spectroscopy in aqueous and ionic solutions. The now well accepted[2] internal reference, tetramethylsilane,[3] is virtually insoluble in such media. However, an ionic derivative of this compound, the anion 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was shown to possess a remarkably favorable balance of properties for general internal referencing of aqueous systems.[1] We here describe the preparation of this useful reference.

The method used was a slight modification of the well-known free-radical addition of bisulfite to olefins.[4,5] Owing to the very low solubility of allyltrimethylsilane in the usual reaction mixture, it was found virtually essential to add a co-solvent, methanol.[5] Alternative initiators (*t*-butyl hydroperoxide, and potassium persulfate) were tried but appeared to be inferior to Kharasch's nitrate-nitrite system.[4]

EXPERIMENTAL

Materials. Allyltrimethylsilane was purchased from Peninsular ChemResearch, Inc., Gainesville, Fla., and was redistilled before use. The other ingredients were of reagent grade.

Sodium 2,2-dimethyl-2-silapentane-5-sulfonate. Into a 500-ml. flask equipped with magnetic stirrer were placed 50.0 g. (0.48 mole) of sodium bisulfite, 5.0 g. (0.072 mole) of sodium nitrate, 5.0 g. (0.059 mole) of sodium nitrate, 150 ml. of distilled water, 250 ml. of methanol, and 25.0 g. (0.22 mole) of allyltrimethylsilane. The flask was tightly stoppered to prevent loss of the volatile silane (the mixture became quite warm) and was stirred without external heat for 2–4 days, at which time a fluffy white precipitate was present. (At this point one might recover a substantial amount of unchanged allyltrimethylsilane by steam distillation; however we did not choose to do so.) The reaction mixture was taken to dryness on the steam bath; we used a rotary evaporator. The dried residue was extracted overnight with 200 ml. of absolute ethanol in a Soxhlet apparatus; the solution was filtered hot through fine filter paper (Whatman No. 5) to remove traces of inorganic salts, and was cooled to crystallize sodium 2,2-dimethyl-2-silapentane-5-sulfonate. Our best yield thus far has been 23.9 g. (46.1%) of the monohydrate of sodium 2,2-dimethyl-2-silapentane-5-sulfonate, after one recrystallization from ethanol; the compound was obtained as the monohydrate.

Anal. Calcd. for $C_6H_{14}NaO_3SiS \cdot H_2O$: H_2O, 7.7; C, 30.5, H, 7.25. Found: H_2O, 7.3 (Karl Fischer); C, 30.5; H, 7.2.

The anhydrous material may be obtained by drying at 130° *in vacuo*.

The monohydrate shows infrared absorption (Nujol mull) at 2.80, 2.88, and 6.20 μ, absent in the anhydrous material; it also has strong sulfonate bands at 8.41 and 9.50 μ with other characteristic bands at 8.01, 11.65, 12.05, 13.24, 13.47, and 14.34 μ.

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Substituent Constants for the Trinitromethyl-, 1,1-Dinitroethyl-, and Related Groups[1]

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Some time ago we pointed out that the rates of reaction of *trans*-3-substituted acrylic acids with diphenyldiazomethane could be correlated with the Hammett *para* substituent constants for the groups used.[2] We wish now to present data on the rates of reaction of several nitro acids and to list the substituent constants for nitroalkyl groups. The rate data, shown in Table I, were obtained as described previously, as were the substituent constants listed in Table II. The substituent constants were calculated from the equations[2]

$$\log k = 0.072 + 1.623\ \sigma_{para}$$

and

$$\log k = -0.105 + 1.174\ \sigma^*$$

TABLE I

RATES OF REACTIONS OF ACIDS WITH $(C_6H_5)_2CN_2$ IN ETHANOL AT 30°

Acid	k, L. Mole^{-1} Min.$^{-1}$
trans-$(O_2N)_3CCH{=}CHCO_2H$	25.3
trans-$(O_2N)_2C(CH_3)CH{=}CHCO_2H$	11.5
trans-$O_2NC(CH_3)_2CH{=}CHCO_2H$	2.49
cis-$O_2NC(CH_3)_2CH{=}CHCO_2H$	3.47
trans-$(O_2N)_2C(C_2H_5)CH{=}CHCO_2H$	13.0
$(O_2N)_3CCH_2CH_2CO_2H$	3.76
$(O_2N)_2C(CH_3)CH_2CH_2CO_2H$	2.03
$(O_2N)_2C(C_2H_5)CH_2CH_2CO_2H$	2.18

TABLE II

SUBSTITUENT CONSTANTS

Substituent	σ_{para}	Substituent	σ^*
Trinitromethyl	0.820	3,3,3-Trinitropropyl	0.579
1,1-Dinitroethyl	0.609	3,3-Dinitrobutyl	0.352
2-Nitro-2-propyl	0.200	3,3-Dinitropentyl	0.377
t-Butyl	−0.197[a]	2,2,2-Trinitroethyl	1.62[b]
1,1-Dinitropropyl	0.642	Trinitromethyl	4.54[b]

[a] From Ref. 3. [b] Obtained by multiplying the value for the substituents with one more methylene group by 2.8.[4]

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[1] Part IV in the series *Polar Effects on Rates and Equilibria*. This investigation was supported by the Department of the Navy, Bureau of Ordnance.

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All of the acids listed were sent to us from the Organic Chemistry Division, U. S. Naval Ordnance Laboratory, Silver Spring, Maryland, by Dr. L. A. Kaplan and Dr. M. J. Kamlet.

It may be noted that the successive replacement of the three methyl groups of *t*-butyl by nitro groups brings about a fairly steady increase in σ_{para}. The σ_{para} and the σ^* values listed for the trinitromethyl group appear to be the largest that have been measured for any electrically neutral group.[3,4]

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An Example of Ester Cleavage by Mechanism $B_{Al}2$

Richard A. Sneen and Arnold M. Rosenberg

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In the course of an investigation into the solvolytic behavior of some isomeric allylic esters we have uncovered an interesting example of the rarely observed $B_{Al}2$ mechanism[1] of ester cleavage: base-catalyzed, bimolecular attack with alkyl-oxygen cleavage. The evidence for this reaction forms the subject matter of this communication.

In particular the methanolysis of α-methyl-γ-phenylallyl *p*-nitrobenzoate had been under study[2] and it had been shown that in the absence of added bases this ester reacts in methanol by an S_N1-type ionization process to furnish *p*-nitrobenzoic acid and both possible isomeric methyl ethers with a first order rate constant at 65° of $k_1 = 1.50 \pm 0.03 \times 10^{-5}$ sec.$^{-1}$ In an attempt to prevent the rather rapid acid-catalyzed equilibration of the initially formed allylic ethers, sodium phenoxide was added as a buffering agent to a methanolic solution of the ester. Interestingly, the rate of production of acid (consumption of base) under these conditions proved to be less than the rate of normal solvolysis of this ester. Furthermore, the reaction appeared to be heading for completion by an essentially second order process, first order in the stoichiometric base concentration. The kinetic data for this run are summarized in Table I. We interpreted these results to mean that the allyl *p*-nitrobenzoate was being consumed by a rapid process to furnish nonacidic products which subsequently underwent a slow base-catalyzed acid-producing reaction, presumably the rate determining step of the reaction.

TABLE I

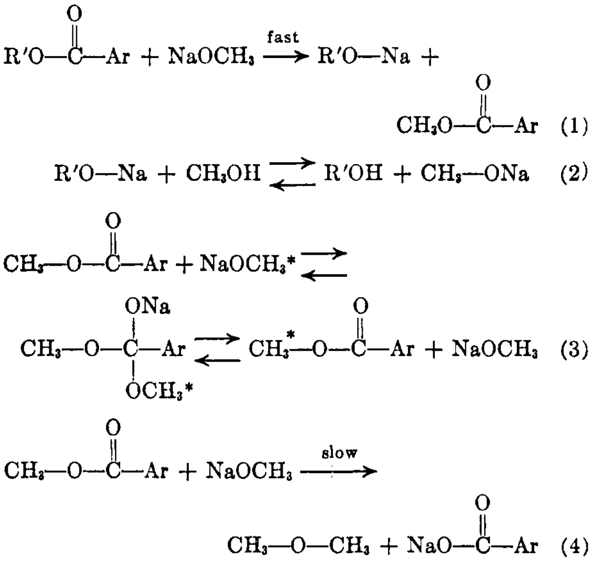
Rate of Reaction of α-Methyl-γ-Phenylallyl *p*-Nitrobenzoate with Sodium Phenoxide in Methanol at 65.0°

$[\text{Ester}]_{\text{initial}} = 0.0184M$
$[\text{NaOC}_6\text{H}_5]_{\text{initial}} = 0.0220M$
Titrant = 0.0209*M* aqueous hydrochloric acid
Quench = 10 ml. acetone
Aliquot = 5 ml.

% Reaction	$\dfrac{-d[\text{NaOC}_6\text{H}_5]/dt \times 10^4}{[\text{NaOC}_6\text{H}_5][\text{R'X}]}$, L. Mole^{-1} Sec.$^{-1\,a}$
12.6	2.39
18.0	2.36
26.0	2.46
37.8	2.34
43.5	2.31
47.2	2.32
	Av. 2.36 ± 0.04

^{a} Derivative obtained by taking tangents to a plot of time *vs.* ml. of titrant.

One sequence of reactions which appeared consistent with these facts is reproduced below (for simplicity in representation the scheme has been modified by assuming base to be present only in the form of sodium methoxide, even though it was introduced in the form of sodium phenoxide):



$$\mathrm{R'O{-}\overset{O}{\overset{\|}{C}}{-}Ar + NaOCH_3 \xrightarrow{fast} R'O{-}Na + CH_3O{-}\overset{O}{\overset{\|}{C}}{-}Ar} \quad (1)$$

$$\mathrm{R'O{-}Na + CH_3OH \rightleftarrows R'OH + CH_3{-}ONa} \quad (2)$$

$$\mathrm{CH_3{-}O{-}\overset{O}{\overset{\|}{C}}{-}Ar + NaOCH_3^* \rightleftarrows CH_3{-}O{-}\overset{ONa}{\underset{OCH_3^*}{C}}{-}Ar \rightleftarrows CH_3^*{-}O{-}\overset{O}{\overset{\|}{C}}{-}Ar + NaOCH_3} \quad (3)$$

$$\mathrm{CH_3{-}O{-}\overset{O}{\overset{\|}{C}}{-}Ar + NaOCH_3 \xrightarrow{slow} CH_3{-}O{-}CH_3 + NaO{-}\overset{O}{\overset{\|}{C}}{-}Ar} \quad (4)$$

R′ = α-methyl-γ-phenylallyl

The first step of this scheme, ester interchange, is presumed to be very fast as required by the observation that the rate of reaction is slower than ordinary solvolysis. (Methyl *p*-nitrobenzoate should, of course, be stable to ionization.) Step 3 is also an ester interchange reaction of mechanism $B_{Ac}2$[1] whose rate is probably very rapid but whose incurrence has no effect on the overall reaction since the products are identical with starting materials. The slow step of the reaction is step 4, the so-called $B_{Al}2$[1] reaction whose presence in most systems is masked by the faster $B_{Ac}2$ reaction. Step 4 is essentially an S_N2 reaction,

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