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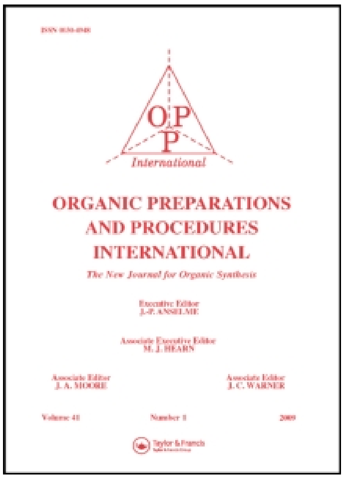

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HYDROLYSIS OF 2-OXOCYCLOPENTYL PHENYL KETIMINE

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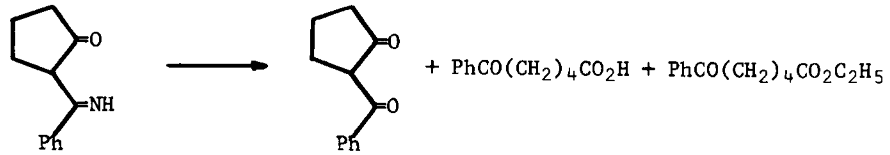

$+ PhCO(CH_2)_4CO_2H + PhCO(CH_2)_4CO_2C_2H_5$

I II III IV

The product from the addition of phenylmagnesium bromide to 2-cyanocyclopentanone was erroneously reported[2] as the diketone II but was subsequently shown[3] to be the imino ketone I.

Different results[4-7] indicate that the hydrolysis of I may give diketone II or the keto acid III in acceptable or unspecified yields. We have found that the experimental conditions are critical in this hydrolysis since we have isolated II, III and keto ester IV in different runs. Shaking I with one equivalent of concentrated HCl at room temperature for 10 minutes gave a 45% yield of II. An 84% yield of II is obtained by refluxing a 1:1 water-ethanol solvent and one equivalent of acid. Shaking I with excess acid for 10 minutes at room temperature gave both II and III in 1:2 ratio respectively. Thus, excess acid must be avoided to maximize the formation of II.

A large excess of aqueous hydrochloric acid and heat gave δ-benzoylvaleric acid in almost 100% yield. High concentrations of ethanol in aqueous ethanol formed ethyl δ-benzoylvalerate directly in the presence of mineral acid. However, this is not the recommended route for the synthesis of the ester.

A summary of 15 hydrolysis runs is presented in the Table.

TABLE

Hydrolysis Conditions and Product Distribution from Ketimine I

Run	Conc. of HCl	Molar Ratio $H^{\oplus}$:imine(I)	Reflux Time	Cosolvent with HCl	% Yield Products[a] II	III[b]	IV
1	2N	1:1	0.5h	35 ml MeOH	60.4	0	-
2	12N	1:1	-[c]	40 ml EtOH[d]	44.5	-	-
3	6N	1:1	0.5h	40 ml EtOH[d]	31.6	0	-
4	12N	11:1	-[c]	none	19.9	36.6	-
5	6N	2:1	0.5h	60 ml EtOH[d]	-	0	41.3
6	12N	11:1	0.5h	60 ml EtOH[d]	-	4.5	42.0
7	6N	2:1	0.5h	30 ml EtOH[d]	-	0	49.0
8	12N	11:1	0.5h	none	-	99.0	-
9	2N	1:1	0.5h	40 ml EtOH/H_2O[e]	83.5	-	-
10	2N	2:1	0.5h	40 ml EtOH/H_2O[e]	62.2	12.5	-
11	2N	1.5:1	0.5h	40 ml EtOH/H_2O[e]	66.2	9.9	-
12	2N	1.25:1	0.5h	40 ml EtOH/H_2O[e]	64.0	8.7	-
13	2N	1:1	0.5h	25 ml EtOH/H_2O[e]	72.4	3.3	-
14	N	1:1	0.5h	40 ml EtOH/H_2O[e]	67.7	0.7	-
15	N	2:1	1.5h	40 ml EtOH/H_2O[e]	49.6	20.2	-

[a] Isolated weight percentages based on using 5g of compound I.
[b] Value of <u>0</u> for acid means no acid isolated by basic extraction of reaction mixture then acidification. [c] Shaken at room temperature in separatory funnel for 10 min. [d] 95% EtOH. [e] 50:50 H_2O/EtOH.

The potential value for the synthesis of various substituted derivatives of I from 2-cyanocycloalkanones[8] and Grignard reagents and the successful hydrolysis of hindered ketimines[8] suggest wide applicability of the sequence leading to compounds of type II. Furthermore, compounds of type III become accessible in high yields.

EXPERIMENTAL[9]

2-Benzoylcyclopentanone (II) was prepared by the procedure of Lamant *et al.*[6] but substituting 2N HCl gave 84% of the diketone (lit. 85%). The product distilled at 180-186°/14mm and after standing in the refrigerator several weeks it solidified, mp. 41-42°, lit. 43°.

5-Benzoylpentanoic Acid (III). A mixture of 5.00 g of I and 24.5 ml of conc. HCl was refluxed for 0.5 hr. then cooled in ice. The solid was filtered and dissolved completely in 10% sodium carbonate and upon acidification gave 5.45 g (~100%) acid, mp. 75.5-76°, lit.[5] mp. 78°.

Ethyl 5-benzoylpentanoate (IV). A mixture of 5.00 g (0.027 mole) of I, 8.9 ml (0.053 mole) of 6N HCl and 30 ml of 95% ethanol was refluxed for 0.5 hr., cooled and extracted with 120 ml of ether. Solid ammonium chloride was removed by filtration. The ethereal extract was washed with 50 ml of water, 20 ml of 10% sodium bicarbonate and 50 ml of water respectively. Acidification of the bicarbonate washing failed to give any acid. After drying ($MgSO_4$) and filtration, the solution was concentrated and the residue was distilled, bp. 189°/10mm or bp. 192.5°/15mm, lit.[7] bp. 180°/8mm. The distillate weighed 3.05 g (49%) and solidified after standing in the refrigerator, mp. 26.5-27°, from 30-60° petroleum ether, lit.[7] mp. 27.5°. The infrared and nmr spectra were identical with those obtained from an authentic sample of IV prepared by esterification of III.

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