

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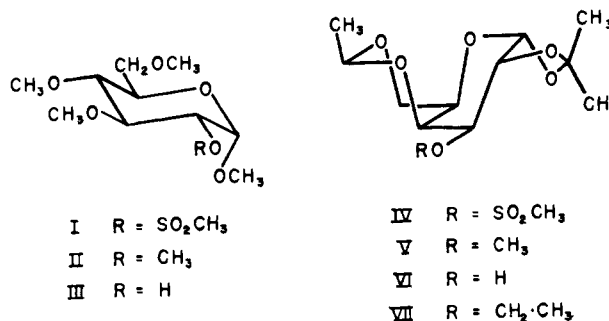
Unexpected Conversion of Carbohydrate Mesyl Esters to Ethers with Retention of Configuration by Reaction with Alkoxides in Dimethyl Sulfoxide

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).

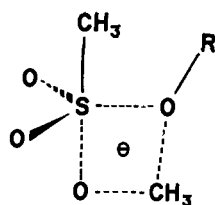
(4) D. H. Ball and J. K. N. Jones, to be published.

(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).



Although there is evidence to suggest that base-catalyzed hydrolysis of a sulfonate ester in water does not involve a true intermediate,^{9,10} it is possible that the high solvating power of dimethyl sulfoxide for large negatively charged species may stabilize an intermediate complex sufficiently to allow a rearrangement to occur. Alternatively, a two-step reaction within the solvent cage might be considered. This work is being extended to include other nucleophiles and other carbohydrate sulfonates and full details will be presented later.

The authors wish to thank M. L. Bazinet for the mass spectral measurements and F. H. Bissett for the n.m.r. spectra.

(9) M. L. Bender, *J. Am. Chem. Soc.*, **73**, 1626 (1951).

(10) D. R. Christman and S. Oae, *Chem. Ind.* (London), 1251 (1959).

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Reactions of 2-Nitrobenzhydrol, Including a Novel Aromatic Nucleophilic Displacement

Sir:

We wish to report two unusual reactions of 2-nitrobenzhydrol, one of which involves an exceptionally facile, high yield, nucleophilic displacement of a benzenoid hydrogen under acidic conditions.

When 2-nitrobenzhydrol was allowed to react with *p*-toluenesulfonyl chloride in pyridine overnight at 5°, a benzene-soluble solid was obtained in 78% yield. Crystallization from ethyl acetate gave a yellow solid (II), m.p. 128–130°, which has been shown to be 2-nitrosobenzophenone rather than the expected 2-nitrobenzhydrol *p*-toluenesulfonate (I).

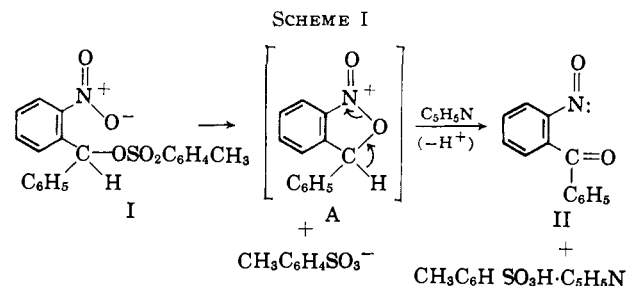
The structural assignment was based on elemental and spectral analyses¹ which indicated that dehydration rather than esterification of 2-nitrobenzhydrol had occurred. *Anal.* Calcd. for C₁₃H₉NO₂: C, 73.92; H, 4.30; N, 6.63; mol. wt. 211. Found: C, 74.06; H, 4.42; N, 6.54; mol. wt. 234 (freezing point in dioxane). Nuclear magnetic resonance spectra showed only a complex aromatic hydrogen multiplet in the region 400–450 c.p.s. (Varian A-60, CDCl₃, external TMS)¹; λ_{max}^{95% EtOH} mμ (ε): 246 (16,366), 278 (infl., 10,349), 307 (infl., 6929); ν_{max}^{KBr} cm.⁻¹: 1670 (vs) and 1482 (vw); ν_{max}^{CHCl₃} cm.⁻¹: 1665 (vs) and 1504 (s).

These data strongly suggested an aromatic ketone, and in fact the infrared spectrum of II was very similar to that of benzophenone, with the exception of a weak band in the solid state at 1482 cm.⁻¹ (KBr) which was

(1) We gratefully acknowledge the cooperation of the Analytical and Physical Chemistry sections in this study. Microanalyses were performed under the direction of Mr. K. D. Fleischer. Spectral data were determined by Dr. F. C. Nachod, Miss C. M. Martini, and Mr. Michael Priznar. Dr. R. K. Kullnig assisted in the interpretation of the n.m.r. data.

greatly intensified and shifted to 1504 cm.⁻¹ in chloroform solution, behavior characteristic of nitroso compounds.² These facts, coupled with the observation that II produces intensely green solutions in several organic solvents, led to the conclusion that II is 2-nitrosobenzophenone, which was confirmed by reduction of II by iron-acetic acid to the known 2-aminobenzophenone, m.p. 106.5–107.³

The formation of II may be assumed to occur *via* the intramolecular displacement of the *p*-toluenesulfonate anion by the nitro group of the presumed intermediate 2-nitrobenzhydrol *p*-toluenesulfonate (I), followed by base-catalyzed collapse of the resulting cation A to 2-nitrosobenzophenone,⁴ as depicted in Scheme I.



Puckowski and Ross⁵ have reported the formation of several 2-nitrobenzhydrol esters by the action of acid chlorides or anhydrides in pyridine,⁶ and have stated that both the alcohol and its esters are transformed into 1,2-di-*o*-nitrophenyl-1,2-diphenylethylene by formic acid.

Since the physical properties of II were similar to those reported for the product of the reaction of 2-nitrobenzhydrol with formic acid, this experiment was repeated according to the published procedure.⁵ The product was identical in every respect (melting point, mixture melting point, infrared, ultraviolet, and n.m.r. spectra) with the 2-nitrosobenzophenone described above. It was thus demonstrated that the substance formerly identified as 1,2-di-*o*-nitrophenyl-1,2-diphenylethylene⁵ is, in fact, 2-nitrosobenzophenone (II).

Attention was therefore directed toward the preparation of a 2-nitrobenzhydrol derivative having a group more difficult to displace than the tosylate anion. To this end, we chose to examine the reaction of 2-nitrobenzhydrol with excess thionyl chloride in refluxing chloroform. Instead of the expected 2-nitrobenzhydrol chloride there was obtained, after crystallization from hexane, a neutral yellow solid (III), m.p. 116–117°, which was clearly the result of both dehydration and chlorination of 2-nitrobenzhydrol. It has now been established that this product is 5-chloro-3-phenyl-2,1-benzisoxazole. *Anal.* Calcd. for C₁₃H₈ClNO: C, 67.98; H, 3.51; Cl, 15.44; N, 6.10. Found: C, 68.04; H, 3.53; Cl, 15.56; N, 5.52. The nuclear magnetic

(2) (a) A. W. Luttko, *Z. Elektrochem.*, **61**, 302 (1957); (b) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 305.

(3) H. H. Szant and C. M. Harmuth, *J. Am. Chem. Soc.*, **81**, 962 (1959).

(4) 2-Nitrosophenyl ketones and aldehydes have been suggested as unstable intermediates in the irradiation-induced decomposition of 2-nitrobenzyl alcohols. The present case appears to be the first direct evidence that such transformation can occur. See F. Sachs and S. Hilpert, *Ber.*, **37**, 3425 (1904), and also W. Reid and M. Wilk, *Ann.*, **590**, 115 (1954).

(5) R. T. Puckowski and W. A. Ross, *J. Chem. Soc.*, 3555 (1959).

(6) H. M. Hoffman, *Chem. Ind.* (London), 336 (1963), has described an elegant procedure for preparing benzhydrol *p*-toluenesulfonates under neutral conditions.