[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Derivatives of Sulfenic Acids. XXII. Studies of Sulfenate Esters (Thioperoxides).[1] Part 2

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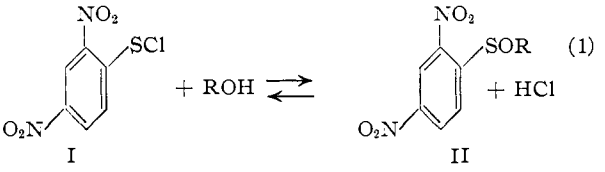
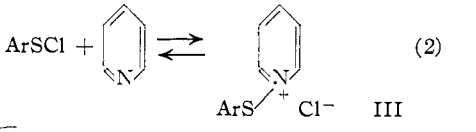
The comparative rates of reaction 1, $ArSCl + CH_3OH \rightleftarrows ArSOCH_3 + HCl$, Ar = 2,4-dinitrophenyl, with and without pyridine present, as well as with the highly hindered amine, N,N-dimethylmesidine, suggest that the powerful catalytic effect of pyridine on reaction 1 involves an intermediate such as 2,4-dinitrobenzenesulfenylpyridinium chloride, $ArSNC_5H_5^+Cl^-$. The attainment of equilibrium 1, in ethylene chloride as solvent, is measurably slow and favors the reactants ($K_{28°} \sim 10^{-3}$). An infrared technique was used to follow the kinetics. Other tertiary amines, as triethylamine, quinoline and acridine, also catalyze reaction 1. An attempt to isolate the presumed intermediate in the case of pyridine was not, however, successful. To evaluate the utility of 2,4-dinitrobenzenesulfenyl chloride for characterizing more complex alcohols, the reactions with ethylene glycol, pinacol, allyl alcohol, cinnamyl alcohol, benzhydrol, triphenylcarbinol, 2-methyl-3-butyne-2-ol and propargyl alcohol were studied. Several new examples of 2,4-dinitrobenzenesulfenate esters are reported and the complexities encountered with various of the above alcohols are illustrated and interpreted.

The pyridine-catalyzed reaction between 2,4-dinitrobenzenesulfenyl chloride (I) and alcohols was previously described as a method of characterizing primary, secondary and tertiary alcohols.[3] The purpose of the present study was to clarify the role of pyridine in this reaction (equation 1) and to examine the reactions of I with more complex alcohols, such as diols, unsaturated alcohols and polyarylcarbinols.[4]



(1)

The function of pyridine in reaction 1 might be simply to neutralize the hydrogen chloride, thereby driving the reaction to completion. In view, however, of the analogies between acyl halides and sulfenyl halides, and since the former are known[5,6] to form acylpyridinium halides which play an important role in the pyridine-catalyzed reactions with alcohols, the formation of an ionic intermediate like III (Ar = 2,4-dinitrophenyl) was suspected in reaction 1.



(2)

The isolation of III and a study of its properties would, of course, be the obvious way to demonstrate its role in reaction 1. Attempts to show that it was present in macroscopic amounts were not, however, successful. The reaction of I with excess pyridine, in ethylene chloride as solvent,[7] gave only unreacted I plus a small amount of disulfide IV, whose formation almost certainly involved the pyridine-catalyzed hydrolysis of I by traces of moisture incurred in carrying out the experiment—since it is known[8] that IV is the major product in the hydrolysis of I and that pyridine strongly catalyzes the hydrolysis.

Our failure to isolate IV recalled the interesting studies of Gold and co-workers,[9] who investigated tertiary amines as catalysts in the hydrolysis of acetic anhydride. In the latter study, using pyridine, the kinetic results were reasonably explained by postulating the intermediate acylpyridinium acetate, $[CH_3CONC_5H_5]^+OAc^-$, but the physical data (spectra, freezing points and conductivities) showed that the pyridinium acetate was not present in amounts detectable by the above methods. These studies also revealed that amines like 2,6-dimethylpyridine were less effective catalysts in the hydrolysis, a result which was ascribed to the steric effects of the *o*-methyl groups in retarding formation of the intermediate pyridinium salt. A similar approach was therefore devised in the present study, using reaction 1-A as a test case, and following the methanolysis of I by an infrared technique. Thus: (a) The uncatalyzed reaction of I with excess methanol (in a solution where compound I was about 0.02 *M* and methanol about 0.12 *M* at the start of the reaction) required about 20 minutes to attain equilibrium, and the value of *K* ($\sim 5 \times 10^{-3}$ at 28°) showed that the equilibrium was in favor of the reactants (*ca.* 20% completion). (b) Adding 1.3 equivalents of pyridine per mole of I, under the same conditions as in (a), caused immedi-

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(2) Stanford Research Institute, Menlo Park, Calif.

(3) N. Kharasch, D. P. McQuarrie and C. M. Buess, THIS JOURNAL, **75**, 2658 (1953).

(4) In the later discussion, the methyl ester (II, R = CH_3) is designated as II-A, and the equation for its formation is referred to as equation 1-A. The reversibility of the reaction in the case of R = methyl was independently demonstrated by formation of I, from II and dry hydrogen chloride, in presence of methanol, in ethylene chloride solution. The conversion of other alkyl arenesuifenates to the sulfenyl chlorides, by treatment with hydrochloric acid, has been reported by other workers; *cf.* N. Kharasch, S. J. Potempa and H. L. Wehrmeister, *Chem. Revs.*, **39**, 326 (1946).

(5) *Cf.* W. R. Gilkerson, W. J. Argersinger and W. E. McEwen, THIS JOURNAL, **76**, 41 (1954).

(6) H. Adkins and Q. Thompson, *ibid.*, **71**, 2242 (1949), as well as references cited therein.

(7) This is the solvent generally used in the pyridine-catalyzed reaction 1. Analogous instances, where complexes between active chlorine compounds and *t*-amines may have been anticipated but were not found, were reported recently by Ziffert, Coulter and Macy, THIS JOURNAL, **75**, 751 (1953), for $POCl_3$ and pyridine; and by Hawthorne and Cram, *ibid.*, **76**, 3452 (1954), for triphenylmethyl chloride and triethylamine.

(8) N. Kharasch, W. King and T. C. Bruice, *ibid.*, **77**, 931 (1955).

(9) S. L. Bafna and V. Gold, *J. Chem. Soc.*, 1406 (1953); V. Gold and E. Jefferson, *ibid.*, 1409 (1953).

ate completion of the reaction.[10] (c) Reaction 1-A was also studied under the same conditions as in (a) above, but with N,N-dimethylmesidine (V) present, and was now found to proceed to completion, but measurably slowly, first order with respect to I, and at a rate dependent on the concentration of V. Product studies of reaction 1-A, using either pyridine or V, gave identical yields of II-A, showing that V does not react by any irreversible process (*e.g.*, nuclear substitution) with I. The results of the rate studies are shown in Figs. 1 and 2.

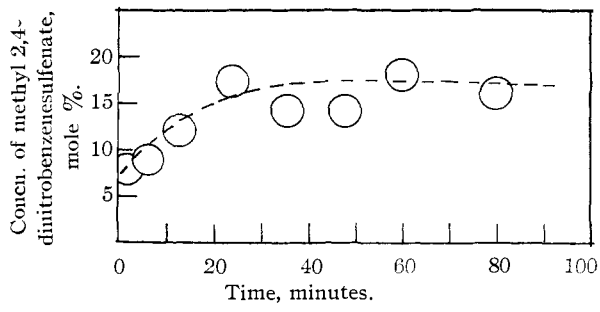


Fig. 1.—Approach to equilibrium in the reaction of 2,4-dinitrobenzenesulfenyl chloride and methanol (equation 1-A) in ethylene chloride solution at 28°; *cf.* experimental part for starting concentrations and other data.

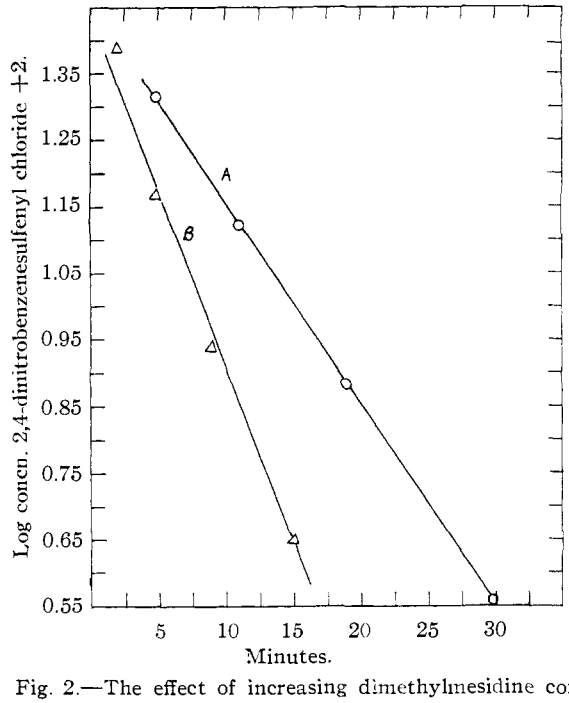


Fig. 2.—The effect of increasing dimethylmesidine concentration on the rate of the reaction of 2,4-dinitrobenzenesulfenyl chloride (I) with methanol, in ethylene chloride solution, at 28°. The faster rate (curve B) represents the higher concentration of mesidine in the two comparable runs; see experimental part for starting concentrations.

The above experiments do not, of course, constitute a full kinetic study of reaction 1-A, but the only explanation which seems logical is that III (or an equivalent pyridine-I complex) is involved in the pyridine-catalyzed reaction of I with methanol. The same type of explanation must also apply to reactions like 1 in which other sulfenyl halides or other tertiary amines are involved (see below).

The choice of N,N-dimethylmesidine as the hindered amine for the above study was made because (1) its base strength (pK_a 5.15)[11] is somewhat greater than is that of pyridine (pK_a 4.38),[12] so that the mesidine should be at least equal to pyridine in its ability to shift equilibrium 1-A; and (2) the mesidine V is strongly hindered to attack at the nitrogen, as shown by its failure to form a quaternary salt with methyl iodide even at 150°,[13] and by its dipole moment.[14] It therefore seems quite certain that V affects the rate of reaction 1-A mainly by retarding the reverse reaction (neutralization of hydrogen chloride), while pyridine has an added effect by forming a complex as III. Other tertiary amines, such as triethylamine, quinoline and acridine (pK_a 4.54)[15] were found to be, qualitatively, as effective as pyridine, suggesting that the reaction is not very sensitive to structural variations in the tertiary amine, unless approach to the nitrogen atom is strongly hindered.

In previous studies involving I, its rate of disappearance was followed by the reaction: $2ArSCl + 2I^- \rightleftarrows ArSSAr + I_2 + 2Cl^-$.[16] This method was considered impractical for the present study because the esters II (R = methyl and ethyl) may compete with the sulfenyl chloride in releasing iodine, as shown by their ability to do so when treated with a solution of sodium iodide in dry acetic acid.[17] An infrared technique (*cf.* Experimental), using an absorption band at 14.25 μ, for II-A, was therefore developed to follow the kinetics. Reaction 1-A was quenched by adding excess cyclohexene, which reacts rapidly and quantitatively[18] to give the 1:1 adduct of J and the olefin VI.[19]

To evaluate reaction 1 more fully as a method for characterizing alcohols, the reactions of I with the alcohols of Table I were studied. The new sulfenate esters obtained are summarized in the table and attendant footnotes, and the results are discussed below. Although it is not reported in this paper, further work in this Laboratory has shown that the use of the pyridine-catalyzed reaction 1 may be extended to other sulfenyl halides, including 2,4-dinitrobezenesulfenyl bromide-, 2-nitro-4-chlorobenzenesulfenyl chloride and 2-nitrobenzenesulfenyl chloride.

Benzyl alcohol had been shown to give high yields of II (R = $C_6H_5CH_2$–), and only traces of the disulfide IV using the pyridine-catalyzed reaction 1. This work was confirmed in the present study, and α-methylbenzyl alcohol reacted similarly. Diphenylmethyl alcohol (benzhydrol), how-

(10) The infrared trace of the reaction mixture two minutes after mixing showed no I and all IIA (*cf.* Experimental).

(11) W. C. Davies and H. W. Addis, *J. Chem. Soc.*, 1622 (1937).
(12) H. C. Brown and B. Kanner, THIS JOURNAL, **75**, 3865 (1953).
(13) A. W. Hofmann, *Ber.*, **5**, 718 (1872).
(14) C. E. Ingham and G. C. Hampson, *J. Chem. Soc.*, 981 (1939).
(15) A. Albert and R. Goldacre, *ibid.*, 454 (1943).
(16) W. L. Orr and N. Kharasch, THIS JOURNAL, **75**, 6030 (1953); N. Kharasch and M. M. Wald, *Anal. Chem.*, **27**, 996 (1955).
(17) J. A. Barltrop, P. M. Hayes and M. Calvin, THIS JOURNAL, **76**, 4358 (1954), commented on the rapid release of iodine, from aqueous hydriodic acid, by $(CH_3)_3C-S-OC_2H_5$.
(18) D. R. Hogg and N. Kharasch, THIS JOURNAL, in press.
(19) N. Kharasch and C. M. Buess, *ibid.*, **71**, 2724 (1949).

TABLE I

NEW SULFENATE ESTERS (THIOPEROXIDES) OBTAINED WITH 2,4-DINITROBENZENESULFENYL CHLORIDE

Alcohol	Type of product (Ar = 2,4-dinitrophenyl)	Yield, %	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Allyl	Ester, ArSOR[e]	14							
	$C_9H_8N_2O_5S$		86–87	42.18	42.28	3.15	3.28	10.94	11.16
Cinnamyl	Ester	35[f]							
	$C_{15}H_{12}N_2O_5S$		120–123 dec.[a]	54.21	54.41	3.71	3.79	8.43	8.14
Ethylene glycol	Monoester	75[g]							
	$C_8H_6N_2O_6S$		113.5–114	36.92	36.77	3.10	3.18	10.77	10.85
Ethylene glycol	Diester	91							
	$C_{14}H_{10}N_4O_{10}S_2$		170–171.5 dec.	36.68	36.71	2.20	2.20	12.22	11.92
Pinacol	Diester[d]	33[h]							
	$C_{18}H_{18}N_4O_{10}S_2$		133.5–135 dec.	42.02	42.50[d]	3.76	3.53	10.89	10.67
α-Phenylethanol	Ester	93							
	$C_{14}H_{12}N_2O_5S$		92–93[b]	52.49	52.59	3.78	3.77	8.75	8.94
2-Methyl-3-butyn-2-ol[i]	Ester	*ca.* 80							
	$C_{11}H_{10}N_2O_5S$		96–97	46.80	47.10	3.57	3.85	9.93	10.15
Benzhydrol	Ester	29[j]							
	$C_{19}H_{14}N_2O_5S$		113 dec.[c]	59.68	60.31 60.57	3.69	4.21 3.97	7.33	7.00
Triphenylcarbinol	……[k]								

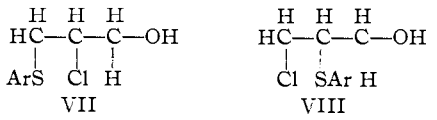
[a] This melting point depends considerably on the rate of heating and temperature of introduction of the sample. [b] The melting point of once-recrystallized sample was 95–96°; further recrystallizations lowered the melting point. [c] This compound melts indefinitely and the melting point drops sharply on recrystallization. The poor analytical figures undoubtedly reflect its instability. [d] *Anal.* Calcd.: S, 12.46; N, 10.89. Found: S, 12.60; N, 10.67. [e] The other product was a viscous yellow oil (44%) whose analysis corresponded to a mixture of VII and VIII. *Anal.* Calcd. for $C_9N_9N_2O_5SCl$: C, 36.93; H, 3.10; N, 9.57; Cl, 12.11. Found: C, 37.11; H, 2.97; N, 9.79; Cl, 12.02. [f] A dark brown, amorphous residue was obtained in this reaction if pyridine was absent. The yield of this, calculated for the 1:1 adduct, was quantitative. *Anal.* Calcd. for the 1:1 adduct of cinnamyl alcohol and I, $C_{15}H_{13}N_2O_5SCl$: C, 48.85; H, 3.55; N, 7.59. Found: C, 48.52; H, 3.84; N, 7.39. [g] The diester, $C_{14}H_{10}N_4O_{10}S_2$ (20% yield), dec. 170–171.5°, was also found. [h] The disulfide IV, in 33% yield, was also found. [i] Kindly supplied by Air Reduction Corporation. Propargyl alcohol (gift of General Aniline and Film Corporation) failed to give any ester; *cf.* discussion. With 2-methyl-3-butyn-2-ol, two crystalline forms of the ester were noted when the crude product (melting partially at 87°, but mainly at 93–97°) was recrystallized from ligroin (b.p. 63–69°): needles, m.p. 87.5–89.5°, and more massive crystals, m.p. 96.2–98°. Both crystal forms are interlocked in the product and difficult to separate. The analysis recorded in the table was made on a crystal melting at 96–97°. A sample which showed melting at 87.5–89.5° and 95.5–97.5° (mixture of both forms) gave: C, 47.90; H, 3.83; N, 10.27. [j] Disulfide IV (39%) and some crude pyridinium 2,4-dinitrobenzenesulfonate also were found. The sulfonic acid no doubt arises by hydrolysis of I, as found by N. Kharasch, W. King and T. C. Bruice, THIS JOURNAL, **77**, 931 (1955); *cf.* also ref. 30. [k] No ester could be obtained. Products included: crude triphenylmethyl chloride (trace); pyridinium 2,4-dinitrobenzenesulfonate (m.p. 196–199°), after recrystallization from ethylene chloride, and not depressing the m.p. of the salt prepared from the sulfonic acid (obtained by oxidizing I with nitric acid) and pyridine. *Cf.* also footnote above. *Anal.* Calcd. for pyridinium 2,4-dinitrobenzenesulfonate, $C_{11}H_9N_3O_7S$: C, 40.37; H, 2.77; N, 12.87; S, 9.82. Found: C, 40.51; H, 2.83; N, 12.82; S, 8.97. Unchanged triphenylcarbinol (m.p. 159–162°) also was found in considerable amount (*cf.* Discussion).

ever, reacted very rapidly with I with excess pyridine present (as evidenced by an immediate, negative test for I with starch–iodide solution)[16,3] but only a 29% yield of II (R = $(C_6H_5)_2CH$–) was isolated, together with 39% of IV. The latter precipitated from the reaction mixture a few minutes after mixing of the reagents, and even though only a slight molar excess of the benzhydrol was used, much of this was recovered unchanged. Reaction of triphenylcarbinol and I, in the presence of excess pyridine, similarly gave rapid precipitation of IV (76.8% isolated yield, based on I), and in this case none of the sulfenate ester [II, R = $(C_6H_5)_3C$–] was detected. Much of the triphenylcarbinol was recovered as such (nearly equivalent amounts of the carbinol and I had been used), and a trace of triphenylmethyl chloride as well as an appreciable amount of pyridinium 2,4-dinitrobenzenesulfonate was isolated. Neither benzhydrol nor triphenylcarbinol gave evidence of reaction with I in the absence of pyridine; but benzyl alcohol and I reacted very slowly (potassium iodide–starch test used as indication of extent of reaction) to deposit an amorphous precipitate, whose analysis was approximately correct for IV, but which had a different physical nature from the well-known, authentic IV. The presence of a small amount of benzaldehyde in the reaction mixture of I and benzyl alcohol was demonstrated by isolating its 2,4-dinitrophenylhydrazone, and the aldehyde was shown not to be an artifact by a control run in which compound (I) was omitted. The properties of the above, possibly polymeric product encountered in this reaction were not investigated further.[20]

The reactions of I with allyl alcohol, cinnamyl alcohol and 2-methyl-3-butyn-2-ol were studied to observe the complications which may arise in reaction 1 when double or triple bonds are present in the alcohol. Allyl alcohol, with pyridine absent, gave the theoretical yield of a highly viscous liquid, whose analysis agreed for the 1:1 adduct. However, attempts to obtain this product in crystalline form by chromatographic separation, or to convert it to a solid derivative were not successful, suggesting that it is probably a mixture of the isomers VII and VIII (Ar = 2,4-dinitrophenyl).

The product from cinnamyl alcohol was also a viscous liquid, whose analysis agreed for a mixture

(20) Major amounts of benzaldehyde and IV (and none of the benzyl ester) were found in the similar reaction of benzyl alcohol with 2,4-dinitrobenzenesulfenyl bromide; L. Goodman and N. Kharasch, unpublished work.



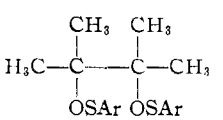
VII VIII

of the isomeric adducts to the olefin bond, but which could not be separated into two components.[21]

The reactions with allyl and cinnamyl alcohols were measurably slow at room temperature (starch–iodide test for I), and complete addition of I to cinnamyl alcohol required a significantly longer time than to allyl alcohol. When excess pyridine was present, however, the starch–iodide test was immediately negative in both cases. From allyl alcohol, there was isolated 14.1% of II (R = H_2C=CH—CH_2—), 44.5% of VII or VIII (or a mixture of these) and 21.2% of disulfide III. With cinnamyl alcohol, the yields were 34.8% of II (R = C_6H_5CH=CH-CH_2—), 24.4% of the product corresponding to 1:1 addition at the olefin bond (analogous to VII or VIII) and 28.1% of IV. The rapidity of the reaction and the relatively high yield of the olefin adduct suggest that pyridine catalyzes the addition of I to the double bond, as would be expected if the pyridinium salt(III) can react rapidly with either of the basic positions in these alcohols, *i.e.*, with the hydroxyl group or with the olefin bond.

2-Methyl-3-butyn-2-ol and I, with excess pyridine present, gave a stable, crystalline ester (II, R = HC≡C—C—$(CH_3)_2$). In contrast, attempts to obtain a similar product from propargyl alcohol failed, although compound I was completely used up, as shown by a negative starch–iodide test. The products were oils; and because they darkened on heating and quickly turned to tars on standing at room temperature, analyses were not performed on them. Since both of the above alcohols contain terminal triple bonds, the above differences in behavior cannot be ascribed to such a gross structural variation. The presence of the *gem*-methyl groups must therefore be associated, in some manner, with the greater stability of the product from 2-methyl-3-butyn-2-ol.

Two glycols, pinacol and ethylene glycol, were subjected to the reaction with I, in the presence of pyridine. When the molar ratio of I to ethylene glycol was 2:1, the diester ArS–OCH_2–CH_2–OSAr (Ar = 2,4-dinitrophenyl) resulted in high yield, while with a large excess of glycol 75% of the monoester (II, R = –CH_2CH_2OH) and 21% of the diester were obtained. Pinacol and compound I (in 1:2 molar ratio) yielded 33% of diester (IX, Ar = 2,4-dinitrophenyl) and 36% of IV. The use of a large excess of pinacol gave 55% of IV, and a viscous, unidentified oil which contained about 8% of chlorine. None of the monoester could be isolated and the above oil appeared to be a mixture, for its analysis did not correspond to any reasonable structure.



IX

(21) The formation of isomeric adducts of I to unsymmetrical olefins, *e.g.*, propylene, has been observed previously: N. Kharasch and C. M. Buess, THIS JOURNAL, **71**, 2724 (1949).

Carefully dried triphenylcarbinol, allyl alcohol, cinnamyl alcohol, pinacol, benzhydrol, as well as *t*-butyl alcohol—when treated with I, in the presence of pyridine—all give relatively high yields of disulfide (compared to the simple primary and secondary alcohols). Since all of these alcohols are of the type which react readily with hydrogen chloride to form water, it seems likely that the higher yields of disulfide IV in these cases are caused by competitive interaction of I with water. This suggestion appears reasonable, since pyridine strongly catalyzes the reaction of I with water, and IV (formed presumably *via* the intermediate sulfenic acid, ArSOH) is a major product of this hydrolysis.[22] The hydrogen chloride required for forming the water is,

$$ROH + Py\cdot HCl \rightleftharpoons HOH + [R^+] + Cl^- + Py \quad (3)$$

of course, available from reaction 1. The equilibrium involved is shown in equation 3 (Py = pyridine). That water is involved in the formation of IV is also supported by the isolation of pyridinium 2,4-dinitrobenzenesulfonate, in the reaction of I with triphenylcarbinol (see above)—for 2,4-dinitrobenzenesulfonic acid is known to be a product in the hydrolysis of I.[22]

As might be expected from the above discussion, it was found that selected examples of II were stable to pyridine alone in dry ethylene chloride (the solvent used for reaction 1) but that addition of pyridine hydrochloride caused slow decomposition. For example, with the cinnamyl ester of I, addition of pyridine hydrochloride to an ethylene chloride solution gave 70% of disulfide IV and the presence of cinnamyl alcohol was detected by isolating its α-naphthylurethan. Similarly, with the allyl ester of I, 60% of IV was formed and, while the decomposition of the methyl ester (II-A) required a much longer time, it eventually gave 69% of IV. In the latter case, there was also found some *m*-dinitrobenzene—a product which may be expected, since it was also found[22] in the hydrolysis of I. These decompositions of the sulfenate esters must involve reversal of reaction 1 and subsequent hydrolysis of the sulfenyl chloride. The required water could arise from the reaction of the alcohol (formed in the reversal of reaction 1) and hydrogen chloride.[23]

Acknowledgment.—The assistance of Mr. Arthur Seibel in carrying out the infrared analyses is gratefully acknowledged. The microanalyses were made by Mr. W. J. Schenck.

Experimental[24]

N,N-Dimethylmesidine (V) was obtained *via* nitromesitylene,[25] reduction of this to aminomesitylene, employing hydrazine–Raney nickel in the procedure described by Balcom and Furst,[26] and methylation of the latter by the procedure

(22) N. Kharasch, W. King and T. C. Bruice, *ibid.*, **77**, 931 (1955).

(23) Although considerable precautions were taken to exclude atmospheric moisture in the above experiments, it may be that a small proportion of the effects ascribed to hydrolysis were caused by traces of water occluded from the atmosphere.

(24) Melting and boiling points are not corrected. Pure, dry reagents, obtained by standard procedures or as recorded in earlier papers of this series, were used throughout. Pyridine was distilled from barium oxide and stored over calcium hydride.

(25) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 449.

(26) D. Balcom and A. Furst, THIS JOURNAL, **75**, 4331 (1953).

of Emerson, *et al.*[27] The product boiling at 74–75° at 5 mm. ($n^{21}D$ 1.5110) was redistilled at atmospheric pressure (b.p. 213–215°). Sixty grams of mesitylene gave 38 g. of final product.

Anal. Calcd. for $C_{11}H_{17}N$: C, 80.92; H, 10.50; N, 8.58. Found: C, 80.35; H, 10.37; N, 8.20.

Rates of Reactions of I with Methanol.—Attempts to follow the rate of methanolysis of I in ethylene chloride solutions by the iodometric procedure[16] were not satisfactory, since II-A, as well as I, liberated iodine under the titration conditions (adding glacial acetic acid and sodium iodide, and titrating the released iodine with standard thiosulfate). The ethyl ester (II, R = ethyl) also liberated iodine under these conditions but more slowly than II-A. The presence of acetic acid hastened the reaction of II-A with iodide, for no iodine release (contrary to the case with I) was noted when II-A was added directly to aqueous sodium iodide. The infrared analytical method was based on the following observations:

The spectrum of II-A in dioxane had a fairly intense peak at 14.25 μ, which could be used analytically, since VI (the cyclohexene adduct of I) did not possess this peak, although both II-A and VI had a common peak of equal intensity at 13.62 μ. Adding a solution of 0.50 g. of I in 10 ml. of ethylene chloride to a mixture of 5 ml. of cyclohexene and 0.5 ml. of methanol showed no absorption at 14.25 μ on examination of the residue obtained after evaporating the volatile components. The reaction with cyclohexene could thus be used to quench reaction 1-A. Examination of the spectrum of chlorocyclohexane in dioxane showed that a peak near 13.62 μ could interfere, making it necessary to remove chlorocyclohexane (which could form by addition of hydrogen chloride to cyclohexene) by pumping at 2 mm. pressure. The empirical calibration curve was prepared by measuring log $I_{14.25\mu}/I_{13.62\mu}$ for known mixtures of II-A and VI dissolved in dioxane. It was also shown that II-A did not react with cyclohexene and could be recovered unchanged under the conditions of reaction 1-A.

Reaction of I with Methanol in Absence of Pyridine.—To obtain data on the uncatalyzed reaction 1-A, a mixture of 100 ml. of ethylene chloride and 5 ml. (0.1223 mole) of dry methanol was prepared at 28°, and 4.1569 g. (0.01772 mole) of I was added, with swirling. Since adding the I and effecting its solution required about 45 seconds, zero time for the reaction was taken at an arbitrary moment, 23 seconds after mixing the reagents. Thereafter, 10-ml. aliquots were withdrawn from the glass-stoppered vessel, at known times, and were pipetted into 5 ml. of purified cyclohexene. The mixtures were evaporated with a stream of nitrogen and pumped at 2 mm. pressure, at room temperature, for several hours. The residual solids were dissolved in dioxane to a 6% solution (weight by volume) and examined in the infrared spectrophotometer (a modified Perkin–Elmer, double-beam model 12-C), using 0.1-mm. sodium chloride cells.

The composition of the reaction mixture at the stated time intervals were (min./mole % II): 2/8; 6/8.8; 13/12; 24/17.4; 36/14; 48/14; 60/18.2; 80/16; 100/22; 100/20. The data are plotted in Fig. 1. Assuming equilibrium at 20 mole % ester, the relative concentrations (moles/volume) at equilibrium of ester, hydrogen chloride, I and methanol are, respectively: 0.0036, 0.0036, 0.0144 and 0.119; and $K_{eq} = (0.0036)^2/0.0144 \times 0.119 = 6 \times 10^{-3}$. This figure is approximate, since the per cent. mole ester at equilibrium is only known to *ca.* ±5%. The order of magnitude is correct, however, since similar values of K_{eq} result, assuming equilibrium, *e.g.*, at 18% ($K_{eq} = 5.8 \times 10^{-3}$) or at 15% ($K_{eq} = 4 \times 10^{-3}$).

That reaction 1-A is, indeed, reversible was independently shown by isolating I in good yield from a mixture of II-A and methanol, in ethylene chloride, by passing dry hydrogen chloride into the solution for two hours at room temperature, then aspirating the mixture to dryness also at room temperature.

Effect of Pyridine on Reaction Rate of I with Methanol.—A similar rate run (as described just above) was set up with 50 ml. of ethylene chloride, 2.00 ml. of dry pyridine and 1.8281 g. (0.007795 mole) of I. The above procedure was followed, except that the evaporated mixtures were washed several times with 5-ml. portions of 0.1 *N* hydrochloric acid and water to remove the pyridine and the samples finally dried for several hours at 80° and 2 mm. in an Abderhalden pistol. The reaction was too rapid to follow, showing essentially 100% ester at the first measured point (2 minutes). The reaction is probably complete well before this time, however, since the sensitive qualitative test for I (using potassium iodide–starch solution) was negative immediately after adding the pyridine.

Determinations of Reaction Rates with N,N-Dimethylmesidine Present.—Run A, Fig. 2: The mesidine (3.2455 g., 0.01988 mole) was mixed with 100 ml. of ethylene chloride and 5.00 ml. (0.1223 mole) of dry methanol. To this was added 4.4542 g. (0.01898 mole) of I, as above, at 28° and aliquots were treated as already described. From the volume and density of the original solution, each aliquot was estimated to have 1.72×10^{-3} mole of I. To avoid errors, three tracings were made, and the relative intensities taken as the average of the three. The plot of log of the molar concentration of I *vs.* time (Fig. 2) gave a straight line for the 5-, 11-, 19- and 30-minute points, with the 2-minute point badly off, probably because of the large timing error at the beginning of the run. The slope of the line was -0.03 min.$^{-1}$.

In run B, Fig. 2, there were used 5.2950 g. (0.03243 mole) of dimethylmesidine (V), 4.4769 g. (0.01907 mole) of I, 100.0 ml. of ethylene chloride and 5 ml. of dry methanol. Each 10-ml. aliquot was estimated to contain, initially, 0.001692 mole of I. The infrared determinations gave the following values for mole % ester/time (min.); 34/2; 54/5; 77.8/9; 88/15; 92.4/20; 94.6/25; 95/32; 100/39; 100/49; 98.4/65. From these data, the plot of log molar concentration of I *vs.* time (curve B, Fig. 2) gave -0.055 min.$^{-1}$ as the slope of the best straight line that could be drawn through the points. In spite of the scattering of some of the points, in comparison with the above run, the positive dependence of the reaction rate on mesidine concentration is demonstrated.

Product Isolation from I with Dimethylmesidine (V) (or Pyridine) and Methanol; and Interaction of I and V.—One-half gram of I, 10 ml. of ethylene chloride and 0.5 ml., each, of dry methanol and V were mixed at room temperature. The test for I with starch–iodide solution was strong immediately after mixing, and could still be detected after 20 minutes (compare instantaneous negative test with pyridine as the amine). Reaction was essentially complete (starch–iodide test) after 30 minutes. After 3.5 hours, the homogeneous mixture was aspirated, at room temperature, giving a red oil, which solidified slowly when water was added. The product was collected, washed with water and dried at 2 mm. (wt. 0.46 g., still containing some V). It was taken up in boiling chloroform, leaving a 25-mg. residue of IV. The filtrate was concentrated to small volume, diluted with ligroin (b.p. 63–69°) and chilled, giving 0.42 g. of II-A (m.p. 117–121°; m.m.p. with authentic II-A, 121–123°). The yields correspond to 87% of the ester II-A and 6% disulfide IV.

The similar reaction was conducted, using dry pyridine in place of V. The yield of II-A (m.p. 121–123°) was 86.6% and that of IV was 5.9%. The test for I was negative immediately after adding the pyridine.

In the reaction of I and V, alone, to 0.42 g. of I, in 10 ml. of ethylene chloride, was added 0.5 ml. of V. The color change to a red solution, indicating interaction of I and V, was very marked. The starch–iodide test for I was strongly positive at 2 hr., and still definite at 20 and 26 hr., but negative after 44 hr. Formation of a precipitate was noted after 1 hr., and after 44 hr. this was collected (273 mg.) and found to melt with decomposition at *ca.* 300° as typical of III. However, darkening of the product at temperatures of about 200° indicated its non-homogeneity. Evaporation of the filtrate to dryness, at the aspirator, gave a gummy reddish residue. This was extracted with boiling ligroin (b.p. 63–69°)/benzene (1:1 by vol.), leaving a residue, which was mainly water-soluble and presumably the hydrochloride of V. Extraction of the residue with ethylene chloride yielded only a little more disulfide IV. The result of this experiment is, no doubt, associated with the amine-catalyzed hydrolysis of I, since the exclusion of traces of water is virtually impossible under the conditions used. The similar interaction of II-A and V, however, gave only recovered II-A.

Recovery of I from Solution in Ethylene Chloride with Excess Pyridine Present.—I (2.35 g., 0.01 mole, m.p. 95–

(27) W. S. Emerson, F. W. Neumann and T. P. Moundres, *ibid.*, **63**, 972 (1941).

96°) was dissolved in 30 ml. of dry ethylene chloride, 15 ml. of solvent removed to ensure dryness and the solution stored in a desiccator. A second solution was prepared from 4 ml. of dry pyridine in 30 ml. of dry ethylene chloride, and 10 ml. of this was removed by azeotropic distillation. The two solutions (hot, to avoid ingress of moisture) were quickly mixed and stored in the desiccator. The solution was clear at mixing, and remained so, but after 38 hr. a trace (1–2 mg.) of solid was noted. After 62 hr., the appearance was the same, and the starch–iodide test was strongly positive. After 5 days, some long needle crystals (later shown to be IV) were noted, and after one week (starch–iodide test still positive) the volatile materials were pumped off at about 5 mm., appreciable loss of material being incurred at this point as a result of "bumping." Extraction of the residue with about 50 ml. of boiling carbon tetrachloride gave 769 mg. of I (first crop, m.p. 94.5–96°) and 915 mg. more (second crystal crop, m.p. 87–94.5°; and having m.m.p. 87–96° with authentic I); total recovery of I 71%. The carbon tetrachloride-insoluble residue (240 mg.) was characterized by its typical decomposition as IV. Formation of IV (*ca.* 12%) suggests that traces of water were picked up in the course of the experiment.

Reactions of I and Other Alcohols.—The sulfenate esters from I and other alcohols, as well as other products encountered in these reactions, are noted in the text and in the body and footnotes of Table I. The preparative details (which generally followed standard techniques, based on our earlier experience with reactions of I) have been filed in a report with the Science Library of the University of Southern California.[28]

N,N-Dimethylmesidine (V) as Base in Reaction of I with Methanol, Allyl Alcohol and Benzhydrol.—The preparative results of using V in place of pyridine were essentially the same as with the pyridine. The results in the case of methanol have been described above in connection with the rate runs.

When compound I (1.0 g.), 1.0 ml. of allyl alcohol, 1.0 ml. of V and 10 ml. of ethylene chloride were mixed, a deep-red solution was formed. After 5 min., the starch–iodide test was still positive, but was negative after 25 min. The volatile components were aspirated, and the residue (a red, viscous oil) was extracted with boiling ligroin (b.p. 63–69°). The ligroin extracts were concentrated and chilled, giving 95 mg. of solid (m.p. 85–87°, with some prior softening). Recrystallization from ligroin (b.p. 63–69°) raised the m.p. to 86–87°, and there was no depression on admixture with authentic allyl ester of I. The residue from the ligroin extracts was dissolved in chloroform, 14 mg. of undissolved IV was collected, and the chloroform filtrate extracted with 3 *M* hydrochloric acid. Evaporation of the chloroform left a viscous liquid containing some IV. Extraction with chloroform left 47 mg. of IV, and evaporation of the chloroform from the filtrate left a viscous oil which still contained some V. The oil was dissolved in benzene, washed with dilute hydrochloric acid and evaporated, leaving 0.96 g. of viscous residue, presumed to be the 1:1 adduct of I at the olefin position of allyl alcohol (see Table I and Discussion). The yields correspond to 77% adduct, 9% ester and 7% IV. The similar reaction, as above, with 0.42 g. of I, 0.39 g. of benzhydrol, 10 ml. of ethylene chloride and 0.5 ml. of V gave a slow completion of reaction and led mainly to recovered benzhydrol (IV) and a low yield of the benzhydrol ester of I. The deep red color formed when I and V interact suggested an attempt to determine whether an isolable complex results. Only IV, however, could be isolated, which probably arises by slow hydrolysis of I by traces of water present in the reaction mixture.

Stabilities of Certain 2,4-Dinitrobenzenesulfenate Esters to Pyridine and Pyridine Hydrochloride.—(a) A mixture of 0.24 g. of cinnamyl 2,4-dinitrobenzenesulfenate (II-A, R = cinnamyl), m.p. 120–123° dec., 0.2 ml. of pyridine and 10 ml. of ethylene chloride was prepared and let stand at room temperature for about 12 hr. The solution remained clear (indicating no formation of IV). Vacuum removal of solvent gave 0.22 mg. of unchanged ester, m.p. 122–123.5° dec. Only a trace of IV was present, since less than 1 mg. of the above residue failed to dissolve in a small volume of hot chloroform.

(b) A solution of pyridine hydrochloride was prepared by adding 0.2 ml. of pyridine to 10 ml. of ethylene chloride, then adding 4.0 ml. of 0.86 *M* dry hydrogen chloride, in dry methyl acetate. The salt was isolated by aspirating the volatile components (anhydrous conditions being maintained), and to it was added 10 ml. of ethylene chloride (warming was necessary to dissolve the salt), 0.1 ml. of dry pyridine and 0.24 g. of cinnamyl 2,4-dinitrobenzenesulfenate (m.p. 122–123° dec.). This mixture was left in a desiccator about 50 hr. at room temperature. At the end of this time, pyridine hydrochloride had precipitated, but heating the mixture still left insoluble material, which proved, when collected, to be 85 mg. of IV. The filtrate was aspirated to dryness, and extracted with 20 ml. of boiling benzene, leaving about 10 mg. of solid which was mostly IV and some cinnamyl alcohol. Evaporation of the benzene extract left an oil, containing also about 5 mg. more of IV, which was removed. The oil formed an α-naphthylurethan, m.p. 106–107° on an admixture of this with the authentic α-naphthylurethan of cinnamyl alcohol (m.p. 111–113°) the m.p. was 110–114°. The total yield of the disulfide IV was 70%.

(c) Allyl 2,4-dinitrobenzenesulfenate (0.25 g., m.p. 86.6–87.6°) was added to a solution of pyridine hydrochloride, prepared as above, in 25 ml. of ethylene chloride containing 0.1 ml. of pyridine. After 0.75 hr., the solution was still clear, but after 14 hr. at room temperature a crystalline precipitate was present. This was collected and proved to be 54 mg. of IV. The filtrate was evaporated to dryness and was extracted with boiling Skellysolve B. Concentration of the extract and chilling yielded 21 mg. of crystalline solid, m.p. 60–85°, giving a mixture m.p. with the starting ester of 73–84°. After extracting the residue (remaining after the ligroin extraction) 63 mg. more of IV remained. The total yield of disulfide IV, based on starting ester, was 60%.

(d) Methyl 2,4-dinitrobenzenesulfenate (0.25 g.) was allowed to react under conditions identical to those in *c* above. There was no precipitate after 6.5 hr., but one was present after 18 hr., and the starch–iodide test at this time was negative. After 90 hr., 132 mg. of IV was collected. The filtrate was aspirated to dryness and the residue extracted with boiling ligroin (b.p. 63–69°). The ligroin extracts, on concentration, yielded 10–15 mg. of pale yellow crystals which melted at 82–86°, and on admixture with authentic *m*-dinitrobenzene melted at 84–88°. More IV (17 mg.) was also obtained from the material which did not dissolve in the ligroin. The total yield of IV was 69%.

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(28) L. Goodman and N. Kharasch, "The Reaction of 2,4-Dinitrobenzenesulfenyl Chloride with Alcohols," Research Report, University of Southern California, 1955.