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Robinson Annelations With A β-Chloroketone In The Presence Of An Acid

P.A. Zoretic*, B. Branchaud[1] and T. Maestrone[1]
Department of Chemistry
Southeastern Massachusetts University
North Dartmouth, Massachusetts 02747

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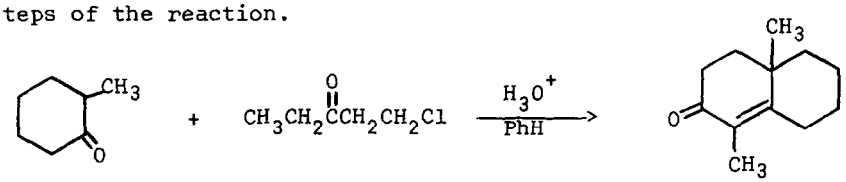
We would like to report that Robinson Annelation reactions can be carried out directly with a β-chloroketone in the presence of an acid. This method presumably utilizes the acid as a catalyst in the in situ generation of the vinylketone[2]; and the acid also serves as a catalyst in both the Michael and Aldol steps of the reaction.



I II III

The synthesis of 1,10-dimethyl-1(9)-octalone-2 (III)[3] was carried out using different molar ratios of (I) and (II) in benzene in the presence of an acid. The experimental results are summarized in Table I. As shown in Table I, the yields of (III) using more than one equivalent of 1-chloro-3-pentanone II range from 46 to 58%.

The experimental procedure employed in the synthesis of (III) is as follows: to a solution of 2-methylcyclohexanone (5.6g, 0.05 mole) and 1-chloro-3-pentanone

Table I

Acid	Molar Ratio I:II	% Yield, III Distilled
H_2SO_4	1:1	32
H_2SO_4	1:1.5	46
p-TsOH	1:1.5	58
H_2SO_4	1:2	52

(9.2g, 0.075 mole) dissolved in benzene (20 ml) was added p-toluenesulfonic acid (300 mg) or concentrated sulfuric acid (0.1 ml) and the resulting mixture was refluxed for 18 hrs. The reaction was cooled to room temperature; poured into

dilute $NaHCO_3$ solution and extracted with Et_2O. The Et_2O extracts were washed with water; dried over anhydrous $MgSO_4$; filtered and concentrated on a rotary evaporatory. Distillation of the residue gave 5.2g (58%) of 1,10-dimethyl-1(9)-octalone-2 (III), b.p. 89° at 0.2 mm. Individual runs are summarized in Table I

Acknowledgement

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References

1. Undergraduate research participants.
2. For examples of acid-catalyzed Robinson Annelations with vinylketones see: a) C.H. Heathcock and J.E. Ellis, Chem. Commun., 1474, 1971 and b) C.H. Heathcock, J.E. Ellis, J.E. McMurry and A. Coppolino, Tet. Let., 4995, 1971.
3. 1,10-Dimethyl-1(9)-octalone-2(III) was shown to be identical (ir, nmr, tlc, vpc) with an authentic sample prepared by an alternate route from the methylation of 10-methyl-1(9)-octalone-2 in the presence of potassium t-butoxide[4] in t-butyl alcohol.
4. N.W. Atwater, J. Am. Chem. Soc., 82, 2847, 1960.