The Chemistry of Nitrilium Salts. Part 1. Acylation of Phenols and Phenol Ethers with Nitriles and Trifluoromethanesulphonic Acid

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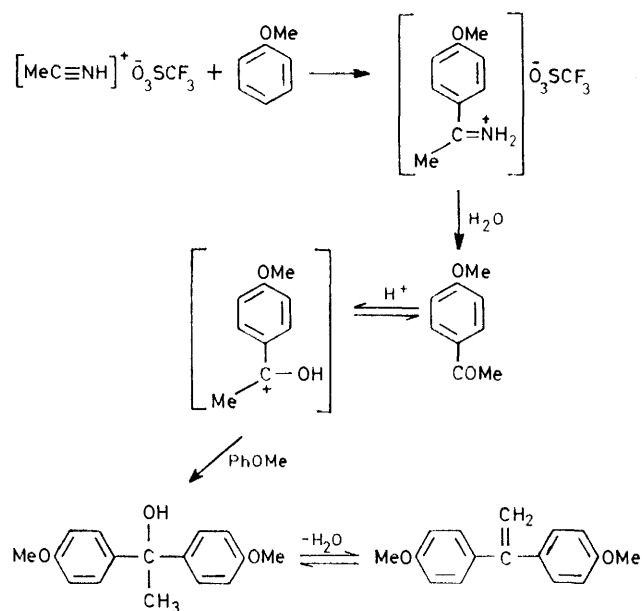
Aliphatic nitriles, RCN (R = Me, Pr^n, CH$_2$Cl, and CCl$_3$), in the presence of trifluoromethanesulphonic acid have been found to react with a number of mono-, di-, and tri-substituted phenols and phenol ethers at room temperature to give ketones after hydrolysis of the reaction mixture. Moderate to good yields of acylation products are obtained in the majority of these reactions. The yield with malononitrile and succinonitrile, which are only slightly soluble in the reaction medium, are generally poor, and reaction involves only one of the available nitrile groups. Attempts to use diethyl ether and dichloromethane as solvents for some of these reactions were unsuccessful, but limited success was achieved with nitromethane.

TRIFLUOROMETHANESULPHONIC ACID [1] (triflic acid) has been shown recently to be an effective catalyst for the Koch carboxylation of alkenes,[2] and the formylation of aromatic compounds with carbon monoxide.[3] This last reaction works well for alkyl-substituted aromatic compounds, but fails completely with anisole. In the early part of this century Hoesch,[4] and later Houben,[5] demonstrated that the acylation of phenols and phenol ethers could be achieved in good yields by reaction with an aromatic or aliphatic nitrile and dry HCl, usually in the presence of a Lewis acid, such as ZnCl$_2$ or AlCl$_3$. This Houben–Hoesch reaction [6] has found wide application not only for the synthesis of ketone derivatives of phenols and phenol ethers, but also for the acylation of pyrroles,[7,8] indoles,[9,10] thiophen,[11] and coumarones.[12] This suggested the possibility that triflic acid might also react with nitriles in the presence of phenols and phenol ethers in an analogous manner. This possibility has now been investigated and the results are now reported.

RESULTS AND DISCUSSION

Reactions of Acetonitrile.—Dropwise addition of acetonitrile to an equimolar amount of triflic acid at room temperature, followed 1 h later, by the addition of a one molar equivalent of anisole with stirring for 4.5 h gave only a 6% yield of 4-methoxyacetophenone after hydrolysis of the mixture. The yield of ketone increased to 9% on storing the mixture of acid, anisole, and nitrile at 0 °C for 72 h before hydrolysis, and extension of the reaction time to 2 weeks resulted in a further improvement to give a 15% yield. In these last reactions 1,1-bis(4,4'-dimethoxyphenyl)ethene (5%) was also isolated from the reaction mixtures. This is thought to arise by the reactions outlined in Scheme 1. Moisture introduced into the reaction vessel possibly on storage for this long period in a refrigerator could cause partial hydrolysis of the intermediate ketiminium salt. As a molecule of water is regenerated in the final dehydration step a trace of moisture only would be necessary to initiate reaction. The order of addition of the reactants also has an effect upon the product yield. Dropwise addition of triflic acid (1 mol equivalent) to a mixture of acetonitrile and anisole gave only 2% of 4-methoxy-

acetophenone. Increasing the amount of nitrile (mol ratio of acid : nitrile : anisole 1 : 10 : 1) did not result in any significant improvement, but increasing the ratio of acid : nitrile has a marked effect as can be seen by reference to the results in Table 1. In these reactions the acid was added slowly to acetonitrile and the mixture was left at room temperature for 2.5 to 3 h before addition of anisole. It was then maintained at room temperature for 2—3 weeks before hydrolysis. Under Houben–Hoesch conditions the reaction of anisole is reported [13] to

SCHEME 1

TABLE 1

Effect of increasing trifluoromethanesulphonic acid concentration on ketone yield [a]

CF$_3$SO$_3$H : CH$_3$CN : PhOMe (mol ratio)	Reaction time/days	4-MeOC$_6$H$_4$COCH$_3$ (%) [b]
1 : 1 : 1	12	15
2 : 1 : 1	13	46
3 : 1.5 : 1	13	58
5 : 1.5 : 1	21	81

[a] All reactions carried out at room temperature. [b] Yield of isolated product based on anisole taken for reaction.

give an unspecified yield of a compound $PhOCH_3 \cdot CH_3$-$CN \cdot 2HCl$, which is presumably the ketiminium salt $[4\text{-}CH_3OC_6H_4C(CH_3)=NH_2]^+$ HCl_2^-, although in the absence of further information this is speculative.

A number of mono-, di-, and tri-hydroxy- and methoxy-substituted benzenes have been acetylated with acetonitrile and triflic acid under similar conditions, and the results are shown in Table 2. Although the long

TABLE 2

Acylation reactions of phenols and phenol ethers with acetonitrile and trifluoromethanesulphonic acid [a]

Aromatic substrate	Reaction time/days	Product	Yield (%) [b]
C_6H_5OMe	12	$4\text{-}MeOC_6H_4COCH_3$	58 (—) [c]
C_6H_5OH	15	$4\text{-}HOC_6H_4COCH_3$	74 (—) [d]
$2\text{-}CH_3C_6H_4OH$	14	$4\text{-}OH\text{-}3\text{-}CH_3C_6H_3COCH_3$	67 (—) [e]
$1,3\text{-}(MeO)_2C_6H_4$	17	$2,4\text{-}(MeO)_2C_6H_3COCH_3$	83 (22) [f]
$1,3\text{-}(HO)_2C_6H_4$ [g]	13	$2,4\text{-}(HO)_2C_6H_3COCH_3$	87 (70 [h], 94 [i])
$1,4\text{-}(MeO)_2C_6H_4$ [j]	12	$2,5\text{-}(MeO)_2C_6H_3COCH_3$	12 (—) [e]
$1,4\text{-}(HO)_2C_6H_4$	15	$2,5\text{-}(HO)_2C_6H_3COCH_3$	— (—) [e]
$1,3,5\text{-}(HO)_3C_6H_3$	12	$2,4,6\text{-}(H)O_3C_6H_2COCH_3$, H_2O	40 (74) [h]
$1,3,5\text{-}(MeO)_3C_6H_3$	15	$2,4,6\text{-}(MeO)_3C_6H_2COCH_3$	71 (85) [k]

[a] Except where stated reactions were carried out at room temperature by addition of the aromatic substrate (0.05 mol) in CH_3CN (12 cm³, 0.023 mol) to a premixed solution of CF_3SO_3H (0.15 mol) and CH_3CN (0.075 mol). [b] Yield of isolated product based on aromatic substrate taken. The values in parentheses are the yield reported for the same reaction carried out under standard Houben–Hoesch conditions with HCl–$ZnCl_2$ catalyst. [c] Reported (ref. 13) to give $C_6H_5OMe \cdot CH_3CN \cdot 2HCl$, m.p. 104—112 °C (decomp.). [d] Reported (ref. 6) to give $[C_6H_5OCMe = \overset{+}{N}H_2]Cl^-$. [e] Reaction has not been reported for Houben–Hoesch conditions. [f] S. Ebine, Sci. Rept. Saitama Univ., 1954, 1A, 157 (Chem. Abs., 1955, 49, 13148e). [g] Addition of resorcinol (0.02 mol) in CH_3CN (15 cm³, 0.29 mol) to a mixture of CH_3CN (0.025 mol) and CF_3SO_3H (0.05 mol). [h] Ref. 4, [i] Ref. 5. [j] 1,4-Dimethoxybenzene (0.05 mol) in CH_3CN (21cm³, 0.04 mol) added to a mixture of CH_3CN (0.05 mol) and CF_3SO_3H (0.05 mol). [k] Ref. 11—this represents the yield of the ketenimine hydrochloride.

reaction times are undoubtedly necessary in the case of anisole it is doubtful whether they are essential for the more reactive phenols and phenol ethers, but optimum conditions have not been established in these cases. Warming these reaction mixtures even within the mild temperature range of 44—48 °C results only in the formation of dark, resinous solids. The yields of ketone products reported to be formed under Houben–Hoesch conditions are included in Table 2 for comparison. The low yield of product isolated from the reaction of phloroglucinol is caused by the difficulty of extracting the ketone from the aqueous phase; this problem is not experienced in the Houben–Hoesch reaction where diethyl ether is usually employed as a solvent.[6] It is noticeable that the reaction of 1,3,5-trimethoxybenzene, where the product is considerably more soluble in organic solvents, gave a much higher product yield. An interesting difference in the results obtained with triflic acid

when compared with those reported under Houben–Hoesch conditions is seen in the reaction of phenol. Phenol is reported to form only the hydrochlorides of iminophenyl esters, $[PhOCR=NH_2]^+$ Cl^- ($R = Me$, CH_2Cl, $CHCl_2$, CCl_3, $PhCH_2$, or Ph) on reaction with the nitriles, RCN, in the presence of HCl with or without zinc chloride.[6] In contrast, both acetonitrile and n-butyronitrile (vide infra) give only the respective C-acylation products in the presence of triflic acid.

A detailed mechanistic investigation of the acylation of phenols and phenol ethers in triflic acid has not been undertaken, but in a separate investigation [14] it has been

SCHEME 2
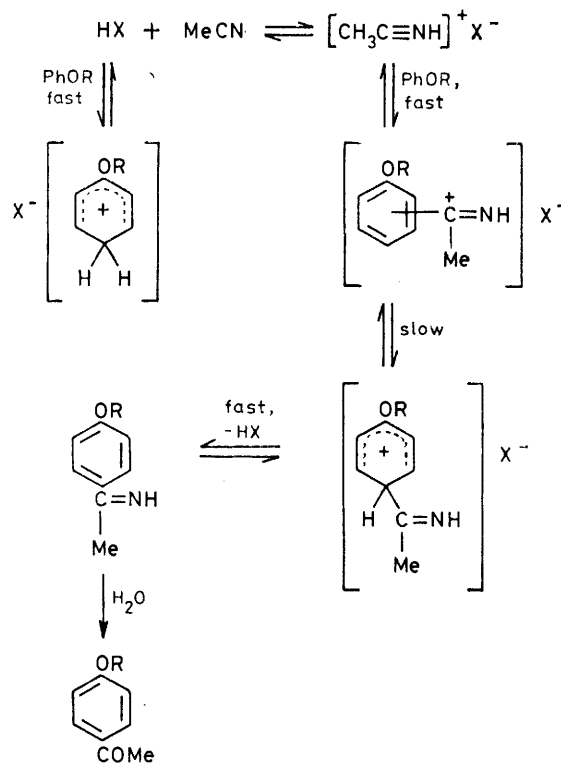
shown that addition of triflic acid to an equimolar amount of acetonitrile under dry nitrogen at room temperature results in the disappearance of the i.r. band at 2 245 cm⁻¹ [$\nu(C\equiv N)$ of nitrile] with the formation of a viscous, red oil having a strong band at 2 300 cm⁻¹. This shift to higher frequency is similar to that observed on formation of the nitrilium salt $[CH_3C\equiv NH]^+$ $SbCl_6^-$ [$\nu(C\equiv N)$ 2 275 cm⁻¹],[15] and the reported values of between 2 300—2 400 cm⁻¹ for the $\nu(C\equiv N)$ bands for N-alkylnitrilium salts having BF_4^-, BCl_4^-, or $SbCl_6^-$ counterions.[15,16] Similar values in the range 2 350—2 400 cm⁻¹ have been found for the N-alkylnitrilium triflate salts $[RC\equiv NCH_3]^+$ $CF_3SO_3^-$ [$R = Me$, Pr^i, Ph, CH_2=$CHCH_2$, and $NC(CH_2)_3$].[14] This strongly suggests that in triflic acid acetonitrile forms the nitrilium triflate salt, $[CH_3C\equiv NH]^+$ $CF_3SO_3^-$, and a mechanism such as that outlined in Scheme 2 may operate in the acylation reactions. The poor ketone yield obtained when the

TABLE 3

Acylation reactions of phenols and phenol ethers with
n-butyronitrile and trifluoromethanesulphonic acid [a]

Aromatic Substrate	Reaction time/days	Product	Yield (%) [b]
C_6H_5OMe [c]	14	4-MeOC$_6$H$_4$COPr^n	40
C_6H_5OH	15	4-HOC$_6$H$_4$COPr^n	78
2-CH$_3$C$_6$H$_4$OH	21	4-HO-3-CH$_3$C$_6$H$_3$COPr^n	75
1,3-(MeO)$_2$C$_6$H$_4$ [d]	14	2,4-(MeO)$_2$C$_6$H$_3$CoPr^n	76
1,3-(HO)$_2$C$_6$H$_4$	14	2,4-(HO)$_2$C$_6$H$_3$COPr^n	77
1,4-(MeO)$_2$C$_6$H$_4$ [d]	14	2,5-(MeO)$_2$C$_6$H$_3$COPr^n	0 [e]
1,4-(HO)$_2$C$_6$H$_4$	18	2,5-(HO)$_2$C$_6$H$_3$COPr^n	0 [e]
1,3,5-(MeO)$_3$C$_6$H$_3$ [d]	13	2,4,6-(MeO)$_3$C$_6$H$_2$COPr^n	67
1,3,5-(HO)$_3$C$_6$H$_3$	16	2,4,6-(HO)$_3$C$_6$H$_2$COPr^n, H$_2$O	45

[a] Except where stated reactions were carried out at room temperature by addition of the aromatic substrate (0.05 mol) in Pr^{n}CN (15 cm^3, 0.17 mol) to a premixed solution of CF$_3$SO$_3$H (0.15 mol) and Pr^{n}CN (0.075 mol). [b] Yield of isolated product based on aromatic substrate taken. [c] Neat anisole (0.5 mol) added to a mixture of CF$_3$SO$_3$H (0.15 mol) and Pr^{n}CN (0.075 mol). [d] Aromatic substrate (0.025 mol) in Pr^{n}CN (15 cm^3, 0.17 mol), added to a mixture of CF$_3$SO$_3$H (0.075 mol) and Pr^{n}CN (0.037 mol). [e] >80% of starting material recovered.

acid is added to a mixture of the nitrile and aromatic substrate may be a result of competition between these two reactants for the available acid. Such competition would lower the concentration of nitrilium salt and deactivate some of the aromatic compound towards electrophilic attack. There is conflicting information on the relative basicities of aromatic ethers and aliphatic nitriles. The pK_a value of acetonitrile, as measured by titration against perchloric acid in glacial acetic acid, is reported to be -4.2,[17] but a much lower value of -10.1 has been calculated from conductivity measurements on solutions of the nitrile in 100% sulphuric acid.[18] The pK_a value for anisole is estimated to be -6.54 ± 0.02 [19] by measurement of the distribution of protonated and non-protonated ether in different solvents. Since this last value lies between the two extreme values for the basicity of acetonitrile competition for the available triflic acid seems not unreasonable. This competition is diminished when the acid and nitrile are mixed and left for several hours before addition of the aromatic substrate, i.e. the procedure followed in the majority of these reactions.

I.r. spectroscopic evidence [14] indicates that protonation of a nitrile by triflic acid is a rapid reaction, but the nitrilium salts formed are only weak electrophiles,[20] and

attack on the aromatic substrate is expected to be slow. Jeffrey and Satchell [21] have suggested that for the reaction between acetonitrile and phloroglucinol with a ZnCl$_2$–HCl catalyst the rate-limiting step is probably the conversion of an initial π-complex intermediate into the σ-complex. In common with many reactions of phenols and phenol ethers with weak electrophiles these acylation reactions are regioselective and attack occurs in the position para to the OH or OCH$_3$ substituent. Where para-substitution is not possible as with 1,4-dimethoxy- and 1,4-dihydroxy-benzene ketone yields are poor. A similar effect has been noted for the related Gattermann reaction.[22]

Reactions of n-Butyronitrile.—Following a similar procedure to that established for the reactions of acetonitrile, reaction between triflic acid, n-butyronitrile, and various phenols and phenol ethers at room temperature over 2—3 weeks gave the acylation products shown in Table 3. The use of n-butyronitrile under Houben–Hoesch conditions has been reported only for resorcinol (no ketone yield given) [23] and phloroglucinol [74% yield of 2,4,6-(HO)$_3$C$_6$H$_2$COPr^n].[24] The low product yield obtained in the reaction of phloroglucinol with triflic acid is again a reflection of the difficulty of isolating the product. In general, the results with n-butyronitrile follow closely those obtained with acetonitrile.

Reactions of Mono- and Tri-chloroacetonitriles.—Limited availability of these more expensive nitriles necessitated a slight change in experimental procedure. Rather than adding a solution of the aromatic substrate in the nitrile to a premixed solution of the nitrile and triflic acid at room temperature, in these reactions the triflic acid was added slowly to a stirred mixture of the nitrile and the aromatic substrate, and the mixture was then stored at room temperature for 11—20 days before hydrolysis and isolation of the acylation products shown in Table 4. For reasons outlined above this procedure has the disadvantage of increasing the possibility of competition between the nitrile and the aromatic substrate for the available acid, but less nitrile is required. Moderate to good yields of ketones are obtained provided the mixture of nitrile and aromatic compound is homogeneous. When this is not the case, as in the reaction between resorcinol and CH$_2$ClCN, a low yield of product results.

TABLE 4

Acylation reactions of phenols and phenol ethers with mono- and tri-chloroacetonitrile and trifluoromethane-sulphonic acid

Nitrile	Aromatic substrate	Reaction time/days	Product	Yield (%) [a]
ClCH$_2$CN [b]	C_6H_5OMe	11	4-MeOC$_6$H$_4$COCH$_2$Cl	63
CCl$_3$CN [c]	C_6H_5OMe	17	4-MeOC$_6$H$_4$COCCl$_3$	59
ClCH$_2$CN [b]	1,3-(HO)$_2$C$_6$H$_4$	14	2,4-(HO)$_2$C$_6$H$_4$COCH$_2$Cl	23
CCl$_3$CN [c]	1,3-(HO)$_2$C$_6$H$_4$	15	2,4-(HO)$_2$C$_6$H$_4$COCCl$_3$	52
ClCH$_2$CN [b]	1,3-(MeO)$_2$C$_6$H$_4$	14	2,4-(MeO)$_2$C$_6$H$_4$COCH$_2$Cl	96
CCl$_3$CN [b]	1,3-(MeO)$_2$C$_6$H$_4$	19	2,4-(MeO)$_2$C$_6$H$_4$COCCl$_3$	59
ClCH$_2$CN [c,d]	1,3,5-(MeO)$_3$C$_6$H$_3$	19	(ClCH$_2$CO)$_2$NH	37 [e]
CCl$_3$CN [c,d]	1,3,5-(MeO)$_3$C$_6$H$_3$	10		[e]

[a] Yield of isolated product based on aromatic substrate taken. [b] Using a mol ratio of acid : nitrile : aromatic substrate of 1.5 : 1.5 : 1 at room temperature. [c] Using a mol ratio of acid : nitrile : aromatic substrate of 3 : 1.5 : 1. [d] With diethyl ether as solvent. [e] Recovery of 1,3,5-(MeO)$_3$C$_6$H$_3$ >87%.

In an effort to overcome this problem a solvent was used for some of the reactions. In the case of 1,3,5-trimethoxybenzene, which was almost insoluble in both CH_2ClCN and CCl_3CN, this was added as a solution in diethyl ether to a stirred suspension of the nitrile and triflic acid; in neither case was any acetylation product observed. The reaction of CH_2ClCN and 1,3,5-trimethoxybenzene was also attempted with dichloromethane as solvent with a similar lack of success. Whereas the reaction of trichloroacetonitrile in ether gave only unchanged starting materials, the reactions of CH_2ClCN gave bis(chloroacetyl)amine in 37 and 16% yields when ether and dichloromethane respectively were used as solvents. In a control experiment the same compound was obtained in 41% yield after hydrolysis of a mixture of chloroacetonitrile and triflic acid (1 : 1 mol ratio)
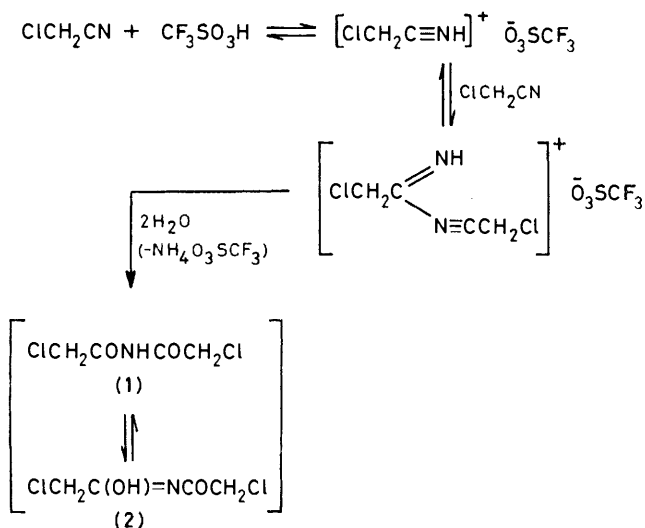
SCHEME 3

after 36 h at room temperature suggesting that it may be formed by the reaction sequence given in Scheme 3. Similar dimerisation reactions of nitriles having α-hydrogens have been reported to take place with HCl at temperatures in the range 0—20 °C.[25-27] Bis(chloroacetyl)amine has been described previously[26] but without spectroscopic detail. I.r. spectroscopy indicates that it is a mixture of the tautomers (1) and (2) as evidenced by bands at 3 247 [ν(OH)], 3 165 [ν(NH)], 1 754 [ν(C=O)], and 1 543 cm^{-1} [ν(C=N)]. Trichloroacetonitrile does not dimerise when mixed with triflic acid even after 6 days, but instead affords an 18% yield of trichloroacetamide after hydrolysis.

Reactions of Malononitrile and Succinonitrile.—A major difficulty in the reactions of aliphatic dinitriles is that they are insoluble in the reaction medium. Successful acylation of anisole to give $4\text{-}MeOC_6H_4COCH_2CN$ (40% yield) was achieved by addition of triflic acid to a suspension of malonitrile in anisole, followed by stirring the mixture at room temperature for 11 days. This procedure was not successful with other phenol ethers and

phenols. The use of a solvent in these reactions has met with only limited success. Houben–Hoesch reactions are usually carried out in diethyl ether or methyl acetate,[6] but triflic acid reacts readily with these and most other common solvents.[1] Attempted reaction between malononitrile and resorcinol by addition of triflic acid to an ethereal solution of the nitrile, followed by addition of a solution of the phenol in the same solvent gave only recovered starting materials after 16 days at room temperature. Reaction between succinonitrile and 1,3-dimethoxybenzene also failed under similar conditions. Aromatic and chlorinated solvents have limited utility as they are invariably poor solvents for phenols and phenol ethers, and of the many solvents investigated only nitromethane was successful. Even with this solvent work-up was difficult and product yields were low. Slow addition of triflic acid to a solution of malononitrile in nitromethane followed, after 40 min, by the addition of 1,3-dimethoxybenzene in nitromethane gave, after 12 days at room temperature, a 39% yield of $2,4\text{-}(MeO)_2C_6H_3COCH_2CN$. Under similar conditions reaction between malononitrile and phloroglucinol in nitromethane gave only a viscous, brown oil, which undoubtedly contained acylation product, but a satisfactory separation procedure could not be achieved. Succinonitrile under comparable conditions gave $2,4\text{-}(HO)_2C_6H_3COCH_2CH_2CN$ (37% yield) with resorcinol.

Despite the limited success of these reactions it is interesting that only one of the nitrile groups react with the aromatic substrate under the conditions employed. Zil'berman *et al.*[25,28] have reported that, with the exception of adiponitrile, the dinitriles $NC(CH_2)_nCN$ ($n = 3, 4, 6, 7,$ and 8) react with HCl under mild conditions to form the corresponding di(chloroimonium) dichlorides, $[H_2N=CCl(CH_2)_nCCl=NH_2]^{2+}$ $2Cl^-$. In the acylation reactions of dinitriles with triflic acid there was no evidence of any products of the type $ArCO(CH_2)_nCOAr$, $ArCO(CH_2)_nCONH_2$, or $ArCO(CH_2)_nCO_2H$ indicative of the formation of dinitrilium salt intermediates. The only report of a reaction of a dinitrile under Houben–Hoesch conditions is that between succinonitrile and resorcinol to give $2,4\text{-}(HO)_2C_6H_3COCH_2CH_2CO_2H$ in unspecified yield.[29] It is not clear from the report of this work whether this is best explained by the formation of di(chloroimonium) salt or dinitrilium salt intermediates, or whether the second nitrile group is only converted into the carboxylic group on final hydrolysis.

EXPERIMENTAL

photometer, [1]H n.m.r. spectra on a Perkin-Elmer R32 spectrometer, and mass spectra on an AEI MS902 instrument.

Reactions of Anisole.—(a) *Preliminary experiments.* Dropwise addition of acetonitrile (8.2 g, 0.2 mol) over a period of 1 h to triflic acid (30.0 g, 0.2 mol) maintained at 15 °C gave a bright yellow solution, which was stirred for a further 1.5 h before dropwise addition of anisole (43.3 g, 0.4 mol) over 2 h, whereupon the reaction mixture turned red. Water (70 cm³) was then added, and the mixture heated under reflux for 1.75 h. The organic phase was washed with water, dried (anhydrous MgSO₄), and distilled giving anisole (34.6 g, 80% recovery), and a pot residue which was recrystallised to give white needles of 4-methoxyacetophenone (1.68 g, 0.012 mol, 6%), m.p. 38—40 °C (lit.,[30] m.p. 38—39 °C).

When triflic acid (15.0 g, 0.1 mol) was added dropwise during 1 h to a stirred mixture of anisole (10.8 g, 0.1 mol) and acetonitrile (4.1 g, 0.1 mol), and stirring was then continued for 2.5 h, hydrolysis of the reaction mixture gave 4-methoxyacetophenone (0.34 g, 0.002 3 mol, 2%).

Dropwise addition of triflic acid (15.0 g, 0.1 mol) during 20 min to acetonitrile (4.1 g, 0.1 mol) cooled to between −12 and −7 °C followed by stirring for 90 min before addition of anisole (10.8 g, 0.1 mol) during 40 min, and storage of the reaction mixture at 0 °C for 12 days gave, after hydrolysis, 4-methoxyacetophenone (2.3 g, 0.015 mol, 15%), together with white crystals of 1,1-bis(4,4′-dimethoxyphenyl)ethene (0.5 g, 0.002 1 mol, 5%), m.p. 139—141 °C (lit.,[31] m.p. 142 °C) [δ(CDCl₃) 3.84 (6 H, s, OCH₃), 5.30 (2 H, s, =CH₂), 6.89 (4 H, d, A part of AA′ XX′ spectrum, J_{AX} 9 Hz), 7.32 (4 H, d, X part); *m/e* 240 (*M*⁺·) 100%].

Addition of acetonitrile (41.0 g, 1.0 mol) dropwise during 1 h to triflic acid (15.0 g, 0.1 mol) cooled to −7 °C, followed by addition of anisole (10.8 g, 0.1 mol) during 1 h while maintaining the same temperature, then stirring for a further 2.5 h followed by hydrolysis, failed to give any ketone product.

(b) *Effect of increasing the trifluoromethanesulphonic acid concentration.* In these experiments the triflic acid was added slowly during a period of 30 min to the acetonitrile with vigorous stirring, and the mixture was then left at room temperature for 3 h before addition of the anisole (5.4 g, 0.05 mol) during 30 min. The mixture was then put aside for a period of 12—21 days at room temperature before hydrolysis. The results are given in Table 1.

Typical Procedure for the Acetylation Reactions with Acetonitrile.—The triflic acid (22.5 g, 0.15 mol) was added dropwise during 30 min to acetonitrile (3.1 g, 0.075) at room temperature, and the mixture was left at room temperature for 1.5—3.5 h before addition of the phenol or phenol ether (0.05 mol) as a solution in acetonitrile (12 cm³). The mixture was then stored at room temperature for 12 to 17 days before addition of water (70 cm³), and heating under reflux for *ca.* 1.5 h. The organic layer was separated, dried (anhydrous MgSO₄), and the excess of acetonitrile was removed by distillation to give a pot residue which was purified by recrystallisation. The results are given in Table 2 and the products were identified from the following data. 4-HOC₆H₄COCH₃: m.p. 107 °C (from Et₂O) (lit.,[30] m.p. 108.5—110 °C), δ(CDCl₃) 2.58 (3 H, s, COCH₃), 6.96 (2 H, d, A part of AA′XX′ spectrum, J_{AX} 8.5 Hz), 7.92 (2 H, d, X part); the signal for OH was not observed.

4-HO-3-CH₃C₆H₃COCH₃: m.p. 105.5—106.5 °C (from H₂O) (lit.,[30] m.p. 104 °C), δ(CDCl₃) 2.25 (3 H, s, CH₃), 2.53 (3 H, s, COCH₃), 6.71 (1 H, d, 5-H, $J_{5,6}$ 8.5 Hz), 7.61 (2 H, dd and d overlapping, 2-H and 6-H, $J_{2,6}$ 2.5 Hz), 7.02—7.32 (1 H, broad s, OH); ν_max. 3 067 (OH) and 1 647 (C=O) cm⁻¹; *m/e* 150 (*M*⁺·) 48.6%.

2,4-(MeO)₂C₆H₃COCH₃: m.p. 35—37 °C (from Et₂O) (lit.,[30] m.p. 39—41 °C), δ(CDCl₃) 2.58 (3 H, s, COCH₃), 3.87 (3 H, s, OCH₃), 3.92 (3 H, s, OCH₃), 6.55 (2 H, dd and d overlapping, 3-H and 5-H, $J_{3,5}$ 2.5 Hz) and 7.86 (1 H, d, 6-H, $J_{5,6}$ 8.5 Hz). The i.r. spectrum was identical to that of an authentic sample.

2,4-(HO)₂C₆H₃COCH₃: m.p. 138—140 °C (from H₂O) (lit.,[32] m.p. 140—141 °C), δ{(CD₃)₂CO} 2.5 (3 H, s, COCH₃), 6.25 (2 H, dd and d overlapping, 3-H and 5-H, $J_{3,5}$ 2.5 Hz), 7.58 (1 H, d, 6-H, $J_{5,6}$ 8.5 Hz), 9.15 (1 H, broad s, OH), and 12.4 (1 H, broad s, OH).

2,5-(MeO)₂C₆H₃COCH₃: yellow oil (lit.,[30] m.p. 18—20 °C), p.p.m. rel. to external *p*-C₆H₄Cl₂ reference (neat liquid) +4.92 (3 H, s, COCH₃), +3.82 (3 H, s, OCH₃), +3.75 (3 H, s, OCH₃), +0.72 (2 H, dd and d overlapping, 3-H and 4-H, $J_{3,4}$ 8 Hz) and +0.34 (1 H, d, 6-H, $J_{4,6}$ 2.5 Hz); *m/e* 180 (*M*⁺·) 52.9%.

2,4,6-(MeO)₃C₆H₂COCH₃: m.p. 98—100 °C (from Et₂O) (lit.,[33] m.p. 100—103 °C), δ(CDCl₃) 2.37 (3 H, s, COCH₃), 3.69 (6 H, s, OCH₃), 3.70 (3 H, s, OCH₃), and 5.97 (2 H, s, 3-H and 5-H); *m/e* 210 (*M*⁺·) 17.6%.

2,4,6-(HO)₃C₆H₂COCH₃,H₂O: m.p. 216—218 °C (from H₂O) (lit.,[21] m.p. 219 °C), δ{(CD₃)₂CO} 2.60 (3 H, s, COCH₃), 3.20 (2 H, broad s, H₂O), 5.94 (2 H, s, 3-H and 5-H), 9.20 (1 H, broad s, OH), and 11.65 (2 h, broad s, OH).

Reactions of n-Butyronitrile.—Triflic acid (22.5 g, 0.15 mol) was added dropwise to n-butyronitrile (5.2 g, 0.075 mol) during 40 min with stirring and the mixture was left at room temperature for 3 h before the phenol or phenol ether (0.05 mol) was added as a solution in n-butyronitrile (12—15 cm³) during a period of 40 min. The mixture was stored for 14 days before addition of water (50 cm³), and heating under reflux for 1 h. The work-up procedure was similar to that used for the reactions of acetonitrile. The results are given in Table 3, and the products were identified from the following data. 4-HOC₆H₄COPr[n]: m.p. 90.5—92 °C (from aq. EtOH) (lit.,[30] m.p. 91 °C), δ(CDCl₃) 1.05 (3 H, t, CH₃, *J* 7 Hz), 1.83 (2 H, sextet, CH₂), 2.98 (2 H, t, CH₂CO, *J* 7 Hz), 7.01 (2 H, d, A part of AA′XX′ spectrum, J_{AX} 8.5 Hz), and 7.96 (2 H, d, X part)—the signal for OH was not seen; *m/e* 164 (*M*⁺·) 26.7%; ν_max. 3 360 (OH) and 1 660 (C=O) cm⁻¹.

4-NO-3-CH₃C₆H₃COPr[n]: m.p. 127—128 °C (from C₆H₆) (lit.,[34] m.p. 132 °C), δ(CDCl₃) 1.02 (3 H, t, CH₃, *J* 7 Hz), 1.78 (2 H, sextet, CH₂), 2.32 (3 H, s, CH₃), 2.92 (2 H, t, CH₂CO, *J* 7 Hz), 6.90 (1 H, d, 5-H, $J_{5,6}$ 8 Hz), 7.76 (2 H, dd and d overlapping, 2-H and 6-H, $J_{2,6}$ 2.5 Hz), and 7.32 (1 H, broad s, OH); *m/e* 178 (*M*⁺·) 45.6%; ν_max. 3 355 (OH) and 1 678 (C=O) cm⁻¹.

2,4-(MeO)₂C₆H₃COPr[n]: yellow oil, b.p. 140—142/1 mmHg (lit.,[33] b.p. 146—147 °C, 2 mmHg), δ(CDCl₃) 0.92 (3 H, t, CH₃, *J* 7 Hz), 1.56 (2 H, sextet, CH₂), 2.82 (2 H, t, CH₂CO, *J* 7 Hz), 3.75 (3 H, s, OCH₃), 3.78 (3 H, s, OCH₃), 6.35 (2 H, dd and d overlapping, 3-H and 5-H, $J_{3,5}$ 2 Hz), and 7.56 (1 H, d, 6-H, $J_{5,6}$ 9 Hz); *m/e* 208 (*M*⁺·) 14%; ν_max. 1 681 (C=O) cm⁻¹.

2,4-(HO)₂C₆H₃COPr[n]: m.p. 65—65.5 °C (from light petroleum) (lit.,[35] m.p. 68—70 °C), δ[(CD₃)₂CO] 0.93 (3 H, t, CH₃, *J* 7 Hz), 1.66 (2 H, sextet, CH₂), 2.84 (2 H, t, CH₂CO, *J* 7 Hz), 6.24 (2 H, dd and d overlapping, 3-H and 5-H,

$J_{3,5}$ 2.5 Hz), 7.60 (1 H, d, 6-H, $J_{5,6}$ 8.5 Hz) and 12.62 (1 H, broad s, OH)—the signal for the OH in the 4-position of the aromatic ring was not seen; m/e 180 ($M^{+\cdot}$) 34.8%; $\nu_{max.}$ 3 322 (OH), and 1 639 (C=O) cm^{-1}.

2,4,6-(MeO)$_3$C$_6$H$_2$COPr^n: yellow oil, b.p. 158—60/1 mmHg (Found: C, 65.3; H, 7.4. C$_{13}$H$_{18}$O$_4$ requires C, 65.5; H, 7.6%), δ(CDCl$_3$) 0.92 (3 H, t, CH$_3$, J 7 Hz), 1.62 (2 H, sextet, CH$_2$), 2.62 (2 H, t, CH$_2$CO, J 7 Hz), 3.69 (6 H, s, OCH$_3$), 3.71 (3 H, s, OCH$_3$), and 5.98 (2 H, s, H$_3$ and H$_5$); m/e 238 (M^+) 6.1%; $\nu_{max.}$ 1 709 (C=O) cm^{-1}.

2,4,6-(HO)$_3$C$_6$H$_2$COPr^n: m.p. 181.5—183 °C (lit.,[24] m.p. 180—181 °C) δ[(CD$_3$)$_2$CO] 0.92 (3 H, t, CH$_3$, J 7 Hz), 1.58 (2 H, sextet, CH$_2$), 2.97 (2 H, t, CH$_2$CO, J 7 Hz), 5.84 (2 H, s, 3-H and 5-H), and 10.0—12.4 (ca. 3 H, broad s, OH); m/e 196 ($M^{+\cdot}$) 27.1%; $\nu_{max.}$ 3 496, 3 448, 3 367 (OH), and 1 612 (C=O) cm^{-1}.

4-MeOC$_6$H$_4$COPr^n: b.p. 135—136 °C/10 mmHg (m.p. 20 °C) (lit.,[36] b.p. 162—163 °C/20 mmHg) δ(CDCl$_3$) 0.95 (3 H, t, CH$_3$, J 7 Hz), 1.65 (2 H, sextet, CH$_2$), 2.75 (2 H, t, CH$_2$CO, J 7 Hz), 3.70 (3 H, s, OCH$_3$), 6.72 (2 H, d, A part of AA'XX' spectrum, J_{AX} 9 Hz), and 7.72 (2 H, d, X part); $\nu_{max.}$ 1 692 (C=O) cm^{-1}; m/e 178 ($M^{+\cdot}$) 14%.

Reactions of Monochloroacetonitrile.—(a) *With triflic acid.* The acid (3.0 g, 0.02 mol) was added slowly to the nitrile (1.5 g, 0.02 mol) cooled at −78 °C. The mixture was allowed to warm to room temperature, and was maintained at this temperature with intermittent shaking for 36 h before being stirred with water (15 cm^3) during 3 h. The white needles which precipitated were identified as bis-(chloroacetyl)amine (0.7 g, 0.008 mol, 41%), m.p. 191—193 °C (from EtOH) (Found: C, 28.4; H, 3.3; Cl, 40.9; N, 8.2. Calc. for C$_4$H$_5$Cl$_2$NO$_2$: C, 28.2; H, 2.9; Cl, 41.9; N, 8.2%), δ[(CD$_3$)$_2$CO] 2.80 (1 H, s, NH) and 4.85 (4 H, s, CH$_2$CO); m/e 169 ($M^{+\cdot}$) 1.8%, 134 (M − Cl)$^+$ 74.8%, 120 (M − CH$_2$Cl)$^+$ 41.6%, 77 (CH$_2$ClCO)$^+$ 100%, 49 (CH$_2$Cl)$^+$ 82.8%, and 42 (CH$_2$=C=O)$^{+\cdot}$ 58.5%.

(b) *With phenols and phenol ethers.* Triflic acid (5.6 g, 0.037 mol) was added during 30 min to a mixture of the nitrile (2.8 g, 0.037 mol) and the aromatic substrate (0.025 mol). The mixture was stirred for 1 h at room temperature and then left at this temperature for 11—19 days. The intense red solution was then stirred with water (25 cm^3) for 1 h, and the product was either filtered off directly and recrystallised, or the solution was extracted repeatedly with diethyl ether, and the product obtained by evaporation of the solvent from the dry extract. In some cases it was necessary to separate the product from the starting material by chromatography (alumina; Et$_2$O eluant). The results are given in Table 4, and the products were identified from the following data. 4-MeOC$_6$H$_4$COCH$_2$Cl: m.p. 98—100 °C (lit.,[37] m.p. 102 °C), δ(CDCl$_3$) 3.92 (3 H, s, OCH$_3$), 4.69 (2 H, s, CH$_2$Cl), 6.98 (2 H, d, A part of an AA'XX' spectrum, J_{AX} 8.5 Hz), and 7.96 (2 H, d, X part); m/e 184 ($M^{+\cdot}$) 2.8% and 135 (M − CH$_2$Cl)$^+$ 100%; $\nu_{max.}$ 1 690 (C=O) cm^{-1}.

2,4-(HO)$_2$C$_6$H$_3$COCH$_2$Cl: m.p. 130—132 °C (lit.,[38] m.p. 130 °C), δ[(CD$_3$)$_2$CO] 4.88 (2 H, s, CH$_2$Cl), 6.65 (2 H, dd and d overlapping, 3-H and 5-H, $J_{3,5}$ 2.5 Hz), 7.92 (1 H, d, 6-H, $J_{5,6}$ 8.5 Hz) and 11.67 (1 H, s, OH)—the signal for the OH in the 4-position of the aromatic ring was not seen; $\nu_{max.}$ 3 289 (OH) and 1 626 cm^{-1} (C=O).

2,4-(MeO)$_2$C$_6$H$_3$COCH$_2$Cl: m.p. 114—116 °C (lit.,[6] m.p. 114—115 °C), [(CD$_3$)$_2$CO] 3.95 (3 H, s, OCH$_3$), 4.05 (3 H, s, OCH$_3$), 4.84 (2 H, s, CH$_2$Cl), 6.68 (2 H, dd and d overlapping, 3-H and 5-H, $J_{3,5}$ 2 Hz), and 7.85 (1 H, d, 6-H, $J_{5,6}$ 8.5 Hz); m/e 214 ($M^{+\cdot}$) 12.2% and 165 (M − CH$_2$Cl)$^+$ 100%; $\nu_{max.}$ 1 667 cm^{-2} (C=O).

(c) *With* 1,3,5-*trimethoxybenzene.* Triflic acid (11.3 g, 0.075 mol) was added during 30 min to chloroacetonitrile (2.8 g, 0.037 mol) and the mixture was stirred for a further 2.5 h at room temperature before dropwise addition of 1,3,5-trimethoxybenzene (4.2 g, 0.025 mol) in diethyl ether (25 cm^3). The mixture was stored at room temperature for 19 days before addition of water (40 cm^3) to give a mixture of 1,3,5-trimethoxybenzene (3.4 g, 87% recovery) and bis(chloroacetyl)amine (1.6 g, 0.01 mol, 37%) separated by chromatography [Al$_2$O$_3$, light petroleum b.p. 30—40 °C and diethyl ether eluants].

A repeat of this reaction but using dichloromethane (30 cm^3) as solvent for the 1,3,5-trimethoxybenzene gave bis-(chloroacetyl)amine (0.5 g, 0.003 mol, 16%) and 1,3,5-trimethoxybenzene (4.1 g, 98%) was recovered.

Reactions of Trichloroacetonitrile.—(a) *With triflic acid.* Slow addition of triflic acid (6.0 g, 0.04 mol) to trichloroacetonitrile (5.8 g, 0.04 mol) at room temperature with stirring, followed, after 6 days, by hydrolysis with iced water (15 cm^3) gave white plates of trichloroacetamide (1.2 g, 0.007 mol, 18%), m.p. 137—138 °C (lit.,[38] m.p. 140—141 °C). The i.r. and ^{1}H n.m.r. spectra of this compound were identical to those of an authentic sample.

(b) *With phenols and phenol ethers.* The quantities of reactants and experimental procedure employed were similar to those described for the reactions of chloroacetonitrile. The results are included in Table 4, and the products were identified from the following data. 4-MeOC$_6$-H$_4$COCCl$_3$: pale yellow oil (after chromatography), b.p. 112—115 °C/1 mmHg (Found: C, 43.1; H, 2.9; Cl, 41.5. C$_9$H$_7$Cl$_3$O$_2$ requires C, 42.6; H, 2.76; Cl, 42.01%), δ(CDCl$_3$) 4.48 (3 H, s, OCH$_3$), 7.57 (2 H, d, A part of AA'XX' spectrum, J_{AX} 9 Hz) and 8.88 (2 H, d, X part); $\nu_{max.}$ 1 701 (C=O) cm^{-1}.

2,4-(HO)$_2$C$_6$H$_3$COCCl$_3$: m.p. 138—141 °C (lit.,[39] m.p. 142.5 °C), δ[(CD$_3$)$_2$CO] 6.56 (2 H, dd and d overlapping, 3-H and 5-H, $J_{3,5}$ 2.5 Hz), 8.3 (1 H, d, H$_6$, $J_{5,6}$ 8.5 Hz), 10.08 (1 H, broad s, OH), and 11.42 (1 H, broad s, OH); m/e 254 ($M^{+\cdot}$) 3.7% and 137 (M − CCl$_3$)$^+$ 100%; $\nu_{max.}$ 3 278 (OH) and 1 639 (C=O) cm^{-1}.

2,4-(MeO)$_2$C$_6$H$_3$COCCl$_3$: b.p. 153 °C/0.5 mmHg (lit.,[40,41] b.p. 153 °C/0.5—0.6 mmHg; m.p. 55 °C), δ(CDCl$_3$) 3.85 (6 H, s, OCH$_3$), 6.54 (2 H, dd and d overlapping, 3-H and 5-H, $J_{3,5}$ 2 Hz), and 7.73 (1 H, d, 6-H, $J_{5,6}$ 9 Hz); m/e 282 ($M^{+\cdot}$) 1.1% and 165 (M − CCl$_3$)$^+$ 100%; $\nu_{max.}$ 1 733 and 1 706 cm^{-1} (C=O)*.

Reactions of Malononitrile.—(a) *With anisole.* Triflic acid (5.6 g, 0.037 mol) was added during 30 min to a stirred suspension of malononitrile (2.4 g, 0.037 mol) in anisole (2.7 g, 0.025 mol), and the mixture was stored for 11 days before addition of water (20 cm^3), and stirring for 3 h in a bath of iced water. The precipitate which formed was filtered off, washed with water, and then with ether, and finally dried to give pale yellow crystals of 4-methoxy-cyanoacetophenone (1.35 g, 0.01 mol, 40%), m.p. 129—131 °C (Found: C, 68.8; H, 5.5; N, 8.1%. Calc. for C$_{10}$H$_9$NO$_2$: C, 68.6; H, 5.2; N, 8.0%), δ[(CD$_3$)$_2$CO] 3.95 (3 H, s, OCH$_3$), 4.50 (2 H, s, CH$_2$CN), 7.09 (2 H, d, A part of AA'XX' spectrum, J_{AX} 8.5 Hz), and 8.02 (2 H, d, X

* The two carbonyl absorptions are probably due to the presence of rotational isomers; similar rotational isomers have been noted previously for chloroacetone, 1,3-dichloroacetone, and α-chloroacetophenone.[42]

part); m/e 175· $(M^{+\cdot})$ 24.2% and 135 $(M - CH_2CN)^+$ 100%; $\nu_{max.}$ 2 258 (C≡N) and 1 688 cm⁻¹ (C=O).

(b) *With 1,3-dimethoxybenzene.* Triflic acid (11.25 g, 0.075 mol) was added during 35 min to a solution of malononitrile (2.4 g, 0.037 mol) in nitromethane (10 cm³) and the mixture was left at room temperature for 40 min before the dropwise addition of a solution of 1,3-dimethoxybenzene (3.5 g, 0.025 mol) in nitromethane (15 cm³) during 40 min. The deep-brown reaction mixture was stored at room temperature for 12 days before addition of ice (50 g), and stirring for 1 h in a bath of iced water. Ether extraction gave a dark-brown oil, which was dissolved in chloroform, decolourised with charcoal, and concentrated before addition of light petroleum, to precipitate 2,4-dimethoxycyanoacetophenone (2.0 g, 0.01 mol, 39%), m.p. 150—151 °C (Found: C, 63.7; H, 5.3; N, 6.8%. Calc. for $C_{11}H_{11}NO_3$: C, 64.4; H, 5.4; N, 6.8%), $\delta(CDCl_3)$ 3.91 (3 H, s, OCH₃), 3.98 (3 H, s, OCH₃), 4.06 (2 H, s, CH₂-CN), 6.58 2 H, dd and d overlapping, 3-H and 5-H, $J_{3.5}$ 2 Hz) and 7.94 (1 H, d, 6-H, $J_{5.6}$ 8.5 Hz); m/e 205 $(M^{+\cdot})$ 40.2% and 165 $(M - CH_2CN)^+$ 100%; $\nu_{max.}$ 2 222 (C≡N) and 1 656 cm⁻¹ (C=O).

Reaction of Succinonitrile with Resorcinol.—Reaction between triflic acid (11.3 g, 0.075 mol), succinonitrile (6.0 g, 0.075 mol) and resorcinol (5.5 g, 0.05 mol) in nitromethane (50 cm³) according to the procedure described in the previous experiment, gave, on hydrolysis after 12 days at room temperature, recovered resorcinol (3.0 g, 55% recovery). Evaporation of the nitromethane gave needles of 2,4-dihydroxy-β-cyanopropiophenone (3.5 g, 0.018 mol, 37%), m.p. 203—205 °C (lit.,[43] m.p. 205.5—207.5 °C) $\delta[(CD_3)_2CO]$ 2.80 (2 H, t, CH₂CO, J 7 Hz), 3.48 (2 H, t, CH₂CN), 6.54 (2 H, dd and d overlapping, 3-H and 5-H, $J_{3,5}$ 2 Hz) and 7.82 (1 H, d, 6-H, $J_{5.6}$ 8.5 Hz); $\nu_{max.}$ 3 226 (OH), 2 222 (C≡N) and 1 631 cm⁻¹ (C=O); m/e 191 $(M^{+\cdot})$ 36.9% and 137 $(M - CH_2CH_2CN)^+$ 100%.

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