339. *The Nitration of Benzilic and Fluorenecarboxylic Acids.*

By Francis L. Rose.

No nitrobenzilic acids appear to have been described, and various methods for the nitration of benzilic acid were therefore investigated. In all cases where nitration took place, the product was a yellow sticky mixture of nitro-acids. From this, about 10% of crystalline 2 : 2′-*dinitrobenzilic acid* was separated as the aniline salt, and the remainder consisted of a mixture (not separated) of anhydro-derivatives, $C_{28}H_{18}O_{13}N_4$, of 2 : 3′- and 3 : 3′-dinitrobenzilic acids. This underwent further dehydration at 100°, giving a mixture of compounds, $C_{28}H_{16}O_{12}N_4$.

Treatment of fluorene-9-carboxylic acid with fuming nitric acid gave only a small yield of a crystalline nitro-acid, the bulk of the product being non-acidic. The use of acetic acid or acetic anhydride as a diluent gave little better results, but by using various other solvents comparatively simple methods for mono- and di-nitration were evolved. The products readily lost carbon dioxide when heated and gave the corresponding nitrofluorenes; many of these have been described, as have also the nitrofluorenones to which they may be oxidised.

2 : 2′-*Dinitrobenzilic Acid.*—Benzilic acid (20 g.) was stirred into HNO_3 (*d* 1·5; 40 c.c.) below 0°, the yellow solution poured on ice, and the solid dissolved, washed, and dried in Et_2O, and then treated with NH_2Ph (10 c.c.).

The pptd. aniline salt was shaken with Et_2O and HCl aq., most of the Et_2O evaporated, and $CHCl_3$ added; 2 : 2′-*dinitrobenzilic acid* separated in colourless prisms (2·8 g.), m. p. 171—172° (decomp.) (Found: C, 52·9; H, 3·2. $C_{14}H_{10}O_7N_2$ requires C, 52·8; H, 3·15%), readily sol. in Et_2O, acetone, and EtOH, but sparingly in $CHCl_3$ and C_6H_6. The addition of a little Zn dust to a hot AcOH solution gave an intense carmine colour, which disappeared as the liquid cooled.

Oxidation of the acid by CrO_3 and AcOH gave 2 : 2′-dinitrobenzophenone, needles, m. p. 187° (Staedel, *Ber.*, 1890, **23**, 2578) (Found: C, 57·3; H, 3·0. Calc.: C, 57·35; H, 2·9%).

The ethereal filtrate from the separation of the aniline salt was shaken with HCl aq. and then with Na_2CO_3 aq. The alkaline solution was freed from Et_2O and treated with dil. HCl, six equal fractions being pptd. These were washed with H_2O and dried in vac. The first two fractions were sticky and coloured. The last three, which were solid and colourless, were united (Found: C, 54·1; H, 3·0. $C_{28}H_{18}O_{13}N_4$ requires C, 54·4; H, 2·9%) and heated in vac. at 100°, giving a non-acidic *compound* (Found: C, 56·1; H, 2·8. $C_{28}H_{16}O_{12}N_4$ requires C, 56·0; H, 2·7%). Oxidation of the last fractions with CrO_3 gave a product (Found: C, 54·5; H, 2·8%) which when fractionated from toluene was separated into 2 : 3′- and 3 : 3′-dinitrobenzophenones, m. p. 127° (Staedel, *loc. cit.*) and 162° (Baeyer, *Annalen*, 1907, **354**, 192) respectively.

2 : 2′-*Diaminobenzilic Acid.*—2 : 2′-Dinitrobenzilic acid (2 g.) was heated during ½ hr. on the water-bath with granulated Sn (4 g.) and conc. HCl (9 c.c.), and the solution diluted, freed from Sn, and evaporated to dryness. The residue crystallised from hot conc. HCl–acetone in colourless needles (Found: Cl, 21·8. $C_{14}H_{14}O_3N_2$,2HCl requires Cl, 21·45%).

2-*Nitrofluorene*-9-*carboxylic Acid.*—Fluorenecarboxylic acid (1 g.) in $CHCl_3$ or CCl_4 (10 c.c.) was shaken with HNO_3 (*d* 1·43; 3 c.c.) during 15 mins. The solid pptd. by H_2O was dried in vac. and crystallised from acetone–$CHCl_3$; yellow needles (0·8 g.), m. p. 186—187° (decomp.) (Found: C, 65·6; H, 3·6. $C_{14}H_9O_4N$ requires C, 65·8; H, 3·5%), readily sol. in acetone and EtOH, sparingly in $CHCl_3$ and C_6H_6. The acid, when heated at its m. p. for a few mins., gave 2-nitrofluorene, m. p. 155° (from AcOH) (Found: C, 73·95; H, 4·4. Calc.: C, 73·9; H, 4·3%), which was oxidised by CrO_3 to 2-nitrofluorenone, m. p. 220° (cf. Diels, *Ber.*, 1901, **34**, 1759; Schultz, *Annalen*, 1880, **203**, 103).

2 : 7-*Dinitrofluorene*-9-*carboxylic acid*, similarly prepared (fluorenecarboxylic acid, 1 g.; CCl_4, 10 c.c.; HNO_3, *d* 1·51, 4 c.c.) and crystallised, formed yellow needles (0·7 g.) (Found: C, 56·1; H, 2·9. $C_{14}H_8O_6N_2$ requires C, 56·0; H, 2·7%), resembling the preceding acid in solubility. At 150° it lost CO_2 and gave 2 : 7-dinitrofluorene, straw-coloured needles which were not melted at 280°* and rapidly darkened at that temp. (Found: C, 60·7; H, 3·2. Calc.: C, 60·9; H, 3·1%). Oxidation with CrO_3 in AcOH gave 2 : 7-dinitrofluorenone, golden-yellow needles, m. p. 290°.

2-*Nitro*-7-*sulphofluorene*-9-*carboxylic Acid.*—2-Nitrofluorenecarboxylic acid (1 g.) was stirred into H_2SO_4 (*d* 1·84; 5 c.c.) and after 15 hrs. the deep red solution was poured on ice (12 g.). The pptd. acid was washed with conc.

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* Although considerable dissension exists about the m. p. of 2 : 7-dinitrofluorene, all agree that it melts above 250° and that 2 : 7-dinitrofluorenone melts at 290° (Morgan and Thomason, J., 1926, 2691).

HCl and dried over KOH. It separated from AcOH, on addition of $CHCl_3$, in small colourless needles, readily sol. in H_2O, acetone, and EtOH but sparingly in C_6H_6. The solution in aq. alkali had a deep blue-green colour, which changed to yellow on heating. A sparingly sol. *potassium* salt (Found: K, 10·4. $C_{14}H_8O_7NSK$ requires K, 10·5%) separated in small yellow prisms when a solution of the acid in H_2O was saturated with KCl. This salt still contained a free acid group, since it was readily sol. in NaOH aq., giving a deep green solution, and formed with PCl_5 a *diacid chloride*, colourless needles, m. p. 159°, from acetone (Found: Cl, 19·3. $C_{14}H_7O_5NCl_2S$ requires Cl, 19·1%).

The monopotassium salt lost CO_2 at 190°, giving the potassium salt of a nitrofluorenesulphonic acid, from which the acid chloride, m. p. 237°, was prepared (Found: Cl, 11·8. Calc.: Cl, 11·45%). Courtot (*Brit. Chem. Abstracts*, 1930, *A*, 1424) gives m. p. 239° for 2-nitrofluorene-7-sulphonyl chloride.

2-*Aminofluorene*-9-*carboxylic Acid*.—The 2-nitro-compound (6 g.) was reduced (conc. HCl, 25 c.c.; granulated Sn, 12 g.) in the usual way. From the tin-freed conc. solution, on cooling, the amino-acid hydrochloride separated in long colourless needles. This was dissolved in a very little H_2O, and NH_3 aq. added, followed by dil. AcOH. The *amino-acid* was practically insol. in neutral organic solvents, but crystallised from much EtOH in small colourless needles, m. p. 207—208° (decomp.) (Found: C, 74·4; H, 5·2. $C_{14}H_{11}O_2N$ requires C, 74·6; H, 4·9%). With Ac_2O, it gave 2-*acetamidofluorene*-9-*carboxylic acid*, which was readily sol. in acetone and crystallised from EtOH in small prisms, m. p. 195° (Found: C, 71·65; H, 5·1. $C_{16}H_{13}O_3N$ requires C, 71·9; H, 4·9%).

2 : 7-*Diaminofluorene*-9-*carboxylic acid* was similarly prepared from the 2 : 7-dinitro-compound. The brittle, colourless, hygroscopic amino-acid hydrochloride was dissolved in a very little H_2O, excess of EtOH added, and then dil. NH_3 drop by drop till the solution was approx. neutral. 2 : 7-Diaminofluorenecarboxylic acid separated in small colourless needles, practically insol. in org. solvents; m. p. 209—210° (decomp.) (Found: C, 69·7; H, 5·1. $C_{14}H_{12}O_2N_2$ requires C, 70·0; H, 5·0%).

With Ac_2O, a *diacetyl* derivative was formed which was almost insol. but was purified by prolonged extraction with hot EtOH; m. p. 263—264° (Found: C, 66·5; H, 4·8. $C_{18}H_{16}O_4N_2$ requires C, 66·7; H, 4·9%).

2-*Amino*-7-*sulphofluorene*-9-*carboxylic Acid*.—The 2-nitro-compound (5 g.) was heated on a water-bath with granulated Sn (7 g.) and conc. HCl (15 c.c.) for ½ hr. The solution was decanted and evaporated to remove the excess of HCl. Colourless rectangular prisms of the *amino-acid* slowly crystallised. These were sparingly sol. in EtOH and H_2O, and darkened at 290° without melting (Found: S, 10·4. $C_{14}H_{11}O_5NS$ requires S, 10·5%).

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