

and XVI showed the following physical constants: yellow powder. mp 55—65° (decomp.). Mass Spectrum: Calcd. for C₁₆H₁₄S: 238, Found: 238 (M⁺), 223 (M⁺-CH₃), 146 (M⁺-CH₃, C₆H₅). NMR (CDCl₃) δ: 6.90—7.70 (11H, m, aromatic H), 2.30 (3H, broad s, CH₃). UV λ_{max}^{EtOH} mμ (log ε): 244 (4.06), 322 (3.53) in a long tail curve. Compared with the isomeric compound (XIV), the structure of XVI was established by its appearance, mass and NMR spectra, and especially by the ultraviolet (UV) spectrum having a characteristic absorption curve. Incidentally, the NMR spectrum does not show the doublet bands of the proton at C-3 in an olefinic region of the ylidic structure in XVI. All new compounds had satisfactory analytical data to support the assignment.

Further studies on the syntheses and reactivities of compounds (XVII) and also on the application of S-alkylthiabenzenes to the medicinal chemistry are now in progress.

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Received June 27, 1974

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[Chem. Pharm. Bull.]
22(11):2757—2758 (1974)

UDC 547.91.04 : 546.215.04

The Preparation and Chemical Reactions of a Peracid Resin

Recent reports from several laboratories have shown the advantageous application of solid phase synthesis¹⁾ to general organic reactions.²⁾ Two groups,^{3,4)} already reported that peracid resins were prepared from cation exchangers and applied to epoxidation of double bonds, however, the peracid resins require some improvements with regard to both stability and reactivity.⁵⁾ We now report the preparation of a new peracid resin and its application to some chemical reactions.

A carboxylic acid resin (I) prepared from styrene-divinylbenzene (2%) copolymer⁶⁾ was oxidized with 87% hydrogen peroxide and methanesulfonic acid in an ice-bath to yield a peracid resin (II; peracid content, 3.06 mmole/g). The resin (II), when it is stored in a brown-bottle at room temperature, is practically stable.⁷⁾

Oxidation reactions with II were smoothly carried out in dioxane or methanol. Chloroform and dichloromethane, which are usually used in *m*-chloroperbenzoic acid (III) oxidation, are unsuitable, probably because they have little activity of swelling the resin (II). Some results are shown in Table I. The resin (II) has sufficient reactivity for practical purposes.

Compared with the reported results on epoxidation with polypermethacrylic acid (IV),⁴⁾ No. 4 and 5 in the table show that the reactivity of II has been considerably improved. When

1) R.B. Merrifield, *J. Amer. Chem. Soc.*, **85**, 2149 (1963).

2) For a review see, C.G. Overberger and K.N. Sannes, *Angew. Chem. internat. Edit.*, **13**, 99 (1974).

3) F. Helfferich and D.B. Luten, *J. Appl. Polymer Sci.*, **8**, 2899 (1964).

4) T. Takagi, *Polymer Letters*, **5**, 1031 (1967).

5) The half-life time of peracid resins prepared from bifunctional cation exchangers is only 2 days.³⁾ Polypermethacrylic acid (IV) can be stored at 0—5° for 2 months without substantial loss of its oxidation capacity, however, at 25° 20% of active oxygen was lost after 60 hr.⁴⁾

6) R.L. Letsinger, M.J. Kornet and V. Manadevan, *J. Amer. Chem. Soc.*, **86**, 5163 (1964).

7) Decomposition of peracid after 2 months storage was less than 1.5%.

TABLE I. Oxidation Reactions with Peracid Resin (II)

No.	Substrate	Peracid (II) Mol. eq.	Solvent ^{a)}	Temp. (°C)	Time (hr)	Product	Yield (%)
1	N,N-Dimethylaniline	1.1	M	0	1	N-oxide	q ^{b)}
2	Nicotine	1.1	M	rt ^{c)}	9	mono-oxide dioxide	37 32
3	Nicotinic acid	1.5	M	rt	24	N-oxide	q
4	Styrene	2.0	D	40	11	epoxide	q
5	<i>t</i> -Stilbene	2.0	D	40	30	epoxide	q
6	Triphenylethylene	2.0	D	40	60	epoxide	81
7	Tetraphenylethylene	2.0	D	40	60	epoxide	26
8	Cholesteryl acetate	2.0	D	rt	26	epoxides $\alpha: \beta = 2:1$	q
9	Undecylenic acid	2.0	D	40	11	epoxide	q
10	Thioanisole	1.1	M	0	0.6	sulfoxide sulfone	86 ^{d)} 14

a) M=methanol, D=dioxane b) q=quantitative yield c) rt=room temperature d) relative yield

substrates have carboxyl groups, it is usually difficult to isolate oxidation products free from contamination due to reagents. In oxidation with II, just filtration gives almost pure products (No. 3 and 9). This is one of principal advantages of II.

On the other hand, an attempted selective α -epoxidation of cholesteryl acetate, expected from the bulkiness of the reagent, was unsuccessful and a result similar to that in oxidation with III was obtained (No. 8). Stepwise oxidation of nicotine (No. 2) and thioanisole (No. 11) was also quite difficult.

Although the peracid resin (II) has some defects for selective oxidation, it can be expected to be a useful reagent in synthetic organic chemistry, because of its sufficient reactivity and stability. Finally, in these experiments the recovered carboxylic acid resin (I) could be easily recycled to the peracid form (II).

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Received July 15, 1974

[Chem. Pharm. Bull.]
22(11)2758-2761(1974)

UDC 547.91.02 : 581.192

Pterosin Q und Pterosid Q aus *Pteris oshimensis* HIERON. und *Histiopteris incisa* (THUNB.) J. SMITH¹⁾

In Fortführung unserer chemischen und chemotaxonomischen Untersuchungen der Gattung *Pteris*, analysierten wir *P. oshimensis* HIERON. (jap. Name: Hachijoshidamodoki). Die oberirdischen Teile dieser Pflanzen wurden mit Methanol heiss extrahiert und der Extrakt

1) Chemische und chemotaxonomische Untersuchungen der Gattung *Pteris* und der verwandten Gattungen V. Mitteil., IV. Mitteil.: T. Murakami, T. Satake, M. Tezuka, K. Tanaka, F. Tanaka und C.M. Chen, *Chem. Pharm. Bull.* (Tokyo), 22, 1686 (1974).