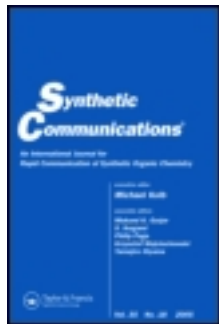


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Highly Selective Oxidative Cleavage of Aryl Substituted Olefins with Pyridinium Chlorochromate

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HIGHLY SELECTIVE OXIDATIVE CLEAVAGE OF ARYL SUBSTITUTED
OLEFINS WITH PYRIDINIUM CHLOROCHROMATE

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After the initial studies on the oxidative properties of pyridinium chlorochromate (PCC) by Corey¹ a little under a decade ago, there have been numerous studies which have revealed the versatility of this reagent for the mild and selective oxidation of a number of organic substrates.² Oxidative cleavage of multiple bonds by PCC is shown to be limited to deoxygenation reactions.^{3,4} In addition, highly activated linear and cyclic enolic carbon-carbon double bonds are reported to be oxidized by this reagent yielding esters and lactones, respectively.⁵ In general, however, pyridinium chlorochromate, in contrast to other oxidant derivatives of chromium(VI), has been reported inactive towards

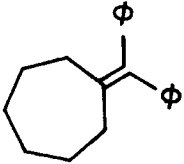
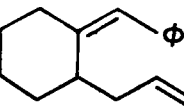
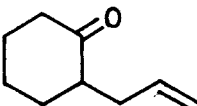
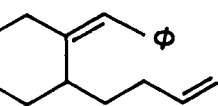
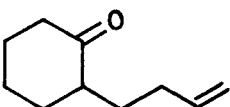
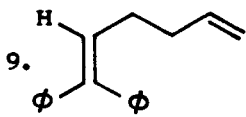
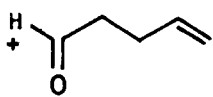
*To whom correspondence should be addressed.

carbon-carbon double bonds¹ and triple bonds.⁶ In the course of our studies on oxidative cyclization we have recently shown that tertiary γ -hydroxy olefins on treatment with PCC give reasonable yields of γ -lactones, with loss of one carbon.⁷ This prompted us to examine in detail the conditions under which olefinic substrates would undergo oxidative cleavage with PCC. In this communication we report a highly selective oxidative cleavage of carbon-carbon double bonds bearing aryl substituents with pyridinium chlorochromate.

Treatment of a number of aryl substituted olefins with pyridinium chlorochromate/Celite in dichloromethane under reflux for 30-45 h resulted in oxidative cleavage yielding the corresponding carbonyl compounds in very good yields. The results of these oxidations are summarized in the Table.

It is evident from these results that aryl substituted acyclic olefins do undergo oxidative cleavage on treatment with PCC (entries 1-6). A noteworthy feature of this methodology is that it is highly selective for aryl substituted olefins since they can be cleaved in the presence of alkyl substituted olefins (entries 7-10). Alkyl substituted acyclic olefins are in general unreactive towards PCC under the same conditions (entries 11 and 12). Cyclic olefins do not undergo

TABLE^a

Entry	Olefin	Molar ratio	Time (h)	Product ^b	Yield
1.	trans-stilbene	1:5	32	Benzaldehyde	90
2.	1,1-Diphenyl-ethylene	1:5	35	Benzophenone	84
3.	1,1-Diphenyl-propene	1:5	26	Benzophenone	92
4.	Tetraphenyl-ethylene	1:5	38	Benzophenone	90
5.	9-Benzylidene-fluorene	1:5	28	Benzaldehyde + Fluorenone	85 86
6.		1:5	30	Benzophenone + Cycloheptanone	90 87
7.		1:5	40	Benzaldehyde + 	85 82
8.		1:5	40	Benzaldehyde + 	84 82
9.		1:5	30	Benzophenone + 	82 72

..contd.

Table (contd.)

Entry	Olefin	Molar ratio	Time (h)	Product ^b	% Yield ^c
10.		1:5	35	Benzaldehyde +	80 76
11.		1:5	35	No reaction	-
12.	trans-2-undecene	1:5	35	No reaction	-
13.	Cyclohexene	1:5	35	2-Cyclohexenone	6 ^d
14.		1:5	40		30 ^d
15.		1:5	40		17 ^d

a. Oxidations were carried out in dichloromethane under gentle reflux.

b. Products were characterised by comparison with authentic samples (spectra, TLC, m.p. and m.p. of 2,4-nitrophenylhydrazones).

c. All yields refer to isolated products.

d. A lot of starting material remained unreacted.

oxidative cleavage with PCC but allylic oxidation is observed, albeit, in low yields (entries 13-15). In summary, it may be mentioned that although oxidation of carbon-carbon multiple bonds does not take place with PCC in the presence of readily oxidizable functional groups,² selective and facile oxidative cleavage of aryl substituted acyclic olefins has been observed for the first time with this reagent. A general procedure for the oxidative cleavage with PCC is given below.

To a solution of the olefin (2 mmol) in dichloromethane (15 ml), a finely powdered and homogenized mixture of pyridinium chlorochromate (10 mmol) and Celite (5.0 g) was added. The reaction mixture was refluxed for 25-40 hr and then diluted with ether (60 ml) and filtered through a short pad of Celite. The filter cake was washed with two 10 ml portions of ether and the combined filtrate was concentrated to reveal the crude product. Flash chromatography yielded the pure compounds.

Acknowledgement

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