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PYRIDINIUM DICHROMATE IN ORGANIC SYNTHESIS: A CONVENIENT OXIDATION OF OLEFIN-IODINE COMPLEXES TO α-IODO KETONES

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Summary: Cyclic α-iodo ketones are obtained directly by oxidation of olefin-iodine complexes with pyridinium dichromate.

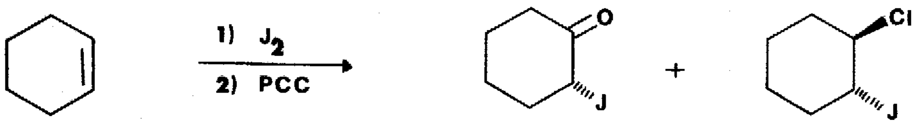
Pyridinium dichromate, PDC, is a stable reagent, recently introduced for the oxidation of a wide range of alcohols to carbonyl compounds[1].

We now wish to report that PDC reacts with cyclic olefin-iodine complexes to give α-iodo ketones (Table).

In a tipical small-scale reaction, iodine (1 mmole) and 4 Å molecular sieves were added to a well stirred solution of olefins (1 mmole) in anhydrous methylene chloride (10 ml), at room temperature under nitrogen. After 30 min, PDC (2.2 mmoles) was rapidly added and the mixture stirred at 45° for several hours. The crude products, after the usual work up[1], were purified by column chromatography on silica gel, eluting with n-hexane/ether.

The ^{1}H-NMR spectra of 6, 8, 9 and 10 showed the C$\underline{H}$-J system as a broad signal with fine structure (W1/2 = 7 - 8 Hz) at δ 4.5 - 4.6 typical for β-equatorial protons in these substrates. The stereochemistry of the reaction can be explained by the formation of a bridged iodonium ion on the less hindered side of the molecule and trans nucleophilic attack of the dichromate anion. PCC, under the same conditions, gave trans 1-chloro-2-iodo-cyclohexane[2], as the main product (66%) and the α-iodo ketone as a by-product (8%).

The reaction seems to be applicable to cyclic olefins but it failed with linear olefins, since only a mixture of unidentified products was obtained (40 - 50%), which decomposed despite several attempts at isolation.



Until now, only one method has been known for the one-step oxidation of olefins to α-iodo ketones[3].

Table

	Olefin	Time reaction (h)		α-iodo ketone[4]	Isolated yield (%)
1	1-cyclohexene	20	6	2-α-iodo-cyclohexanone	50
2	1-cyclooctene	23	7	2-iodo-cyclooctanone	60
3	4-t-butyl-1-cyclohexene	3.5	8	trans 2-α-iodo-4-t-butyl-cyclohexanone	62
4	1-phenyl-1-cyclohexene	1.5	9	cis 1-phenyl-2-α-iodo-cyclohexanol	60
5	2-cholestene	23	10	3-α-iodo-cholestan-2-one	70

References and notes

1) E. J. Corey and G. Schmidt, Tetrahedron Letters, 399 (1979);

2) a) W. C. Baird, Jr, J. H. Surridge, M. Buza, J. Org. Chem., 36, 2088 (1971);
b) A. Onoe, S. Uemura, M. Okano, Bull. Chem. Soc. Jpn., 47, 2818 (1974);

3) G. Cardillo and M. Shimizn, J. Org. Chem., 42, 4268 (1977);

4) 6: IR (1% CCl$_4$, ν_{max} cm^{-1}): 1715; NMR (CCl$_4$, δ): 4.60 (m, 1 H, CHJ), 3.18 (m, 1 H, H$_{ax}$ at C$_6$). 7: IR (1% CCl$_4$, ν_{max} cm^{-1}): 1710; NMR (CCl$_4$, δ): 4.40 (dd, 1 H, CHJ, J$_1$ = 13 Hz, J$_2$ = 5 Hz), 2.80 (m, 1 H). 8: IR (1% CCl$_4$, ν_{max} cm^{-1}): 1710; NMR (CCl$_4$, δ): 4.50 (m, 1 H, CHJ), 3.05 (m, 1 H, H$_{ax}$ at C$_6$). 9: IR (1% CCl$_4$, ν_{max} cm^{-1}): 3560; NMR (CCl$_4$, δ): 7.30 (m, 5 H, H$_{arom}$), 4.53 (m, 1 H, CHJ), 1.80 (s, 1 H, -OH). 10: IR (1% CCl$_4$, ν_{max} cm^{-1}): 1708; NMR (CCl$_4$, δ): 4.50 (m, 1 H, CHJ), 3.00 (d, 1 H, H$_{ax}$ at C$_1$, J = 13.5 Hz), 2.16 (d, 1 H, H$_{eq}$ at C$_1$, J = 13.5 Hz).

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