A New, Convenient Synthesis of Cyclopropyl Ketones

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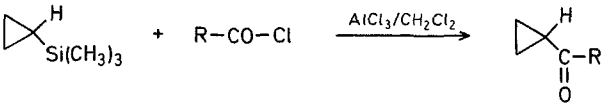
Various synthetic routes to cyclopropyl ketones have been reported[1,2,3]. In all cases a carbonyl compound is used as starting material and the cyclopropyl ring is formed in the last step. We now propose a simple and general synthesis of cyclopropyl ketones **3** starting from acyl chlorides **2** and cyclopropyltrimethylsilane (**1**) according to the scheme.



1 **2** **3**

Table. Preparation of Cyclopropyl Ketones **3** from Acyl Chlorides **2** and Cyclopropyltrimethylsilane (**1**)

Compound	R	Yield (%)	b.p./torr	Molecular formula[a]	I.R. Spectra (film) ν cm^{-1} (C=O)	(C=C)	^{1}H-N.M.R. Spectra (CCl_4) δ ppm AA'BB' shift	X shift	Other shifts
3a	CH_3	60	115°/760	C_5H_8O (84.1)	1715	—	0.75	1.80	2.05 (s, CH_3)
3b	C_2H_5	55	128°/760	$C_6H_{10}O$ (98.1)	1710		0.80	1.80	1.00 (t, 3H), 2.4 (q, 2H)
3c	i-C_3H_7	60	55°/25	$C_7H_{12}O$ (112.2)	1695		0.70	1.88	0.98 (d, 6H, 2 CH_3), 2.5 (sept. 1H, $\geqslant$CH)
3d	C_6H_5	50	130°/30	$C_{10}H_{10}O$ (146.2)	1670		1.05	2.55	7.35 (m, 3H_{arom}, *m*- and *p*-H's) 7.85 (m, 2H_{arom}, *o*-H's)
3e	H_3C—CH=CH—	65	75°/30	$C_7H_{10}O$ (110.2)	1665–1685	1635	0.82	2.02	ABX_3 spectrum: 1.68 (X_3), 5.85 and 6.05 (B), 6.45 to 7.05 (1) total 5H for H_3C—CH=CH—
3f	$(H_3C)_2C$=CH—	75	90°/30	$C_8H_{12}O$ (112.2)	1680	1630	0.85	1.75	1.85 and 2.05 (undoubled s, 6H, 2CH_3), 4.1 (broad, =CH—)
3g	H_2C=C(CH_3)—	40	71°/37	$C_7H_{10}O$ (110.2)	1670		0.9	2.4	1.85 (m, 3H, CH_3), 5.7 and 6.0 (broad, 2H, H_2C=)

[a] All products gave satisfactory microanalyses (C ± 0.2%, H ± 0.2%).

Under the reaction conditions used, products resulting from a ring opening process are detected in only very low proportions (< 1% as determined by distillation). This is unexpected as it is well known that the action of an acyl chloride on cyclopropane or methylcyclopropane leads exclusively to chloroketones resulting from ring opening (e.g. R—CO—$(CH_2)_3$—Cl and R—CO—$CH(CH_3)$—CH_2—Cl from cyclopropane[4]). It is thus apparent that the presence of the trimethylsilyl group modifies the reactivity of the cyclopropyl ring. However, in addition to the cyclopropyl ketones **3**, we have separated very small amounts of starting materials and also observed the formation of tars.

As shown in the Table, reactions of α,β-unsaturated acyl chlorides give rise to α,β-unsaturated cyclopropyl ketones. To the best of our knowledge, products **3e, f,** and **g** are new compounds.

Preparation of Cyclopropyltrimethylsilane (1):
This product was obtained by cyclopropanation of trimethylvinylsilane using diiodomethane and a zinc-copper couple according to the Simmons-Smith process as modified by Rawson and Harrison[5]; yield: 70%; b.p. 95°/760 torr.

Preparation of Cyclopropyl Ketones 3; General Procedure:
Aluminium chloride (7.35 g, 0.055 mol) is added in small portions within 30 min to a solution of cyclopropyltrimethylsilane (5.7 g, 0.05 mol) and the acyl chloride (0.05 mol) in dichloromethane (50 ml). The mixture is stirred at 25° for 60 h, then cooled to −5°, and chlorotrimethylsilane and dichloromethane removed by evaporation under reduced pressure. The residual solution is diluted with diethyl ether (30 ml) and is poured on to an ice/salt mixture. The product is extracted into ether, the organic phase is washed to neutrality, dried with sodium sulfate, and the product separated by distillation.

The ^{1}H-N.M.R. of all the cyclopropyl ketones exhibit an AA'BB'X spectral pattern typical for the cyclopropyl ring protons when the ring bears an electron-withdrawing substituent. The ^{1}H-N.M.R. data are given in the Table.

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