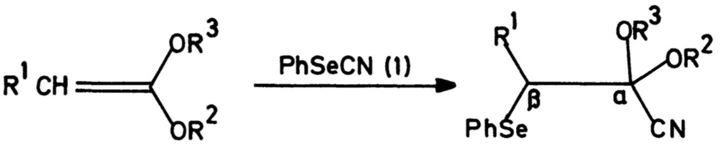
CHEMISTRY LETTERS, pp. 1733-1734, 1982.

CYANOSELENENYLATION OF KETENE ACETALS. SYNTHESIS OF CARBONYL-PROTECTED α-OXO CARBONITRILES[1)]

Shuji TOMODA,* Yoshito TAKEUCHI, and Yujiro NOMURA
Department of Chemistry, College of General Education
The University of Tokyo, Komaba, Meguro-ku, Tokyo 153

The reaction of ketene acetals with phenyl selenocyanate afforded a new type of compounds, α,α-dioxy-β-phenylseleno carbonitriles(carbonyl-protected α-oxo carbonitriles), in good yields. Oxidation of these vicinal cyanoselenenylation products gave β,γ-unsaturated α,α-dioxy carbonitriles in excellent yields.

In earlier communications, we reported efficient addition reaction of phenyl selenocyanate (1)[2)] to olefins, such as enamines[3)] and simple alkenes.[4)] This reaction, which we call cyanoselenenylation, is among a few reactions which can introduce a cyano group directly into the carbon-carbon double bond.[5)] We now wish to report that cyanoselenenylation can also be effected with ketene acetals (2) to provide α,α-dioxy-β-phenylseleno carbonitriles (3)(carbonyl-protected α-oxo carbonitriles[6)]), a new structural type of compounds which are of considerable potential utility to construct latent α-amino ketone unit[7)] frequently found in alkaloids.



2 3

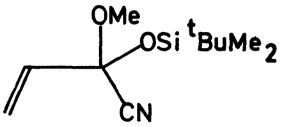
Both ketene dialkyl acetal[8)] and ketene alkyl silyl acetals[9)] undergo regioselective cyanoselenenylation with phenyl selenocyanate (1) as shown in the Table.[10)] Thus ketene diethyl acetal (2a) reacted with a slight excess of 1 in ethanol at room temperature under argon to afford 3a in 73% yield after purification by column chromatography. The ^{1}H-NMR spectrum of 3a showed a singlet at δ 3.32 due to the methylene group carrying the phenylseleno moiety besides three other absorptions; δ($CDCl_3$) 7.21(m, 5H, SePh), 3.68(q, J=7 Hz, 4H, OCH_2), and 1.20(t, J=7 Hz, 6H, CH_3). The presence of a cyano group was clearly demonstrated by IR(2230 cm^{-1}) and ^{13}C-NMR(δ 115.7). Similarly 1-tert-butyldimethylsiloxy-1-methoxyethylene (2b) gave 3b in 64% yield. Interestingly, the cyanoselenenylation of ketene acetals (2) appears neither stereospecific nor stereoselective unlike other olefins previously reported.[3,4)] Thus, 2c, obtained as a 7:3 mixture of stereoisomers from the enolate anion of methyl propionate[11)], provided a single adduct 3c in 78% yield, whereas 2d afforded two stereoisomeric adducts 3d in 7:2 ratio. No regioisomers were found in either case.

Upon oxidation with 30% hydrogen peroxide, the α,α-dioxy-β-phenylseleno carbonitriles (3c and 3d) were readily converted into β,γ-unsaturated α,α-dioxy carbonitriles (4c and 4d) in 91 and 94% yields, respectively(CH_2Cl_2, r.t., 4 h).[12)]

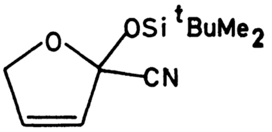
Table Cyanoselenenylation of Ketene Acetals (2) with Phenyl Selenocyanate (1)[a]

Compd. number suffix	2			3		
	R^1	R^2	R^3	Yield(%)	ν(CN)(cm^{-1})[b]	^{13}C-NMR(CN)(δ)[c]
a	H	Et	Et	73	2230	115.7
b	H	Me	^{t}BuMe$_2$Si	64	2215	116.7
c	Me	Me	^{t}BuMe$_2$Si	78	2220	116.5
d	-CH_2CH_2-		^{t}BuMe$_2$Si	56(major)	2215	117.7
				16(minor)	2220	117.5

[a] Reactions were run in ethanol(2a) or in dichloromethane(2b, 2c and 2d) using 1.2 mole equiv. of 1 for 8-18 h(TLC control) at room temperature under argon. [b] Obtained as a thin film. [c] Measured in $CDCl_3$ with tetramethylsilane as an internal standard.



4c



4d

The reaction products described herein (3 and 4) are regarded as α-oxo carbonitrile derivatives in which carbonyl group is protected as an acetal from nucleophilic attack. In view of the general observation that nucleophiles preferentially attack the carbonyl group of α-oxo carbonitriles with concomitant displacement of the cyano group,[6] these compounds (3 and 4) would be especially suited to construct the α-amino ketone structure by selective nucleophilic reactions at the cyano carbon. Further studies are now in progress.

References

1) Organoselenium Chemistry 6. Part 5; S. Tomoda, Y. Takeuchi, and Y. Nomura; Ref. 4.
2) S. Tomoda, Y. Takeuchi, and Y. Nomura, Chem. Lett., 1981, 1069.
3) S. Tomoda, Y. Takeuchi, and Y. Nomura, Tetrahedron Lett., 23, 1361(1982).
4) S. Tomoda, Y. Takeuchi, and Y. Nomura, J. Chem. Soc. Chem. Commun., 1982, in press.
5) Recent examples; (a) B. M. Trost, T. Shibata, and S.J. Martin, J. Am. Chem. Soc., 104, 3228 (1982). (b) J. Backvall and O.S. Andell, J. Chem. Soc. Chem. Commun., 1981, 1098. (c) P.S. Elmes and W.R. Jackson, J. Am. Chem. Soc., 101, 6128(1979).
6) For a recent review on α-oxo carbonitriles(acyl cyanides), see; S. Hünig and R. Schaller, Angew. Chem. Int. Ed. Engl., 21, 36(1982).
7) (a) D.E. Enders and H. Lotter, Tetrahedron Lett., 23, 639(1982). (b) D.E. McClure, B.H. Ariso, J.H. Jones, and J.J. Baldwin, J. Org. Chem., 46, 2431(1981).
8) S.M. McElvain and D. Kundiger, Org. Synth. Coll. Vol. 3, 506(1955).
9) J.K. Rasmussen, Synthesis, 1977, 91.
10) Structures of 3 were consistent with combustion analysis, IR and NMR(^{1}H and ^{13}C) spectral data.
11) M.V. Rathke and D.F. Sullivan, Synth. Commun., 3, 67(1973).
12) Structures of 4c and 4d were consistent with IR and NMR(^{1}H and ^{13}C).

(Received September 6, 1982)