Journal of

The Chemical Society,

Chemical Communications

NUMBER 24/1974 **18 DECEMBER**

Preparation of a Polymer-supported Per-acid and its Use to Oxidize Olefins to Epoxides

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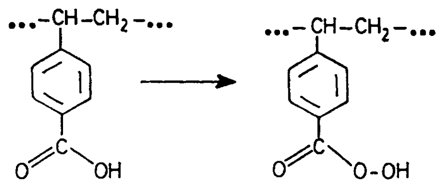
Summary A polymeric per-acid has been prepared and used to oxidize several olefins to their epoxides in good yield.

There has recently been considerable interest in polymer-supported organic reagents.[1] We now report the preparation of a polymeric per-acid and its reactions with some olefins. Use of the polymeric reagent allows the epoxide and any unchanged olefin to be separated from the excess and the spent reagent simply by filtration or centrifugation. A resin capable of epoxidizing olefins has been described previously[2] but it contains aliphatic per-acid residues and explodes very readily on impact.[3] The resin we now describe contains aromatic per-acid residues and despite numerous attempts to make it explode by impact it has never done so.



(I) (II)

Carboxy groups were introduced *via* chloromethylation and oxidation into *ca.* 83% of the phenyl rings of a polystyrene resin cross-linked with either 1% or 2% of divinylbenzene.[4] Treatment of the product (I) in methanesulphonic acid at 25° with 85% hydrogen peroxide overnight gave a per-acid resin (II). The oxidation capacity, as estimated by iodometry, was usually 3·5 to 4·0 mE g^{-1}, indicating that *ca.* 75 to 87% of the carboxy groups had been converted to per-acid groups. The oxidation capacity is comparable to that (5·0 mE g^{-1}) of commercial 85% *m*-chloroperoxybenzoic acid. There was no significant

Table

Reactions of per-acid resins with olefins in tetrahydrofuran at 40° for 4h

Olefin	Equivalents of reagent used[a]	Yield of oxide/%[b]	Recovered olefin/%[b]
Methylcyclohexene	2	65[c]	0
Cholesteryl acetate	3	42[d,e]	52[d]
trans-Oct-2-ene	3	76	9
cis-Oct-2-ene	2	50	13
trans-β-Methylstyrene	3	62	8
	3[f]	65	15
Cyclo-octene	2	95	2
	2[f]	84	12
Cyclododecene	3	82	16
Styrene	2	7	60
Methyl undec-10-enoate	2	1	82

[a] Unless indicated otherwise, the reagent was prepared from polystyrene cross-linked with 1% of divinylbenzene. [b] Unless indicated otherwise, yields were determined using g.l.c. The yields are based on the amount of olefin treated with the reagent. Compare with yields given in, for example, ref. 6. [c] The product was mainly 2-methylcyclohexanone formed by rearrangement of the oxide. [d] Products isolated using p.l.c. [e] Triol monoacetate also obtained in 6% yield. [f] Reagent prepared from polystyrene cross-linked with 2% of divinylbenzene.

loss of activity over several months when the resin was stored at −20°, but when it was stored at 20° it lost half the activity in 70 days.

Several olefins were treated with the reagent. Tetrahydrofuran was the most satisfactory of several solvents investigated even though in some instances a small amount of the reagent was consumed in oxidising tetrahydrofuran to γ-butyrolactone.[5] The polymeric reagent was suspended in a solution of the olefin at 40°. After 4 h the polymer was filtered or centrifuged off and the solution examined by g.l.c. or p.l.c. The results are summarised in the Table. It can be seen that (i) in most instances the epoxides were obtained in good yield, (ii) the poor yields were obtained with monosubstituted olefins, *i.e.* those olefins known to be relatively unreactive towards organic per-acids,[7] and (iii) in some instances only about 60—70% of the starting material was accounted for. This last is probably partly due to the carboxylic acid residues on the polymer reacting with the epoxides to give hydroxy esters As the reagent was polymeric these would be removed, together with the excess and spent reagent, by filtration.

We thank the S.R.C. for financial support.

(*Received, 23rd September* 1974; *Com.* 1200.)

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[5] There appears to be no previous report of per-acids effecting this oxidation, although it is known that it can be brought about by other oxidants. See, *e.g.* L. M. Berkowitz and P. N. Rylander, *J. Amer. Chem. Soc.*, 1958, **80**, 6682; Ger. P. 1,222,034 (*Chem. Abs.*, 1966, **65**, 15,238a).

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