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Preliminary Communication

Cobalt-catalyzed methoxycarbonylation of naphthalene mono- and di-sulfonates to naphthalene mono- and di-esters *

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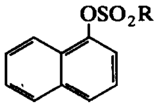
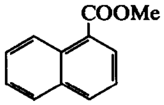
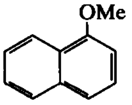
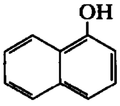
Abstract

The methoxycarbonylation of naphthalene mono- and di-sulfonates under mild reaction conditions catalyzed by cobalt complexes generated *in situ* from either $[Co(CO)_4]^-/Me_2SO_4$ or $[Co(CO)_4]^-/BrCH_2COOEt$ is reported.

Naphthalene dicarboxylic esters are particularly important monomers/comonomers for specialty polyesters [1] but their widespread use has been hampered till now by their relatively high cost. Although synthetic efforts have been devoted mainly towards oxidation of lateral alkyl chains, there are few reports on transition metal-catalyzed carbonylation of dihalonaphthalenes [2]. In particular, the carbonylation of aromatic halides may be carried out with palladium phosphine complexes [3,4] or, more conveniently, with alkylcobalt complexes as catalysts [5]. However, all these methods suffer from the lack of simple regioselective syntheses of the starting dihalides when naphthalene diesters are the target compounds. The possibility of carbonylating the more accessible naphthalene diols or hydroxy naphthoic acid derivatives appears very attractive.

Palladium-catalyzed alkoxycarbonylations of aryl triflates are known [6]; however, these substances are very expensive and of limited stability. In contrast, palladium-based complexes do not catalyze the carbonylation of cheap and readily available sulfonates such as mesylates and tosylates [7]. Because of our previous experience with aryl halides [5], we checked the efficiency of alkylcobalt complexes in the alkoxy carbonylation of aryl sulfonates by comparing several 1-naphthyl sulfonates using alkylcobalt complexes gen-

TABLE 1. Cobalt-catalyzed carbonylation of 1-naphthyl sulfonates. Effect of sulfonate on the yield of 1-methoxycarbonylnaphthalene

					
Entry	R	Conversion %	Yield %	Yield %	Yield %
1	p-$MeOC_6H_4$	44	40	1.5	2.5
2	p-MeC_6H_4	70	70	–	–
3	C_6H_5	67	65	< 1	1
4	p-FC_6H_4	97	67	10	20
5	p-ClC_6H_4	71	64	3	3
6	p-$NO_2C_6H_4$	5	tr.	4	1
7	Me	n.d.	59	6	7
8	CF_3	n.d.	53	tr.	tr.
9 [a]	p-MeC_6H_4	88	87	tr.	tr.

In a typical procedure, to a mixture of 1-naphthyl sulfonate (4.12 mmol), K_2CO_3 (4.8 mmol) and $Na[Co(CO)_4]$ (0.4 mmol) in MeOH (18 ml) at 45°C under CO, were added 0.7 ml of a 1.33 M solution of Me_2SO_4 in MeOH during 90 min.
[a] 0.7 ml of a 0.665 M solution of $BrCH_2COOEt$ in MeOH was added in place of Me_2SO_4 over 90 min.

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* Dedicated to Professor Gian Paolo Chiusoli on the occasion of his 70th birthday and in recognition of his important contributions to organometallic chemistry and its applications in organic synthesis.

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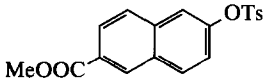
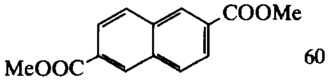
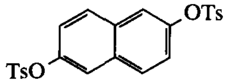
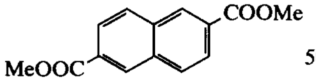
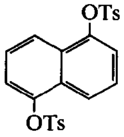
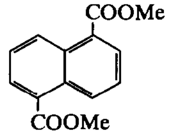
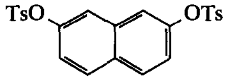
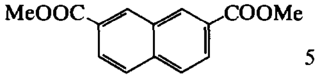
TABLE 2. Cobalt-catalyzed methoxycarbonylation of various naphthalene mono- and di-sulfonates [a]

Entry	Substrate	Conversion %	Carbonylation product Yield % (Selectivity %)
1		62	 60 (96)
2		54	 50 (93)
3		45	 42 (93)
4		55	 52 (94)

[a] Experimental conditions as in entry 9 of Table 1.

erated *in situ* from $[Co(CO)_4]^-$ and a suitable activator (EX).

$$ArOSO_2R + CO + MeOH + B \xrightarrow[45°C,\ 1\ atm.]{[Co(CO)_4]^-/EX} ArCOOMe + RSO_2O^-BH^+ \quad (1)$$

$R = p\text{-}MeOC_6H_4,\ p\text{-}MeC_6H_4,\ C_6H_5,\ p\text{-}FC_6H_4,\ p\text{-}ClC_6H_4,\ Me,\ CF_3$

$B = K_2CO_3$

$EX = Me_2SO_4,\ BrCH_2COOEt$

From Table 1, where several sulfonates of 1-naphthol are compared, it appears that the *p*-toluensulfonyl group (Ts) is best in terms of selectivity (almost complete) and yield of the desired product (70%, entry 2) using Me_2SO_4 as the activator.

Even better results were achieved under the same reaction conditions but with $BrCH_2COOEt$ as activator (Table 1, entry 9). Subsequent experiments were directed to synthesis of diesters from aryl tosylates, with $BrCH_2COOEt$ as cocatalyst (Table 2).

Yields are moderate to good, but the selectivity is always very high. The high reactivity of monosulfonate esters is evident because in no case were they isolated from the reaction mixture when disulfonates were used (entries 2–4, Table 2).

The preparation of naphthyl tosylates and their subsequent methoxycarbonylation can be carried out conveniently on a large scale under very mild reaction conditions.

This easy and efficient homologation of naphthols and naphthalene diols to the corresponding naphthyl esters may provide an alternative route to aromatic esters hitherto difficult to prepare.

References

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7 The palladium-catalyzed alkoxycarbonylation of aryltosylates in the presence of bidentate phosphines gave the corresponding aromatic esters in low yield (< 25%). W. Cabri and S. De Bernardinis, unpublished results.