H's); IR (KBr) 3110, 2950, 1750, 1530, 1350, 1180 cm^{-1}. Anal. Calcd for $C_{11}H_{13}NO_7S$: C, 43.56; H, 4.29; N, 4.62. Found: C, 43.69; H, 4.26; N, 4.55.

Methyl 2-cyclohexyl-2-(((*p*-nitrophenyl)sulfonyl)oxy)acetate (2i) was prepared by method B from 1-(trimethylsiloxy)-1-methoxy-2-cyclohexylethylene (**1i**) (2.1 mmol), pNBSP (2.0 mmol), and MeOH (10 mmol) as a colorless oil (69%) after purification by flash chromatography (hexane/ethyl acetate (90:10 to 80:20)): NMR ($CDCl_3$) δ 1.2–2.4 (set of m, cyclohexyl H's), 3.19 (s, 3 H, CH_3), 8.21 and 8.40 (two d, 4 H, aromatic H's); IR (neat) 3100, 2940, 1740, 1530, 1350, 1160 cm^{-1}. Anal. Calcd for $C_{14}H_{17}NO_7S$: C, 49.00; H, 4.96; N, 4.08. Found: C, 49.56; H, 5.05; N, 3.97.

2-(((*p*-Nitrophenyl)sulfonyl)oxy)valerolactone (2j) was prepared by method A from 2-(trimethylsiloxy)-1-oxacyclohex-2-ene (**1j**) (1.5 mmol), pNBSP (1.0 mmol), and NaOMe (1.6 mmol) as a white solid (73%) after purification by flash chromatography (hexane/ethyl acetate (60:40 to 50:50)): mp 97–98 °C; NMR ($CDCl_3$) δ 2.02–2.70 (m, 4 H, CH_2CH_2), 2.38 (m, 2 H, OCH_2), 5.20 (t, 1 H, OC*H*), 8.18 and 8.42 (two d, 4 H, aromatic H's); IR (CH_2Cl_2, NaCl) 3050, 2970, 1760, 1530, 1350 1190 cm^{-1}. Anal. Calcd for $C_{11}H_{11}NO_7S$: C, 43.85; H, 3.65; N, 4.66. Found: C, 44.24; H, 3.77; N, 4.61. Use of method A gave a low yield (15%) of **2j**.

2-(((*p*-Nitrophenyl)sulfonyl)oxy)butyrolactone (2k) was prepared by method B from 2-(trimethylsiloxy)-1-oxacyclopent-2-ene (**1k**) (3.0 mmol), pNBSP (2.0 mmol), and NaOMe (3.1 mmol) as a white solid (61%) after purification by flash chromatography (hexane/ethyl acetate (60:40)): mp 136 °C; NMR (acetone-d_6) δ 2.50 (m, 1 H, $-CH_2CH_2O-$), 2.80 (m, 1 H, $-CH_2CH_2O-$), 4.46 (m, 2 H, $-CH_2CH_2O-$), 5.64 (t, 1 H, $OCHCH_2-$), 8.38 and 8.58 (two d, 4 H, aromatic H's); IR (KBr) 3100, 2920, 1790, 1565, 1350, 1180 cm^{-1}. Anal. Calcd for $C_{10}H_9NO_7S$: C, 41.81; H, 3.14; N, 4.88. Found: C, 41.98; H, 3.15; N, 4.66.

Studies of the Solvolysis of 2-Adamantyl Pentafluorobenzenesulfonate: A Y_{PFBS} Scale[1]

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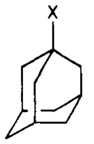
The original Grunwald–Winstein equation (eq 1) defines a scale of solvent ionizing power (Y) based on the specific rates of solvolysis of *tert*-butyl chloride at 25 °C. In eq

$$\log (k/k_0) = mY \qquad (1)$$

1, k/k_0 represents the specific rate of solvolysis in the solvent under consideration (k) relative to that in 80% ethanol (k_0), the standard solvent. For *tert*-butyl chloride, m, which represents the sensitivity of the solvolysis to solvent ionizing power, is defined as unity. Though intended as a model for solvolysis by a limiting mechanism, *tert*-butyl chloride has since been shown to solvolyze with some degree of nucleophilic participation, which results in inclusion of a small nucleophilic solvation component in the *tert*-butyl chloride Y scale.[2,3]

In 1-adamantyl substrates (I), backside nucleophilic attack is sterically prohibited by the rigid, caged structure of the adamantyl skeleton.[4] The 2-adamantyl system (II) has also been shown to lack sensitivity to solvent nucleophilicity,[5,6] It has been demonstrated that solvent effects on the reactivity of 1-adamantyl *p*-toluenesulfonate (tosylate) (I, X = OTs) are virtually identical with those of 2-adamantyl tosylate (II, X = OTs).[7] Consequently, both 1-adamantyl and 2-adamantyl substrates are excellent compounds for defining scales of solvent ionizing power.



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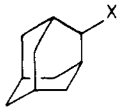

II

Recent investigations[8,9] have given strong support to the viewpoint[3,7,10,11] that each leaving group requires a separate consideration of the influence of solvent variation upon its leaving-group ability. Y_X scales of solvent ionizing power have been developed for a number of nucleofuges based on the solvolyses of 1-adamantyl and 2-adamantyl derivatives (I, X = Cl,[3] Br,[3] I,[12] and picrate;[13] II, X = OTs,[7,10,11] OTf,[9,13] and $OClO_3$[8,13]). In this paper we present an additional scale of solvent ionizing power for pentafluorobenzenesulfonates (Y_{PFBS}) based on the solvolysis of 2-adamantyl pentafluorobenzenesulfonate (II, X = PFBS). This new scale of solvent ionizing power, for a sulfonate leaving group bridging the 10^5–10^6-fold nucleofugality gap between tosylate and trifluoromethanesulfonate (triflate),[14] will be compared with presently existing scales.

Results

Solvolyses in Ethanol, Methanol, Acetic Acid, and 80% Ethanol. Specific rates of solvolysis were determined at four temperatures in the 16–55 °C range. Constant integrated first-order rate coefficients were obtained throughout each kinetic run. The averages of all of the values for the integrated first-order rate coefficients for duplicate runs are reported in Table I. Solvent ionizing power values (Y_{PFBS}) based on 2-adamantyl pentafluorobenzenesulfonate as the standard substrate at 25.0 °C are also presented in Table I. Activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$) calculated with the data of Table I are listed in Table II.

Solvolyses in Solvents of Varying Ionizing Power. A study has been made at 25.0 °C in the following aqueous organic solvents: 100–70% ethanol (four compositions), 100–80% methanol (three compositions), 95–60% acetone (five compositions), 95–70% dioxane (four compositions), and 100–80% 2,2,2-trifluoroethanol (TFE) (four compositions). A study was also made over a full range of TFE–ethanol mixtures (six compositions). Table III lists the averages of all of the integrated first-order rate coefficients for duplicate runs in each of the solvent mixtures studied, with the exception of those already listed in Table I. Calculated Y_{PFBS} values are also listed within Table III.

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Table I. First-Order Rate Coefficients[a] for the Solvolysis of 2-Adamantyl Pentafluorobenzenesulfonate[b] and Y_{PFBS} Values

	10^6k, s^{-1}			
T, °C	80% EtOH	MeOH	EtOH	CH_3CO_2H
16.10	15.8 ± 0.1	1.39 ± 0.01	0.265 ± 0.001	
25.00	62.2 ± 0.5	5.95 ± 0.05	1.200 ± 0.008	2.40 ± 0.03
35.00				11.76 ± 0.09
37.10	322 ± 3	35.1 ± 0.4	7.55 ± 0.07	
45.00				47.0 ± 0.8
50.20	1476 ± 17	212 ± 2	45.6 ± 0.4	
55.00				171 ± 2
Y_{PFBS}[c]	0.000	−1.019	−1.715	−1.414

[a] With associated standard deviations. [b] Concentration ca. 0.0048 M. [c] $\log (k/k_0)_{2\text{-AdPFBS}}$ at 25 °C, where k_0 refers to the specific rate in 80% ethanol.

Table II. Enthalpies ($\Delta H^{\ddagger}$) and Entropies ($\Delta S^{\ddagger}$) of Activation for Solvolysis of 2-Adamantyl Pentafluorobenzenesulfonate[a]

solvent	$\Delta H^{\ddagger}_{298}$, kcal/mol	$\Delta S^{\ddagger}_{298}$, (cal/mol)/K
80% EtOH[b]	24.1 ± 0.5	+3.0 ± 1.7
MeOH	26.8 ± 0.2	+7.3 ± 0.5
EtOH	27.4 ± 0.3	+6.4 ± 0.9
CH_3CO_2H	27.0 ± 0.4	+6.4 ± 1.4

[a] Calculated with data of Table I and with associated standard errors. [b] On a volume–volume basis at 25 °C.

Table III. First-Order Rate Coefficients for the Solvolysis of 2-Adamantyl Pentafluorobenzenesulfonate[a] in Aqueous Organic Solvents at 25.0 °C and Y_{PFBS}[b]

solvent[c,d]	10^6k, s^{-1}	Y_{PFBS}[e]
90% EtOH	14.6 ± 0.2	−0.630
70% EtOH	169 ± 2	0.433
90% MeOH	31.8 ± 0.4	−0.291
80% MeOH	132.7 ± 1.3	0.328
95% acetone	0.483 ± 0.005	−2.111
90% acetone	1.69 ± 0.01	−1.567
80% acetone	9.56 ± 0.06	−0.814
70% acetone	36.1 ± 0.4	−0.238
60% acetone	125 ± 0.9	0.304
95% dioxane	0.113 ± 0.001	−2.740
90% dioxane	0.618 ± 0.006	−2.004
80% dioxane	4.64 ± 0.04	−1.127
70% dioxane	21.6 ± 0.2	−0.461
100% TFE[f]	792 ± 8	1.105
97% TFE	884 ± 8	1.153
90% TFE	1010 ± 8	1.211
80% TFE	1238 ± 15	1.298
80% T–20% E[g]	165 ± 1	0.422
60% T–40% E	37.5 ± 0.2	−0.220
40% T–60% E	9.78 ± 0.08	−0.804
20% T–80% E	3.10 ± 0.02	−1.303

[a] Concentration ca. 0.0048 M; rate coefficients presented with associated standard deviations. [b] For additional values, see Table I. [c] With water as the other component, except for TFE–EtOH (T–E) mixtures. [d] On a volume–volume basis, at 25 °C, except for TFE–H_2O mixtures, which are on a weight–weight basis. [e] For definition, see footnote *c* of Table I. [f] 2,2,2-Trifluoroethanol. [g] 2,2,2-Trifluoroethanol–ethanol mixtures.

Discussion

Comparisons between the rates of solvolysis of 2-adamantyl pentafluorobenzenesulfonate and those of the corresponding tosylate and triflate are presented in Table IV. The order of reactivity (OTs < PFBS < OTf) is in agreement with the observation by Sheppard that the inductive electron-withdrawing ability of the pentafluorophenyl substituent is intermediate between those of the phenyl and trifluoromethyl substituents.[14]

Table IV. Relative Rates of Solvolysis of Various 2-Adamantyl Sulfonates at 25 °C

solvent	k_{PFBS}/k_{OTs}[a]	k_{PFBS}/k_{OTF}[b]
80% EtOH	2590	2.92 × 10^{-3}
MeOH	2040	2.11 × 10^{-3}
EtOH	2790	3.22 × 10^{-3}
CH_3CO_2H	404	5.15 × 10^{-3}

[a] Rate coefficients for solvolyses of 2-adamantyl tosylate at 25 °C; data from ref 10. [b] Rate coefficients for solvolyses of 2-adamantyl triflate at 25 °C; data from ref 9.

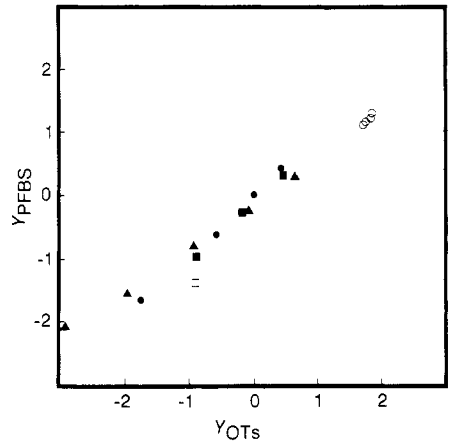

Figure 1. Grunwald–Winstein solvent ionizing power: plot of Y_{PFBS} against Y_{OTs}. The symbols are as follows: (●) aqueous ethanol; (■) aqueous methanol; (▲) aqueous acetone; (○) aqueous TFE; (□) acetic acid.

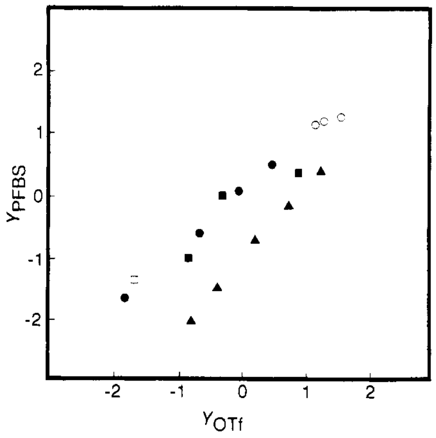

Figure 2. Grunwald–Winstein solvent ionizing power: plot of Y_{PFBS} against Y_{OTf}. The symbols are assigned as in Figure 1.

Y_{PFBS} values are compared with Y_X scales developed for tosylates and triflates, which have been based upon solvolyses of their adamantyl derivatives. Plots of Y_{PFBS} against Y_{OTs} and Y_{OTf} are presented in Figures 1 and 2. Slopes and intercepts for these plots are given in Table V. For individual mixed-solvent systems, good correlations are generally obtained for Y_{PFBS} against either Y_{OTs}

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Table V. Slopes (m) and Intercepts (c) for Plots of Y_{PFBS} against Y_{OTs} or Y_{OTf}[a]

	EtOH–H_2O[b]	acetone–H_2O[d]	acetone–H_2O[d]	overall[e]
m_{OTs}	0.98	0.97	0.67	0.75
c_{OTs}	–0.02	0.12	–0.17	–0.18
r_{OTs}[f]	1.000	1.000	0.999	0.984
m_{OTf}	0.92	0.85	1.16	0.87
c_{OTf}	–0.03	–0.25	–1.16	–0.42
r_{OTf}[f]	1.000	0.998	0.999	0.880

[a] Using Y_{OTs} values from ref 7, 8, and 10 and Y_{OTf} values from ref 9 (except that the Y_{OTf} value for 80% MeOH is revised from 0.905 to 0.708 and Y_{OTs} values for 70% acetone and 90 and 80% TFE are obtained by interpolation). [b] 100–70% ethanol (four compositions). [c] 100–80% methanol (three compositions). [d] 95–60% acetone (five compositions). [e] Using all of the data presented in Figures 1 and 2. [f] Correlation coefficient.

or Y_{OTf}. Since the Y_X values lie within a very narrow range for the studied water–TFE solvents, correlations for this system are not reported. The plot against Y_{OTf} values contains one less point because the value for 80% TFE has not been reported.

In water–ethanol and water–methanol mixtures, the correlation of Y_{PFBS} against Y_{OTs} gives slopes of close to unity and intercepts not far removed from zero. For these mixtures, the correlation of Y_{PFBS} against Y_{OTf} leads to slightly reduced slopes, suggesting a reduced sensitivity to solvent ionizing power for 2-adamantyl pentafluorobenzenesulfonate. This, however, may be due in part to temperature differences. Y_{PFBS} values are defined at 25 °C while the Y_{OTf} values used in the correlations were defined at -20 °C.[9] Usually, the sensitivities of the rates of solvolysis to solvent ionizing power are reduced with increasing temperature.[15]

The correlation of Y_{PFBS} against Y_{OTs} for water–acetone mixtures gives a slope of 0.67. The rates of solvolysis of 2-adamantyl pentafluorobenzenesulfonate in water–acetone mixtures rich in acetone are greater than would be predicted on the basis of Y_{OTs} values. The correlation of Y_{PFBS} against Y_{OTf} leads to the opposite result. The increased slope of 1.16 and large negative intercept indicate that the rates of solvolysis of 2-adamantyl triflate are markedly underestimated by Y_{PFBS} values. That 2-adamantyl triflate shows faster rates in water–acetone mixtures than those predicted from tosylate solvolyses has been previously reported.[9,13]

When all of the solvents of Figures 1 and 2 are considered, the Y_{PFBS} values correlate much better with Y_{OTs} values than with Y_{OTf} values (Table V). Grunwald–Winstein Y values, based on *tert*-butyl chloride solvolysis, are available[16] for 24 of the 25 solvents studied at 25.0 °C (all except 95% dioxane), and Y_{PFBS} values correlate with Y values with a slope of 0.82 and an intercept of –0.11 (correlation coefficient of 0.983). The values for these parameters and for the correlation coefficient are very close to the corresponding values obtained in the correlation against Y_{OTs} values.

The data for the solvolyses in TFE–ethanol mixtures have not been included in the figures because Y_{OTs} values for these solvents are not available; the six Y_{PFBS} values, for ethanol, TFE, and the four TFE–ethanol mixtures (Tables I and III), correlate excellently with both traditional Y values[16] (slope of 0.91, intercept of +0.07, correlation coefficient of 0.998) and Y_{OTf} values[9] (slope of 0.92, intercept of +0.07, correlation coefficient of 0.997).

Values of the rate ratio $[k_{EW}/k_{AcOH}]_Y$, a measure of the deviation of data for acetic acid from the correlation line for water–ethanol mixtures based on *tert*-butyl chloride Y values,[16] have previously been used to estimate the degree of electrophilic assistance involved in the solvolyses of other adamantyl substrates.[12,17] The order of increasing values of this ratio [OTs (0.13) < PFBS (1.09) < OTf (1.63)] is identical with the order of increasing leaving-group ability for these sulfonates. This suggests that better sulfonate leaving groups require less electrophilic assistance during solvolysis. This observation can be rationalized in terms of charge dispersal; that is, the better a developing sulfonate ion can disperse a developing negative charge internally, the less dependent bond heterolysis is upon charge dispersal through electrophilic assistance.

Experimental Section

Materials. The purifications of acetone, dioxane, ethanol, and methanol were as previously described.[17] The purifications of acetic acid[18] and 2,2,2-trifluoroethanol[19] were also performed by using previously reported procedures. 2-Adamantanol (Aldrich) was recrystallized from hexane prior to use. The *n*-butyllithium used was a 1.6 M solution in hexane (Aldrich). Pentafluorobenzenesulfonyl chloride (Aldrich) was used without further purification.

2-Adamantyl Pentafluorobenzenesulfonate. To a flame-dried apparatus purged with nitrogen were added 2-adamantanol (6.17 g, 0.04 mol) and 300 mL of anhydrous ethyl ether (Fisher, maximum water content 0.01%). After the mixture was cooled to 0 °C, 1 equiv of *n*-butyllithium (1.6 M *n*-BuLi/hexane, 25.3 mL) was added via syringe, and the mixture was stirred for 20 min. At this point, a 10% molar excess of pentafluorobenzenesulfonyl chloride (12 g) was added and stirring was continued for 1 h. The mixture was then filtered and the solvent evaporated. Recrystallization from hexane gave a 73% yield: mp 120–122 °C; ^1H NMR ($CDCl_3$) δ 1.58–2.12 (m, 14), 5.06 (s, 1, $CHOSO_2C_6F_5$); IR (KBr pellet) includes peaks at 910, 998, 1105, 1192, 1307, 1387, 1500, 1520 (sh), 1642, 2865, 2925 cm^{-1}.

Anal. Calcd for $C_{16}H_{15}SO_3F_5$: C, 50.26; H, 3.95; S, 8.38; F, 24.84. Found: C, 50.40; H, 4.15; S 8.89; F, 24.22.

Kinetic Procedures. Substrate concentrations of ca. 4.8×10^{-3} M were used. Fifty milliliters of the solvent under investigation, maintained at the required temperature, was transferred to a flask (tightly stoppered) containing an appropriate amount of the solid substrate. After mixing and a brief period for temperature reequilibration, 5-mL portions were removed at suitable time intervals. For all kinetic runs except those in acetic acid, the aliquots were quenched by pipetting into 25 mL of acetone containing Lacmoid (resorcinol blue) indicator, cooled within a solid CO_2–acetone slush bath. The previously produced acid was then titrated with a standardized solution of sodium methoxide in methanol. For runs in acetic acid, aliquots were quenched in 25 mL of acetic acid containing bromophenol blue indicator and cooled within an ice bath, and they were titrated with a standarized solution of sodium acetate in acetic acid. All runs were performed at least in duplicate. Calculation of first-order rate coefficients was as previously described.[20] For the slower runs, specific rates of less than about 3×10^{-5} s^{-1}, the interval prior to infinity determination was reduced by the transfer of a 5-mL portion to the 50.2 °C bath.

In the preparation of a 4.8×10^{-3} M solution, solubility problems were observed for solvents more aqueous than those reported. For example, even in an ultrasonic bath,[11,13] sufficiently rapid dissolution at 25.0 °C could not be obtained in 70% methanol, 60% ethanol, or 50% acetone.

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Registry No. II (X = PFBS), 115095-87-9.

Preparation of 10-g Quantities of 15-*O*-Acetyl-4-deoxynivalenol

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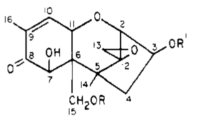
The most common trichothecenone produced by strains of *Fusarium graminearum* isolated from Eastern Canadian and United States grain is 15-*O*-acetyl-4-deoxynivalenol (15-*O*-acetyl-DON) (1, R = Ac, R^1 = H).[1] Although we have examined 51 isolates of this fungus for their ability to produce this mycotoxin in laboratory culture, the best yield obtained was only 40 mg L^{-1}. The relative inaccessibility of this compound has resulted in the use of deoxynivalenol (= DON = vomitoxin, 1, R = R^1 = H) for most toxicological studies with laboratory animals,[2] despite the known differences in partition coefficient (and hence pharmacology) of the acetate and alcohol in lipid–aqueous systems.



1

By contrast, 3-*O*-acetyl-DON (1, R = H, R^1 = Ac) is readily available[3] and could serve as starting material for a partial synthesis of the 15-acetate. This conversion has now been achieved by two routes. The preferred route involves only two steps, hydrolysis of 3-*O*-acetyl-DON to DON with ammonium hydroxide followed by regiospecific Steglich esterification,[4] with acetic acid and dicyclohexylcarbodiimide (DCC) in the presence of 4-(dimethylamino)pyridine (DMAP), giving 15-*O*-acetyl-DON in 82% yield or 67% overall, together with a small amount of 3,15-di-*O*-acetyl-DON,[5] which is easily removed by column chromatography. This procedure was superior to acetylation with 1 equiv of acetic anhydride in the presence of DMAP,[6] which was also regiospecific, giving 15-*O*-acetyl-DON containing <5% 3-*O*-acetyl-DON but in only 69% yield. When pyridine was used instead of DMAP, the reaction was essentially nonspecific, giving the 15- and 3-acetates in the ratio 3:2.

The second route involves six steps using standard protecting group chemistry and gives the 15-acetate in 54% overall yield, but is more laborious and time-consuming. The 15-*tert*-butyldimethylsilyl ether (1, R = t-BuMe$_2$Si, R^1 = Ac) of 3-*O*-acetyl-DON was hydrolyzed with ammonium hydroxide to the diol (1, R = t-BuMe$_2$Si, R^1 = H), which readily formed the 3-tetrahydropyranyl (THP) ether (1, R = t-BuMe$_2$Si, R^1 = THP). Removal of the silyl group with tetrabutylammonium fluoride, regiospecific acetylation at position 15 of the resulting diol (1, R = H, R^1 = THP), and deprotection gave the 15-acetate (1, R = Ac, R^1 = H). With the exception of the silyl ether (1, R = t-BuMe$_2$Si, R^1 = Ac), the intermediate products were gums (this is normally the case with diastereoisomeric THP ethers) and were not analyzed. An envisaged six-step procedure using the trityl ether (1, R = Ph$_3$C, R^1 = Ac) broke down through failure to find a protecting group for the diol (1, R = Ph$_3$C, R^1 = H) that would both permit perferential removal of the trityl residue and also undergo fission without solvolysis of a 15-acetate residue. The 15-phenylurethane (1, R = CONHPh, R^1 = Ac) was also prepared.

Acetylation of 3-*O*-acetyl-DON under most conditions gives the known 3,7,15-triacetate,[7,8] but Steglich esterification gave the 3,15-diacetate (1, R = R^1 = Ac). This on mild alkaline hydrolysis gave a mixture of the 15- and 3-acetates in the ratio 3:2. The reaction between DON and 1 equiv of dihydropyran was also not regiospecific, and after acetylation of the product and deprotection, the 15- and 3-acetates were obtained in the ratio 1:1.

A crystalline precipitate consisting of about 80% 3-*O*-acetyl-DON can be obtained from the crude extract of *Fusarium culmorum* (HLX 1503) fermentations.[3] When this material was hydrolyzed on the 10-g scale and the resulting crude DON was acetylated under the preferred conditions described above, the 15-acetate (1, R = Ac, R^1 = H) was obtained, after chromatography in about 60% yield.

Experimental Section

A. Experimental Details for Work Carried Out at the University of Sussex. Melting points (Kofler block) are corrected. Merck silica gel 7734 was used in column chromatography. All reactions and chromatographic separations were monitored by analytical thin-layer chromatography (TLC) (UV detection) on Merck silica gel 60 F_{254} in chloroform–methanol (9:1). In this system DON has R_f 0.03, mono-*O*-acetyl-DON has R_f 0.55, and 3,15-di-*O*-acetyl-DON has R_f 0.73. Triethylamine was used, where possible, in preference to pyridine, which also has R_f 0.55.

In mixtures of 3-*O*-acetyl- and 15-*O*-acetyl-DON, integration of the ^{1}H NMR (80 MHz) signals from 3-HOAc at δ 5.28 (CDCl$_3$, Me$_4$Si internal standard) and 15-H_2OAc at δ 4.28 gave the ratio. The same could be checked by integration of the common H-10 signal at δ 6.68. Identifications were confirmed by comparison of the IR spectra which are for mulls in Nujol. Methylene chloride was distilled from calcium hydride.

Hydrolysis of 3α-Acetoxy-7α,15-dihydroxy-12,13-epoxytrichothec-9-en-8-one (1, R = H, R^1 = Ac; 3-*O*-Acetyl-DON). 3-*O*-Acetyl-DON (1.00 g) in methanol (20 mL) and ammonium hydroxide (1.5 N, 10 mL) was stirred at room temperature for 6 h. The solution was concentrated under reduced pressure (bath, 40 °C) to 6 mL and extracted with ethyl acetate saturated with water (10 × 6 mL). The recovered foam (895 mg) crystallized from ethyl acetate gave DON (722 mg, 82%), mp 150–152 °C (lit.[8] mp 151–153 °C).

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