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STEREOCHEMICAL STUDIES ON THE DECOMPOSITION OF AN α-SULFONYL PERESTER*

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In investigations reported from several laboratories α-sulfonyl carbanions generated from optically active precursors have been shown to be capable of maintaining their asymmetry.[1,2,3] The studies on α-sulfonyl free radicals which we wish to describe here were undertaken with the intention of determining the effect of a sulfonyl group on the stereochemistry of an adjacent radical center. Our approach to this problem was to study the stereochemical fate of a sulfone, III, formed by the decomposition of an optically active α-sulfonyl peroxyester, II, a reaction proceeding via the intermediacy of potentially asymmetric α-sulfonyl free radicals.

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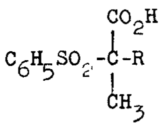
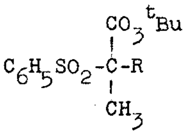
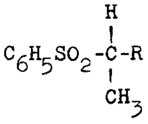

$C_6H_5SO_2\text{-}\overset{CO_2H}{\underset{CH_3}{C}}\text{-}R$


$C_6H_5SO_2\text{-}\overset{CO_3{}^tBu}{\underset{CH_3}{C}}\text{-}R$


$C_6H_5SO_2\text{-}\overset{H}{\underset{CH_3}{C}}\text{-}R$

I R = *n*-C_6H_{13} II R = *n*-C_6H_{13} III R = *n*-C_6H_{13}

IV R = *n*-C_2H_5 V R = *n*-C_2H_5 VI R = *n*-C_2H_5

(+)-2-Benzenesulfonyl-2-methyloctanoic acid, I, $[\alpha]_D^{25}$ +15.5, was prepared by the method of Cram and Wingrove.[2c*] Thionyl chloride (15 ml.) was added to the acid (11.87 g., 3.98 x 10^{-2} mole), and the mixture was refluxed for 3 hours. Excess thionyl chloride was removed by distillation, and the product acid chloride was added to sodium *t*-butylhydroperoxide (6.43 g., 5.74 x 10^{-2} mole) in 250 ml. of ice-cold ether. The resultant mixture was warmed to room temperature and allowed to stand for 17 hours. In the next step it was washed with water (200 ml.), 10°/₀ sulfuric acid (200 ml.), saturated sodium carbonate (200 ml.), and finally again with water (200 ml.). The ethereal solution was then dried over calcium chloride, the ether and excess *t*-butyl hydroperoxide were removed by distillation at reduced pressure, and the *t*-butyl ester of 2-benzenesulfonyl-2-methylperoxyoctanoic acid (13.2 g., 3.56 x

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10^{-2} mole, 90°/₀ crude yield) was obtained. Chromatography of the crude material on Florisil with pentane-ether solvent mixtures yielded 8.83 g. of pure peroxyester, II, $[\alpha]_D^{30}$ +10.9° (chloroform) as an oil.

The decomposition of the optically active peroxyester, II, was first studied under vigorous conditions. The t-butyl peroxyester (0.93 g., 2.5×10^{-3} mole) was dissolved in 15 ml. of cumene, and the mixture was added over a period of 1 hour to 50 ml. of refluxing cumene and then refluxed for 2 1/2 additional hours. The solvent, cumene, was removed by distillation, and chromatography of the residue on a Florisil column using pentane and pentane-ether mixtures gave racemic (less than 5°/₀ optically active) 2-octyl phenyl sulfone, III, (0.127 g., 5.0×10^{-4} mole) which was identical with authentic (±)-2-octyl phenyl sulfone prepared by the decarboxylation of (±)-2-benzenesulfonyl-2-methyloctanoate.*

In another experiment the possibility that optically active III might be obtained if the decomposition of the peroxyester, II, were carried out in the presence of a very good hydrogen donor was explored. The peroxyester, II, (0.93 g., 2.5×10^{-3} mole) was dissolved in 15 ml. of cumene, and this solution was added over a period of one hour to 50 ml. of refluxing cumene containing 4-toluenethiol (1.24 g., 1.00×10^{-2} mole). The mixture was refluxed for

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* For comparative purposes, (+)-2-octyl phenyl sulfone $[\alpha]_D^{25}$ +12.6 was prepared by the decarboxylation of the quinine salt of (+)-2-benzenesulfonyl-2-methyloctanoic acid. A control experiment showed that the optically active sulfone was not racemized by chromatography on Florisil.

2 1/2 hr. more, the cumene was removed by distillation, and the sulfone, III, (0.115 g., 4.5×10^{-4} mole) was isolated by chromatography on Florisil. III was found again to be racemic.

The peroxyester, II, was decomposed photochemically also. A solution of II (1.00 g., 2.7×10^{-3} mole) in 35 ml. of isopropyl alcohol was placed in a reaction tube, the tube was evacuated on a high vacuum line (mercury diffusion pump) and sealed. The sample was then photolyzed through Pyrex with a 450 watt Hg arc Hanovia lamp for 24 hours at room temperature. After photolysis was completed the isopropyl alcohol was removed with a rotary evaporator, and the racemic sulfone, III, (0.076 g., 3.0×10^{-4} mole) was isolated by chromatography.

Although it seemed unlikely to us that racemization of the sulfone, III, occurred after its formation (for example, by hydrogen abstraction reactions), this was a conceivable complication which we wished to check. (±)-2-Benzenesulfonyl-2-methylbutanoic acid, IV, was prepared and then converted to the corresponding _t_-butyl peroxyester, V, by a route analogous to that given for II.* A solution containing the optically active sulfone (+)-III, (1.0 g., 3.94 $\times 10^{-3}$ mole) and the racemic peroxyester, (±)-V, (1.0 g., 3.18 $\times 10^{-3}$ mole) in isopropyl alcohol (35 ml.) was irradiated as described above, and the product mixture was analyzed by preparative vapor phase chromatography on a column of 5% SE 30 silicone gum rubber

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* Satisfactory analytical and spectral data were obtained for V.

on Chromosorb W at 180°. Isolation of the two sulfones, III (0.75 g., 3.0×10^{-3} mole) and VI (0.084 g., 4.2×10^{-4} mole), and measurement of their optical rotations revealed that III had retained its optical activity entirely and that VI was racemic. Hence, racemization of the sulfone, III, is not induced during the decomposition of the peroxyester.

In an attempt to explore the stereochemistry of hydrogen abstraction by the α-sulfonyl free radicals, the decomposition of the optically active peroxyester, (+)-II, was carried out in (-)-menthol. A solution of (+)-II (1.5 g., 4.1×10^{-3} mole) in 25 g. of (-)-menthol was heated at 100° for a period of 48 hr. The resultant mixture was dissolved in pentane and filtered through a Florisil column. The column was then eluted with 500 ml. of ether, the ether solvent was evaporated, and the residue was chromatographed on Florisil with pentane and pentane-ether solvents. The fractions containing the sulfone, III, were combined, and the sulfone (0.073 g., 2.9×10^{-4} mole) was isolated by preparative vapor phase chromatography and found to be racemic.*

Our experiments, thus, all indicate that racemic sulfone, III, is produced from the decomposition of the optically active peroxyester, II. These observations can be explained either by the hypothesis that the intermediate α-sulfonyl free radicals are not asymmetric or that they are asymmetric but do not abstract hydrogen atoms in a stereospecific fashion (or by a combination of these

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* Of course, this does not preclude the possibility that other optically active solvents and other experimental conditions might be found which would give rise to the formation of an optically active product.

hypotheses). This problem and other aspects of the stereochemistry of heteroatom-substituted free radicals are under further investigation in our laboratory.

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