PYRYLIUM SALTS FROM FRIEDEL-CRAFTS ACYLATION OF ISOPARAFFINS : ISOOCTANE

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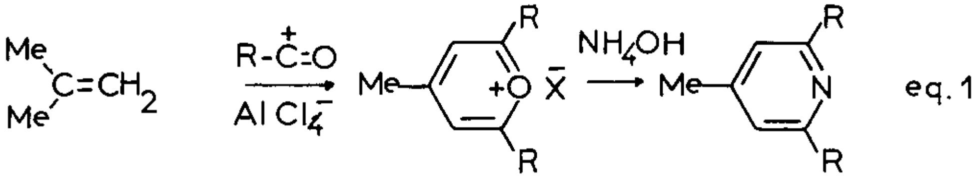
Abstract - It is shown that acylation of isooctane in $AlCl_3/CHCl_3$ medium leads to 2,6-dialkyl-4-methylpyrylium salts, unsaturated ketones and isobutane. Compared to acylation of other isoparaffins, better yields are obtained due to an autocatalytic process.

2,6-Dialkyl-4-methylpyrylium salts have been obtained through various synthetic routes[1]. Among these, the diacylation of isobutene is well documented (eq. 1) : tert-butyl alcohol, tert-butyl chloride or diisobutylene[2] have been used as isobutene precursors. We want to report the first example of acylation of isooctane which shows the formation of pyrylium salts under mild conditions. The 2,6-dialkyl-4-methylpyrylium salts were converted into the corresponding pyridines upon treatment of the crude reaction mixture with NH_4OH (eq. 1).

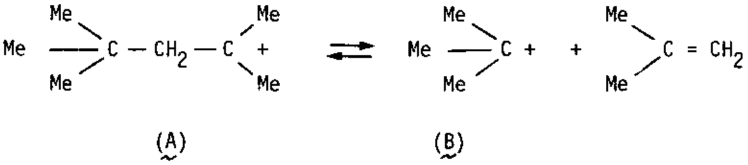


eq. 1

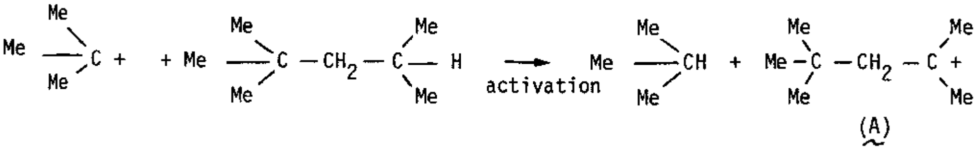
Example : A mixture of 0.2 mole $AlCl_3$, 0.2 mole CH_3COCl and 0.1 mole isooctane in 200 ml of chloroform which was prepared at 0° C, was allowed to react 23 h at 35° C. An abundant evolution of gas is observed. It consists of HCl and pure isobutane (N.M.R. 0.85 ppm D ; 1.65 ppm M ; solvent $CDCl_3$). The crude reaction mixture is then treated under cooling with 350 ml of 34 % NH_4OH. The crude organic phase consists of pure 2,4,6-trimethylpyridine, mesityl oxide and a trace of methyl isobutyl ketone. Acid and base treatments afford 4.3 g of pure trimethylpyridine and 6.1 g of mesityl oxide. The yield of the pure isolated pyridine is 36 % mole/mole of isooctane. The same procedure was followed for the propionyl and isobutyril chlorides. The Friedel-Crafts acetylation of isoparaffins has been studied by Nenitzescu and his group and Hopff since 1931 and, depending on experimental conditions, saturated or unsaturated ketones were obtained[3]. More recently Tabushi et al. reported the formation of mesityl oxide by treatment of isooctane by $AlCl_3$/AcCl in chloroform[4]. We have shown recently that isoparaffins, 2-methylbutane and isomeric isohexanes can undergo di- or tri-acylation under Friedel-Crafts conditions[6]. But it was pointed out that the yields were very low in chloroform. In the reaction of isooctane a high improvment of the yield comes from the autocatalytic process as shown below.

The initiation step of the acylation of isooctane is the generation of carbenium ion A by hydride shift to some protonated or Lewis-acid complexed acylium ion salts, or possibly by acid catalyzed ($HCl/AlCl_3$) hydride abstraction (eq.2)[5]. A is in equilibrium with the trimethyl carbenium ion (B) and isobutene (eq. 3). The trimethyl carbenium ion B can be reduced to isobutane according to equation 4 while isobutene is acylated according to equation 1. Thus, the formation of isobutane and 2,6-dimethyl-4-methylpyrylium salt is simply accounted for in terms of a chain process. It is clear that in the acylation of 2-methylbutane or isomeric hexanes the initiation step is the same but the autocatalytic step 4 is impossible, accounting for the very low yield in chloroform for these reactions.

eq. 2



eq. 3



eq. 4

Table : acylation of isooctane[a] in $AlCl_3/CHCl_3$

Reagents	Products[b]
CH_3COCl	2,4,6-Trimethylpyridine (38 %) ; mesityl oxide (62 %)
EtCOCl	2,6-Diethyl-4-Me-pyridine (18 %) ; nmr ($CDCl_3$) : 1.26 (6H,t) ; 2.26 (3H,s) ; 2.75 (4H,q) ; 6.75 (2H,s) ; ms (80 ev) ; m/e (%) : 149 (46), 148 (100), 133 (14.3), 121 (23.4), 77 (12.8), 39 (15.4). 2-Methyl-2-hexene-4-one (38 %) ; nmr ($CDCl_3$) : 1.5 (3H,t) ; 1.95 (3Hs) ; 2.25 (3H,s) ; 2.5 (2H,q) ; 6.3 (1H,s) ; ms (80 ev) ; m/e (%) : 112 (15.8) ; 83 (100), 55 (54), 39 (10.8).
i PrCOCl	2,6-Diisopropyl-4-Me-pyridine[c] (5 %) ; nmr ($CDCl_3$): 1.25 (6H,d) ; 2.25 (3H,s) ; 2.95 (2H, sept), 6.72 (2H,s) ; ms (80 ev) ; m/e (%) : 177 (26.3), 176 (34.1), 162 (100), 149 (28.4), 147 (11.7), 146 (16.5), 135 (13.7), 91 (11.1), 41 (13), 39 (11.8). 2,5-Dimethyl-2-hexene-4-one (44 %) ; nmr ($CDCl_3$) : 1.15 (6h,d), 1.9 (3H,s), 2.15 (3H,s), 2.5 (1H,sept), 6.1 (1H,s) ; ms (80 ev) ; m/e (%) : 126 (8.7), 83 (100), 55 (100, 55 (39.5), 39 (13.6).

a) The experimental conditions are given in the text.

b) After treatment with NH_4OH.

c) The poor yield results from the steric effect of the isopropyl groups which are involved in several steps of the reaction.

More general and fundamental studies show that the activation of iso-paraffins can be performed in an acylation medium by any source of carbenium ions (alcohols, alkyl halides). Application of this type of activation in the pyrylium synthesis from isoparaffins is underway.

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