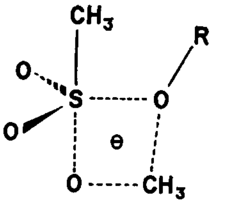

Although there is evidence to suggest that base-catalyzed hydrolysis of a sulfonate ester in water does not involve a true intermediate,[9,10] it is possible that the high solvating power of dimethyl sulfoxide for large negatively charged species may stabilize an intermediate complex sufficiently to 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.

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[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.

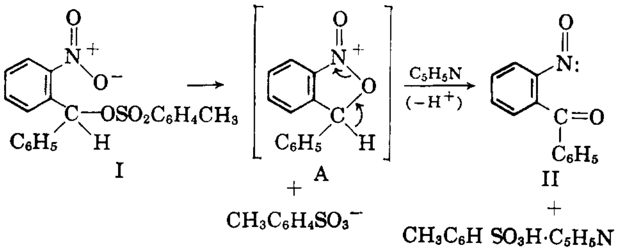
When 2-nitrobenzhydrol was allowed to react with *p*-toluenesulfonyl chloride in pyridine overnight at 5°, a benzene-soluble solid was obtained in 78% yield. Crystallization from ethyl acetate gave a yellow solid (II), m.p. 128–130°, which has been shown to be 2-nitrosobenzophenone rather than the expected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

The structural assignment was based on elemental and spectral analyses[1] which indicated that dehydration rather than esterification of 2-nitrobenzhydrol had occurred. *Anal.* Calcd. for $C_{13}H_9NO_2$: 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, $CDCl_3$, external TMS)[1]; $\lambda_{max}^{95\%\ EtOH}$ mμ (ϵ): 246 (16,366), 278 (infl., 10,349), 307 (infl., 6929); ν_{max}^{KBr} cm.$^{-1}$: 1670 (vs) and 1482 (vw); $\nu_{max}^{CHCl_3}$ 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 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-nitrobenzhydryl *p*-toluenesulfonate (I), followed by base-catalyzed collapse of the resulting cation A to 2-nitrosobenzophenone,[4] as depicted in Scheme I.

SCHEME I



Puckowski and Ross[5] have reported the formation of several 2-nitrobenzhydryl 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-diphenylethylene[5] is, in fact, 2-nitrosobenzophenone (II).

Attention was therefore directed toward the preparation of a 2-nitrobenzhydryl 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-nitrobenzhydryl 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 $C_{13}H_8ClNO$: 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

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[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.

[2] (a) A. W. Luttke, *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. Szmant 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).

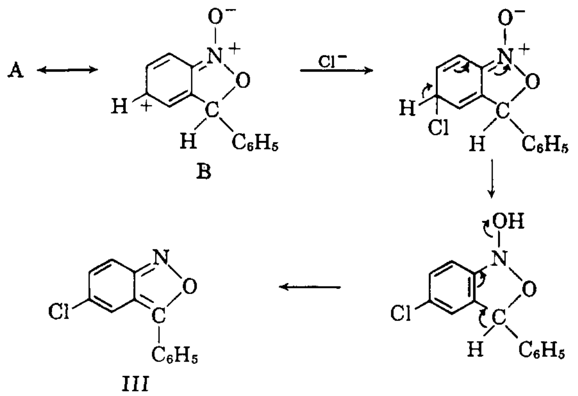
[5] R. T. Puckowski and W. A. Ross, *J. Chem. Soc.*, 3555 (1959).

[6] H. M. Hoffman, *Chem. Ind.* (London), 336 (1963), has described an elegant procedure for preparing benzhydryl *p*-toluenesulfonates under *neutral* condi tions.

resonance spectrum showed only a complex aromatic hydrogen multiplet in the region 450–520 c.p.s. ($CDCl_3$, external TMS); $\lambda_{max}^{95\%\ EtOH}$ mμ (ϵ): 213 (25,451), 217 (infl., 24,279), 248 (14,159), 257 (16,603), and 352 (15,350); ν_{max}^{KBr} cm.$^{-1}$: 1626 (s), 1542 (s), 1482 (s), 1055 (s), 930 (s), 810 (vs), 762, 733 (vs), 732, 738 (vs), 680 (vs), and 664 (s).

These data clearly indicated a highly conjugated aromatic structure quite unlike the benzophenone previously obtained. The following mechanistic consideration then led to the postulate that this product was 5-chloro-3-phenyl-2,1-benzisoxazole (III). An initially formed chlorosulfite ester was envisaged as cyclizing to the previously proposed intermediate ion A, which is resonance-stabilized by forms like B. In the absence of pyridine (see above), proton abstraction is suppressed and nucleophilic attack by chloride ion on the cyclic cation B supravenes, followed by rearomatization and dehydration to give III, as depicted in Scheme II.

SCHEME II



An authentic specimen of 5-chloro-3-phenyl-2,1-benzisoxazole was therefore prepared from *p*-chloronitrobenzene and phenylacetonitrile,[7] and unequivocally identified with that produced from the interaction of thionyl chloride and 2-nitrobenzhydrol by mixture melting point and infrared, ultraviolet, and n.m.r. spectral determinations.

In our opinion, the formation of 5-chloro-3-phenyl-2,1-benzisoxazole by the action of thionyl chloride on 2-nitrobenzhydrol under acidic conditions represents one of the most facile displacements of a benzenoid hydrogen by a weak nucleophile that has yet been reported.

(7) R. B. Davis and L. C. Pizzini, *J. Org. Chem.*, **25**, 1884 (1960).

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Phenylation with Nitrosoacetanilides[1]

Sir:

Phenylation of aromatic hydrocarbons with nitrosoacetanilides has long aroused mechanistic interest because it leads to biaryls in good yields[2,3] and yet the "acetoxy radicals" which one might expect to be formed in the decomposition of the initially formed[4] diazonium acetate surprisingly do not lead to[5] carbon dioxide and methyl radicals. Instead, the acetoxy moiety ends up as acetic acid (possibly *via* acetate anions).

In a previous publication[3] we had, on the basis of circumstantial evidence, ascribed the apparent difference in behavior between benzoyl peroxide as an arylating agent on one hand and nitrosoacetanilide (NAA) and phenylazotriphenylmethane (PAT) on the other (particularly with respect to the absence of dihydrobiphenyl formation from the latter two reagents) to the operation of a cage effect in the case of NAA and PAT. In the meantime, however, it has been amply shown[6–8] that no cage effect is operative in the case of PAT but that the lack of dimerization and disproportionation of the phenylcyclohexadienyl radicals (from addition of phenyl radicals to benzene) in this case is due to the high stationary state concentration of triphenylmethyl radicals concomitantly formed in the primary act of decomposition; these radicals then abstract hydrogen from phenylcyclohexadienyl radicals or combine with them with great efficiency to give biphenyl and triphenylmethane or 3-phenyl-6-triphenylmethyl-1,4-cyclohexadiene.[6] Not enough phenylcyclohexadienyl radicals build up to disproportionate (to dihydrobiphenyl) or dimerize (to tetrahydroquaterphenyl) by reactions second-order in these radicals.

In view of recent indications[9,10] that the NAA reaction also does not involve a cage effect, we wish to record our own experimental observations, though incomplete, which strongly point in the same direction, *i.e.*, militate against a cage effect with NAA.

The essential experimental data are shown in Table I. Nitrosoacetanilide was decomposed in aromatic solvents at room temperature in the presence of iodine in low concentrations (0.02–0.05 *M*). Under these conditions it is unlikely that iodine can compete efficiently with a reaction of NAA occurring in a benzene cage to give biphenyl, nitrogen, and acetic acid. Yet, Table I shows that 80–85% of the NAA was converted to iodobenzene.[11] In view of the fact[3,4] confirmed in the present study (see Table I) that the yield of biaryl from NAA is in the 80–90% region, one may calculate that 90–100% of the phenyl radicals from NAA are scavenged by iodine in low concentration. This almost certainly indicates that the phenyl radicals formed from NAA are free and not caged, although there is a possible complication in the hard-to-ascertain possibility that NAA complexes with iodine prior to decomposition.

Unfortunately, though our results are incompatible with the previously proposed[3,12] cage mechanism for

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(1) Research was carried out in the Radiation Laboratory, operated under contract with the Atomic Energy Commission. This is AEC Document No. COO-38-359.

(2) E. C. Butterworth and D. H. Hey, *J. Chem. Soc.*, 116 (1938).

(3) E. L. Eliel, M. Eberhardt, O. Simamura, and S. Meyerson, *Tetrahedron Letters*, 749 (1962).

(4) R. Huisgen and L. Krause, *Ann.*, **574**, 157, 171 (1951).

(5) Such decomposition normally occurs rapidly [L. Jaffe, E. J. Prosen, and M. Szwarc, *J. Chem. Phys.*, **27**, 416 (1957)] and, in the decomposition of acetyl peroxide, may be concerted [M. J. Goldstein, *Tetrahedron Letters*, 1601 (1964)]. The pertinent studies refer to temperatures above 80° considerably higher than that (*ca.* 25°) in the present work.

(6) D. Hey, M. J. Perkins, and G. H. Williams, *Tetrahedron Letters*, 445 (1963).

(7) J. F. Garst and R. S. Cole, *ibid.*, 679 (1963).

(8) G. A. Russell and R. F. Bridger, *ibid.*, 737 (1963).

(9) D. B. Denney, N. E. Gershman, and A. Appelbaum, *J. Am. Chem. Soc.*, **86**, 3180 (1964).

(10) C. Dickermann, private communication.

(11) Excluding runs 3, 7, and 12 where an insufficient amount of iodine was employed; see below.

(12) R. Huisgen and G. Horeld, *Ann.*, **562**, 137 (1949).