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SHORT COMMUNICATIONS

Synthesis and Rearrangement of *p*-Tolyl Chloroacetate

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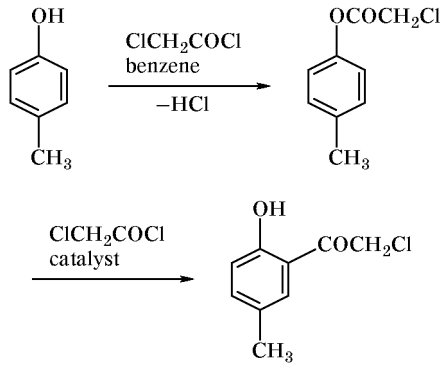
Rearrangements of phenol esters into hydroxy ketones in the presence of $AlCl_3$ have been well documented (see, e.g., [1–4]). However, there are no published data on rearrangements of esters derived from cresol in the presence of small amounts of metal salts. The present communication describes the synthesis and rearrangement of *p*-tolyl chloroacetate in the presence of $FeCl_3$, $FeCl_3 \cdot 6H_2O$, $Fe_2(SO_4)_3$, $ZnCl_2$, and iron acetylacetonate. The reactions followed the scheme given below:



Optimal conditions for the formation of *p*-tolyl chloroacetate were found. The rearrangement of *p*-tolyl chloroacetate was carried out in the temperature ranges from 180 to 200°C and from 200 to 230°C at various ester-to-catalyst ratios. The results are summarized in table. The yields of the rearrangement product in the presence of $FeCl_3$, $FeCl_3 \cdot 6H_2O$, and $Fe_2(SO_4)_3$ at 180–200°C were low; in the presence of $ZnCl_2$ and $Fe(acac)_3$ at the same temperature the yields of 2-hydroxy-5-methylphenacyl chloride were 36 and 60%, respectively. Raising the temperature to 230°C strongly increases the yield of the final product in the rearrangements catalyzed by $FeCl_3$, $FeCl_3 \cdot 6H_2O$, $ZnCl_2$, and $Fe(acac)_3$. The best results were obtained with $FeCl_3$ as catalyst (yield 98%).

***p*-Tolyl chloroacetate.** A mixture of 10.8 g (0.1 mol) of *p*-cresol, 11.3 g (0.1 mol) of chloroacetyl chloride, and 50 ml of dry benzene was refluxed for 17 h (until hydrogen chloride no longer evolved). The mixture was washed with a dilute solution of NaOH, and the aqueous phase was extracted with benzene. The benzene extract was dried over $CaCl_2$, the solvent was distilled off, and *p*-tolyl chloroacetate was distilled under reduced pressure. Yield 16.6 g (90%), bp 145–150°C (20 mm).

Rearrangement of *p*-tolyl chloroacetate. *a.* A mixture of 3.69 g (0.02 mol) of *p*-tolyl chloroacetate and 0.025 g (1.5×10^{-4} mol) of anhydrous $FeCl_3$ was heated for 3 h at 180–200°C and was then distilled under reduced pressure. We isolated 3.39 g (92%) of a product with bp 140–145°C (20 mm) which contained (according to the GLC data) 97.9% of *p*-tolyl chloroacetate and 2.1% of 2-hydroxy-5-methylphenacyl chloride.

b. A mixture of 3.69 g (0.02 mol) of *p*-tolyl chloroacetate and 0.05 g (3×10^{-4} mol) of $FeCl_3$ was heated for 3 h at 200–230°C. Vacuum distillation gave 3.3 g (89%) of a liquid with bp 140–145°C (20 mm) which contained (GLC) 2% of *p*-tolyl chloroacetate and 98% of 2-hydroxy-5-methylphenacyl chloride.

Thin-layer chromatography was performed on Silufol UV-254 plates using carbon tetrachloride–chloroform (1:1) as eluent; chromatograms were developed with iodine vapor. *p*-Tolyl chloroacetate, R_f 0.7; 2-hydroxy-5-methylphenacyl chloride, R_f 0.09. The products were separated by column chromatography on Silicagel L (100/160 μm) or Al_2O_3, and their melting points were determined. *p*-Tolyl chloroacetate, mp 29–30°C (published data [2]: mp 30–32°C); 2-hydroxy-5-methylphenacyl chloride: bp 140–145°C (20 mm), mp 63–65°C (published data [2]: mp 65°C).

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Rearrangement of *p*-tolyl chloroacetate in the presence of $FeCl_3$, $FeCl_3 \cdot 6H_2O$, $Fe_2(SO_4)_3$, $ZnCl_2$, and $Fe(acac)_3$ (reaction time 3 h)

Substrate-to-catalyst molar ratio	Temperature, °C	Yield, %	Fraction of *p*-tolyl chloroacetate,[a] %	Fraction of 2-hydroxy-5-methylphenacyl chloride,[a] %
		$FeCl_3$		
$1:7.7\times10^{-3}$	180–200	91.8	97.9	2.1
$1:1.5\times10^{-2}$	180–200	89.4	93.4	6.6
$1:1.5\times10^{-2}$	200–230	81	2.00	98
		$FeCl_3 \cdot 6H_2O$		
$1:4.6\times10^{-3}$	180–200	89.1	80.8	19.2
$1:9.2\times10^{-3}$	180–200	86.4	75.5	24.5
$1:9.2\times10^{-3}$	200–230	75.6	4.4	95.6
		$Fe_2(SO_4)_3$		
$1:3.1\times10^{-3}$	180–200	83.7	94.8	5.2
$1:6.2\times10^{-3}$	180–200	81.0	91.6	8.4
$1:6.2\times10^{-3}$	200–230	72.2	77.5	22.5
		$ZnCl_2$		
$1:9.1\times10^{-3}$	180–200	78.3	80.00	20.00
$1:2\times10^{-2}$	180–200	72.9	64.20	35.8
$1:2\times10^{-2}$	200–230	64.9	11.2	88.8
		$Fe(acac)_3$		
$1:3.5\times10^{-3}$	180–200	75.6	63.5	36.5
$1:7\times10^{-3}$	180–200	70.2	40.00	60.00
$1:7\times10^{-3}$	200–230	59.4	13.8	86.2

[a] In the crude mixture (GLC data).

The reaction mixtures and products were analyzed by GLC on an LKhM-8MD chromatograph using a 2000×5-mm column packed with 3% of SKTFT-50-Kh on Chromaton U-A; oven temperature 190°C; thermal conductivity detector; hydrogen flow rate 55 ml/min. The fractions of the components were calculated as described in [5].

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