271. *The Benzoylation of* as-*Phenylethylurea.*

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ATTEMPTS to prepare a benzoyl derivative of *as*-phenylethylurea (Gebhardt, *Ber.*, 1884, **17**, 2095) by the action of phenylethylcarbamyl chloride upon benzamide (cf. acylation of benzamide, Titherley, J., 1904, **85**, 1684) have proved fruitless, the following reaction taking place:

$$NPhEt{\cdot}COCl + Ph{\cdot}CO{\cdot}NH_2 \longrightarrow NHPhEt,HCl + CO_2 + PhCN$$

The *benzoyl* derivative has, however, been obtained by the action of benzoyl chloride on the urea in pyridine solution at the ordinary temperature. In the preparation of the p-*nitrobenzoyl* derivative under similar conditions, a small quantity of cyanuric acid was produced.

The action of benzoyl chloride upon *as*-phenylethylurea at 100° leads to the production of cyanuric acid, *N*-ethylbenzanilide, and hydrogen chloride:

$$3NPhEt{\cdot}CO{\cdot}NH_2 + 3Ph{\cdot}COCl = 3Ph{\cdot}CO{\cdot}NPhEt + C_3H_3O_3N_3 + 3HCl$$

as-Phenylethylurea was prepared in quantitative yield by the action of dry ammonia on phenylethylcarbamyl chloride in benzene or other suitable solvent at the ordinary temperature and was more readily purified than that obtained by Gebhardt's method (*loc. cit.*).

EXPERIMENTAL.

The Action of Phenylethylcarbamyl Chloride on Benzamide.—An intimate mixture of phenylethylcarbamyl chloride (4·5 g.) and benzamide (3·8 g.) was heated during 2½ hours at 180—200°. Benzonitrile (1·2 g.) distilled over and there remained a red oil, which yielded ethylaniline hydrochloride (2 g.) when it was extracted with a little cold acetone.

When the operation was carried out at 110—120° in the presence of pyridine or anhydrous sodium carbonate, the ethylaniline reacted with unchanged phenylethylcarbamyl chloride, giving *NN'*-diphenyl-*NN'*-diethylurea, which crystallised from light petroleum in lustrous prisms, m. p. and mixed m. p. 74°. Michler (*Ber.*, 1876, **9**, 712) gives m. p. 79° and Gradmann (*ibid.*, p. 1913) m. p. 70°.

as-*Phenylethylurea.*—Dry ammonia was led into a solution of phenylethylcarbamyl chloride (15 g.) in a mixture of benzene (50 c.c.) and absolute alcohol (20 c.c.) until no more ammonium chloride was deposited. After some time the solution was filtered, the filtrate evaporated, and the syrupy residue extracted with benzene; on evaporation the filtered extract gave a faintly brown syrup, which crystallised in plates (14·5 g.), m. p. 60°, in a vacuum after 24 hours. Gebhardt (*loc. cit.*) gives m. p. 62°.

The Action of Benzoyl Chloride on as-*Phenylethylurea.*—A solution of the urea (2 g.) in benzoyl chloride (2·2 g.) was heated on the water-bath for 30 minutes, hydrogen chloride being evolved and a colourless solid deposited. This, after being washed with light petroleum, crystallised from hot water in characteristic prisms, identical in properties with cyanuric acid. The light petroleum extract was evaporated, and the unchanged benzoyl chloride decomposed with cold

sodium carbonate solution. A small quantity of oil remained undissolved and after extraction with ether crystallised in small plates, m. p. 52°, and 51—52° in admixture with authentic *N*-ethylbenzanilide.

as-*Phenylethylbenzoylurea*.—Benzoyl chloride (1·8 g.) was dropped, with stirring, into a solution of *as*-phenylethylurea (2 g.) in anhydrous pyridine (4 c.c.) at the ordinary temperature. After 2 hours, the mixture was warmed on the water-bath for 15 minutes, and water (20 c.c.) added; the oily precipitate, which rapidly solidified, was washed with dilute hydrochloric acid and crystallised from hot alcohol, forming long needles (2 g.), m. p. 121° [Found: N (Kjeldahl), 10·2. $C_{16}H_{16}O_2N_2$ requires N, 10·45%].

as-*Phenylethyl*-p-*nitrobenzoylurea*.—A mixture of *p*-nitrobenzoyl chloride (2·0 g.), *as*-phenylethylurea (2 g.), and anhydrous pyridine was maintained at 60—80° for 1 hour, water (20 c.c.) added, and the precipitated solid dried and extracted with benzene. The aqueous solution yielded a small quantity of cyanuric acid on evaporation. The benzene solution gave a glue-like residue, which solidified when stirred with light petroleum. By systematic crystallisation from ether, in which the material was moderately easily soluble, two substances were finally isolated. The less soluble compound crystallised in long needles, m. p. 175°, and was as-*phenylethyl*-p-*nitrobenzoylurea* (Found: N, 13·6. $C_{16}H_{15}O_4N_3$ requires N, 13·4%). The mother-liquors gave well-defined, pale yellow prisms, m. p., after several crystallisations from alcohol, 119°, not depressed by *N*-ethyl-*p*-nitrobenzanilide (Found: C, 66·2; H, 5·3. Calc. for $C_{15}H_{14}O_3N_2$: C, 66·6; H, 5·2%).

The same three products were obtained when the reaction was carried out at the ordinary temperature.

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