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α -Hydrogen Exchange in the Reaction of 2-Phenylethyldimethylsulphonium Ion with Base in Aqueous Solution and of 2-Phenylethyltrimethylammonium Ion with Base in Aqueous and Alcoholic Solution*

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α -Hydrogen exchange during the elimination from 2-phenylethyldimethylsulphonium bromide with OD^- in deuterium oxide has been found to be almost complete under certain reaction conditions. The product, trimethylamine, from the analogous reaction of 2-phenylethyltrimethylammonium iodide with either ethoxide ion in ethanol- $\text{O}-d$ or with OD^- in deuterium oxide was found to contain no detectable amount of deuterium above natural abundance.

A mass-spectrometric method for the determination of small amounts of deuterium is described. Doering and Hoffmann¹ measured the deuterioxide-catalysed hydrogen exchange of methyl »onium« salts and found that trimethylsulphonium iodide and tetramethylphosphonium iodide exchange hydrogen very rapidly while tetramethylammonium iodide exchanges hydrogen very slowly. This was explained in terms of *d*-orbital resonance which lowers the energy of the transition state from the phosphonium and sulphonium ions.

It was previously observed^{2,3} that 1,1-dideutero-2-phenylethyldimethylsulphonium bromide with aqueous base exchanges deuterium during elimination. This exchange has now been thoroughly reexamined and it was found that under certain conditions it is almost quantitative.

The α -hydrogen exchange in the reaction of 2-phenylethyltrimethylammonium iodide with ethoxide ion in ethanol- $\text{O}-d$ and with deuterioxide in deuterium oxide solution was also examined; no exchange could be observed. This exchange was studied by mass-spectrometric determination of ratio of masses 60/59 in the trimethylamine collected from the elimination reaction. Any increase of deuterium above natural abundance would increase the ratio 60/59 and indicate that α -hydrogen exchange had occurred during elimination. Mass 60 results from the carbon-13, nitrogen-15 and deuterium content. Thus, only 1 per cent of deuterium in trimethylamine above natural

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abundance would increase mass 60 approximately from 3.7 to 4.7 per cent of mass 59. Since one tenth of this increase could have been determined the analyses were appreciably more accurate than the deuterium analyses by the usually employed »falling drop method« which has an error of about 1 per cent^{1,4}.

RESULTS

1. α -Hydrogen Exchange in the Reaction of 2-Phenylethyldimethylsulphonium Bromide with Hydroxide Ion in Aqueous Solution

In the first series of experiments the reaction of 0.1 M 2-phenylethyldimethylsulphonium bromide with 0.2 M OD⁻ in deuterium oxide at 58.9° was carried to 30% completion. The rate constant amounts to 1.14×10^{-4} sec.⁻¹ mole⁻¹ l at that temperature⁵. The unreacted sulphonium salt was then recovered and reduced with lithium aluminium hydride⁶. A liquid reaction product was obtained. The dominant component was methyl-2-phenylethyl sulphide. The highest mass in the mass-spectrum was 157 corresponding to C₆H₅CH₂CD₂SCD₃. When the elimination was carried out in aqueous solution with hydroxide ion under the same conditions as in deuterated media, the product of reduction of the unreacted sulphonium salt with lithium aluminium hydride had the highest mass 152 corresponding to C₆H₅CH₂CH₂SCH₃. Mass-spectra showed that the extent of α -hydrogen exchange in the sulphonium salt was approximately 99%. The initial sulphonium salt also gave upon lithium aluminium hydride reduction a liquid product with the highest mass 152.

The reduction of 2-phenylethyldimethylsulphonium ion to the methyl-2-phenylethyl sulphide has not been previously reported. The composition of the liquid reduction product-mixture is being investigated.

When 2-phenylethyldimethylsulphonium bromide was dissolved in deuterium oxide and left under the reaction conditions of the elimination without added base for a time corresponding to 30% completion of the reaction, the product of the reduction with lithium aluminium hydride of the regenerated sulphonium salt had the highest mass 152, showing that no exchange occurs without base.

In the second series of experiments the reaction of 0.1 M 2-phenylethyldimethylsulphonium bromide with 0.2 M OD⁻ in deuterium oxide was carried out to completion at 97°C. The reaction time was approximately 150 min.⁵ Dimethyl sulphide was expelled from the reaction solution and collected in a liquid air trap. After purification the mass-spectra were recorded. The main and the highest mass was 68 corresponding to S(CD₃)₂. Masses 63, 67, 66, 65, 64, 63, and 62 were measured and the relative magnitudes determined as 721, 94, 212, 20, 7, 4, and 19. From these data it was calculated that dimethyl sulphide contained approximately 88% of deuterium. In the first series of experiments the exchange was much higher (99%) because in the recovered sulphonium salt an accumulation of deuterium took place.

In the third series of experiments the reaction of 0.1 M 2-phenylethyldimethylsulphonium bromide and 0.2 M OD⁻ in deuterium oxide was carried out at 71° to completion. The rate constant⁵ at 70.70° amounts to 4.32×10^{-4} sec.⁻¹ mole⁻¹ l. Styrene was collected in the liquid air trap. Dimethyl sulphide was removed *in vacuo* and styrene distilled under reduced pressure. The

highest mass found in the mass-spectrum of styrene was 106, corresponding to $C_6H_5CH=CD_2$. In undeuterated aqueous media, blanks showed that the highest mass was 104.

2. *α*-Hydrogen Exchange in the Reaction of 2-Phenylethyltrimethylammonium Iodide with Base

In the first series of experiments the reaction of 0.1 *M* 2-phenylethyltrimethylammonium iodide and 0.2 *M* OD^- in deuterium oxide was carried out to completion and trimethylamine collected in a liquid air trap and purified. Mass-spectra of trimethylamine showed that the ratio of masses 60/59 remained practically equal to the ratio of the same masses in trimethylamine collected from the reaction in aqueous undeuterated media.

In the second series of experiments the reaction of 0.04 *M* 2-phenylethyltrimethylammonium iodide and 0.14 *M* ethoxide ion in ethanol-*O-d* at 45° was carried out to completion. The rate constant at 40.0° amounted to 5.2×10^{-4} sec.⁻¹ mole⁻¹ l. The reaction time for 99% completion of the reaction was calculated for 40.0°. The ratio of masses 60/59 in the collected trimethylamine was compared with the same ratio in trimethylamine collected from the reaction in undeuterated media under the same conditions. All ratios obtained in both series of experiments were also compared with that of commercial trimethylamine. A slight decrease of the ratio of masses 60/59 was observed in the trimethylamine from ethanol-*O-d* solution. It was probably caused by impurities in ethanol-*O-d*. The results are given in Table I.

TABLE I

Mass 60/59 Ratio in Trimethylamine Determined by Mass-spectrometry

A. From the reaction of 0.1 <i>M</i> PhCH ₂ CH ₂ N(CH ₃) ₃ I at 97° with:	Masses 60/59 × 100
0.2 <i>M</i> OH ⁻ in H ₂ O	3.73
0.2 <i>M</i> OD ⁻ in D ₂ O	3.76
B. From the reaction of 0.04 <i>M</i> PhCH ₂ CH ₂ N(CH ₃) ₃ I at 45° with:	
0.14 <i>M</i> EtO ⁻ in EtOH	3.77 ^a
0.14 <i>M</i> EtO ⁻ in EtOD	3.59 ^b
commercial N(CH ₃) ₃	3.73 ^c
theoretical ratio	3.78

^a Average of: 3.73 and 3.81

^b Average of: 3.59 and 3.58

^c Average of: 3.77, 3.71, 3.80 and 3.67

It can be concluded that no *α*-hydrogen exchange occurs in the reaction of the ammonium salt.

DISCUSSION

Doering and Hoffmann¹ found a small deuterium exchange of 1.13% in 0.3 *M* tetramethylammonium iodide with 0.3 *M* deuterioxide in deuterium oxide solution after 358 hours at 100°. We could not find a measurable exchange in trimethylamine collected during elimination from the 2-phenylethyltrimethylammonium salt. It is very likely that the exchange of the *α*-methylene-groups of the ammonium salt during elimination is also

negligible since the phenyl group should not have an important influence on the acidity of these hydrogens. The total reaction time of the elimination in aqueous solution at 97° was approximately 60 hours and in alcoholic solution at 45° approximately 14 hours. These conditions were milder than those of Doering and Hoffmann.

Analogous mass-spectrometric measurements make possible the study of β -hydrogen exchange in the »onium« salts during elimination.

EXPERIMENTAL

Materials

2-Phenylethyldimethylsulphonium Bromide

The preparation was described earlier⁵.

Anal. C₁₀H₁₅BrS (247.21) calc'd: Br. 32.33% found: Br. 32.56%

2-Phenylethyltrimethylammonium Iodide

A batch previously prepared and analysed was used⁷.

Ethanol-O-d

The procedure of Salas and Wilson was applied⁸. The deuterated alcohol contained about 3% of deuterium oxide which was not removed.

Regeneration of the Unreacted 2-Phenylethyldimethylsulphonium Salt

To the reaction solution solid silver nitrate was added which removed the base and also precipitated bromide ions. The precipitate was filtered off and styrene extracted with ether. Deuterium oxide was evaporated *in vacuo* and the sulphonium salt dried in a vacuum desiccator.

Reduction of 2-Phenylethyldimethylsulphonium Bromide

2-Phenylethyldimethylsulphonium bromide was reduced with two molar excess of lithium aluminium hydride in refluxing ether during 3 hours. The procedure of Amundsen and Nelson⁶ was further applied. Ether was removed *in vacuo* and the remaining liquid distilled under reduced pressure. The product, predominantly methyl-2-phenylethyl sulphide, was then introduced into the mass-spectrometer.

Collection and Purification of Dimethyl Sulphide Samples

To the reaction vessel immersed in a water-bath held at 97° a condenser was attached to hold back most of the water vapour. Nitrogen, purified by passage through Ascarite and sulphuric acid, was bubbled through the reaction solution to expel the dimethyl sulphide which was collected in a liquid air trap. Purification of dimethyl sulphide samples was carried out as previously described⁵.

Collection and Purification of Trimethylamine Samples

Trimethylamine was expelled from the reaction vessel in the same way as dimethyl sulphide. When the elimination from the 2-phenylethyltrimethylammonium iodide was carried out in alcoholic media trimethylamine expelled with nitrogen contained appreciable quantity of ethanol. A washing bottle with concentrated sodium hydroxide kept at 70° held back ethanol. Trimethylamine freed from alcohol was then trapped in liquid air trap. It was further purified in a vacuum line analogously to dimethyl sulphide⁵, except that calcium oxide was used for drying (instead of phosphorous pentoxide used for drying of dimethyl sulphide).

Mass-spectrometry

A Niers's type mass-spectrometer with a resolution of 1:350 was used⁹.

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IZVOD

Izmjena α -vodika u reakciji 2-feniletildimetilsulfonijeva iona s bazom u vodenoj otopini i 2-feniletiltrimetilamonijeva iona s bazom u vodenoj i alkoholnoj otopini

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Nađeno je da je izmjena α -vodika u reakciji eliminacije 2-feniletildimetilsulfonijeva bromida sa OD⁻ u teškoj vodi pod određenim uvjetima gotovo potpuna.

Također je ustanovljeno da u analognoj reakciji 2-feniletiltrimetilamonijevog jodida sa etoksi ionom u etanolu-O-d, odnosno sa OD⁻ u teškoj vodi, reakcioni produkt trimetilamin, ne sadrži deuterija iznad prirodnoga sadržaja, što znači da u reakciji amonijeve soli ne dolazi do izmjene α -vodika.

Opisana je također metoda spektrografije mase za određivanje malih količina deuterija.

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