Oxidative *C*—*C* Cleavage of Phenyloxiranes by Pyridinium Chlorochromate

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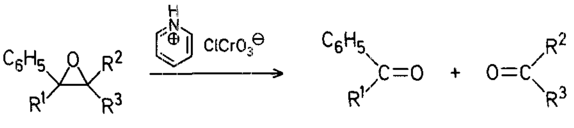
The typical procedures for the *C*—*C* cleavage of oxiranes, leading to carbonyl compounds, generally require a two-step sequence involving conversion of the oxiranes into glycols followed by oxidation with lead(IV) acetate or sodium metaperiodate. The one-step fission of the *C*—*C* bond of oxiranes is a rather unusual process, which has only seldom been reported[1,2,3].

A general method for this *C*—*C* cleavage, based on the irradiation of oxiranes in the presence of oxygen-transfer reagents, such as ozone, pyridine *N*-oxide, diethyl persulphoxide etc. has been reported, but in every case the yields of carbonyl compounds are low so that this process is unsatisfactory from a preparative point of view.

In the course of investigations on the reactivity of pyridinium chlorochromate[5], we have found that this reagent is able to effect the *C*—*C* bond cleavage of phenyloxiranes (**1**) to yield the carbonyl compounds **2**.



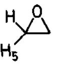
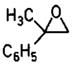
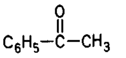
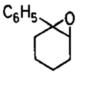
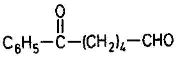
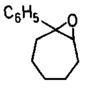
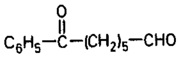
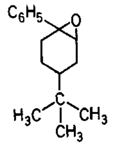
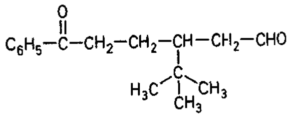
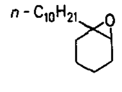
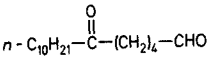
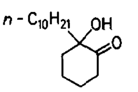
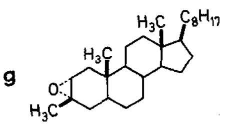
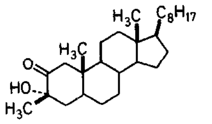
1 **2**

This new method is of synthetic value since the conversion is carried out under mild and simple conditions and the yields are notably higher than those obtained by the only hitherto available method[4].

It has to be noted that the presence of a phenyl group seems to be essential for efficient *C*—*C* cleavage by our method. In fact, alkyloxiranes (**1f, g**) are prevalently converted into *α*-hydroxyketones (**3f, g**). Only from the attempted cleavage of **1f** could a small amount (< 10%) of cleavage product (**2f**) be isolated. When longer reaction times and/or a large excess of pyridinium chlorochromate are used with educts **1f, g** the yields of products **2f** and **3f, g** decrease.

Phenyloxirane (**1a**) is commercially available. The other oxiranes were prepared by epoxidation of the corresponding alkenes according to literature procedures: **1b, c, d**[7]; **1e**[8] (used as an unresolved *cis/trans* mixture); **1f, g**[9]. The structures of these compounds **1** were confirmed their physical (m.p., b.p.) and spectrometric data (M.S., I.R., ^{1}H-N.M.R.).

Table 1. Oxidation of Oxiranes (**1**) with Pyridinium Chlorochromate

Educt		Product(s)		Reaction time and temperature [h], [°C]	Yield[a] [%]	m.p. or b.p./torr [°C]	Molecular formula[b] or Lit. Data [°C]	M.S. *m/e* (M$^+$)
1a		**2a**	C_6H_5-CHO	4, 20°	52	b.p. 63-65°/12	b.p. 62°/10[6]	
1b		**2b**	 $C_6H_5-\overset{O}{\overset{\|}{C}}-CH_3$	5, 20°	65	b.p. 82-84°/12	b.p. 79°/10[6]	
1c		**2c**	 $C_6H_5-\overset{O}{\overset{\|}{C}}-(CH_2)_4-CHO$	0.75, 40°	75	m.p. 33-34° (light petroleum)	$C_{12}H_{14}O_2$ (190.2)	190
1d		**2d**	 $C_6H_5-\overset{O}{\overset{\|}{C}}-(CH_2)_5-CHO$	0.75, 40°	72	m.p. 79-81° (light petroleum)	$C_{13}H_{16}O_2$ (204.3)	204
1e		**2e**	 $C_6H_5-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\underset{\underset{CH_3}{H_3C-\overset{\|}{C}-CH_3}}{\underset{\|}{CH}}-CH_2-CHO$	3, 40°	68	m.p. 138-140° (light petroleum)	$C_{16}H_{22}O_2$ (246.3)	246
1f		**2f**	 $n-C_{10}H_{21}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-CHO$ +	1.5, 20°	9	m.p. 51-53° (light petroleum)	$C_{16}H_{30}O_2$ (254.4)	254
		3f			66	oil (n_D^{22}: 1.4633)	$C_{16}H_{30}O_2$ (254.4)	254
1g		**3g**		[30, 40°]	50	m.p. 198-199° (ethanol)	m.p. 196-199°[10]	416

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[a] Yield of isolated product. In experiments **a-e**, 10-15% of the oxirane **1** was recovered.

[b] The microanalyses were in good agreement with the calculated values: C, ±0.10; H, ±0.12.

Table 2. Spectral Data of Compounds **2** and **3**

Compound	I.R. (CCl_4) ν [cm^{-1}]	^{1}H-N.M.R. (CCl_4/TMS_{int}) δ [ppm]
2c	3060, 2940, 2820, 2720, 1735, 1698, 1605, 710	9.4 (m, 1 H); 7.8 (m, 2 H); 7.4 (m, 3 H); 2.9 (m, 2 H); 2.45 (m, 2 H); 1.7 (m, 4 H)
2d	3040, 2940, 2715, 1745, 1697, 705	9.75 (m, 1 H); 7.9 (m, 2 H); 7.45 (m, 3 H); 2.96 (t, 2 H, $J = 8$ Hz); 2.4 (m, 2 H); 1.7 (m, 6 H)
2e	3060, 2960, 2710, 1730, 1695, 1600 700	9.5 (m, 1 H); 7.7 (m, 2 H); 7.3 (m, 3 H); 2.8 (m, 2 H); 0.89 (s, 9 H)
2f	2925, 2850, 2708, 1727, 1718, 1258, 1096	9.45 (m, 1 H); 2.2 (m, 6 H); 0.78 (m, 3 H)
3f	3490, 2925, 2850, 1709, 1460, 1450	3.60 (s, 1 H, the signal disappears after shaking with D_2O); 0.84 (m, 3 H)
3g	(in $CHCl_3$): 3590, 2925, 1702, 1452	(in $CDCl_3$): 2.60 (d, 1 H, $J = 12$ Hz); 2.28 (d, 1 H, $J = 12$ Hz); 1.30 (s, 3 H); 0.75 (s, 3 H); 0.68 (s, 3 H)

Reaction of Oxiranes (1, Epoxides) with Pyridinium Chlorochromate; General Procedure:

A solution of the oxirane (**1**; 4 mmol) in dry dichloromethane (50 ml) is rapidly added to a stirred suspension of pyridinium chlorochromate (1.725 g, 8.0 mmol) and 4 Å molecular sieves (3 g) in dry dichloromethane (75 ml) under nitrogen. The mixture is stirred under the conditions given in Table 1. Then, ether (150 ml) is added, the mixture filtered through a small amount (10 g) of silica gel, and the silica gel eluted with ether. The solvent is removed under reduced pressure at 40°C and the residue is column-chromatographed on silica gel. The pure products **2** and/or **3** are obtained by elution with light petroleum/ether (4/1) or hexane/ether (9/1), respectively.

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[1] E. A. Mayeda, L. L. Miller, J. F. Wolf, *J. Am. Chem. Soc.* **94**, 6812 (1972).

[2] D. Milstein, O. Buchman, J. Blum, *J. Org. Chem.* **42**, 2299 (1977).

[3] V. G. Dryuk, *Tetrahedron* **32**, 2855 (1976).

[4] Y. Ito, T. Matsuura, *J. Chem. Soc. Perkin Trans. 1* **1981**, 1871.

[5] For a review on the synthetic applications of pyridinium chlorochromate, see: G. Piancatelli, A. Scettri, M. D'Auria, *Synthesis* **1982**, 245.

[6] *Handbook of Chemistry and Physics*, CRC Press, Inc., Boca Raton, Florida, 63rd Edn., 1982–1983.

[7] A. C. Cope, P. A. Trumbull, E. R. Trumbull, *J. Am. Chem. Soc.* **80**, 2844 (1956).

[8] G. Berti, B. Macchia, F. Macchia, *Tetrahedron* **24**, 1755 (1968).

[9] D. H. R. Barton, A. da S. Campos-Neves, R. C. Cookson, *J. Chem. Soc.* **1956**, 3500.

[10] J. R. Bull, A. Tuinman, *J. Chem. Soc. Perkin Trans. 1* **1976**, 212.