A New Preparation of Aliphatic Nitro Compounds by S_H2' Reactions of *gem*-Halo Nitro Compounds with Allyltributylstannane

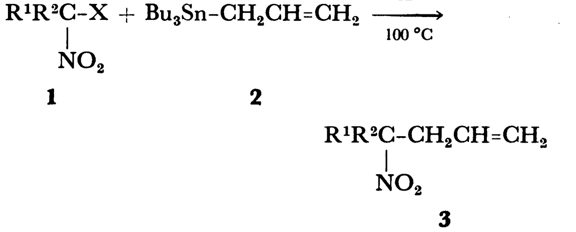
Noboru ONO,* Klaus ZINSMEISTER, and Aritsune KAJI*
Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606

(Received October 3, 1984)

Synopsis. α-Nitroalkyl radicals generated from *gem*-halo nitro compounds are reactive enough to undergo the carbon–carbon bond forming reaction with allyltributylstannane *via* radical chain processes, which provides a new method for the introduction of an allyl group into nitroalkanes.

The chemistry of aliphatic nitro compounds has recently recieved much attention because of their importance in organic synthesis.[1] Although aliphatic nitro compounds can be prepared by numerous methods, a new method is still desired. The method *via* the carbon–carbon bond formation at the α-position of the nitro function is particularly useful among them. This has be done so far mainly by Michael addition reactions of nitroalkanes,[1] nitro-aldol condensation reactions,[1] or single-electron transfer reactions involving α-nitroalkyl radicals as intermediates.[2] However, it is very difficult to introduce alkyl groups such as methyl, ethyl, or allyl groups at the α-position of the nitro function, for reactions of alkyl halides with the α-anions of nitroalkanes give exclusive *O*-alkylation products in general,[1] and the inverse reactions using *gem*-halo nitro compounds and alkyl anions such as Grignard reagents or alkyllithium reagents fail to give the alkylated products.[3] In this paper we wish to report a simple method for the introduction of an allyl group at the α-position of the nitro function by application of S_H2'reactions of allyltin compounds developed by Migita and his coworkers[4] to the reaction of *gem*-halo nitro compounds (**1**) with allyltributylstannane (**2**).

Various *gem*-halo nitro compounds (**1**) were allowed to react with **2** in the presence of a radical initiator (azobisisobutyronitrile, AIBN) at 100 °C. The reaction was also initiated by light, which was achieved by using a conventional medium-pressure mercury lamp equipped with a pyrex filter at 25 °C. Monoallylated products (**3**) were isolated from the reaction mixture by distillation and further purified by chromatography. The results are summarized in the Table.



$$\underset{\substack{|\\ NO_2\\ \mathbf{1}}}{R^1R^2C\text{-}X} + \underset{\mathbf{2}}{Bu_3Sn\text{-}CH_2CH{=}CH_2} \xrightarrow[100\,^{\circ}C]{AIBN} \underset{\substack{|\\ NO_2\\ \mathbf{3}}}{R^1R^2C\text{-}CH_2CH{=}CH_2}$$

Thus, *gem*-bromo nitro or *gem*-chloro nitro compounds undergo S_H2' reactions, but the reactions of *gem*-iodo nitro compounds with **2** proceed in the different way from S_H2' reactions. Although it is reported that simple alkyl halides such as isopropyl bromide react with **2** to give the allylated products in good yields,[4] **1** is much more reactive than simple alkyl halides in the present S_H2' reactions. For example, treatment of a mixture of 2-bromo-2-nitropropane and isopropyl bromide with **2** resulted in selective formation of **3a** was recovered unchanged.

TABLE. PREPARATION OF 4-NITRO-1-ALKENES

R^1	R^2	X	Time/h	Yield of **3**/%[a]
Me	Me	Br	24	**3a**, 67 (65)[b]
Me	Me	Cl	24	**3a**, 65
Me	Me	I	24	**3a**, 0[c]
Me	Et	Br	24	**3b**, 45
$-(CH_2)_4-$		Br	24	**3c**, 55
Me	H	Br	15	**3d**, 70
Et	H	Br	15	**3e**, 60
H	H	Br	15	**3f**, 35

a) Yields refer to pure and isolated products. b) Photoinitiation at 25 °C. c) Allyl iodide was formed.

Although the reactions of various organic halides with **2** have been already reported,[4] the present alkylation of **1** with **2** may find its synthetic value, because compounds **3** cannot be prepared by ordinary S_N2 reactions of allyl bromides with the α-carbanions of nitroalkanes,[5] and also **3** can be converted into various important compounds such as ketones, aldehydes, carboxylic acids, nitriles, oximes, or amines through the manipulation of the nitro function.[1]

Experimental

Materials. Allyltributylstannane was prepared by the reaction of allymagnesium bromides with tributyltin chloride in diethyl ether.[4] *gem*-Halo nitro compounds were prepared according to the literature method; 2-bromo-2-nitropropane[6] (bp 72—75 °C/50 mmHg, 1 mmHg=133.32 Pa), 2-bromo-2-nitrobutane[7] (bp 65—68 °C/30 mmHg), 1-bromo-1-nitrocyclopentane[7] (bp 100—103 °C/20 mmHg), 1-bromo-1-nitroethane[8] (bp 70 °C/50 mmHg), 1-bromo-1-nitropropane[8] (bp 70—74 °C/50 mmHg), bromonitromethane[9] (bp 143—145 °C), 2-chloro-2-nitropropane[6] (bp 57 °C/50 mmHg), 2-iodo-2-nitropropane.[6]

Preparation of 4-Methyl-4-nitro-1-pentene (3a). Method A: A mixture of 2-bromo-2-nitropropane (1.7 g, 10 mmol), **2** (6.5 g, 15 mmol), and AIBN (0.5 g, 3 mmol) was heated at 100 °C for 24 h. In the course of the reaction, AIBN was added in three portions. The products were distilled off by Kugelrohr distillation and purified by column chromatography on silica gel with hexane to give pure **3a** (0.86 g, 67% yield). IR (neat) 3040, 1610, 1540, 1380 cm⁻¹; ¹H-NMR ($CDCl_3$) δ=1.56

(s, 6H), 2.66 (d, 2H, J=7.5 Hz), 4.9—5.2 (m, 2H), 5.5—5.8 (m, 1H). Found: C, 55.72; H, 8.76; N, 10.92%. Calcd for $C_6H_{11}NO_2$: C, 55.72; H, 8.53; N, 10.86%. Method B: The same procedures of method A using 2-chloro-2-nitropropane (1.3 g, 10 mmol) gave **3a** in 65% yield. Method C: A solution of 2-bromo-2-nitropropane (0.51 g, 3 mmol) and **2** (2 g, 4.5 mmol) in 100 ml of benzene was internally irradiated for 10 h with a 300 W medium-pressure mercury lamp using a Pyrex filter. The same work-up as described in method A have pure **3a** in 65% yield.

Following compounds were prepared by the method A.

4-Methyl-4-nitro-1-hexene (3b): IR (neat) 3040, 1610, 1535, 1375 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=0.88 (t, 3H, J=7.0 Hz), 1.52 (s, 3H), 1.6—2.1 (m, 2H), 2.5—2.7 (m, 2H), 4.9—5.2 (m, 2H), 5.5—5.8 (m, 1H). Found: C, 58.38; H, 9.14; N, 9.63%. Calcd for $C_7H_{13}NO_2$: C, 58.76, H, 9.09; N, 9.78%.

1-Allyl-1-nitrocyclopentane (3c): IR (neat) 3040, 1610, 1540, 1380 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.2—1.4 (m, 8H), 2.50 (d, 2H, J=7.2 Hz), 4.9—5.2 (m, 2H), 5.4—5.8 (m, 1 H). Found: C, 61.74; H, 8.13; N, 9.16%. Calcd for $C_8H_{13}NO_2$: C, 61.95; H, 8.39; N, 9.03%.

4-Nitro-1-pentene (3d): IR (neat) 3040, 1610, 1540, 1380 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.54 (d, 3H, J=7.0 Hz), 2.4—2.8 (m, 2H), 4.4—4.8 (m, 1H), 5.0—5.2 (m, 2H), 5.5—5.9 (m, 1H). Found: C, 52.19; H, 8.12; N, 12.35%. Calcd for $C_5H_9NO_2$: C, 52.16; H, 7.88; N, 12.17%.

4-Nitro-1-hexene (3e): IR (neat) 3030, 1610, 1540, 1380 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=0.98 (t, 3H, J=7.0 Hz), 1.7—2.1 (m, 2H), 2.4—2.8 (m, 2H), 4.2—4.6 (m, 1H), 5.0—5.2 (m, 2H), 5.4—5.8 (m, 1H). Found: C, 55.63; H, 8.83; N, 11.04%. Calcd for $C_6H_{11}NO_2$: C, 55.79; H, 8.53; N, 10.86%.

4-Nitro-1-butene (3f): IR (neat) 3030, 1610, 1540, 1380 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ=2.8 (q, 2H), 4.6 (t, 2H), 5.2—5.5 (m, 2H), 5.6—6.2 (m, 1H). These spectral data are in good agreement with those of authentic sample of **3a** which is prepared from 4-bromo-1-butene.[1]

References

1) D. Seebach, E. W. Colvin, F. Lehr, and T. Weller, *Chimia*, **33**, 1 (1979); N. Ono and A. Kaji, *Yuki Gosei Kagaku Kyokai Shi*, **38**, 115 (1980).

2) N. Kornblum, *Angew. Chem., Int. Ed. Engl.*, **14**, 734 (1975).

3) G. A. Russell, M. Jawdosiuk, and M. Makosza, *J. Am. Chem. Soc.*, **101**, 2355 (1979).

4) T. Migita, K. Nagai, and M. Kosugi, *Bull. Chem. Soc. Jpn.*, **56**, 2480 (1980), and references therein.

5) D. Seebach and F. Lehr, *Helv. Chim. Acta*, **62**, 2239 (1979), in which the dianions derived from primary nitroalkanes are carbon-allylated with allyl bromides. Thus, **3d** and **3e** can be prepared by the method using dianions of nitroalkanes.

6) L. W. Seigle and H. B. Hass, *J. Org. Chem.*, **5**, 102 (1940).

7) D. C. Iffland and G. X. Criner, *J. Am. Chem. Soc.*, **75**, 4047 (1953).

8) A. S. Erickson and N. Kornblum, *J. Org. Chem.*, **42**, 3764 (1977).

9) J. Tscherniak, *Justus Liebigs Ann. Chem.*, **180**, 123 (1876).