

p-character in the carbon atomic orbital of the CN bonds is 79% in $(\text{CH}_3)_3\text{N}$ and 87% in $(\text{CH}_3)_4\text{N}^+$. As expected, the $\text{C}^{13}\text{-H}$ coupling constant for trimethylamine N-oxide shows that the electronegativity of N^+ in the N-oxide is nearly the same as the electronegativity of N^+ in quaternary ammonium salts so that the NO bond in N-oxides must be almost completely $\text{N}^+\text{-O}^-$.

Pauling has concluded⁶ from the structural data on amides that the dipolar form, $\text{-C}=\text{N}^+\text{O}^-$, contributes 40% of the total structure of amides. A linear dependence of $\text{C}^{13}\text{-H}$ coupling constant on the amount of positive charge on nitrogen would therefore predict a coupling constant in N,N-dimethylamides of 138–139 c.p.s. depending on the $\text{C}^{13}\text{-H}$ coupling constant one uses for N^+ ; this is consistent with the data in Table I. Therefore, $\text{C}^{13}\text{-H}$ coupling constants can be used as an experimental measure of the amount of positive charge on atoms bonded to methyl groups; this, in turn, can give information concerning bonding and structure.

We therefore have used this method on simple compounds containing PO and SO bonds. Trimethylphosphine shows a lower coupling constant than trimethylamine, and the increase on quaternization is smaller, as might be expected, because the C–P bond should be about 0.4 Å. longer than the C–N bond. The $\text{C}^{13}\text{-H}$ coupling constant for trimethylphosphine oxide in D_2O solution (Table I) indicates that the phosphorus atom in $(\text{CH}_3)_3\text{PO}$ more closely resembles a neutral P than a P^+ . We conclude that the phosphorus atom in $(\text{CH}_3)_3\text{PO}$ is nearly neutral, and the PO bond is best described as a double bond.^{7,12}

Considerations of solvation and changes in hybridization at phosphorus reinforce this conclusion. (1)

(6) L. Pauling in "Symposium on Protein Structure," A. Neuberger, Ed., John Wiley and Sons, Inc., New York, N. Y., 1958.

(7) The conclusions in this paper are in agreement with some previous comments⁸ on P=O and S=O bonds but do not agree with the results of a recent paper⁹ on molecular orbital calculations on phosphoryl compounds. Our conclusion from experimental values should be more reliable. However, it may be useful to record S_{dpp} overlap integrals^{10,11} for P=O and S=O bonds: S_{dpp} (P=O, phosphine oxide) = 0.06; S_{dpp} (S=O, sulfoxide) = 0.06; S_{pdp} (S=O, sulfone) = 0.17. These values can be compared with S_{pp} (C=O, ketone) = 0.23. Overlap integrals using Slater orbitals are always approximate and are undoubtedly especially crude here because of the sensitivity of the integral to a small amount of positive charge on phosphorus or sulfur; e.g., S_{dpp} (P=O, phosphine oxide) = 0.11 if the P–O bond is one-fourth dipolar. Also, there is undoubtedly mixing of orbitals so that the phosphorus orbitals used in π -bonding will actually have some p-character.

(8) J. R. Van Wazer, *J. Am. Chem. Soc.*, **78**, 5709 (1956); D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel and L. E. Sutton, *J. Chem. Soc.*, 332 (1954).

(9) E. L. Wagner, *J. Am. Chem. Soc.*, **85**, 161 (1963).

(10) H. H. Jaffé, *J. Chem. Phys.*, **21**, 258 (1953); interpolation makes the S values quite approximate but the error is undoubtedly no worse than the errors in the approximate descriptions of the wave functions.

(11) R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 4493 (1950).

(12) A referee has objected to our reasoning on the basis of Juan and Gutowsky's theory¹³ that unshared electron pairs on an atom bonded to C has a large effect on the $\text{C}^{13}\text{-H}$ coupling constant. This argument was advanced to explain data such as the change in $\text{C}^{13}\text{-H}$ coupling constant from 126 c.p.s. in ethane to 151 c.p.s. in methyl iodide despite the similarity of the electronegativities of iodine and carbon. However, it appears to us that Muller and Pritchard⁴ had a more reasonable explanation for this data; they attributed the larger-than-expected $\text{C}^{13}\text{-H}$ coupling constant in methyl iodide to the longer bond length which would allow more s-character to be in the C–H bonds. Muller and Pritchard's explanation is substantiated by the nearly linear dependence of $\text{C}^{13}\text{-H}$ coupling constants on electronegativity within any one row of the periodic table.¹⁴ Therefore our reasoning should be valid since it only involves comparisons of closely related compounds. The data for amides also substantiate our arguments.

(13) C. Juan and H. Gutowsky, *J. Chem. Phys.*, **37**, 2203 (1962);

(14) D. Tyssee, unpublished results.

Solvation: since the phosphine oxide spectrum was run in D_2O , H-bonding would tend to enhance the contribution of the polar form I. (2) Hybridization: one would expect a change in the hybridization of the atomic orbitals of phosphorus in the CP bonds from very little s-character in $(\text{CH}_3)_3\text{P}^{15}$ to about 25% s in $(\text{CH}_3)_3\text{PO}$. This would cause a change in orbital electronegativity which should lead to an increase in the $\text{C}^{13}\text{-H}$ coupling constant for $(\text{CH}_3)_3\text{PO}$ compared to $(\text{CH}_3)_3\text{P}$; the change from 25% s, $(\text{CH}_3)_4\text{C}$, to about 33% s, $(\text{CH}_3)_2\text{C}=\text{CH}_2$, is accompanied by an increase of about 2 c.p.s. in the $\text{C}^{13}\text{-H}$ coupling constants for the methyl groups.⁵

Although analogous compounds of the second row are not available for comparison with dimethyl sulfoxide and dimethyl sulfone, the conclusion seems clear; SO bonds are best described as double bonds.^{7,12} The results clearly show that the electronegativity of the sulfur atom in sulfoxides and sulfones closely resembles that in sulfides and is quite different from sulfonium salts. The result for dimethyl sulfone in D_2O is especially convincing.

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(15) The C–P–C angles in trimethylphosphine are about 100°: H. D. Springall and L. O. Brockway, *J. Am. Chem. Soc.*, **60**, 996 (1938).

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Acidity of Hydrocarbons. XV. Relative Stabilities of Triphenylmethyl and Bridgehead Triptycyl Carbanions¹

Sir:

As part of our continuing study of base-catalyzed proton-exchange reactions between hydrocarbons and cyclohexylamine we have found that cesium cyclohexylamide (CsCHA) is some $10^3\text{--}10^4$ times more reactive than lithium cyclohexylamide (LiCHA). Despite this large difference in reactivity, relative rates of exchange of different hydrocarbons are closely similar with both catalysts; for example, tritium exchange rates relative to benzene-*t* are given as follows for LiCHA at 50° and CsCHA at 25°, respectively: cumene- α -*t*, 0.84, 1.34; 2-phenylbutane-2-*t*, 0.31, 0.39°; toluene-2-*t*, 0.12, 0.20; toluene-3-*t*, 0.54, 0.57; toluene-4-*t*, 0.46, 0.48.³ Note that both benzylic C–T and aromatic C–T bonds are being compared. With the CsCHA catalyst we are able to study C–T bonds that exchange with LiCHA at inconveniently slow rates.

(1) This work was supported in part by grants from the Petroleum Research Fund of the American Chemical Society and by the Air Force Office of Scientific Research. Paper XIV: A. Streitwieser, Jr., and C. Perrin, *J. Am. Chem. Soc.*, in press.

(2) 0.43 at 50°.

(3) The LiCHA rates are based largely on work of R. G. Lawler, to be published soon.

With CsCHA in cyclohexylamine we obtained the following rates relative to benzene-*t*: triptycene-1-*t*, 0.24 at 25°; cyclohexane-*t*, 1.1×10^{-8} at 50°. Triptycene-1-*t* was prepared from anthracene-9-*t* using the method of Friedman and Logullo.⁴ Cyclohexane was run with tritiated cyclohexylamine; the cyclohexane was isolated from each kinetic aliquot by g.c. and the radioactivity was obtained by liquid scintillation counting to give an initial rate constant for exchange. The bridgehead position of triptycene is clearly comparable in acidity to aromatic hydrogens and its acidity is much greater than that of saturated hydrocarbons.⁵ This enhanced acidity of triptycene can only be attributed to the inductive effect of the attached benzene rings since resonance conjugation with these rings is unlikely.

With LiCHA at 25° we find the following rates relative to toluene- α -*t*: diphenylmethane- α -*t*, 270; triphenylmethane- α -*t*, 1100.⁶ Since toluene- α -*t* is 106 times as reactive as benzene-*t* toward LiCHA,³ it follows that triphenylmethane- α -*t* is 1.1×10^{13} more reactive than cyclohexane-*t* but only 5×10^5 more reactive than triptycene. We conclude that more than half of the enhanced acidity of triphenylmethane over saturated hydrocarbons is due to the inductive effect of the three benzene rings and that less than half can be attributed to resonance stabilization of the carbanion. To the extent that relief of steric strain contributes to the acidity of triphenylmethane, the role of resonance is still less.

(4) L. Friedman and F. M. Logullo, *J. Am. Chem. Soc.*, **85**, 1549 (1963).

(5) This conclusion differs from that derived by E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Company, New York, N. Y., 1959, pp. 370-371, from the metalation experiments with 1-bromotriptycene of P. D. Bartlett and E. S. Lewis, *J. Am. Chem. Soc.*, **72**, 1005 (1950).

(6) The rate ratio, Ph₃CT:Ph₃CHT 4.1, is substantially smaller than the equilibrium constant difference toward CsCHA of about 40 (A. Streitwieser, Jr., and J. H. Hammons, to be published). The difference may be due to steric hindrance to exchange at the tertiary position. This difference will affect the argument to follow quantitatively but not qualitatively.

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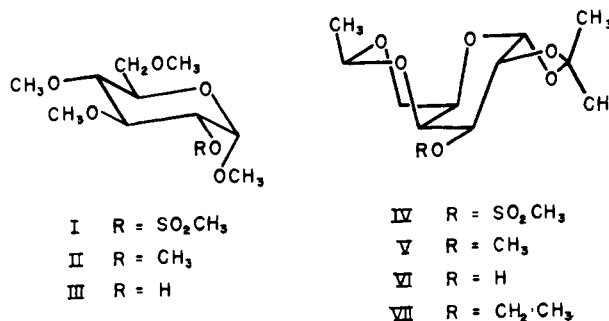
Unexpected Conversion of Carbohydrate Mesyl Esters to Ethers with Retention of Configuration by Reaction with Alkoxides in Dimethyl Sulfoxide

Sir:

Recent interest in the use of dipolar aprotic solvents in base-catalyzed reactions¹⁻³ and our current interest in sulfonyl esters of carbohydrates has led to a study of the reactions of the latter with bases in dimethyl sulfoxide (DMSO).

Treatment of methyl 2-*O*-mesyl-3,4,6-tri-*O*-methyl- α -D-glucoside (I) with sodium methoxide in anhydrous DMSO for 1 hr. at 70° gave a mixture of methyl 2,3,4,6-tetra-*O*-methyl- α -D-glucoside (II) and methyl 3,4,6-tri-*O*-methyl- α -D-glucoside (III) in approximately equal amounts. Under similar conditions, 4,6-*O*-ethylidene-1,2-*O*-isopropylidene-3-*O*-mesyl-D-galactose (IV)⁴ gave a mixture of 4,6-*O*-ethylidene-1,2-*O*-iso-

propylidene-3-*O*-methyl-D-galactose (V) and 4,6-*O*-ethylidene-1,2-*O*-isopropylidene-D-galactose (VI). When sodium ethoxide was used, VI and the corresponding 3-*O*-ethyl derivative (VII) were formed.



The reactions were followed by thin-layer chromatography on silica gel and the products were isolated by fractionation of the reaction mixtures on columns of silica gel. The products were characterized by comparison of melting point, infrared and n.m.r. spectra, and gas-liquid chromatography (g.l.c.) with authentic compounds. DMSO alone gave no reaction with either I or IV when maintained at above 100° for several hours.

When I was treated with sodium methoxide in dimethylformamide under similar conditions, a very slow reaction occurred and after 24 hr. I was still the major component of the mixture. Two other compounds present were tentatively identified (g.l.c.) as II and III.

Saponifications of "isolated" carbohydrate secondary sulfonate esters usually proceed with difficulty and by O-S cleavage to give the alcohol with retention of configuration (pp. 167-170 in ref. 5). The mechanism of such reactions is believed to occur by a nucleophilic displacement on sulfur in compounds whose stereochemistry makes attack on carbon unfavorable⁶; however, there appears to be no previous report of reaction of an "isolated" secondary sulfonate ester with alkoxide to give an ether with the original configuration. The slight possibility of neighboring group participation by a methoxyl group⁷ in I is excluded since no such possibility exists in IV.

To ascertain whether or not the C-O bond of the ester was broken, I was treated with ¹⁸O-labeled sodium methoxide under the conditions described above. The methyl tetra-*O*-methyl- α -D-glucopyranoside formed was isolated and its mass spectrum was compared with that of unlabeled II. The spectra were identical indicating that no ¹⁸O was incorporated and, therefore, that the C-O bond was not broken during the reaction.

Since the alkyl group, but not the ether oxygen, originates in the alkoxide ion, it seems that an initial nucleophilic attack by alkoxide on sulfur is followed by rearrangement of an intermediate complex. The most probable stereochemistry of such an intermediate appears to be that of a trigonal bipyramid resulting from sp³d-hybridization of the sulfur-bonding orbitals.⁸ In one such intermediate, as shown, an internal rearrangement between the entering and leaving groups is sterically feasible.

(1) C. H. Snyder and A. R. Soto, *J. Org. Chem.*, **29**, 742 (1964).

(2) F. C. Chang, *Tetrahedron Letters*, No. 6, 305 (1964).

(3) A. J. Parker, *Quart. Rev. (London)*, **16**, 163 (1962).

(4) D. H. Ball and J. K. N. Jones, to be published.

(5) R. S. Tipson, *Advan. Carbohydrate Chem.*, **8**, 107 (1953).

(6) C. A. Bunton and Y. F. Frei, *J. Chem. Soc.*, 1872 (1951).

(7) B. Capon, *Quart. Rev. (London)*, **18**, 45 (1964).

(8) G. Cilento, *Chem. Rev.*, **60**, 147 (1960).