A Useful Preparation of Cyclopentenones

Steven WOLFF, William C. AGOSTA

Laboratories of The Rockefeller University, New York, New York 10021, U.S.A.

The various general methods[1] that are available for conversion of saturated ketones to α,β-unsaturated compounds typically involve two separate operations and proceed in modest overall yield. In earlier work[2], for example, we employed a bromination-dehydrobromination procedure[3] for conversion of cyclopentanones into cyclopentenones in

Table. Preparation of Cyclopentenones (**2a–c**)[a]

Product	R	Yield (%)[b]	Empirical Formula[c]	^{1}H-N.M.R. (220 MHz, CCl_4) δ ppm
2a	CH_3	70	$C_7H_{10}O$ (110.2)	Compatible with reported[6] spectrum.
2b	$CH_2CH(CH_3)_2$	64	$C_{10}H_{16}O$ (152.2)	7.30 (d, J=6 Hz), 5.93 (d, J=6 Hz, 1H), 2.22 (d, J=18 Hz, 1H), 2.00 (d, J=18 Hz, 1H), 1.61 (m, 1H), 1.5 (dd, J=14, 5 Hz, 1H), 1.3 (dd, J=14, 7 Hz, 1H), 1.1 (s, 3H), 0.92 (d, J=7 Hz, 3H), 0.90 (d, J=7 Hz, 1H).
2c	$CH_2CH_2CH_2CH_3$	60	$C_{10}H_{16}O$ (152.2)	7.38 (d, J=6 Hz, 1H), 6.0 (d, J=6 Hz, 1H), 2.18 (d, J=18 Hz, 1H), 1.98 (d, J=18 Hz, 1H), 1.59–1.09 (br m, 6H), 1.20 (s, 3H), 0.90 (t, J=7 Hz, 3H).

[a] **2a–c** all showed strong infrared absorption at 1721 cm^{-1}.

[b] Estimated by gas chromatography; conditions: 3 m × 0.635 cm column of 25% QF-1 on Chromosorb W at 192° and helium flow rate of 73 ml/min.

[c] Analytical samples obtained by preparative gas chromatography; conditions: 3 m × 0.95 cm column of 30% Carbowax 20 M on Chromosorb W at 190° and helium flow rate of 150 ml/min. Compounds **2b** and **2c** gave satisfactory elemental analyses (C ± 0.17%, H ± 0.14%).

yields of 30–40%. Since that time we have had continuing need for a better method of carrying out this transformation. For our purposes complete conversion, improved yield, and convenience of operation on a small scale were primary considerations. It appeared that previous observations and exploratory experiments[4] concerning the dehydrogenation of ketones by palladium(II) compounds offered the basis for a practical procedure that would meet our needs. This has proved to be the case, and we report here conditions for oxidation of 3,3-disubstituted cyclopentanones to the corresponding cyclopentenones in a single operation with yields of 60–70%. The ketone in acetic acid/dioxan is treated with chloranil plus an equivalent of palladium(II) chloride in a small volume of concentrated hydrochloric acid, and the resulting reaction mixture is stirred at 110° for 2–3 days. Simple work up and bulb-to-bulb distillation furnishes the unsaturated ketone in good purity. These conditions have been applied successfully for conversion of ketones **1a–c** to the corresponding cyclopentenones **2a–c**. A typical procedure is detailed below.

1a-c **2a-c**

a R = CH_3

b R = $CH_2-CH(CH_3)_2$

c R = n-C_4H_9

Preparation of 3-Isobutyl-3-methyl-5-oxocyclopentene (2b):
Palladium chloride (887 mg, 5 mmol) was dissolved in concentrated hydrochloric acid (0.5 ml) by warming on a steam bath; a homogeneous red-brown oil remained after removal of most of the aqueous acid in vacuo. To this was added 3-isobutyl-3-methylcyclopentanone (**1b**; 761 mg, 4.94 mmol)[5], chloranil (1.230 g, 5 mmol), glacial acetic acid (5 ml) and dioxan (2.5 ml) and the mixture was stirred at 110° for 48 h. The reaction mixture was poured into pentane and filtered through Hyflo Super-Cel; the pentane solution was washed with water, 5% sodium hydroxide, water, and brine and was dried over magnesium sulfate. After removal of the pentane by distillation through a Vigreux column, the residue was distilled bulb-to-bulb (120–140°/18 torr) to give a colorless oil; yield: 481 mg. V.P.C. analysis of the distillate indicated virtually pure cyclopentenone **2b** with < 1% of the starting material remaining.

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[1] For extensive references and discussions of new methods see H. J. Reich, J. M. Renga, I. L. Reich, *J. Am. Chem. Soc.* **97**, 5434 (1975).
J. M. Townsend, I. D. Reingold, M. C. R. Kendall, T. A. Spencer, *J. Org. Chem.* **40**, 2976 (1975).

[2] W. C. Agosta, A. B. Smith, III, *J. Am. Chem. Soc.* **93**, 5513 (1971).
S. Wolff, W. L. Schreiber, A. B. Smith, III, W. C. Agosta, *J. Am. Chem. Soc.* **94**, 7792 (1972).

[3] E. W. Garbisch, Jr., *J. Org. Chem.* **30**, 2109 (1965).

[4] R. J. Theissen, *J. Org. Chem.* **36**, 752 (1971).
B. Bierling, K. Kirschke, H. Oberender, and M. Schulz, *J. Prakt. Chem.* **314**, 170 (1972).

[5] This compound was prepared by conjugate addition of isobutylmagnesium bromide to 3-methylcyclopentenone and characterized by I.R. and N.M.R. spectra, and elemental analysis.

[6] A. J. Bellamy, *J. Chem. Soc.* [B] **1969**, 449.