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

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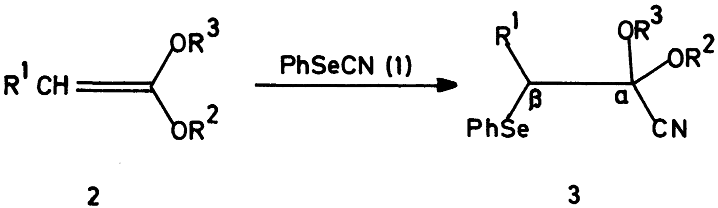
The reaction of ketene acetals with phenyl selenocyanate afforded a new type of compounds, α,α-dioxy-β-phenylseleno carbonitriles(carbonyl-protected α-oxo carbonitriles), in good yields. Oxidation of these vicinal cyanoselenenylation products gave β,γ-unsaturated α,α-dioxy carbonitriles in excellent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

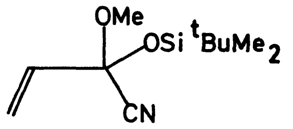
Both ketene dialkyl acetal[8] and ketene alkyl silyl acetals[9] undergo regioselective cyanoselenenylation with phenyl selenocyanate (1) as shown in the Table.[10] Thus ketene diethyl acetal (2a) reacted with a slight excess of 1 in ethanol at room temperature under argon to afford 3a in 73% yield after 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]

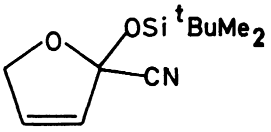
Table Cyanoselenenylation of Ketene Acetals (2) with Phenyl Selenocyanate (1)[a]

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	$^tBuMe_2Si$	64	2215	116.7
c	Me	Me	$^tBuMe_2Si$	78	2220	116.5
d	$-CH_2CH_2-$		$^tBuMe_2Si$	56(major) 16(minor)	2215 2220	117.7 117.5

[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

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