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THE REARRANGEMENT OF 1-NAPHTHYL SULPHAMIC ACID TO 1-NAPHTHYLAMINE-4-SULPHONIC ACID

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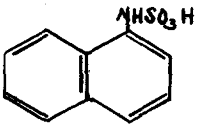
The rearrangement of 1-naphthylsulphamic acid (I) to 1-naphthylamine-4-sulphonic acid (II) has been a controversial subject. An initial report[1] that (I) rearranged to compound (II) on heating was quickly disproved[2]. Shilov[3] then reported that heating the sodium salt of (I) with 1-naphthylamine and sulphuric acid yielded both the 1,2-isomer (III), 60% and the 1,4-isomer (II), 7%. However, compound (II) could arise[4] by sulphonation of the 1-naphthylamine present. We now report the transformation of compound (I) to (II) under conditions where 1-naphthylamine is not sulphonated. We have examined the mechanism of this rearrangement using radio-labelling and find evidence for a substantial intramolecular contribution to the process.

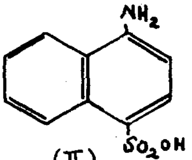
Twin sealed ampoules containing equimolar quantities of (I) (sodium salt) and concentrated sulphuric acid in dry dioxane were maintained at the appropriate temperatures and times and were then cooled and broken. The contents of one such ampoule were diluted with water and analysed for sulphate. The contents of the other ampoule were added to ethanol and the 1,4-acid (II) crystallised out. The identification of the acid (II) was based on the identity of its i.r. and n.m.r. spectra and S-benzylthiouronium derivative (m.p. 96-98°) with authentic samples.

The corresponding spectra and S-benzylthiouronium salts of the acid (III), S-benzyl derivative, m.p. 183-184° and of starting material (I) S-benzyl derivative, m.p. 141-143°, were markedly different from those of compound (II). The yields of sulphate (formed in excess of the sulphuric acid already present) and of (II) with various reaction times were as follows ; 20 minutes: SO_4^{-2}, 77%; (II), 5.4%; 100 minutes: SO_4^{-2}, 59%; (II) 23.4%; 24 hours : SO_4^{-2}, 35.3%, (II), 44.4% ; 55 hours: SO_4^{-2}, 29%, (II) 42.2%. Samples of the crude crystalline material obtained in each ampoule, in each run, were also subjected to thin-layer chromatographic analysis. Compounds (I) (R_f, 0.46), (II) (R_f, 0.34), (III) (R_f, 0.40) and 1-naphthylamine

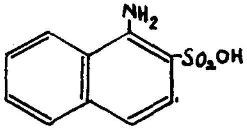
(Rf, 0.80) were separated on Silica Gel – PF_{254} (250 mμ, air-dried overnight) using an n-butanol-water-ethanol (23:2:1 v/v) solvent system. However no chromatographic evidence for the formation of any compound (III) was obtained in any run.



(I)



(II)



(III)

These product runs reveal that compound (I) can be converted into the isomeric material (II) in reasonable yield, - but at a continuously falling rate. The data show a reasonable correlation between sulphate consumed and sulphonic acid formed. The following additional experiments are also relevant. The standard reaction mixture (in twin ampoules) was maintained for 20 minutes at room temperature, one ampoule was treated with concentrated NH_4OH solution until basic and was then analysed for sulphate. The contents of the other ampoule were dissolved in warm water and analysed for sulphate. Unreacted sulphamate did not hydrolyse under the first (basic) conditions and did under the second (acidic) conditions, so that the difference in the sulphate formed represented unreacted sulphamate. After 20 minutes at room temperature 33% of starting sulphamate (I) remained in the reaction medium whereas after 20 minutes at 100° none remained. Therefore whatever is slowly producing the 1,4-substituted compound (II) during the reaction cannot be the sulphamate (I). It could possibly[5] be the N-disubstituted acid $C_{10}H_7N(SO_3H)_2$ but the hydrolysis tests which established the non-survival of sulphamate also attest to the absence of an N,N-disulfonic acid.

We established that 1-naphthylamine did not undergo appreciable sulphonation under our reaction conditions over 55 hours[6]. Thus, whatever is generating the 1,4-compounds does not appear to be free naphthylamine and sulphuric acid. The remaining alternative is that the species generating compound (II) is probably a multiply sulphonated-1-naphthylamine acid[7] which both desulphonates to form (II) and can also resulphonate the available 1-naphthylamine. Such reactions have some precedent[3].

We next examined the rearrangement of (I) using two kinds of radiolabelling technique, namely rearrangement of unlabelled (I) in dioxane containing S^{35}-labelled H_2SO_4, and secondly reaction of radiolabelled (I) in an unlabelled H_2SO_4 medium. The relevant data are summarised in the Table.

TABLE 1 : Radiochemical Results

Reaction Time (hours)	Compound Counted	Specific Activity[a] (cpm/mmole x 10^{-6}) Na^+	NH_4^+	S^+	% Exchange Exper.	Theor.[b]
1.66	1-naphthylamine-4-	1.26	-	-	34.3	51.7
	sulphonic acid[c]	1.12	-	-	30.4	51.7
24	,, [c]	-	1.18	1.19	32.3	,,
55	,, [c,d]	0.26	-	-	30.8	,,
55	1-naphthylamine-4-sulphonic acid[e]	0.0028	-	-	0.33	
24	1-naphthylamine-4-	-	0.054[f]	-	68.3	50
	sulphonic acid	-	0.035[g]	-	68.6	-

[a] Sulphonic acids were counted as their sodium (Na^+), Ammonium (NH_4^+) or S-benzylthiouronium salts (S^+) using the counting procedure described previously[illegible]. [b] For a 1 : 1 molar ratio of sulphamate (I). $1H_2O$ to radiosulphuric acid, this theoretical figure is based on rapid and 77% pooling of sulphate. With labelled anhydrous starting sulphamate, this 51.7 becomes 50. [c] Product isolated from rearrangement runs using unlabelled (I) and $^{35}S-H_2SO_4$ of specific activity 3.69 x 10^6 cpm/mmole. [d] Product isolated using a $^{35}S-H_2SO_4$ of specific activity 8.44 x 10^5 cpm/mmole. [e] Product from a run using unlabelled (II) and $^{35}S-H_2SO_4$ of specific activity 8.44 x 10^5 cpm/mmole. [f] Product from a run using ^{35}S- radiolabelled sodium salt of (I), specific activity 7.9 x 10^4 cpm/mmole and unlabelled H_2SO_4. [g] Run using ^{35}S- radiolabelled (I) , (sodium salt), specific activity 5.1 x 10^4 cpm/mmole.

The radiochemical results establish first that the specific activity of the samples of compound (II) actually isolated does not vary when the reaction time is varied from 100 minutes to 55 hours. Secondly, we have established that compound (II) does not exchange with the sulphuric acid of the medium. Thirdly, the formation of radiolabelled (II) from unlabelled (I) and $^{35}S-H_2SO_4$ in the medium demonstrates some pooling of the sulphamate-SO_3H with the sulphuric acid of the medium. There is an imbalance however in the mixing, the samples of (II) isolated from the runs : unlabelled (II) + $^{35}S-H_2SO_4$, being substantially too low in activity for complete pooling to have occurred; similarly the (II) isolated from the runs ^{35}S-labelled (II) + unlabelled H_2SO_4 being too high. This imbalance can be simply represented in each case by assuming a 55% pooling of sulphate is liberated from (I), (i.e. a reaction involving intermolecular character) and 45% of a reaction involving non-pooling (or intramolecular) character.

These radiochemical results are in striking contrast to those which we obtained with phenylsulphamic acid, under identical conditions[8].

References

(1) A.M. Berkenheim and M.P. Filimonov, Zhur.Obschei Khim., 7, 610 (1937)

(2) N.N. Vorozhtsov, V.V. Kozlov, B.B. Aristov, A.I. Baryshev and M.F. Fedulov, Zhur.Obschei. Khim., 10, 894 (1940)

(3) E.A. Shilov, M.N. Bogdanov and A.E. Shilov, Doklady Akad.Nauk. S.S.S.R., 92, 93 (1953)

(4) V.V. Kozlov, Zhur.Obschei.Khim., 27, 1146 (1957)

(5) Compare Z. Urba and Z.J. Allan, Tetrahedron Letters, no. 43, 4507 (1968)

(6) Naphthylamine is converted to 1-naphthylamine-4-sulphonic acid in conc. H_2SO_4, cf. H. Erdmann, Ann., 247, 313 (1888). We have also found that the conversion (I) $\longrightarrow$ (II) can be effected in conc.H_2SO_4

(7) Z. Urba and Z.J. Allan, Coll.Czech.Chem.Comm., 33, 4426 (1968)

(8) W.J. Spillane and F.L.Scott, J.Chem.Soc. [B], 779 (1968)