ESR spectra of Ga-ethylene and In-ethylene complexes. More detailed analyses of the spectra presented here and those of Ga- and In-ethylene complexes will be reported shortly.

References and Notes

(1) P. S. Skell and L. R. Wolf, *J. Am. Chem. Soc.*, **94**, 7919 (1972).
(2) P. H. Kasal, *Acc. Chem. Res.*, **4**, 329 (1971).
(3) The spectrum due to Al atoms has been observed in heavily concentrated matrices where the degeneracy of the 3p orbitals is removed by the lattice distortions. J. H. Ammeter and D. C. Schlosnagle, *J. Chem. Phys.*, **59**, 4784 (1973); L. B. Knight and W. Weltner, Jr., *ibid.*, **55**, 5066 (1971).
(4) P. H. Kasai, *J. Am. Chem. Soc.*, **94**, 5950 (1972).
(5) For the analyses of hyperfine coupling tensors, see, for example, P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals", Elsevier, Amsterdam, 1967.
(6) H. M. McConell, *J. Chem. Phys.*, **24**, 764 (1956); H. M. McConell and D. B. Chestnut, *ibid.*, **28**, 107 (1958).

Paul H. Kasai,* D. McLeod, Jr.
Union Carbide Corporation, Tarrytown Technical Center
Tarrytown, New York 10591

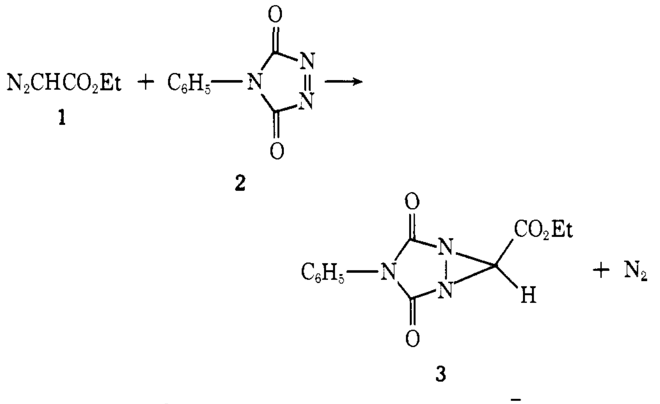
Received May 13, 1975

1,2-Addition Reaction of Ethyl Diazoacetate and 4-Phenyl-1,2,4-triazoline-3,5-dione

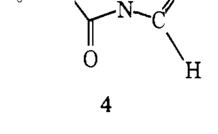
Sir:

The formation of three-membered carbocyclic ring systems by the reaction of carbene intermediates with olefinic and acetylenic sites has been well documented. However, the analogous reaction of these intermediates with azo compounds to give diaziridine derivatives has not been reported. Carbene sources such as ethyl diazoacetate have been found to react with *trans*-diacyldiimides by 1,4- rather than 1,2-addition.[1] When the groupings about the azo linkage are forced to occupy a cis configuration, 1,4-addition is no longer possible. Instead 1,2-addition is likely to occur. We wish to present evidence of the first known example of this latter type of addition.

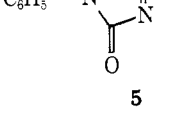
Ethyl diazoacetate (**1**) reacted vigorously in a mildly exothermic manner with 4-phenyl-1,2,4-triazoline-3,5-dione (**2**)[2] in either methylene chloride or benzene solution at 0° to form a one-to-one adduct, mp 175–177° dec, *m/e* 261, in near quantitative yield.[3,4] The structure of the product was assigned as 6-carbethoxy-3-phenyl-1,3,5-triazabicyclo[3.1.0]hexane-2,4-dione (**3**) rather than that of the bicyclic compound **4** or the triazolinium-*N*-ylide **5**. There is literature analogy for compounds of type **4** and **5**.[5-7] Generally, however, compounds of type **4** which have three adjacent saturated heteroatoms are unstable and readily rearrange to ylide structures.[6,7] The adduct is a white solid whereas ylides are colored and give a visible spectrum. The ir spectrum shows the carbonyl absorptions centered at 1745 cm^{-1}. Ylides containing the $-N{=}N^{+}{}^{-}CHCO_2Et$ grouping have their carbonyl absorption at 1645–1660 cm^{-1} [5,6] owing to the delocalization of the negative charge on to the carbonyl oxygen. The behavior of the product in the presence of either acid or base was inconsistent with both **4** and **5**. It was recovered unchanged when treated with 15% hydrochloric acid for 48 hr but decomposed immediately in 5% sodium hydroxide. It failed to react with excess acetic acid (60:1) and acetic anhydride in methylene chloride solution at room temperature over a 3-week period. However, when the reaction was repeated and a small excess (2:1) of either lead diacetate or sodium acetate was added to the reaction mixture, the diacetoxytriazole **6** was recovered in high yield.[8] This reaction can best be rationalized as a double nucleophilic displacement by acetate anion at C-6 of **3** to give 4-phenylurazole followed by diacetylation of the urazole ring with acetic anhydride.[9] Thus the above results strongly support **3** as the structure of the product.



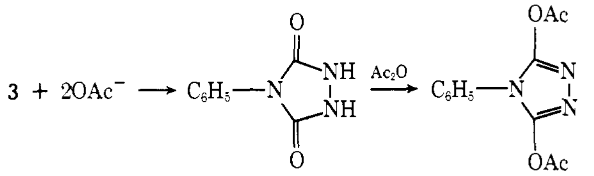
1 **2** **3**



4

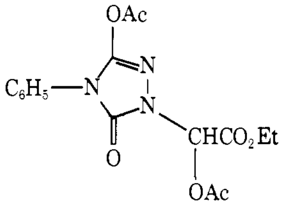


5



6

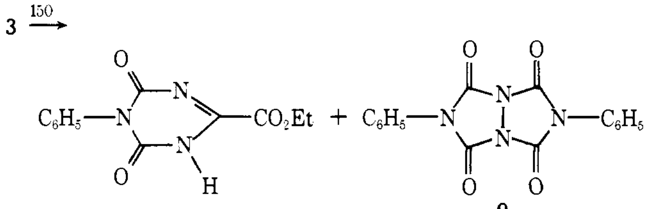
The in situ reaction of **2**, prepared by the lead tetraacetate oxidation of 4-phenylurazole,[2] with **1** also gave **3** (30–40%). In addition a small quantity (1–3%) of 1-(acetoxycarbethoxymethyl)-3-acetoxy-4-phenyl-1,2,4-triazoline-5-one (**7**)[10] was isolated which was possibly formed by ring-opening of **3** under the reaction conditions.



7

The ^{1}H NMR spectrum of **3** showed two complex and broad multiplets for the ethoxy protons. Only slight changes in the appearance of the multiplets were observed as the temperature was varied between −78 and 80°. A 10^{-3} M solution of **3** in chloroform did not give an ESR spectrum. The proton decoupled ^{13}C NMR spectrum[11] showed signals at 13.8 (CH_3), 63.4, and 64.7 ($O-CH_2$ and C-H) ppm downfield from internal TMS in addition to the carbonyl and aromatic absorptions. All of the signals were considerably broadened. The presence of a single set of ethoxy absorptions indicates that only one isomer, presumably the exo isomer, was formed in high yield. The cause of the broadening of both the ^{1}H and ^{13}C NMR signals is most likely due to either the presence of a low concentration of a paramagnetic species that was not detected by ESR spectroscopy or to an effect of slow inversion of the phenyl group about the nitrogen atom and/or slow rotation of the carbethoxy group about the C—C=O bond.[12]

The diaziridine compound **3** is thermally unstable. Heating 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.

References and Notes

(1) R. Breslow, C. Yaroslavsky, and S. Yaroslavsky, *Chem. Ind.* (*London*), 1961 (1961).
(2) R. C. Cookson, S. S. Gupte, I. D. R. Stevens, and C. T. Watts, *Org. Synth.*, **51**, 121 (1971).
(3) We thank the Research Triangle Center for Mass Spectrometry, Durham, N.C. for the mass spectral determinations.
(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.
(5) S. F. Gait, C. W. Rees, and R. C. Storr, *Chem. Commun.*, 1545 (1971).
(6) S. F. Gait, M. J. Rance, C. W. Rees, and R. C. Storr, *J. Chem. Soc., Chem. Commun.*, 688 (1972).
(7) S. R. Challand, C. W. Rees, and R. C. Storr, *J. Chem. Soc., Chem. Commun.*, 837 (1973).
(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.
(12) The origin of the broadening of the NMR signals is under study.
(13) R. Stolle, *Chem. Ber.*, **45**, 273 (1912).
(14) V. Dave and E. W. Warnhoff, *Org. React.*, **18**, 217 (1970).
(15) R. Fusco in "Pyrazoles, Pyrazolines, Pyrazolidines, Indazoles, and Condensed Rings", R. H. Wiley, Ed., Interscience, New York, N.Y., 1967, p 197.

Robert A. Izydore,* Samuel McLean
Department of Chemistry, North Carolina Central University
Durham, North Carolina 27707
Received May 30, 1975

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}.

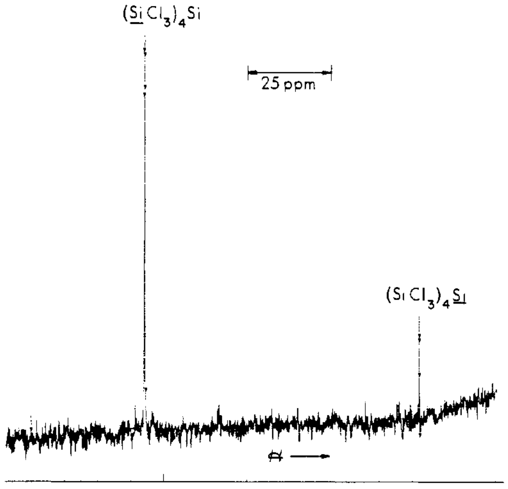


Figure 1. Silicon-29 NMR spectrum of neo-Si_5Cl_{12}, 0.42 *M* in $CDCl_3$, with added $Cr(acac)_3$ (0.03 *M*).

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-