Preparation of carboxylic esters from alkanes and formates

M. Garni, V. Lazzeri, P. Deschamps, R. Gallo *

URA 1410 CNRS, ENSSPICAM, Faculté des Sciences St-Jérôme, Av. Normandie-Niemen, 13397 Marseille Cedex 20, France

Abstract

Dehydroesterification of iso and cycloalkanes has been carried out with methyl formate and H_2SO_4 at atmospheric pressure slightly above room temperature. The yields range from 32 to 70%. The reaction takes place at tertiary carbon; no fragmentation of the hydrocarbon skeleton is observed. The reaction fails with normal alkanes. The effect of reaction conditions is discussed. A mechanism involving an hydride transfer for the activation of the alkane is given. The reaction is extended to other alkyl formates. © 1997 Elsevier Science B.V.

Keywords: Carboxylic asters; Sulfuric acid; Hydride transfer

1. Introduction

Selective functionalization of alkanes is not an easy task, due to their chemical inertness toward most of the usual reagents, but it is a topic of continuing interest in catalysis [1,2], because saturated hydrocarbons are readily available and inexpensive materials. Moreover esters of tertiary alkyl carboxylic acids find several industrial applications due to their high stability [3]. It is therefore interesting to prepare carboxylic esters directly from alkanes by simple methods.

Using a modification of the Koch reaction [4], carboxylic esters have been prepared by reacting alkenes (or functional derivatives) with carbon monoxide and an alcohol, with a mineral acid (H_2SO_4, H_3PO_4) at high temperature and pressure. If formic acid is used in place of CO (the Koch–Haaf procedure) the reaction can be run at low temperature and atmospheric pressure [5].

More recently carboxylic esters have been prepared by reacting alkenes [6,7] (or halides [8,9]) with alkyl formates. So far however, to the best of our knowledge, this reaction has not been carried out with alkanes (in place of alkenes or halides). It is this new synthesis of carboxylic esters from alkanes and formates that we describe in this paper.

2. Experimental

GC analyses were carried out using a Shimadzu GC 14 gas Chromatograph equipped with a Shimadzu C-RGA integrator, a flame ioniza-

* Corresponding author. Tel.: +33-491-288600; fax: +33-491-027776.

Table 1

Preparation of carboxylic esters from alkanes and methyl formate $RH + HCO_2Me + Me_3CX \xrightarrow{H_2SO_4} RCO_2Me + Me_3CH + HX$

Entry	RH	Me_3CX	RCO_2Me (yield)
1	2,3-dimethylbutane	Me_3CCl	methyl-2,2,3-trimethylbutanoate (60%)
2	1-methylcyclohexane	Me_3CCl	methyl-1-methylcyclohexanoate (68%)
3	decaline	Me_3COMe	methyl-9-decalincarboxylate (32%)
4 [c]	adamantane	Me_3COMe	methyl-1-adamantanoate (70%)
5	1-methylcyclohexane	Me_3COMe	methyl-1-methylcyclohexanoate (58%)
6	hexane	Me_3CCl	no reaction
7	1-methylcyclohexane	Me_3CBr	methyl-1-methylcyclohexanoate (15%)
8 [a]	1-methylcyclohexane	Me_3CCl	methyl-1-methylcyclohexanoate (17%)
9 [b]	adamantane	Me_3COMe	methyl-1-adamantanoate (45%)
10 [d]	adamantane	Me_3COMe	methyl-1-adamantanoate (< 5%)

Reaction temperature: 35°C if not otherwise stated.

[a] Addition of Cu_2O.

[b] Ambient temperature.

[c] 35–40°C.

[d] 50°C.

tion detector and a packed column with Chromosorb WAP 80/100 and 3% OV 101 (200 cm length, 2.2 mm section) operated between 100 and 280°C with a temperature gradient of 15°C/min and 2 bars pressure of dinitrogen.

GC-MS data were recorded using a Delsi Di 700 gas chromatograph, a Ribermag R 100-10 mass spectrometer and a Sidar mass spectral data system.

3. Procedure for the esterification of alkanes

A 250 ml flask, fitted with a mechanical stirrer, dropping funnel, reflux condenser and thermometer was charged with 0.25 mol of the alkane and 80 ml of 98% H_2SO_4. The resultant mixture was stirred slightly above ambient tem-

perature (Table 1). 0.5 mol of the formate and 0.125 mol of the precursor (Me_3CX) were added dropwise and stirring was continued for 2 h. 0.75 mol of alcohol (the same as the alcohol moiety of the formate) was added dropwise and stirring was continued for 1 h at 40°C. The reaction medium was quenched with 200 g of crushed ice. The two phases were separated and the aqueous phase was extracted with 100 ml of hexane. The combined organic phases were neutralized, washed with 50 ml of water and dried over sodium sulfate. The solvent was removed by rotary evaporation. The reaction products were analyzed by GC and GC-MS. The yields reported in Tables 1 and 2 are calculated by GC using authentic samples. With adamantane the procedure is as above, except that adamantane is introduced after solubilization in 50 ml of

Table 2

Preparation of carboxylic esters from alkanes and alkyl formates $RH + HCO_2R' + Me_3CX \xrightarrow{H_2SO_4} RCO_2R' + Me_3CH + HX$

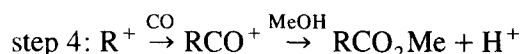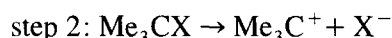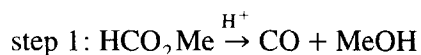| Entry	RH	Me_3CX	HCO_2R'	RCO_2R' (yield)
11	2,3-dimethylbutane	Me_3CCl	HCO_2Et	Et-2,2,3-trimethylbutanoate 40%
12	Methylcyclohexane	Me_3CCl	HCO_2Et	Et-1-methylcyclohexanoate 42%
13	adamantane	Me_3COEt	HCO_2Et	Et-1-adamantanoate 45%
14	methylcyclohexane	Me_3CCl	HCO_2nPr	Pr-1-methylcyclohexanoate 57%
14	methylcyclohexane	Me_3CCl	HCO_2iPr	iPr-1-methylcyclohexanoate 31%

carbon tetrachloride and after quenching in crushed ice the aqueous phase is extracted with 100 ml of carbon tetrachloride.

4. Results and discussion

The dehydroesterification of alkanes with methyl formate gives methyl esters of carboxylic acids according to Eq. (1):

$$RH + HCO_2MeS \xrightarrow[-Me_3CH]{\substack{+Me_3CX \\ +H_2SO_4}} R\text{-}CO_2Me + HX$$

$$(1)$$
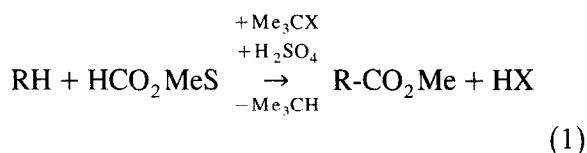
More precisely this reaction of methyl formate and of an alkane (preferably iso or cycloalkane) at atmospheric pressure, in the presence of sulfuric acid and of a tert-butyl cation precursor (tert-butyl chloride or MTBE), gives as a major product the methyl ester of the carboxylic acid obtained from the alkane by carbonylation at a tertiary carbon (Table 1) together with isobutane which comes from the reduction of the promoter (Me_3CX); this reaction involves the following steps:

step 1: $HCO_2Me \xrightarrow{H^+} CO + MeOH$

step 2: $Me_3CX \rightarrow Me_3C^+ + X^-$

step 3: $RH \xrightarrow[-Me_3CH]{+Me_3C^+} R^+$

step 4: $R^+ \xrightarrow{CO} RCO^+ \xrightarrow{MeOH} RCO_2Me + H^+$

Step 1 corresponds to the decomposition of HCO_2Me, catalyzed by H_2SO_4, into CO and MeOH, which has been already described [10]. Step 2 corresponds to the heterolytic decomposition of Me_3CX to give the corresponding cation Me_3C^+. The presence of RCO_2Me (obtained from the alkane) and of Me_3CH are indicative of an activation by hydride transfer [11] of the alkane into a cation (step 3) which further reacts to give the ester through an acylium intermediate (step 4).

The experiments of entries 1–4 in Table 1 were carried out with typical iso-, monocyclo-, dicyclo and tricyclo alkanes (2,3-dimethylbutane, methylcyclohexane, decaline and adamantane) slightly above room temperature; they give besides the carboxylic ester derived from the alkane, small amounts (5–7%) of the corresponding carboxylic acid due to the competition in the acylium being trapped by MeOH or by H_2O.

Tert-butyl chloride and tert-butyl methyl ether (MTBE) were used as promoters because they give a tertiary carbon necessary for an efficient hydride transfer [11] and also because they give, upon reduction, isobutane which is evolved as a gas from the reaction medium, and which can be trapped (at $-80°C$) to follow kinetically the hydride transfer step. Moreover the decomposition of MTBE, in the presence of H_2SO_4, gives MeOH (in addition to Me_3C^+) which can be involved in the esterification step. However this presence of additional methanol resulted in no significant increase in yield (entries 2 and 5). Tert-butyl bromide was less efficient as a promoter (entries 7 and 2). The addition of Cu_2O reduced the yield of the reaction (from 68% to 17% in entries 2 and 8); this was unexpected since Cu_2O (or $FeSO_4$) increases the yield of Koch–Haaf reactions carried out with an excess of carbon monoxide [12,13]. However in the case of the reaction of formate, (where CO is delivered by decomposition of HCO_2Me), CO is trapped by elements of the Ib group, which gives 'more time' to carbocations for oligomerization before carbonylation; this is evidenced by the presence of methyl esters of higher carboxylic acids.

Selectivity is an important feature of the reaction described here. No fragmentation of the alkane framework was observed (to the contrary of carboxylation of alkanes, catalyzed by super acids, which occurs mostly with fragmentation of the hydrocarbon skeleton [14]). No rearrangement was detected either, because in all cases a stable tertiary cation is formed almost exclusively in the alkane, which gives the methyl

ester of a tertiary carboxylic acid (no ester of secondary carboxylic acid was detected by GC). In addition no diester was observed when several tertiary carbons are present in the alkane (2 in dimethylbutane, 2 in decaline and 4 in adamantane). When a linear alkane was tested (entry 6) under the reaction conditions used for iso- and cycloalkanes, no reaction occurred. This is consistent with an order of reactivity in the alkane under acidic conditions: tertiary CH > secondary CH ≫ primary CH [15,16].

A monitoring of reaction conditions indicates (i) that the yield reaches a steady value after 3–5 h, (ii) stirring must be efficient enough (mechanical rather than magnetic) and (iii) that concentrated sulfuric acid ($\geq 95\%$) is needed. The reaction can be run at ambient temperature but an optimum is obtained at 30–35°C (cf. entries 4, 9 and 10); above 40–50° oligomerization becomes important (as in most reactions involving cations) and the yield is strongly reduced.

A self-explanatory reaction mechanism, in agreement with all the results discussed, is described in Scheme 1.

It is comparable to mechanisms previously proposed in functionalizations of alkanes under acidic conditions (like halogenations [17], Friedel–Crafts alkylation [18], hydroxylation [19], the Ritter reaction [20] or the Clay reaction [21] which all involve an activation of the alkane

by hydride transfer followed by reaction of the cation derived from the alkane by the appropriate nucleophile (CO + MeOH) in the reaction reported here).
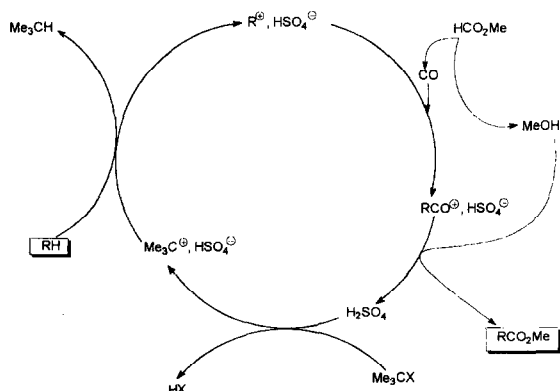
Table 2 shows that other carboxylic esters can be obtained from alkanes and different alkyl formates. For a sake of comparison the reactions were conducted under the same conditions as with HCO_2Me, but since steric effects reduce the rate of esterification [22], the yields are slightly smaller (31–57%). However an appropriate optimization procedure could easily allow to increase the yields.

5. Conclusion

We have shown that alkanes can be directly converted to carboxylic esters under mild conditions. Alkyl formates, which are produced by petroleum industry, can be used as liquid carriers of CO in this reaction. The activation by hydride transfer appears an interesting and promising method for selective functionalization of alkanes.

Scheme 1. Mechanism of dehydro-esterification of alkanes by methyl formate involving a hydride transfer.

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