under conditions closely approximating those for the photolytically generated crystals. The main spectral features in the two sets of spectra are, within instrumental limits of resolution, identical. We must conclude that the pentasilane common to both systems does in fact possess the neo structure, $Si(SiCl_3)_4$.

Two mechanistic pathways to the observed series of perchloropolysilanes produced by the $SiCl_3H$ photolysis seem plausible to us. The first involves disproportionation of $SiCl_3$ radicals on recombination and the subsequent intermediacy of $SiCl_2$.[26] An alternative mechanism involves facile chlorine atom abstraction from silanes by various silyl radicals, with the polysilane products resulting from radical recombinations. We have at present no direct evidence in support of either mechanism; however, the abstraction route is consistent with our preliminary observation that mercury-sensitized cophotolysis of SiF_3H and $SiCl_4$ generates SiF_3Cl ($SiCl_4$ itself is unaffected by $Hg(^3P)$ under the conditions employed). Further work related to mechanistic pathways and additional silicon NMR studies on perchloropolysilanes is in progress.

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(24) ^{29}Si spectra were run on JEOL Models FT-1A and FT-1M in 5 mm o.d. tubes at ambient temperature. Additional spectral parameters are given in conjunction with the figure.
(25) These values follow the convention that positive shifts correspond to resonances at lower field than the standard.
(26) The work of P. L. Timms (*Inorg. Chem.*, **7**, 387 (1968)) demonstrates the ability of $SiCl_2$ to insert into Si–Cl bonds at "ordinary temperatures".

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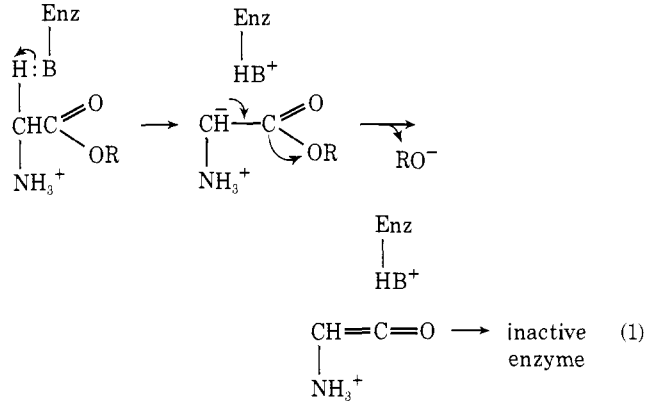
Novel Inactivators of Plasma Amine Oxidase

Sir:

Studies of the mechanism of action of plasma amine oxidase have indicated that at some stage during the oxidation a proton is abstracted from the carbon atom which is oxidized.[1] We have reported that propargylamine and 2-chloroallylamine irreversibly inactivate plasma amine oxidase[2] and proposed a mechanism of inactivation which is based on the ability of the enzyme to abstract a proton from these inactivators. An additional approach to the irreversible inactivation of that enzyme was suggested to us by the report that esters with sufficiently good leaving groups can undergo elimination reactions to form ketenes.[3] Generation of a reactive ketene species at the active site of an enzyme might lead to enzyme inactivation, probably by acylation of a group on the enzyme. Glycine esters appear to be good candidates for this kind of enzyme inactivation. We expected that plasma amine oxidase would catalyze the abstraction of a proton from the α-position of a glycine ester to form a carbanion, which could undergo either the normal oxidative process or an elimination reaction (eq 1) to produce an enzyme bound ketene.



Results obtained with several glycine esters are summarized in Table I. All are good substrates relative to benzylamine. Only the two α-amino esters which have good leaving groups inactivate the enzyme. Ethyl glycinate and the β-amino ester do not inactivate the enzyme. Furthermore, "R" is larger for the phenyl than the *p*-nitrophenyl ester, which implies that as the leaving group becomes better, partitioning between inactivation and oxidation favors inactivation. When phenyl glycinate is added to plasma amine oxidase, the rate of oxygen consumption decreases to zero