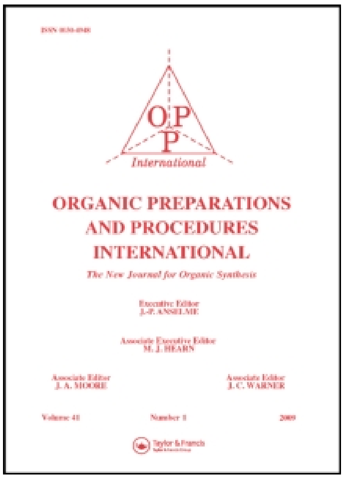

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SYNTHESIS OF γ-UNSATURATED METHYLKETONES

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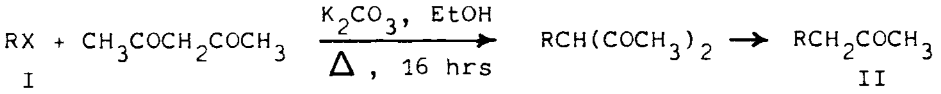
Previous publications[1,2] had described the preparation of ketones II (R = n-C_4H_9, $CH_2=C(CH_3)CH_2$, $ArCH_2$) from the reaction of the corresponding halide I (X = Cl or Br) with acetylacetone and ethanolic potassium carbonate. We have



$$\underset{\text{I}}{RX} + CH_3COCH_2COCH_3 \xrightarrow[\Delta\text{, 16 hrs}]{K_2CO_3\text{, EtOH}} RCH(COCH_3)_2 \longrightarrow \underset{\text{II}}{RCH_2COCH_3}$$

extented this reaction to several α-unsaturated and α,γ-unsaturated halides and we obtained, in a one-pot procedure, the γ-ethylenic ketones IIa-f, the γ-acetylenic ketones IIg-i, the γ-allenic ketone IIj, the γ,ε-diethylenic ketone IIk and the γ-ethylenic-ε-acetylenic ketones IIl,m. The same reaction works well with an α-haloester, leading to the γ-ketoesters IIn,o. Yields are generally fair (40-60 %), alkyl chlorides giving better yields than alkyl bromides (see footnotes b and c of Table 1). With the primary α-ethylenic, α-acetylenic or α,γ-unsaturated halides, the normal alkylation product was obtained ; in no case have we been able to detect any ketone corresponding to an allylic or a propargylic rearrangement. No ketone was obtained when we tried the same reaction with halides Ip-r.

This one-step procedure is a very convenient method to prepare ketones RCH_2COCH_3 where R is an α-unsaturated or an α,γ-unsaturated group ; ketones IIa[3,4], IIb[3,4], IIc[3], IIf[4,5], IIg[6,7,8], IIh[9], IIj[10,11], IIk[12] and IIl[12] have

Table 1. γ-Unsaturated Methylketones[a]

RX (I)	Yield(%) of II	bp./torr	n_D^{20}
a) $CH_2=CHCH_2Cl$[b]	42	40-41°/14	1.4203
b) $CH_3CH=CHCH_2Cl$ (trans)	60	61-62°/25	1.4319
c) $C_6H_5CH=CHCH_2Cl$ (trans)	60	156-157°/15	1.5480
d) $(CH_3)_2C=C(CH_3)CH_2Cl$	40	83-84°/18	1.4500
e) $ClCH=CHCH_2Cl$ (cis + trans)	55	74-78°/14	
f) $CH_2=CClCH_2Cl$	40	63°/13	1.4532
g) $HC\equiv CCH_2Cl$[c]	60	71-72°/48	1.4369
h) $CH_3C\equiv CCH_2Cl$	60	66-67°/15	1.4490
i) $HOCH_2C\equiv CCH_2Cl$	25	93-95°/0.05	1.4809
j) $CH_2=C=CHCH_2Br$	60	61-62°/12	1.4625
k) $CH_2=CHCH=CHCH_2Cl$ (trans)	58	76-77°/12	1.4760
l) $HC\equiv CCH=CHCH_2Br$ (trans)	60	86-87°/12	1.4741
m) $HC\equiv CC(CH_3)=CHCH_2Br$ (trans)	62	95-96°/12	1.4801
n) $C_2H_5OCOCH_2Br$	60	91°/13	1.4225
o) $C_2H_5OCOCHBrCH_3$	45	96-97°/15	1.4239
p) $HC\equiv CCH(Cl)CH_3$	-	-	-
q) $ClCH_2CH=CHCH_2Cl$ (trans)	-	-	-
r) $(C_2H_5O)_2CHCH_2I$	-	-	-

a. Satisfactory elemental analysis, purity by glc and spectral data (IR and NMR ^1H) were obtained for all the products (see Table 2).

b. With $CH_2=CHCH_2Br$, the yield was 35 %.

c. With $HC\equiv CCH_2Br$, the yield was 45 %.

Table 2. Elemental Analysis and Partial Spectral Data

	Elemental Analysis % Calculated (% Found)				
II	C	H	Cl	NMR $^1H^a$	IR^b
IIa	73.43	10.27		2.10(s,3H),2.30(m, 4H),	1715,1640,
	(73.51)	(10.25)		4.95(m, 3H)	990, 910
IIb	74.95	10.79		1.55(d,3H),2.05(s,3H),	1720,1670,
	(74.90)	(10.73)		2.30(m,4H),5.40(m,2H)	970
IIc	82.72	8.10		2.00(s,3H),2.40(m,4H),	1715,1650,
	(82.63)	(8.17)		6.20(m,2H),7.15(s,5H)	1600, 965
IId	77.09	11.53		1.60(m,9H),2.05(s,3H),	1715,1670
	(77.00)	(11.58)		2.35(m,4H)	
IIe	54.35	6.84	26.74	2.05(s,3H),2.40(m,4H),	1715,1635,
	(54.42)	(6.90)	(26.68)	5.85(m,2H)	935
IIf	54.35	6.84	26.74	2.10(s,3H),2.60(m,4H),	1720,1640,
	(54.32)	(6.88)	(26.80)	5.25(m,2H)	885
IIg	74.97	8.38		1.90(t,1H),2.10(s,3H),	3280,2120,
	(75.05)	(8.43)		2.50(m,4H)	1715, 635
IIh	76.32	9.15		1.70(t,3H),2.05(s,3H),	2250,1720
	(76.41)	(9.20)		2.40(m,4H)	
IIi	66.64	7.99		2.10(s,3H),2.55(m,4H),	3420,2250,
	(66.59)	(8.04)		3.15(s,1H),4.25(m,2H)	1715
IIj	76.32	9.15		2.05(s,3H),2.35(m,4H),	1960,1720,
	(76.39)	(9.11)		4.65(m,2H),5.05(m,1H)	1060, 850
IIk	77.37	9.74		2.05(s,3H),2.30(m,4H),	1720,1650,
	(77.43)	(9.70)		5.60(m,5H)	1600,1000,
					950, 900
IIl	78.65	8.25		2.10(s,3H),2.40(m,4H),	3280,2100,
	(78.59)	(8.21)		2.65(d,1H),5.80(m,	1715,1650,
				J=16Hz, 2H)	960, 635
IIm	79.36	8.88		1.80(d,3H),2.10(s,3H),	3280,2100,
	(79.45)	(8.83)		2.40(m,4H),2.60(s,1H),	1715,1650,
				5.80(m,1H)	830, 635
IIn	58.31	8.39		1.25(t,3H),2.10(s,3H),	1730,broad
	(58.38)	(8.32)		2.55(m,4H),4.10(q,2H)	1150,broad
IIo	60.74	8.91		1.10(d,3H),1.25(t,3H),	1730 broad
	(60.80)	(8.96)		2.10(s,3H),2.70(m,3H),	1150 broad
				4.10(q,2H)	

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a. Recorded on a Perkin-Elmer R 24 A spectrometer, expressed in δ relative to TMS.

b. Recorded on a Beckman IR 4240 spectrometer, expressed in cm^{-1}.

already been prepared, but by multi-steps methods.

EXPERIMENTAL

Halides Ia, Ib, Ie, If, Ig, In, Io et Iq are commercial products ; they were purified by distillation before use. Halides Ic[13,14], Ih[15], Il[16,17] and Im[16,17] were obtained from the corresponding primary alcohols. Halide Id was prepared[18] from 2,3-dimethyl-1-buten-3-ol, halide Ik[12,19] from 1,4-pentadien-3-ol and halide Ip[15] from 1-butyn-3-ol. Halide Ii was prepared[20] from 2-butyn-1,4-diol. Halide Ij was obtained[21,22] from halide Ii. Halide Ir was prepared[23] by halogen exchange from corresponding bromide (commercial product).

Synthesis of ketones II. General procedure. - A mixture of 0.275 mole (27.5 g) of acetylacetone, 0.25 mole of alkyl halide, 0.28 mole (39 g) of anhydrous potassium carbonate and 150 ml of commercial anhydrous ethanol was refluxed (70°-75°) for 18-24 hrs in a 500 ml round-bottomed flask equipped with a condenser. The ethanol and the ethyl acetate were removed by distillation and the residue was shaken with ice water (300 ml) to dissolve the salts. The mixture was extracted with ether (4 x 50 ml). The combined ethereal extracts were washed with a saturated sodium chloride solution (2 x 50 ml), dried over anhydrous potassium carbonate and filtered. The solvent was removed and the residue was distilled under reduced pressure.

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REFERENCES AND NOTES

1. S. Boatman, T. M. Harris and C. R. Hauser, J. Org. Chem., 30, 3321 (1965).
2. S. Boatman and C. R. Hauser, Organic Syntheses, Coll. Vol. V, 767 (1973).
3. W. Kimmel and A. C. Cope, J. Am. Chem. Soc., 65, 1992 (1943).

4. Th. Cuvigny, M. Larcheveque and H. Normant, Ann., 719 (1975).
5. J. F. Tinker and T. E. Whatmough, J. Am. Chem. Soc., 74, 5235 (1952).
6. M. Gaudemar, Ann. Chim. France, [13], 1, 161 (1956).
7. J. Colonge and R. Gelin, Bull. Soc. Chim. France, 208 (1954).
8. G. Eglinton and M. C. Whiting, J. Chem. Soc., 3052 (1953).
9. S. R. Kurowsky and H. Morrison, J. Am. Chem. Soc., 94, 507 (1972).
10. J. W. Wilson and S. A. Sherrod, Chem. Comm., 143 (1968).
11. J. K. Crandall and C. F. Mayer, J. Org. Chem., 34, 2814 (1968).
12. L. Crombie, S. H. Harper and D. Thompson, J. Chem. Soc., 2906 (1951).
13. R. H. Dewolfe and W. G. Young, Chem. Rev., 56, 753-901 (1956).
14. H. Gilman and S. A. Harris, Rec. Trav. Chim. Pays-Bas, 50, 1052 (1931).
15. L. Brandsma, Preparative Acetylenic Chemistry, p. 157, Elsevier, Amsterdam, 1971.
16. H. B. Henbest, E. R. H. Jones and I. M. S. Walls, J. Chem. Soc., 3646 (1950).
17. G. Courtois and L. Miginiac, J. Organometal. Chem., 117, 201 (1976).
18. Reaction of methyllithium with methyl methylacrylate at -78°, gave 2,3-dimethyl-1-buten-3-ol in 81 % yield (bp. 52°/17 torr). The reaction of this alcohol with 12N HCl gave (yield : 65 %) a 60/40 mixture (bp. 68-73°/95 torr) of chloride Id together with the tertiary isomeric chloride. On fractional distillation, a sample of pure chloride Id (bp. 72°/95 torr) was obtained.
19. Ph. Miginiac, Ann. Chim. France, [13], 7, 445 (1962).
20. G. Dupont, R. Dulou and G. Lefebvre, Bull. Soc. Chim. France, 816 (1954).
21. W. J. Bailey and C. R. Pfeiffer, J. Org. Chem., 20, 1337 (1955).

22. W. H. Carothers and G. J. Berchet, J. Am. Chem. Soc., 55, 2807 (1933).
23. T.A. Narvid and A. I. Meyers, J. Org. Chem., 39, 2572 (1974).

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