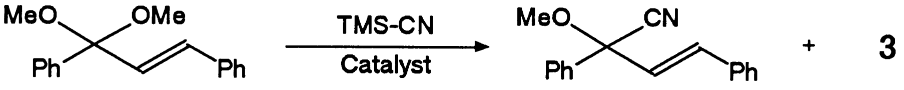
CHEMISTRY LETTERS, pp. 1259-1262, 1990. © 1990 The Chemical Society of Japan

Reactions of Acetals of α,β-Unsaturated Ketones with Silylated Nucleophiles as Trimethylsilyl Cyanide and Phenylthiotrimethylsilanes

Teruaki MUKAIYAMA, Haruhiro TAKENOSHITA,
Masaaki YAMADA, and Tsunehiko SOGA
Department of Applied Chemistry, Faculty of Science,
Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162

A result of the reaction between phenylthiotrimethylsilane and (E)-chalcone dimethyl acetal let us to reinvestigate the structure of the isomerized products obtained from the reaction of acetals of (E)-chalcone derivatives with trimethyl cyanide recently reported from our laboratory. It was found consequently that previously assigned isomerized products were not Z-isomer of α-methoxy-β,γ-unsaturated nitriles, but γ-methoxy-α,β-unsaturated nitriles produced by double transfer of double bond and methoxy group. Reactions of thus formed nitriles with several silylated nucleophiles are also described.

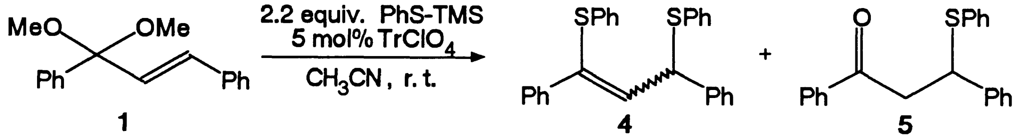
In the previous paper,1) we reported that in the presence of a catalytic amount of di-μ-chloro-bis(1,5-cyclooctadiene)dirhodium or trityl perchlorate ($TrClO_4$), trimethylsilyl cyanide (TMS-CN) reacts with (E)-chalcone dimethyl acetal (1) to yield (E)-2,4-diphenyl-2-methoxy-3-butenenitrile (2) and its isomerized compound 3.



1 (E)-2

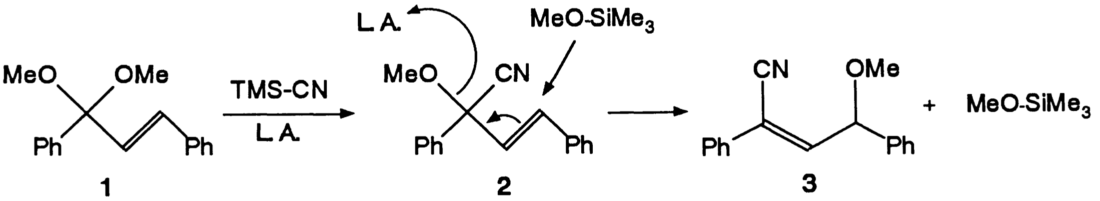
2 mol% $[Rh(COD)Cl]_2$, CH_2Cl_2, r.t., 40 h, 89% yield, 2 : 3 = 20 : 80
5 mol% $TrClO_4$, CH_3CN, r.t., 3 h, 92% yield, 2 : 3 = 0 : 100

We judged that the structure of the above compound 3 was Z-isomer of 2 resulted by isomerization of double bond based on the value of coupling constant (J=9.2 Hz) characteristic to cis olefinic protons by ^1H NMR measurement. However, at that time, the reason for the perfect isomerization from E to Z-isomer was not explained clearly. In order to extend the scope of the above reaction, dithioacetalization of 1 was tried with phenylthiotrimethylsilane (PhS-TMS) in the presence of a catalytic amount of $TrClO_4$ in CH_3CN. It was found there that 1,3-bis(phenylthio)-1,3-diphenyl-1-propene (4) (mixture of E and Z-isomer, 1:4), formed by transfer of double bond, and 1,3-diphenyl-3-phenylthio-1-propanone (5), the Michael adduct, were obtained in 60% and 34% yield, respectively. The structure of 4 was determined mainly by ^1H and ^{13}C NMR measurement.2) E or Z-isomer of dithioacetal of chalcone was not isolated under the above conditions.



The above result let us to study again on assigned structure of compound 3 resulted from the reaction between 1 and TMS-CN, because there considered another possibility of isomerization by double transfer of double bond and methoxy group in the above mentioned cyanation reaction of 1. So, we carefully reinvestigated the structure of the above isomerized product 3.

^{13}C NMR spectra of compound 3 were measured and it showed a signal at δ=82.2. This signal was assigned to a carbon atom bonded to methoxy group and this carbon atom was determined to be a tertiary carbon by off-resonance measurement. The above data indicated that compound 3 was not Z-isomer of 2. Further, ^{13}C NMR spectra showed other two signals at δ=116.2(s) and 116.5(s). One of these signals could be assigned to a carbon atom of cyano group and another signal could be assigned to 2-position carbon of conjugated unsaturated nitrile. Based on these data, it is reasonable to consider that 3 was produced according to the following reaction.



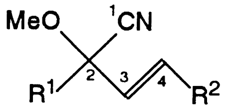
Trimethylsilyl methoxide, formed by the reaction of 1 with TMS-CN, would attack onto 4-position carbon of 2 by promotion of Lewis acid to form a conjugated nitrile 3 accompanied with transfer of double bond.[3)] Concerning the geometry of double bond in 3, only one isomer was observed by ^{1}H and ^{13}C NMR measurement and the geometry was considered Z-configuration because of a value of coupling constant between 1-position carbon and 3-position proton ($^3J_{C1,H3}$=13.9 Hz) by ^{13}C NMR measurement[4)] and steric effect of C1-phenyl group.

Isomerization of isolated 2 to 3 was tried under various conditions (Table 1) and it was found that the isomerization did not occur in the presence of only $TrClO_4$ catalyst, on the other hand, the isomerization was completed within 3 h in the presence of 5 mol% of $TrClO_4$ and 2 equiv. of TMS-OMe. This result supported the

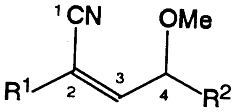
Table 1. Isomerization from Isolated 2 to 3 [a)]

Entry	Reagent	Time/h	Ratio of 2 : 3 [b)]	Isolated yield/%
1	$TrClO_4$ (5 mol%)	18	100 : 0	-
2	$TrClO_4$ (5 mol%) - TMSOMe (2 equiv.)	3	0 :100	96
3	$SbCl_5$ (5 mol%)	3	8 : 92	87
4	$SbCl_5$ (5 mol%) - TMSOMe (1.5 equiv.)	1.5	0 :100	83

a) Reactions were carried out in CH_3CN at r.t.
b) Determined by ^{1}H NMR.



6



7

Table 2. δ Values of Main Signals of **6** and **7** on ^{1}H and ^{13}C NMR Spectra

R^1	R^2	**6** [a] C1 (s)	C2 (s)	3-H (J=16 Hz)	4-H (J=16 Hz)	**7** [b] C1 and C2 (s) (s)	C4 (d)	3-H (J=9 Hz)	4-H (J=9 Hz)
Ph	Ph	117.2	81.2	6.18	7.01	116.2 and 116.5	82.2	6.84	5.34
p-Me-Ph	Ph	117.3	81.1	6.18	6.98	117.1 and 117.2	82.9	6.79	5.33
p-MeO-Ph	Ph	117.3	80.7	6.18	6.94	116.1 and 116.4	82.2	6.70	5.32
p-NO_2-Ph	Ph	116.3	80.6	6.07	7.11	114.3 and 115.3	82.2	7.03	5.35
Ph	p-NO_2-Ph	116.7	81.0	6.36	7.05	116.0 and 118.1	81.1	6.74	5.46
Ph	α-Naphthyl	117.3	81.3	6.24	-	116.2 and 117.2	80.6	7.06	5.93
Ph	β-Naphthyl	117.2	81.3	6.30	7.16	116.3 and 116.6	82.3	6.92	5.51
p-MeO-Ph	p-NO_2-Ph	116.8	80.5	6.37	6.97	116.1 and 117.7	81.2	6.59	5.43

a) **6** were prepared by using 1.5 equiv. of TMS-CN and 5 mol% of $CoCl_2$ in CH_3CN for 0.5 - 3 h.

b) **7** were prepared by using 1.5 equiv. of TMS-CN and 5 mol% of $TrClO_4$ or $SbCl_5$ in CH_3CN for 3 - 24 h. Yields of **7** were described in the previous paper.[1)]

above mechanism of the isomerization. In case of using $SbCl_5$ catalyst (stronger Lewis Acid), the isomerization took place even in the absence of TMS-OMe.

δ values of main signals on ^{1}H and ^{13}C spectra of all compounds listed in the previous paper[1)] were shown in Table 2. These data also supported the isomerized structure of **7**, therefore, we would like to correct the previously assigned structure (Z)-**6** to **7** with our sincere apology.

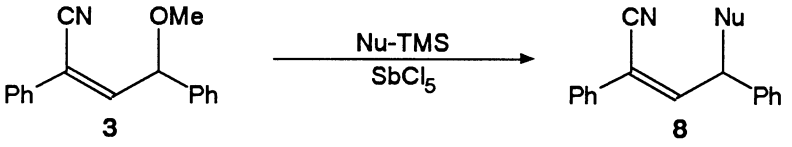
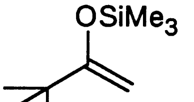
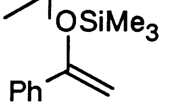
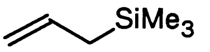


Table 3. Reactions of **3** with Various Silylated Nucleophiles[a)]

Entry	Nucleophile	Temp / °C	Yield/%
1		- 78	96
2		- 78	76
3		0	64[b)]
4	TMS-CN	- 23	87

a) Reactions were carried out by using 1.5 - 1.8 equiv. of nucleophiles and 1.1 equiv. of $SbCl_5$ in CH_2Cl_2 for 1 h.

b) Starting material **3** was recovered in 22% yield.

Concerning the utility of the isomerized compound **3**, there is a possibility of substitution at allyl ether position by silylated nucleophiles⁵⁾ in addition to an availability as an α,β-unsaturated nitrile. The reactions of **3** with various silylated nucleophiles by the promotion of $SbCl_5$ are demonstrated in Table 3.

It is noted that the use of a catalytic amount of $TrClO_4$ promotes the cyanation of (E)-chalcone dimethyl acetal derivatives with TMS-CN yielding the γ-methoxy-α,β-unsaturated nitriles accompanied with double transfer of double bond and methoxy group. The similar isomerization was observed in the reaction of chalcone dimethyl acetal with PhS-TMS. Further studies directed to the possible use of the other nucleophiles and acetals of α,β-unsaturated ketones are currently in progress.

References

1) T. Mukaiyama, H. Takenoshita, M. Yamada, and T. Soga, *Chem. Lett*, **1990**, 229.

2) Pure major isomer of **4** was obtained by recrystallization from ethanol. The geometry of double bond in major isomer was considered Z-configuration because of a chemical shift of a olefinic proton by ^{1}H NMR measurement. Major isomer: mp 103-5 °C; ^{1}H NMR ($CDCl_3$) δ=5.85 (1H,d,J=10.1 Hz), 6.59 (1H,d,J=10.1 Hz); ^{13}C NMR ($CDCl_3$) δ=53.3(d). Minor isomer: ^{1}H NMR ($CDCl_3$) δ=4.90 (1H,d,J=11.0 Hz), 6.13 (1H,d,J=11.0 Hz); ^{13}C NMR ($CDCl_3$) δ=52.7(d).

3) Analytical data of **3**: IR(neat) 2220, 1495, 1450, 1085, 755, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.43 (3H,s), 5.34(1H,d,J=9.2Hz), 7.3-7.6(10H,m); ^{13}C NMR ($CDCl_3$) δ=56.8(q), 82.2(d), 116.2(s), 116.5(s), 126.0(d), 126.6(d), 128.6(d), 129.0(d and d, 2C), 129.3(d), 133.5(d), 135.0(s), 137.4(s). Found: *m/z* 249.1124. Calcd for $C_{17}H_{15}NO$: M, 249.1154.

4) U. Vögeli and W. von Philipsborn, *Org. Magn. Reson.*, **7**, 617 (1975).

5) T. Mukaiyama, H. Nagaoka, M. Ohshima, and M. Murakami, *Chem. Lett.*, **1986**, 1009; M. Murakami, T. Kato, and T. Mukaiyama, *ibid.*, **1987**, 1167.

(Received April 26, 1990)