ELSEVIER

Journal of Organometallic Chemistry 518 (1996) 69–77

Journal of Organometallic Chemistry

Additions of organomanganese reagents to conjugated nitroolefins [1]

I.N.N. Namboothiri, Alfred Hassner *

Department of Chemistry, Bar-Ilan University, Ramat Gan 52900, Israel

Received 9 November 1995

Abstract

Additions of organomanganese reagents to aromatic and aliphatic conjugated nitroolefins were examined for the first time. In most cases reaction proceeded rapidly at −30°C. Unlike Mn reagents lacking β-hydrogens (Me, Ph), which lead to oxidative coupling and reductive dimerisation of nitrostyrenes, benzylmanganese chloride gives 1,4-addition in yields exceeding Grignard or Cu-assisted additions. At 0°C alkyl(Bu, Pr)–manganese reagents undergo an addition–migration–elimination process with nitrostyrenes providing a convenient and stereospecific entry into arylated *trans*-olefins.

Keywords: Manganese; Organomanganese reagents; Conjugated nitroolefins; Addition reaction; Alkenes

1. Introduction

Conjugate addition of organomagnesium reagents to nitroolefins [2] has so far met with only limited success, despite the latter's well-documented versatility as powerful Michael acceptors [3]. This is primarily due to the complications arising from concomitant 1,2-additions as well as diadditions that take place, particularly in the case of aliphatic nitroolefins [2a,b,f]. Recently, Cahiez and Alami [4–6] demonstrated that organomanganese reagents were superior to their Mg and Li counterparts in 1,4-additions to α,β-ethylenic ketones [4], aldehydes [5] and esters [6]. Several disadvantages associated with classical conjugate addition protocols viz. requirement of very low temperatures, various stabilizing and solubilising additives, etc. were reported to have been overcome when manganese reagents were used as Michael donors. Furthermore, catalytic amounts of Cu(I) salts and stoichiometric amounts of trimethylsilyl chloride (Me_3SiCl) were found to accelerate the 1,4-additions. Alternatively, Grignard reagents themselves have been known for quite some time to add with great 1,4-selectivity to various Michael acceptors under mild, Cu(I)-catalyzed conditions in the presence or absence of Me_3SiCl and other additives [7]. Our own interest in additions of nucleophiles to nitroolefins [8] prompted us to examine in detail reactions of Grignard and organomanganese reagents with nitroolefins, the results of which are described herein (Scheme 1).

2. Results and discussion

2.1. 1,4-Additions

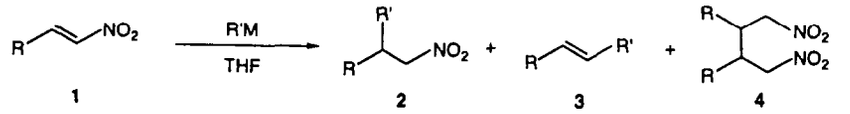
Although it has been reported that addition of alkyl groups to aliphatic nitroolefins furnishes a complex mixture of 1,4-addition products, oximes and hydroxylamines (Scheme 2), the response of aromatic conjugated nitroolefins (nitrostyrenes) to similar additions remains obscure [2]. Our preliminary experiments using BuMgCl and nitrostyrene as the substrate (Table 1) under a wide range of conditions revealed that stabilizing and solubilising additives have hardly any effect on the 1,4-addition. It is also important, however, to note that traces (less than 5%) of 1,2-addition–elimination products **3Aa** were isolated in these reactions at −30°C (Table 1). Nevertheless, the 1,4-addition product **2Aa** turned out to be the sole product at low temperatures in these practically instantaneous reactions. Formation of 1,2-addition–elimination product **3Aa** in small amounts at −30°C and its plausible mechanistic pathway will be discussed later.

We subsequently employed organomanganese reagents, freshly generated or generated in situ. All the

[1] Synthetic Methods 46. For paper 45, see Ref. [1].

* Corresponding author.

PII S0022-328X(96)06150-5



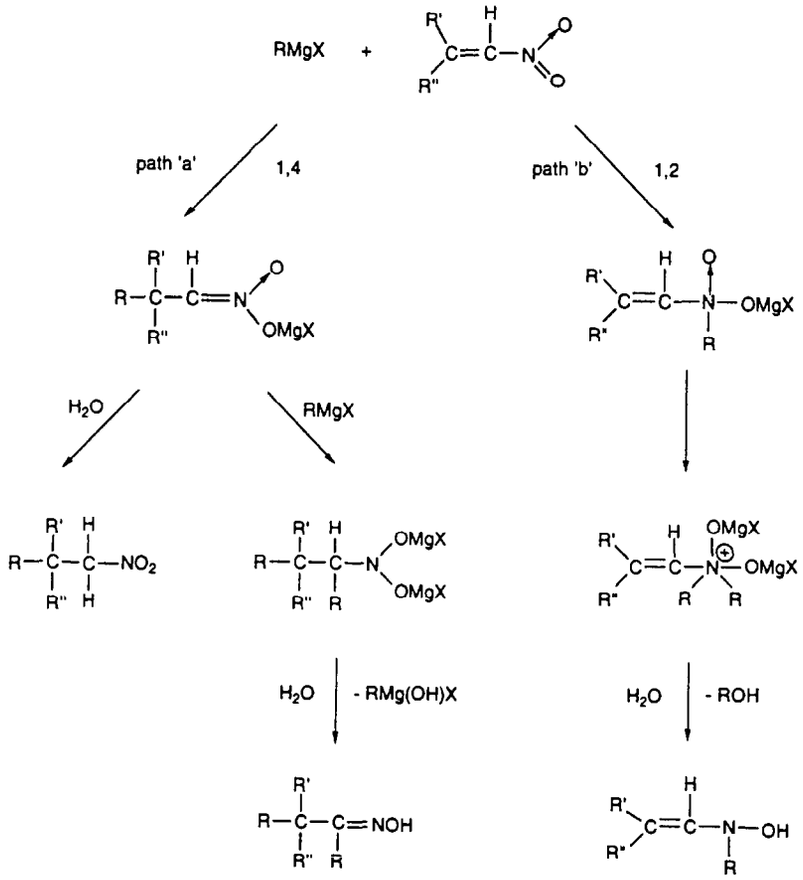
1 2 3 4

1A : R = Ph
1B : R = *p*-OMe-Ph
1C : R = *p*-Cl-Ph
1D : R = *i*-Pr

2Aa, 3Aa : R = Ph, R' = *n*-Bu
2Ba, 3Ba : R = *p*-OMe-Ph, R' = *n*-Bu
2Ca, 3Ca : R = *p*-Cl-Ph, R' = *n*-Bu
2Ab : R = Ph, R' = Me
2Bb, 3Bb : R = *p*-OMe-Ph, R' = Me

2Ac : R = Ph, R' = Bn
2Bc : R = *p*-OMe-Ph, R' = Bn
2Cc : R = *p*-Cl-Ph, R' = Bn
2Ad, 3Ad : R = Ph, R' = *n*-Pr
2Dc : R = *i*-Pr, R' = Bn

Scheme 1.



Scheme 2.

Table 1
Addition of *n*-butylmagnesium chloride [a] to *β*-nitrostyrene (**1A**) [b]

Entry	Catalyst Cu(I), 5%	Additives		Temp (°C)	Isolated yields (%) of products	
		Me_3SiCl (equiv.)	Others (equiv.)		1,4-Addition **2Aa**	1,2-Addition **3Aa**
1.	—	—	—	−30	75	4
2. [c]	CuCl	—	—	−30	76	3
3. [c]	CuCl	1.2	—	−30	73	1
4. [c]	CuBr	1.2	—	−30	73	1
5. [c]	CuBr	1.2	DMAP (1.2)	−30	68	3
6.	—	—	—	−90	77	—
7. [d]	$CuCl_3Li_2$	—	—	−90	77	—
8. [e]	CuBr	1.2	HMPA (1.2)	−90	76	—

[a] 1.2 Equiv.
[b] In THF. [c] Ref. [15a]. [d] Ref. [7d]. [e] Ref. [15b].

Table 2
Addition of organomanganese chloride [a] to *p*-methoxy-β-nitrostyrene (**1B**) [b]

Entry	R′	Isolated yields (%) of products		
		1,4-Addition **2**	1,2-Addition **3**	β-Reductive dimerisation **4**
1.	^{n}Bu	21	21	— [c]
2.	Me	—	10	18 [d]
3.	Ph	—	—	17 [e]

[a] 1.2 Equiv. [b] In THF at −30°C. [c] 13% of the substrate was recovered. [d] 53% of the substrate was recovered. [e] Substrate polymerized.

organomanganese reagents have been generated from the corresponding organomagnesium reagents and the THF-soluble "ate" complex $MnCl_4Li_2$, following the procedures of Cahiez and Alami [6a] (see also Experimental section). A wide array of aromatic and aliphatic nitroolefins was subjected to our studies, aimed at probing their reactivity towards both alkyl and aryl groups. The reaction of butyl-, methyl- and phenylmanganese reagents with *p*-methoxy-β-nitrostyrene at −30°C in THF (Table 2) was unsatisfactory owing to the decomposition of the reagent prior to and/or upon addition of the nitroolefin leading to partial consumption of the substrate and/or its polymerization. However, it seemed possible to draw a distinction between butyl and the other two reagents (Me and Ph), in that the former afforded a mixture of 1,4- and 1,2-addition–elimination products (**2** and **3**) in comparable amounts, while the latter two gave rise mainly to β-reductive dimerisation products (**4**).

In stark contrast to the behavior of the butyl-, methyl- and phenylmanganese reagents, benzylmanganese chloride afforded the expected 1,4-addition products in excellent yields without any apparent side reactions (Table 3). In fact, benzylic organometallic reagents have been sparingly used owing partly to their thermal instability

Table 3
Conjugate addition of benzylmanganese chloride [a] to nitroolefins [b]

Entry	Nitroolefin	Isolated yield (%) of 1,4-adduct
1.	**1A**	87
2.	**1B**	89
3.	**1C**	95
4.	**1D**	73
5.	**6**	73

[a] 1.2 Equiv. [b] In THF at −30°C.

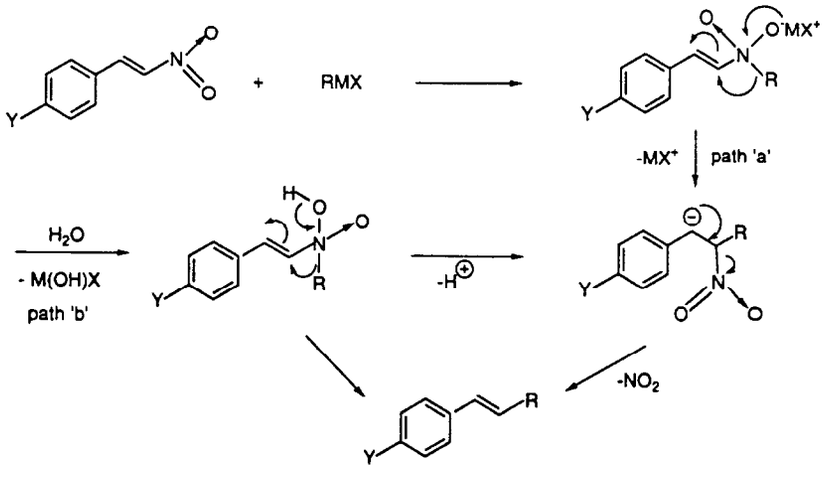
Table 4
Conjugate addition of benzyl–metal reagents to β-nitrostyrene (**1A**) [a]

Entry	R′M	Isolated yield (%) of 1,4-adduct **2Ac**
1.	BnMgCl [b]	79
2.	BnMnCl [b]	87
3.	$Bn_3MnMgCl$ [c]	77
4.	Bn_2Mn [d]	81

[a] In THF at −30°C. [b,c,d] 1.2, 0.4 and 0.6 equiv. respectively.

[9]. The only example, to our knowledge, for the addition of a benzyl group to a nitroolefin was reported in 1947, in which case the crude 1,4-addition product (2-nitro-1-benzylcyclohexane, **6**) was isolated in 43% yield when benzylmagnesium halide was treated with 1-nitrocyclohexene (**5**) [2f]. Therefore, it is noteworthy that the use of a manganese reagent not only improved the yield substantially but demonstrated the generality of the procedure as well. Moreover, there has been no report until now of 1,4-addition of benzylmanganese reagents to any of the common acceptors, viz. α,β-ethylenic ketones, aldehydes and esters.

The fact that the performance of organomanganese halide (RMnX) is superior, albeit marginally, to its magnesium analog and other manganese reagents generated from different stoichiometric ratios of Grignard reagent vs. $MnCl_4Li_2$ is evident from Table 4. Use of



Scheme 3.

Li reagents per se, or in place of Grignard reagents for the generation of Mn reagents, did not give satisfactory results [10].

2.2. Addition–migration–elimination

In order to circumvent the problem of partial consumption of the substrate in the addition of butyl- and methylmanganese reagents, the reagents were generated in situ [4b] (see also Experimental section) by carefully adding Grignard reagent to a stirred solution of $MnCl_4Li_2$ and nitroolefin in THF.

Table 5 shows that a mixture of 1,4-addition products and products arising from a 1,2-addition–elimination process, with the latter predominating, is formed in the case of the butylmanganese reagent. Similar behavior is exhibited by propylmanganese reagent as well. The stereochemistry of β-alkylstyrenes isolated was shown to be *trans* (at least 99%) by ^1H and ^{13}C NMR spectroscopy. This can be rationalized in terms of the stereospecific elimination of the nitro group from the intermediate anion (Scheme 3) under thermodynamic control.

Well-established procedures [11] are indeed available for the synthesis of myriad olefins, both alkylated and arylated, but many lack stereoselectivity, leading to a mixture of *cis*- and *trans*-isomers. Controlled introduction of the C–C double bond is a non-trivial task, often involving separation of intermediate diastereomers [11e], requirement of sensitive organometallic reagents and metal complexes as catalysts [11f,g], cumbersome experimental setup and longer reaction times. Formation of *trans* 1,2-alkyl–aryl olefins in 15–40% yield by reaction of dialkylzinc reagents with 2-aryl-1-nitroalkenes was reported by Seebach et al. [10j]. It is known that nitroalkenes with electron-withdrawing substituents (e.g. RSO_2) undergo similar vinylic substitution reactions [10k–o]. We now show for the first time that alkylmanganese reagents provide a stereospecific route to a variety of arylated *trans*-alkenes in respectable yields involving simple reagents, conditions and separation procedures.

Table 5
Addition of alkyl Grignard reagents [a] in the presence of $MnCl_4Li_2$ [b] to β-nitrostyrenes (**1A–C**) [c]

Entry	Nitro-styrene **1**	R′	Isolated yields (%) of products		
			1,4-Addition	1,2-Addition	β-Reductive dimerisation
			2	**3**	**4**
1.	**1A**	n-Bu	33	56	—
2.	**1A**	n-Pr	40	54	— [d]
3.	**1A**	Me	12	—	20 [e]
4.	**1B**	n-Bu	40	40	—
5.	**1B**	Me	15	—	28 [e]
6.	**1C**	n-Bu	25	62	—

[a] 1.5 Equiv. [b] 1.2 Equiv. [c] In THF at 0°C. [d] Grignard reagent freshly prepared. [e] Substrate polymerized.

Table 6
Addition of *n*-butylmagnesium chloride [a] to *p*-Methoxy-nitrostyrene (**1B**) in the presence of different quantities of $MnCl_4Li_2$ [b]

Entry	$MnCl_4Li_2$ (equiv.)	Isolated yields (%) of products	
		1,4-Addition **2Ba**	1,2-Addition **2Bb**
1.	—	68	4
2.	0.1	57	27
3.	0.3	46	37 [c]
4.	1.2	40(43) [d]	40(27) [d]
5.	2.0	33	43 [e]

[a] 1.5 Equiv. [b] In THF at 0°C. [c] With 0.3 equiv. of $MnCl_2$ the 1,4- and 1,2-adducts isolated were 51 and 21% respectively. [d] In the presence of CuCl (5%) and Me_3SiCl (1.2 equiv.). [e] 7% of the substrate was recovered.

It was extremely intriguing to see 1,2-addition taking place at a rate comparable with or greater than 1,4-addition in the presence of Mn salts. This, in fact, contravenes the prevailing impression that Mn salts preferentially accelerate 1,4-addition [6]. The role of Mn salts in catalyzing 1,2-addition of alkyl groups to β-nitrostyrenes is amply supported by Table 6, which also suggests that the presence of Mn salts in increasing amounts leads to an increase in the rate of 1,2-addition. However, it was observed that increasing amounts of Grignard reagents were required for the completion of the reaction when the quantity of Mn salts was increased (Table 6, Entry 5). Therefore, it was economical to use 1.2 equiv. of $MnCl_4Li_2$ vs. 1.5 equiv. of Grignard reagents (Table 5). It may be noted that even 0.3 equiv. of $MnCl_4Li_2$ is sufficient to achieve satisfactory yields (Table 6, Entry 3).

Entries 1, 4 and 6 in Table 5 indicate that the nature of a remote *p*-substituent on the benzene ring can have a bearing on the extent of 1,2-addition, with the electron-donating OMe group minimizing the 1,2-addition and the electron-withdrawing Cl group enhancing it. This gives insight into the mechanism of this alkylation process, and there seems little doubt that the alkylation initially takes place on N (as in Scheme 2, path b). Subsequently, the alkyl group migrates to the α-carbon, triggering elimination of the nitro group in an overall addition–migration–elimination sequence (Scheme 3). It is also clear that migration of the R group can be modulated by the *p*-substitution on the benzene ring.

Cahiez and Alami [4a] observed some time ago that reaction of three different butylmanganese species (RMnX, R_2Mn and R_3MnMgX) with cyclohexenone provides a mixture of 1,4-addition, 1,2-addition and β-reductive dimerisation products in varying yields. The procedure was subsequently improved by using catalytic amounts of CuCl, often in conjunction with molar equivalents of Me_3SiCl to achieve excellent yields of

1,4-adducts [4b]. However, in the case of nitroalkenes we noted that use of Cu(I) salt and Me_3SiCl did not alter the ratio (Table 6, Entry 4) to any significant extent. This may be attributable to the instantaneous nature of the reaction.

2.3. Reagent stability and substrate sensitivity

Various modes of decomposition of organomanganese reagents and Grignard reagents in the presence of transition metal halides, including $MnCl_2$, were extensively investigated by Kochi and coworkers [12]. The highlights of their observations are that those reagents possessing β-hydrogens (e.g. ethyl, iso-propyl and tert-butyl) are more vulnerable to decomposition by disproportionation than others (e.g. methyl, neopentyl, phenyl, vinyl and benzyl). However, an alternative mode (oxidative coupling) is available for those groups devoid of β-hydrogens. In the case of methyl–metal species, decomposition to methane was also regarded as a predominant pathway. All these decomposition processes were found to be enhanced by the presence of styrene, although the yield of ethylbenzene was much higher with those reagents possessing β-hydrogens.

Insofar as our studies are concerned, the butyl group, which has a greater tendency to undergo decomposition via disproportionation, reacted reasonably well only when the *trans*-metallation was performed in situ. We were pleasantly surprised to note that only traces of coupling dimer (1,2-diphenylethane) were isolated in the case of benzylmanganese reagents, even as phenyl– and methyl–metal reagents underwent large scale decomposition. The smaller tendency of benzyl carbanions to undergo decomposition has been accounted for in terms of the high energy requirement for the conversion of benzylic carbanion to the corresponding free radical as compared with the alkyl and phenyl cases [13]. Whereas the coupling dimer (biphenyl) was isolated in greater than 90% yield in the case of phenyl, no attempt has been made to estimate methane or ethane apparently evolved as a result of the decomposition of methyl–metal reagent.

Recent investigations pertaining to the conjugate addition of organomanganese reagents to α,β-ethylenic esters showed that 1,4-adducts are formed only in moderate yields (approximately 50%) in the case of methyl and phenyl groups [6b]. Although no explanation has been advanced, it is presumably due to the poor nucleophilicity of methyl and phenyl groups coupled with their susceptibility to undergo oxidative coupling in spite of the fact that these species are considered to be relatively stable. In the light of the above, the concordant behavior of methyl- and phenylmanganese reagents towards nitroolefins can be rationalized. It is also unique that β-reductive dimerisation of the substrate is the major pathway in both the Me and Ph cases (see Table 2), which in all probability takes place via radical intermediates. The intermediacy of radicals is much in evidence from the polymerization of at least 50% of the substrate under the conditions employed (see Table 2, Entry 3 and Table 5, Entry 3).

The possible role of styrenic π-ligand in the substrate in catalyzing the decomposition of the reagents as observed by Kochi and coworkers [12] needs to be considered. In the first place, no β-nitroethylbenzene was isolated even in the additions of alkyl groups possessing β-hydrogens to nitrostyrene. Secondly, benzylmanganese reagents displayed exceptional stability and reacted extremely well to afford exclusively 1,4-addition products in excellent yields. However, polymerization on a large scale of β-nitrostyrenes on treatment with methyl- and phenylmanganese reagents does implicate the potential catalytic role being played by the styrenic π-ligand.

Previous investigations disclosed that the presence of an amino group in the substrate or in the medium is undesirable in reactions of organomanganese reagents [14]. Whether the nitro group may have an influence on the stability of manganese reagents is still uncertain.

3. Conclusions

Three distinctly different processes, viz. 1,4-addition, 1,2-addition and β-reductive dimerisation were encountered, often individually but sometimes collectively, when a broad spectrum of nitroolefins was treated with organomanganese reagents. Unlike methyl or phenyl reagents, benzylmanganese reagent leads to high yields of 1,4-addition. The relative stability and reactivity of the reagent appear to be key factors in determining the reaction pathway. A convenient methodology to prepare a variety of arylated *trans*-olefins has evolved from our studies.

4. Experimental

4.1. General

All organometallic reactions were carried out under a positive, dry argon atmosphere using standard experimental techniques. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone ketyl. Column chromatography was performed on Merck silica gel 60 (230–400 mesh), and pre-coated Merck silica gel plates (60F-254) were used for TLC. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200 or AM 300 FT spectrometer. High resolution mass spectra (CI in methane) were recorded at 60–70 eV on VG-Fisons "AutoSpec" spectrometer.

Unless otherwise specified, standardized (2 M or 3 M) Grignard reagents (in THF) were used as purchased from Aldrich. Anhydrous $MnCl_2$ (Fluka) and LiCl were dried at 180°C for 2 h and at 180°C overnight respectively prior to use. Nitrocyclohexene (Aldrich) was used as purchased and all other nitroolefins were prepared as described [2a,8d].

4.2. General procedure for the addition of Grignard reagents to nitroolefins (cf. Table 1)

4.2.1. Entries 1–6 [15a]

To a stirred solution of nitroolefin (1 mmol) in THF (1 ml), cooled to −30 or −90°C, was added Grignard reagent (1.2 equiv. in THF). CuX (5 mol.%) and other additives were added prior to the addition of Grignard reagent as specified in Table 1.

4.2.2. Entries 7,8 [7d,15b]

To the Cu salt (5 mol.%) in THF (0.5 ml), cooled to −90°C, were successively added Grignard reagent, other additives (as specified in Table 1) and finally nitrostyrene in THF (1 ml).

4.2.3. Entries 1–8

The reaction mixture was quenched with saturated aqueous NH_4Cl (2 ml), stirred at room temperature for 1 h, poured into water and extracted with ether. The extracts were washed with brine, dried (anhydrous $MgSO_4$), evaporated and the residue was chromatographed (petroleum ether/ethyl acetate).

4.3. General procedure for the addition of organomanganese reagents to nitroolefins (cf. Tables 2–4)

Organomanganese reagents were quantitatively generated as described [6a] from the "ate" complex, $MnCl_4Li_2$ (1.2 equiv.), and Grignard reagent (1.2 equiv. in THF). To the freshly generated reagent, cooled to −30°C, was added nitroolefin (1 mmol) in THF (1 ml). The reaction mixture was quenched with 10% aqueous HOAc (2 ml) and worked up as above.

4.4. General procedure for the reaction of nitroolefins with Grignard reagents in the presence of $MnCl_4Li_2$ (cf. Tables 5 and 6)

To a stirred solution of the "ate" complex, $MnCl_4Li_2$ (1.2 mmol), in THF (1 ml) were added consecutively nitroolefin (1 mmol) in THF (1 ml) and then, at 0°C, Grignard reagent in THF (1.5 equiv.). The reaction mixture was then quenched with 10% aqueous acetic acid (2 ml) and worked up as above.

In general, the order of elution of products was 1,2-addition–migration–elimination, 1,4-addition and β-reductive dimerisation.

2Aa. Light yellow oil. ^{1}H NMR δ ($CDCl_3$, ppm): 0.83 (t, $J = 7$ Hz, 3H, CH_3), 1.17 (m, 2H, CH_3CH_2), 1.28 (sext, $J = 7$ Hz, 2H, $CH_3CH_2CH_2$), 1.68 (bq, $J = 8$ Hz, 2H, $CH_3CH_2CH_2CH_2$), 3.43 (quint, $J = 8$ Hz, 1H, $CHCH_2NO_2$), 4.52 and 4.56 (AB of ABX, $J_{AB} = 13$ Hz, $J_{AX} = 8.5$ Hz, $J_{BX} = 7.5$ Hz, 2H, $CH_AH_BNO_2$), 7.16–7.20 and 7.22–7.36 (m, 5H, Ar*H*). ^{13}C NMR δ ($CDCl_3$, ppm): 13.80 (CH_3), 22.41 (CH_3CH_2), 29.05 ($CH_3CH_2CH_2$), 32.77 ($CH_3CH_2CH_2CH_2$), 44.39 ($CHCH_2NO_2$), 81.05 (CH_2NO_2), 127.60, 128.90 (Ar), 139.60 (*ipso*-C). MS: *m/z* (relative intensity) 415 (MMH^+, 6), 251 (43), 206 (16), 161 (81), 118 (100). HRMS (*m/z*): Found 415.2565, $C_{24}H_{35}N_2O_4$ (MMH^+) Calc. 415.2597.

2Ba. Light yellow oil. ^{1}H NMR δ ($CDCl_3$, ppm): 0.85 (t, $J = 7$ Hz, 3H, CH_3), 1.18 (m, 2H, CH_3CH_2), 1.28 (sext, $J = 7$ Hz, 2H, $CH_3CH_2CH_2$), 1.65 (ddd, $J = 15/8/2$ Hz, 2H, $CH_3CH_2CH_2CH_2$), 3.40 (bquint, $J = 8$ Hz, 1H, $CHCH_2NO_2$), 3.80 (s, 3H, OCH_3), 4.48 and 4.58 (AB of ABX, $J_{AB} = 12.5$ Hz, $J_{AX} = 8.5$ Hz, $J_{BX} = 7.5$ Hz, 2H, $CH_AH_BNO_2$), 6.83–6.89 and 7.07–7.13 (m, 4H, Ar*H*). ^{13}C NMR δ ($CDCl_3$, ppm): 13.83 (CH_3), 22.40 (CH_3CH_2), 29.07 ($CH_3CH_3CH_2$), 32.78 ($CH_3CH_2CH_2CH_2$), 43.64 ($CHCH_2NO_2$), 55.10 (OCH_3), 81.21 (CH_2NO_2), 114.23 and 128.47 (Ar), 131.49 (*ipso*-C), 158.85 (CH_3OC). MS: *m/z* (relative intensity) 237 (M^+,45), 191 (61), 177 (100), 148 (51). HRMS (*m/z*): Found 237.1353, $C_{13}H_{19}NO_3$ (M^+) Calc. 237.1365.

2Ca. Colorless oil. ^{1}H NMR δ ($CDCl_3$, ppm): 0.84 (t, $J = 7$ Hz, 3H, CH_3), 1.16 (m, 2H, CH_3CH_2), 1.28 (sext, $J = 7$ Hz, 2H, $CH_3CH_2CH_2$), 1.65 (m, 2H, $CH_3CH_2CH_2CH_2$), 3.42 (quint, $J = 8$ Hz, 1H, $CHCH_2NO_2$), 4.49 and 4.55 (AB of ABX, $J_{AB} = 13$ Hz, $J_{AX} = 8.5$ Hz, $J_{BX} = 7.5$ Hz, 2H, $CH_AH_BNO_2$), 7.09–7.14 and 7.28–7.33 (m, 4H, Ar*H*). ^{13}C NMR δ ($CDCl_3$, ppm): 13.76 (CH_3), 22.33 (CH_3CH_2), 28.99 ($CH_3CH_2CH_2$), 32.70 ($CH_3CH_2CH_2CH_2$), 43.77 ($CHCH_2NO_2$), 80.71 (CH_2NO_2), 128.82 and 129.07 (Ar), 133.34 (Cl–*C*), 138.08 (*ipso*-C). MS: *m/z* (relative intensity) 243 ($[M + 2]^+$, 40), 241 (0.38), 197 (21), 195 (70), 183 (20), 181 (59), 153 (43), 139 (37), 127 (33), 125 (100). HRMS (*m/z*): Found 241.0860, $C_{12}H_{16}ClNO_2$ (M^+) Calc. 241.0870.

2Ac. Colorless oil. ^{1}H NMR δ ($CDCl_3$, ppm): 2.95 and 3.02 (AB of ABX, $J_{AB} = 14$ Hz, $J_{AX} = 8$ Hz, $J_{BX} = 8$ Hz, 2H, $PhCH_AH_B$), 3.76 (quint, $J = 8$ Hz, 1H, $CHCH_2NO_2$), 4.57 and 4.61 (AB of ABX, $J_{AB} = 13$ Hz, $J_{AX} = 8.5$ Hz, $J_{BX} = 7.5$ Hz, 2H, $CH_AH_BNO_2$), 7.04–7.08 and 7.13–7.33 (m, 10H, Ar*H*). ^{13}C NMR δ ($CDCl_3$, ppm): 39.99 ($PhCH_2$), 45.94 ($CHCH_2NO_2$), 79.54 (CH_2NO_2), 126.73, 127.45, 127.63, 128.52, 128.80 and 129.00 (Ar), 137.75 and 139.09 (*ipso*-Cs). MS: *m/z* (relative intensity) 240 ($[M–H]^+$, 1), 195 (5), 181 (18), 117 (100). HRMS (*m/z*): Found 240.0998, $C_{15}H_{14}NO_2$ ($[M–H]^+$) Calc. 240.1025.

2Bc. M.p. 75–77°C. ^{1}H NMR δ ($CDCl_3$, ppm): 2.92 and 2.98 (AB of ABX, J_{AB} = 14 Hz, J_{AX} = 7.5 Hz, J_{BX} = 7.5 Hz, 2H, PhCH_AH_B), 3.70 (quint, J = 7.5 Hz, 1H, CHCH_2NO_2), 3.75 (s, 3H, OCH_3), 4.55 (d, J = 7.5 Hz, 2H, CH_2NO_2), 6.79–6.86, 7.03–7.10 and 7.15–7.29 (m, 9H, ArH). ^{13}C NMR δ ($CDCl_3$, ppm): 39.97 (PhCH$_2$), 45.20 (CHCH$_2$NO$_2$), 55.11 (OCH$_3$), 79.77 (CH$_2$NO$_2$), 114.14, 126.60, 128.43 and 128.95 (Ar), 130.92 and 137.88 (*ipso*-Cs), 158.87 (CH$_3$OC). MS: m/z (relative intensity) 271 (M^+,9), 239 (7), 225 (30), 211 (100). HRMS (m/z): Found 271.1220, $C_{16}H_{17}NO_3$ (M^+) Calc. 271.1208.

2Cc. M.p. 104–106°C. ^{1}H NMR δ ($CDCl_3$, ppm): 2.94 and 2.97 (AB of ABX, J_{AB} = 13.5 Hz, J_{AX} = 7.5 Hz, J_{BX} = 7.5 Hz, 2H, PhCH_AH_B), 3.75 (quint, J = 7.5 Hz, 1H, CHCH_2NO_2), 4.57 (d, J = 7.5 Hz, 2H, CH_2NO_2), 7.02–7.10 and 7.19–7.29 (m, 9H, ArH). ^{13}C NMR δ ($CDCl_3$, ppm): 39.86 (PhCH$_2$), 45.35 (CHCH$_2$NO$_2$), 79.28 (CH$_2$NO$_2$), 126.87, 128.60, 128.82, 128.94, 128.97 (Ar), 133.45 (Cl–C), 137.30 and 137.51 (*ipso*-Cs). MS: m/z (relative intensity) 277 ([M + 2]$^+$, 0.6), 275 (2), 230 (13), 228 (34), 153 (21), 151 (63), 138 (100). HRMS (m/z): Found 275.0690, $C_{15}H_{14}ClNO_2$ (M^+) Calc. 275.0713.

2Ab [2i]. Colorless oil. ^{1}H NMR δ ($CDCl_3$, ppm): 1.38 (d, J = 7 Hz, 3H, CH_3), 3.63 (sext, J = 7 Hz, 1H, CHCH$_3$), 4.49 and 4.54 (AB of ABX, J_{AB} = 12 Hz, J_{AX} = 8.5 Hz, J_{BX} = 7.5 Hz, 2H, CH_AH_B), 7.20–7.37 (m, 5H, ArH). ^{13}C NMR δ ($CDCl_3$, ppm): 18.72 (CH$_3$), 38.65 (CHCH$_3$), 81.88 (CH$_2$), 126.88, 127.56 and 128.97 (Ar), 140.95 (*ipso*-C). MS: m/z (relative intensity) 119 (M^+–NO_2, 100), 105 (19), 91 (66). HRMS (m/z): Found 119.0847, C_9H_{11}(M^+–NO_2) Calc. 119.0861.

2Bb. Colorless oil. ^{1}H NMR δ ($CDCl_3$, ppm): 1.35 (d, J = 7 Hz, 3H, CH_3), 3.59 (sext, J = 7.5 Hz, 1H, CHCH$_3$), 3.79 (s, 3H, OCH_3), 4.44 and 4.50 (AB of ABX, J_{AB} = 12 Hz, J_{AX} = 8 Hz, J_{BX} = 7.5 Hz, 2H, CH_AH_B), 6.84–6.89 and 7.12–7.17 (m, 4H, ArH). ^{13}C NMR δ ($CDCl_3$, ppm): 18.84 (CHCH$_3$), 37.97 (CHCH$_3$), 55.30 (OCH$_3$), 82.15 (CH$_2$), 114.42 and 127.87 (Ar), 132.95 (*ipso*-C), 158.97 (CH$_3$OC). MS: m/z (relative intensity) 195 (M^+, 75), 149 (100), 148 (89), 135 (65), 121 (27). HRMS (m/z): Found 195.0890, $C_{10}H_{13}NO_3$ (M^+) Calc. 195.0895.

2Ad. Colorless oil. ^{1}H NMR δ ($CDCl_3$, ppm): 0.87 (t, J = 7.5 Hz, 3H, CH_3), 1.22 (sext, J = 7.5 Hz, 2H, CH$_3$CH_2), 1.66 (m, 2H, CH$_3$CH$_2$CH_2), 3.46 (quint, J = 8 Hz, 1H, CHCH$_2$NO$_2$), 4.52 and 4.56 (AB of ABX, J_{AB} = 12 Hz, J_{AX} = 8 Hz, J_{BX} = 8 Hz, 2H, CH_AH_B NO$_2$), 7.16–7.36 (m, 5H, ArH). ^{13}C NMR δ ($CDCl_3$, ppm): 13.73 (CH$_3$), 20.11 (CH$_3$$CH_2$), 35.27 (CH$_3CH_2$$CH_2$), 44.17 ($CHCH_2NO_2$), 81.02 ($CH_2NO_2$), 127.52 and 128.89 (Ar), 139.65 (*ipso*-C). MS: m/z (relative intensity) 193 (M^+, 5), 147 (47), 118 (57), 91 (100). HRMS (m/z): Found 193.1120, $C_{11}H_{15}NO_2$ (M^+) Calc. 193.1103.

2Dc. Colorless oil. ^{1}H NMR δ ($CDCl_3$, ppm): 0.97 (d, J = 7 Hz, 3H, C$H_{(A)3}$), 1.00 (d, J = 7 Hz, 3H, C$H_{(B)3}$), 1.82 (heptd, J = 7/3.5 Hz, 1H, CH$_3$CHCH$_3$), 2.47 (m, 2H, PhCH_AH_B and CHCH$_2$NO$_2$), 2.80 (dd, J = 19/10 Hz, 1H, PhCH$_A$$H_B$), 4.21 and 4.35 (AB of ABX, J_{AB} = 12.5 Hz, J_{AX} = 7 Hz, J_{BX} = 5.5 Hz, 2H, CH_AH_BNO$_2$), 7.15–7.33 (m, 5H, ArH). ^{13}C NMR δ ($CDCl_3$, ppm): 18.65 (C_AH$_3$), 18.75 (C_BH$_3$), 27.87 (CH$_3$$CHCH_3$), 34.30 (Ph$CH_2$), 45.16 ($CHCH_2NO_2$), 76.74 ($CH_2NO_2$), 126.51, 128.59 and 128.91 (Ar), 138.85 (*ipso*-C). MS: m/z (relative intensity) 208 (MH^+, 5), 161 (34), 119 (26), 105 (83), 91 (100). HRMS (m/z): Found 208.1326, $C_{12}H_{18}NO_2$ (MH^+) Calc. 208.1338.

6 [2f]. Colorless oil. Inseparable mixture of two isomers in approximately 10:1 ratio. ^{1}H NMR δ ($CDCl_3$, ppm): 1.64–1.93 (m, 6H, CH$_2$CHCH_2CH_2-CH_2), 2.13–2.24 (m, 2H, CH_2CHNO$_2$), 2.25–2.37 (m, 1H, CHCHNO$_2$), 2.59 and 2.63 (AB of ABX, J_{AB} = 14 Hz, J_{AX} = 9 Hz, J_{BX} = 6.5 Hz, 2H, PhCH_AH_B), 4.57 (dt, J = 7/4 Hz, 1H, CHNO$_2$), 7.10–7.16 and 7.17–7.32 (m, 5H, ArH). ^{13}C NMR δ ($CDCl_3$, ppm) major (*cis*) isomer: 21.96 (CH$_2$CHCH$_2$$CH_2$), 22.48 ($CH_2CH_2$CHNO$_2$), 26.39 (PhCH$_2CHCH_2$), 27.87 ($CH_2$CHNO$_2$), 35.82 (Ph$CH_2$), 41.21 ($C$HCHNO$_2$), 85.88 ($CHNO_2$), 126.31, 128.45 and 128.92 (Ar), 139.18 (*ipso*-C); minor (*trans*) isomer: 24.47 (CH$_2$CHCH$_2$$CH_2$), 24.65 ($CH_2CH_2$CHNO$_2$), 29.22 (PhCH$_2CHCH_2$), 32.16 ($CH_2$CHNO$_2$), 38.97 (Ph$CH_2$), 42.43 ($C$HCHNO$_2$), 90.94 ($CHNO_2$), 128.31, 128.70 and 129.33 (Ar), 138.40 (*ipso*-C). MS: m/z (relative intensity) 173 (M^+–NO_2, 100), 119 (6), 105 (8), 91 (20). HRMS (m/z): Found 218.1170, $C_{13}H_{16}NO_2$ ([M–H]$^+$). Calc. 218.1181.

3Aa [11g,h]. Colorless oil. ^{1}H NMR δ ($CDCl_3$, ppm): 0.93 (t, J = 7 Hz, 3H, CH_3), 1.40 (m, 4H, CH$_3$CH_2CH_2), 2.25 (bqd, J = 7/1.5 Hz, 2H, CH_2CH=), 6.25 (dt, J = 16/7 Hz, 1H, CH$_2$CH=), 6.40 (bd, J = 16 Hz, 1H, PhCH=) 7.14–7.21 and 7.24–7.36 (m, 5H, ArH). ^{13}C NMR δ ($CDCl_3$, ppm): 13.92 (CH$_3$), 22.28 (CH$_3$$CH_2$), 31.60 (CH$_3CH_2$$CH_2$), 32.70 ($CH_2$CH=), 125.93, 126.71 and 128.44 (Ar), 129.80 (CH$_2$$C$H=), 131.19 (Ph$C$H=), 138.07 (*ipso*-C). MS: m/z (relative intensity) 161 (MH^+, 100), 147 (11), 117 (29), 105 (10), 91 (56). HRMS (m/z): Found 161.1323, $C_{12}H_{17}$ (MH^+) Calc. 161.1330.

3Ba. Colorless oil. ^{1}H NMR δ ($CDCl_3$, ppm): 0.93 (t, J = 7 Hz, 3H, CH_3), 1.40 (m, 4H, CH$_3$CH_2CH_2), 2.15 (bqd, J = 7/1.5 Hz, 2H, CH_2CH=), 3.80 (s, 3H, OCH_3) 6.10 (dt, J = 16/7 Hz, 1H, CH$_2$CH=), 6.33 (bd, J = 16 Hz, 1H, ArCH=), 6.79–6.85 and 7.23–7.29 (m, 4H, ArH). ^{13}C NMR δ ($CDCl_3$, ppm): 13.96 (CH$_3$), 22.28 (CH$_3$$CH_2$), 31.71 (CH$_3CH_2$$CH_2$), 32.70

(CH_2CH=), 55.28 (OCH_3), 113.91 (Ar), 126.93 (CH=CH), 129.03 (Ar), 130.86 (*ipso*-C), 158.61 (CH_3OC). MS: *m/z* (relative intensity) 191 (MH^+, 100), 190 (99.7), 147 (32). HRMS (*m/z*): Found 191.1441, $C_{13}H_{19}O$ (MH^+) Calc. 191.1436.

3Ca. Colorless oil. ^{1}H NMR δ ($CDCl_3$, ppm): 0.92 (t, J = 7 Hz, 3H, CH_3), 1.24–1.50 (m, 4H, CH_3CH_2-CH_2), 2.19 (qd, J = 7/1 Hz, 2H, CH_2CH=), 6.19 (dt, J = 16/7 Hz, 1H, CH_2CH=), 6.30 (dt, J = 16/1 Hz, 1H, ArCH=), 7.24 (s, 4H, ArH). ^{13}C NMR δ ($CDCl_3$, ppm): 13.92 (CH_3), 22.30 (CH_3CH_2), 31.47 ($CH_3CH_2CH_2$), 32.70 (CH_2CH=), 127.09 (Ar), 128.56 (Ar and CH_2CH=), 131.92 (ArCH=), 132.29 (Cl–*C*), 136.50 (*ipso*-C). MS: *m/z* (relative intensity) 197 ([M + 2]H^+, 36), 196 (26), 195 (100), 194 (50), 167 (6), 153 (27). HRMS (*m/z*): Found 195.0953, $C_{12}H_{16}Cl$ (MH^+) Calc. 195.0941.

3Ad [lli, j, k]. Colorless oil; ^{1}NMR δ ($CDCl_3$, ppm): 0.95 (t, J = 7.5Hz, 3H, CH_3), 1.50 (sext, J = 7.5Hz, 2H, CH_3CH_2), 2.18 (qd, J = 7.5/1.5Hz, 2H, CH_2CH=), 6.22 (dt, J = 16/7.5Hz, 1H, CH_2CH=), 6.37 (bd, J = 16Hz, 1H, PhCH=) 7.13–7.20 and 7.23–7.35 (m, 5H, ArH); ^{13}CNMR δ ($CDCl_3$, ppm): 13.69 (CH_3), 22.57 (CH_3CH_2), 35.12 (CH_2CH=), 125.93, 126.72 and 128.42 (Ar), 129.98 (CH_2CH=), 130.91 (PhCH=), 138.00 (*ipso*-C); MS: *m/z* (relative intensity) 146 (M^+, 100), 117 (73), 104 (11), 91 (36), 91 (56); HRMS (*m/z*): Found 146.1090, $C_{11}H_{14}$ (M^+) Calc. 146.1096.

3Bb. Colorless oil. ^{1}H NMR δ ($CDCl_3$, ppm); 1.85 (dd, J = 7/1.5 Hz, 3H, CH_3CH=), 3.80 (s, 3H, OCH_3), 6.04 (dd, J = 16/7 Hz, 1H, CH_3CH=), 6.09 (dd, J = 16/1.5 Hz, 1H, ArCH=), 67.9–6.85 and 7.22–7.28 (m, 4H, ArH). ^{13}C NMR δ ($CDCl_3$, ppm): 18.37 (CH_3CH=), 55.30 (OCH_3), 113.96 (Ar), 123.49 (CH_3CH=), 126.91 (Ar), 130.41 (ArCH=), 130.90 (*ipso*-C), 158.66 (CH_3OC). MS: *m/z* (relative intensity) 149 (MH^+, 100), 121 (10), 113 (7). HRMS (*m/z*): Found 149.0958, $C_{10}H_{13}O$ (MH^+) Calc. 149.0966.

4A. M.p. 101–103°C. ^{1}H NMR δ ($CDCl_3$, ppm): 3.95 (bquint, J = 5 Hz, 2H, 2 × PhCH), 4.57 and 4.74 (similar to AB of ABX, J_{AB} = 13.5 Hz, J_{AX} = 7.5 Hz, J_{BX} = 6.5 Hz, 4H, 2 × CH_AH_BNO$_2$), 6.77–6.83 and 7.21–7.32 (m, 10H, 2 × ArH). ^{13}C NMR δ ($CDCl_3$, ppm): 45.55 (PhCH), 77.20 (CH_2), 128.46, 128.60 and 128.91 (Ar), 134.14 (*ipso*-C). MS: *m/z* (relative intensity) 301 (MH^+, 0.2), 254 (37), 207 (100), 193 (89). HRMS (*m/z*): Found 301.1164, $C_{16}H_{17}N_2O_4$ (MH^+) Calc. 301.1188.

4B. M.p. 129–131°C. Inseparable mixture of two isomers (dl and *meso*) in approximately 6:1 ratio. Major (dl) isomer: ^{1}H NMR δ ($CDCl_3$, ppm): 3.78 (s, 6H, 2 × OCH_3), 3.86 (bquint, J = 6 Hz, 2H, 2 × ArCH), 4.49 and 4.66 (similar to AB of ABX, J_{AB} = 13 Hz, J_{AX} = 7.5 Hz, J_{BX} = 7.5 Hz, 4H, 2 × CH_AH_BNO$_2$), 6.69–6.81 (m, 8H, 2 × ArH). ^{13}C NMR δ ($CDCl_3$, ppm): 44.83 (ArCH), 55.24 (OCH_3), 77.51 (CH_2), 114.00 (Ar), 125.85 (*ipso*-C), 130.15 (Ar), 159.59 (CH_3OC). Minor (*meso*) isomer: ^{1}H NMR δ ($CDCl_3$, ppm): 3.66 (bquint, J = 4.5 Hz, 2H, 2 × ArCH), 3.80 (s, 6H, 2 × OCH_3), 4.25 (similar to A of ABX, B part is obscured, J_{AB} = 12.5 Hz, J_{AX} = 4 Hz, 2H, 2 × CH_AH_BNO$_2$), 6.90–7.27 (m, 8H, 2x ArH). ^{13}C NMR δ ($CDCl_3$, ppm): 46.96 (ArCH), 55.24 (OCH_3), 79.32 (CH_2), 115.08 (Ar), 128.08 (*ipso*-C), 128.76 (Ar), 159.60 (CH_3OC). MS: *m/z* (relative intensity) 360 (M^+, 4), 314 (4), 300 (35), 253 (46), 206 (15), 180 (100). HRMS (*m/z*): Found 360.1351, $C_{18}H_{20}N_2O_6$ (M^+) Calc. 360.1321.

Acknowledgements

Support of this research by a grant from the Israel Science Foundation is gratefully acknowledged. We thank Dr. H.E. Gottlieb for valuable help with NMR spectra.

References and notes

[1] T. Yechezkel, E. Ghera, D. Ostercamp and A. Hassner, *J. Org. Chem., 60* (1995) 5135.

[2] (a) E. Muller (ed.), *Houben-Weyl: Methoden der Organische Chemie.*, Vol. 10/1, Thieme, Stuttgart, 1971, pp. 9–462 and references cited therein. (b) V.V. Perekalin, *Unsaturated Nitro Compounds*, Israel Program for Scientific Translations, Jerusalem, 1964, p. 249 and references cited therein. (c) E.P. Kohler and J.F. Stone, Jr., *J. Am. Chem. Soc., 52* (1930) 761. (d) A. Lambert, J.D. Rose and B.C.L. Weeden, *J. Chem. Soc.*, (1949) 42. (e) G.D. Buckley, *J. Chem. Soc.*, (1947) 1494. (f) G.D. Buckley and E. Ellery, *J. Chem. Soc.*, (1947) 1497. (g) J. Colonge and G. Lartigau, *Bull. Chem. Soc. Fr.*, (1965) 738. (h) T. Severin, D. Scheel and P. Adhikary, *Chem Ber., 102* (1969) 2966. (i) S.B. Bowlus, *Tetrahedron Lett.*, (1975) 3591.

[3] (a) D. Seebach, E.W. Colwin, F. Lehr and T. Weller, *Chimia, 33* (1979) 1. (b) A.G.M. Barrett and G.G. Graboski, *Chem. Rev., 86* (1986) 751 and references cited therein. (c) A.G.M. Barrett, *Chem. Soc. Rev., 20* (1991) 95.

[4] (a) G. Cahiez and M. Alami, *Tetrahedron Lett., 27* (1986) 569; (b) *30* (1989) 3541.

[5] G. Cahiez and M. Alami, *Tetrahedron Lett., 30* (1989) 7365.

[6] (a) G. Cahiez and M. Alami, *Tetrahedron, 45* (1989) 4163; (b) *Tetrahedron Lett., 31* (1990) 7423.

[7] (a) B.H. Lipshutz and S. Sengupta, *Organic Reactions, 41* (1992) 135 and references cited therein. (b) E. Erdik, *Tetrahedron, 40* (1984) 641 and references cited therein. (c) G. Cahiez and M. Alami, *Tetrahedron Lett., 31* (1990) 7425. (d) M.T. Reetz and A. Kindler, *J. Chem. Soc., Chem. Commun.*, (1994) 2509.

[8] (a) A. Hassner, J.M. Larkin and J.E. Dowd, *J. Org. Chem., 33* (1968) 1733. (b) A. Hassner and W. Chau, *Tetrahedron Lett., 23* (1982) 1989. (c) A. Hassner and W. Dehaen, *J. Org. Chem., 55* (1990) 5505; (d) *Chem. Ber., 124* (1991) 1181. (e) E. Ghera, T. Yechezkel and A. Hassner, *J. Org. Chem., 58* (1993) 6716.

[9] (a) R.J. Linderman, A. Godfrey and K. Horne, *Tetrahedron, 45* (1989) 495. (b) S.C. Berk, M.C.P. Yeh, N. Jeong and P. Knochel, *Organometallics, 9* (1990) 3053. (c) P.S. van Heer-

den, B.C.B. Bezuidenhoudt, J.A. Steenkamp and D. Ferreira, *Tetrahedron Lett., 33* (1992) 2383. (d) B.K. Mehta, H. Ila and H. Junjappa, *Tetrahedron Lett., 36* (1995) 1925.

[10] For the addition of organolithium reagents to nitroolefins, see (a) Refs. [2h] and [3a]. (b) D. Seebach and H.F. Leitz, *Angew. Chem., 81* (1969) 1047. (c) D. Seebach, H.F. Leitz and V. Ehrig, *Chem. Ber., 108* (1975) 1924. (d) D. Seebach, V. Ehrig, H.F. Leitz and R. Henning, *Chem. Ber., 108* (1975) 1946. (e) V. Ehrig and D. Seebach, *Chem. Ber., 108* (1975) 1961. (f) C.D. Bedford and A.T. Neilsen, *J. Org. Chem., 43* (1978) 2460. (g) P. Knochel and D. Seebach, *Tetrahedron Lett., 22* (1981) 3223. (h) D. Seebach and P. Knochel, *Helv. Chim. Acta, 67* (1984) 261. (i) A.G.M. Barrett, G.G. Graboski and M.A. Russell, *J. Org. Chem., 51* (1986) 1012. (j) D. Seebach, H. Schaefer, B. Schmidt and M. Schreiber, *Angew. Chem., 104* (1992) 1680; *Angew. Chem., Int. Ed. Engl., 31* (1992) 1587. (k) W.D. Emmons and J.P. Freeman, *J. Org. Chem., 22* (1957) 456. (l) Z. Rappoport and A. Gazit, *J. Org. Chem., 50* (1985) 3184. (m) B.J. Barnes, P.J. Newcombe, R.K. Norris and K. Wilson, *J. Chem. Soc., Chem. Commun.*, (1985) 1408. (n) C. Jubert and P. Knochel, *J. Org. Chem., 57* (1992) 5431. (o) K.P. Park, I. Yi and C. O, *J. Org. Chem., 59* (1994) 1053.

[11] (a) A. Hassner and B. Stumer, *Organic Synthesis based on Name Reactions and Unnamed Reactions*, Tetrahedron Organic Chemistry Series, Vol. 11, Elsevier, 1994 and references cited therein. (b) B.E. Maryanoff and A.B. Reitz, *Chem. Rev., 89* (1989) 863. (c) J. Boutagy and R. Thomas, *Chem. Rev., 74* (1974) 87. (d) R.F. Heck, *Organic Reactions, 27* (1982) 345. (e) D.J. Ager, *Organic Reactions, 38* (1990) 1. (f) G. Zweifel and J.A. Miller, *Organic Reactions, 32* (1984) 375. (g) E. Negishi and S. Baba, *J. Chem. Soc., Chem. Commun.*, (1976) 596. (h) N. Miyaura, T. Yoshinari, M. Itoh and A. Suzuki, *Tetrahedron Lett.*, (1974) 2961. (i) T. Mole and J.R. Surtees, *Austr. J. Chem., 17* (1964) 1229. (j) H. Lehmkuhl, D. Reinehr, D. Henneberg, G. Schomburg and G. Schroth, *Liebigs Ann. Chem.*, (1975) 119. (k) H. Lehmkuhl and W. Bergstein, *Liebigs Ann. Chem.*, (1978) 1436.

[12] (a) M. Tamura and J. Kochi, *J. Organomet. Chem., 29* (1971) 111; (b) *Bull. Chem. Soc. Jpn., 44* (1971) 3063. See also (c) R.P.A. Sneeden and H.H. Zeizz, *J. Organomet. Chem.*, 22 (1970) 713.

[13] Organolithium and magnesium reagents can react with nitro compounds lacking α-hydrogens to provide nitrones, A. Hassner and D.R. Fitchmun, *Tetrahedron Lett.*, (1966) 1991.

[14] (a) J.F. Normant and G. Cahiez, *Modern Synthetic Methods, 3* (1983) 173. (b) G. Friour, A. Alexakis, G. Cahiez and J.F. Normant, *Tetrahedron, 40* (1984) 683. (c) G. Friour, G. Cahiez and J.F. Normant, *Synthesis*, (1985) 50.

[15] (a) G. Cahicz and M. Alami, *Tetrahedron Lett.*, 31 (1990) 7425. (b) Y. Horiguchi, S. Matsuzwa, E. Nakamura and I. Kuwajima, *Tetrahedron Lett., 27* (1986) 4025.