Reaction of Group IV Organometallic Compounds. XXXI.[1] The Reaction of *N*-Trimethylsilyl- and -stannyl-(diphenylmethylene)amine with Diketene

Hiroharu Suzuki, Isamu Matsuda,* Kenji Itoh, and Yoshio Ishii

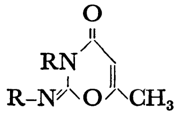
Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464

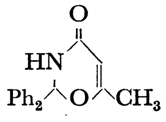
(Received July 15, 1974)

Linear 1/1 adducts and oxazinone derivative were obtained by the reaction of *N*-trimethylsilyl- and -stannyl-(diphenylmethylene)amine; $Ph_2C=N-MMe_3$ (M=Si, Sn) with diketene. Consecutive demetallation reaction by ethanethiol for the organostannyl 1/1 adduct, and by methanol for the organosilyl 1/1 adduct gave a piperidine derivative and an oxazinone derivative, respectively.

N-Trimethylsilyl- and -stannyl(diphenylmethylene)-amine; $Ph_2C=N-MMe_3$ ((I) for M=Si and (II) for M=Sn) have been reported to induce insertion and consecutive cyclization reactions with heterocumulene compounds,[1–4] aldehydes,[3] and acrylonitrile.[3]

Diketene is an attractive component for the preparation of six-membered heterocyclic compounds, because the acyl-oxygen bond cleavage of diketene provides a synthetic equivalence of acetylketene; $CH_3CO-CH=C=O$. For example, the addition of diketene to some carbodiimides and the parent diphenylmethyleneamine gave the corresponding oxazinone derivatives III[5] and IV,[6] respectively.

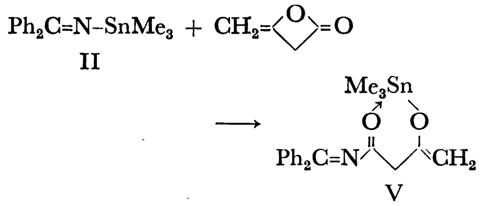

III


IV

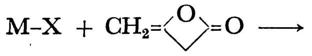
In this paper we describe an insertion of diketene to the metal-nitrogen bond of I and II, and the subsequent cyclization reactions by way of demetallation treatment. The difference of products in both insertion and demetallation steps by changing the metal atom is discussed.

Results and Discussion

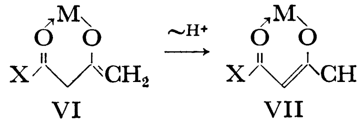
The Reaction of N-*Trimethylstannyl(diphenylmethylene)-amine (II).* N-Trimethylstannyl(diphenylmethylene)amine; $Ph_2C=N-SnMe_3$ (II) reacted exothermically with equimolar amounts of diketene to give the 1/1 adduct (V) as the fairly air-stable crystals in 96% yield. The strong IR absorption band around 1574 cm^{-1} indicates the presence of the carbonyl oxygen atom coordinated to the organotin moiety. Another absorption band at 1673 cm^{-1} was assigned to the C=N stretching frequency. The ^{1}H NMR spectrum of 1/1 adduct (V) showed resonance peaks at τ 7.05 (2H, m), 5.71 (1H, d, J=1.5 Hz), and 4.43 (1H, m), which were assigned to the methylene and terminal vinylic protons, respectively. The above spectroscopic results are consistent with the depicted structure V in Eq. (1). The participation of the diphenylmethylene group in the 1/1 reaction may be ruled out, since any cyclic product which includes the diphenylmethylene group in the ring skeleton was not obtained at all. Organometallic insertion reactions of diketene have been reported[7,8] to give only one product VII, which involves intramolecular 1,3-shift of a central methylene proton from VI.



(1)

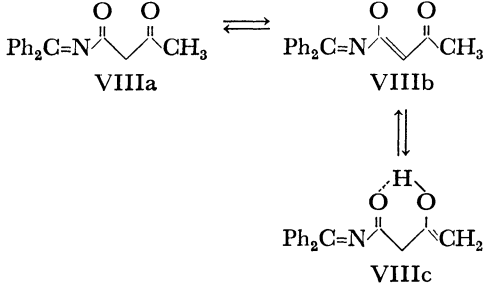


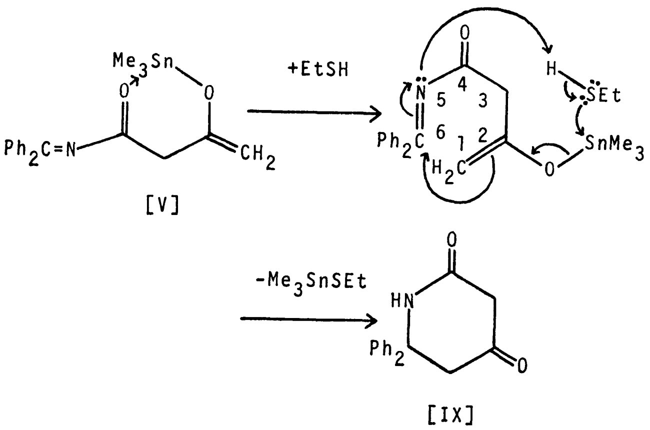
$M=o\text{-}C_6H_4O_2B$ $X=NEt_2$[7]
Me_3Sn NMe_2[7]
Et_2Al NMe_2[8]
Et_2Al SEt[8]



(2)

It is noteworthy that the product (V) obtained in the reaction of *N*-trimethylstannyl(diphenylmethylene)-amine with diketene is the first stable organometallic insertion product which does not induce a 1,3-proton shift. The structure of V is also confirmed by the following destannylation reaction. Ethanethiol was added to the 1/1 adduct (V) in order to substitute the trimethylstannyl group with proton. The expected products were the isomers VIIIa—VIIIc; however, the ^{1}H NMR spectrum of the obtained destannylation product exhibited unexpectedly neither methyl protons nor vinylic protons. Only two pairs of methylene protons (τ 6.95, 2H, s, and τ 6.68, 2H, s) and the one proton attached to the nitrogen atom (τ 2.32, 1H, s, confirmed by D_2O exchange) were observed.





Scheme 1.

Moreover, two strong absorption bands at 1728 and 1661 cm^{-1} are assigned to a ketone and an amide carbonyl stretching frequencies, respectively. The above-mentioned spectroscopic results are consistent with 6,6-diphenylpiperidin-2,4-dione (IX), whose formation may be shown in Scheme 1. The addition of ethanethiol firstly causes the cleavage of the intramolecular coordinated structure because of the difference in the affinity of the tin atom toward oxygen and sulfur atoms. Then the ring closure is induced exclusively by the nucleophilic attack of the terminal carbon atom C(1) to the *exo* double bond at C(6), accompanied by the elimination of trimethylstannyl ethylsulfide. In the present case, diketene behaves as a component $\dot{C}O-CH_2CO-\dot{C}H_2$ to [4+2] cycloaddition. This is quite different from the general behavior of diketene which acts as a synthetic equivalence of $CH_3CO-CH=C=O$ as described before.

The Reaction of N-Trimethylsilyl(diphenylmethylene)amine (I). *N*-Trimethylsilyl(diphenylmethylene)amine (I) reacted with diketene under more vigorous condition than the tin analogue (II) (60 °C, 14 hr). The 1/1 reaction mixture was purified by vacuum distillation (bp 108.0—116.0 °C/0.02 mmHg) and was confirmed as a 1/1 adduct by analysis, whereas the adduct did not show a simple ^{1}H NMR spectrum (Fig. 1). The detailed measurement of the proton ratio and coupling patterns revealed the presence of three isomers XI, XIII, and XV, structures of which were given in Scheme 2.

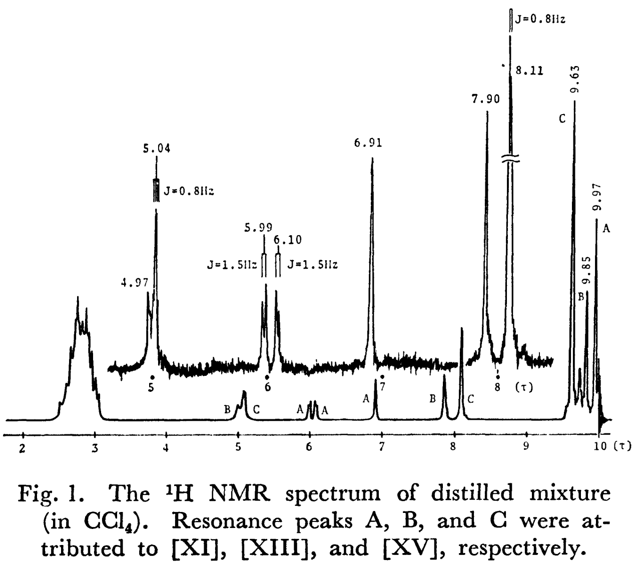
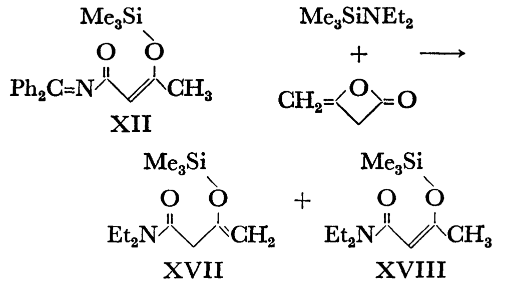


Fig. 1. The ^{1}H NMR spectrum of distilled mixture (in CCl_4). Resonance peaks A, B, and C were attributed to [XI], [XIII], and [XV], respectively.

There is the possibility of the presence of the structure XII in the 1/1 adduct as reported in the paper[9] that diketene reacted with equimolar amounts of trimethylsilyldiethylamine to give the mixture of XVII and XVIII as shown in Eq. (3).



(3)

However, it can be excluded because of the absence of the allyl coupling which is expected in the structure XII.

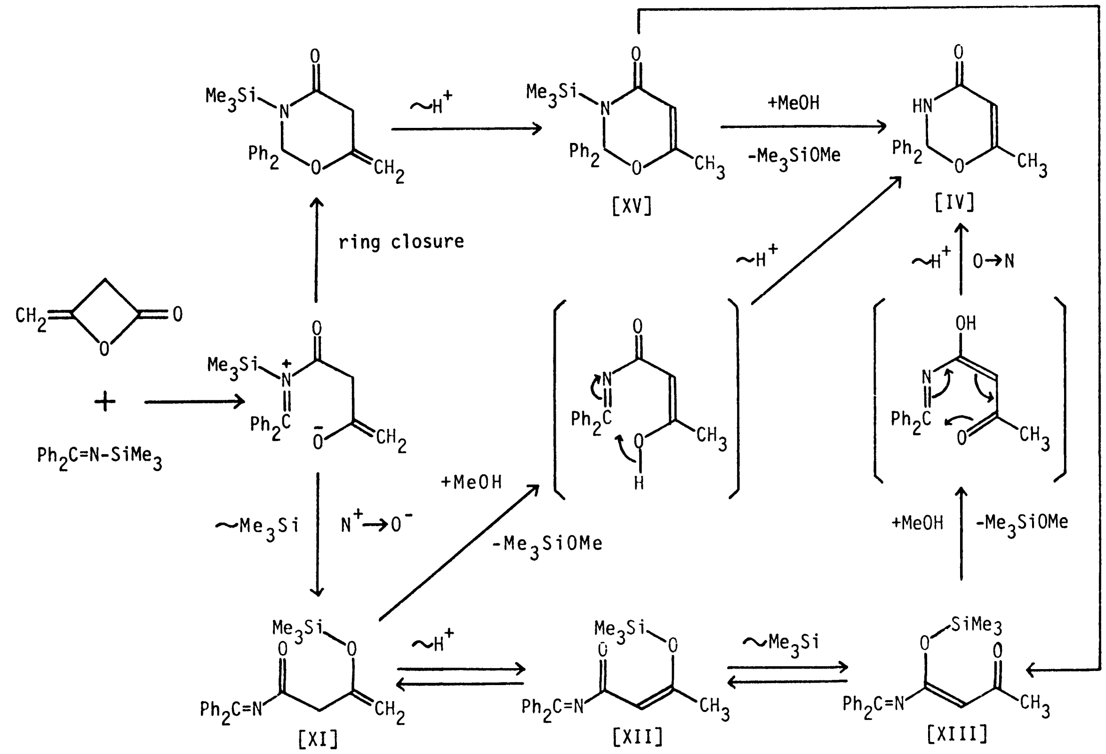
Table 1.

Reaction temp. (°C)	Total yield of XI, XIII, and XV (%)	Isomer ratio XI : XIII : XV
60	73	3.5 : 1 : 8.0
115	68	0.9 : 1 : 1.3
120	71	0.4 : 1 : 0.8

The observed isomer ratio in the 1/1 adducts was dependent on the reaction temperature as shown in Table 1. The isomer ratio of XI and XV decreased, and that of XIII increased as the elevation of the reaction temperature. This result definitely showed XI and XV were convertible to XIII, which would be thermodynamically the most stable product. Although the 1/1 adduct is composed of three isomers, XI, XIII, and XV, only 2,2-diphenyl-3,4-dihydro-6-methyl-2(1*H*)-1,3-oxazin-4-one (IV) was isolated on desilylation reaction. The yields are quantitative from the methanolysis of the purified 1/1 adduct, and 72% from the methanolysis of the 1/1 reaction mixture. The IV has been prepared by [4+2] cycloaddition reaction of the parent amine; $Ph_2C=NH$ with diketene.[6] The above results are summarized in Scheme 2.

The first step is a nucleophilic attack of the nitrogen atom in *N*-trimethylsilyl(diphenylmethylene)amine to the carbonyl carbon of diketene. In the second step, two paths are possible. First possibility is the migration of the trimethylsilyl group from the nitrogen to the oxyanion in X to give XI and XIII. Secondly, a direct ring closure accompanying a 1,3-prototropy gives XV, similar to a reaction of the parent diphenylmethyleneamine with diketene.[6]

It is extremely interesting that two isomeric heterocyclic compounds; IX and IV may be obtained from diketene only by changing the organometallic moiety in another component; *N*-organometallyldiphenylmethyleneamine.



Scheme 2.

Experimental

The mp of V was determined in a sealed capillary filled with argon. Analyses of organometallic compounds were carried out by Alfred Bernhardt Mikroanalytisches Laboratorium, West Germany. IR spectra were recorded on Japan Spectroscopic Co., Ltd., IR-S and DS-403G instruments. Proton NMR spectra were measured with Japan Electron Optics Co., Ltd., C-60HL instrument.

N-Trimethylsilyl(diphenylmethylene)amine[2] and *N*-trimethyltannyl(diphenylmethylene)amine[10] were prepared according to the published procedure. Diketene was distilled before use.

Reaction of N-*Trimethylstannyl(diphenylmethylene)amine with Diketene.* To a solution of 0.870 g (2.53 mmol) of *N*-trimethylstannyl(diphenylmethylene)amine in *ca.* 3 ml of benzene was added 0.268 g (3.19 mmol) of diketene at 0 °C under nitrogen. The reaction proceeded exothermically. The adduct was precipitated as pale yellow crystals by the addition of *ca.* 4 ml of *n*-hexane after the completion of the reaction. This was identified as 1/1 adduct (V), after the purification by reprecipitation from the mixed solvent of benzene and *n*-hexane (2/4) (1.044 g, 96%). Mp 130.0—133.0 °C. Found: C, 56.29; H, 5.54%. Calcd for $C_{20}H_{23}NO_2Sn$: C, 56.11; H, 5.41%. IR (in $CHCl_3$) 1673 and 1574 cm^{-1}. ^{1}H NMR (in $CDCl_3$) τ 9.57 (Me_3Sn, $J^{117/119}$Sn–C–H=65.0/68.0 Hz), 7.05 (2H, m), 5.71 (1H, d, J=1.5 Hz) and 4.43 (1H, m).

Destannylation of V. Addition of ethanethiol (2 ml) to a benzene solution (15 ml) of the 1/1 adduct (V) (0.900 g, 2.10 mmol) afforded the destannylated product (IX) (0.513 g, 1.94 mmol) as white prisms in 93% yield. Mp 179.5—181.5 °C. Found: C, 77.17; H, 5.72; N, 5.20%. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.69; N, 5.27%. IR (in KBr) 3120, 1728, and 1661 cm^{-1}. ^{1}H NMR (in $CDCl_3$) τ 6.95 (2H, s), 6.68 (2H, s), 2.72 (10H), and 2.32 (NH, br. s).

Reaction of N-*Trimethylsilyl(diphenylmethylene)amine with diketene.* The mixture of 1.916 g (7.58 mmol) of *N*-trimethylsilyl(diphenylmethylene)amine and 0.819 g (9.75 mmol) of diketene was heated at 60 °C for 40 hr in a sealed tube. The isomer ratio of [XI]: [XIII]: [XV] was decided by the intensities of proton signals of trimethylsilyl group in ^{1}H NMR spectrum of the reaction mixture. The reaction mixture was purified by vacuum distillation (bp 108.0—116.0 °C/0.02 mmHg) (1.85 g, 73%). Found: C, 71.22; H, 6.68%. Calcd for $C_{20}H_{23}NO_2Si$: C, 71.18; H, 6.78%. In the ^{1}H NMR spectrum (in CCl_4), the assignment of proton signals are as follows. XI: τ 9.97 (Me_3Si, 9H, s), 6.91 (2H, s), 6.10 (1H, d, J=1.5 Hz), and 5.99 (1H, d, J=1.5 Hz). XIII: τ 9.85 (Me_3Si, 9H, s), 7.90 (3H, s), and 4.97 (1H, s). XV: τ 9.63 (Me_3Si, 9H, s), 8.11 (3H, d, J=0.8 Hz), and 5.04 (1H, q, J=0.8 Hz).

A mixture of XI, XIII, and XV (2.55 g, 7.57 mmol) was desilylated by the treatment with methanol (5 ml). The desilylated product was isolated in 72% yield (1.45 g) and was identified to IV by the comparison with the authentic sample.[6]

References

1) Part XXX, H. Suzuki, K. Itoh, I. Matsuda, and Y. Ishii, This Bulletin, in press.

2) I. Matsuda, K. Itoh, and Y. Ishii, *J. Chem. Soc., Perkin I*, **1972**, 1678.

3) P. G. Harrison, *ibid.*, **1972**, 130.

4) M. F. Lappert, J. McMeeking, and D. E. Palmer, *J. Chem. Soc., Dalton*, **1973**, 151.

5) R. Lacey, *J. Chem. Soc.*, **1959**, 2134.

6) T. Kato and H. Sakamoto, *Yakugaku Zasshi*, **87**, 1322 (1967).

7) J. R. Horder and M. F. Lappert, *J. Chem. Soc., Ser. A*, **1969**, 173.

8) K. Urata, K. Itoh, and Y. Ishii, *J. Organometal. Chem.*, **63**, 11 (1973).

9) I. F. Lutsenko, Y. I. Baukov, A. S. Kostyuk, N. I. Savelyeva, and V. K. Krysina, *ibid.*, **17**, 241 (1969).

10) L. H. Chan and E. G. Rochow, *ibid.*, **9**, 231 (1967).