Pergamon

Tetrahedron Letters 39 (1998) 811–812

TETRAHEDRON LETTERS

Synthesis of (*E*)-Nitro Olefins by Isomerisation of (*Z*)-Nitro Olefins with Polymer-Supported Triphenylphosphine

Peter Stanetty* and Manfred Kremslehner

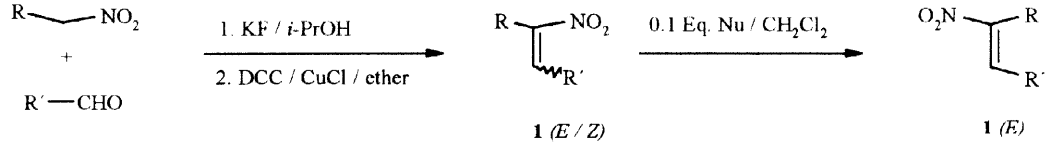
Institute of Organic Chemistry, Vienna University of Technology
Getreidemarkt 9/154, A-1060 Vienna, Austria

Received 29 September 1997; revised 27 November 1997; accepted 4 December 1997

Abstract: We have found that (*Z*)-nitro olefins or mixtures of (E)- and (Z)-compounds can be converted to the pure (*E*)-isomers by treatment with catalytic amounts of triethylamine or polymer-bound triphenylphosphine, respectively.

Nitro olefins are very useful and versatile building blocks in organic synthesis. Due to the strong electron withdrawing character of the nitro group the double bond is highly activated for Michael additions as well as cycloaddition reactions.[1] After transformation of the activated double bond the nitro group can be replaced by hydrogen[2] or reduced to an amino or carbonyl group,[3-4] respectively. The most popular method for the preparation of nitro olefins is the dehydration[5] of β-nitro alcohols which are readily available by nitroaldol reaction.[6] However, in the case of nitro olefins bearing an alkyl group in the α-position to the nitro group, this method furnish mixtures of the (*E*)- and (*Z*)-isomers.
In the course of our synthetic work we developed a new method for the isomerisation of (*Z*)-nitro olefins into their (*E*)-isomers simply by treatment with catalytic amounts of a suitable nucleophile.

Table 1. Isomerisation of (E/Z)-Nitroolefin Mixtures into Pure (E)-Isomers (**1a-1f**) with Polymer-Supported TPP



1 (*E* / *Z*) **1** (*E*)

entry	educt (*E*/*Z*)	R	R′	*E* : *Z*[a]	Nu	time [h]	product[b] (*E*)	*E* : *Z*[a]	yield [%][c]
1	**1a**	Me	Pr	55 : 45	TEA	4	**1a**	--	--
2	**1a**	Me	Pr	55 : 45	TPP	20	**1a**	100 : 0	100
3	**1b**	Me	$(CH_2)_2COOEt$	90 : 10	TPP	20	**1b**	100 : 0	100
4	**1c**	Et	Pr	60 : 40	TPP	40	**1c**	100 : 0	100
5	**1d**	Me	Ph	80 : 20	TEA	24	**1d**	100 : 0	96
6	**1d**	Me	Ph	80 : 20	TPP	20	**1d**	100 : 0	100
7	**1e**	Ph	Pr	80 : 20	TPP	20	**1e**	90 : 10	100
8	**1f**	Me	SPh	0 : 100	TEA	17	**1f**	65 : 35	97
9	**1f**	Me	SPh	0 : 100	TPP	48	**1f**	65 : 35	100

[a] Ratio determined by nmr spectroscopy, [b] For nmr data see reference 9, [c] All yields refer to isolated, pure compounds.

Thus, we prepared some representative nitro olefins **1a-e** by nitroaldol reaction with potassium fluoride in 2-propanol[7] and subsequent dehydration of the nitro alcohols with DCC and CuCl in refluxing diethyl ether.[5a] The obtained (*E*/*Z*)-mixtures were used for the nucleophile-mediated isomerisation and the change of the (*E*/*Z*)-ratio was monitored by nmr spectroscopy. In our first attempt, a solution of **1a** in dichloromethane was stirred with 0.1 eq. of triethylamine (TEA) at room temperature (entry 1, Table 1). After 4h the (*Z*)-olefin was completely isomerized, however, about 10% of the nonconjugated 2-nitro-3-hexene was formed as a by-product of the (*E*)-olefin due to a base-induced shift of the double bond. This isomerisation is known to take place also when β-nitro alcohols are dehydrated with methanesulfonyl chloride

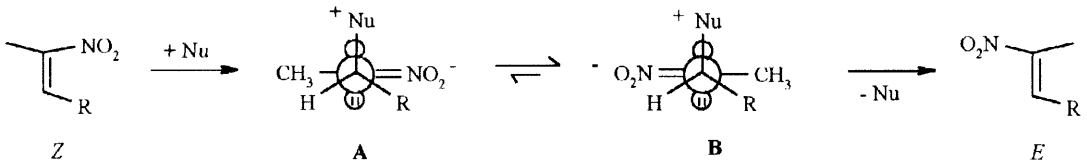
0040-4039/98/$19.00
PII: S0040-4039(97)10789-4

and TEA[5b] and can be used for the synthesis of allylic nitro compounds from nitro olefins.[8] To avoid this side-reaction we used 0.1 eq. of triphenylphosphine (TPP) as a nucleophilic but less basic catalyst. For further improvement, polymer-supported TPP (purchased from Aldrich) was applied to avoid the necessity of purification by distillation or chromatography.[9] After 20h the pure (*E*)-olefin was obtained quantitatively (entry 2). This method can also be applied for the stereoselective preparation of (*E*)-5-nitro-4-hexenoic acid ethylester **1b** which we needed for our synthesis of functionalized decahydroquinolines (entry 3).

As shown in Table I the stereoselectivity of the *E/Z*-isomerisation is retained when the methyl group in α-position is replaced by the sterically more demanding ethyl group (**1c**) as well as by changing the aliphatic chain in β-position to phenyl (**1d**). Of course, in the case of nitrostyrene **1d** due to the lack of acidic hydrogens in γ-position TEA is equally effective as a catalyst (entry 5 *vs* 6). This is in agreement with its perpendicular orientation in conformation **A** and **B**.

On the other hand, introduction of the phenyl group in α-position (**1e**) or a phenylthio group in the β-position (**1f**)[10] reduces the stereoselectivity to an *E/Z*-ratio of 90:10 or 65:35, respectively (entry 7-9). With some selected examples we have shown, that our new method for the stereoselective preparation of (*E*)-nitro olefins[11] can be applied for a wide range of substitution patterns on the double bond (linear alkyl in α-position and alkyl or aryl in β-position, respectively). In combination with the very mild KF-induced nitroalodol reaction and dehydration of the nitro alcohol with DCC it is also compatible with many other, especially base sensitive functional groups.

The mechanism of this isomerisation should proceed *via* attack of the nucleophile to the activated double bond, interconversion of the intermediate **A** to **B** and subsequent elimination of the nucleophile. Rotamer **B** and the corresponding transition state of the elimination should be energetically favoured due to the reduced allylic 1,3-strain (NO_2 and H in **A** *vs.* NO_2 and R in **B**).



REFERENCES and NOTES

1. For a review see: Barrett, A. G. M.; Graboski, G. G. *Chem. Rev.* **1986,** *86,* 751-762.
2. For a review see: Ono, N.; Kaji, A.; *Synthesis* **1986,** 693-704.
3. For a review see: Hemmer, R.; Lürken, W. in *Houben-Weyl Methoden der Organischen Chemie*; Klamann, D., Ed.; Thieme Verlag: Stuttgart, **1992;** Vol. E16d, pp. 815-865.
4. McMurry, J.; Melton, J. *J. Org. Chem.* **1973,** *38,* 4367-4372.
5. (a) Knochel, P.; Seebach, D. *Synthesis* **1982,** 1017-1018. (b) Melton, J.; McMurry, J. *J. Org. Chem.* **1975,** *40,* 2138-2139.
6. For a review see: Rosini, G. in *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I., Ed.; Pergamon Press: New York, **1991;** Vol. 2; pp. 321-340.
7. Kambe, S.; Yasuda, H.; *Bull. Chem. Soc. Jpn.* **1968,** *41,* 1444-1446.
8. (a) Tamura, R.; Sato, M.; Oda, D. *J. Org. Chem.* **1986,** *51,* 4368-4375. (b) Ono, N.; Hamamoto, I.; Kamimura, A.; Kaji, A.; Tamura, R. *Synthesis* **1987,** 258-260.
9. General procedure: A solution of 3 mmol nitro olefin in 10 ml of dry dichloromethane and 100mg (~0.3 mmol) of polymer-supported triphenylphosphine (Aldrich) was stirred for 20 h. The catalyst was filtered off and the solvent was removed in *vacuo* to obtain the pure (*E*)-olefin **1a-d** in quantitative yield. **1a:** ^{13}H NMR (200 MHz, $CDCl_3$) δ 1.00 (t, *J* = 7 Hz, 3H), 1.55 (hex, *J* = 7 Hz, 2H), 2.10-2.28 (m, 5H), 7.15 (t, *J* = 7Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 12.2, 13.5, 21.4, 29.8, 135.9, 147.5.**1b:** ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.28 (t, *J* = 7 Hz, 3H), 2.20 (s, 3H), 2.45-2.65 (m, 4H), 4.15 (q, *J* = 7 Hz, 2H), 7.1 (bt, *J* = 6 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 12.4, 14.1, 23.3, 32.4, 60.7, 133.8, 148.4, 171.7. **1c:** ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.00 (t, *J* = 7 Hz, 3H), 1.12 (t, *J* = 7 Hz, 3H), 1.55 (hex, *J* = 7 Hz, 2H), 2.22 (q, *J* = 7 Hz, 2H), 2.62 (q, *J* = 7 Hz, 2H), 7.05 (t, *J* = 7 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 12.5, 13.7, 19.8, 21.7, 29.6, 135.6, 153.2. **1d:** mp. 63-65 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.48 (s, 3H), 7.45 (s, 5H), 8.10 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.9, 128.8, 129.8, 132.3, 133.4, 147.6.
10. Ono, N.; Kamimura, A.; Kaji, A. *J. Org. Chem.* **1986,** *51,* 2139-2142.
11. For the preparation of *(Z)*-nitro olefins see: Ono, N.; Kamimura, A.; Kawai, T.; Kaji, A. *J. Chem. Soc., Chem. Commun.* **1987,** 1550-1551.