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The Arylation of Nitroalkanes and Nitronate Salts with Aryllead Triacetates

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Nitroalkanes and their nitronate salts undergo α-arylation in good yield when treated with an aryllead triacetate in dimethyl sulfoxide.

We have recently shown that aryllead triacetates are particularly useful C-arylating agents, giving high yields of α-arylated β-dicarbonyl compounds, under particularly mild conditions, with a wide range of β-diketones,[1] β-keto esters,[2] Meldrum's acid derivatives[3] and α-hydroxymethylene ketones.[4] Less acidic carbonyl compounds, such as malonic esters[3] and simple ketones,[4] cannot be α-arylated under the same conditions; however, salts of some of these compounds have been found to react with these reagents to give useful yields of the α-aryl carbonyl compound.[4] Since the ease of reaction appeared to be largely dependent on the acidity of the substrate, we have been examining other classes of pseudo acids with pK$_a$'s within the range of those of the above compounds. Nitroalkanes were obvious candidates, and we now wish to report that their α-arylation can be achieved with aryllead triacetates in preparatively useful yields.

Unlike the β-dicarbonyl compounds, the reaction of nitro compounds did not proceed well in chloroform/pyridine; however, in dimethyl sulfoxide at 40° reaction with the aryllead compound was complete in approximately 30 hours in most cases, and yields of α-nitroalkylaromatic compounds were in the range 60-80% (Table 1). Thus the reaction provides a convenient route to a variety of such compounds. Although the scope of the reaction has not been fully investigated, a number of comments can be made at this stage. Whereas 2-nitropropane (entry 1), nitrocyclohexane (entry 5), nitrocyclopentane (entry 8), and nitroethane (entry 11) reacted with phenyllead triacetate to give the α-phenyl derivative in good yield, nitromethane, under the same conditions, gave a complex mixture from which no pure products could be isolated. Also, nitroethane gave mainly 1-nitro-1-phenylethane when treated with 1 equivalent of phenyllead triacetate, while reaction with 2 equivalents of the same reagent yielded 1,1-diphenyl-1-nitroethane. This is in contrast to the behaviour of β-dicarbonyl compounds with two replaceable hydrogens, which give the diarylated product, even with one equivalent of lead compound.[1-3]

The method would appear to be applicable to the introduction of a wide range of aryl groups, since it proceeded equally well with phenyllead triacetate, *p*-tolyllead triacetate, *p*-methoxyphenyllead triacetate, and biphenyl-4-yllead triacetate (entries 1-10). Unless oxygen was rigorously excluded from the reactions of nitroethane and phenyllead triacetate (entries 11 and 12), small amounts of acetophenone were also produced. This was presumably due to autoxidation of 1-nitro-1-phenylethane, since in an oxygen atmosphere the yield of acetophenone increased to 40%. In the reaction of nitrocyclopentane and *p*-methoxyphenyllead triacetate (entry 10), the initial product of arylation could not be isolated, since a very rapid elimination of nitrous acid occurred to give 1-(*p*-methoxyphenyl)-1-cyclopentene.

Table 1. Reaction of aryllead triacetates with nitroalkanes[a]

Entry	Substrate	$ArPb(OAc)_3$ Ar =	Product (Yield %)[b]
1	2-nitropropane	C_6H_5	α-nitrocumene (75)
2	"	p-MeC_6H_4	p-methyl-α-nitrocumene (75)
3	"	p-MeOC_6H_4	p-methoxy-α-nitrocumene (62)
4	"	p-PhC_6H_4	α-nitro-p-phenylcumene (71)
5	nitrocyclohexane	C_6H_5	1-nitro-1-phenylcyclohexane (76)
6	"	p-MeC_6H_4	1-(p-methylphenyl)-1-nitrocyclohexane (71)
7	"	p-MeOC_6H_4	1-(p-methoxyphenyl)-1-nitrocyclohexane (65)
8	nitrocyclopentane	C_6H_5	1-nitro-1-phenylcyclopentane (70)
9	"	p-MeC_6H_4	1-(p-methylphenyl)-1-nitrocyclopentane (69)
10	"	p-MeOC_6H_4	1-(p-methoxyphenyl)-1-cyclopentene (64)
11	nitroethane	C_6H_5 (1.1 equiv)	1-nitro-1-phenylethane (58-65), acetophenone (0-9) 1,1-diphenyl-1-nitroethane (0-5)
12	nitroethane	C_6H_5 (2.2 equiv)	1-nitro-1-phenylethane (0-5), acetophenone (0-6) 1,1-diphenyl-1-nitroethane (66-74)

[a] The nitro compound (1.5 mmol) and aryllead triacetate (1.65 mmol) were stirred in DMSO (3-5 ml) under nitrogen at 40° for 30 h, except for entry 12 in which the amount of phenyllead triacetate was doubled.

[b] Yields by n.m.r. spectroscopy using dibromomethane as internal standard.

Similar yields of the products listed in Table 1 were obtained by replacing the nitro compound by the corresponding sodium nitronate. These reactions, which were carried out in dry dimethyl sulfoxide, were all complete within 30 minutes.

The phenylation of 2-nitropropane with triphenylbismuth carbonate and pentaphenylbismuth has recently been reported by Barton and coworkers.[5]

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