

## Preparation of Polymer-supported Peroxy-acids and their Use to Oxidise Olefins to Epoxides <sup>1</sup>

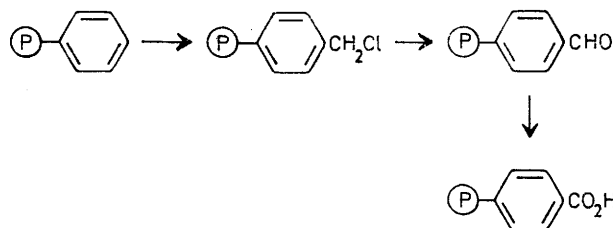
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Treatment of carboxy-substituted polystyrene resins with hydrogen peroxide in methanesulphonic acid gave resins containing aromatic peroxy-acid residues (3.5—4.0 mmol g<sup>-1</sup>). The resins generally reacted with di- and tri-substituted olefins in tetrahydrofuran at 40 °C to give epoxides (or products derived from epoxides) in yields greater than 50%. Monosubstituted olefins reacted poorly. In cases where mixtures of stereoisomeric epoxides were formed the proportions of the isomers were essentially the same as those obtained by using monomeric aromatic peroxy-acid reagents.

POLYMER-SUPPORTED organic reagents have several attractive features, one of which is that reactions in which they are used can often be worked up simply by filtration or centrifugation.<sup>2</sup> We describe here the preparation of some resins containing peroxy-acid residues and their use to epoxidise olefins. Several resins containing aliphatic peroxy-acid residues have been described previously but those purely aliphatic resins which reacted with olefins to give good yields of epoxides<sup>3</sup> were explosive,<sup>4</sup> and those which also contained aromatic sulphonic acid residues reacted with olefins to give diols<sup>5</sup> or low yields of epoxides.<sup>6</sup> The reagents we now describe contain aromatic peroxy-acid residues and are not explosive. They react with many di- and tri-substituted olefins to give good yields of epoxides. Since our work was completed Fréchet and Haque have described some similar resins.<sup>7</sup> They were mainly concerned with the preparation of the resins and one of their methods was similar to the main method we used. They studied the epoxidation of only one olefin. An important difference between their resins and ours is that ours has *ca.* 80% of the phenyl residues substituted whereas theirs had only *ca.* 15%. This may result in substantial differences in the swelling properties of the resins and hence in the availability of the reactive groups in a given solvent.

**Preparation of Polymeric Peroxy-acids.**—The starting materials were cross-linked polystyrene resins containing carboxy-substituents. These were conveniently prepared by introducing carboxy-groups into commercial polystyrene beads by the sequence shown in the Scheme.<sup>8</sup> From polystyrenes cross-linked with 1% and also with 2% of *p*-divinylbenzene (DVB), carboxy-resins with 83% of the rings substituted were prepared. A more

direct way of preparing the carboxy-resin was by copolymerisation of methyl *p*-vinylbenzoate, styrene, and DVB, followed by hydrolysis of the ester group, but the resin prepared in this way tended to break down under the conditions used to produce the peroxy-acid.



SCHEME

The carboxy-resins prepared according to the Scheme could be converted into peroxy-acid resins by treatment with 85% hydrogen peroxide in methanesulphonic acid at 25 °C for 16 h. The peroxy-acid resins generally had an activity (measured by iodimetry) of *ca.* 3.5—4.0 mmol [O] per g, indicating that *ca.* 70% of the carboxy-groups had been converted into peroxy-acid groups. This oxidative capacity is about 4 times greater than that of Fréchet and Haque's resins<sup>7</sup> and is comparable to that (5.0 mmol g<sup>-1</sup>) of commercial 85% *m*-chloroperbenzoic acid.

Treatment of the carboxy-resin prepared by the second of the above methods with hydrogen peroxide under the above conditions resulted in breakdown of the resin, but a shorter reaction time (4 h) gave a resin with satisfactory physical properties and an activity of 2.51 mmol [O] per g. This resin was not used in the investigations described below.

An alternative method of preparing the peroxy-acid

<sup>1</sup> C. R. Harrison and P. Hodge, *J.C.S. Chem. Comm.*, 1974, 1009.

<sup>2</sup> C. G. Overberger and K. N. Sannes, *Angew. Chem. Internat. Edn.*, 1974, **13**, 99; C. C. Leznoff, *Chem. Soc. Rev.*, 1974, **3**, 65.

<sup>3</sup> T. Takagi, *J. Polymer Sci., Part B, Polymer Letters*, 1967, **5**, 1031.

<sup>4</sup> T. Takagi and M. Aoyama, *J. Polymer Sci., Part B, Polymer Letters*, 1974, **12**, 681; C. R. Harrison, P. Hodge, and G. M. Perry, unpublished observations.

<sup>5</sup> F. Helfferich and D. B. Luten, *J. Appl. Polymer Sci.*, 1964, **8**, 2899.

<sup>6</sup> W. J. Hamilton, K. J. Krause, and H. B. Wagner, *J. Appl. Polymer Sci.*, 1974, **18**, 1039.

<sup>7</sup> J. M. J. Fréchet and K. E. Haque, *Macromolecules*, 1975, **8**, 130.

<sup>8</sup> C. R. Harrison, P. Hodge, J. Kemp, and G. M. Perry, *Makromol. Chem.*, 1975, **176**, 267.

resin was to treat the formyl resin (Scheme) in methanesulphonic acid with hydrogen peroxide. This procedure allows the peroxy-acid to be prepared from the formyl resin in one step and it gives material comparable in activity to that from the carboxy-resin, but it is only convenient to carry the reaction out on a small scale otherwise the strongly exothermic reaction is difficult to control.

There was no significant loss of activity over several months when the resins were stored at  $-20^{\circ}\text{C}$ , but at  $20^{\circ}\text{C}$  they lost half their activity in *ca.* 70 days. As some resins containing aliphatic peroxy-acid residues are known to be explosive, we made numerous attempts

We next sought to optimise the reaction time and the quantity of reagent. Treating several substrates with the resins in THF at  $40^{\circ}\text{C}$  for various periods showed that 4 h was the most satisfactory reaction time. The yield of epoxide did not usually increase significantly after this period and in some instances it actually fell. As not all the peroxy-acid residues on the resin were likely to be accessible to the substrate, an excess of reagent was used. Usually 2 mol. equiv. were used but some reactions were also carried out with 3 and 4.5 mol. equiv. The results (Table 3) show that increasing the molar ratio from 2 : 1 to 3 : 1 markedly increased the yields of epoxides but that further increases caused the

TABLE 1  
Effect of solvent on reaction yield <sup>a</sup>

Substrate	Yield of epoxide (%) in various solvents						
	THF	DMF	Dioxan	EtOAc	CHCl <sub>3</sub>	PhH	CH <sub>2</sub> Cl <sub>2</sub>
Cyclo-octene	95		69		3	2	2
Cyclododecene	57	45					
$\alpha$ -Methylstyrene <sup>b</sup>	50		41	28	0	0	
<i>trans</i> - $\beta$ -Methylstyrene <sup>c</sup>	52		52	40	7		4

<sup>a</sup> Yields of epoxide (determined by g.l.c.) obtained by treating olefin in solvent at  $40^{\circ}\text{C}$  for 4 h with 2 mol. equiv. of reagent prepared from 1% cross-linked polystyrene. <sup>b</sup> The product from  $\alpha$ -methylstyrene was a mixture (see text); yields given are the total of those for all products. <sup>c</sup> Reagent prepared from 2% cross-linked polystyrene.

to detonate our peroxy-acids by impact, but on no occasion did an explosion occur.

*Effect of Various Factors on the Efficiency with which the Peroxy-acid Resins react with Olefins.*—Ideally, the reaction conditions used with polymer-supported reagents should cause the polymer to swell so as to facilitate access to the reactive groups. A major factor determining the extent of swelling is the solvent. We treated a number of olefins with peroxy-acid resins in a range of solvents under standard conditions and determined the yields of epoxide. Typical results (Table 1) show that tetrahydrofuran (THF) is marginally superior to dioxan and dimethylformamide (DMF), which in turn are better than ethyl acetate. Benzene, chloroform, and methylene chloride, solvents commonly used with monomeric peroxy-acids,<sup>9</sup> are poor solvents. Interestingly this order is approximately the same as that of the solubility of *m*-chloroperbenzoic acid (CPBA) in these solvents.<sup>10</sup>

A second major factor in determining the extent of swelling is the degree of cross-linking; the lower this is the more the resin swells. Although the chloromethylation reactions used in the preparation of the reagents almost certainly increased the extent of cross-linking,<sup>11</sup> the peroxy-acids prepared from 1% cross-linked polystyrene usually gave greater yields of epoxide than those prepared from 2% cross-linked polystyrene. Some typical results are summarised in Table 2. Other workers have reported that decreasing the percentage of cross-linking improves reaction yields.<sup>12</sup>

<sup>9</sup> H. O. House, 'Modern Synthetic Reactions,' 2nd edn., Benjamin, Menlo Park, California, 1972, ch. 6.

<sup>10</sup> L. F. Fieser and M. Fieser, 'Reagents for Organic Synthesis,' Wiley, New York, 1967, p. 136. *m*-Chloroperbenzoic acid has a solubility in THF and dioxan of more than 150 g per 100 g at  $25^{\circ}\text{C}$ .

yields to fall. The latter effect stems partly from the difficulty of efficiently recovering the product from the relatively large amount of resin.

TABLE 2

Effect of percentage of cross-linking on reaction yield <sup>a</sup>

Substrate	Solvent	1%	2%
		cross-linked reagent <sup>c</sup>	cross-linked reagent <sup>c</sup>
<i>trans</i> -oct-2-ene	THF	48	35
Cyclo-octene	THF	95	72
Cyclo-octene	Dioxan	69	66
Cyclododecene	THF	57	51
$\alpha$ -Methylstyrene	THF	50	68
$\alpha$ -Methylstyrene <sup>b</sup>	Dioxan	41	20
<i>trans</i> - $\beta$ -Methylstyrene	THF	54	52

<sup>a</sup> Yield of epoxide (determined by g.l.c.) obtained by treating the olefin in solvent at  $40^{\circ}\text{C}$  with two mol. equiv. of peroxy-acid for 4 h. <sup>b</sup> See note b, Table 1. <sup>c</sup> Reagents prepared from 1 and 2% cross-linked polystyrenes. As noted in the text, the actual percentage of cross-linking in the peroxy-acid resin is probably higher.

*Reaction of the Polymer-supported Peroxy-acids with a Range of Olefins.*—A range of olefins was treated with the peroxy-acid resins using the best general conditions established by the above work. The polymer was filtered or centrifuged off and the filtrate was analysed, usually by g.l.c. The results are given in Table 4. With most tri- and di-substituted olefins, yields of epoxide in excess of 50% were obtained, but with monosubstituted olefins the yields were poor. This is not surprising as the resin reagent used in THF would be expected to be less reactive than both CPBA and perbenzoic acid used

<sup>11</sup> J. A. Patterson in 'Biochemical Aspects of Reactions on Solid Supports,' ed. G. R. Stark, Academic Press, New York, 1971, p. 204.

<sup>12</sup> W. Heitz and R. Michels, *Angew. Chem. Internat. Edn.*, 1972, **11**, 298.

in chloroform, and the latter often react far from quantitatively with tri- and di-substituted olefins and often only poorly with monosubstituted olefins.<sup>9</sup> The resin reagent would be expected to be less reactive because it is an alkyl-substituted perbenzoic acid (electron-releasing substituents decrease the reactivity<sup>13</sup>)

that these resin reactions, particularly that of cyclooctene, are markedly slowed by the need for the substrate to diffuse into the resin, and/or by the inaccessibility of some of the peroxy-acid residues, and/or by microenvironmental effects. It is not clear why the polymeric reagent was more stable than the monomeric.

TABLE 3  
Effect of an excess of reagent on reaction yield<sup>a</sup>

Substrate	Cross-linking in reagent <sup>c</sup>	Reaction time (h)	Yield of epoxide (%)		
			2 equiv. reagent	3 equiv. reagent	4.5 equiv. reagent
<i>trans</i> -Oct-2-ene	1	4	54	76	30
Cyclododecene	1	4	64	82	68
$\alpha$ -Methylstyrene <sup>b</sup>	2	22	74	91	
<i>trans</i> - $\beta$ -Methylstyrene	2	4	52	65	
4-Methoxycarbonylcyclohexene	1	4	36		19

<sup>a</sup> Yield of epoxide (determined by g.l.c.) obtained by treating the substrate in THF with various amounts of reagent <sup>b</sup> See note b, Table 1. <sup>c</sup> See note c, Table 2.

and because it is used in an ethereal solvent.<sup>14</sup> The reactions with the resin reagent might also be slower because the substrate needs to diffuse into the resin to react. In an attempt to throw light on this, cyclooctene and *trans*- $\beta$ -methylstyrene were each separately

Use of the resin reagent simplifies the reaction procedure by allowing the excess of and spent reagent to be separated from the product by filtration. This is particularly useful when the substrate is acidic. A common side reaction in epoxidations is reaction of the epoxide with the carboxylic acid (spent peroxy-acid) to give hydroxy-esters. These also would be removed by

TABLE 4  
Reactions of peroxy-acid resins with various olefins in THF at 40 °C for 4 h<sup>a</sup>

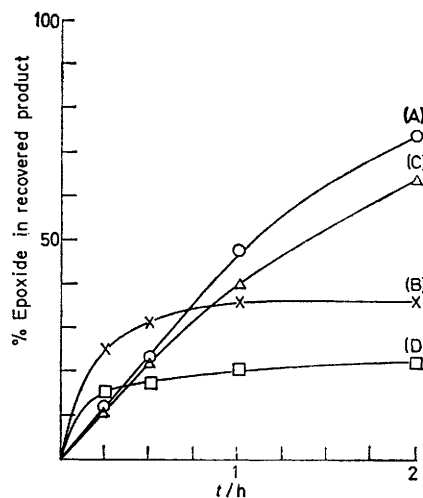
Olefin	Equiv. of reagent	Yield of epoxide (%)	Unchanged olefin (%)
Methylcyclohexene	2	65 <sup>b</sup>	0
Cholesteryl acetate	3	42 <sup>c</sup>	52
<i>trans</i> -Oct-2-ene	3	76	9
<i>cis</i> -Oct-2-ene	2	50	13
Elaidic acid	3	53	40
$\alpha$ -Methylstyrene	2 <sup>d</sup>	50 <sup>e</sup>	12
<i>trans</i> - $\beta$ -Methylstyrene	3	62	8
Cyclo-octene	2	95	2
Cyclododecene	3	82	16
4-Methoxycarbonylcyclohexene	2	36	28
4-Carboxycyclohexene	3 <sup>d</sup>	35	31
3-Acetylcyclohexene	3	3	91
3-Hydroxycyclohexene	3	28	3
Norbornene	2 <sup>d</sup>	54	8
Styrene	2	7	60
Methyl undec-10-enoate	2	1	82

<sup>a</sup> Unless indicated otherwise the reagent was prepared from 1% cross-linked polystyrene and yields were determined by g.l.c. <sup>b</sup> Product was 2-methylcyclohexene. <sup>c</sup> Products isolated by p.l.c.; triol monoacetate also obtained (6%). <sup>d</sup> Reagent prepared from 2% cross-linked polystyrene. <sup>e</sup> Complex mixture of oxidation products (see Experimental section).

treated with *p*-*t*-butylperbenzoic acid and with the resin peroxy-acid in THF at 40 °C and the reactions were followed by g.l.c. The results (Figure) show that the monomeric reagent reacted faster with both substrates initially but it also decomposed faster, with the net effect that higher yields were obtained with the resin reagents. The magnitude of the differences in the initial rates of the epoxidations indicates, especially as the monomeric reagent was decomposing more rapidly,

<sup>13</sup> B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1955, 1525.

<sup>14</sup> P. Renolen and J. Ugelstad, *J. Chim. phys.*, 1960, 57, 634; N. N. Schwartz and J. H. Blumbers, *J. Org. Chem.*, 1964, 29, 1976.



Reactions of peroxy-acids with olefins in THF at 40°: (A), cyclooctene and resin peroxy-acid; (B), cyclo-octene and *p*-*t*-butylperbenzoic acid; (C),  $\beta$ -methylstyrene and resin peroxy-acid; (D),  $\beta$ -methylstyrene and *p*-*t*-butylperbenzoic acid

filtration as they would be attached to the polymer, and this is probably the main reason why not all the starting material was accounted for.

In two reactions the initially formed epoxide was converted into other products. The epoxide from 1-methylcyclohexene simply rearranged to 2-methylcyclohexanone,<sup>15</sup> but in the epoxidation of  $\alpha$ -methylstyrene other reactions occurred as well. Thus, acetophenone was obtained in addition to  $\alpha$ -phenylpropionaldehyde. The complexity of the reaction is not a consequence of

<sup>15</sup> R. Filler, B. R. Camara, and S. M. Naqvi, *J. Amer. Chem. Soc.*, 1959, 81, 658.

using the polymeric reagent, as the same products were obtained by using CPBA. A few products, mainly those from the less reactive olefins, contained small amounts of  $\gamma$ -butyrolactone produced by oxidation of the THF. When a suspension of the peroxy-acid in THF was heated for 4 h, sufficient  $\gamma$ -lactone was formed to account for 9% of the oxidation capacity of the resin.

Several of the olefins listed in Table 4 could afford a mixture of stereoisomers and it was of interest to see whether the polymeric reagent gave different stereochemical results from the monomeric reagents. The reactions of 4-methoxycarbonyl- and 4-carboxy-cyclohexene both gave mixtures of stereoisomers, but in each case the ratio (*cis* : *trans* 30 : 70 and 33 : 67, respectively) was essentially the same as that (31 : 69) obtained by treating the ester with CPBA in THF. Previous workers found a ratio of 34 : 66 from treatment of the ester with perbenzoic acid in ether<sup>16</sup> and a ratio of 29 : 71 with the ester and CPBA in chloroform.<sup>17</sup> Unfortunately 3-acetoxycyclohexene was too unreactive for a completely satisfactory study to be made, but 3-hydroxycyclohexene gave stereoisomeric epoxides in the ratio 91 : 9. This is similar to that reported (*cis* : *trans* 90 : 10) for the reaction of this olefin with perbenzoic acid in ether at 5 °C.<sup>18</sup> We could only detect one product, the *exo*-epoxide, from the norbornene oxidation whether the resin reagent or CPBA was used. This is in agreement with other workers who claim that the *exo*-epoxide is the exclusive<sup>19</sup> or almost exclusive product,<sup>20</sup> but Kwart and Takeshita have reported that both isomers are formed, the *exo* : *endo* ratio being 94 : 6.<sup>21</sup> Hence it appears from this limited number of examples that the polymeric reagent gives essentially the same stereochemical results as the monomeric reagents.

#### EXPERIMENTAL

The polystyrene resins used were Biobeads SX1 and SX2 (Bio-Rad Laboratories, California). These were styrene-1% *p*-divinylbenzene and styrene-2% *p*-divinylbenzene copolymers, respectively, in the form of 200–400 mesh beads. Resins were filtered off by using no. 4 grade sintered glass filters and were dried in a vacuum oven (0.1 mmHg). G.l.c. was carried out with a Pye 104 machine (flame ionisation detector) and a 5 ft column containing either Apiezon L or SE30 as stationary phase. Peak areas were determined by triangulation except in those reactions where a mixture of stereoisomers was obtained; in these cases a curve resolver was used. Unless indicated otherwise, ratios were determined by comparison with authentic mixtures. All the olefins and most of the epoxides used in this work were obtained commercially. The other epoxides were prepared by standard methods.

*Introduction of Carboxy-groups into Polystyrene Resins.*—This was carried out as described previously<sup>8</sup> (Scheme).

<sup>16</sup> G. Bellucci, F. Marioni, and A. Marsili, *Tetrahedron*, 1972, **28**, 3393.

<sup>17</sup> J. W. Huffman, C. B. S. Rao, and T. Kamiya, *J. Org. Chem.*, 1967, **32**, 697.

<sup>18</sup> P. Chamberlain, M. L. Roberts, and G. H. Whitham, *J. Chem. Soc. (B)*, 1970, 1374.

From Biobeads SX1 a carboxy-resin with 83% of the rings substituted was obtained. Biobeads SX2 also gave a product in which 83% of the rings were substituted. Comparable results were obtained on subsequent occasions.

*Copolymerisation of Methyl p-Vinylbenzoate, Styrene, and p-Divinylbenzene: Hydrolysis of the Product.*—Methyl *p*-vinylbenzoate was prepared by methylating *p*-vinylbenzoic acid<sup>22</sup> with diazomethane. Nitrogen was bubbled through a rapidly stirred solution (*ca.* 350 rev. min<sup>-1</sup>) of polyvinyl alcohol (3.0 g;  $\bar{M}$  125 000) in water (400 ml) at 95 °C. To this solution was added a mixture of benzoyl peroxide (0.3 g), methyl *p*-vinylbenzoate (10.0 g), and *p*-divinylbenzene (0.7 ml of a 1 : 1 mixture of *p*-divinylbenzene and 1-ethyl-4-vinylbenzene). Heating and stirring under nitrogen were continued overnight. The flask was then cooled to 20 °C and water (700 ml) added. The beads were allowed to settle and the liquid was decanted. The beads were washed with hot water then transferred to a filter, washed with acetone and methylene chloride, and dried (60 °C). This gave white beads (8.4 g, 81%),  $\nu_{\max}$  (KBr) 1 730 cm<sup>-1</sup>.

The ester groups were hydrolysed by treating the resin for 16 h with an excess of the potassium butoxide-water reagent in 1,2-dimethoxyethane heated under reflux.<sup>9</sup> The carboxy-resin had  $\nu_{\max}$  (KBr) 1 735m and 1 690s cm<sup>-1</sup>.

*Preparation of Polymeric Peroxy-acids from Carboxy-resins.*—(a) A stirred mixture of the carboxy-resin (5 g; from Biobeads SX1) and methanesulphonic acid (15 ml) was kept at 25–30 °C while hydrogen peroxide (85%; 10 ml) in methanesulphonic acid (10 ml) was carefully added dropwise. Control of temperature is important. When the addition was complete the mixture was stirred for 16 h at 20 °C. The resin was then filtered off, washed successively with THF and methylene chloride, and dried under vacuum (20 °C). It was stored at –20°. To determine the activity of the product a portion (120–140 mg) was treated with methylene chloride (2 ml), potassium iodide (340 mg), and sulphuric acid (5 ml; 6N). The mixture was set aside with occasional shaking for 1 h. It was then titrated against sodium thiosulphate (0.1N), starch indicator being added near the end-point. The resin had an activity of 3.90 mmol [O] per g, corresponding to 70% of the carboxy-groups being oxidised. Similar reactions generally gave resins with activities of 3.5–4.0 mmol g<sup>-1</sup>.

(b) Similar treatment of the carboxy-resin from Biobeads SX2 gave a peroxy-acid resin with an activity of 3.82 mmol g<sup>-1</sup> (69% of carboxy-groups oxidised).

(c) The carboxy-resin obtained *via* polymerisation of methyl *p*-vinylbenzoate was treated with hydrogen peroxide as above. This gave a rubbery product which was partially soluble in methanesulphonic acid. A reaction time of 4 h gave a resin with satisfactory physical properties and an activity of 2.51 mmol g<sup>-1</sup> (*ca.* 41% of carboxy-groups oxidised).

*Preparation of Peroxy-acid Resin from Formyl Resin.*—(a) A stirred mixture of formyl resin<sup>8</sup> (1.0 g; from Biobeads SX2) and methanesulphonic acid (2.5 ml) was treated dropwise with an ice-cold solution of hydrogen peroxide (1.0 ml; 85%) in methanesulphonic acid (7.5 ml) so that the interna

<sup>19</sup> S. B. Soloway and S. J. Cristol, *J. Org. Chem.*, 1960, **25**, 327

<sup>20</sup> H. C. Brown, J. H. Kawakami, and S. Ikegami, *J. Amer. Chem. Soc.*, 1970, **92**, 6914.

<sup>21</sup> H. Kwart and T. Takeshita, *J. Org. Chem.*, 1963, **28**, 670.

<sup>22</sup> J. R. Leebrick and H. E. Ramsden, *J. Org. Chem.*, 1958, **23**, 935.

temperature was kept between 25 and 30 °C. More hydrogen peroxide (1.0 ml) was then added and the mixture was stirred at 20 °C for 5 h. The resin was then filtered off, washed with methanesulphonic acid, and re-treated with hydrogen peroxide, but this time the mixture was stirred overnight. The product was filtered off, washed, and dried as before. The product had an activity of 4.29 mmol g<sup>-1</sup> (78% of formyl groups oxidised).

(b) The formyl resin prepared from Biobeads SX1 reacted similarly.

*Oxidation of Cyclo-octene by Polymeric Peroxy-acid.*—A mixture of cyclo-octene (55 mg, 0.5 mmol), THF (2 ml), and peroxy-acid resin (256 mg of activity 3.90 mmol g<sup>-1</sup>, 1.0 mmol) was stirred at 40 °C for 4 h, cooled, and filtered. The resin was washed several times with small portions of THF. G.l.c. analysis of the combined filtrates showed that the yield of epoxy-cyclo-octane was 95% and that 2% of the cyclo-octene was unchanged.

*Other Oxidations (Tables 1—3).*—The reactions summarised in the Tables are only representative. About twice as many reactions were actually carried out by the above procedure, except that in some instances the resin was removed by centrifugation. Different batches of resin gave similar results. The reproducibility of the yields was estimated to be ±10% of the values given. The combined yields of oxidation products and unchanged starting material usually exceeded 80%, except when 4.5 mol. equiv. of reagent were used.

*Reactions summarised in the Figure.*—*p-t*-Butylperbenzoic acid was prepared by the reported method.<sup>23</sup> The substrates (0.5 mmol) in THF (10 ml) at 40 °C were separately treated with the peroxy-acids (1 mmol) in the usual manner. Periodically, samples were removed and the ratio of epoxide to olefin was determined by g.l.c., the samples from the reactions with the monomeric reagents being first treated with sodium sulphite to quench the peroxy-acid and sodium carbonate to remove the carboxylic acid. The g.l.c. analyses showed that the amounts of epoxide and olefin present were sufficient to account for most of the starting material.

*Reactions summarised in Table 4.*—These were carried out by a procedure similar to that for the oxidation of cyclo-octene.

The product from the oxidation of 1-methylcyclohexene was identified as 2-methylcyclohexanone by g.l.c., <sup>1</sup>H n.m.r., and i.r. analysis (comparison with an authentic sample).

The crude product from the oxidation of cholesteryl acetate was separated by preparative t.l.c. (Kieselgel HF<sub>254</sub>; chloroform-hexane). This gave starting material (52%), the epoxide as a solid (42%), and triol monoacetate

(6%). Each compound was identified by t.l.c. comparison with authentic samples. The first two products also had satisfactory <sup>1</sup>H n.m.r. spectra.

The product from one oxidation of  $\alpha$ -methylstyrene was analysed by g.l.c. and by <sup>1</sup>H n.m.r. and i.r. spectroscopy (comparison with authentic samples). It contained  $\alpha$ -methylstyrene (27%),  $\alpha$ -phenylpropionaldehyde (21%), and acetophenone (13%). The last was isolated as the 2,4-dinitrophenylhydrazone. Treatment of  $\alpha$ -methylstyrene in methylene chloride at 40 °C with CPBA for 2 h also gave a mixture of  $\alpha$ -methylstyrene oxide,  $\alpha$ -phenylpropionaldehyde, and acetophenone.

The product from 4-methoxycarbonylcyclohexene contained (g.l.c. analysis on the SE30 column) the *cis*- and *trans*-epoxides in a ratio of 31 : 69 when 2 mol. equiv. of resin peroxy-acid were used (Table 4), and a ratio of 29 : 71 when 4.5 mol. equiv. were used (Table 3). The same substrate in THF reacted with CPBA at 40 °C to give a 40% yield of epoxides with a *cis* : *trans* ratio of 31 : 69. A similar reaction at 0 °C gave the epoxides in the ratio 30 : 70. Authentic samples of the two epoxides were not available and the g.l.c. peaks were assigned by assuming that the major product (which had the shorter retention time) was the *trans*-isomer. Previous workers using silicone columns found this to be the case.<sup>16</sup> The product from 4-carboxycyclohexene was methylated (diazomethane) prior to g.l.c. analysis. The *cis* : *trans* ratio was 33 : 67.

The product from 3-acetoxycyclohexene contained (g.l.c. analysis on the SE30 column) two epoxides in approximately equal amounts. The product from 3-hydroxycyclohexene, analysed similarly, contained two epoxides in the ratio 91 : 9, the major isomer having the shorter retention time. As authentic samples of the two epoxides were not available the peaks could not be assigned unambiguously.

The product from norbornene was analysed by g.l.c. (SE30 column). Kwart and Takeshita<sup>21</sup> also used a silicone column. Only one epoxide peak was obtained under various operating conditions. It had a retention time the same as that of authentic *exo*-epoxide. The <sup>1</sup>H n.m.r. spectrum of the crude product by comparison with that of authentic *exo*-epoxide, indicated that this epoxide was the major, if not the only product. A similar result was obtained when norbornene was treated with CPBA in THF. The yield of epoxide was 80%.

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[5/2027 Received, 17th October, 1975]

<sup>23</sup> L. S. Silbert, E. Siegel, and D. Swern, *J. Org. Chem.*, **1962**, **27**, 1336.