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A CONVENIENT SYNTHESIS OF SUBSTITUTED 1-BROMO-1-NITROALKENES

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ABSTRACT: The reaction of aldehydes with bromonitromethane in the presence of tri-n-butylarsine affording substituted 1-bromo-1-nitroalkenes in good yields is described.

Synthesis of conjugated nitroalkenes is attracting much interest since such compounds are good acceptor in the Michael addition of carbonyl compounds and they provide an umpolung of reactivity of carbonyl compounds, nitro group being synthetically equivalent to carbonyl groups.[1] The synthetic potential of conjugated nitroalkenes also lies in the remarkable versatility of nitro groups in the interconversions of organic functional groups.[1] 1-Bromo-1-nitroalkenes also are useful intermediates in organic synthesis, particularly in the synthesis of heterocyclic compounds.[2] The general method for their preparation was bromination-dehydrobromination of nitro-

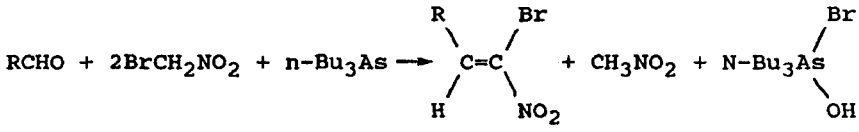
Table 1. Preparation of 1-Bromo-1-nitroalkenes.

Compound	R	Condition		Yield[a]
		Temp./°C	Time/h	(%)
2a	C_6H_5	60	15	60
2b	4-$NO_2C_6H_4$	60	10	64
2c	4-$CH_3C_6H_4$	60	30	64
2d	2-ClC_6H_4	60	20	67
2e	2,4-$Cl_2C_6H_3$	60	12	69
2f	C_6H_5CH=CH	60	20	62

[a] Isolated yields.

alkenes,[3] but a mixture of E- and Z-isomers was obtained.[2] Therefore to develop an effective method for their preparation would be valuable. Recently we found that tri-n-butylarsine could be used as halophilic reagent and applicable to the synthesis of α,β-unsaturated esters[4] and cyano esters.[5] We now wish to report the reaction of aldehydes with bromonitromethane in the presence of tri-n-butylarsine giving substituted 1-bromo-1-nitroalkenes in Z-isomer exclusively and 60-69% yields.

The reaction is shown as follows:



1 **2**

The results are summarized in Table 1.

This one-pot synthesis of the title compounds is quite convenient and the reaction gave Z-isomer exclusively as compared with the NMR data reported in the literature.[6]

EXPERIMENTAL

All melting points were uncorrected. Infrared spectra of solid products were obtained as KCl disks on a Shimadzu IR-440 spectrometer. NMR spectra (chemical shifts in ppm from TMS) were obtained on a Varian EM-360 spectrometer at 60 MHz or XL-200 spectrometer at 200 MHz.

General procedure:

Bromonitromethane (4 mmol) was injected dropwise and slowly into a suspension of aldehyde (2 mmol) and tri-n-butylarsine (2 mmol) under nitrogen.[7] The mixture was stirred and heated for several hours (see Table 1). After the disappearance of the aldehyde, chromatography on silica gel eluting with light petroleum ether (bp 60-90°C)-ethyl acetate (85:15) gave the product **2**.

Z-1-Bromo-1-nitro-2-phenyl ethene (**2a**):

2a was obtained in 60% yield, m.p. 63-64°C [Lit. 67-68°C[3]], IR(KCl): 1600(s), 1570(s), 1530(s) 1310(s) cm^{-1}. ^1H NMR($CDCl_3$/TMS): 7.40-7.60(m,3H); 7.80-8.00(m,2H); 8.60(s,1H) ppm.

Z-1-Bromo-1-nitro-2-(4-nitrophenyl) ethene (**2b**):

2b was obtained in 64% yield, m.p. 133-134°C [Lit.

135°C[8]], IR(KCl): 1600(s), 1510(s), 1350(s), 1310(s) cm^{-1}. ^1H NMR($CDCl_3$/TMS): 7.90(d,2H,J=9.0Hz); 8.32(d,2H,J=9.0Hz); 8.57(s,1H) ppm.

Z-1-Bromo-1-nitro-2-(4-methylphenyl) ethene (**2c**):

2c was obtained in 64% yields, m.p. 65-67°C [Lit. 67-67.5°C[9]], IR(KCl): 1600(s), 1530(s), 1510(s), 1300(s)cm^{-1}. ^1H NMR($CDCl_3$/TMS): 7.08(d,2H,J=8.0Hz); 7.47(d,2H,J=8.0Hz); 8.35(s,1H) ppm.

Z-1-Bromo-1-nitro-2-(2-chlorophenyl) ethene (**2d**):

2d was obtained in 67% yield, m.p. 58-59°C [Lit. 60-61°C[9]], IR(KCl): 1590(s), 1520(s), 1300(s), 1280(s) cm^{-1}. ^1H NMR($CDCl_3$/TMS): 7.05-7.85(m,4H); 8.55(s,1H) ppm.

Z-1-Bromo-1-nitro-2-(2,4-dichlorophenyl) ethene (**2e**):

2e was obtained in 69% yield, m.p. 70-72°C[10], IR(KCl): 1580(s), 1530(s), 1460(s), 1320(s) cm^{-1}. ^1H NMR($CDCl_3$/TMS): 7.10-7.45(m,3H); 8.50(s,1H) ppm.

Z-1-Bromo-1-nitro-4-phenyl-1,3-butadiene (**2f**):

2f was obtained in 62% yield, m.p. 82-84°C[11], IR(KCl): 1580(s), 1520(s), 1300(s) cm^{-1}. ^1H NMR($CDCl_3$/TMS): 6.60-7.50(m,7H); 8.10(d,1H,J=9Hz) ppm.

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