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CARBONYLATION OF TERTIARY ALKYL HALIDES
SYNTHESIS OF PIVALOYL HALIDES

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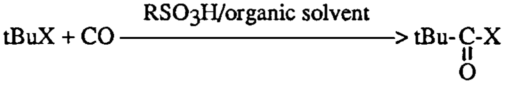
Abstract: The carbonylation of tert-butyl halides in a two-phase system, RSO_3H/CCl_4, under carbon monoxide pressure affords the corresponding pivaloyl halides in good yields and selectivities.

No efficient preparation of tertiary carboxylic acids and derivatives by Reppe reactions has ever been achieved.[1,2] The best way to obtain these compounds by carbonylation reactions lies in the so-called Koch reactions[3] which can now be conducted under low pressure in the presence of Group 11 metals of the periodic table.[4] Moreover, although the synthesis of carboxylic acid derivatives by carbonylation of various structures is well known, the direct preparation of acyl halides has been less studied.[1,5] Actually, only one process has been reported that allows the preparation of pivaloyl chloride by a carbonylation reaction.[6] This reaction involves the conversion of tert-butyl chloride under high carbon monoxide pressure in the presence of aluminium trichloride and/or iron trichloride.

We now wish to report that the synthesis of pivaloyl chloride and bromide from the corresponding tert-butyl halides can be brought about in good yield and selectivity in a two-phase reaction medium consisting of a sulfonic acid, RSO_3H ($R = CF_3$, Cl) and a non-miscible organic solvent (Eq 1).



$$tBuX + CO \xrightarrow{RSO_3H/\text{organic solvent}} tBu\text{-}\underset{\underset{O}{\|}}{C}\text{-}X \qquad (1)$$

X = Cl, Br

At the end of the reaction, the gaseous phase contains only CO and HCl (no traces of isobutene could be detected). ^{1}H NMR, IR and GC analyses of the organic phase show the presence of pivaloyl chloride and unreacted tert-butyl chloride only. Last, the acid phase contains some side-products among which 2,2,5 trimethyl hex-4-ene-3-one and the mixed anhydride $CF_3SO_3(CO)$-tBu were found to be the main ones. One of the major advantages of the above reaction is the easy elimination of side products by simple separation of the phases, affording a very clean organic phase.

The reaction is sensitive to four main parameters: (i) the relative ratio of sulfonic acid to tert-butyl chloride, (ii) the amount of organic solvent, (iii) the reaction temperature and (iv) the carbon monoxide pressure. The main results of the systematic study of these parameters are summarized in Table 1.

Table 1. Carbonylation of tert-butyl chloride^a: influence of the main parameters

Run	CF_3SO_3H (%)	T (°C)	P_{CO} (bar)	CCl_4 (ml)	Conversion (%)^b	tBuCOCl yield (%)^b	Selectivity (%)^b
1	10	0	50	20	21	7	33
2	35	0	50	20	55	18	33
3	50	0	50	20	76	19	25
4	35	0	20	20	51	9	18
5	35	0	50	40	54	22	41
6	50	-25	50	40	84	42	50
7	50	-25	75	40	87	47	54

a) tBuCl: 45 mmol; reaction time = 1 hour; b) determined by GC and ^{1}H NMR analyses.

For example, tert-butyl chloride (45 mmol) was added, at -25°C, in a 100-ml glass-lined 316 STI autoclave containing CF_3SO_3H (22.5 mmol) and CCl_4 (40 ml) under 50 bar of carbon monoxide. After 1 hour stirring (1100 rpm, magnetic) at - 25°C, the autoclave was slowly depressurized. After careful separation of the phases, IR and ^{1}H NMR analysis (90 MHz with 1,2,4-trichlorobenzene as internal standard) of the crude organic phase indicate the presence of 19 mmol pivaloyl chloride (42% yield) and 7.2 mmol unreacted tert-butyl chloride (run 6, Table 1). When the same reaction was conducted with tert-butyl bromide, a 40% yield of pivaloyl bromide was obtained (53% selectivity). Under the same conditions, 1,2-dichloro- 2-methylpropane *selectively* led to 3-chloro-2,2-dimethyl propionyl chloride (24% yield, 53% selectivity).

Further experiments showed that the preparation of pivaloyl chloride can be brought about, with the same yields, by substituting the inexpensive $ClSO_3H$ for CF_3SO_3H (trifluoroacetic acid is inactive). The reaction can also be conducted in other conventional halogenated organic solvents (Table 2). The critical feature of the process is that the organic solvent must be completely non-miscible with the sulfonic acid used in order to prevent decomposition of the pivaloyl halide.

Table 2. Carbonylation of tert-butyl chloride in various solvents[a]

Run	Solvent	Conversion (%)[b]	tBuCOCl yield (%)	Selectivity ^{b}(%)[b]
8	CCl_4	84	42	50
9	CCl_3F	82	32	39
10	CCl_3F[c]	69	50	72
11	Cl_2FCCF_2Cl	68	29	39
12	$Cl_3C\text{-}CCl_2H$	81	39	48

a) CF_3SO_3H: 50%, tBuCl: 45 mmol, solvent: 40 ml, P_{CO} = 50 bar, T = -25°C, reaction time = 1 hour; b) determined by GC and ^1H NMR analyses; c) T = -45°C.

The reaction was also performed on a 450 mmol tert-butyl chloride scale (750 mL Hastelloy autoclave) in order to ensure preparative applicability. For this purpose, a two-phase system, CF_3SO_3H/pentachloroethane was selected (pentachloroethane, Bp = 163°C). After 1 hour stirring (700 rpm, mechanically) at -25°C under 50 bar of carbon monoxide, the phases were carefully separated. Distillation of the organic phase at atmospheric pressure allowed to obtain 18 g (33% yield) of pivaloyl chloride of very high purity (Bp = 105-106°C).

Kinetic investigations were conducted on 450 mmol scale reactions (CF_3SO_3H/CCl_4 biphasic medium) by withdrawing small aliquots from the organic phase at regular intervals. GC analysis with an internal standard of both the formed pivaloyl chloride and the remaining tert-butyl chloride led to the curves reported on Figure 1. It thus appears that the consumption of tBuCl is faster than the formation of pivaloyl chloride.

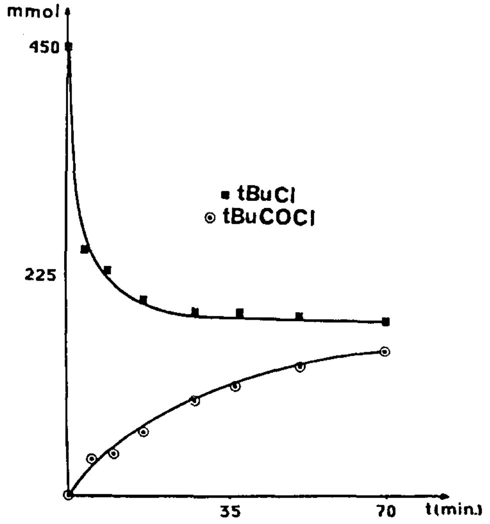
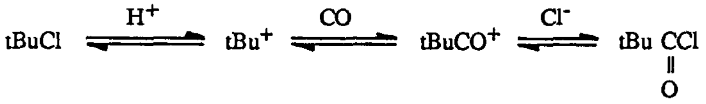


Fig. 1. Evolution of the composition of the organic phase with time

Furthermore, examination of the variation of carbon monoxide pressure with time shows that the major consumption occurs in the early 15 min of the reaction. These results suggest the intervention of the equilibria depicted in eqn 2.[7]



$$\mathrm{tBuCl} \xrightleftharpoons{\mathrm{H^+}} \mathrm{tBu^+} \xrightleftharpoons{\mathrm{CO}} \mathrm{tBuCO^+} \xrightleftharpoons{\mathrm{Cl^-}} \mathrm{tBu\,\underset{\underset{O}{\|}}{C}Cl} \qquad (2)$$

The determining step of the reaction is thus believed to be the formation of tBuCOCl from the chloride ion and the pivaloyl cation. This hypothesis is supported by the observation that improved yields of pivaloyl chloride can be obtained by bringing about the reaction under 50 bar CO/HCl (9:1) pressure. (46% yield, 57% selectivity, all other conditions being those of run 6, Table 1).

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