Tetrahedron Letters,Vol.27,No.26,pp 3025-3028,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

# LEWIS ACID CATALYZED SUBSTITUTION OF ALLYLIC NITRO COMPOUNDS WITH CYANOTRIMETHYLSILANE

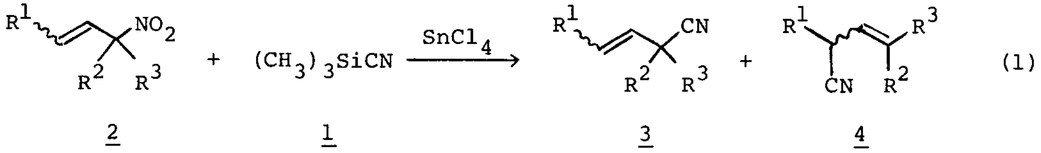
Hideyoshi Miyake* and Kimiaki Yamamura

Department of Chemistry, College of General Education,
Kobe University, Nada, Kobe 657, Japan

Summary: The nitro group in allylic nitro compounds is replaced by cyano group on treatment with cyanotrimethylsilane in the presence of Lewis acid.

Allylic nitro compounds are easily prepared by well established procedures with carbon-carbon bond forming reaction under mild conditions[1,2)], and the nitro group of them can be replaced by various functional groups[2,3)]. Therefore, they are versatile intermediates in organic synthesis. Now, we wish to describe a new and convenient method to replace a nitro group at an allylic position with cyano group by the reaction with cyanotrimethylsilane (1)[4)] in the presence of Lewis acid catalyst.

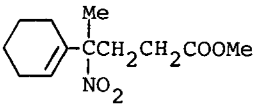
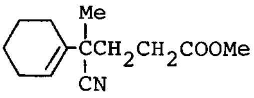
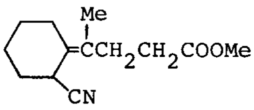
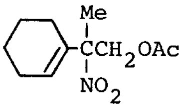
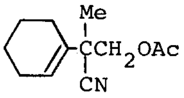
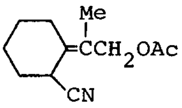
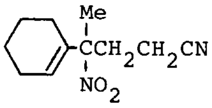
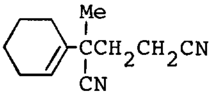
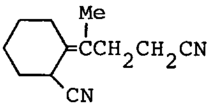
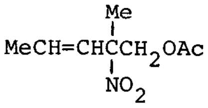
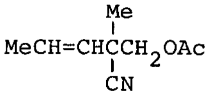
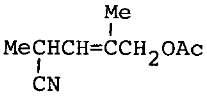
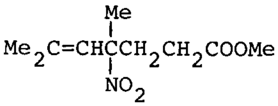
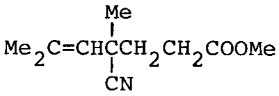
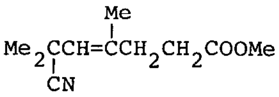
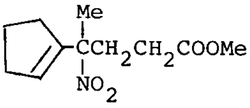
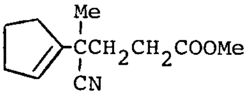
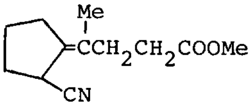
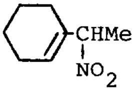
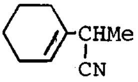
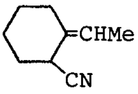
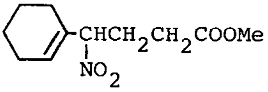
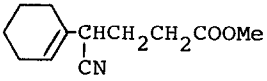
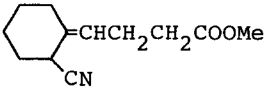
Cyanotrimethylsilane(1),which is readily available[4a)], was very useful reagent for the synthesis of silyl ether of cyanohydrines[4b)], tertiary nitriles[4c)], and isonitriles[4d)]. Those reactions are often catalyzed by Lewis acids, such as $SnCl_4$, $TiCl_4$, and $ZnCl_2$.



When allylic nitro compounds(2) were treated with 1 in the presence of Lewis acid catalyst, the nitro group was replaced by cyano group, and corresponding β,γ-unsaturated nitriles(3 and 4) were obtained (Eq.1). Of all the Lewis acids we used, $SnCl_4$ was the most effective catalyst for this reaction, and $TiCl_4$ was also effective. However, other Lewis acids such as $ZnCl_2$, $AlCl_3$, and $BF_3 \cdot OEt_2$ were not so effective as $SnCl_4$ and $TiCl_4$; the reaction proceeds much slower and the yield of the nitriles was lower.

The results are summarized in Table. The nitro group of tertiary allylic nitro compounds was replaced by cyano group smoothly at room temperature in good yield without destruction of other functional groups, such as ester group and cyano group.

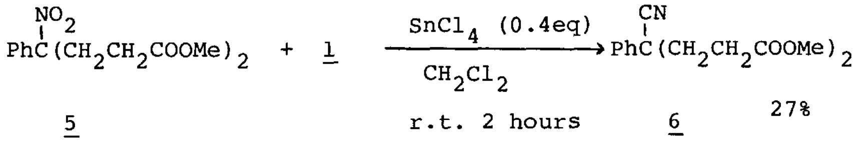
Table. Replacement of the Nitro Group by Cyano Group

| Entry | R-$NO_2$ | Products | | Yield a) | |
|---|---|---|---|---|---|
| | 2 | 3 | 4 b) | (%) | 3:4 |
| 1 |  |  |  | 75<br>54 | 3:7 d)<br>2:8 c,d) |
| 2 |  |  |  | 69 | 5:5 d) |
| 3 |  |  |  | 78 | 3:7 e) |
| 4 |  $\mathrm{MeCH{=}CH\overset{Me}{\underset{NO_2}{C}}CH_2OAc}$ b) |  $\mathrm{MeCH{=}CH\overset{Me}{\underset{CN}{C}}CH_2OAc}$ |  $\mathrm{Me\underset{CN}{C}HCH{=}\overset{Me}{C}CH_2OAc}$ | 61 | 5:5 e) |
| 5 |  $\mathrm{Me_2C{=}CH\overset{Me}{\underset{NO_2}{C}}CH_2CH_2COOMe}$ |  $\mathrm{Me_2C{=}CH\overset{Me}{\underset{CN}{C}}CH_2CH_2COOMe}$ |  $\mathrm{Me_2\underset{CN}{C}CH{=}\overset{Me}{C}CH_2CH_2COOMe}$ | 73 | 5:5 e) |
| 6 |  |  |  | 65 | 2:8 d) |
| 7 |  |  |  | 39 | 5:5 f) |
| 8 |  |  |  | 50 | 5:5 d) |

a) Isolated yield. b) E/Z ratio was not determined. c) $TiCl_4$ was used as catalyst. d) Determined by GLPC. e) Ratio of pure isolated compounds. f) Determined by $^1H$ NMR.

The regio-selectivity of this reaction was low, and the mixture of the isomers (3 and 4) was obtained (entries 1-6). The nitro group of secondary allylic nitro compounds was also replaced by cyano group under the same conditions. However, the yield of the nitriles was lower (entries 7 and 8). In all cases, regio-selectivity of the replacement was low. It is one of the most important unsolved problem, and we are under studying to improve the regio-selectivity.

Benzylic nitro compound (5) also reacted with 1 in the presence of $SnCl_4$ to give the corresponding nitrile (6). However 5 was less reactive than allylic nitro compounds, and considerable amount of 5 remained under the same conditions. Therefore, we used 3 equivalents of 1 and 0.4 equivalent of $SnCl_4$ to improve the yield of 6 (Eq.2).



$$\underset{\underline{5}}{\overset{NO_2}{PhC}(CH_2CH_2COOMe)_2} + \underline{1} \xrightarrow[CH_2Cl_2 \text{ r.t. 2 hours}]{SnCl_4 \text{ (0.4eq)}} \underset{\underline{6} \quad 27\%}{\overset{CN}{PhC}(CH_2CH_2COOMe)_2} \qquad (2)$$

When the nitro compounds were neither allylic nor benzylic, they were much less reactive. The nitro group of them was not replaced by cyano group under any conditions we studied, and most of the starting nitro compound was recovered.

General procedure: Allylic nitro compounds were prepared according to the reported procedures[1,2]. Replacement of the nitro group with cyano group was carried out by the procedures as follows. To a solution of allylic nitro compound (2) (4.0 mmol) and cyanotrimethylsilane (1) (8.8 mmol) in 5 mL of dichloromethane was added $SnCl_4$ (0.2 g, 0.8 mmol). The resulting solution was kept at room temperature for 30 minutes and the reaction mixture was poured into water (30 mL) and extracted with ether three times. The organic layer was washed with water, dried over anhydrous magnesium sulfate, and evaporated. The residue was purified by column chromatography on silica gel to give β,γ-unsaturated nitriles 3 and 4[5]. In the cases of entries 3-5, the nitriles 3 and 4 were obtained independently. However, in other cases (entries 1,2, and 6-8), the mixture of 3 and 4 was obtained. When $TiCl_4$ (0.15g, 0.8 mmol) was used as catalyst, longer reaction time (2 hours) was necessary, and other procedures were carried out in the same way. Replacement of the nitro group of 5 was also carried out by the resemble procedures.

Acknowledgement: The present work was partially supported by the Research Aid of Inoue Foundation for Science.

## References

1) T.Severin and D.König, Chem. Ber., 107, 1499 (1974); H.Lerche, D.König, and T.Severin, Chem. Ber., 107, 1509 (1974); R.Tanikaga,H.Sugihara, K.Tanaka, and A.Kaji, Synthesis, 1977, 299

2) R.Tamura and L.S.Hegedus, J. Am. Chem. Soc., 104, 3727 (1982); N.Ono, I.Hamamoto, and A.Kaji, J. Chem. Soc., Chem. Commun., 1982, 821.

3) R.Tamura, K.Hayashi, Y.Kai, and D.Oda, Tetrahedron Lett., 25, 4437 (1984); R.Tamura, K.Hayashi, M.Kakihana, M.Tsuji, and D.Oda, Tetrahedron Lett., 26, 851 (1985); N.Ono, I.Hamamoto, T.Yanai, and A.Kaji, J.Chem.Soc., Chem. Commun., 1985, 523; R.Tamura, K.Hayashi, M.Kakihana, M.Tsuji, and D.Oda, Chem. Lett., 1985, 229; N.Ono, I.Hamamoto, and A.Kaji, J. Chem. Soc., Chem. Commun., 1984, 274; N.Ono, H.Miyake, R.Tamura, and A.Kaji, Tetrahedron Lett., 22, 1705 (1981); N.Ono, H.Miyake, A.Kamimura, I.Hamamoto, R.Tamura, and A.Kaji, Tetrahedron, 41, 4013 (1985).

4) Review of synthetic application of cyanotrimethylsilane; W.C.Groutas and D.Felker, Synthesis, 1980, 861.
a) P.Cazeau, F.Moulines, O.Laporte, and F.Duboudin, J. Organometal. Chem., 201, C9 (1980); F.Duboudin, P.Cazeau, F.Moulines, and O.Laporte, Synthesis, 1982, 213; M.T.Reetz and I.Chatziiosifidis, Synthesis, 1982, 330; b) S.Hünig and G.Wehner, Synthesis, 1975, 180; P.G.Gassman and J.J.Talley, Tetrahedron Lett., 19, 3773 (1978); L.H.Foley, J. Org. Chem., 50, 5204 (1985), and references cited therein. c) M.T.Reetz and I.Chatziiosifidis, Angew. Chem. Int. Ed., 20, 1017 (1981). d) P.G.Gassman and T.L.Guggenheim, J. Am. Chem. Soc., 104, 5849 (1982).

5) All the products were identified with IR and $^1$H NMR spectra. The IR spectra of 3 and 4 have the absorption of cyano group at 2220-2255 cm$^{-1}$. The product 3 in entries 1-3 and 5-7 has the characteristic signal of methyl protons (β-position of cyano group) at 1.4-1.5 ppm. The product 4 in entries 1-7 has characteristic signal of allylic methyl protons at 1.65-1.8 ppm. The products 3 and 4 were also confirmed by MS or elemental analysis.

(Received in Japan 12 April 1986)