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Chemoselective and Stereospecific Conjugate Alkenyl Group Transfer to α-Nitroolefins using Diisobutylalkenylalanes

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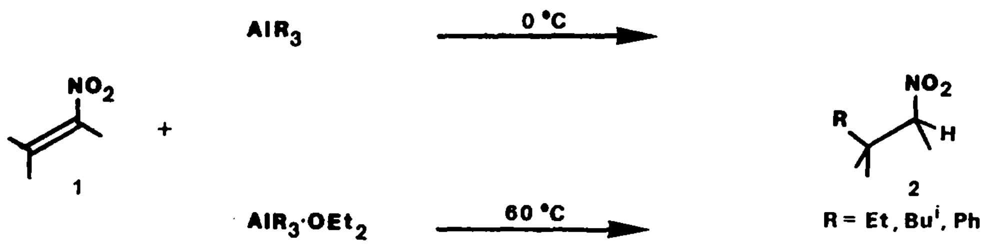
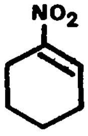
Abstract: Diisobutylalkenylalanes, easily prepared by hydroalumination of terminal, α-branched and internal alkynes, react with α-nitroolefins to give pure E-γ-nitroolefins in almost quantitative yields. The reaction described is a convenient and simple approach to E-β,γ-unsaturated carbonyl compounds.

In a recent study we found that triorganoalanes (AlR_3) and the corresponding etherate complexes ($AlR_3 \cdot OEt_2$) are very effective reagents in conjugate alkyl or aryl group transfer to α-nitroolefins[1] (Scheme 1).

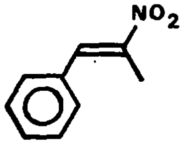
Scheme 1



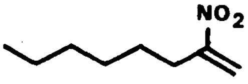
Independently of the nature of the substrates **1**, such a reaction supplied the products **2** that are easily recovered in very good yields. Since compounds **2** are valuable intermediates in organic synthesis,[2] we decided to test whether unsaturated aluminum derivatives could be successfully employed too, in order to extend the scope of the reaction described.



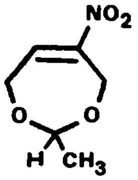
1a



1b



1c

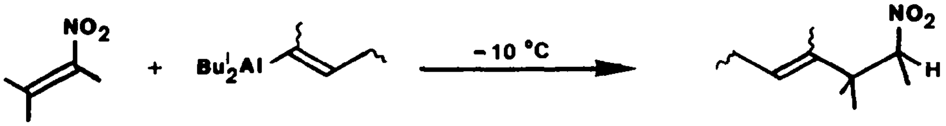


1d

Diisobutylalkenylalanes, easily prepared "in situ" from either terminal or internal alkynes and DIBAL,[3] react with nitroolefins **1a-d** in mild reaction conditions, transferring only the unsaturated group with retention of the double bond configuration (Scheme 2). Vinylalanes have already been employed in reactions with other substrates such as carbon dioxide,[4] carbonyl compounds[5] and α, β-unsaturated ketones,[6] but, in all instances, low yields (30-60%) of products resulting from a trans-hexenyl group transfer were recovered. A competing hydride or isobutyl group transfer,[5] as well as polymerization of the substrates,[6] are factors that might be responsible for the moderate yields obtained.

In the case of **1a-d**, the reaction is very clean and the E-γ-nitroolefins **3a-j** are recovered in almost quantitative yields independently of the nature of the precursors (Table). The lower yield (79%) obtained by starting from **1d** (Table , run 10) is due to the sensitivity of the product **3j** to the acidic work-up used (see experimental). It should be noted that, with the work-up employed, no traces of carbonyl compounds resulting from the solvolytic Nef reaction[7,8] were detected.

Scheme 2



1a-d **3a-j**

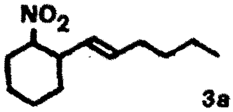
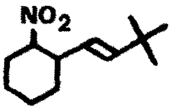
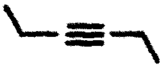
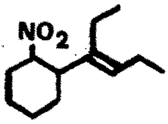
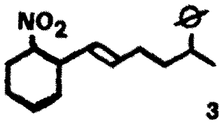
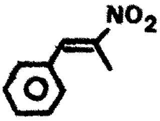
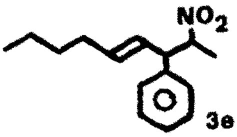
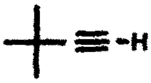
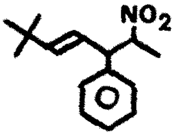
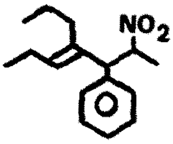
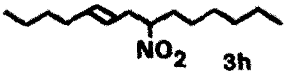
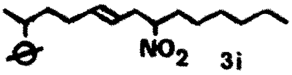
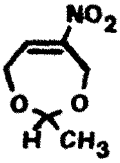
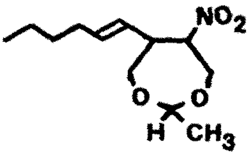
The diastereoisomeric composition of the products recovered was determined by glc and the configuration of the predominant stereoisomer was established on the basis of ^{1}H and ^{13}C NMR spectral data[9]. The cis configuration of **3a-d** main isomers was determined by the characteristic upfield shift of the ^{13}C NMR signals[10] relative to the $\underline{C}$-NO$_2$ ($\sim$87 ppm) with respect to the corresponding one of the trans isomers ($\sim$90 ppm). On the other hand, the ^{1}H NMR signals of C$\underline{H}_3$-CH-NO$_2$ (doublet, $\sim$1.60-1.30 ppm) were used to identify the erythro and threo isomers of **3e-g**: in the erythro isomers a specific upfield shift ($\sim$0.25 ppm) is induced by the gauche phenyl group.[11]

Moreover, the quantitative evaluation of the erythro-threo ratios obtained by ^{1}H NMR, that well agreed with those obtained by glc, allowed the gaschromatographic identification of each diastereoisomer: in all instances the erytrho isomers showed a lower retention time.

Noteworthy products **3a-d** were obtained in an almost pure cis configuration: such a result is consistent with the well-known kinetic control occurring in the hydrolysis of nitronate anions.[12] Indeed, when hydrolysis was performed at a higher temperature (see table 1, run 2), a smaller cis diastereoselectivity was observed.

The alkenylation procedure described herein proves the extraordinary selectivity and effectiveness of alane reagents towards nitroolefins. Moreover, considering that the -NO$_2$ group can be easily converted into a carbonyl by many different protocols,[13] the E-γ-nitroolefins obtained are direct precursors of E-β, γ-unsaturated carbonyl derivatives **4** that are now readily accessible "via" a simple

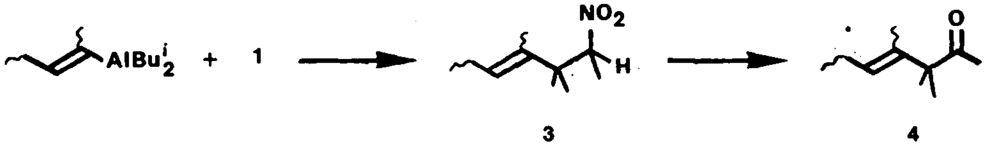
TABLE

Run	Nitroolefin	Alkyne	Product	Recovered yield	a)
1	 1a		 3a	97	96/ 4
2			 3b	95	94/ 6 (73/27)^{b}
3			 3c	92	100
4			 3d	98	100
5	 1b		 3e	89	65/35
6			 3f	96	68/32
7			 3g	91	30/70
8	 1c		 3h	94	==
9			 3i	95	==
10	 1d		 3j	79	c)

a) cis/trans or erythro/threo diastereoisomeric ratio (glc); b) work-up performed at room temperature; c) diastereoisomeric mixture.

two-step procedure (Scheme 3).

Scheme 3



Experimental Section

Material and Instrumentation. All the reactions were performed in dry apparatus under argon. Diisobutylaluminumhydride was employed as 1.0 M hexane solution (Aldrich). 1-nitrocyclohexene (**1a**), 1-phenyl-2-nitropropene (**1b**) were prepared according to described procedures.[14,15] 2-Nitro-1-octene (**1c**) and 5-nitro-2-methyl-1,3-dioxep-5-ene (**1d**) were obtained following the experimental procedure reported for similar compounds.[14] Hexane and benzene were purified by standard methods and redistilled from $LiAlH_4$ before use.

Glc analyses were performed on a Perkin Elmer F-30 instrument (SE-30, 2mx0.29cm columns) equipped with flame ionization detectors and N_2 as the carrier gas.

Ir spectra (ν cm^{-1}) were obtained on a Perkin Elmer FT IR 1750 spectrophotometer using liquid films (20μ).

^1H NMR and ^{13}C NMR spectra were recorded on a Varian XL-100 (100 MHz and 25.2 MHz) spectrometer. All NMR data were obtained in $CDCl_3$ solution and chemical shifts are reported as δ values referred to Me_4Si (TMS) as the internal reference. Values marked with * are referred to the isomer present in smaller quantities.

Mass spectra (m/e, I%) were taken on VG-Analytical 7070 GC-MS instrument.

All the compounds described in this paper gave satisfactory elemental analyses (0.2%).

Analytical TLC were performed on silica gel (Merck, SiO_2 60); all crude products were purified by flash chromatography on silica gel column (Merck, SiO_2 60, 230-400 mesh) using ethyl acetate/light petroleum (10/90) or ethyl ether/light petroleum (5/95).

General Procedure. 13 ml of a 1.0M solution of DIBAL in n-hexane were added to a cooled (0 °C) solution of the alkyne (13 mmol) in the same solvent (15 ml). The resulting colorless solution was heated at 50 °C for the required time (2 hr for 1-alkynes, 6 hr for 3-hexyne). The mixture was then cooled at ca. -15 °C and the nitroolefin (10 mmol in hexane/benzene) was added dropwise. The mixture was stirred at room temperature for 30 min. and then poured into a separatory funnel containing 250 ml of cold (ca. -10 °C) 0.2 N HCl/NaCl solution and extracted into ether. Drying and evaporating the solvents yielded an almost colorless liquid residue (>95% pure, glc) which was purified[16] by flash chromatography.

The pure products recovered showed:

3a: MS 181(3), 165(3), 135(3), 121(8), 111(36), 95(88), 81(56), 67(85), 55(100); IR 1546, 1378, 970; ^1H-NMR 5.60-5.40 (m,2H), 4.55-4.45 (m,1H), 2.95-2.85 (m,1H), 2.50-1.00 (m,14H), 0.95-0.80 (m,3H); ^{13}C-NMR 134.30, 133.30*, 129.15*, 125.88, 90.37*, 87.06, 44.65*, 42.23, 32.29, 31.45, 29.76, 26.28, 23.05, 22.09, 21.46, 13.86;

3b: MS 196(4), 181(20), 165(3), 149(23), 111(45), 95(87), 83(100), 69(80); IR 1546, 973; ^{1}H-NMR 5.50-5.37 (m,2H), 4.63-4.33 (m,1H), 3.03-2.70 (m,1H), 2.20-1.10 (m,8H), 0.96 (s,9H); ^{13}C-NMR 145.19, 144.30*, 123.59*, 120.29, 90.87*, 87.15, 45.11*, 41.99, 32.95, 29.60, 29.46 (3C), 26.10, 22.98, 21.33;

3c: MS 165(2), 123(10), 109(8), 95(17), 81(58), 67(34), 57(100); IR 1550, 863; ^{1}H-NMR 5.11 (t,7Hz,1H), 4.97-4.73 (m,1H), 2.50-1.20 (m,13H), 1.20-0.73 (m,6H); ^{13}C-NMR 138.76, 128.23, 84.64, 44.50, 29.78, 25.35, 24.74, 23.02, 20.95, 20.23, 14.37, 13.59;

3d: MS 270(4), 257(12), 240(33), 239(51), 197(18), 183(25), 131(17), 118(29), 105(100), 91(35); IR 1546, 1378, 971, 762, 702; ^{1}H-NMR 7.35-7.10 (m,5H), 5.57-5.35 (m,2H), 4.50-4.43 (m,1H), 2.95-0.85 (m,17H); ^{13}C-NMR 147.09, 133.96, 128.11, 126.85, 125.83, 125.66, 86.92, 42.14, 39.12, 37.66, 30.60, 29.69, 25.99, 23.00, 22.19, 21.19;

3e: Gc-MS (erythro isomer) 217(4), 200(65), 173(29), 157(18), 143(35), 129(38), 117(98), 105(42), 91(100); (threo isomer) 200(56), 173(23), 157(21), 143(42), 129(41), 117(100), 105(25), 91(98); IR 1551, 969, 761, 701; ^{1}H-NMR 7.40-7.20 (m,5H), 5.75-5.48 (m,2H), 4.90-4.75 (m,1H), 3.85-3.60 (m,1H), 2.10-1.90 (m,2H), 1.59 (d,6.5Hz,1.1H)*, 1.34 (d,6.5Hz,1.9H), 1.30-1.20 (m,4H), 0.90-0.80 (m,3H);

3f: Gc-MS (erythro isomer) 217(4), 200(26), 185(53), 173(25), 157(24), 143(23), 131(72), 117(26), 105(55), 91(100); (threo isomer) 200(40), 185(69), 173(30), 157(34), 143(27), 131(91), 117(31), 105(42), 91(100); IR 1553, 973, 762, 702; ^{1}H-NMR 7.35-7.15 (m,5H), 5.67-5.43 (m,2H), 4.77 (dq,10Hz,6Hz,1H), 3.95-3.40 (m,1H), 1.55 (d,6Hz,0.9H)*, 1.30 (d,6Hz,2.1H), 0.97 (s,2.7H)*, 0.90 (s,6.3H); ^{13}C-NMR 146.33*, 145.15, 139.58*, 138.95, 128.86, 128.60*, 127.78, 127.65*, 127.31, 127.14*, 122.45, 121.11*, 88.06, 87.31*, 54.18, 53.85*, 33.22*, 32.95, 29.37* (3C), 29.29 (3C), 17.69, 17.25*;

3g: Gc-MS (erythro isomer) 200(10), 171(28), 159(10), 143(25), 131(26), 117(40), 105(51), 91(49), 57(100); (threo isomer) 200(16), 171(49), 159(19), 143(41), 131(57), 117(67), 105(42), 91(73), 57(100); IR 1552, 870, 754, 702; ^{1}H-NMR 7.30-7.10 (m,5H), 5.33 (t,7Hz,1H), 5.11 (dq,11Hz,6Hz,1H), 3.71 (d,11Hz,1H), 2.33-1.71 (m,4H), 1.60 (d,6Hz,2.1H), 1.33 (d,6Hz,0.9H)*, 1.20-0.70 (m,6H); ^{13}C-NMR 139.05*, 138.80, 138.42, 138.30*, 129,19, 128.57*, 128.31, 127.73, 127.36*, 127.23, 86.44, 85.21*, 56.48, 55.49*, 23.61*, 23.31, 21.10, 20.96*, 19.35*, 19.16, 14.28, 13.34, 12.99*;

3h: MS 194(19), 123(10), 110(26), 95(20), 81(41), 67(54), 55(100); IR 1551, 970; ^{1}H-NMR 5.50-5.17 (m,2H), 4.52-4.13 (m,1H), 2,60-0.70 (m,24H); ^{13}C-NMR 135.56, 122.70, 88.53, 36.99, 33.18, 32.07, 31.41, 28.61, 25.67, 22.43, 22.05, 13.95, 13.82;

3i: MS 270(1), 145(10), 131(16), 118(32), 105(100), 91(27); IR 1551, 971, 762, 701; ^{1}H-NMR 7.33-7.10 (m,5H), 5.55-5.20 (m,2H), 4.55-4.15 (m,1H), 2.55-0.65 (m,23H); ^{13}C-NMR 146.97, 135.17, 128.14, 126.81, 125.72, 123.02, 88.56, 39.18, 37.66, 36.96, 33.20, 31.42, 30.48, 28.60, 25.68, 22.44, 22.21, 13.96;

3j: MS 196(1), 183(5), 153(4), 139(5), 123(24), 109(7), 95(11), 81(48), 67(100); IR 1553, 1145, 1097, 973; ^{1}H-NMR 5.70-5.17 (m,2H), 5.03-4.90 (m,1H), 4.65-4.45 (m,5H), 3.10-2.65 (m,1H), 2.10-1.95 (m,2H), 1.40-1.20 (m,7H), 0.95-0.83 (m,3H).

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References and Notes

1. A.Pecunioso, R.Menicagli, J.Org.Chem., in the press;
2. a) D.Seebach, E.W.Colvin, F.Lehr, T.Weller, Chimia, **33**,1 (1979); b) G.Rosini, M.Petrini, P.Sorrenti, Synthesis, 515 (1985), and references cited therein; c) N.Ono, A.Kaji, ibidem, 693 (1986);
3. a) J.J.Eisch, W.C.Kaska, J.Am.Chem.Soc., **88**, 2213 (1966); b) G.Wilke, H.Muller, Justus Liebigs Ann. Chem., **629**, 222 (1960);
4. G.Zweifel, R.B.Steele, J.Am.Chem.Soc., **89**, 2724 (1967);
5. H.Newman, Tetrahedron Lett., 4571 (1971);
6. J.Hooz, R.B.Layton, Can.J.Chem., **51**, 2098 (1973);
7. See ref. 2 a);
8. Variable amounts of carbonyl derivatives have already been detected in the mixtures recovered from the reactions of nitroolefins and trialkylalanes (see ref. 1);
9. Compound **3j** was recovered as a mixture of three diastereoisomers the configuration of which was not established;
10. a) D.K.Dalling, D.M.Grant, J.Am.Chem.Soc., **89**, 6612 (1967); b) J.D.Roberts, F.J.Weigert, J.I.Kroschwitz, H.J.Reich, ibidem, **92**, 1338 (1970); c) M.Cristl, H.J.Reich, J.D.Roberts, ibidem, **93**, 3463 (1971);
11. For exemples see: a) M.Mladenova, F.Gaudemar-Bardonne, S.Simova, R.Couffignal, Bull.Chem.Soc.Fr., 479 (1986) and ref. cited therein; b) L.Engman, J.Org.Chem., **52**, 4585 (1987) and ref. cited therein;
12. H.E.Zimmerman, T.E.Nevins, J.Am.Chem.Soc., **79**, 6559 (1957);
13. M.Steliou, M.Poupart, J.Org.Chem., **50**, 4971 (1985), and ref. cited therein;
14. E.J.Corey, H.Estreicher, J.Am.Chem.Soc., **100**, 6294 (1978);
15. C.B.Gairaud, G.R.Lappin, J.Org.Chem., **18**, 1 (1953);
16. Partial decomposition of the products occurred during distillation.