9.90, 10.16, 10.48, 10.70, and 11.27 μ] in the ratio 2:3 as judged by the gas chromatogram. The major component of this mixture should be the *meso* isomer 9 since the double bond in unsaturated ketone 5 appears from models to be somewhat hindered by the proximate methyl group.[8] Ketones 8 and 9 differed from 3 according to the infrared spectra and gas chromatographic behavior. However, desulfurization of the thioketal derivative of ketone 9 afforded the same hydrocarbon 6 previously obtained from β-vetivone. Ketones 3 and 9 must therefore be epimeric at the spiro ring junction. Ketone 8, when similarly treated, afforded hydrocarbon 7 [λ_{max}^{film} 7.24, 8.63, 9.42, 10.25, 10.75, 10.95, and 11.33 μ] which closely resembled 6. These hydrocarbons could be cleanly separated by gas chromatography.

The above transformations require that β-vetivone be formulated as III, or the mirror image. The choice of III can be made from Yosioka and Kimura's work in which hinesol (now formulated as V) was converted to (+)-β-vetivone (VI).[9] The absolute configuration of hinesol (V) follows from its degradation to (+)-α-

V   VI
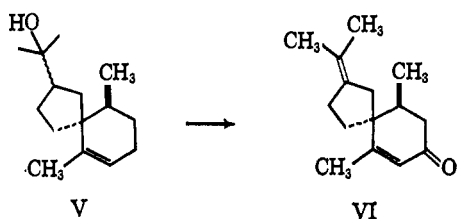
methylglutaric acid by Šorm and co-workers.[10]

In view of the findings recorded above and in our previous report,[1] the list of sesquiterpenes containing a spiro[4.5]decane ring system which previously contained only the acrorones[11] and agarospirol[12] must now be expanded to include β-vetivone, hinesol[10] (a close relative of agarospirol[12]), bicyclovetivenol,[13] α-isovetivenene, and β-isovetivenene.[3]

(8) This methyl group probably prefers an axial conformation to avoid *gauche* butane interactions with the adjacent spiro methylenes. Such an orientation may be particularly favored with olefin 5 because the double bond alleviates or removes the unfavorable *gauche* interactions normally associated with an axial methylcyclohexane: *Cf.* E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, pp 42ff, 109ff.

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(13) G. Chiurdoglu and J. Decot, *ibid.*, 4, 1 (1958).

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The Acidities of Weak Acids in Dimethyl Sulfoxide (DMSO) Solutions. III. Comments on the H_- Acidity Scales

Sir:

There has been some apparent disparity between the acidity scale in cyclohexylamine solvent developed by Streitwieser[1] and his co-workers and one which we reported earlier[2] for DMSO, aqueous DMSO, and methanolic DMSO. We present here some recent results which bring the two scales into better over-all agreement but which indicate a significant difficulty in basing the scales satisfactorily on the aqueous reference state.

In our previous communication[2] we reported a ΔpK between fluorene (FH) and 9-phenylxanthene (PXH) of 3.7–3.8. Subsequent work showed that the actual ΔpK was too great to relate the indicators directly, and an intermediate indicator, 1,1,3-triphenylpropene (TPH), has now been used. The result is that the pK of indicators less acidic than fluorene must be increased by about 1.6 units. This gives a pK span of 9.7 units between FH and our least acidic indicator, diphenylmethane (DH), as compared to Streitwieser's span of 10.4. This is surprisingly good agreement considering the vast difference in the acidities involved and the difference in solvent systems.

A second point of inconsistency is the assignment of absolute pK values. We based our scale on 4-nitroaniline (NAH), the pK of which was reported to be 18.4 by Stewart and O'Donnell,[3] a valued based on the aqueous reference state. Streitwieser's scale is based on 9-phenylfluorene (PFH), the pK of which is reported to be 18.5 by Langford and Burwell[4] and 18.6 by Bowden and Stewart.[5] We have related FH to NAH, FH to PFH, and PFH to NAH, and find that PFH is significantly more acidic than previously reported. Ritchie has also found this to be the case.[6] With these results our ΔpK between PFH and DH is 13.6 while Streitwieser's is 14.6—still excellent agreement. Furthermore, if both scales are based on the same reference compound the absolute pK values are within 1 pK unit throughout.

Absolute pK values have been avoided intentionally in the above discussion. The reason is that large deviations have been found between the hydrocarbon indicators, PFH and FH, and the nitroanilines in aqueous DMSO, and this causes uncertainties in basing the acidity scale on the aqueous reference state. This is shown graphically in Figure 1 where the H_- of 10 mM KOH solutions in aqueous DMSO is plotted against $-\log$ [H_2O] using the different indicators. Values calculated from the data of Stewart, O'Donnell, and Dolman[7] are also included. They used Me_4N^+ as the cation. The pK values of the nitroanilines are assumed to be those reported by Stewart and O'Donnell.[3]

(1) (a) A. Streitwieser, Jr., J. H. Hammons, E. Ciuffarin, and J. I. Brauman, *J. Am. Chem. Soc.*, 89, 59 (1967); (b) A. Streitwieser, Jr., E. Ciuffarin, and J. H. Hammons, *ibid.*, 89, 63 (1967).

(2) E. C. Steiner and J. M. Gilbert, *ibid.*, 87, 382 (1965).

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(5) K. Bowden and R. Stewart, *Tetrahedron*, 21, 261 (1965).

(6) C. D. Ritchie and R. E. Uschold, *J. Am. Chem. Soc.*, 89, 2752 (1967).

(7) (a) R. Stewart and J. P. O'Donnell, *Can. J. Chem.*, 42, 1694 (1964); (b) R. Stewart and D. Dolman as presented in a review by K. Bowden, *Chem. Rev.*, 66, 119 (1966).
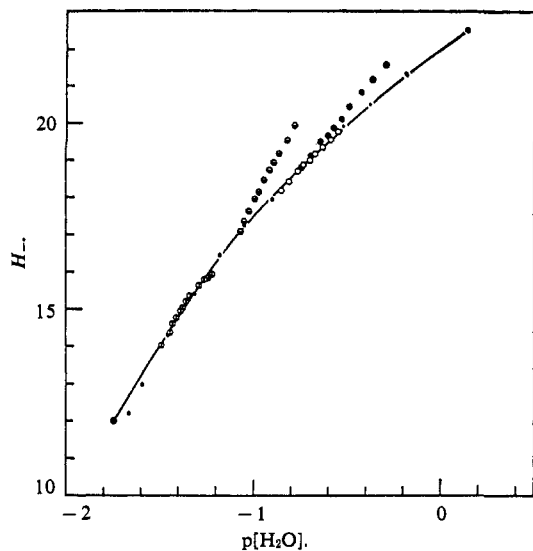
Figure 1. Base strength of aqueous DMSO solutions as a function of water concentration: ☉, 2,4-dinitrodiphenylamine, [KOH] = 10 mM; O, 4-nitroaniline, [KOH] = 10 mM; •, calculated from data in ref 7, [Me₄N⁺OH⁻] = 11 mM adjusted to 10 mM; ◑, 9-phenylfluorene (pK = 18.1 assumed), [KOH] = 10 mM; ●, fluorene (pK = 21.1 assumed), [KOH] = 10 mM.

The pK's of PFH and FH are set at 18.1 and 21.1 so that H_- values measured with them conform to the aniline scale at the higher water concentrations. Clearly, the two types of indicators do not behave ideally relative to each other since the curves are not parallel. Furthermore, the ΔpK between, say, NAH and PFH will depend strongly on solvent composition, and therefore a large uncertainty is inevitable when absolute pK values are assigned to the less acidic hydrocarbons. This same sort of discrepancy obtains also in methanolic DMSO, although it is not as serious. The discrepancy is negligible in ethanolic DMSO.

The causes of the deviations have not been investigated, but it seems likely that the nitro groups are an important factor. Thus if the anion of 4-nitroaniline is stabilized by hydrogen bonding to water, an increase
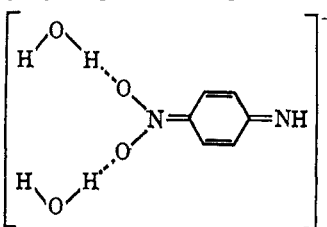
in water concentration would increase the acidity of NAH relative to that of PFH, as is observed. Salting out of the un-ionized hydrocarbon by water, another possible source of nonideality, should have an effect opposite to that observed. It is interesting to note that H_- data measured in methanolic DMSO with 4-nitrotriphenylmethane and with bis(4-nitrobenzyl) sulfone[8] parallel very closely the data from the nitroanilines.

At the present time it appears to us that the nitroaniline scale is the most firmly anchored in the aqueous reference state. Furthermore, it is fairly consistent in a number of aqueous and alcoholic DMSO solutions as well as in pure DMSO. As such, it can be a useful tool. The nonideality between the anilines and the

(8) Measured in our laboratory by R. H. Imes in cooperation with Dr. F. G. Bordwell.

more acidic hydrocarbons creates large uncertainties in the pK values assigned to the hydrocarbons, but since the aniline scale is the only available link between the hydrocarbons and the aqueous reference state there is little choice but to use it temporarily as the base for the hydrocarbons. If the hydrocarbon scale can be satisfactorily related directly to the pH scale, then perhaps a more valid and widely applicable H_- scale can be developed. A more detailed description of the H_- scale in a number of alcoholic DMSO mixtures will be given in a subsequent communication.

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Acidity in Nonaqueous Solvents. V. Acidity Scales in Dimethyl Sulfoxide Solution[1,2]

Sir:

Using the potentiometric method recently described,[2] we have determined the "absolute"[3] acidities of several additional carbon acids in dimethyl sulfoxide solution. The new data, presented in Table I, along with some pertinent previously reported data, provide an explanation of major discrepancies between reported relative acidities in dimethyl sulfoxide and cyclohexylamine solution[4] and provide further insight into the nature of the effect of changing solvent on the relative acidities of various acids.

Table I. Comparison of Acidities in Various Solvents

Acid	pK(DMSO)[a]	pK(H₂O)[b]	pK(CHA)[c]
9-Carbomethoxyfluorene	10.3	12.9[d,e]	...
p-Nitrophenol	10.4[f]	7.1	...
Acetic acid	11.6[f]	4.8	...
Malononitrile	11.0	11.1[g,e]	...
Benzoylacetone	12.1[f]	9.6	...
Tris(p-nitrophenyl)-methane	12.2[f]	14.3[d,e]	...
Acetylacetone	13.4	9.0	...
2,4-Dinitroaniline	14.8[f]	14.7[d]	...
Nitromethane	15.9[f]	10.2	...
9-Phenylfluorene	16.4	18.6[d,e]	(16.4)
Indene	18.5	18.2[d]	17.8
9-Methylfluorene	19.7[f]	...	...
4,5-Methylenephenanthrene	20.0	...	20.5
Fluorene	20.5	20.5[d]	20.6
Triphenylmethane	∼28	28.8[d,h]	29.4

[a] Standard state in dimethyl sulfoxide solution. Estimated accuracy: ±0.3 pK unit (see ref 2). All measurements at 25.0°. [b] Those values not referenced were actually determined in aqueous solution. Others have been determined by acidity function techniques. [c] Values taken from ref 4 and adjusted to pK = 16.4 for 9-phenylfluorene. [d] Values determined by acidity function techniques. [e] From ref 5. [f] Values from ref 2. [g] Value determined in aqueous solution and used as the standard for establishment of an H_- scale. See ref 5. [h] Personal communication from Dr. E. C. Steiner.

(1) This work was supported by Grant No. GM 12832 from the Public Health Service, National Institutes of Health.
(2) For previous papers in this series, see: C. D. Ritchie and R. E. Uschold, *J. Am. Chem. Soc.*, **89**, 1721 (1967), and earlier references cited there.
(3) The word "absolute" is used in the sense that the equilibrium constants are referred to a standard state in the solvent in which they are measured.
(4) A. Streitwieser, Jr., E. Ciuffarin, and J. H. Hammons, *J. Am. Chem. Soc.*, **89**, 63 (1967).