versity, and Professor I. R. C. Bick, University of Tasmania, for generous gifts of comparison samples.

Registry No.—**1**, 52674-06-3; **1** HCl, 52759-92-9; **2**, 52674-07-4; **3**, 6391-64-6; **4**, 35611-57-5; **5**, 52674-08-5; **6**, 52674-09-6; **9**, 52674-10-9; **10**, 52729-64-3; **13**, 52729-65-4; **18**, 52674-11-0.

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Notes

Synthesis and Properties of *N*-Acetimidoyl Derivatives of Glycine and Sarcosine[1a]

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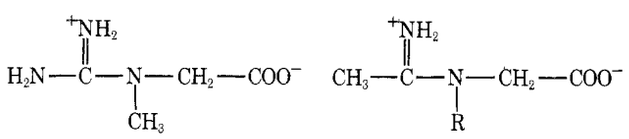
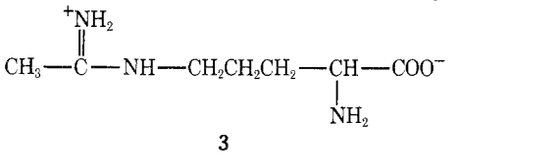
Analogs of creatine **1** which have been prepared and tested for their properties have been restricted to *N*-amidino derivatives (*i.e.*, guanidino compounds) of appropriate amino acids.[2,3] No attempts have been made, however, to test other derivatives, such as *N*-acetimidoylamino acids (*i.e.*, amidines) that are structurally related to creatine and may provide interesting information concerning their biological properties. In fact, acetimidoyl compounds of biological interest in relation to their amidino counterparts have been noted; for example, N^5-acetimidoyl-L-ornithine (**3**), an L-arginine **4** antagonist, has recently been isolated by Scannell, *et al.*[4]



1

2a, R = H
b, R = CH_3



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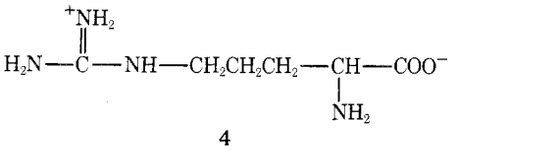
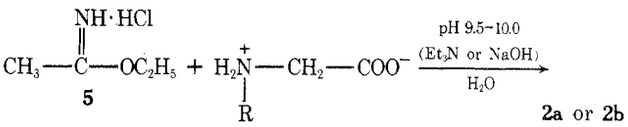


4

We, therefore, synthesized acetimidoyl derivatives of glycine **2a** and sarcosine **2b** in an attempt to understand their properties including those of biological interest.

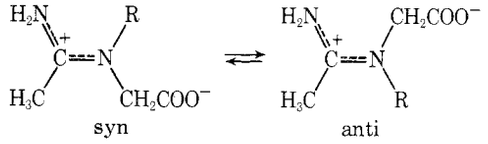
Results and Discussion

The well-known imido ester–amine reaction[5] is useful in the synthesis of amidines **2** derived from amino acids. Most products have been obtained in high yields by carrying out reactions in alcoholic solvents at elevated temperature (60–160°).[6] We have synthesized two new amidines, *N*-acetimidoylglycine (**2a**) and *N*-acetimidoylsarcosine (**2b**), in aqueous media at pH 9.5–10.0 and room temperature, utilizing the pH–rate relationship of the reactions of imidoester with amines,[7] amino acids,[8] and proteins.[8]



5 **2a** or **2b**

Both compounds have characteristic ir absorption bands for the carboxylate and C=N groups. Their nmr spectra reveal that, like other aminidium ions,[9] the rotation about the C–N bond is restricted, and both compounds can exist in syn and anti forms, which result in two sets of proton signals for each compound (Table I).



syn anti

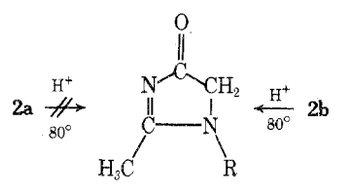
The chemical shifts are assigned to the syn and anti forms by analogy with *N*,*N*-dimethylformamide.[10] The acetimidoyl methyl protons in the syn form absorb at higher field presumably because of an electric field effect arising from the carboxylate group that lies on the same side. The low syn/anti ratio for **2a** is in accord with the preference of the anti form of *N*-methylacetamidium ion in D_2O (syn/anti, 0.04).[11] It is of interest to note that the syn preference in the internal salt **2b** is opposite to that of the neutral *N*-acetylsarcosine methyl ester in DMSO-d_6 (syn/anti, 0.4).[12] Downfield shifts of α protons in **2a** and **2b** in acidic medium are of the same magnitude observed for amino acids and peptides.[13] In trifluoroacetic acid, the spin–spin coupling of N–H and N–CH_2 in **2a** indicates that no protonation occurs on the substituted α-amino nitrogen.

Table I
Nmr Data of *N*-Acetimidoylglycine (2a) and *N*-Acetimidoylsarcosine (2b)

Compd	Solvent	Syn/anti ratio[b]	δ, ppm[a] $-CH_2-COO^-$ Syn	$-CH_2-COO^-$ Anti	$CH_3-C=N$ Syn	$CH_3-C=N$ Anti	CH_3-N Syn	CH_3-N Anti	N–H[c] and/or $=NH_2$
2a	D_2O (neutral)	0.05	4.42	4.39	2.68	2.78			
	D_2O (H^+)	0.05	4.73	4.70	2.78	2.87			
	CF_3COOH	0.05	4.30[d]		2.37	2.45			7.45, 7.62, 7.87
2b	D_2O (neutral)	2.3	4.59	4.54	2.72	2.82	3.60	3.70	
	D_2O (H^+)	2.3	4.85	4.80	2.79	2.88	3.70	3.77	
	CF_3COOH	2.3	4.46		2.42	2.46	3.29	3.34	7.16, 7.64

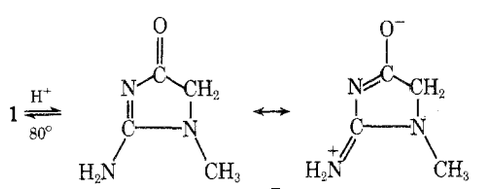
[a] External TMS standard. Assignments for syn and anti forms are consistent with the intensity distribution in the spectra. [b] Approximate integration ratio. [c] Broad bands. [d] A doublet, $J = 5.4$ Hz.

Both compounds, **2a** and **2b**, remain unaltered on heating in neutral aqueous solution at 80° for 15 hr. This observation is in agreement with that of Ried, *et al.*[6b] They found that aliphatic imido esters, unlike their aromatic counterparts, give only amidines and generally fail to cyclize to give imidazolones due to relatively higher basicity of the acetimidoyl nitrogen. Heating in acidic media, however, presents a striking difference between **2a** and **2b** in their cyclization behavior; although **2a** remains unchanged after standing at 80° for 15 hr, **2b** cyclizes to give 1,2-dimethyl-2-imidazolone-4 (**6b**) at 80°.



6a, R = H
b, R = CH_3

An examination of creatine **1** and 1-carboxymethyl-2-iminoimidazolidine (**8**), a substrate of creatine phosphokinase,[2] revealed the same difference in their cyclization behavior; **1** cyclizes to creatinine **7** in hot acidic medium, but **8** remains unaltered under the same conditions.



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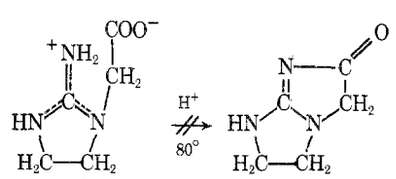


8

Apparently, the cyclization process in these cases is controlled by factors other than the basicity of the acetimidoyl or amidino nitrogen. One of these factors may be the release of the steric hindrance between the two methyl groups in **2b** and **1**, which are nearly coplanar with N···C···N. In **6b**, N–CH_3 can be expected to avoid crowding with C–CH_3 by assuming an out-of-plane position, and in **7**, conjugation may occur through the exocyclic nitrogen as noted by Kowalsky, *et al.*[14] No such gain is likely in the cyclization of **2a** and **8**, and the molecules may exist largely as the open-chain, zwitterion structure.

In light of the above results of cyclization, we carried out some color reactions of **2a** and **2b** with reagents that usually develop colors with creatine or creatinine (Table II). That both **1** and **2b** give positive reactions with alkaline picrate solution only after pretreatment with acid and neither **2a** nor **8** gives a color under the same conditions is in accord with the acidic cyclization behavior of these compounds.

Table II
Color Reactions[a]

Compd	FCNP	Reagent: Alkaline picrate	Reagent: Diacetyl-α-naphthol
2a	Red	Negative, negative[b]	Negative
2b	Red	Negative,[c] red[b]	Negative
1	Red	Negative, red[b]	Red
8	Blue	Negative, negative[b]	Negative
7		Red	Negative

[a] In neutral medium and at room temperature unless otherwise stated. [b] Samples allowed to stand at pH 1–2 for 30 hr. [c] Very sluggish development of a red color was noted.

In order to know if **2a** and **2b** possess biological properties due to their structural resemblance to creatine, we have examined one of the biochemical aspects considered most relevant, namely, their reactivity toward creatine phosphokinase, which converts creatine to phosphocreatine in the presence of metals, such as magnesium.[15]

Our preliminary results show that in Trizma buffer solution at 30° and pH 9, while 4.8 m*M* of creatine shows an initial rate of 0.054 *A*/min and 6.3 m*M* of **8** shows 0.016 *A*/min, the initial rate of **2a** or **2b** (3–20 m*M*) with the same quantity of enzyme is zero. At a **2a** or **2b**/**1** ratio (**1**, 2 m*M*) of 10, no inhibition of the transformation of creatine to phosphocreatine by **2a** and **2b** was observed. One may attribute the insignificant interaction of **2a** and **2b** with creatine phosphokinase to the possibility that the acetimidoyl methyl group may not be able to occupy the site of the enzyme that will accommodate the smaller primary amino group or that the presence of two amino groups from the guanidino moiety in creatine may be necessary for activity.

Experimental Section

Melting points were measured on a Fisher-Johns melting point apparatus unless otherwise stated and are uncorrected. Ir, nmr, and mass spectra were recorded on Beckman IR-9, Varian A56/60, and LKB Shimadzu Gas Chromatograph-Mass Spectrometer 9000S, respectively. Elementary analyses were performed by the Elek Microanalytical Laboratories, Torrance, Calif.

Materials. All chemicals and solvents used in this work are commercially available. Rabbit muscle creatine phosphokinase (ATP:Creatine phosphotransferase; E.C. No. 2.7.3.2; 115 units/mg protein) and reagents for the uv determination of creatine phosphokinase (No. 40-UV) were purchased from Sigma Chemical Co.

Preparation of *N*-Acetimidoylglycine (2a). *The following experiment was carried out in a well-ventilated hood.* To a well-stirred solution of 40 g (0.53 mol) of glycine in 500 ml of H_2O is added slowly about 60 ml of Et_3N[16] to bring the pH to 10.0 (measured with a pH meter), then 100 g (0.81 mol) of powdered ethyl acetimidate hydrochloride is added in small portions with concurrent dropwise addition of Et_3N from a separatory funnel to maintain the pH of the reaction mixture at 9.5–10.0. After standing at room temperature for 2 hr (a longer reaction time is not necessary), the solution is decolorized with acid-washed charcoal and filtered. Evaporation of the filtrate *in vacuo* to complete dryness gives a solid mixture, from which the desired white product is washed free from $Et_3N \cdot HCl$ and minor by-products by stirring thoroughly in 400 ml of absolute EtOH, collected on a Büchner funnel, washed twice with 20 ml of fresh EtOH, and pressed dry. The total yield is 45–50 g (71–81%, based on glycine). An analytical sample is obtained by crystallization from an H_2O–EtOH mixture: mp 202–205° dec; ir (KBr) 1608, 1385 (COO^-), 1660 (C=N), 1710 (probably N–H; a sample obtained from D_2O does not have this absorption band), 3300, 3220, and 3120 cm^{-1} (broad, N–H);[17] nmr Table I; mass spectrum (70 eV, source 230°, probe 165°) *m/e* (rel intensity, %) 117 (1.1; $M^+ + 1$, dependent upon sample pressure), 116 (1.9; M^+, calcd 116), 98 (25.9, $M^+ - H_2O$), 72 (12.9), 71 (30.6), 55 (25.3), 54 (9.4), 43 (15.9), 42 (100).

Anal. Calcd for $C_4H_8N_2O_2$: C, 41.73; H, 6.94; N, 24.12. Found: C, 41.29; H, 6.59; N, 24.48.

This compound is liable to become discolored unless stored in a vacuum desiccator.

2a HCl is prepared by adding several drops of concentrated HCl to a solution of 100 mg of **2a** in 0.5 ml of H_2O. The solvent is removed in an evacuated desiccator over concentrated H_2SO_4 overnight. The crude product (125 mg) is crystallized from absolute EtOH: mp 171–173° dec; nmr Table I; ir (KBr) 1725, 1420, 1202 (COOH), 1680, 1633, 1345 (N—C=N^+H_2), 2620, 2530, 2490, 2400 (a series of weak bands, probably COOH and/or =N^+H_2), 3330, 3290, and 3130 cm^{-1} (broad, N–H).[17]

Preparation of *N*-Acetimidoylsarcosine (2b). The procedure for the preparation of **2b** is the same as the one described above, except that 2*N* NaOH is used instead of Et_3N to adjust the pH of the reaction mixture.

A total of 150 g (1.22 mol) of ethyl acetimidate hydrochloride is added to a solution of 100 g (0.80 mol) of sarcosine hydrochloride in 200 ml of H_2O at pH 10.0. The pH of the reaction mixture is maintained at 9.5–10.0. After standing at room temperature for 3 hr, the solution is neutralized to pH 6.5–7.0, filtered, and evaporated *in vacuo* to dryness. The product obtained at this stage contains water of hydration and is soluble in EtOH. The residual solid is stirred with a mixture of EtOH–*i*-PrOH (1:1). The insoluble solid (mainly NaCl) is filtered off, and the filtrate is concentrated under reduced pressure. The residue is an oil. The desired product can be separated out as a solid powder by first treating the residual oil with 300 ml of a mixture of Et_2O–C_6H_6 (10:1) followed by addition of 10–20 ml of absolute EtOH, with vigorous stirring. Evaporation of some solvent mixture on a rotary evaporator at this stage aids considerably the separation of the solid, presumably due to removal of the remaining H_2O. The white solid is filtered off, washed with Et_2O, and pressed dry. This solid (75–85 g) usually contains about 10% of NaCl and can be purified by dissolving it in a minimum amount of hot EtOH and separating it out with Et_3N. An analytical sample is obtained by crystallization from a mixture of EtOH–Et_3N (1:1) at 4°: mp 190–200° dec; nmr Table I; ir (KBr) 1620, 1388 (COO^-), 1660 (C=N), 1318 (C–N), 3420, and 3220 cm^{-1} (broad, N–H);[17] mass spectrum (70 eV, source 230°, probe 115°) *m/e* (rel intensity, %) 131 (0.31, $M^+ + 1$), 130 (1.3; M^+; calcd 130), 112 (65.4, $M^+ - H_2O$), 86 (7.3), 56 (30.4), 44 (28.1), 43 (69.2), 42 (100), 41 (20.8), 36 (13.8).

Anal. Calcd for $C_5H_{10}N_2O_2$: C, 46.14; H, 7.74; N, 21.52. Found: C, 44.28; H, 7.78; N, 20.61. (This corresponds to a 96% purity, an improvement from 87% of the crude product: C, 40,15; H, 7.01; N, 18.35.)

2b $(H_2SO_4)_{1/2}$ is prepared by adding concentrated H_2SO_4 to a solution of 2.5 g of **2b** in 1.5 ml of H_2O. A total of 2.9 g of product is separated with EtOH, which is further purified by crystallization from H_2O–EtOH: mp 169–70°; nmr Table I; ir (KBr) 1725, 1428, 1275 (COOH), 1697, 1647, 1358 (N—C=N^+H_2), 2490, 2440 (broad, COOH and/or =N^+H_2), 3280, and 3100 cm^{-1} (broad, N–H).[17]

Preparation of 1-Carboxymethyl-2-Iminoimidazolidine (8). *The following experiment was carried out in a well-ventilated hood.* A solution of $ClCH_2COONa$ is first prepared by adding 159 g (1.5 mol) of anhydrous Na_2CO_3 in small portions to a well-stirred solution of 283.5 g (3 mol) of $ClCH_2COOH$ in 300 ml of H_2O at room temperature. This solution is then added dropwise to a well-stirred solution of 200 ml (3 mol) of ethylenediamine in 200 ml of H_2O over a period of 1 hr. The initial temperature of the ethylenediamine solution is about 80° due to heat of hydration, and the temperature of the reaction mixture is kept at 70–80° during the addition of $ClCH_2COONa$ solution. After standing at the same temperature for 1.5 hr, the brown solution is cooled to room temperature, and 120 g (3 mol) of NaOH in 120 ml of H_2O is then added. Ethylenediamine monoacetate is formed at this stage.

The resultant mixture is cooled in an ice bath, and a solution of 318 g (3 mol) of cyanogen bromide in 400 ml of absolute MeOH is added dropwise over a period of 1.5–2 hr, with vigorous sitrring, while the temperature is maintained at 30°. A white solid starts to separate from the solution in about 10 min after the addition of cyanogen bromide. After complete addition of the reagent, the suspension is kept under stirring at room temperature for 1 hr. The solid is then collected on a Büchner funnel, washed with a small amount of H_2O to remove a contaminating yellow substance, and pressed dry. The total yield is 125–135 g (29.1–31.5%, based on cyanogen bromide). Purification can easily be achieved by crystallization from hot H_2O (30 g in 400 ml): mp 310° dec (measured in a sealed mp tube, lit.[2] 341–342°); nmr (external TMS standard) (D_2O, neutral) 4.40 (2 H) and 4.22 ppm (4 H, symmetrical multiplets with two shoulder peaks at 4.22 ± 0.023 and two well-resolved smaller peaks at ± 0.081 ppm; this is likely to be a AA′BB′ pattern with identical chemical shifts of the two methylene groups;[18] the 220-MHz spectrum in ref 2 shows a typical AA′BB′ pattern), (D_2O, H^+) 4.68 (2 H) and 4.28 ppm (4 H); ir (KBr) 1610, 1390 (COO^-), 1654 (C=N), 1318 (C–N), 1700, 1717 (probably due to N–H; a sample obtained from D_2O does not exhibit absorption bands in this region), 3250, 3160, and 3060 cm^{-1} (N–H).[17]

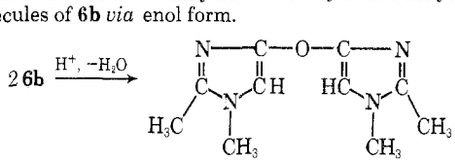
Anal. Calcd for $C_5H_9N_3O_2$: C, 41.95; H, 6.34; N, 29.35. Found: C, 41.90; H, 6.41; N, 29.54.

This is a new, simple procedure for the preparation of **8.** The product is identical with that obtained by the literature method,[2] which requires a large amount of KCN.

Cyclization Experiments. Neutral (pH ~6.5) and acidic (pH 1–2) solutions of 40 mg of each of **2a, 2b,** and 8 in 0.5 ml of D_2O are placed in the nmr tubes and are allowed to stand at room temperature or at 80° for 15 hr.

Nmr spectra show that all three compounds in both neutral and acidic media are stable at room temperature and **2a** and 8 remain unchanged on heating at 80° for 15 hr. The latter was further confirmed by paper chromatography. Spraying with alkaline FCNP revealed red spots at R_f (solvent) 0.54 (aged *n*-PrOH–HOAc–H_2O, 14:5:1), 0.48 (80% pyridine), 0.92 (80% phenol), and 0.40 (65% 2,4-lutidine) for **2a** and blue spots at 0.54, 0.36, 0.94, and 0.36 for **8.** Mixed spots of respective solutions with and without heating are inseparable in all solvent systems employed.

Heating of **2b** at 80° for 15 hr results in a change in the nmr signals. The product, which is likely to be 1,2-dimethyl-2-imidazolone-4 (**6b**), gives three singlets at 3.70 (3 H), 3.77 (2 H), and 4.00 ppm (3 H) (external TMS standard). Evaporation of the solvent gives an unstable oil, which gives a red color upon exposure to the air. This is a common property of imidazolones.[6b] The formation of **6b** was further confirmed by its parent peak *m/e* 112 in the mass spectrum. A by-product, *m/e* 206, presumably **9,** and its protonated forms, *m/e* 207 and 208, were also detected in the mass spectrometer at 11.5 eV. It may be formed by acidic dehydration of two molecules of **6b** *via* enol form.



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Color Reactions. Results are summarized in Table II.

FCNP. To a solution of 5 mg of sample in 1 ml of water is added several drops of FCNP solution consisting of 2.5% of NaOH, potassium ferricyanide, and sodium nitroprusside.

Alkaline Picrate (Jaffe Method[19a]). To 5 mg of sample in 1 ml of 5% Na_2CO_3 is added 1 to 2 drops of saturated picric acid.

Diacetyl-α-naphthol.[19b] To 5 mg of sample in 1 ml of water is added 2 ml of alkaline α-naphthol solution (5 mg of α-naphthol, 0.6 g of NaOH, and 1.6 g of Na_2CO_3 in 10 ml of water) and 1 ml of freshly prepared 0.05% diacetyl solution.

Reaction with Creatine Phosphokinase. The procedure described in Sigma Technical Bulletin No. 40-UV, May 1972, is fol-

lowed. The change in the absorbance A of β-DPNH at 340 mμ with respect to time (in minutes) is measured on a Colman Junior II spectrophotometer, which is equal to the rate of creatine phosphokinase reaction. The results are given in the Results and Discussion section.

Acknowledgments. I am deeply indebted to Professor James B. Walker for his generous assistance in this research while working as a Welch Postdoctoral Fellow under his supervision. I am also grateful to Professor Edward S. Lewis of the Chemistry Department for kindly making his laboratory facilities available to me, especially at the beginning of this work.

Registry No.—**2a,** 52555-34-7; **2a** HCl, 52555-35-8; **2b,** 52555-36-9; **2b** $(H_2SO_4)_{1/2}$, 52555-37-0; **5,** 2208-07-3; **6b,** 52555-38-1; **8,** 35404-50-3; **9,** 52555-39-2; glycine, 56-40-6; sarcosine HCl, 637-96-7; sodium chloroacetate, 3926-62-3; ethylenediamine, 107-15-3.

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(1) (a) This work was supported by Grant C-153 from the Robert A. Welch Foundation to Professor James B. Walker; (b) Department of Cell Biophysics, Baylor College of Medicine, Houston, Texas 77025.
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Some New Arenesulfonate Leaving Groups Less Reactive Than the *p*-Toluenesulfonate Group

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The wide use and advantages of sulfonate, and particularly arenesulfonate, leaving groups in the study of reaction mechanisms are well known. Their reactivity spread, which is one of their advantages, has been successfully extended in the direction of groups more reactive than the usual *p*-toluenesulfonate,[2] but not so in the opposite direction.

Our attempts to moderate the solvolytic reactivity of some 3-aryl-2-butyl sulfonate derivatives had led us to a search for such "poor" sulfonate leaving groups. Of such groups synthesized and studied, the arenesulfonate derivatives of 3-*p*-tolyl-2-butanol (Table I) and their solvolytic reactivities, as measured by their polarimetric[3] rate of solvolysis in 65% aqueous ethanol (Table II), are reported in this communication.

Table I
Summary of Physical and Analytical Data of Some Arenesulfonyl Chlorides and (+)-*threo*-3-*p*-Tolyl-2-butyl Arenesulfonates

Compd[a]	Registry no.	Mp, °C	$[\alpha]^{25}D$[b]
2,4,6-$(MeO)_3$-I[c]	52499-93-1	134–136	
$(Me)_5$-I[c]	52499-94-2	80–81	
II[d]	52499-95-3	43–44	35.2
III[e]	52499-96-4	43–44	29.5
4-Me-III	52499-97-5	69–70	21.2
$(Me)_5$-III	52499-98-6	112–113	29.1
4-MeO-III	52499-99-7	46–47	22.5
2,4,6-$(MeO)_3$-III	52522-72-2	76–77	8.0

[a] Satisfactory combustion analytical data (±0.7% for C and H) have been provided for all of the compounds in this table. Ed. [b] In benzene solution (1.3%). [c] I = benzenesulfonyl chloride. [d] II = (+)-*threo*-3-*p*-tolyl-2-butyl methanesulfonate. [e] III = benzenesulfonate ester of (+)-*threo*-3-*p*-tolyl-2-butanol.

Table II
Relative Leaving Group Abilities Based on Polarimetric Rates in the Solvolysis of Some (+)-*threo*-3-*p*-Tolyl-2-butyl Arenesulfonates in 65% (Wt/Wt) Aqueous Ethanol[a]

			50 °C		
Compd	Temp,[b] °C	$k \times 10^2$, min^{-1}[c]	$k \times 10^2$, min^{-1}[d]	k_{OTs}/k	k_{III}/k
II[e]	63.43	7.243 ± 0.033	1.722	1.26	1.66
	58.80	4.593 ± 0.022			
	53.54	2.540 ± 0.021			
III[f]	53.54	4.211 ± 0.022	2.859	0.76	1.00
	46.45	1.923 ± 0.024			
4-Me-III	53.54	3.223 ± 0.051	2.168	1.00	1.32
	46.45	1.445 ± 0.023			
4-MeO-III	60.50	3.646 ± 0.017	1.135	1.91	2.52
	53.54	1.696 ± 0.017			
2,4,6-$(MeO)_3$-III	72.28	2.924 ± 0.009	0.273	7.94	10.47
	69.90	2.333 ± 0.031			
	66.48	1.626 ± 0.016			
$(Me)_5$-III	72.28	3.123 ± 0.013	0.255	8.50	11.21
	66.48	1.665 ± 0.018			

[a] Containing 35.0% (wt/wt) water (Karl Fischer determination), and being 0.03 M in NaOAc and 0.02 M in the ester. [b] The temperatures given are those inside the polarimeter cell. [c] Each rate constant represents the average of two to three rate constant determinations followed from 12 to 83% reaction. [d] Rate constants extrapolated to 50°. [e] (+)-*threo*-3-*p*-Tolyl-2-butyl methanesulfonate. [f] Benzenesulfonate ester of (+)-*threo*-3-*p*-tolyl-2-butanol.

The methanesulfonate derivative has also been studied. Methanesulfonates have been reported to be some three times less reactive than tosylates,[4] thus being the slowest reacting sulfonate derivatives known.[5] In our hands and in the solvolytic system used, the mesylate proved to be only 26% less reactive than the tosylate at 50° (Table II). Against this minimal deceleration achieved with the methanesulfonate group and the small retardation by the *p*-methoxybenzenesulfonate group (mosylate, –OMos), 1.9-fold at 50°, the decelarations realized with the now reported 2,4,6-trimethoxybenzenesulfonate group (trimosylate or trosylate, –OTmos or –OTms), 7.9-fold at 50°, and even more that with the pentamethylbenzenesulfonate group (pesylate, –OPmes or –OPms), 8.5-fold, become quite substantial. Of these two new arenesulfonate groups,