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Amide N-Arylation with *p*-Tolyllead Triacetate

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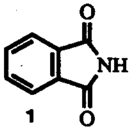
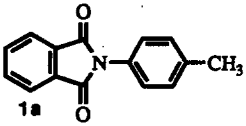
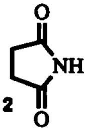
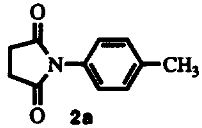
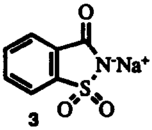
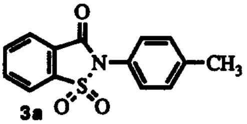
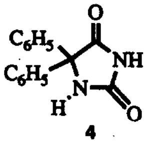
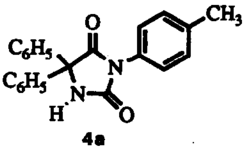
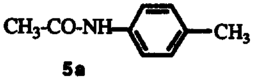
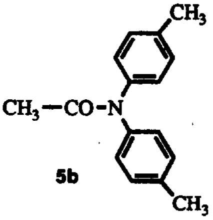
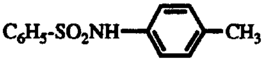
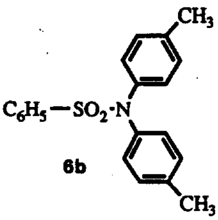
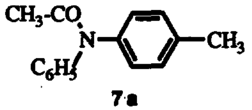
Abstract.- *The N-arylation of several types of amidic nitrogen atoms, including those found in carboxamides, sulfonamides, carboxylic acid imides, mixed carboxylic-sulfonic imides and hydantoin systems was carried out by treatment of their sodium salts with p-tolyllead triacetate in the presence of copper (II) acetate.*

In spite of recent progress[1], the development of general methods for the arylation of organic compounds continues to attract intensive research efforts. The most promising methods are based on the use of organometallic compounds, including arylpalladium species (the Heck arylation), pentavalent bismuth reagents and aryllead triacetates. The latter compounds[2] have received relatively little attention, in spite of their efficiency in the arylation of several types of carbon atoms[3-5] and inorganic nucleophilles such as iodide and azide anions[6]. More recently, copper (II)-catalyzed N-arylation of amines[7] and azoles[8] by aryllead triacetates has also been described.

Certain amides have been arylated by traditional methods. Thus, heating anilides and aryl halides at high temperature in the presence of potassium carbonate and copper (I) iodide affords the corresponding N-aryl derivatives (Goldberg reaction)[9]; N-arylation of other carboxamides[10], as well as imides[11] and sulfonamides[12], is also possible under related conditions. In spite of the existence of a simplified experimental protocol based on the use of phase-transfer catalysis[13], the very high temperatures required, the limited range of aryl iodides that can give the reaction and the moderate yields often obtained make the Goldberg and related reactions unsuitable for many potential applications. Although the use of diaryliodonium reagents[14,15] has served as an alternative in some cases, there is still a clear need for a mild, general method for the N-arylation of amides and related compounds. We wish to report here our findings on the use of aryllead triacetates for this purpose.

As shown in Table 1, amide anions react cleanly with *p*-tolyllead triacetate (**1**)[2b] to give the corresponding N-arylated compounds. A variety of substrates bearing several structural types of amidic

Starting cmpd.	Eqs. of		Time/h	Temp./°C	Solvent	Yield/%[a]	Product(s)
	NaH	1					
 1	1.2	1.2	1	70	Cl_2CH_2-DMF (3:0.5)	82	 1a
 2	-	1.2	7	70	Cl_2CH_2-DMF (2:0.5)	86	 2a
 3	b	1.2	5	60	Cl_2CH_2-DMF (1:1.5)	98	 3a
 4	1.2	1.2	7	80	Cl_2CH_2-DMF (3:1)	75	 4a
CH_3-CO-NH_2 5	1.1	1.1	16	80	Cl_2CH_2	76	 5a
						10	 5b
C_6H_5-SO_2-NH_2 6	1.1	1.1	5	90	Cl_2CH_2-DMF (3:1)	73	 6a
						9	 6b
	2.4	2.4	6	90	Cl_2CH_2-DMF (3:1)	85	6b

Starting cmpd.	Eqs. of		Time/h	Temp./°C	Solvent	Yield/%	Product(s)
	NaH	**1**					
CH_3-CO-NH-C_6H_5 **7**	2	1.2	48	80	Cl_2CH_2	75[c]	 **7a**

Notes: [a]Yields are given for isolated, purified products. [b]Purchased as the sodium salt. [c]91%, based on unrecovered 7

TABLE 1

nitrogen were employed, including carboxamides, sulfonamides, carboxylic acid imides, mixed carboxylic-sulfonic imides and hydantoins. Typical reaction conditions involve the preparation of the amide anion by treating a dichloromethane-dimethylformamide solution of the starting compound with a slight excess of sodium hydride at room temperature, addition of the aryllead triacetate and a catalytic amount of copper (II) acetate, and heating at 60-80 °C for one to several hours. All reactions were clean and reliable, and invariably gave good to excellent yields. In the case of imides, the reaction could also be performed in the absence of sodium hydride, albeit in slightly harsher conditions (entry 2). Excellent monodiarylation/diarylation selectivities were achieved in the case of compounds bearing two N-H bonds upon use of a slight excess of arylating reagent (entries 5 and 6); a large excess led exclusively to diarylation (entry 6). N-substituted carboxamides required longer reaction times and temperatures, as shown by the reaction starting with acetanilide (entry 7).

In conclusion, we have shown that *p*-tolyllead triacetate is an excellent reagent for the mild, high-yielding N-arylation of amidic compounds.

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