upon this tripositive complex[7] is 7.2×10^{-3} sec^{-1}, about 170 times faster than for the dipositive cupric complex. That this factor is about twice as large as might be predicted from the difference of one unit of positive charge in the two transition metal ion complexes may be due to only about half the cupric complexes being chelated at any one time or to a greater polarizing power for cobaltic ion at the carbonyl oxygen.

The rate constant from the second paragraph of $10^{2.5}$ sec^{-1} for water attack at carbonyl oxygen protonated ester of unit positive charge exceeds by $10^{6.9}$ and $10^{4.6}$ the respective rate constants for water attack of $10^{-4.4}$ sec^{-1} at the dipositive cupric chelate and $10^{-2.1}$ sec^{-1} at the tripositive cobaltic chelate of glycine ethyl ester. On the basis of the argument so far presented, the large rate advantages for the protonated ester over the transition metal ion chelates suggest that acid-catalyzed ester hydrolysis proceeds much too rapidly to be accounted for by water attack on the small concentrations of preprotonated ester existing in weakly acid solutions. The argument presented is an electrostatic one based on considerations of specific rate constants of species of known charge distribution. It is generally recognized, however, that the polarizing power of the proton even when hydrated is greater than that of metal ions in similar solvents. It is necessary, therefore, to attempt an estimate of the relative charge densities at the carbonyl carbon, where water attack takes place, due to the different polarizing powers of the hydrated proton and cupric or cobaltic ions located at the carbonyl oxygen atom.

The relative σ-bond polarizing powers due to the hydrated proton and cations at an atom attached to oxygen may be estimated from the acid ionization constants for loss of a proton from their respective hydration spheres according to eq 1, where H^+ is an abbreviation for the hydrated proton.

$$M(H_2O)_n^{Z} \rightleftharpoons M(H_2O)_{n-1}(OH^-)^{Z-1} + H^+ \qquad (1)$$

For M as H^+, Cu^{2+}, and Co^{3+}, the respective pK_a values[8] for eq 1 are -1.7, 7.3, and 1.7, indicating that the polarizing power of the proton is about $10^{9.0}$ and $10^{3.4}$ times greater than for the aquo metal cations. However, when cobaltic ion is combined with five nitrogen donors, its polarizing power appears much decreased since for eq 2 pK_a[8] is 6.2. A steady increase in pK_a for ionization from water

$$Co(NH_3)_5H_2O^{3+} \rightleftharpoons Co(NH_3)_5OH^{2+} + H^+ \qquad (2)$$

occurs as nitrogen is substituted for oxygen donors about the cobaltic ion.[8] The hydrated proton appears to be $10^{7.9}$ times more polarizing than cobaltic ion with five nitrogen donors. No corresponding information seems to be available for cupric ion where the pK_a for coordinated water ionization from a complex with one nitrogen donor is desired. Allowing one log unit per nitrogen donor, we may estimate the hydrated proton to be 10^{10} times more polarizing than cupric ion with one nitrogen donor.

Rate constants for water attack at carbonyl oxygen protonated esters may now be calculated by multiplying the rate constant for water attack at each metal ion chelate of glycine ethyl ester by the relative polarizing powers of hydrated proton and cation. We obtain for the cobaltic chelate, $10^{-2.1} \times 10^{7.9} = 10^{5.8}$ sec^{-1} and for the cupric chelate, $10^{-4.4} \times 10^{10} = 10^{5.6}$ sec^{-1}. These values are about $10^{3.2}$ times greater than the experimental value of $10^{2.5}$ sec^{-1} so that this last rate constant appears to be an attainable one. We conclude that acid-catalyzed hydrolysis of ordinary esters may well proceed by water attack on preprotonated ester.

Because of the symmetrical nature of ester hydrolysis and formation reactions[9] and the similar values of carboxylic acid and ester ionization constants[3] as suggested by their comparable dipole moments,[10] the conclusion advanced here is applicable to the formation as well as the hydrolysis reaction. Partitioning of the tetrahedral carbon addition intermediate to yield ester or acid is comparable in both acid[11] and metal ion[12] catalyzed reactions so that the conclusions are not affected by a change in the rate-limiting step.

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[7] M. D. Alexander and D. H. Busch, *J. Am. Chem. Soc.*, **88**, 1130 (1966).

[8] "Stability Constants," Special Publication, No. 17, The Chemical Society, London, 1964.

[9] R. B. Martin, *J. Am. Chem. Soc.*, **84**, 4130 (1962); **86**, 5709 (1964).

[10] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p 304.

[11] M. L. Bender, *J. Am. Chem. Soc.*, **73**, 1626 (1951); M. L. Bender, R. D. Ginger, and J. P. Unik, *ibid.*, **80**, 1044 (1958).

[12] M. L. Bender and B. W. Turnquest, *ibid.*, **79**, 1889 (1957).

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N-Sulfonylamines

Sir:

We wish to report the generation of a new class of electrophilic amine derivatives designated as N-sulfonylamines ($RN{=}SO_2$). Unlike the related N-sulfinylamines[1] ($RN{=}S{=}O$), the N-sulfonylamines studied so far appear to be stable only at low temperature in solution. Ethylsulfamoyl chloride[2] (II) reacts rapidly with 1 equiv of triethylamine in toluene solution at −78° to afford a nearly quantitative yield of precipitated triethylamine hydrochloride. Filtration at this temperature provides solutions of I, which undergoes mildly exothermic polymerization upon warming. Successful interception of the N-sulfonylethylamine was accomplished by the addition to this solution of a nucleophile such as aniline which results in a 21% yield of N-phenyl-N′-ethylsulfamide (III).[3,4]

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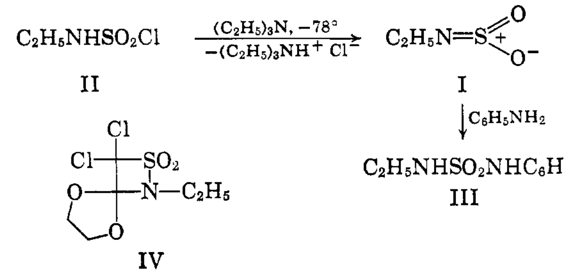
[1] G. Kresze, *et al.*, *Angew. Chem. Intern. Ed. Engl.*, **1**, 89 (1962).

[2] Prepared by the interaction of ethylamine hydrochloride and sulfuryl chloride in diethyl ether solution: N. C. Hansen, *Acta Chem. Scand.*, **17**, 2141 (9163); G. Schulze and G. Weiss, Belgian Patent 667,311 (1966).

[3] Identified by mixture melting point (where appropriate) and infrared spectral comparison with an authentic sample.

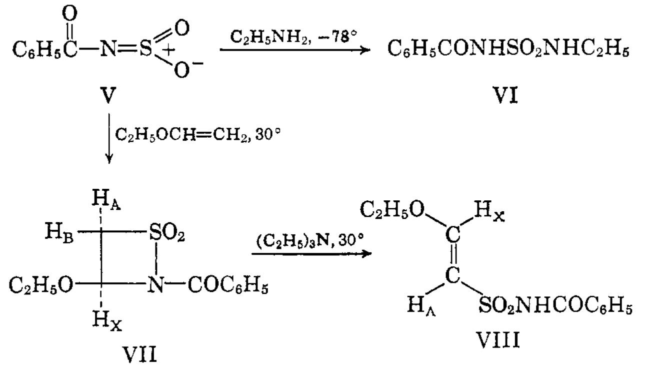
[4] A. Dorlars in Houben-Weyl's "Methoden der Organischen Chemie," Vol. 8, E. Muller, Ed., Georg Thieme Verlag, Stuttgart, Germany, 1952, pp 720–721.

The generation of I at room temperature in the presence of 2-(dichloromethylene)-1,3-dioxalane[5] affords a nearly quantitative yield of a cycloadduct, mp 74–75°, assigned the 1,2-thiazetidine 1,1-dioxide structure IV.[6]



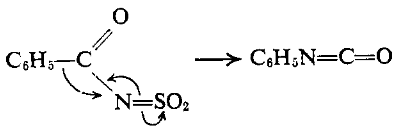
The mass spectrum of IV displayed a molecular ion[7] at *m/e* 262 and prominent ions at *m/e* 107 ($C_2H_5NSO_2^+$) and 154 ($C_4H_4O_2Cl_2^+$) resulting from 1,4 and 2,3 bond cleavage only; therefore our proposed orientation of this cycloadduct rests upon the mechanistic consideration that the transition state polarization of I is $-\bar{N}-S^{+}O_2$.

More electrophilic[8] N-sulfonylamines such as N-sulfonylbenzamide (V) were prepared in toluene solution at −78° in an analogous manner from benzoylsulfamoyl chloride.[9] The existence of V was likewise established by the formation of N-benzoyl-N′-ethylsulfamide[3] in 66% yield upon quenching with ethylamine at −78°.[10]



The formation of V in the presence of excess ethyl vinyl ether at 30° in benzene solution affords a 71% yield of a cycloadduct, mp 87–88°, for which structure VII is proposed based on the following evidence. The nmr spectrum ($CDCl_3$, 60 Mc) displayed quartets for H_A, H_B, and H_X centered at τ 6.53, 6.20, and 4.07, respectively, with $J_{AB} = 14$ cps, $J_{AX} = 9$ cps, and $J_{BX} = 3$ cps, and the molecular ion appeared at *m/e* 255 in the mass spectrum. Treatment of VII with a benzene solution of triethylamine at 30° provided in nearly quantitative yield an isomer, mp 135–136°, assigned structure VIII.[11] The nmr spectrum ($CDCl_3$, 60 Mc) of VIII indicated a doublet for H_X centered at τ 4.08 coupled ($J = 12$ cps) with H_A, whose absorption was superimposed on the aromatic and imide proton signals at τ 2.1–2.7. This evidence supports the structural assignment and establishes the orientation of the cycloaddition reaction leading to VII.

If a toluene solution of V at −78° is allowed to warm to room temperature in the absence of a trapping agent exclusive rearrangement to phenyl isocyanate[3] occurs. It is interesting to speculate that this reaction may represent an α elimination of sulfur dioxide, *i.e.*



Studies are in progress on the synthetic usefulness of N-sulfonylamines in elaborating small-ring heterocycles.

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[5] S. M. McElvain and M. J. Curry, *J. Am. Chem. Soc.*, **70**, 3781 (1948).

[6] Satisfactory elemental analyses were obtained for all new compounds reported herein.

[7] The appearance of a M + 2 and M + 4 ion resulting from the possible isotopic combinations substantiated the dichloro assignment for IV.

[8] N-Sulfonylethylamine fails to react at room temperature with olefins of low nucleophilicity such as ethyl vinyl ether.

[9] Prepared by the interaction of chlorosulfonyl isocyanate and benzoic acid in benzene solution. See ref 4, p 700.

[10] Currently under investigation is the possibility that the reactive species present is the triethylamine adduct, $C_6H_5CO\bar{N}{-}SO_2N^+(C_2H_5)_3$. Analogous adducts of certain sulfenes have been reported recently by G. Spitz and D. Bucher, *Tetrahedron Letters*, **43**, 5263 (1966).

[11] This imide was isolated as the triethylamine salt which was converted to VIII upon silica gel chromatography. This salt also results from the reaction of ethyl vinyl ether with VI in the presence of excess triethylamine.

Photoreduction of Acetone by Tributylstannane

Sir:

The intermediacy of the triplet states of ketones in their photoreductions is so well established[1–3] that there has been some doubt whether the corresponding excited singlet states have any chemical reactivity in bimolecular reactions in solutions. When it became clear that aliphatic ketones undergo type-II photoelimination from both singlet and triplet excited states,[4] we suggested[5] that the n,π^* excited singlet states of carbonyl compounds may in general be just as reactive

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[1] (a) G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, **57**, 1686 (1961); (b) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961); (c) W. M. Moore and M. Ketchum, *ibid.*, **84**, 1368 (1962); (d) J. A. Bell and H. Linschitz, *ibid.*, **85**, 528 (1963).

[2] G. S. Hammond and P. A. Leermakers, *ibid.*, **84**, 207 (1962).

[3] P. J. Wagner, *ibid.*, **88**, 5672 (1966).

[4] (a) P. J. Wagner and G. S. Hammond, *ibid.*, **87**, 4009 (1965); (b) T. J. Dougherty, *ibid.*, **87**, 4011 (1965).

[5] P. J. Wagner and G. S. Hammond, *ibid.*, **88**, 1245 (1966).