Stereospecific Conversion of Olefins into Aziridines by *p*-Tolylsulphonylhydroxylamine

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Summary The reactions of *O*-*p*-tolylsulphonylhydroxylamine with olefins proceed stereospecifically to give aziridines in moderate to high yield

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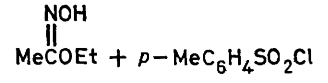
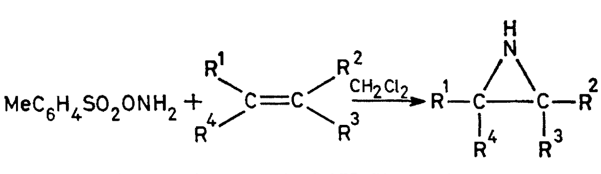
The stereospecific conversion of olefins into epoxides using peroxy acids has been known for more than half a century, but to date no analogous conversion of olefins into aziridines has been devised The peroxy acid analogue, *O*-*p*-tolylsulphonylhydroxylamine,[1] has proved capable of effecting such a transformation and typical olefins have been transformed into their corresponding aziridines in moderate to high yields In addition, the reaction rates appear to be highly dependent on the number of substituents on the olefin, as is the case with the reaction of olefins with peroxy acids [2]

O-*p*-Tolylsulphonylhydroxylamine was prepared by reaction of ethyl acetohydroximate[3] with toluene-*p*-sulphonyl chloride in dimethylformamide (DMF), followed by hydrolysis of the resulting product in 70% perchloric acid [equation (1)] [4] The reagent was extracted into methylene chloride and used in solution, as it is very unstable In a typical run, the reagent (*ca* 6 mmol) was stirred with the olefinic substrate (3 mmol) in 5 ml of CH_2Cl_2 until the starch–iodine test for *O*-*p*-tolylsulphonylhydroxylamine was negative (usually 12—24 h) [equation (2)]



$$\overset{\text{NOH}}{\overset{\|}{\text{MeCOEt}}} + p\text{-MeC}_6\text{H}_4\text{SO}_2\text{Cl} \xrightarrow{\text{Et}_3\text{N}} \xrightarrow{\text{DMF}} \xrightarrow{70\%\,\text{HClO}_4} p\text{-MeC}_6\text{H}_4\text{SO}_2\text{ONH}_2$$

(1)



(2)

Commercial cyclododecene was converted into the corresponding aziridine in 90% yield by this method, *cis*- and *trans*-di-isopropylaziridine (m p s 64 and 12 °C, respectively) were obtained in 30% yield from *cis*- and *trans*-di-isopropylethylene, respectively, and 2-decylaziridine was obtained in 30% yield from dodec-1-ene The stilbenes did not react to give appreciable quantities of aziridines Mixing of *O*-*p*-tolylsulphonylhydroxylamine with 2-methylbut-2-ene resulted in an immediate exothermic reaction with concomitant suppression of the positive starch–iodine test.

Unambiguous i.r., ^{1}H n.m.r., and mass spectra have been obtained for all these aziridines. The spectral data and m.p. of the phenylcarbamoyl derivative of *trans*-di-isopropylaziridine agree with those reported by Hassner and his co-workers.[5]

Owing to the short half-life of the hydroxylamine reagent, unreactive olefins do not give high yields of aziridines. Optimization of yields thus requires further study of other *O*-substituted hydroxylamines which are more stable and yet have the same reactivity toward olefins.

I thank Professor Glenn Berchtold for financial support *via* an N.I.H. grant, and Professor Schrock and his group for samples of pure *cis*- and *trans*-di-isopropylethylene.

(*Received*, 17*th March* 1980; *Com.* 292.)

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