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A Convenient Samarium-Promoted Synthesis of Aliphatic (*E*)-Nitroalkenes under Mild Conditions†

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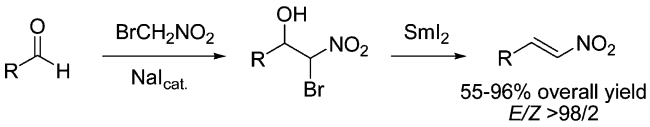

A samarium-promoted synthesis of (*E*)-nitroalkenes from 1-bromo-1-nitroalkan-2-ols in high yields and with total selectivity is reported. This reaction together with the easy and efficient preparation of the 1-bromo-1-nitroalkan-2-ols constitutes a simple and advantageous alternative toward nitroalkenes with total *E*-stereoselectivity. A mechanism is proposed to explain the *E*-stereoselectivity of the β-elimination reaction.

Nitroalkenes are synthetically important products since they have been used as important reagents as Michael acceptors or dienophiles in the Diels−Alder reactions among others.[1] Moreover, nitroalkenes prepared from aromatic aldehydes are especially useful for natural product synthesis.[2] For these reasons, various methods have been described for their preparation. Hence, aromatic nitroalkenes can be very readily obtained through a base-catalyzed reaction of the corresponding aromatic aldehyde with the nitroalkane (Knoevenagel reaction).[3] However, no aliphatic nitroalkenes are, in general, accessible using this process. The most important method for the synthesis of aliphatic nitroalkenes is the dehydration of the corresponding β-nitro alcohol. This process is generally carried out using phthalic anhydride,[4] $CH_3SO_2Cl-NEt_3$,[5] dicyclohexylcarbodiimide,[6] $Ac_2O-AcONa$,[7] PPh_3-CCl_4,[8] TFAA−NEt_3,[9] or Al_2O_3.[10] Other methods starting from materials other than conventional Henry adducts have also appeared in the literature.[11]

Introduced by Kagan in 1977,[12] samarium diiodide has been used to perform a wide variety of organic reactions, including carbon−carbon bond formation and olefination of carbonyl compounds.[13] However, to the best of our knowledge, the transformation of Henry adducts into nitroalkenes, promoted by samarium diiodide, has not been described to date. Taking into account that samarium diiodide is a nontoxic reagent and given the high selectivity generally shown by SmI_2-mediated reactions, it would be useful to develop a method promoted by SmI_2 to access nitroalkenes.

Very recently, we described the addition reaction of bromonitromethane to aldehydes, catalyzed by NaI, to yield 1-bromo-1-nitroalkan-2-ols.[14] In this note, we describe a novel and totally stereoselective β-elimination reaction of 1-bromo-1-nitroalkan-2-ols promoted by SmI_2 under mild reaction conditions, to obtain 1-nitroalkenes. This reaction, together with the ready availability of the requisite 1-bromo-1-nitroalkan-2-ols,[14] constitutes an efficient route to (*E*)-1-nitroalkenes. A mechanism is also proposed to explain the *E*-stereoselectivity of the β-elimination reaction from a mixture of diastereoisomers of the starting compounds.

Thus, 1-bromo-1-nitroalkan-2-ols **2** were readily available by reaction of bromonitromethane with various aldehydes **1** in the presence of catalytic amounts of NaI at room temperature (Scheme 1). The crude reaction mixtures obtained (without purification) were treated with SmI_2 at room temperature, affording the corresponding nitroalkenes **3** in high yield and with total *E*-stereoselectivity.

† This paper is dedicated with best wishes to Professor Miguel Yus on the occasion of his 60th birthday.

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SCHEME 1. Synthesis of Nitroalkenes 3.

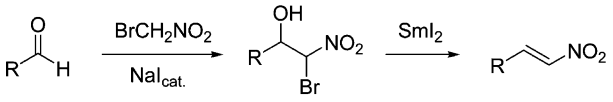

TABLE 1. Synthesis of Nitroalkenes 3

entry	3	R	*E*/*Z*[a]	yield (%)[b]
1	**3a**	*n*-C_7H_{15}	>98/2	78(70)
2	**3b**	*i*-Bu	>98/2	65(59)
3	**3c**	*s*-Bu	>98/2	60(55)
4	**3d**	Cy	>98/2	95(92)
5	**3e**	$PhCH_2$	>98/2	97(96)
6	**3f**	$CH_2{=}CH(CH_2)_8$	>98/2	89(85)
7	**3g**	(Z)-$PrCH{=}CH(CH_2)_4$	>98/2	84(82)

[a] *E*/*Z* ratio was determined by GC-MS and/or 300 MHz ^{1}H NMR analysis of the crude products **3**. [b] Isolated yield of pure compounds **3** after column chromatography based on crude compounds **2**. Isolated yield of compounds **3** based on compounds **1** are shown in parentheses.

The key step in the synthesis of nitroalkenes **3** is the β-elimination reaction, and this process seems to be general as shown by the results compiled in Table 1. Thus, linear, branched, cyclic, and aromatic aldehydes were succesfully used as starting materials. Three points are worth noting: (a) this process can be carried out using readily enolizable aldehydes (Table 1, entry 5); (b) other C=C double bonds and their stereochemistry remained unaltered during the process (Table 1, entries 6 and 7); (c) the starting compounds **2** were used as a diastereoisomeric mixture (approximately 1/1). It should also be emphasized that bromohydrins **2** were employed without purification before the β-elimination reaction was carried out. So, the synthesis of crude bromohydrins **2** combined with the β-elimination reaction constitutes an easy and efficient route to (*E*)-nitroalkenes. As it is shown in Table 1, nitroalkenes **3** were obtained in good overall yields from aldehydes **1**.

The *E*/*Z* ratio was determined on the crude reaction products by GC-MS and/or ^{1}H NMR spectroscopy. The relative *E* configuration of the double bond was established based on the value of ^{1}H NMR coupling constant between the olefinic protons in compounds **3**.[15]

The synthesis of nitroalkenes from aldehydes constitutes an advantageous alternative to the methods previously described in the literature due to the following reasons: (a) this process took place under very mild reaction conditions and no basic media were necessary; (b) the reaction took place with total stereoselectivity affording nitroalkenes with *E*/*Z* ratio >98/2; (c) in general, this method afforded nitroalkenes **3** in similar or higher yield than those preparations of aliphatic nitroalkenes previously reported in the literature such as **3a**,[11a] **3d**,[6b,9a,11c] and **3e**.[11d,e]

The synthesis and the observed stereochemistry of products **3** might be explained by assuming a chelation control model similar to those previously published by our group.[16] Thus, treatment of compounds **2** with 1 equiv of samarium diiodide would generate a radical **4**, which could be reduced to the samarium nitronate intermediate **5** after the addition of another 1 equiv of SmI_2. Chelation of the oxophilic Sm^{III} center with the oxygen atom of the alcohol group produces a six-membered ring, which increases the leaving group aptitude of the hydroxyl group. On the basis of the oxophilic nature of samarium (III),[17] we propose a half-chair transition state model **I**, with the bulkier R group in the equatorial orientation in order to avoid 1,3-diaxial interactions with the samarium coordination sphere. Consequently, elimination from this intermediate **5** affords (*E*)-nitroalkenes **3** (Scheme 2).

The isolation of **3** with total *E*-stereoselectivity from the mixture of diastereoisomers **2** can be explained by assuming the fact that after metalation of **2** by SmI_2, the mixture of diastereoisomers of **2** would be transformed into a mixture of the samarium nitronate enantiomers **5**. So, the β-elimination of **5** would generate only one diastereoisomer.[18]

In summary, we have described an easy, efficient, and general route to aliphatic nitroalkenes with total *E*-stereoselectivity through two successive reactions. First, 1-bromo-1-nitroalkan-2-ols **2** are readily obtained by a NaI-catalyzed reaction of aldehydes with bromonitromethane. In the second reaction, the SmI_2-promoted a β-elimination reaction on the obtained crude compounds **2** with total *E*-stereoselectivity. Both reactions take place under mild reaction conditions. The development of further methodologies for the catalytic use of SmI_2 in β-elimination processes is currently under investigation within our laboratory.

Experimental Section

Compounds **2a**−**e** and **3d** have been previously characterized, and their NMR spectral data were in good agreement with the literature data. References for the reported compounds are also cited in the Supporting Information.

General Procedure for the Synthesis of Nitroalkenes 3 from Aldehydes 1. NaI (0.12 mmol, 0.15 equiv) was added to a stirred solution of bromonitromethane (0.8 mmol, 1 equiv) and the corresponding aldehyde **1** (0.8 mmol, 1 equiv) in THF (10 mL). After stirring the reaction at room temperature for 2 h, it was quenched by addition of aqueous HCl (10 mL, 0.1 M) before the organic material was extracted with dichloromethane. The combined extracts were washed with an aqueous saturated solution of $Na_2S_2O_3$ and then dried over Na_2SO_4. Finally the solvent was removed under reduced pressure affording pure compound **2**. A solution of SmI_2 (2.0 mmol, 2.5 equiv) in THF (20 mL) was then added to a stirred solution of corresponding crude product **2** in THF (5 mL). After stirring the reaction at room temperature for 2 h, it was quenched by addition of aqueous HCl (10 mL, 0.1 M) before the organic material was extracted with dichloromethane. The combined extracts were washed with an aqueous saturated solution of $Na_2S_2O_3$ and then dried over Na_2SO_4, and the solvent was removed under reduced pressure affording crude products **3**.

1-Bromo-1-nitrododec-11-en-2-ol (2f): Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.87 (d, J = 2.8 Hz, 1H), 5.74−

(15) The coupling constant between the olefinic protons of compounds **3** ranging between J = 13.0 and 13.8 Hz were in accordance with the average literature values for J_{trans}: Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. In *Spectrometric Identification of Organic Compounds*; John Wiley and Sons: New York, 1991; Chapter 4, Appendix F, p 221.

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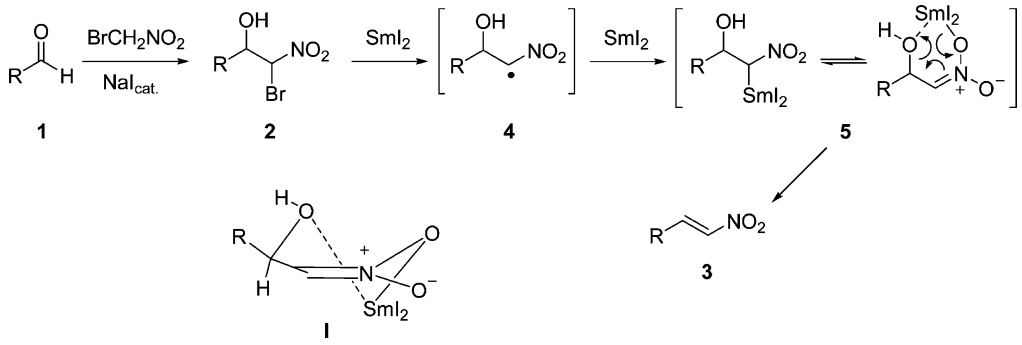
SCHEME 2. Mechanistic Proposal for the Conversion of 2 into 3



5.60 (m, 3H), 4.88−4.77 (m, 4H), 4.08 (m, 2H), 1.94−1.87 (m, 4H), 1.75−1.06 (m, 28H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.0 (2 × CH), 114.0 (2 × CH_2), 86.3 (CH), 81.5 (CH), 73.2 (CH), 72.5 (CH), 33.6 (2 × CH_2), 33.5 (2 × CH_2), 31.8 (2 × CH_2), 29.2 (2 × CH_2), 29.0 (2 × CH_2), 28.9 (2 × CH_2), 28.7 (2 × CH_2), 25.0 (CH_2), 24.7 (CH_2); IR (neat) 3416, 2926, 2855, 1640, 1567, 1465, 1356 cm^{-1}; R_f 0.20 (hexane/EtOAc 10/1); Anal. Calcd for $C_{12}H_{22}BrNO_3$: C, 46.76; H, 7.19; N, 4.54. Found: C, 47.01; H, 6.99; N, 4.45.

(*Z*)-1-Bromo-1-nitroundec-7-en-2-ol (2g): Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.87 (d, J = 3.4 Hz, 1H), 5.61 (d, J = 7.9 Hz, 1H), 5.28−5.13 (m, 4H), 4.16−4.06 (m, 2H), 2.92 (br s, 1H), 1.95−1.66 (m, 8H), 1.44−1.08 (m, 16H), 0.82 (t, J = 7.3 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 131.7 (2 × CH), 128.7 (2 × CH), 86.3 (CH), 81.5 (CH), 73.2 (CH), 72.5 (CH), 33.5 (CH_2), 31.8 (CH_2), 29.3 (2 × CH_2), 28.6 (2 × CH_2), 26.7 (2 × CH_2), 24.9 (CH_2), 24.6 (CH_2), 20.3 (2 × CH_2), 14.2 (2 × CH_3); IR (neat) 3424, 3005, 2930, 2857, 1638, 1567, 1462, 1357 cm^{-1}; R_f 0.20 (hexane/EtOAc 10/1); Anal. Calcd for $C_{11}H_{20}BrNO_3$: C, 44.91; H, 6.85; N, 4.76. Found: C, 44.85; H, 6.93; N, 4.79.

(*E*)-1-Nitronon-1-ene (3a): Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27 (dt, J = 6.4, 13.6 Hz, 1H), 6.97 (d, J = 13.6 Hz, 1H), 2.29−2.22 (m, 2H), 1.53−1.05 (m, 10H), 0.87 (t, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.8 (CH), 139.5 (CH), 31.55 (CH_2), 28.9 (CH_2), 28.8 (CH_2), 28.3 (CH_2), 27.6 (CH_2), 22.5 (CH_2), 13.9 (CH_3); HRMS (70 eV) calc. for [$C_9H_{17}NO_2$−Me] 156.1025, found 156.1010; IR (neat) 2927, 2856, 1558, 1528, 1466, 1357 cm^{-1}; R_f 0.4 (hexane/EtOAc 5/1); Anal. Calcd for $C_9H_{17}NO_2$: C, 63.13; H, 10.01; N, 8.18. Found: C, 63.02; H, 10.25; N, 8.11.

(*E*)-4-Methyl-1-nitropent-1-ene (3b): Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.15−7.05 (m, 1H), 6.83 (dt, J = 1.1, 13.6 Hz, 1H), 2.03−1.98 (m, 2H), 1.75−1.62 (m, 1H), 0.81 (d, J = 6.8 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.7 (CH), 139.9 (CH), 37.0 (CH_2), 27.5 (CH), 22.0 (2 × CH_3); HRMS (70 eV) calc. for $C_6H_{11}NO_2$ 129.0790, found 129.0794; IR (neat) 2929, 1732, 1645, 1556, 1523, 1450, 1350 cm^{-1}; R_f 0.37 (hexane/EtOAc 5/1); Anal. Calcd for $C_6H_{11}NO_2$: C, 55.80; H, 8.58; N, 10.84. Found: C, 55.55; H, 8.67; N, 10.92.

(*E*)-3-Methyl-1-nitropent-1-ene (3c): Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.04 (dd, J = 8.4, 13.5 Hz, 1H), 6.79 (dd, J = 1.1, 13.5 Hz, 1H), 2.25−2.15 (m, 1H), 1.39−1.29 (m, 2H), 0.98 (d, J = 6.7 Hz, 3H), 0.77 (t, J = 7.3 Hz, 3H) ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.3 (CH), 138.5 (CH), 34.9 (CH), 28.4 (CH_2), 18.4 (CH_3), 11.3 (CH_3); HRMS (70 eV) calc. for $C_6H_{11}NO_2$ 129.0790, found 129.0755;IR (neat) 2924, 1718, 1557, 1462, 1380 cm^{-1}; R_f 0.4 (hexane/EtOAc 5/1); Anal. Calcd for $C_6H_{11}NO_2$: C, 55.80; H, 8.58; N, 10.84. Found: C, 55.91; H, 8.50; N, 10.87.

(*E*)-3-Phenyl-1-nitroprop-1-ene (3e): Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48−7.05 (m, H), 6.85 (d, J = 13.5 Hz, 1H), 3.49 (d, J = 7.05 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.0 (CH), 140.2 (CH), 135.6 (C), 128.9 (2 × CH), 128.6 (2 × CH), 127.3 (CH), 34.5 (CH_2); HRMS (70 eV) calc. for $C_9H_9NO_2$ 163.0633, found 163.0639; IR (neat) 3015, 2925, 2833, 1561, 1467, 1355 cm^{-1}; R_f 0.5 (hexane/EtOAc 5/1); Anal. Calcd for $C_9H_9NO_2$: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.55; H, 5.43; N, 8.46.

(*E*)-1-Nitrododeca-1,11-diene (3f): Brown oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.15 (dt, J = 7.3, 13.0 Hz, 1H), 6.85 (d, J = 13.0 Hz, 1H), 5.74−5.60 (m, 1H), 4.85 (d, J = 20.0 Hz, 1H), 4.79 (d, J = 11.3 Hz, 1H), 2.2−2.1 (m, 2H), 1.99−1.87 (m, 2H), 1.51−1.11 (m, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.7 (CH), 139.4 (CH), 138.9 (CH), 114.1 (CH_2), 33.6 (CH_2), 29.1 (CH_2), 29.0 (CH_2), 28.9 (CH_2), 28.8 (CH_2), 28.7 (CH_2), 28.3 (CH_2), 27.6 (CH_2); IR (neat) 2927, 2855, 1641, 1557, 1527, 1465, 1352 cm^{-1}; R_f 0.25 (hexane/EtOAc 10/1); Anal. Calcd for $C_{12}H_{21}NO_2$: C, 68.21; H, 10.02; N, 6.63. Found: C, 68.55; H, 10.22; N, 6.56.

(1*E*,7*Z*)-1-nitroundeca-1,7-diene (3g): Brown oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.14 (dt, J = 7.3, 13.8 Hz, 1H), 6.85 (d, J = 13.8 Hz, 1H), 5.28−5.12 (m, 2H), 2.17−2.10 (m, 2H), 1.94−1.85 (m, 4H), 1.45−1.12 (m, 6H), 0.81 (t, J = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.6 (CH), 139.4 (CH), 131.8 (CH), 128.5 (CH), 29.1 (CH_2), 28.5 (CH_2), 28.3 (CH_2), 27.5 (CH_2), 26.7 (CH_2), 20.4 (CH_2), 14.2 (CH_3); IR (neat) 3004, 2936, 2857, 1649, 1556, 1527, 1462, 1352 cm^{-1}; R_f 0.25 (hexane/EtOAc 10/1); Anal. Calcd or $C_{11}H_{19}NO_2$: C, 66.97; H, 9.71; N,7.10. Found: C, 67.05; H, 9.55; N, 7.15.

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Supporting Information Available: General information, and copies of ^{1}H and ^{13}C NMR spectra for all new compounds **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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