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ACID-CATALYZED ROBINSON ANNELATIONS

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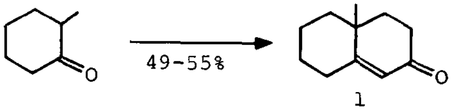
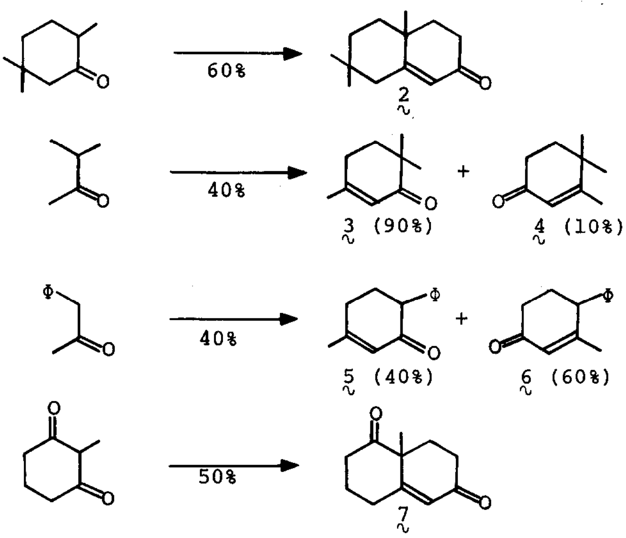
We wish to point out a particularly convenient method for the synthesis of cyclohexenones by the Robinson Annelation. The method involves the use of acid, rather than base, as the catalyst for both the Michael and aldol stages of the sequence. A typical procedure follows:

Synthesis of 4a-Methyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3H)-one ($\underset{\sim}{1}$): A mixture of 45 g (0.4 moles) of 2-methylcyclohexenone, 36 g (0.5 moles) methyl vinyl ketone and 0.3 ml conc. sulfuric acid in 100 ml is refluxed for 16 hours. The solution is cooled and diluted with 100 ml hexane. After washing with 100 ml of 5% aqueous potassium hydroxide, the solution is dried, then concentrated on a rotary evaporator. Distillation of the residue affords 32.78 g of octalone $\underset{\sim}{1}$ (49%), boiling at 112-115° (5 Torr). In a number of similar runs, the yield ranged from 49% to 55%. In one run, a yield of 75% was obtained.

Cyclohexenones which have been prepared by essentially the above procedure, along with the yields realized, are given below.



$\underset{\sim}{1}$



Yields obtained are usually comparable to or better than those obtained in the normal base-catalyzed variation of the Robinson Annelation.[1] The process fails with ketones which do not enolize readily (2-butanone, 4-methyl-2-pentanone, cyclopentanone) and is obviously not applicable to the synthesis of cyclohexenones which also contain acid-sensitive functional groups. Even though the method is of limited utility, it complements the base-catalyzed method and is superior in many cases.

Reference

1. J. A. Marshall and W. I. Fanta, *J. Org. Chem.*, **29**, 2501 (1964) and references therein.