sulfuric acid yielded a 2,4-dinitrophenylhydrazone, m.p. 152–153° (cor.) after recrystallization from aqueous ethanol.

Anal. Calcd. for $C_{17}H_{24}N_4O_5$: C, 56.03; H, 6.64. Found: C, 56.21; H, 6.56.

Reaction of Carvenone and Methanol.—In two attempts to carry out this reaction under the conditions described above for carvone, quantitative recovery of starting material (identified by boiling point, refractive index and semicarbazone) was obtained.

Reduction of VI to VIII.—A solution of VI (0.65 g.) in absolute methanol (10 ml.) was stirred with palladium-on-carbon catalyst (0.5 g.) under hydrogen at room temperature and pressure. The calculated volume for one mole of hydrogen was taken up in 1 hour. After removal of the catalyst by filtration, the solution was concentrated under reduced pressure. A portion of the colorless product yielded a 2,4-dinitrophenylhydrazone which did not show a constant m.p. on repeated recrystallization. The infrared spectrum of a second portion, after distillation through a small Hickman column, appeared to be identical with that of VIII. A third portion (100 mg.) of the product was heated under reflux with a 10% solution of sodium methoxide in methanol for 1 hour. The mixture was poured into water, the organic material extracted into ether, washed with water, dried over magnesium sulfate and concentrated under reduced pressure to a liquid which yielded a 2,4-dinitrophenylhydrazone, m.p. 149–151° (cor.), recrystallized from aqueous ethanol. Admixture with the 2,4-dinitrophenylhydrazone prepared from VIII did not depress this value.

CAMBRIDGE, MASSACHUSETTS

Organic Peroxides. III. The Mechanism of the Reaction of Alkyl Methanesulfonates with Hydrogen Peroxide

BY HOMER R. WILLIAMS AND HARRY S. MOSHER

The sequence of reactions: 2-heptanol → 2-heptyl methanesulfonate → 2-heptyl hydroperoxide → 2-heptanol, has been studied using optically active 2-heptanol. *Dextrorotatory* 2-heptanol was converted by these steps to *levorotatory* 2-heptanol with 90% of the rotation of the starting alcohol. These results clearly establish the reaction of alkyl methanesulfonates with hydrogen peroxide in the presence of base as a typical S_N2 displacement which proceeds by inversion.

A study has been made of the stereochemical course of the reactions involved in the preparation of 2-heptyl hydroperoxide by the action of 2-heptyl methanesulfonate on hydrogen peroxide in the presence of a base. This example was chosen because of the ease of resolution of 2-heptanol[1] and the satisfactory yield obtained in the preparation of 2-heptyl hydroperoxide. Dextrorotatory 2-heptanol (97.5% optical purity) was converted to dextrorotatory 2-heptyl methanesulfonate by the method of Sekera and Marvel[2] in 70% yield. This 2-heptyl methanesulfonate was then converted to levorotatory 2-heptyl hydroperoxide by the method employed for the preparation of the normal and secondary alkyl hydroperoxides,[3] and described in detail in the experimental section. The levorotatory 2-heptyl hydroperoxide was then reduced with lithium aluminum hydride to give levorotatory 2-heptanol.
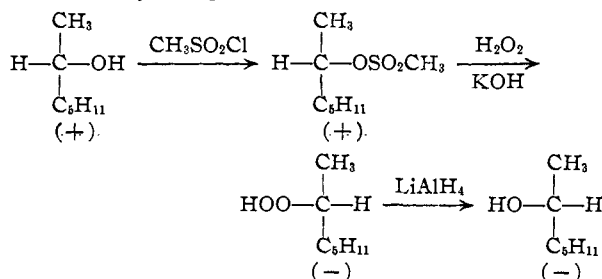
The optical rotation of the final alcohol was opposite in sign and 90% of the starting alcohol. Since there appears to be no reasonable mechanism whereby inversion can occur during the first or last step it follows that the inversion resulted from a backside attack of the hydroperoxy ion on the alkyl methanesulfonate by an S_N2 mechanism.
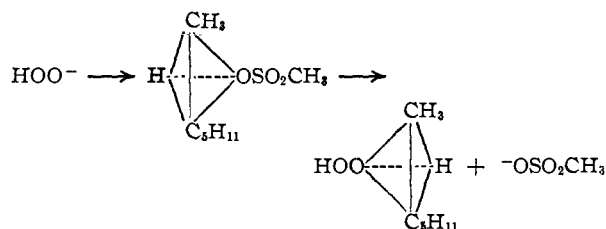
The data show that 95% of the reaction goes by such a mechanism. This reaction is then completely analogous to the established inversion of tosylates by reagents such as the carboxylate and alkoxide ions.[4] It can safely be assumed that the same mechanism operates in the case of the reaction of hydrogen peroxide in basic solution on the *n*-alkyl sulfonates[4] and very probably in the method of Baeyer and Villiger[5] as well. This mechanism is in contrast to the carbonium ion mechanism[6] which undoubtedly operates in the preparation of tertiary hydroperoxides by the action of hydrogen peroxide on tertiary alcohols in the presence of strong acid catalysts.[6,7] The application of both S_N1 and S_N2 reactions to the alkylation of hydrogen peroxide now makes potentially available all types of aliphatic primary, secondary and tertiary hydroperoxides.

(1) R. H. Pickard and J. Kenyon, *J. Chem. Soc.,* **99**, 45 (1911).

(2) V. Sekera and C. S. Marvel, THIS JOURNAL, **55**, 345 (1933).

(3) H. R. Williams and H. S. Mosher, *ibid.,* **76**, 2987 (1954).

(4) R. H. Phillips, *J. Chem. Soc.,* **127**, 2552 (1925).

(5) A. Baeyer and V. Villiger, *Ber.,* **33**, 3387 (1900); **34**, 738 (1901).

(6) D. G. Davies, R. V. Foster and A. M. White, *J. Chem. Soc.,* 1541 (1953).

(7) N. A. Milas, U. S. Patent 2,273,807 (Dec. 3, 1940); N. A. Milas and D. M. Surgenor, THIS JOURNAL, **68**, 205, 643 (1946).

Experimental

The Resolution of 2-Heptanol.—This was accomplished essentially according to the method of Pickard and Kenyon.[1] The (+)-2-heptanol obtained had the following properties: b.p. 149–150°, n^{20}D 1.4204, α^{26}D +4.12° (l = 0.5 dm., neat), d^{25}_4 0.815 as compared with the following reported[2] values: b.p. 150°, n^{20}D 1.4209, d^{20}_4 0.8185, $[\alpha]^{20}$D +10.32°.

Optically Active 2-Heptyl Methanesulfonate.—A mixture of 11.5 g. (0.10 mole) of methanesulfonyl chloride and 11.6 g. (0.10 mole) of (+)-2-heptanol was stirred in an ice-bath while 16.8 g. (0.20 mole) of pyridine was added slowly. After three hours, the mixture was worked up as previously described[4] to give 13.5 g. (70%) of (+)-2-heptyl methanesulfonate, b.p. 77–79° (1 mm.), n^{20}D 1.4338, d^{25}_4 1.027, α^{25}D +20.96° (l = 2 dm., neat).

Optically Active 2-Heptyl Hydroperoxide.—A one-phase reaction mixture was prepared from 12.5 g. (0.065 mole) of optically active 2-heptyl methanesulfonate, 32 g. (0.28 mole) of 30% hydrogen peroxide, 100 ml. of methanol, 8 ml. of water and 8.1 g. (0.072 mole) of 50% aqueous potassium hydroxide, which was added with cooling. The mixture was maintained in a water-bath at room temperature for 24 hours and worked up in the manner previously described[4] to give 2.00 g. (24.5%) of optically active 2-heptyl hydroperoxide, b.p. 39–41° at 0.8 mm., n^{20}D 1.4242, d^{20}_4 0.877, α^{25}D −9.96° (l 2 dm., neat), $[\alpha]^{25}$D −5.66.[8]

The infrared spectrum of this sample was identical to that of the 2-heptyl hydroperoxide previously reported.[4] There was no detectable change in the spectra or the optical rotation after storage for eight months in the dark at 5°. Titration for active oxygen[9] gave the following results. *Anal.* Calcd. for $C_7H_{16}O_2$: O, 12.1. Found: O, 11.45, 11.59, 11.49.

The Reduction of Optically Active 2-Heptyl Hydroperoxide with Lithium Aluminum Hydride.[10]—A suspension of 100 mg. (2.7 moles) of powdered lithium aluminum hydride in 2.5 ml. of ether was cooled while 406 mg. (3.1 moles) of (−)-

2-heptyl hydroperoxide was added slowly in 2.5 ml. of ether. Methanol was then added dropwise until the excess lithium aluminum hydride was destroyed, after which 2 ml. of 10% potassium hydroxide was added. The aqueous layer was extracted twice with 1-ml. portions of ether, and the combined ether fractions were dried over sodium sulfate. The ether was evaporated on a steam-bath to leave 231 mg. (84%) of (−)-2-heptanol, n^{20}D 1.4207, α^{25}D −3.70° (l = 0.5 dm., neat). The infrared spectrum of this product was identical to that of 2-heptanol.

The Platinum-catalyzed Reduction of Optically Active 2-Heptyl Hydroperoxide.—A mixture of 415 mg. (3.14 moles) of (−)-2-heptyl hydroperoxide, 15 mg. of platinum oxide and 1.5 ml. of methanol was stirred at 25° in a hydrogen atmosphere. There was a rapid initial uptake of hydrogen until 50 ml. (64% of the theoretical requirement) was absorbed. The product failed to give a positive test for hydroperoxide. The catalyst was centrifuged from the solution, and the methanol was evaporated to leave 233 mg. (82%) of (−)-2-heptanol, n^{20}D 1.4203, α^{25}D −3.78° (l = 0.5 dm., neat). The infrared spectrum of this sample corresponded with that of 2-heptanol with the exception of a very weak band at 5.85 μ which corresponded to a very strong band of 2-heptanone. That the theoretical amount of hydrogen was not absorbed in this reduction was due to a platinum-catalyzed decomposition of the hydroperoxide[8] as indicated in the following experiment.

Platinum oxide (4.5 mg.) in 0.2 ml. of methanol was reduced in a hydrogen atmosphere over a five-minute period. The platinum suspension was boiled, and the reaction flask was thoroughly flushed with air. Pure 2-heptyl hydroperoxide (200 mg., 1.51 moles) was added in 0.8 ml. of methanol and stirred for 23 hours. At the end of this time, an iodide test for hydroperoxide indicated the presence of only a trace in the reaction mixture. The platinum was removed by centrifugation, and the methanol was boiled off to leave 171 mg. of residue. The infrared spectrum showed absorption maxima at all points corresponding to the spectrum of 2-heptanol. In addition, there was appreciable absorption at 5.85 μ, and there were weak inflections at the other strong absorption points of 2-heptanone. A band at 9.66 μ did not correspond to the spectrum of either 2-heptanol or 2-heptanone. The lithium aluminum hydride reduction method is therefore to be preferred.

STANFORD, CALIFORNIA

---

(8) It is interesting to note that the sign of rotation of the 2-heptyl hydroperoxide is the same as that of the alcohol of the corresponding configuration but the magnitude is approximately one half.

(9) C. D. Wagner, R. H. Smith and E. D. Peters, *Anal. Chem.*, **19**, 976 (1947).

(10) The use of lithium aluminum hydride for the reduction of hydroperoxides has been described previously by D. A. Sutton, *Chemistry and Industry*, 272 (1951).

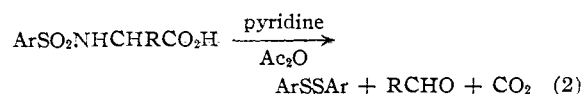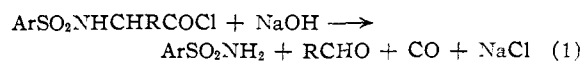# Base-catalyzed Decomposition of Substituted α-(Benzenesulfonamido)-carboxylic Acids and their Acyl Chlorides

BY RICHARD H. WILEY AND RICHARD P. DAVIS[1]

In a continuation of previous studies the pyridine–acetic anhydride decarboxylation of twelve additional α-(arylsulfonamido)-carboxylic acids has been shown to give 33–97% of carbon dioxide, 18–70% of benzaldehyde, 0–7% of arylsulfonamide and 0–49% of aryl disulfide; the aqueous alkaline decomposition of ten additional α-(arylsulfonamido)-acyl chlorides has been shown to give 37–98% of carbon monoxide, 0–58% of arylsulfonamide and 22–80% of benzaldehyde. The unusual reactions involved have been reinterpreted in terms of a cyclic intermediate I for the pyridine decarboxylation and a displacement reaction at the α-carbon atom (reaction 3) for the alkaline decomposition. Both proposals are consistent with effects produced by introduction of electron donor groups at the α-carbon or in the aryl nucleus and with recognized similar effects.

In preceding papers[2,3] we have described two reactions which take place in the base-catalyzed decomposition of α-(benzene- and p-toluenesulfonamido)-phenylacetyl chloride and the related acetic acids. These two reactions are differentiated in that the acyl chlorides decompose when treated with aqueous alkali to give an arylsulfonamide and carbon monoxide (reaction 1) and the acids themselves decompose when heated with pyridine to give an aryl disulfide and carbon dioxide (reaction 2). Aldehydes are obtained from phenylacetic acid (R = C_6H_5) but not from propionic acid (R = CH_3) derivatives.

$$ArSO_2NHCHRCOCl + NaOH \longrightarrow$$
$$ArSO_2NH_2 + RCHO + CO + NaCl \quad (1)$$

$$ArSO_2NHCHRCO_2H \xrightarrow[Ac_2O]{pyridine}$$
$$ArSSAr + RCHO + CO_2 \quad (2)$$

(1) Research Corporation graduate research assistant.

(2) R. H. Wiley and N. R. Smith, THIS JOURNAL, **73**, 4719 (1951).

(3) R. H. Wiley, H. L. Davis, D. E. Gensheimer and N. R. Smith, *ibid.*, **74**, 936 (1952).