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Short Communication

Tetrafluoro- and 2,4,5-trifluororesorcinol

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2,4,5,6-Tetrafluororesorcinol is of interest as a condensation polymer intermediate and has been used in the preparation of polycarbonates[1] and other polyesters. A good preparation of this compound however has not hitherto been described.

Pummer and Wall[2] first obtained 2,4,5,6-tetrafluororesorcinol in low yield as a by-product from the preparation of pentafluorophenol by the reaction between aqueous potassium hydroxide and hexafluorobenzene. Burdon *et al.*[3] later obtained it in higher yield by treating pentafluorophenol with potassium hydroxide in t-butanol solution and isolating the product as the dimethyl derivative after methylation. For several years now we have prepared 2,4,5,6-tetrafluororesorcinol in good yield by the reaction between aqueous potassium hydroxide and pentafluorophenol at 150°.

In early preparations we used the theoretical amount of potassium hydroxide (3 moles per mole of pentafluorophenol) and obtained 25–30% yields with *ca.* 50% conversion of pentafluorophenol. When the amount of potassium hydroxide was increased to 6 moles, other quantities and conditions remaining the same, 50–60% yields of tetrafluororesorcinol and virtually complete conversion of pentafluorophenol were obtained. A possible contribution to the increased rate and extent of conversion may be made by the higher concentration of non-hydrated hydroxyl ions which exists in the more concentrated solution[4].

When 2,3,5,6-tetrafluorophenol was used as a substrate under the same conditions with aqueous potassium hydroxide, 2,4,5-trifluororesorcinol was obtained in only 9% yield. Unless there is a large difference in the solubility of the potassium salts of pentafluorophenol and 2,3,5,6-tetrafluorophenol, under the reaction conditions, the much reduced conversion of the latter probably reflects its lower susceptibility to nucleophilic attack by virtue of it having only four fluorine atoms. In these reactions temperature control is important because below *ca.* 140° the rate is unacceptably low, while much charring and loss of product occurred in a reaction where the temperature rose to 180°.

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Since pentafluorophenol has been obtained[2] from aqueous potassium hydroxide and hexafluorobenzene it should be possible to prepare tetrafluororesorcinol in one stage from hexafluorobenzene, but it is probable that vigorous agitation of the initially heterogeneous reaction mixture would be necessary to promote the reaction. This agitation was not essential in the present work because hydrated potassium pentafluorophenate was quite soluble in aqueous potassium hydroxide solution under the reaction conditions.

After the 2,4,5,6-tetrafluororesorcinol was recrystallised once from benzene, its IR spectrum was compared with the reference spectra of tetrafluorocatechol and tetrafluorohydroquinone. If either isomer were present as an impurity in the tetrafluororesorcinol its concentration must be less than 5% (limit of detection). The NMR spectrum showed the presence of at least 95% of the *m*-isomer in the product. TLC indicated that tetrafluorohydroquinone was not present, but it was not a useful technique to detect the tetrafluorocatechol. The overall conclusion was that the tetrafluororesorcinol had a minimum isomeric purity of 90–95%.

The 2,4,5-trifluororesorcinol produced could not be purified from a non-isomeric impurity by recrystallisation, and a satisfactory elemental analysis was obtained only from material purified *via* its diacetate derivative. The orientation in this compound was confirmed by ^{1}H and ^{19}F NMR spectroscopy. Reference samples of possible isomeric impurities were not available for further study.

Experimental

Infrared spectra were measured on a Perkin–Elmer 337 spectrophotometer. TLC analyses were carried out with silica gel (Kieselgel GF_{254}) coated plates and 9:1 v/v chloroform, glacial acetic acid mixture. Melting points are uncorrected.

2,4,5,6-Tetrafluororesorcinol

Pentafluorophenol (185 g, 1 mole) and a solution of 85% purity potassium hydroxide (402 g, 6.06 moles) in water (500 ml) were shaken together in a 950 ml capacity stainless-steel autoclave at 150° for 5 h. The product, a slurry of crystals, was poured into hydrochloric acid (1.3 l, 9 *N*) and the resultant solution was extracted with methylene chloride (6 × 200 ml). Evaporation of the dried extracts gave pentafluorophenol (4.8 g).The residual aqueous acid solution was extracted with diethyl ether (3 × 500 ml, 3 × 300 ml). The combined dried extracts were evaporated and the residue (146.3 g) was distilled through a 15 cm indented column giving 2,4,5,6-tetrafluororesorcinol (109.7 g, 58% yield) b.p. 110–114°/15 mmHg, as a white solid, 95% by GLC (2 m × 6 mm silicone oil–Chromosorb W (15:85) at 150° and He carrier gas). The solid was dissolved in boiling benzene (450 ml) and moisture removed with a Dean–Stark trap. When allowed to cool the precipitated crystals were filtered off and dried *in vacuo* (0.1 mmHg/3 h) losing benzene to give 2,4,5,6-tetrafluororesorcinol as a white powder (95 g, 52% yield), m.p. 96.5–98.5° (sealed tube), b.p. 218°/760 mmHg, 99+% by GLC on the silicone oil column at 150°. (Found: C, 39.6; H, 1.2; F, 41.6. Calc. for $C_6H_2F_4O_2$: C, 39.6;

H, 1.1; F, 41.7%.) The IR spectrum was consistent with the proposed structure, $\nu_{\max.}$ (CCl_4) 3500 cm^{-1} (–OH) *ca.*1510 cm^{-1} (fluorinated aromatic ring), which was confirmed by NMR spectroscopy. TLC analysis showed only a single spot for this material.

A bis-*p*-toluenesulphonate derivative (nc) had m.p. 114–115° (ethanol). (Found C: 49.0; H, 2.8. $C_{20}H_{14}F_4O_6S_2$ requires C, 49.0; H, 2.9%.)

2,4,5,6-Tetrafluororesorcinyl diacetate (nc)

2,4,5,6-Tetrafluororesorcinol (4.46 g, 0.03 mole) and acetic anhydride (37 g) containing freshly fused anhydrous sodium acetate (2 g), were heated on a steam bath for 0.75 h. The hot mixture was poured into water (100 ml) and the precipitated white solid was filtered off and dried (5.87 g), m.p. 47–48°. A portion recrystallised from aqueous ethanol had a m.p. 47–48°. (Found: C, 45.1; H, 2.3; F, 28.7. $C_{10}H_6F_4O_4$ requires C, 45.1; H, 2.3; F, 28.5%.) TLC showed only one spot for this material which had a consistent IR spectrum. Acid hydrolysis of the diacetate gave 2,4,5,6-tetrafluororesorcinol with an IR spectrum practically identical to that of material produced by reaction between potassium hydroxide and pentafluorophenol.

2,4,5-Trifluororesorcinol (nc)

2,3,5,6-Tetrafluorophenol (166 g, 1.0 mole) and a solution of 85% pure potassium hydroxide (402 g, 6.06 moles) in water (500 ml) were shaken together in a 950 ml capacity stainless-steel autoclave at 150° for 5 h. The product was poured into hydrochloric acid (1.3 l, 9 *N*) and the solution was extracted with methylene chloride (5 × 200 ml). Evaporation of the combined dried extracts gave 2,3,5,6-tetrafluorophenol (81 g, 0.49 mole). The aqueous acid solution remaining was extracted with diethyl ether (5 × 200 ml) and the dried combined extracts were evaporated to leave a residue (36 g).

This material was sublimed (60–80°/0.04 mmHg) giving a white solid (31.8 g), m.p. 80–82° which was purified as described below by conversion to the diacetate and subsequent hydrolysis to 2,4,5-trifluororesorcinol (14.3 g, 9% yield), m.p. 82–84° (sealed tube) with an IR spectrum identical to that of authentic material prepared in the small-scale hydrolysis described below.

2,4,5-Trifluororesorcinyl diacetate (nc)

2,4,5-Trifluororesorcinol (4.1 g, 0.025 mole) and acetic anhydride (31 g) containing freshly-fused anhydrous sodium acetate (1.7 g) were heated together on a steam bath for 5 h. The reaction product was poured into water (100 ml) and the precipitate filtered off, washed with sodium bicarbonate solution and dried *in vacuo* over phosphoric oxide. Recrystallisation (50% v/v aqueous ethanol) gave 2,4,5-trifluororesorcinyl diacetate (3.85 g) m.p. 67–67.5° showing a single spot by TLC and having an IR spectrum consistent with the proposed structure. (Found: C, 48.3; H, 2.8; F, 23.0. $C_{10}H_7F_3O_4$ requires C, 48.3; H, 2.8; F, 23.0%.)

Hydrolysis of the diacetate (3.17 g) with sulphuric acid (60 ml, 5 *N*) gave 2,4,5-trifluororesorcinol (2.2 g) which was recrystallised (benzene) to give pure

2,4,5-trifluororesorcinol (1.32 g) m.p. 83–86° (sealed tube) which showed only a single spot by TLC (conditions as for the diacetate). (Found: C, 43.2; H, 2.2; F, 35.2. $C_6H_3F_3O_2$ requires C, 43.9; H, 1.8; F, 34.7%.) The structure was confirmed by the IR spectrum $\nu_{max.}$ (KBr) *ca.* 3250 cm^{-1} (–OH), *ca.* 1520 cm^{-1} (fluorinated aromatic ring) and by the NMR spectrum.

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