The undesired isomer **5b** was carefully removed by distillation on an annular spinning band still: bp 68° (1.0 mm); pmr spectrum δ 1.19 (s, 3, CH_3), 1.45 (broad s, 3, vinyl CH_3), 1.56 (m, 3, vinyl CH_3), 1.72–2.19 (m, 4, two CH_2), 2.42 (broad t, 2, J = 6 Hz, $HOCH_2CH_2$), 3.57 (t, 2, J = 7.5 Hz, $HOCH_2CH_2$), 3.77 (s, 1, $HOCH_2CH_2$); ir spectrum 3300 (broad OH), 1350 cm^{-1} (sharp, olefinic CH_3). The desired isomer **1a** boiled at 73° (1.0 mm) and had spectra identical with those of the natural material.

Registry No.—**1a,** 28117-21-7; **1b,** 34502-18-6; **3,** 33194-47-7; **4,** 34566-68-2; **5a,** 34502-20-0; **5b,** 34502-21-1.

Diphenylacetylene from the Decomposition of 2,2-Diphenyl-1-tosylazoethylene[1]

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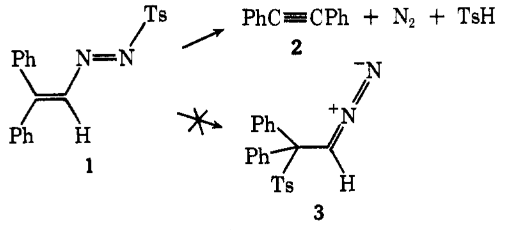
During the last few years we have investigated the chemistry of azoalkenes. In some reactions (1:4 additions,[2a] isomerizations[2b]) the S–N bond of tosylazoalkenes is retained, whereas in other cases (cycloadditions,[3] reactions with alcohols[4]) this bond is cleaved.

Earlier we reported the thermal degradation, at 90° in benzene and at 25° in chloroform, of aryl-substituted tosylazoalkenes having a vinylic proton on the carbon β to the azo group.[5] One degradation path apparently involves the formation of a vinylic carbonium ion which loses a proton from the adjacent carbon forming a triple bond as well as another principal path in which the tosylazoalkene rearranges to the corresponding α-tosyldiazo derivative which then undergoes acid-catalyzed decomposition.[5]

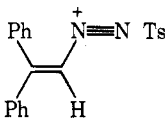
In order to extend our earlier studies, we have examined the thermal decomposition of 2,2-diphenyl-1-tosylazoethylene (**1**) which does not possess a proton on the vinylic carbon adjacent to the azo group.

In benzene at 90° and in chloroform[6] at 25°, **1** gives diphenylacetylene (**2**) as the main product (85–90%), nitrogen, and *p*-toluenesulfinic acid, without formation of 2-tosyl-2,2-diphenyl-1-diazoethane (**3**) or the decomposition products expected from **3** (Chart I).

Chart I



Although the detailed mechanism for the decomposition of **1** has not been established, it seems likely that the azoalkene gives rise to the diazonium ion pair **4** which may rearrange to **2** either in a concerted manner or through the formation of a vinylic carbonium ion[7–12] **5** or a divalent intermediate[9,13,14] **6**.



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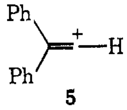

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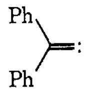

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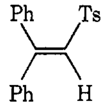
However, all attempts to trap intermediates such as **5** and **6** were unsuccessful. For example, compounds **7**–**9** (expected by-products from the carbonium ion **5**) were not detected in the reaction mixture.



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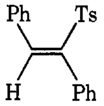

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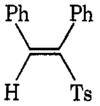

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Introduction of cyclohexene did not afford any carbenoid adducts. Thus if **5** or **6** are intermediates they are too short lived to undergo any intermolecular reactions.

Experimental Section

Melting points are uncorrected. Spectra were recorded on Beckman IR-5A, Unicam SP-800, and Minimar Jeolco spectrometers. Nmr spectra were recorded using TMS as internal standard. Microanalyses were performed using C, H, N Analyzer Model 185 of Hewlett-Packard Co. Diphenylacetaldehyde and tosylhydrazine are commercial materials. Analytical-grade solvents were purified by standard methods and distilled through a Vigreux column before use.

2,2-Diphenyl-1-tosylazoethylene (**1**).—Diphenylacetaldehyde (5.0 g, 2.5×10^{-2} mol) was dissolved in 200 ml of diethyl ether, and 4.0 g (2.5×10^{-2} mol) of bromide was added dropwise. The ethereal solution obtained was shaken with an aqueous solution of sodium carbonate and then washed several times with water. The ethereal solution was dried (Na_2SO_4), and the ether was evaporated. Part (2.0 g, 7.2×10^{-3} mol) of the crude 2-bromo-2,2-diphenylacetaldehyde was dissolved in 200 ml of ether, and 1.3 g (7.2×10^{-3} mol) of tosylhydrazine was added with magnetic stirring. When the solution turned red it was shaken with a saturated aqueous solution of sodium carbonate and then washed several times with water, dried (Na_2SO_4), filtered, and concentrated under reduced pressure at room temperature until precipitation of a yellow-orange product occurred. The crystals of **1** were collected, washed with *n*-hexane, and dried (yield 65%): mp 82° dec; uv max (Et_2O) 348 mμ (ε 20,400); ir (KBr) 3000 (vw), 1580 (m), 1550 (w), 1480 (w), 1440 (m), 1415 (s), 1335 (vs), 1290 (w), 1250 (w), 1210 (vw), 1185 (m), 1160 (vs), 1120 (vs), 1080 (vs), 1025 (w), 1015 (w), 985 (m), 928 (w), 878 (m), 830 (s), 810 (s); nmr (C_6D_6) δ 7.60 (s, 1, vinylic proton), 1.85 (s, 3, methyl of tosyl group).

Anal. Calcd for $C_{21}H_{18}N_2O_2S$: C, 69.61; H, 4.97; N, 7.73. Found: C, 69.57; H, 5.00; N, 7.75.

Decomposition of 2,2-Diphenyl-1-tosylazoethylene (**1**). **Route**

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[1] Work was effected with financial support of the Italian Research Council (C. N. R.).

[2] (a) L. Caglioti, A. Dondoni, and G. Rosini, *Chim. Ind.* (*Milan*), **50**, 122 (1968); (b) L. Caglioti, A. Dondoni, G. Rosini, and G. Mossa, *J. Chem. Soc. B*, 1404 (1968).

[3] W. Barbieri, L. Bernardi, P. Masi, L. Caglioti, and G. Rosini, *Tetrahedron Lett.*, 1343 (1970); W. Barbieri, L. Bernardi, P. Masi, A. Vigevani, L. Caglioti, and G. Rosini, *Tetrahedron*, in press.

[4] L. Caglioti and G. Rosini, *Chem. Ind.* (*London*), 1093 (1969).

[5] G. Rosini and R. Ranza, *J. Org. Chem.*, **36**, 1915 (1971).

[6] Methanol-free chloroform was used.

[7] M. S. Newman, and A. E. Weinberg, *J. Amer. Chem. Soc.*, **78**, 4654 (1956).

[8] M. S. Newman and A. Kutner, *ibid.*, **73**, 4199 (1951).

[9] D. Y. Curtin, J. A. Kampmeir, and B. R. O'Connor, *ibid.*, **87**, 863 (1965).

[10] D. Y. Curtin, J. A. Kampmeir, and M. L. Farmer, *ibid.*, **87**, 873 (1965).

[11] W. M. Jones and F. W. Miller, *ibid.*, **89**, 1960 (1967).

[12] A. C. Day and M. C. Whiting, *J. Chem. Soc. B*, 991 (1967).

[13] See J. Hine, "Divalent Carbon," Ronald Press, New York, N. Y., 1964.

[14] M. S. Newman and A. O. M. Okorodudu, *J. Amer. Chem. Soc.*, **90**, 4189 (1968).

A.—1 (3.0 g, 8.2 × 10^{-3} mol) dissolved in 100 ml of dried benzene in a sealed tube was heated in an oil bath at 90°. After a few minutes the color of the benzene solution disappeared with evolution of nitrogen. The colorless solution was cooled and concentrated under reduced pressure, and then a chromatographic separation was performed on a silica gel column using benzene as eluent. Diphenylacetylene was obtained in 85–90% yield, mp 59–60° (lit.[15] mp 60–61°); spectroscopic data are in agreement with those recorded on a sample independently prepared.[15]

Anal. Calcd for $C_{14}H_{10}$: C, 94.34; H, 5.66. Found: C, 94.25; H, 5.68.

Route B.—1 (3.0 g, 8.2 × 10^{-3} mol) was dissolved in 100 ml of chloroform and the solution was allowed to stand at 25° until the color disappeared (3–4 days); by evaporation of solvent under reduced pressure and chromatographic separation on a silica gel column using benzene as eluent, diphenylacetylene in 85–90% yield was obtained.

Registry No.—**1,** 34220-14-9; **2,** 501-65-5.

Acknowledgment.—We wish to thank Professor Luciano Caglioti for his interest in this work and Mr. R. Bonoli, who carried out some of the experiments.

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[15] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath, Boston, Mass., 1955, p 181.

The Effects of Group IVA Organometallics on the Reaction of Ethoxycarbonylnitrene with Cyclohexene[1a]

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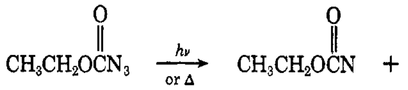
It has recently been reported that C–H bonds involving the carbon atom directly linked to a group IV metal (silicon and tin) are inert to dichlorocarbene generated by the thermal decomposition of phenyl(bromodichloromethyl)mercury. However, secondary or tertiary β C–H bonds underwent insertion readily.[2] Furthermore, the activating effect of a metal β to a C–H bond is in the order Sn > Ge > Si.[3]

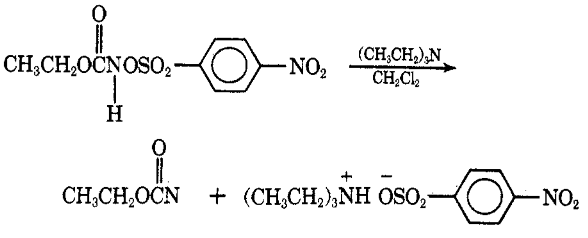
We wish to report that tetramethyltin (α C–H bonds), as well as trimethylisobutyltin (β C–H bond), is inert to insertion by ethoxycarbonylnitrene generated under a variety of reaction conditions.

Ethoxycarbonylnitrene can be generated by the thermal or photolytic decomposition of ethoxycarbonyl azide[4] (eq 1) or by base-induced α elimination from *N*-*p*-nitrobenzenesulfonyloxyurethane (eq 2)[5] and gives addition and insertion reactions similar to carbenes.[6]

However, we have found that thermal decomposition of ethoxycarbonyl azide in pure tetramethyltin or solutions of tetramethyltin in carbon tetrachloride or methylene chloride as inert solvents gave only recovered organotin starting compound, a few per cent yield of urethane, $CH_3CH_2OC(=O)NH_2$, from hydrogen abstraction by the nitrene, and small amounts of viscous, polymeric orange-red oils as products. A polymeric gum was also observed when pivaloylnitrene was generated in unreactive solvents such as methylene chloride.[7]



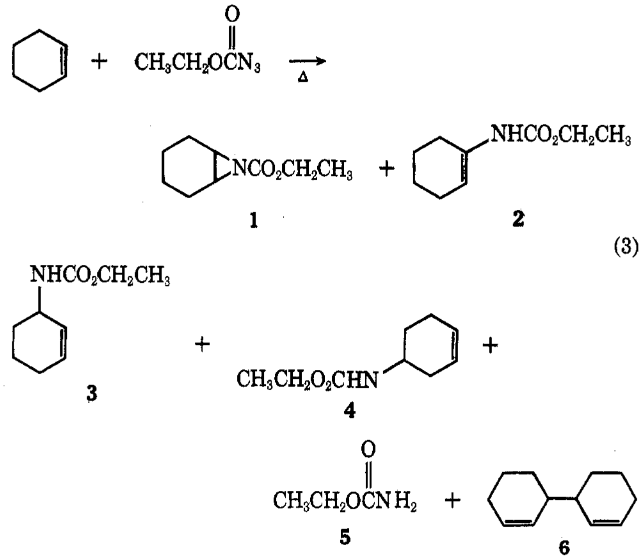
$$CH_3CH_2O\overset{\overset{O}{\|}}{C}N_3 \xrightarrow[\text{or }\Delta]{h\nu} CH_3CH_2O\overset{\overset{O}{\|}}{C}N + N_2 \qquad (1)$$



(2)

The α elimination reaction (eq 2) with 33 mol % tetramethyltin in methylene chloride gave a 97% yield of triethylammonium *p*-nitrobenzenesulfonate and, upon work-up, yielded only recovered tetramethyltin and a small amount of urethane. Since a tertiary, β C–H bond is the most reactive toward dichlorocarbene for tetraalkyltin, -germanium, or -silicon compounds, trimethylisobutyltin was prepared and allowed to react in acetonitrile solution with thermally generated ethoxycarbonylnitrene. However, gas chromatography after concentration of the reaction mixture showed peaks only for solvent, starting organotin compound, and urethane.

Since insertion into C–H bonds is attributed to the carbonylnitrene principally in the singlet electronic state,[8] the effect of organometallic group IVA compounds on the singlet–triplet character of this nitrene was evaluated. The major products obtained upon thermal decomposition of ethoxycarbonylazide in cyclohexene are given in eq 3.[4] The insertion products (2, 3, and 4) are mainly due to reaction of cyclohexene with singlet nitrene, products 5 and 6 are from triplet nitrene, and product 1 is from either singlet or triplet.[8]



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[1] (a) This work was supported by a grant from the Research Corporation and by grants from the California State College, Fullerton Foundation; (b) undergraduate research assistant.

[2] D. Seyferth, *et al.*, *J. Amer. Chem. Soc.*, **92**, 4405 (1970).

[3] D. Seyferth, *et al.*, *J. Organometal. Chem.*, **29**, 371 (1971).

[4] W. Lwowski and T. W. Mattingly, Jr., *J. Amer. Chem. Soc.*, **87**, 1947 (1965).

[5] W. Lwowski and T. J. Maricich, *ibid.*, **87**, 3630 (1965).

[6] W. Lwowski, *Angew. Chem., Int. Ed. Engl.* **6**, 897 (1967).

[7] S. Linke, G. T. Tisue, and W. Lwowski, *J. Amer. Chem. Soc.*, **89**, 6308 (1967).

[8] W. Lwowski, editor, "Nitrenes," Interscience Publishers, New York, N. Y., 1970, pp 200–207.