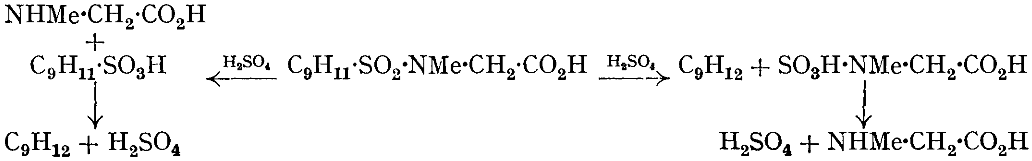
355. *Preparation of the Simpler α-Alkylamino-acids. Part II.*

By Wesley Cocker.

The method of Johnson and Ambler (*J. Amer. Chem. Soc.*, 1914, **36**, 371) for the preparation of sarcosine by the decomposition of its *N*-benzylsulphonyl derivative with hydrochloric acid is elegant, since the unwanted product (benzyl chloride) is volatile and only sarcosine hydrochloride remains. The investigation now described was an attempt to extend the above principles by the use of the derivatives of other sulphonic acids known to be unstable in hot acid, yielding volatile products. Amino-acid derivatives of 2-methoxynaphthalene-1-sulphonic acid, mesitylenesulphonic acid, and *m*-xylene-4-sulphonic acid have been prepared and from the last two compounds good yields of sarcosine and *N*-ethylglycine have been obtained.

Pechmann (*Ber.*, 1873, **6**, 534) showed that benzylsulphonyl chloride dissociates almost quantitatively into sulphur dioxide and benzyl chloride on heating, and Johnson and Ambler (*loc. cit.*) found that benzylsulphonamides are transformed into benzyl chloride and sulphur dioxide when heated with hydrochloric acid at 130—150°. Crafts (*Ber.*, 1901, **34**, 1352) showed that *m*-xylene-4-sulphonic acid is unstable at comparatively low temperatures in presence of mineral acid, and Rasik Lal Datta (*J. Amer. Chem. Soc.*, 1921, **43**, 310) obtained trichloromesitylene by leading chlorine through mesitylenesulphonic acid. Hoogewerf and van Dorp (*Rec. trav. chim.*, 1902, **21**, 359) showed that mesitylenesulphonic acid gives mesitylene when heated with 50% acetic acid. Lapworth (*Chem. News*, 1895, **71**, 206) found that potassium 2-ethoxy- and 2-methoxy-naphthalene-1-sulphonates are decomposed by boiling water to 2-ethoxy- and 2-methoxy-naphthalene. It has now been found that on hydrolysis of *N*-*m*-xylene-4-sulphonylsarcosine and *N*-mesitylenesulphonylsarcosine with 60% sulphuric acid xylene and mesitylene, particularly the latter, are readily evolved; the results obtained by the use of 2-methoxynaphthalene-1-sulphonyl derivatives were not encouraging. In neither of the successful hydrolyses was sulphur dioxide evolved, but presumably sulphuric acid was produced, and the amino-acid was readily isolated. There is insufficient evidence to state what is the mechanism of hydrolysis, since two are possible :



$$\begin{tikzcd}
\begin{array}{c}\mathrm{NHMe{\cdot}CH_2{\cdot}CO_2H}\\+\\\mathrm{C_9H_{11}{\cdot}SO_3H}\end{array} \arrow[d] & \mathrm{C_9H_{11}{\cdot}SO_2{\cdot}NMe{\cdot}CH_2{\cdot}CO_2H} \arrow[l, "H_2SO_4"'] \arrow[r, "H_2SO_4"] & \mathrm{C_9H_{12} + SO_3H{\cdot}NMe{\cdot}CH_2{\cdot}CO_2H} \arrow[d] \\
\mathrm{C_9H_{12} + H_2SO_4} & & \mathrm{H_2SO_4 + NHMe{\cdot}CH_2{\cdot}CO_2H}
\end{tikzcd}$$

In either case there is at some stage attack of proton at the nuclear carbon atom to which $SO_2{\cdot}NX$ is attached, a reaction rendered facile by the accumulative effect of the methyl groups in mesitylene.

EXPERIMENTAL.

(A) *Attempted Preparation of Sarcosine from its* 2-*Methoxynaphthalene*-1-*sulphonyl Derivative.*—N-2-*Methoxynaphthalene*-1-*sulphonylglycine,* prepared in 93% yield from the sulphonyl chloride in benzene and glycine in *N*-sodium hydroxide, consists of six-sided plates, m.p. 184·5° (instantaneous m.p.), soluble in benzene, alcohol and ethyl acetate (Found: N, 4·9. $C_{13}H_{13}O_5NS$ requires N, 4·7%).

N-2-*Methoxynaphthalene*-1-*sulphonylsarcosine,* prepared in 90% yield from the above compound by methylation with methyl sulphate, consists of transparent rectangular prisms, m.p. 145°, soluble in hot water and alcohol (Found: C, 54·45; H, 5·05; N, 4·7. $C_{14}H_{15}O_5NS$ requires C, 54·4; H, 4·85; N, 4·5%). Attempted hydrolysis with boiling 60% sulphuric acid produced a little 2-methoxynaphthalene and much tar. A little sarcosine was obtained as the phenylcarbamido-derivative. Below 125° the hydrolysis scarcely proceeded at all.

(B) *Preparation of Sarcosine from its Mesitylenesulphonyl Derivative.*—*Mesitylenesulphonylglycine,* prepared from the sulphonyl chloride (Demény, *Rec. trav. chim.*, **1931**, **50**, 55) and glycine in the manner described above, consists of long, colourless, transparent prisms, m.p. 154·5°, soluble in hot water and benzene (Found: N, 5·6. $C_{11}H_{15}O_4NS$ requires N, 5·45%).

Methylation with methyl sulphate gives *mesitylenesulphonylsarcosine* in 80% yield as transparent feathery prisms, m.p. 164—165°, shrinking 157·5°, soluble in boiling water, alcohol and benzene (Found: N, 5·4. $C_{12}H_{17}O_4NS$ requires N, 5·2%).

Hydrolysis. The latter compound (37·5 g.), suspended in a mixture of 38 c.c. of concentrated sulphuric acid and 45 c.c. of water, is heated to boiling in a Claisen flask, carbon dioxide being passed in to facilitate removal of mesitylene and water added to keep the volume constant; the reaction is complete in 2 hours. Sarcosine is isolated from the solution, containing only sarcosine sulphate and sulphuric acid, by the method of Cocker and Lapworth (J., **1931**, 1397). The yield of almost pure sarcosine, m. p. 213° (decomp.), is 10·5—11 g. (85—90% of the theoretical) (Found: N, 15·7. Calc.: N, 15·7%).

(C) *Preparation of Sarcosine and* N-*Ethylglycine from their* m-*Xylene*-4-*sulphonyl Derivatives.*—By the method used by Demény (*loc. cit.*) for mesitylenesulphonyl chloride, *m*-xylene-4-sulphonyl chloride is prepared in 50% yield from *m*-xylene and chlorosulphonic acid. m-*Xylene*-4-*sulphonylglycine,* obtained in 75% yield, separates from hot water as the monohydrate, m.p. 76° (Found: N, 5·6. $C_{10}H_{13}O_4NS,H_2O$ requires N, 5·4%). It loses water when heated for 10 minutes at its m.p. and then has m.p. 110°. It also loses water on recrystallisation from benzene. The anhydrous compound consists of long transparent prisms, m.p. 110—110·5°, soluble in alcohol, ether and hot benzene (Found: N, 5·8. $C_{10}H_{13}O_4NS$ requires N, 5·8%).

m-*Xylene*-4-*sulphonylsarcosine,* prepared in 75% yield by methylation of the preceding compound with methyl sulphate, consists of transparent prisms, m.p. 104·5—105°, soluble in hot water, benzene and high-boiling ligroin (Found: N, 5·6. $C_{11}H_{15}O_4NS$ requires N, 5·45%). It is best recrystallised from ligroin. When hydrolysed as described under (B), it yields 50—55% of sarcosine.

N-m-*Xylene*-4-*sulphonyl*-N-*ethylglycine* is obtained in 61% yield by heating a mixture of *m*-xylene-4-sulphonylglycine in 3*N*-sodium hydroxide and ethyl *p*-toluenesulphonate on the water-bath, with agitation. It consists of large transparent pyramids, m.p. 108—109° (Found: N, 5·3. $C_{12}H_{17}O_4NS$ requires N, 5·2%). Ethyl iodide gives a yield of 74% of the theoretical. Hydrolysis as under (B) gives *N*-ethylglycine in 34% yield, m.p. 181·5° (decomp.) (compare Cocker, this vol., p. 1693; Heintz, *Annalen*, **1864**, **129**, 35) (Found: N, 13·8. Calc.: N, 13·6%) (benzenesulphonyl derivative, m.p. 116·5°; compare Johnson and McCollum, *Amer. Chem. J.*, **1906**, **35**, 61).

The author thanks Professor A. Lapworth, F.R.S., for his interest during the investigation.

THE UNIVERSITY, MANCHESTER.
UNIVERSITY COLLEGE, EXETER.

[*Received, August* 26*th*, **1937**.]