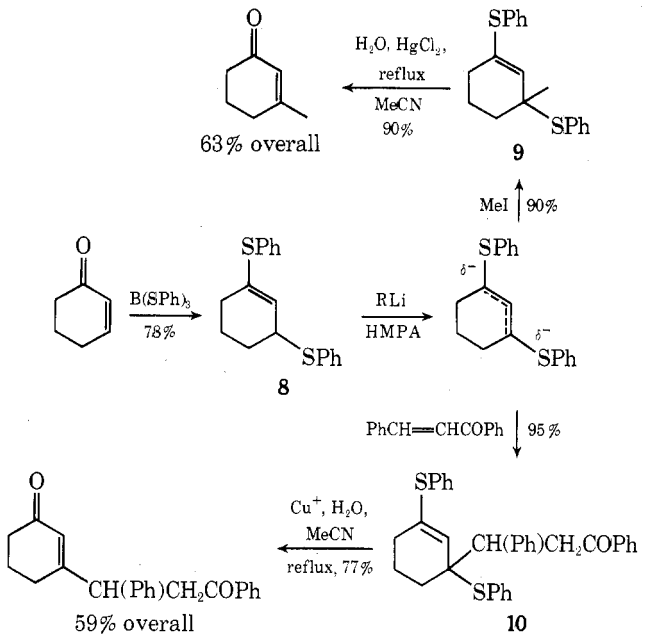
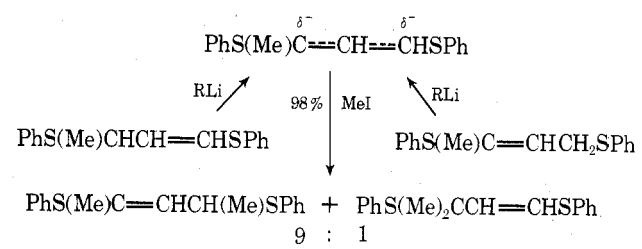
Scheme III



Scheme IV



which yield unsymmetrical anions, this procedure will result in a substitutive 1,3-carbonyl transposition[16] in some cases. Presumably, in the case of unsymmetrical anions with different steric requirements at the partially negative carbon atoms, the least hindered of the latter will be alkylated most readily as in Scheme IV. Methods of reversing this regioselectivity and of exploiting the interesting implications of this aspect are now under investigation, as are alternative uses of the 1,3-bis(phenylthio)alkenes.

Acknowledgment. We thank the National Institutes of Health for Grant GM20707 in support of this work. We also thank Mr. Richard Gapinski for technical assistance.

References and Notes

(1) Triethyl thioborate is reported[2] to form a normal thioacetal with α,β-unsaturated aldehydes. In view of the known allylic rearrangements of allylic thioethers,[3] we intended to perform the thermal or Lewis acid catalyzed rearrangements of these unsaturated thioacetals. However, both reactions apparently occur in the same reaction mixture with triphenyl thioborate, presumably because of the Lewis acid behavior of the latter and the superior leaving ability of thiophenoxide.
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(3) H. Kwart and N. Johnson, *J. Am. Chem. Soc.*, **92**, 6064 (1970); Y. Makisumi and T. Sasatani, *Tetrahedron Lett.*, 1975 (1969).
(4) A modification of the literature procedure [J. Brault and J. M. LaLancette, *Can. J. Chem.*, **42**, 2903 (1964)] consisting of heating B_2S_3 (Alpha) with thiophenol in refluxing benzene for 48 h gives a nearly quantitative yield of triphenyl thioborate as white crystals which can be handled rapidly in air and stored in a desiccator.
(5) The presence of galvinoxyl does not influence this result: G. W. Kabalka, H. C. Brown, A. Suzuki, S. Honma, A. Arase, and M. Itoh, *J. Am. Chem. Soc.*, **92**, 710 (1970).
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(9) The same sequence is also successful starting from methacrolein. A subsequent publication will elaborate on eliminations from such tris-(phenylthio) compounds by means of cuprous triflate.
(10) Corey has shown that the lithio derivative of 1,3-bis(methylthio)propene behaves as a synthetic equivalent of the hypothetical β anion of acrolein: E. J. Corey, B. W. Erickson, and R. Noyori, *J. Am. Chem. Soc.*, **93**, 1724 (1971); E. J. Corey and R. Noyori, *Tetrahedron Lett.*, 311 (1970). See also K. Oshima, H. Yamamoto, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, **48**, 1567 (1975); R. G. Carlson and W. S. Mardis, *J. Org. Chem.*, **40**, 817 (1975).
(11) Hydrolysis of this compound was also successful (quantitatively, according to ^{1}H NMR) using the cupric chloride method[12] but in this case it was necessary to separate the product from diphenyl disulfide.
(12) T. Mukaiyama, K. Narasaka, and M. Furusato, *J. Am. Chem. Soc.*, **94**, 8641 (1972).
(13) Unpublished work of Richard Gapinski indicates that this method is also successful with a third 1,3-bis(phenylthio)propene which was prepared by a different procedure.
(14) A similar solution can be prepared more easily by adding water to a solution formed by heating cupric triflate and copper metal in acetonitrile: C. L. Jenkins and J. K. Kochi, *J. Am. Chem. Soc.*, **94**, 843 (1972).
(15) The only other method of which we are aware for preparing β-acyl vinyl anion equivalents directly from enones requires four separate operations in some cases and five in others: K. Kondo and D. Tunemoto, *Tetrahedron Lett.*, 1007 (1975).
(16) B. M. Trost and J. L. Stanton, *J. Am. Chem. Soc.*, **97**, 4018 (1975).
(17) A. W. Mellon Predoctoral Fellow.

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Received March 16, 1976

Nitrogen Acids. 1. Carboxamides and Sulfonamides

Summary: Measurement of the equilibrium acidities in Me_2SO of carbon, nitrogen, and oxygen acids has revealed the expected order, i.e., GOH $\gg$ GNH_2 $\gg$ GCH_3, when G is Ph, CH_3SO_2, or F_3CSO_2, but when G is CH_3CO or PhCO the carbon and nitrogen acids have comparable acidities.

Sir: Carboxamides are too weakly acidic to allow equilibrium acidities to be measured in water by ordinary methods. In fact, to our knowledge, no report of an *absolute* acidity measurement for a simple carboxamide has been recorded in the literature in the 48 years since Branch and Clayton reported the equilibrium constant of acetamide in water to be 8.3×10^{-16}.[1,2] Measurements on carboxamides in strongly basic aqueous media by acidity function techniques are made difficult, if not impossible, by hydrolysis, and pK data are scarce for this important class of weak nitrogen acids.[2] We wish to report that absolute equilibrium acidity measurements in dimethyl sulfoxide solution can be made accurately and conveniently for carboxamides, as well as for sulfonamides, by the competitive indicator method developed for carbon acids.[4] These nitrogen acids differ from oxygen acids in this respect, the latter having a strong tendency to undergo hydrogen bonding ("homoconjugation") with their conjugate bases (e.g., $RO^-\cdot\cdot\cdot HOR$), which makes measurements more difficult.[4,5] The pK's in Me_2SO for a few carboxamides and sulfonamides are compared in Table I with those of their carbon and oxygen analogues.

Examination of Table I shows that the pK for dissociation of the N–H bond in acetamide is much higher in Me_2SO than in water (25.5 vs. 15.1). This is consistent with results obtained with other acids in which the negative charge in the anion is concentrated on oxygen where it can be stabilized by strong H bonding in water, but not in Me_2SO.[4] Judging from preliminary results with *N,N*-dimethylacetamide, the pK for dissociation of the C–H bond in acetamide is above 32 in Me_2SO, which places the acidity more than 7 units higher than the pK in water estimated from deuterium exchange rates.[6]

The order of acidities of carbon, nitrogen, and oxygen acids is seen from Table I to be $GCH_3 \ll GNH_2 \ll$ GOH, when G

Table I. Comparison of the Equilibrium Acidities of Analogous Carbon, Nitrogen, and Oxygen Acids in Dimethyl Sulfoxide Solution

Acid	pK	Acid	pK	Acid	pK
$PhCH_3$	~47[a]	$PhNH_2$	30.7[b]	PhOH	16.4,[c] ~18.5[d]
CH_3COCH_3	26.5[e]	CH_3CONH_2	25.5	CH_3COOH	12.6[c]
CH_3COCH_2Ph	19.8[f]	$CH_3CONHPh$	21.45		
$C_6H_5COCH_3$	24.7[e]	$C_6H_5CONH_2$	23.35	C_6H_5COOH	11.1[c]
$C_6H_5COCH_2Ph$	17.7[f]	$C_6H_5CONHPh$	18.8		
$CH_3SO_2CH_3$	31.1[e]	$CH_3SO_2NH_2$	17.5	CH_3SO_2OH	1.62[g]
$F_3CSO_2CH_3$	18.8[h]	$F_3CSO_2NH_2$	9.7	F_3CSO_2OH	0.31[g]

[a] Estimated by extrapolation. [b] Preliminary value. [c] Reference 11. [d] Z. Margolin, unpublished results. [e] Reference 4. [f] Reference 9. [g] Reference 12. [h] Reference 10.

is Ph, CH_3SO_2, or F_3CSO_2. In these systems there is nearly the same difference in acidity between the carbon and nitrogen acids as between the nitrogen and oxygen acids. The difference is ~15 pK units when G is Ph or CH_3SO_2, and ~9.5 pK units when G is F_3CSO_2. When G is CH_3CO or PhCO the difference in acidities between nitrogen and oxygen acids (12 to 13 pK units) appears to be in line with that expected by analogy with the corresponding acids where G is Ph or CH_3SO_2, but the difference in acidities between the carbon and nitrogen acids is only ~1.5 pK units in each instance. Furthermore, the carbon acids in which a phenyl group has been substituted for a hydrogen atom at the acidic site, i.e., CH_3COCH_2Ph and $C_6H_5COCH_2Ph$, are actually over 1 pK units *more* acidic than their nitrogen analogues, $CH_3CONHPh$ and $C_6H_5CONHPh$. In comparing the acidities of carboxamides to ketones it is clear that some factor is present that negates the intrinsically greater acidity of the N–H bond as compared to the C–H bond. It seems likely that the strong resonance stabilization of the undissociated carboxamide is responsible. Judging from the results with the other carbon, nitrogen, and oxygen acid systems (Table I), the difference in acidities between ketones and carboxamides should be as large as between carboxamides and carboxylic acids or ~7 pK units (half the difference in acidities between the carbon and oxygen acids). If "extra" resonance in the carboxamide is the cause of the much smaller difference actually observed (1.5 pK units), this would require a resonance energy of ~7.5 kcal/mol. It is interesting to note in this connection that the barrier to rotation around the C–N bond in carboxamides is high, ranging from about 14 to 18 kcal/mol at the appropriate coalescence temperatures.[8]

Resonance between the electron pair on nitrogen and the function to which the nitrogen atom is attached no doubt occurs in the undissociated forms of all of the nitrogen acids listed in Table I. Evidently, this resonance in aniline and in the sulfonamides is relatively much weaker than in the carboxamides.

Acknowledgment. We are grateful to the National Science Foundation (MP 574-12665) for support of this research. A sample of trifluoromethanesulfonamide was kindly furnished by Professor James Hendrickson.

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Received March 19, 1976