Pergamon

Tetrahedron Vol. 51, No. 14, pp. 4173-4182, 1995

0040-4020/95 $9.50+0.00

0040-4020(95)00133-6

A Novel Reactivity of α-Nitro Ketone Tosylhydrazones with DBU. Synthesis of α,β-Unsaturated Enone Tosylhydrazones.

Roberto Ballini,* and Gianni Giantomassi
Dipartimento di Scienze Chimiche dell'Università, Via S. Agostino 1, 62032 Camerino - Italy

Abstract: Treatment of α-nitro ketone tosylhydrazones with DBU gives 1,4-elimination of nitrous acid affording 1-tosylazoalkenes which, under basic conditions (DBU), tautomerize to the more stable enone tosylhydrazones. The obtained tosylhydrazones may be used as starting material for a wide range of other functionalities. Removal of the hydrazone affords conjugated enones in good yields. Due to the possibility to prepare the nitro ketones with the nitro group in α or α' position, by this method it is possible to obtain α,β-unsaturated carbonyl compounds with the complete regioselectivity.

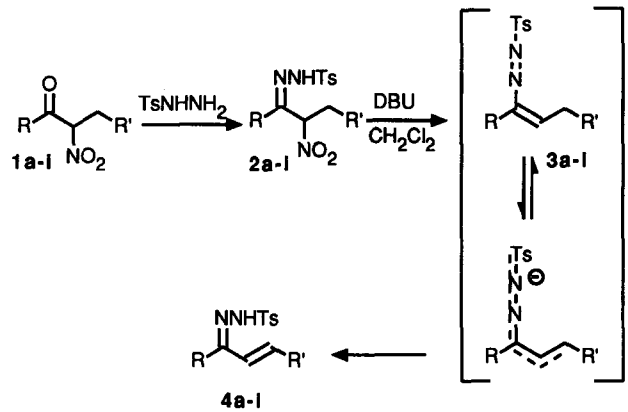
Aliphatic nitro compounds can be considered as versatile building blocks and intermediates[1] and, in special case, only if electron-withdrawing groups exist at the β-position of the nitro function, elimination of nitrous acid takes place readily to give olefins in good yields.[2] However, if the nitro group is in α-position the elimination of nitrous acid is impraticable.

α-Nitro ketones are a class of compounds readily available from: (i) Ketones,[3] (i) Alkenes,[3a,f] (iii) aldehydes,[4] (iv) nitroalkanes,[5] and (v) Nitroalkenes.[6]

Given the well known chemical differences of the carbonyl group and the carbon-nitro group moiety, their juxtaposition on two adiacent positions offers a new reactivity pattern, peculiar to α-nitro ketones. In the recent years, their remarkable versatility has ensured long standing interest of their utilization in organic synthesis.[3a,f,7]

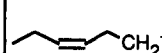
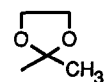
In the course of our effords to discover new potentialities of α-nitro ketones we reported that hydride reduction of their tosylhydrazones produced, at 0 °C, the replacement of the nitro group by hydrogen[8] or deuterium,[9] while at 60-80 °C we observed the tandem denitration-deoxygenation of α-nitro ketones.[10,11]

On the basis of these previous results we have found the first method for the elimination of nitrous acid

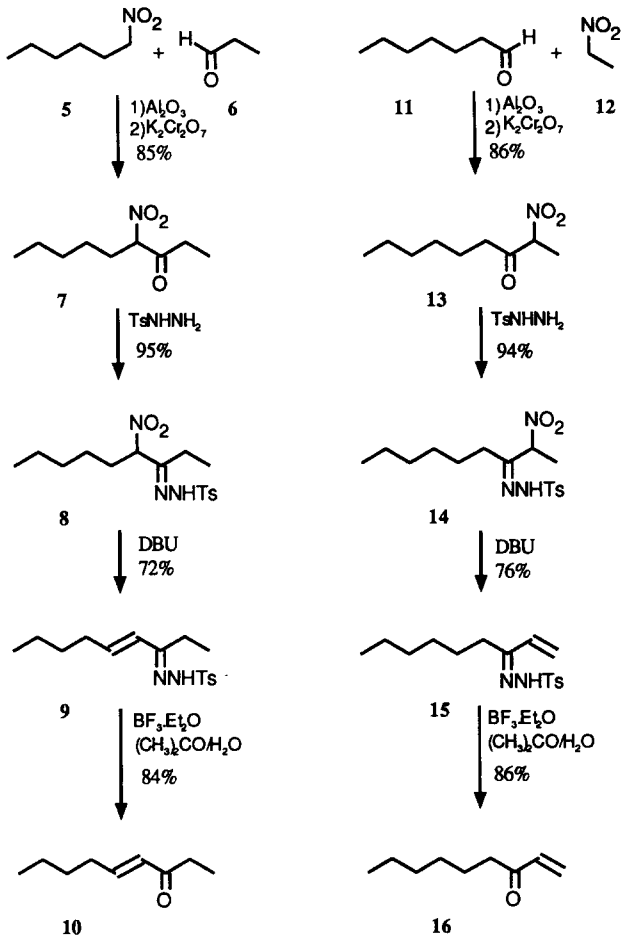


Scheme 1

Table I. Conversion of α-Nitro Ketones (1) to Enone Tosylhydrazones (4)

	R	R'	Yield (%) (2)	Yield (%) (4)
a	$-(CH_2)_3-$		95	70
b	$-(CH_2)_4-$		93	60
c	$-(CH_2)_5-$		91	60
d	$-(CH_2)_8-$		93	75
e	$-(CH_2)_9-$		96	73
f	$-(CH_2)_{12}-$		98	79
g	$C_6H_5(CH_2)_2-$	H	93	60
h		H	92	70
l	$C_6H_5(CH_2)_2-$		80	74[a]

[a] 100% *E*-isomer


NO2
H
O
5
6
11
12
1)Al2O3
2)K2Cr2O7
85%
86%
7
13
TsNHNH2
95%
94%
NNHTs
8
14
DBU
72%
76%
9
15
BF3.Et2O
(CH3)2CO/H2O
84%
86%
10
16

Scheme 2

from α-nitro ketones, with recovery of the double bond, *via* their tosylhydrazones, under basic conditions. Then (Scheme 1), treatment of the latter **2** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 1.5 mol), in dichloromethane at room temperature gives, after 15 min, the α,β-unsaturated ketone tosylhydrazones **4**.

We suggested that formation of **4** takes place as follow: 1,4-elimination of nitrous acid from **2** affords the 1-tosylazoalkenes **3** which, under basic conditions (DBU), tautomerize to the more stable[12] enone tosylhydrazones **4**. The azo-diazo conversion of **3** to **4** can be related to the electron-withdrawing power of the tosyl group which, through the conjugated double bonds system, strongly polarizes the allylic hydrogens of alkene.

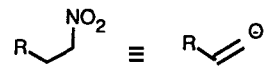
Satisfactory to high yields of isolated products were observed both in the conversion of α-nitro ketones **1** into the corresponding tosylhydrazones **2** as well as in the formation of **4** (Table I). Tosylhydrazones are, in general, cristalline and it is possible to obtain pure compounds easily by recristallization.

The versatility of tosylhydrazones in synthesis is noteworthy as in their complementary relationship to other key functional group. In fact, tosylhydrazones may be used as starting compounds for a wide variety of preparatively, useful further transformations.[7h,8,13]

Moreover, enone tosylhydrazones may be readily cleaved to give the corresponding enones by a multitude of procedures,[14] so that our method also represents a new synthesis of α,β-unsaturated ketones from α-nitro ketones.

Because it is possible to prepare nitro ketones with the nitro group in either the α- (**7**) or α'-position (**13**) from the appropriate starting material[4g] (Scheme 2), our method offers a regioselective approach for the synthesis of α,β-unsaturated carbonyl compounds. Thus, solvent-free nitroaldol reaction (**5** with **6** or **11** with **12**) on alumina and *in situ* oxidation, under phase transfer conditions, with potassium dichromate affords, one pot and in 85% and 86% yields, **7** and **13** respectively. Following our procedure **7** and **13** are converted to **9** and **15** (72% and 76% yields) which, after regeneration of ketone with acetone/water/boron trifluoride etherate,[14a] give *(E)*-4-nonen-3-one **10** and 1-nonen-3-one **16** in 84% and 86% yields (overall yields 49% (**10**) and 53% (**16**) in four steps).

In this context the nitro alkanes can be regarded as synthetic equivalents of the vinyl anion synthons **a**.



a

By this method, when the formation of both *Z*- and *E*-isomers is plausible, exclusively the latter is obtained. Functionalities such as *(Z)*-double bond and ketal are preserved. Of particular interest is the example **4i** which is an immediate precursor of the *(E)*-enedione system.[15]

Thus, such new reactivity of α-nitro ketone tosylhydrazones gives a rapid elimination of nitrous acid and, due to great versatility of tosylhydrazones, can provide different elaborations to a variety of synthetic building blocks. On the other hand, although there are a number of methods[16-21] for performing the preparation

of α,β-unsaturated carbonyl compounds (the most important of which are: α-bromination-dehydrobromination,[17] elimination of selenoxides[19] or sulfoxides groups,[20] aldolization-dehydration,[16] and *via* enol derivatives[21]), frequently requirement of harsh reaction conditions or the need of toxic substances severe limits them, moreover an effective control of the regioselectivity is often a problem, so our procedure promotes the α-nitro ketones as a new, useful source for the regioselective synthesis of α,β-unsaturated enones. Additionally, because by our approach the latter can also be prepared by the connection of two carbon-skeletons (Scheme 2), it can be regarded as a valid alternative to the aldolization-dehydration.[16]

Finally, the reported method represents an important, new utilization of α-nitro ketones in organic synthesis.

Experimental

General. All ^{1}H NMR spectra were recorded in $CDCl_3$ at 300 MHz on a Varian VXR 300; *J* values are given in Hz. IR spectra were recorded with a Perkin Elmer 257 spectrophotometer. Melting points are uncorrected. The reactions were monitored by TLC and/or GC analyses, performed on a Carlo Erba Fractovap 4160 using a capillary column of duran glass (0.32 mm x 25 m), stationary phase OV1 (film thickness 0.4-0.45 nm). Literature methods were followed for the synthesis of α-nitro ketones (**1**).[3,4g]

General Procedure fo the preparation of α-Nitro Ketone (*p*-tolylsulfonyl)hydrazones (2). A solution of *p*-toluenesulfonylhydrazine (3.72 g, 20 mmol) in methanol (15 ml) was added to a solution of equimolar amount of α-nitro ketone **1** in methanol (15 ml) and the mixture was allowed to stand at room temperature for 13-15 h. The crystalline **2**, which crystallizes upon cooling of the solution, was isolated by suction, dried in vacuo, and used in the next step without further purification. An analytical sample may be prepared by recrystallization from methanol/water.

2a: mp 133-134 °C; IR ν 3205, 1555, 1340 and 1170 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.3-2.55 (8H, m), 2.45 (3H, s), 5.02 (1H, t, *J* = 3.8 Hz), 7.57 (4H, AA' BB' pattern, *J* = 8.0 Hz).

2b: mp 118-119 °C; IR ν 3210, 1550, 1320 and 1168 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.08-2.61 (10H, m), 2.43 (3H, s), 5.15 (1H, t, *J* = 7.5 Hz); 7.57 4H, (AA' BB' pattern, *J* = 8.0 Hz).

2c: mp 157-158 °C; IR ν 3230, 1535, 1340 and 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.12-2.48 (12H, m), 2.42 (3H, s), 5.02 (1H, m), 7.47 (4H, AA' BB' pattern, *J* = 8.0 Hz).

2d: mp 144-145 °C; IR ν 3200, 1540, 1340 and 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.05-2.48 (18H, m), 2.42 (3H, s), 5.12 (1H, dd, *J* = 3.9 and 11.4 Hz), 7.57 (4H, AA' BB' pattern, *J* = 8.0 Hz).

2e: mp 172-174 °C; IR ν 3210, 1540, 1340 and 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.9-2.6 (20H, m,), 2.42 (3H,

s), 5.15 (1H, dd, J = 3.7 and 12.1 Hz), 7.57 (4H, AA' BB' pattern, J = 8.0 Hz).

2f: mp 130-132 °C; IR ν 3210, 1540, 1370 and 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.1-2.4 (26H, m), 2.42 (3H, s), 5.0 (1H, t, J = 7.4 Hz), 7.57 4H, (AA' BB' pattern, J = 8.0 Hz).

2g: mp 105-106 °C; IR ν 3200, 1552, 1345 and 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.55 (2H, d, J = 7 Hz), 2.42 (3H, s), 2.5-2.8 (4H, m), 4.9 (1H, q, J = 7 Hz), 6.9-7.8 (9H, m).

2h: mp 87-88 °C; IR ν 3210, 1545, 1340 and 1165 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9 (3H, m, J = 7.6 Hz), 1.15-2.5 (12H, m), 1.65 (3H, d, J = 6.9 Hz), 2.45 (3H, s), 5.1-5.28 (2H, m), 5.3-5.5 (1H, m), 7.57 (4H, AA'BB' pattern, J = 8.0 Hz).

2i: mp 113-114 °C; IR ν 3230, 1550, 1340 and 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28 (3H, s), 2.35-2.95 (6H, m), 2.43 (3H, s), 3.78-3.98 (4H, m), 5.05-5.25 (1H, m), 6.95-7.9 (9H, m).

8: mp 90-92 °C; IR ν 3200, 1540, 1370 and 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (3H, t, J = 7.3 Hz), 1.05 (3H, t, J = 7.7 Hz), 1.1-2.3 (10H, m), 2.42 (3H, s), 5.02 (1H, dd, J = 6.7 and 8.1 Hz), 7.57 (4H, AA' BB' pattern, J = 8.0 Hz).

14: mp 89-90 °C; IR ν 3210, 1550, 1340 and 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9 (3H, t, J = 7.0 Hz), 1.1-1.5 (8H, m), 1.65 (3H, d, J = 6.9 Hz), 2.2 (2H, m), 2.42 (3H, s), 5.25 (1H, , J = 6.9 Hz), 7.57 (4H, AA' BB' pattern, J = 8.0 Hz).

Elimination of Nitrous Acid from (2). General Method for the Preparation of Conjugated Enone(*p*-tolylsulfonyl)hydrazones (4). To a stirred solution of **2** (10 mmol) in CH_2Cl_2 (50 ml) DBU (2.28 g, 15 mmol) was added at room temperature. After stirring the solution for 15 min the solvent was evaporated and the crude product **4** was purified by crystallization from methanol/water. Only the products **4g,h** were purified by flash chromatography with cyclohexane/EtOAc (8:2) as eluent.

4a: mp 168-169 °C; IR ν 3210, 1585, 1350 and 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.7-1.8 (2H, m, J = 6.3 Hz), 2.1-2.2 (2H, m), 2.22-2.3 (2H, m, J = 6.7 Hz), 2.42 (3H, s), 6.15 (1H, dt, J = 1.6 and 10.1 Hz), 6.28 (1H, dt, J = 4 and 10.1 Hz), 7.57 (4H, AA' BB' pattern, J = 8.0 Hz).

4b: mp 141-142 °C; IR ν 3210, 1584, 1340 and 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.6-1.8 (4H, m), 2.22-2.4 (4H, m), 2.42 (3H, s), 5.86-5.98 (1H, dt, J = 1.7 and 12.5 Hz), 6.04-6.15 (1H, dt, J = 4.8 and 12.5 Hz), 7.58 (4H, AA' BB' pattern, J = 8.0 Hz).

4c: mp 119-121 °C; IR ν 3210, 1585, 1340 and 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.3-2.6 (10H, m), 2.42 (s, 3 H), 5.92 (1H, dt, J = 7.7 and 12.4 Hz), 6.18 (1H, d, J = 12.4 Hz), 7.57 (4H, AA' BB' pattern, J = 8.0 Hz).

4d: mp 114-115 °C; IR ν 3200, 1340 and 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05-2.48 (16H, m), 2.42 (3H, s), 5.97 (1H, dt, *J* = 7.1 and 16 Hz), 6.15 (1H, d, *J* = 16 Hz), 7.47 (4H, AA' BB' pattern, *J* = 8.0 Hz).

4e: mp 118-119 °C; IR ν 3200, 1580, 1340 and 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05-1.6 (14H, m), 2.1-2.23 (2H, m), 2.24-2.35 (2H, m), 2.42 (3H, s), 6.03 (1H, dt, *J* = 0.9 and 15.6 Hz), 6.2 (1H, dt, *J* = 7.0 and 15.6 Hz), 7.57 (4H, AA' BB' pattern, *J* = 8.0 Hz).

4f: mp 121-123 °C; IR ν 3200, 1585, 1370 and 1165 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05-2.3 (24H, m), 2.42 (3H, s), 6.05 (2H, m), 7.57 (4H, AA'BB' pattern, J = 8.0 Hz).

4g: liquescent; IR n 3210, 1600, 134 and, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.42 (3H, s), 2.58-2.9 (4H, m), 5.45 (1H, d, *J* = 11 Hz), 5.55 (1H, d, *J* = 18 Hz), 6.35 (1H, dd, *J* = 11 and 18 Hz), 7.05-7.35 (5H, m), 7.47 (4H, AA' BB' pattern, *J* = 8.0 Hz).

4h: liquescent; IR ν 3210, 1595, 1340 and 1165 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85-2.4 (9H, m), 2.42 (3H, s), 5.1-5.4 (2H, m), 5.43 (1H, d, *J* = 11 Hz), 5.52 (1H, d, *J* = 18 Hz), 6.35 (1H, dd, *J* = 11 and 18 Hz), 7.57 (4H, AA' BB' pattern, *J* = 8.0 Hz).

4i: mp 115-116 °C; IR ν 3210, 1595, 1340 and 1168 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.42 (3H, s), 2.42 (3H, s), 2.6-2.8 (4H, m), 3.8-4.0 (4H, m), 5.86 (1H, d, *J* = 16 Hz), 6.35 (1H, d, *J* = 16 Hz), 6.98-7.2 (5H, m), 7.57 (4H, AA' BB' pattern, *J* = 8.0 Hz).

9: mp 83-84 °C; IR ν 3200, 1590, 1330 and 1160 cm^{-1}; ^1H NMR (C_6D_6) δ 0.8-1.4 (9H, m), 0.82 (3H, t, *J* = 7.7 Hz), 1.7-2.0 (2H, m), 1.8 (3H, s), 5.55-5.72 (1H, dt, *J* = 6.9 and16.2 Hz), 6.1-6.2 (1H, dt, *J* = 1.4 and 16.2 Hz), 7.43 (4H, AA' BB' pattern, *J* = 8.2 Hz).

15: mp 103-105 °C; IR ν 3210, 1600, 1340 and 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9 (3H, t, *J* = 7.0 Hz), 1.3-1.4 8H, m), 2.2-2.35 (2H, m), 2.42 (3H, s), 5.41 (1H, d, *J* = 11 Hz), 5.5 (1H, d, *J* = 18 Hz), 6.35 (1H, dd, J = 11 and 18 Hz), 7.57 (4H, AA' BB' pattern, J = 8.0 Hz).

Preparation of α-Nitro Ketones (7) and (13). General Procedure. A mixture of aldehyde (**6** or **11**, 25 mmol) and the nitroalkane (**5** or **12**, 25 mmol) was mechanically stirred for 5 min and then cooled in an ice-bath. After the addition of chromatographic alumina (7 g, activity I) and stirring for 2 h at room temperature, the mixture was allowed to stand for 20 h, then CH_2Cl_2 (50 ml) tetra-*n*-butylammonium hydrogen sulfate (0.85 g, 2.5 mmol) were added. Under stirring and cooling to -10 °C, 30% sulfuric acid (30 ml) and potassium dichromate (9.55 g, 32.5 mmol) were simultaneously added, keeping the inner temperature at -10 °C. After stirring for 2 h at -10 °C, the organic solvent was removed under reduced pressure and the crude product distilled.

7: bp 80 °C/0.1 Torr; IR ν 1725 and 1550 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (3H, t, *J* = 7.0 Hz), 1.05 (3H, t, *J* = 7.2 Hz), 1.2-1.4 (6H, m), 1.88-2.27 2H, m), 2.54 (2H, q, *J* = 7.2 Hz), 5.25 (1H, dd, *J* = 4.7 and 9.9 Hz).

13: bp 85°C/0.25 Torr; IR ν 1730 and 1550 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9 (3H, t, J = 7.0 Hz), 1.2-1.65 (8H, m), 1.7 (3H, d, J = 7.1 Hz), 2.4-2.5 (2H, m), 5.25 (1H, q, J = 7.1 Hz).

Regeneration of Ketones from Enone(*p*-tolylsulfonyl)hydrazones. Preparation of Enones (10) and (16). General Procedure. The tosylhydrazone (**9** or **15**, 10 mmol) was dissolved in acetone/water (60 ml, 10:1), distilled boron trifluoride etherate (1.9 ml, 1.5 mmol) was added and the mixture was stirred at room temperature for 25 h. Evaporation of the acetone in vacuo and dissolution of the crude residue in hexane, followed by filtration of the acetone tosylhydrazone and removal of the hexane, at reduced pressure, yielded the pure carbonyl compounds **10** and **16**.

10: bp 63 °C/4 Torr; IR ν 1705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9 (3H, t, J = 7 Hz), 1.2-1.6 (9H, m), 2.2 (2H, m), 2.35 (2H, t, J = 7 Hz), 6.1 (1H, dt, J = 1.5 and 16 Hz), 6.8 (1H, dt, J = 6.8 and 16 Hz).

16: bp 65 °C/5 Torr; IR ν 1708 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9 (3H, t, J = 7 Hz), 1.2-1.7 (8H, m), 2.35 (2H, t, J = 7 Hz), 5.8 (2H, dd, J = 1.8 and 10 Hz), 6.8 (1H, dd, J = 10 and 18.8 Hz).

Acknowledgements: We thank the Consiglio Nazionale delle Ricerche (C.N.R.)-Italy and Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST)-Italy for financial support.

References

1. (a) Seebach, D.; Leher, F. *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 505. (b) Baker, D. C.; Putt, S. R. *Synthesis* **1978**, 478. (c) Crumbie, R. L.; Nimitz, J. S.; Mosher, H. S. *J. Org. Chem.* **1982**, *47*, 4040. (d) Ono, N.; Fuji, M.; Kaji, A. *Synthesis* **1987**, 532.
2. (a) Patterson, J. W.; McMurry, J. E. J. *Chem. Soc. Chem. Commun.* **1971**, 488. (b) Ono, N.; Eto, H.; Tamura, R.; Hayami, J.; Kaji, A. *Chem. Lett.* **1976**, 2371. (c) Seebach, D.; Hoekstra, M. S.; Protschuk, G. *Angew. Chem. Int. Ed., Engl.* **1977**, *16*, 321. (d) Danishefsky, S.; Prisbylla, M. P.; Hiner, S. *J. Am. Chem. Soc.* **1978**, *100*, 2918. (e) Bakuzis, P; Bakuzis, M. L. F.; Weingartner, T. F. *Tetrahedron Lett.* **1978**, 2371. (f) Ono, N.; Miyake, H.; Tanikaga, R.; Kaji, A. *J. Org. Chem.* **1982**, *47*, 5017.
3. (a) Fisher, R. H.; Weitz, H. M. *Synthesis* **1980**, 261. (b) Ozbal, H.; Zajac jr, W. W. *J. Org. Chem.* **1981**, *46*, 3082. (c) Dampawan, P.; Zajac jr, W. W. *J. Org. Chem.* **1982**, *47*, 1176. (d) Cushman, M.; Mathew, J. *Synthesis* **1982**, 397. (e) Rathore, R.; Lin, Z.; Kochi, J. K. *Tetrahedron Lett.* **1993**, *34*, 1859. (f) Rosini, G.; Ballini, R.; Petrini, M.; Marotta, E.; Righi, P. *Org. Prep. Proc. Int.* **1990**, *22*, 707.
4. (a) Sele, K. *Israel J. Chem.* **1966**, *4*, 7; *C. A.* **1967**, *66*, 28479. (b) Canonica, L.; Cardani, C. *Gazz. Chim. Ital.* **1949**, *79*, 262. (c) Levy, N.; Scaife, C. W. *J. Chem. Soc.* **1946**, 1103. (d) Hurd, C. D.; Nilson, M. E. *J. Org. Chem.* **1955**, *20*, 927. (e) Rosini, G.; Ballini, R. *Synthesis* **1983**, 543. (f) Adams, L. L.; Luzzio, F. A. *J. Org. Chem.* **1989**, *54*, 5387. (g) Rosini, G.; Ballini, R.; Sorrenti, P.; Petrini, M. *Synthesis* **1984**, 607. (h) Melot, J. M.; Texier-Boullet, F.; Foucaut, A. *Tetrahedron Lett.*

1986, *27*, 493.

5. (a) Seebach, D.; Leher, F. *Angew. Chem. Int. Ed, Engl.* **1976**, *15*, 505. (b) Baker, D. C.; Putt, S. R. *Synthesis* **1978**, 478. (c) Crumbie, R. L.; Nimitz, J. S.; Mosher, H. S. *J. Org. Chem.* **1982**, *47*, 4040. (d) Ono, N.; Fuji, M.; Kaji, A. *Synthesis* **1987**, 532.
6. Ashwell, M. A.; Jackson, R. F. W. *Synthesis* **1988**, 229.
7. Dampawan, P.; Zajac jr, W. W. *Tetrahedron Lett.* **1982**, *23*, 135. (b) Cookson, R. C.; Ray, P. S. *Tetrahedron Lett.* **1982**, *23*, 3521. (c) Ono, N.; Miyake, H.; Kaji, A. *J. Chem. Soc. Chem. Commun.* **1983**, 875. (d) Ono, N.; Miyake, H.; Kaji, A. *J. Org. Chem.* **1984**, *49*, 4997. (e) Ono, N.; Hamamoto, I.; Kaji, A. *J. Org. Chem.* **1986**, *51*, 2832. (f) Denmark, S. E.; Sternberg, J. A.; Lueoend, R. *J. Org. Chem.* **1988**, *53*, 1251. (g) Stach, H.; Hesse, M. *Tetrahedron* **1988**, *44*, 1573. (h) Rosini, G.; Ballini, R. *Synthesis* **1988**, 833. (i) Rosini, G.; Ballini, R.; Marotta, E. *Tetrahedron* **1989**, *45*, 5935. (j) Ballini, R.; Petrini, M.; Rosini, G. *Tetrahedron* **1990**, *46*, 7531. (k) Ballini, R.; Bartoli, G.; Castagnani, R.; Marcantoni, E.; Petrini, M. *Synlett* **1992**, 64. (l) Ballini, R.; Petrini, M.; Polzonetti, V. *Synthesis* **1992**, 355. (n) Ballini, R.; Bartoli, G.; Giovannini, R.; Marcantoni, E.; Petrini, M. *Tetrahedron Lett.* **1993**, *34*, 3301. (o) Ballini, R.; Bartoli, G.; Gariboldi, P. V.; Marcantoni, E.; Petrini, M. *J. Org. Chem.* **1993**, *58*, 3368. (p) Attanasi, O.; Ballini, R.; Liao, Z.; Santeusanio, S.; Serra-Zanetti, F. *Tetrahedron* **1993**, *49*, 7027.
8. Rosini, G.; Ballini, R. *Synthesis* **1983**, 137.
9. Rosini, G.; Ballini, R. *Synthesis* **1983**, 228.
10. Ballini, R.; Petrini, M.; Rosini, G. *J. Org. Chem.* **1990**, *55*, 5159.
11. Ballini, R.; Castagnani, R.; Marcantoni, E. *J. Chem. Soc. Perkin Trans 1* **1992**, 3161.
12. Dondoni, A.; Rosini, G.; Mossa, G.; Caglioti, L. *J. Chem. Soc. Sect. B* **1968**, 1404.
13. (a) Hutchins, R. O.; Natale, N. R. *J. Org. Chem.* **1978**, *43*, 2299. (b) Kabalka, G. W.; Maddox, J. T.; Bogas, E. *J. Org. Chem.* **1994**, *59*, 5530.
14. See for example: (a) Sacks, C. E.; Fuchs, P. L. *Synthesis* **1979**, 207. (b) Caglioti, L.; Gasparrini, F.; Misiti, D.; Palmieri, G. *Synthesis* **1979**, 207. (c) Attanasi, O.; Grossi, M.; Serra-Zanetti, F. *J. Chem. Res. (S)* **1983**, 322. (d) Ballini, R.; Petrini, M. *J. Chem. Soc. Perkin Trans 1* **1988**, 2563. (e) Kumar, P.; Hedge, V. R.; Pandey, B.; Ravindranathan, T. *J. Chem. Soc. Chem. Commun.* **1993**, 1553. (f) Altamura, A.; Curci, R.; Edwards, J. O. *J. Org. Chem.* **1993**, *58*, 7289.
15. See for example: (a) Pinder, A. R.; Staddin, B. W. *J. Chem. Soc.* **1965**, 2955. (b) Buchi, G.; Wuest, H. *J. Org. Chem.* **1966**, *31*, 977. (c) Floyd, M. B. *J. Org. Chem.* **1978**, *43*, 1641. (d) Elliot, J. D.; Hetmanski, M.; Stoodley, J. *J. Chem. Soc. Perkin Trans 1* **1981**, 1782. (e) Williams, P. D.; Le Golf, E. *J. Org. Chem.* **1981**, *46*, 4143.
16. Patai, S.; Rappoport, Z. in *The Chemistry of Enones* (1989) part. 1 and 2; J. Wiley & Sons, Chichester.
17. (a) Braude, E. A.; Evans, E. A. *J. Chem. Soc.* **1954**, 607. (b) Garbisch jr, E. W. *J. Org. Chem.* **1965**, *30*, 2109. (c) Stotter, P. L.; Hill, K. L. *J. Org. Chem.* **1973**, *38*, 2576. (d) Miller, B.; Wong, H. S. *Tetrahedron* **1972**, *28*, 2369. (e) Hussey, C. W. T.; Pinder, A. R. *J. Chem. Soc.* **1961**, 3525. (f) Brenner, J. E. *J. Org. Chem.* **1961**, *26*, 22.
18. (a) Marx, J. N.; Cox, J. H.; Norman, L. R. *J. Org. Chem.* **1972**, *37*, 4489. (b) Walker, D.; Hiebert, J. D. *Chem. Rev.* **1967**, *67*, 153. (c) Thomas, A. F.; Ozainne, M. *J. Chem. Soc. Chem. Commun.* **1973**, 746. (d) Theissen, R. J. *J. Org. Chem.* **1971**, *36*, 752. (e) Cohen, T.; Shaw, C. K.; Jenkins, J. A. *J. Org. Chem.* **1973**, *38*, 3737.
19. (a) Sharpless, K. B.; Lauer, R. F.; Teranishi, A. Y. *J. Am. Chem. Soc.* **1973**, *95*, 6137. (b) Reich, H.

J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434. (c) Liotta, D.; Barnum, C.; Puleo, R.; Zima, G.; Bayer, C.; Kezar III, H. S. *J. Org. Chem.* **1981**, *46*, 2920. (d) Engman, L. *Tetrahedron Lett.* **1985**, *26*, 6385. (e) Barton, D. H. R.; Lester, D. J.; Ley, S. V. *J. Chem. Soc., Perkin Trans* **1980**, 2209. (f) Eaton, P. E.; Bunnelle, W. H. *Tetrahedron Lett.* **1984**, *25*, 23.

20. Trost, B. M.; Salzmann, T. N.; Hiroi, K. *J. Am. Chem. Soc.* **1976**, *98*, 4887.
21. (a) Ito, Y.; Hirao, T.; Saegusa, T. *J. Org. Chem.* **1978**, *43*, 1011. (b) Tsuji, J.; Minami, I.; Shimizu, I. *Tetrahedron Lett.* **1983**, *24*, 1973.

(*Received in UK* 17 *January* 1995; *revised* 6 *February* 1995; *accepted* 9 *February* 1995)