277. *The Orton Rearrangement. Part II.*[1] *The Reactions of Several Substituted* N-*Bromoacylanilides in Various Media causing Rearrangement.*

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The reactions of a number of *o*-substituted *N*-bromoacetanilides with trichloroacetic acid in chlorobenzene have been studied. Preparations of several new derivatives of *N*-bromoacetanilide are described.

In Part I [1] we described the preparation and rearrangement of *N*-bromo-2 : 6-dimethylacetanilide; this substance showed some unusual properties, owing presumably to the steric influence of the two *o*-methyl groups. We have accordingly examined the rearrangements of a number of *ortho*-substituted derivatives of *N*-bromoacetanilide to obtain further information concerning the steric effects of the substituents and to prepare the way for kinetic studies.

The compounds examined were the *o*-methyl-, *o*-fluoro-, *o*-chloro-, *o*-bromo-, *o*-nitro-, *o*-phenyl, 2 : 4 : 6- and 2 : 4 : 5-trichloro-, and 2 : 6-diethyl derivatives of *N*-bromoacetanilide. Of these the last three compounds and *N*-bromo-*o*-fluoroacetanilide are new; 2-*N*-bromoacetamidodiphenyl had not previously been obtained pure (cf. Scarborough and Waters [2]).

An improved synthesis of *o*-fluoroaniline was devised, namely, oxidation of *o*-fluorotoluene to *o*-fluorobenzoic acid followed by a Schmidt reaction.

All the monosubstituted *N*-bromoacetanilides rearranged smoothly to *p*-bromoacetanilides on treatment with trichloroacetic acid in chlorobenzene, except the nitro-derivative; in this case *o*-nitroacetanilide and *p*-bromochlorobenzene were formed, but normal rearrangement, to 4-bromo-2-nitroacetanilide, took place with trichloroacetic acid in carbon tetrachloride.

The diethyl derivative rearranged normally in boiling water, but gave intractable mixtures with trichloroacetic acid in chlorobenzene. This *N*-bromo-compound was surprisingly unstable, rearranging in the solid state even over phosphoric oxide in a vacuum in the dark.

Both the trichloro-derivatives attacked the solvent, giving free anilide and *p*-bromochlorobenzene.

An attempt to prepare *N*-bromopivalanilide failed; bromination of pivalanilide in acetic acid gave *p*-bromopivalanilide in good yield.

Experimental

2-N-*Bromoacetamidodiphenyl.*—The following modification of Scarborough and Waters's procedure [2] gave a much purer product. 2-Acetamidodiphenyl (10 g.) in warm dioxan (100 ml.) was added slowly with stirring to bromine (10 ml.) and potassium hydrogen carbonate (4 g.) dissolved in 0·25N-sodium hydroxide (2 l.). The yellow precipitate was isolated with chloroform which was then evaporated to a small volume, and hot light petroleum (b. p. 40—60°) was added. 2-*N*-Bromoacetamidodiphenyl separated, on cooling, in yellow prisms (9 g., 68%), m. p. 116—118° (decomp.) (Found : active Br, 27·4, 27·6. Calc. for $C_{14}H_{12}ONBr$: Br, 27·5%).

o-*Fluorobenzoic Acid.*—*o*-Fluorotoluene (44 g.) and potassium permanganate (75 g.) in water (1·25 l.) were boiled under reflux for 2 hr. Further potassium permanganate (37·5 g.) was then added and heating continued until the permanganate colour had disappeared. After steam-distillation of the excess of fluorotoluene, the solution was filtered and acidified, giving *o*-fluorobenzoic acid (25·6 g., 45%), m. p. 125—126° (lit., 126°).

N-*Bromo*-o-*fluoroacetanilide.*—*o*-Fluoroacetanilide (5 g.) (from *o*-fluoroaniline [3]) in chloroform (100 ml.) was shaken with an excess of hypobromous acid containing a little mercuric

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[1] Part I, Dewar and Scott, *J.*, 1955, 1845.

[2] Scarborough and Waters, *J.*, 1927, 89.

[3] Minor and Van der Werf, *J. Org. Chem.*, 1952, **17**, 1425; Harris, Potter, and Turner, *J.*, 1955, 145.

oxide. The N-*bromo-amide*, isolated as before, crystallised in needles (3 g., 40%), m. p. 82—84° (Found: active Br, 34·4, 34·3. C_8H_7ONBrF requires Br, 34·4%).

p-*Bromo*-o-*fluoroacetanilide*.—*o*-Fluoroacetanilide was brominated in acetic acid, and the crude *bromofluoroacetanilide* (1·8 g., 92%) crystallised several times from aqueous alcohol (norite), forming needles, m. p. 158—160° (Found: C, 41·0; H, 3·6; N, 6·0; Br, 34·5. C_8H_7ONBrF requires C, 41·4; H, 3·0; N, 6·0; Br, 34·4%).

N-*Bromo*-2 : 4 : 6-*trichloroacetanilide*.—A solution of 2 : 4 : 6-trichloroacetanilide (15 g.) in chloroform (1·5 l.) was stirred very vigorously with bromine (10 ml.) and potassium hydrogen carbonate (8 g.) dissolved in 0·25N-sodium hydroxide (2 l.). After 1 hr. the N-*bromoanilide* was isolated as before, forming pale yellow prisms (15 g., 60%), m. p. 135—137° (Found: active Br, 25·2. $C_8H_5ONCl_3Br$ requires Br, 25·2%).

N-*Bromo*-2 : 4 : 5-*trichloroacetanilide*, prepared in the same way (50%) yield), crystallised from light petroleum (b. p. 40—60°) in prisms m. p. 96—98° (Found: active Br, 25·0%).

N-*Bromo*-2 : 6-*diethylacetanilide*.—Prepared in the same way as the *o*-phenyl derivative, this N-*bromoanilide* crystallised from light petroleum (b. p. 40—60°) in blades, m. p. 72—75° (Found: active Br, 26·7, 26·2. $C_{12}H_{16}ONBr$ requires Br, 26·6%).

p-*Bromopivalanilide*.—(*a*) *p*-Bromoaniline with pivalyl chloride in pyridine gave crude p-*bromopivalanilide* (2·6 g., 86%) which crystallised from chloroform–light petroleum in needles, m. p. 156—157° (Found: C, 51·8; H, 5·6; Br, 31·2. $C_{11}H_{14}ONBr$ requires C, 51·6; H, 5·5; Br, 31·2%). (*b*) The same compound was obtained in 69% yield by bromination of pivalanilide in acetic acid.

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