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Preliminary communication

Silicon–carbon multiple-bonded (p_π–p_π) intermediates. Reactions with acetonitrile and its derivatives

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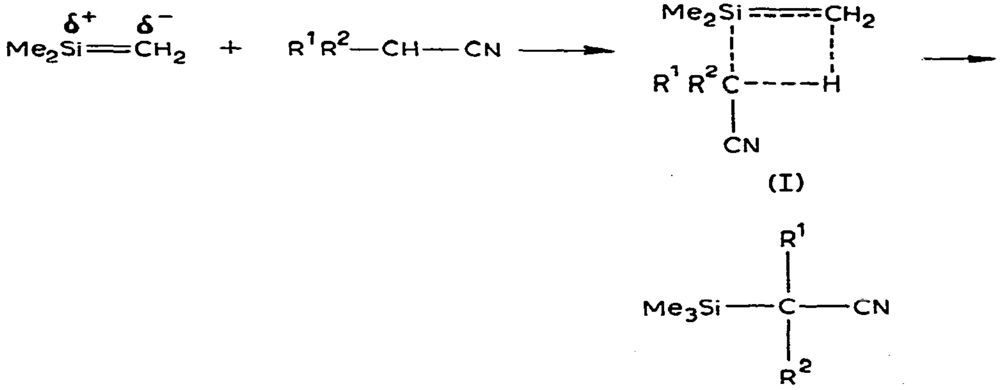
SUMMARY

1,1-Dimethylsilacyclobutane has been pyrolyzed at 610°C with acetonitrile and alkyl- and aryl-substituted acetonitriles to yield, in some cases, the corresponding α-trimethylsilyl-substituted acetonitriles.

In recent papers we have described reactions of the silicon–carbon double bond with aldehydes and ketones[1,2]. In these reactions there were two major reaction pathways: (1) A pseudo Wittig reaction in which a carbonyl moiety is transformed into an olefin, and (2) the formation of a silyl enol ether from an enolizable ketone or aldehyde.

Reported below are the results of the pyrolysis of 1,1-dimethylsilacyclobutane at 610°C with acetonitrile and substituted acetonitriles in a nitrogen flow system. The products are thought to arise by the reaction of dimethylsilylethylene with an acetonitrile via a four-centered transition state, which can be formulated according to eqn. 1.



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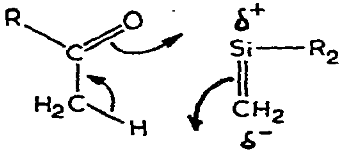
1,1-Dimethylsilacyclobutane (20.0 mmole) was pyrolyzed at 610°C in a nitrogen flow system with acetonitrile (122 mmole) in benzene solvent (9.33 mmole) to form trimethylsilylacetonitrile in 34% isolated yield[*]. The pyrolysis apparatus was a quartz tube 23 mm i.d. × 34 cm heated over a length of 30 cm by a 750 watt furnace. In all reactions the flow rate of the nitrogen carrier gas was 25 ml/min. The reaction solutions were added to the quartz tube at a rate of between 0.3 and 0.4 g/min. The yields were reproducible and did not vary significantly with minor changes in addition rate. Contact times are difficult to calculate because flash vaporization of the volatile components of the reaction solution caused temporary flow rates which were much greater than that of the carrier gas. The actual contact times were much shorter than the value of 5.0 min calculated using only the carrier gas flow rate. The benzene was needed to dissolve solid reactants and reduce mechanical losses by increasing the volume of the solutions which were pyrolyzed.

IR(CCl_4): ν(CN) 2243, (MeSi) 1255 cm^{-1}; NMR (CCl_4 with external TMS): δ 0.13 (s, 9), δ 1.51 (s, 2). This reaction can be explained by a four-centered mechanism in which the silicon atom becomes attached to the α-carbon of the nitrile and the carbon atom of the silicon—carbon double bond becomes attached to the α-hydrogen of the nitrile. This is approximately as shown in Eq. (1) with the added caution that addition may not be completely concerted.

Other more complex multi-step mechanisms involving interaction between silicon and nitrogen appear less probable and would, for an intramolecular process, involve a 1—3 shift of Me_3Si from nitrogen to the methylene in an allenic type system; such a shift seems highly improbable from a geometrical viewpoint. We cannot, however, rule out an intermolecular exchange process of this sort but we tend to favor the simpler alternative of a four-centered mechanism.

Reaction of acetonitrile-d_3 with 1,1-dimethylsilacyclobutane at 610°C yields deuteriotrimethylsilyldeuterioacetonitrile $N{\equiv}C{-}CD_2{-}Si(CH_2D)Me_2$ (II). The general course of the above reaction suggests that in the reaction of the silicon—carbon double bond with enolizable ketones and aldehydes[2], the ketone or aldehyde need not be in the enol form to react, and that a six-centered mechanism[2] may be involved as in III.



(III)

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[*] All products reported in this paper have been isolated by preparative GLC. The thermal stability of trimethylsilylacetonitrile was determined by pyrolysis in benzene at 610° and recovery by preparative GLC in 66% yield.

For II: exact mass of *P*-Me, $C_4H_5D_3SiN$: found 101.0632; calcd. 101.0623 *m/e* 101 (*P* − Me), 100 (*P* − CH_2D), and 74 (*P* − CD_2CN). NMR (CCl_4, ext. TMS): δ 0.20 (s). IR (CCl_4): 2970, 2240, 1400, 1250, 1170, 1070, 970 cm^{-1}.

When 1,1-dimethylsilacyclobutane was pyrolyzed with excess benzonitrile, no adduct was detected and 83% of the benzonitrile was recovered. This result is in accord with our proposed mechanism for acetonitrile.

It was also of interest to determine the effect of steric and electronic factors on the reactivity of the silicon—carbon double bond. This was done by varying the substituents on acetonitrile. Table 1 summarizes these results. If the reaction involves mainly nucleophilic attack of the α-carbon of the nitrile on the electron deficient silicon, then alkyl substituents on the nitrile should inductively increase the reactivity. Alkyl groups should also, however, have a steric effect which would decrease the reactivity of the nitrile. From the results summarized in Table 1 it seems that steric factors are important.

TABLE 1

SILICON—CARBON DOUBLE BOND REACTIONS WITH ACETONITRILES

Reactant	*Product*	*Isolated*[a] *yield (%)*
CH_3CN	Me_3SiCH_2CN	34
$MeCH_2CN$	$Me_3SiCH(Me)CN$	22
Me_2CHCN	$Me_3SiC(Me)_2CN$	11
$PhCH_2CN$	$Me_3SiCH(Ph)CN$	4
Ph_2CHCN	$Me_3SiC(Ph)_2CN$	0

[a] Isolated yields were obtained by preparative GLC.

1,1-Dimethylsilacyclobutane (10.0 mmole) when pyrolyzed at 610°C with propionitrile (30.0 mmole) yields α-trimethylsilylpropionitrile[4] in 22% isolated yield. IR (CCl_4): 2990, 2900, 2910, 2240, 1260; NMR (CCl_4, ext. TMS): δ 0.13 (s, 9), δ 1.31 (d, 3), δ 1.83 (m, 1). Here the yield of α-trimethylsilylpropionitrile has decreased by 12% compared to that of trimethylsilylacetonitrile.

1,1-Dimethylsilacyclobutane (12.0 mmole) when pyrolyzed with dimethylacetonitrile (55.0 mmole) at 610° yields 11% of trimethylsilyldimethylacetonitrile: (nc) exact mass $SiC_7H_{15}N$: found 141.0990; calcd. 141.0973. *m/e* 126 (*P* − Me), 73 $(Me_3Si)^+$. IR (CCl_4): 2965, 2220, 1420, 1250. NMR (CCl_4, ext. TMS): δ 0.167 (s, 9) and δ 1.31 (s, 6). Here again the steric effects of two methyl groups can account for the low yield.

1,1-Dimethylsilacyclobutane (9.46 mmole) when pyrolyzed with phenylacetonitrile (30.0 mmole) at 610° affords a 4% yield of trimethylsilylphenylacetonitrile[5]. IR (CCl_4): 2990, 2240, 1260; NMR (CCl_4, ext. TMS): δ 0.13 (s, 9), δ 3.25 (s, 1) and δ 7.47 (m, 5). The low yield observed probably results from delocalization of the negative charge on the α-carbon by the phenyl substituent, thus making that carbon a poorer nucleophile toward the positive silicon. This indicates that in reactions of acetonitrile with silicon—carbon double bonds the rate-controlling stage involves nucleophilic attack at the positive silicon center rather than electrophilic attack of an α-hydrogen at the negative carbon center. A silicon—carbon double bond certainly must possess zwitterion character as indicated by the following resonance formulation:

$$R_2Si{=}CH_2 \leftrightarrow R_2\overset{+}{Si}{-}\overset{-}{C}H_2$$

1,1-Dimethylsilacyclobutane was pyrolyzed with diphenylacetonitrile at 610°C and GLC analysis showed no products corresponding to trimethylsilyldiphenylacetonitrile.

ACKNOWLEDGMENT

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