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NEW EPOXIDATION REAGENTS DERIVED FROM ALUMINA AND SILICON

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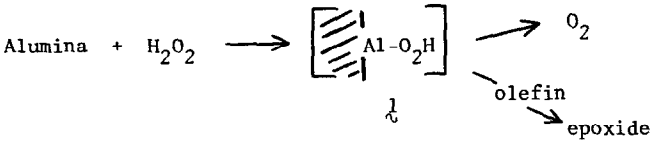
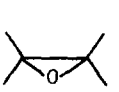
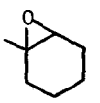
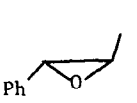
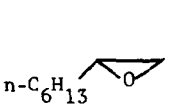
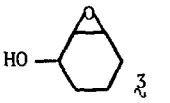
Summary: Hydrogen peroxide or tert butyl hydroperoxide in contact with basic alumina will epoxidize olefins. Triphenylsilyl hydroperoxide behaves similarly to peracids toward olefins, ketones and allylic alcohols.

The altered reactivity observed with many reagents when in contact with chromatographic adsorbents has led us to examine the activity of H_2O_2 on alumina. This system was carefully described by Leffler[1] who found that surface-bound hydroperoxides, e.g. 1, are formed rapidly, then disappear slowly as oxygen is evolved. We find that the intermediates can be intercepted by olefins to yield epoxides.



Typically, .5 ml of 90% H_2O_2 was added to a stirred slurry of 5 g alumina (Woelm Basic, Activity I) in 10 ml dry ether containing 1 mmol olefin. The yields (gc, nmr) of epoxides after several hours at ambient temperature were low (Table), but control experiments established that this was largely due to their further reactions with the surface.[2] The substitution of tert butyl hydroperoxide for H_2O_2 gave similar results, as did minor variations in procedure.

Epoxidation Yields from Corresponding Olefins

Reagent					
Alumina/H_2O_2	40	12	8%	< 1	-
Alumina/Me_3C-O_2H	27	11	27	-	-
Ph_3Si-O_2H	70	70	89	64	77

A preparatively useful reagent for epoxidation was found in the crystalline[3] silyl hydroperoxide 2. Yields reported in the table were obtained when 2 (2 equiv., based on titrated active oxygen content) was added to 1 mmol olefin in 5 ml CH_2Cl_2 followed by stirring at 25° for 1 day. Like peracids, 2 shows little preference for cis vs. trans stilbenes in epoxidations, gives high (19:1) syn/anti epoxidation of 3 and converts cyclopentanone to δ-valerolactone (56%).

Ho[4] has recently reported that Me_3SiCl in the presence of H_2O_2 converts olefins to chlorohydrins in high yield. Our results with 2 confirm Ho's suggestion that silyl hydroperoxides can indeed epoxidize olefins, and implicate epoxide intermediates in his procedure.

$Ph_3Si\text{-}O_2H$

2

REFERENCES

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2. G. Posner, Angew. Chem. Internat. Ed., 17, 487 (1978).
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4. T.-L. Ho, Syn. Commun., 9, 37 (1979).
5. This research was supported by the National Institutes of Health.

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