Detection of Acetophenone Oxime O-Sulphonic Acid—the True Rearranging Species in the Beckmann Rearrangement in Concentrated Sulphuric Acid

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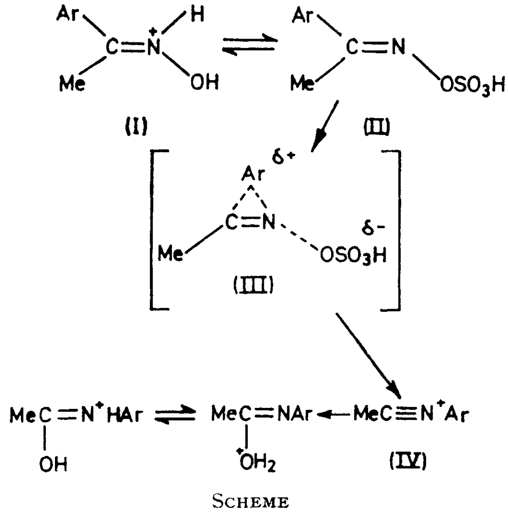
Summary Acetophenone oxime *O*-sulphonic acid was detected by n.m.r. spectroscopy in the Beckmann rearrangement of acetophenone oxime in conc. sulphuric acid.

RECENTLY, Schofield and his co-workers[1] reported that the mechanism of the Beckmann rearrangement of acetophenone oximes (I) in conc. sulphuric acid is described as shown in the Scheme. They detected spectroscopically the *N*-arylnitrilium ion (IV) as an intermediate in the case of *ortho*-substituted acetophenone oximes. They failed to detect any acetophenone oxime *O*-sulphonic acid (II) in 98% sulphuric acid, and (II) was considered to be formed in a fast, reversible step. We now report that in 99·0% sulphuric acid at 60° unsubstituted acetophenone oxime (I; Ar = Ph) rearranges through an intermediate which is readily detected by n.m.r. spectroscopy† and is thought to be the oxime *O*-sulphonic acid (II; Ar = Ph).



SCHEME

In connection with the isotope effect study of the Beckmann rearrangement in concentrated sulphuric acid[2–4] the possibility of hydrolysis of acetophenone oxime to acetophenone during the course of the reaction was examined. A series of ^{1}H n.m.r. spectra of the reaction solution (210 mg of the oxime in 6 ml of 99·0% sulphuric acid) taken at 60° showed not only the absence of hydrolysis[1,5] but also the detailed features of the rearrangement.

The change observed first was the appearance of a new methyl signal at 3·17 p.p.m. together with that of the oxime at 2·88 p.p.m. This is not one of the methyl signals of acetanilide (2·70 and 2·38 p.p.m.) nor that of acetophenone (3·28 p.p.m.). Schofield and his co-workers[1] reported the values of 3·65—3·85 p.p.m. for the chemical shifts of the α-methyl groups of three *ortho*-substituted *N*-arylnitrilium ions in conc. sulphuric acid. The observed

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† ^{1}H n.m.r. spectra were taken with a Varian A60 spectrometer and chemical shifts were p.p.m. values from external Me$_4$Si.

^{1}H n.m.r. spectroscopic data in concentrated sulphuric acid

Species	Chemical shifts and assignment (p.p.m. from external Me_4Si)
Acetophenone oxime (I, Ar = Ph)	2.88 (3H, Me), 7.73 (5H, Ar)
Acetophenone oxime *O*-sulphonic acid (II, Ar = Ph)	3.17 (3H, Me), 7.7 (5H, Ar)
Acetanilide	2.70 and 2.38 (3H, Me), 7.50 (5H, Ar)
N-Acetylsulphanilic acid	2.80 and 2.57 (3H, Me), 7.85 and 8.12 (4H, Ar, AA'BB', *J* 7 Hz)
Sulphanilic acid	7.80 and 8.20 (4H, Ar, AA'BB', *J* 9 Hz)
Acetic acid	2.75 (Me)
Acetophenone	3.28 (3H, Me), 7.65—8.53 (5H, Ar)

difference of 0.5—0.7 p.p.m. is too large to be attributed to a substituent effect and, therefore, the species which shows the methyl resonance at 3.17 p.p.m. should not be the *N*-phenylnitrilium ion. For comparison, acetophenone oxime *O*-sulphonic acid (II, Ar = Ph) was prepared[6] and dissolved in conc. sulphuric acid. The spectrum obtained was similar to that of the reaction solution at an early stage: a small methyl signal at 3.17 and a large one at 2.88 p.p.m., which indicated that most of (II) was hydrolysed to the original oxime. Furthermore, kinetic treatment of n.m.r. intensities of these methyl signals gave a linear plot with $k = 1.9 \times 10^{-4}\,s^{-1}$ when the compound showing an absorption at 3.17 p.p.m. was regarded as a species *before* the rearrangement step. The rate constant agrees closely with the value obtained by the gravimetric method using 2,4-dinitrophenylhydrazine ($k = 1.90 \times 10^{-4}\,s^{-1}$) under the same conditions (2.0 g of the oxime in 60 ml of 99.0% sulphuric acid at 60.00°).[2] In addition, the intensity ratio of the two peaks at 2.88 and 3.17 p.p.m. remained constant at 10 : 1 until 60% of the reaction was completed, after which the peak at 3.17 p.p.m. was too small to be measured accurately. From these results the observed intermediate is concluded to be acetophenone oxime *O*-sulphonic acid (II, Ar = Ph) which is, as Schofield and his co-workers pointed out,[1] in equilibrium with protonated acetophenone oxime (I, Ar = Ph). The reason why the presence of (II) was not detected is not clear but the position of the equilibrium may be sensitive to many factors such as the strength of sulphuric acid, the structure of the oxime, the concentration of the reaction solution, and the temperature applied.

The acetanilide produced was sulphonated quite rapidly under the rearrangement conditions to give *N*-acetylsulphanilic acid, which was hydrolysed slowly to acetic acid and sulphanilic acid. The n.m.r. data are summarized in the Table.

Discussions about the structure of the transition state of the rate-determining step (III) will be published elsewhere[2] in connection with a carbon-14 isotope effect study.

(*Received, September 27th*, 1971; *Com.* 1676.)

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