78. N-*Nitrosoaceto*-1-*naphthalide.*

By Herbert H. Hodgson and Ewart Marsden.

N-*Nitrosoaceto*-1-*naphthalide* is formed when a solution of aceto-1-naphthalide in glacial acetic acid is added to nitrosylsulphuric acid. Its reactions are similar to those of a diazonium compound in mineral acid (*e.g.*, Sandmeyer reaction) and of a diazo-compound (*e.g.*, coupling) in neutral, weak acid, and alkaline solution.

Grieve and Hey (J., **1935**, 689) failed to obtain *N*-nitrosoaceto-1-naphthalide by passing nitrous fumes into a solution of aceto-1-naphthalide in glacial acetic acid. We also failed, using an ethyl-alcoholic solution. Complete and rapid formation of N-*nitrosoaceto*-1-*naphthalide*, however, occurred when aceto-1-naphthalide was treated by the Hodgson–Walker method of diazotisation (J., **1933**, 1620). Crystals were actually obtained, but with difficulty; nevertheless, the tarry product gave 1-chloronaphthalene with the Sandmeyer reagent, a mixture of 2- and 4-nitro-1-naphthols with ethyl alcohol, and naphthalene together with the above nitronaphthols with copper powder. In these reactions, the nitroso-compound must have been hydrolysed into the diazonium salt prior to decomposition. Moreover, *N*-nitrosoaceto-1-naphthalide coupled rapidly with β-naphthol in alkaline solution, readily with α- and β-naphthylamine in acetic acid, and more slowly with α-naphthol, α-naphthylamine, and H-acid in neutral environment. These couplings indicate that hydrolysis and consequent formation of a reactive diazo-compound (cf. Bamberger and Müller, *Annalen*, 1900, **313**, 126) precede coupling.

α-Naphthylamine itself is stated to be incapable of diazotisation by nitrosylsulphuric acid (E.P. 355,970; D.R.-P. 519,729), but is nitrosated in the *p*-position to the amino-group. Acylation of the amino-group consequently inhibits this *p*-nitrosation, and, in effect, promotes diazotisation.

Experimental.

Nitrosation of Aceto-1-*naphthalide*.—A solution of aceto-1-naphthalide (18·5 g.) in glacial acetic acid (185 c.c.) was added during 1 hour to an ice-cooled solution of sodium nitrite (7·7 g.) in sulphuric acid (60 c.c., *d* 1·84); a vigorous reaction occurred and the temperature had to be maintained below 20°. After 30 minutes, the mixture was poured into ice-water (2 l.); the yellowish tar which slowly settled was separated from the aqueous layer, washed with water (200 c.c.), dried, and washed with carbon tetrachloride and carbon disulphide, in which it was insoluble. On keeping at −20°, yellow needles (0·7 g.) of N-*nitrosoaceto*-1-*naphthalide* formed, m. p. 8—10°, which were rapidly pressed between filter-paper (Found : N, 13·0. $C_{12}H_{10}O_2N_2$ requires N, 13·1%). They were very unstable and changed into a yellow oil which decomposed smoothly and rapidly at room temperature with evolution of nitrogen. That the tar consisted essentially of *N*-nitrosoaceto-1-naphthalide was established by the following experiments.

(*a*) When the tar (from 18·5 g. of aceto-1-naphthalide) was added to a solution of cuprous chloride (20 g.) in hydrochloric acid (50 c.c., *d* 1·16), a violent reaction began. After 30 minutes, the mixture was steam-distilled, α-chloronaphthalene (10 g.; yield, 61·8%) passing over.

(*b*) Another batch of tar, prepared as above, was mixed with ethyl alcohol (100 c.c.), kept overnight, heated to 80° on the water-bath, and then steam-distilled; a small amount of 2-nitro-1-naphthol passed over. The residual liquor was filtered hot; on cooling, it deposited a mixture of 2- and 4-nitro-1-naphthols (10·02 g.; 53·7% yield). These were separated by means of the difference in solubility of their potassium salts in water (Hodgson and Kilner, J., 1924, **125**, 808), 45% of 2-nitro-1-naphthol and 54% of 4-nitro-1-naphthol being obtained. The addition of copper powder to the alcoholic mixture was without effect on the products of the reaction.

(*c*) The initially prepared solution of *N*-nitrosoaceto-1-naphthalide (above) was mixed with copper powder (6·3 g.) at 20—30° and kept overnight. On steam-distillation, naphthalene (0·9 g.; 8% yield) was obtained, together with 2- and 4-nitro-1-naphthols (48% yield) and a tar (0·6 g.). The nitronaphthols were present in the proportion 52% of the 1 : 2- and 48% of the 1 : 4-isomeride.

(*d*) The tar, prepared as above, was stirred into a faintly alkaline solution of β-naphthol (14·3 g.) in aqueous sodium hydroxide, to which sodium carbonate was subsequently added. After keeping overnight, 1-1′-naphthaleneazo-2-naphthol was precipitated (23·0 g.; 78% yield).

(*e*) The Gomberg reaction did not occur when the tar was dissolved in benzene and kept overnight; nitronaphthols were formed, but no 1-phenylnaphthalene was observed.

(*f*) Coupling occurred in the following experiments, immediately in (i) and (iv), slowly in (ii) and (iii). (i) The *N*-nitrosoaceto-1-naphthalide solution (188 c.c.) prepared from 18·5 g. of aceto-1-naphthalide was divided into two equal parts, each of which was further diluted with acetic acid and then treated with sodium acetate until it gave no blue colour with Congo-red paper. The two solutions were then added gradually at 0—5° to solutions of α- and β-naphthylamine (5 g.) in glacial acetic acid (40 c.c.) diluted with water (100 c.c.) in which sodium acetate had been dissolved. (ii) α-Naphthol (5 g.) was dissolved in just sufficient sodium carbonate (2n), the solution faintly acidified with hydrochloric acid, the excess of acid neutralised with calcium carbonate, and ethyl alcohol (150 c.c.) added. The tar (prepared from 9·25 g. of aceto-1-naphthalide and made neutral by calcium carbonate) was stirred into the above mixture. (iii) A solution of α-naphthylamine (5 g.) in ethyl alcohol (100 c.c.) was diluted with ice and water to 250 c.c., calcium carbonate (20 g.) stirred into the suspension, and tar, prepared and neutralised as above, stirred into the mixture. (iv) A solution of H-acid (5 g.) in just sufficient sodium carbonate (2n) was diluted with ice and water to 250 c.c. and faintly acidified with dilute hydrochloric acid, calcium carbonate added in excess, followed by neutral tar prepared as above.

The authors thank I.C.I. (Dyestuffs) Ltd. for gifts of chemicals.

Technical College, Huddersfield. [*Received, December* 19*th*, 1942.]