bonding, and a sensitive and simple method to know the relative strength of bases in organic solvent. This method is quite simple and should be useful for the system composed of both weak acid and base, especially for those where infrared spectroscopic method is not applicable because of overlapping of the absorption band caused by addition of organic base.

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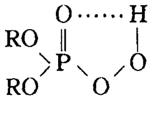
New Methods and Reagents in Organic Synthesis. 15.[1] Epoxidation of Olefins with Diethyl Phosphorocyanidate (DEPC) and Hydrogen Peroxide

A mixture of diethyl phosphorocyanidate (DEPC) and hydrogen peroxide in the presence of 2-hydroxypyridine or 1,2,4-triazole functions as an epoxidizing agent for olefins.

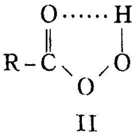
Keywords——diethyl phosphorocyanidate; hydrogen peroxide; epoxidation; 2-hydroxypyridine; 1,2,4-triazole; peroxyphosphoric acid

Recent efforts of our laboratories have unveiled that diethyl phosphorocyanidate (DEPC, $(C_2H_5O)_2P(O)CN$)[2] plays a role of a condensation-dehydration reagent[3] as well as a cyanation reagent.[4] Our continuing interest on the synthetic use of DEPC has led us to develop a new method for the epoxidation of olefins[5] using DEPC.

We have conceived that the action of DEPC on hydrogen peroxide would produce diethyl ester of peroxyphosphoric acid (Ia) which would have an epoxidizing power since it is isosteric to peroxycarboxylic acid (II). The only peroxyphosphoric acid ever known is peroxymonophosphoric acid (Ib)[6] which has been reported to epoxidize *trans*-stilbene.[7] However, its preparation is rather tedious and it is so acidic as to be apt to proceed the reaction further.

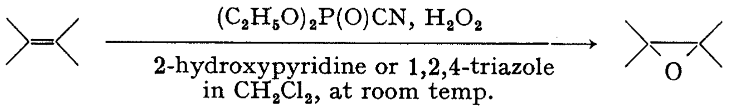


Ia: $R=C_2H_5$
Ib: $R=H$



II

We now wish to report that a mixture of DEPC and hydrogen peroxide smoothly epoxidizes olefins at room temperature in the presence of 2-hydroxypyridine or 1,2,4-triazole in methylene chloride solution:



A Typical Experimental Procedure for the New Epoxidation is as follows

Method A——To a stirred mixture of an olefin (2 mmol) and 2-hydroxypyridine (380 mg, 4 mmol) in methylene chloride (10 ml) was added 20% anhydrous ethereal solution of hydrogen peroxide[8] (2 ml) under nitrogen, followed by the addition of DEPC (652 mg, 4 mmol) in methylene chloride (5 ml). The mixture was stirred at room temperature for 3 hr. After dilution with ethyl acetate–benzene (2: 1, 100 ml) or methylene chloride (150 ml), the mixture was successively washed with 40 ml portions of saturated aqueous sodium bicarbonate, water, 10% aqueous citric acid, water, and saturated aqueous sodium chloride. Drying over sodium sulfate followed by evaporation of the solvent afforded the crude epoxide which was purified by column chromatography on silica gel (Mallinckrodt Silic AR CC-7 special or Merck silica gel No. 7734).

Method B——When 1,2,4-triazole was used as an additive, 4 equivalents of the triazole and 2 equivalents of DEPC were used together with 9.5% anhydrous *tert*-amyl alcohol solution of hydrogen peroxide[9] (4 ml) and the reaction time was 2 hr.

No epoxidation occurred without DEPC. Addition of 2-hydroxypyridine or 1,2,4-triazole was not essential, but the yield of the epoxides severely decreased when the epoxidation was conducted without one of these. Although pyrazole or 1,2,3-benzotriazole effected similarly, imidazole, 3,5-dimethylpyrazole, 1,5-diazabicyclo[5.4.0]undec-5-ene, or 8-hydroxyquinoline showed no or little effect on epoxidation. Methylene chloride seemed to be a solvent of choice.

TABLE I. Epoxidation of Olefins with DEPC/H_2O_2

Run	Olefin	Epoxidation method[a]	Isolated yield (%) of epoxide
1	*trans*-Stilbene	A	66 (89)[b]
2	*trans*-Stilbene	B	59 (82)[b]
3	Cyclododecene	A	84
4	Cyclododecene	B	85
5	1-Dodecene	A	61 (76)[b]
6	Geranyl acetate	A	35
7	Linalool	A	76
8	Cholesteryl acetate	A	90
9	Cholesteryl acetate	B	93
10	Isophorone	A	Trace[c]

[a] Epoxidation was carried out as in the text.
[b] Allowing the recovery of the starting olefin.
[c] Recovery yield of the enone was 75%.

The results are summarized in Table I. Various olefins were epoxidized in good yields. *trans*-Stilbene and 1-dodecene which are less susceptible to electrophilic attack of peroxycarboxylic acids (II)[10] smoothly underwent the new epoxidation reaction. Although geranyl acetate upon the epoxidation afforded a mixture of the 2,3-epoxide (2%) and the 6,7-epoxide (33%), linalool mainly afforded the 6,7-epoxide under similar reaction conditions. Cholesteryl acetate furnished a mixture of α- and β- epoxides. Since isophorone containing a conjugated double bond did not give almost any epoxidation product, the new epoxidation procedure will be specific to isolated double bonds.

The Baeyer–Villiger oxidation also occurred when bicyclo[3.2.0]hept-2-en-6-one (III)$^{11)}$ was treated with a mixture of DEPC (4 eq) and hydrogen peroxide (4 eq) in methylene chloride at 0° for 1 hr and then at room temperature for 6 hr, giving a mixture of 2-oxabicyclo[3.3.0]-oct-6-en-3-one (IV, 11%),$^{11,12)}$ the *cis-syn-cis* and *cis-anti-cis* oxido lactones (Va, 21%; Vb, 50%).$^{12)}$ The γ-lactone (IV) afforded a mixture of Va and Vb in 79% yield under similar reaction conditions. The ratio of Va to Vb was 0.68 in contrast with the epoxidation result using *m*-chloroperoxybenzoic acid (Va/Vb=2.3).$^{12)}$

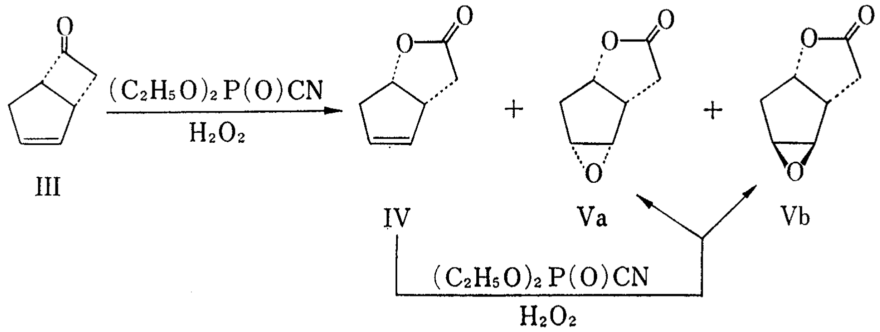


Chart 1

Although it should be still investigated whether the real reactive species is diethyl ester of peroxyphosphoric acid (Ia) or not,$^{13)}$ a combination of DEPC and hydrogen peroxide in the presence of 2-hydroxypyridine or 1,2,4-triazole provides a new epoxidation procedure for olefins.

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