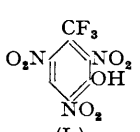
538. *Organic Fluoro-compounds. Part III. 2 : 4 : 6-Trinitro-3-hydroxybenzotrifluoride—a New Reagent for the Characterisation of Amines and Pyranol Bases.*

By W. B. Whalley.

The nitration of *m*-hydroxybenzotrifluoride gives 2 : 4 : 6-trinitro-3-hydroxybenzotrifluoride, a compound which shows considerable possibilities as a reagent for the characterisation of amines and pyranol bases.

In Part I (*J.*, 1949, 3016) it was recorded that the nitration of *m*-hydroxybenzotrifluoride gave rise to a complex mixture of nitrophenols. However, it has now been shown that vigorous nitration with fuming nitric acid readily furnishes 2 : 4 : 6-trinitro-3-hydroxybenzotrifluoride (I), unaccompanied by easily detectable quantities of other nitrophenols. The orientation of (I) was initially inferred by analogy with the behaviour of *m*-hydroxybenzoic acid which contains an electronic system comparable with that present in *m*-hydroxybenzotrifluoride and gives rise to 2 : 4 : 6-trinitro-3-hydroxybenzoic acid under similar nitration conditions (Wolffenstein and Paar, *Ber.*, 1913, **46**, 598). Because of the resistance of the trifluoromethyl group in (I) to hydrolysis with concentrated acid and alkali the orientation was established from the production of (I) by the nitration of 2-nitro-3-hydroxybenzotrifluoride (II), 4-nitro-3-hydroxybenzotrifluoride (III; $R^1 = NO_2$, $R^2 = OH$) (De Brouwer, *Bull. Soc. chim. Belg.*, 1930, **38**, 298), and 2-nitro-5-hydroxybenzotrifluoride (IV) (Part I, *loc. cit.*). Phenols (II) and (III; $R^1 = NO_2$, $R^2 = OH$) were characterised as the *p*-nitrobenzoates.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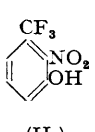
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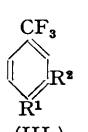
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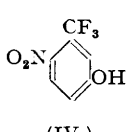
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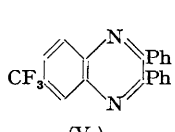
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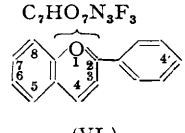
(VI.)

2 : 4 : 6-Trinitro-3-hydroxybenzotrifluoride (I), like picric acid, is readily soluble in aqueous sodium hydrogen carbonate and forms well-defined highly crystalline complexes with primary, secondary, and tertiary amines (including cyclic amines). The number of reagents available for the characterisation of primary and secondary amines is considerable, but very few are suitable for use with tertiary amines, particularly in aqueous solution (compare "Organic Reagents for Organic Analyses," 1944, London, p. 24). The trinitrohydroxybenzotrifluoride

(I) with amines readily gives derivatives which in most cases have melting points (see Table) appreciably different from those of the corresponding picrates.

The number of salts preparable from pyranol bases for characterisation is also rather limited. With the selection of pyranol bases examined the reagent readily furnishes, in good yield, highly crystalline derivatives of type (VI) which in general exhibit only moderate solubility in solvents. Unlike picric acid, this reagent does not appear readily to form solid complexes with hydrocarbons or with ethers.

The catalytic reduction of 4-nitro-3-aminobenzotrifluoride (III; $R^1 = NO_2$, $R^2 = NH_2$) gave rise to 3 : 4-diaminobenzotrifluoride (III; $R^1 = R^2 = NH_2$) characterised by the formation of the 2 : 3-diphenylquinoxaline (V).

Experimental.

2 : 4 : 6-*Trinitro*-3-*hydroxybenzotrifluoride* (I).—*m*-Hydroxybenzotrifluoride (10 g.) was added during 15 minutes to stirred fuming nitric acid (30 ml.) without cooling. A vigorous reaction occurred and on its being kept some product crystallised. 24 Hours later the mixture was poured on crushed ice (50 g.), and the crystalline precipitate collected and washed with ice-cold water (100 ml.). 2 : 4 : 6-*Trinitro*-3-*hydroxybenzotrifluoride* (7 g.) separated from benzene in colourless rhombic plates, m. p. 88°, containing benzene of crystallisation which rapidly vaporised when the crystals were exposed to the atmosphere. Crystallisation from ethyl acetate–light petroleum gave the product in rhombic prisms, m. p. 122° (Found: C, 28·6; H, 0·8; N, 15·3; F, 19·4. $C_7H_2O_7N_3F_3$ requires C, 28·3; H, 0·7; N, 14·2; F, 19·2%). The compound is sparingly soluble in water to a yellow solution, soluble in aqueous sodium carbonate and sodium hydrogen carbonate with the evolution of carbon dioxide, easily soluble in ethyl acetate, alcohol, and acetone, moderately soluble in benzene, and very sparingly soluble in light petroleum.

2- and 4-Nitro-3-aminobenzotrifluorides were obtained by the nitration of *m*-acetamidobenzotrifluoride with acetyl nitrate (Rouche, *Bull. Acad. roy. Belg. Classe Sci.*, 1927, **13**, 346), and were subsequently converted into the corresponding nitrophenols by prolonged hydrolysis with 6N-sodium hydroxide solution (De Brouwer, *Bull. Soc. chim. Belg.*, 1930, **39**, 298). 2-Nitro-3-hydroxybenzotrifluoride (II) gave a p-*nitrobenzoate* which separated from aqueous methyl alcohol in slender prisms, m. p. 130° (Found: N, 8·1. $C_{14}H_7O_6N_2F_3$ requires N, 7·9%). 4-Nitro-3-hydroxybenzotrifluoride (III; $R^1 = NO_2$, $R^2 = OH$) furnished a p-*nitrobenzoate* in clusters of stout prisms, m. p. 103°, from aqueous methyl alcohol (Found: N, 7·5. $C_{14}H_7O_6N_2F_3$ requires N, 7·9%). The nitration of 2-nitro-3-hydroxy-, 4-nitro-3-hydroxy-, and 2-nitro-5-hydroxy-benzotrifluoride (Part I, *loc. cit.*) with fuming nitric acid by this method readily gave rise, in each case, to 2 : 4 : 6-trinitro-3-hydroxybenzotrifluoride, the product from each preparation being identical with the others and with that from *m*-hydroxybenzotrifluoride.

The Characterisation of Amines.—The reagent is conveniently employed in saturated aqueous or alcoholic solution and on admixture with an aqueous or alcoholic solution of the amine the crystalline derivative separates rapidly, and is collected and recrystallised, usually from alcohol or aqueous alcohol containing about 0·5% of the reagent, until of constant m. p. One recrystallisation is usually sufficient. Occasionally the use of a benzene solution of the reagent and amine is more convenient (where the latter is easily available in the anhydrous condition). The Table records details of a series of amine derivatives.

Characterisation of Pyranol Bases.—An excess of a saturated alcoholic solution of the reagent is added to a solution of the pyranol base in the same solvent. The crystalline salt separates immediately and is recrystallised from methyl or ethyl alcohol containing about 0·5% of the reagent.

The pyranol bases required for the preparation of the derivatives described were obtained from the corresponding chlorides by standard methods. The chlorides were prepared by the condensation in ethyl acetate of the appropriate acetophenone and *o*-hydroxy-aldehyde in the presence of dry hydrogen chloride.

The following pyrylium *trifluoromethylpicrates* were so prepared (all crystallised from methanol; those marked * exhibited rather sparing solubility; the temperatures given in parenthesis after the m. p. indicate the point at which darkening was first observed); *7-*hydroxy*-2-*phenylbenzopyrylium*, shimmering red-brown plates with a green reflex, m. p. 236–238° (decomp.) (180°) (Found: C, 51·5; H, 2·4; N, 8·1; F, 10·1. $C_{22}H_{12}O_9N_3F_3$ requires C, 50·9; H, 2·3; N, 8·1; F, 11·0%); *7-*hydroxy*-2-p-*tolylbenzopyrylium*, shimmering red-brown plates exhibiting a green reflux, m. p. 220—222° (decomp.) (170°) (Found: C, 52·7; H, 2·9; N, 8·1; F, 10·2. $C_{23}H_{14}O_9N_3F_3$ requires C, 51·8; H, 2·6; N, 7·9; F, 10·8%); *7-*hydroxy*-5-*methyl*-2-p-*tolylbenzopyrylium*, shimmering orange-red plates, m. p. 207° (decomp.) (200°) (Found: C, 52·0; H, 3·0; N, 7·8; F, 10·1. $C_{24}H_{16}O_9N_3F_3$ requires C, 52·6; H, 2·9; N, 7·7; F, 10·4%); *7-*hydroxy*-2-*phenyl*-5-*methylbenzopyrylium*, shimmering red-brown plates with a green sheen, m. p. 220—222° (decomp.) (Found: C, 51·4; H, 2·5; N, 8·1; F, 10·2. $C_{23}H_{14}O_9N_3F_3$ requires C, 51·8; H, 2·6; N, 7·9; F, 10·7%); 6-*methoxy*-2-*phenylbenzopyrylium*, green-brown silky needles, m. p. 178° (decomp.) (164°) (Found: C, 50·8; H, 3·3; N, 8·4; F, 10·2. $C_{23}H_{14}O_9N_3F_3,0{\cdot}5H_2O$ requires C, 50·9; H, 2·8; N, 7·9; F, 10·5%); 6-*methoxy*-2-p-*tolylbenzopyrylium*, orange-brown silky needles which changed on being kept in contact with the solvent to glistening, slender, almost black parallelograms with a green sheen, m. p. 160—163° (decomp.) (Found: C, 52·5; H, 2·5; N, 7·9; F, 9·7. $C_{24}H_{16}O_9N_3F_3$ requires C, 52·6; H, 2·9; N, 7·7; F, 10·4%); 7-*hydroxy*-2-*phenyl*-5: 6-*dimethylbenzopyrylium*, rosettes of red-brown needles, m. p. 241—243° (decomp.) (220°) (Found: C, 53·0; H, 3·3; N, 7·4; F, 9·7. $C_{24}H_{16}O_9N_3F_3$ requires C, 52·6; H, 2·9; N, 7·7; F, 10·4%); *7-*hydroxy*-2-p-*tolyl*-5: 6-*dimethylbenzopyrylium*, greenish-brown shimmering plates, m. p. 243—244° (decomp.) (220°) (Found: C, 52·4; H, 3·2; N, 7·4; F, 9·6. $C_{25}H_{18}O_9N_3F_3,0{\cdot}5H_2O$ requires C, 52·6; H, 3·3; N, 7·5; F, 10·0%); *7-*methoxy*-6-*ethoxy*-2-p-*tolylbenzopyrylium*, greenish-brown needles, m. p. 182—185° (decomp.) (Found: C, 51·3; H, 3·6; N, 7·3; F, 8·7.

$C_{26}H_{20}O_{10}N_3F_3,H_2O$ requires C, 51·3; H, 3·6; N, 6·9; F, 9·4%); and *6 : 7-*dimethoxy*-2-p-*tolylbenzopyrylium*, glistening greenish-brown stout tablets, m. p. 184—185° (decomp.) (180°) (Found : C, 51·7; H, 3·1; N, 7·3; F, 9·1. $C_{25}H_{18}O_{10}N_3F_3$ requires C, 52·0; H, 3·1; N, 7·3; F, 9·9%).

Amine.	M. p. of derivative.	M. p. of picrate.[4]	Crystalline form.	Formula.	Found, %. N.	Found, %. F.	Requires, %. N.	Requires, %. F.
Aniline	182—183° (decomp.)	165°	Yellow slender needles [2]	$C_{13}H_9O_7N_4F_3$	14·5	14·1	14·4	14·6
Quinoline	203	203	Deep-yellow slender needles [1]	$C_{16}H_9O_7N_4F_3$	13·1	12·8	13·1	13·4
Morpholine	238—242 (decomp.)	146	Pale yellow massive tablets [1]	$C_{11}H_{11}O_8N_4F_3$	14·2	14·5	14·4	14·7
Pyridine	179	167	Bright-yellow slender prisms [1]	$C_{12}H_7O_7N_4F_3$	14·6	15·2	14·9	15·2
n-Butylamine	156	151	Yellow massive long prisms [1]	$C_{11}H_{13}O_7N_4F_3$	14·8	15·3	15·1	15·4
*iso*Propylamine	157	—	Bright-yellow long flat prisms [3]	$C_{10}H_{11}O_7N_4F_3$	15·9	15·8	15·7	15·7
Triethylamine	93	173	Yellow short stout pale prisms [3]	$C_{13}H_{17}O_7N_4F_3$	13·9	14·3	14·1	14·3
o-Toluidine	171	185	Straw-coloured slender needles [2]	$C_{14}H_{11}O_7N_4F_3$	13·8	14·1	13·9	14·1
Dimethylaniline	165	162	Pale yellow stout tablets [2]	$C_{15}H_{13}O_7N_4F_3$	13·7	13·4	13·3	13·6
Diethylamine	113	—	Bright-yellow short stout tablets [2]	$C_{11}H_{13}O_7N_4F_3$	15·2	15·0	15·1	15·4
Lepidine	202	212	Orange-yellow plates [1]	$C_{17}H_{11}O_7N_4F_3$	12·6	12·7	12·8	12·9
Benzidine	250—252 (decomp.)	—	Rosettes of yellow stout prisms [2]	$C_{26}H_{18}O_{14}N_8F_6$	14·6	13·9	14·4	14·6
Diethylaniline	92	142	Greenish-yellow prisms [2]	$C_{17}H_{17}O_7N_4F_3$	13·0	11·7	12·5	12·7
4-*m*-Xylidine	183—184 (decomp.)	209	Pale yellow thin plates [2]	$C_{15}H_{13}O_7N_4F_3$	13·6	13·4	13·4	13·6
α-Naphthylamine	192 (decomp.)	161	Rosettes of pale yellow needles [2]	$C_{17}H_{11}O_7N_4F_3$	12·7	12·7	12·7	12·9
Quinaldine	198	191	Bright lemon-yellow long slender needles [1]	$C_{17}H_{11}O_7N_4F_3$	12·7	12·7	12·6	12·9

[1] Methyl alcohol containing 0·5% of the reagent used for crystallisation.
[2] Aqueous methyl alcohol containing 0·5% of the reagent used for crystallisation.
[3] Water containing 0·5% of the reagent used for crystallisation.
[4] The picrate m. p.s recorded are those given in " Organic Reagents for Organic Analyses," 1944, London.

3 : 4-*Diaminobenzotrifluoride.*—The reduction of 4-nitro-3-aminobenzotrifluoride (2·5 g.) in methyl alcohol (100 ml.) with a palladium–charcoal catalyst [from charcoal (0·5 g.) and palladium chloride (0·3 g.)] proceeded rapidly, and after evaporation of the solvent 3 : 4-*diaminobenzotrifluoride* was obtained. It crystallised from light petroleum–benzene in rosettes of small prisms, m. p. 58°. Sublimation at 140°/0·1 mm. gave rhombic plates, m. p. 58° (Found : N, 16·6. $C_7H_7N_2F_3$ requires N, 15·9%).

2 : 3-*Diphenyl*-6-*trifluoromethylquinoxaline.*—A solution of the diamine (0·2 g.) and benzil (0·2 g.) in methyl alcohol (5 ml.) was warmed on the steam-bath for 30 minutes and then cooled, whereupon 2 : 3-*diphenyl*-6-*trifluoromethylquinoxaline* (V) (0·2 g.) separated; it crystallised from methyl alcohol in shimmering, colourless, rectangular plates, m. p. 127° (Found : N, 8·3. $C_{21}H_{13}N_2F_3$ requires N, 8·0%).

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