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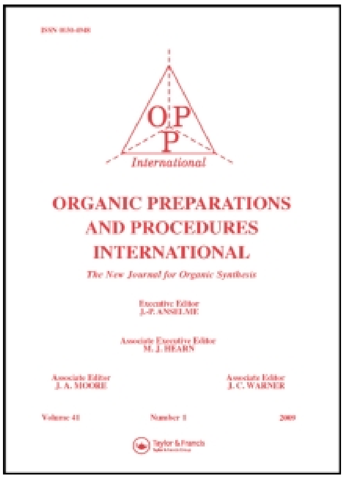

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SYNTHESIS OF γ, δ-UNSATURATED KETONES

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SYNTHESIS OF γ,δ-UNSATURATED KETONES

Submitted by
(10/27/86)

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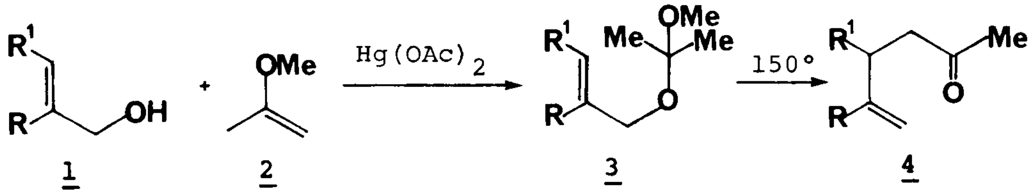
In connection with ongoing synthetic studies, we required a variety of γ,δ-unsaturated methyl ketones. Compounds of this type have been prepared by the Claisen rearrangement of allyl vinyl ethers,[1] via alkylation of ketimines with allylic halides,[2] and by the conjugate addition of vinyl cuprates to enones.[3] We now report a convenient, one-step synthesis of γ,δ-unsaturated ketones from allylic alcohols via the Claisen rearrangement.



1a: 2-propen-1-ol; 1b: 2-methyl-2-propen-1-ol; 1c: 2-buten-1-ol; 1d: 3-methyl-2-buten-1-ol; 1e: 2-methyl-3-buten-2-ol; 1f: 1-cyclohexen-1-methanol; 1g: 1-penten-3-ol.

Heating a solution of alcohols 1 and mercuric acetate in 2-methoxypropene (2) at 150° gives the ketones 4 in uniformly good yields with primary and secondary alcohols and in fair yield with the one tertiary alcohol tried. This procedure is a combination of the mercury catalyzed addition of alcohols to vinyl ethers[7] and of the Claisen rearrangement[8] of allyl isopropenyl ethers.[9]

When the mixture of alcohol 1f and mercuric acetate in 2-methoxypropene was heated to 110° and then distilled an 81% yield of the mixed acetone ketal 3f was obtained. This indicates that the initial step in this reaction is addition of the alcohol to 2-methoxypropene and not exchange. Thermal elimination of methanol from 3f and rearrangement to 4f occur when the compound is heated to 150°.

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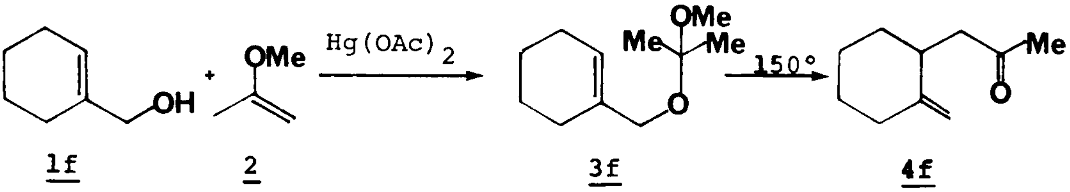

TABLE 1. γ,δ-UNSATURATED KETONES

Alcohol	Ketone	Yield (%)	bp. (°C)	lit. bp. (°C)
1a	5-hexen-2-one (4a)	81	60°/34	128°/745[1]
1b	5-methyl-5-hexen-2-one (4b)	88	65°/35	50°/20[2]
1c	4-methyl-5-hexen-2-one (4c)	75	70°/30	62°/50[3]
1d	4,4-dimethyl-5-hexen-2-one (4d)	82	70°/36	58-60°/22[3]
1e	6-methyl-5-hepten-2-one (4e)	53	76°/36	58°/12[4]
1f	1-(2-methylenecyclohexyl)-2-propanone (4f)	83	95°/15	90-95°/1.3[5]
1g	E-5-octen-2-one* (4g)	89	68°/41	60-65°/12[6]

*97:3 E:Z

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EXPERIMENTAL SECTION

1-(2-Methylenecyclohexyl)-2-propanone (1f) Typical Procedure.- 1-Cyclohexene-1-methanol[10] (1f, 1.5 g, 13.4 mmoles), 2-methoxypropene (4.5 g, 62 mmoles, Aldrich), and mercuric acetate (0.1 g, freshly recrystallized) were stirred together at room temperature for 0.5 hour. The solution was placed in a 75 ml stainless steel cylinder (Whitey #HDF2-75) fitted with an inlet valve (Whitey 43M4-S4), a relief valve (Napro 4CPA2-350), and a pressure gauge. A few milligrams of hydroquinone were added and the apparatus purged with nitrogen. It was pressurized to 150 psi with nitrogen and then placed in an oil bath which covered the cylinder up to its neck. The temperature of the oil bath was slowly increased to 150° and was maintained at this temperature overnight. The cooled reaction mixture was evaporated at reduced pressure and the residue distilled (Kugelrohr) at 95°/15 mm to give 1.69 g (83%) of a colorless oil, lit.[5] bp. 90-95°C/1.3 mm. IR (neat): 1715, 1645, 890 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 4.67 and 4.46 (bs, 1 H, vinyl), 2.15 (s, 3H, CH$_3$). MS: m/e 152 (5%, M$^+$), 109 (100, M-CH$_3$CO), 94 (56, M-CH$_3$COHCH$_2$).

2-(1-Cyclohexene-1-methoxy)-2-methoxypropane (3f).- A mixture of 1f (1.0 g, 8.9 mmoles), 2-methoxypropene (4 g), mercuric acetate (0.1 g), and hydroquinone was heated to 110°. The reaction mixture was evaporated at reduced pressure and then distilled to yield 1.33 g (81%) of a colorless oil, bp. 120°/30 mm. ^{1}H NMR ($CDCl_3$): δ 5.70 (b,1H,vinyl); 3.78 (s, 2H, CH_2O); 3.23 (s, 3H, CH_3O); 1.33 (s, 6H, CH_3). MS: m/e 152 (3.7%, M-CH_3OH); 95 (32, $C_7H_{11}^+$); 73 (100, M-$C(CH_3)_2$-OCH_3).

Anal. Calcd. for $C_{11}H_{20}O_2$: C,71.70; H, 10.94

Found: C,71.89; H, 10.88

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