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An Unexpected Reaction between 2-Aryl-1-nitro-1-alkenes and Trialkylgallium Compounds

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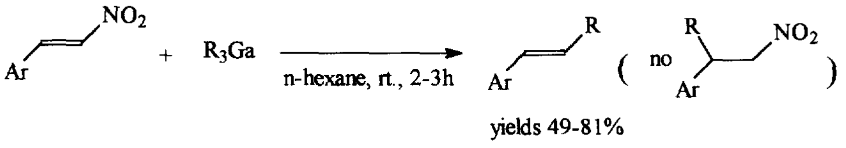
Abstract: A novel reaction between 2-aryl-1-nitro-1-alkenes and trialkylgallium compounds via NO_2 / alkyl substitution is found, and a possible mechanism is propose. Copyright © 1996 Elsevier Science Ltd

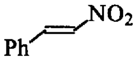
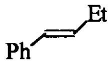
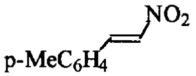
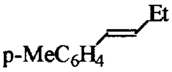
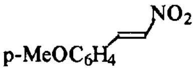
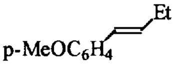
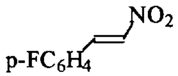
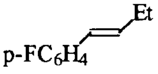
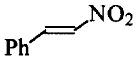
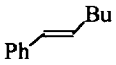
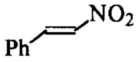
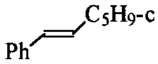
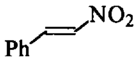
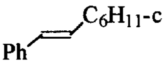
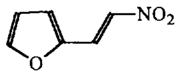
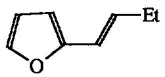
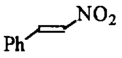
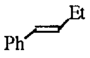
In continuation of our studies on the synthetic application of metallic gallium and its compounds[1], the synthetic utility of the long-forgotten group 13 organometallics: gallium, indium and thallium[2-3], we tried the Michael addition of gallates with nitroolefins[4]. However, to our surprise we found that the reaction of trialkylgallium to ω-nitrostyrene gave a product in which the nitro group was substituted by an alkyl group via radical intermediates.



Scheme 1

Under the optimized conditions shown in **Scheme 1**, 2-aryl, and 2-heteroarylnitroethenes reacted with both primary and secondary trialkylgallium compounds, to afford the substitution products in 49 to 81%(**Table**). All products have (E) configuration according to their 300 MHz ^{1}H NMR spectra, even if a (E / Z) mixed starting material (nitroolefin)[5] was used. The substitution reaction was not successful with triphenylgallium. The solvent used has definite effect on this reaction. In hydrocarbon solvents, substitution products were obtained in moderate to good yields. However, in ethereal solvents(THF or Et_2O) neither substitution product nor Michael addition product could be obtained. This presumably resulted from the corporation of oxygen atom in ethereal solvent to gallium and then weakened the nucleophilic ability of triorganogallium compounds. Under refluxing n-hexane, the substitution reaction was completed in 3-5 minutes.

Table. The substitution reaction resulting between triorganogalliums and nitro olefins[a]

Entry	Substrate	R_3Ga[b]	Product[c]	Yield(%)[d]
1		Et_3Ga		68
2		Et_3Ga		62
3		Et_3Ga		74
4		Et_3Ga		60
5		Bu_3Ga		74
6		$(c\text{-}C_5H_9)_3Ga$		81
7		$(c\text{-}C_6H_{11})_3Ga$		54
8		Et_3Ga		49
9		Et_3Ga		63[e]

a. All of reactions were carried out with 0.5 eq. nitroolefins, 2eq. triorganogallium compound at room temperature for 2-3h in drying n-hexane under Ar. b. All triorganogallium were obtained by means of the reaction of gallium trichloride and Grignard reagents respectively in Et_2O. c. All of products were (E)-olefin, estimated by 300 ^1H NMR spectra. d. Isolated yields based on nitroolefins. e. Under refluxing n-hexane, the reaction carried out during 3-5 minutes.

It is particularly noteworthy that, using 2-nitro-1-phenylpropene or 1-nitro-1-bromo-2-phenylethene as starting material, we did not obtain any substitution product probably due to the reaction is very sensitive to steric hindrance.

Nitro group is usually used as an activator in Michael addition[6] and addition-elimination processes[7]. But we find only a few cases [8] to show a substitution of a nitro group at its original position, where nitro group served as a leaving group. In order to understand the nature of these reactions, the substitution reaction of 2-aryl-1-nitro-1-alkenes and triethylgallium was studied by ESR at room temperature. Their ESR spectrum was determined. When the spin trap 2-methyl-2-nitrosopropane(MNP) was added to the above-mentioned reaction systems. The ESR spectrum of 1:2:3:3:2:1 sextet peak with super-hyperfine was obtained (**Fig. 1**). The structural assignment of the spin adduct $PhCH{=}CH{-}N(O^{\cdot})Bu^{t}$was based on its ESR spectrum and the simulated spectrum. Their ESR spectral parameters were as follow: $a_N = a_{H1} = 1.5$ mT, $a_{H2} = 3.12$ mT, $a_H^p =$ 0.37 mT, $a_H^o = 0.35$ mT, $a_{Hm} = 0.12$ mT. The reaction seems probably to be initiate by an electron transfer(ET) between acceptor 2-aryl-1-nitro-1-alkene and donor trialkylgallium.. The reaction mechanism will be further studied in details.

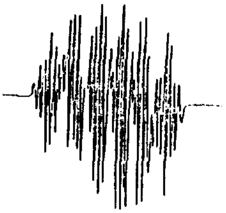


Fig. 1. ESR spectrum of the reaction of 1-nitro-2-phenyl ethene, triethylgallium and ^{t}BuNO in hexane at rt.

In conclusion, we have described a novel radical reaction between trialkylgalliums and α,β-unsaturated nitroolefins via NO_2 / alkyl substitution. This not only gives a new synthetic method of (E)-olefins but also find the first example of reaction of organometallic reagent with α,β-unsaturated nitroolefins. The reaction would broaden the scope of utility of organogallium reagents in organic synthesis.

Typical synthetic procedure: A solution of 75.5 mg (0.5 mmol) of 1-nitro-2-phenyl ethene in 5 ml n-hexane, under argon at room temperature was treated with 2 mmol pure triethylgallium(using a syringe). After 3 h, the mixture was passed a silica gel column (15 × 3 cm, ca. 100 ml ethyl acetate), and the solvent evaporated in vacuum. The residue was chromatographed on a silica plate or column(light petroleum b. p. 6090°C) to give (E)-1-phenyl butene in 68% yield. ^{1}H NMR($CDCl_3$, TMS, 300MHz) δ_H(ppm): 1.09(t, 3H, J 7.35 Hz), 2.23(m, 2H), 6.30(m, 1H), 6.40(d, 1H, J 15.9 Hz), 7.32(m, 5H). EIMS m/z(relative intensity): 133(M+1, 5.71), 132(M^+, 50.28), 131(M-1,, 11.98), 117($M-CH_3$, 100.00), 104($M-CH{=}CH_2$, 3.59).

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