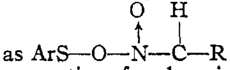
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

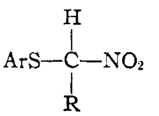
Derivatives of Sulfenic Acids. XII. Studies of α-Nitro Sulfides. Part 3

BY MAURICE B. SPARKE, J. LORNE CAMERON AND NORMAN KHARASCH

RECEIVED APRIL 9, 1953

In accord with earlier studies, reaction of 2,4-dinitrobenzenesulfenyl chloride with the sodium salt of 1-nitrobutane led to 2,4-dinitrophenyl 1′-nitrobutyl sulfide (75%). However, in the corresponding reactions of 4-chlorobenzenesulfenyl chloride and 2,4-dichlorobenzenesulfenyl chloride with the sodium salt of 1-nitropropane, the sulfur-containing products were 4-chlorophenyl 4′-chlorobenzenethiolsulfonate and bis-(2,4-dichlorophenyl) disulfide, respectively—none of the expected α-nitro sulfides being found. 1-Chloro-1-nitropropane was also a product in the reaction of 2,4-dichlorobenzenesulfenyl chloride. The possibility that an intermediate such as  $\mathrm{ArS{-}O{-}\overset{\overset{O}{\uparrow}}{N}{-}\overset{\overset{H}{|}}{C}{-}R}$ is involved in the reactions of sulfenyl halides with the nitroalkane salts is considered, and evidence suggestive of such an intermediate is presented from a study of the reaction of 2,4-dinitrobenzenesulfenyl chloride and the sodium salt of nitroethane. Some related studies of the syntheses, hydrolyses, alcoholyses and characterizations of the above sulfenyl halides are also recorded.

In extending our studies of α-nitro sulfides,[1] interest in the potential insecticidal activities of compounds related to I led us to attempt the syntheses of IA, IB and IC.

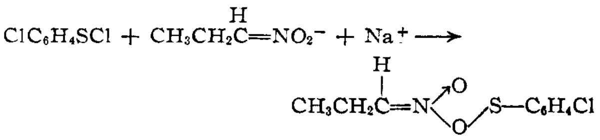


$$\mathrm{ArS{-}\underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}}{-}NO_2}$$

IA, Ar = 2,4-dinitrophenyl; R = *n*-propyl
IB, Ar = 4-chlorophenyl; R = ethyl
IC, Ar = 2,4-dichlorophenyl; R = ethyl

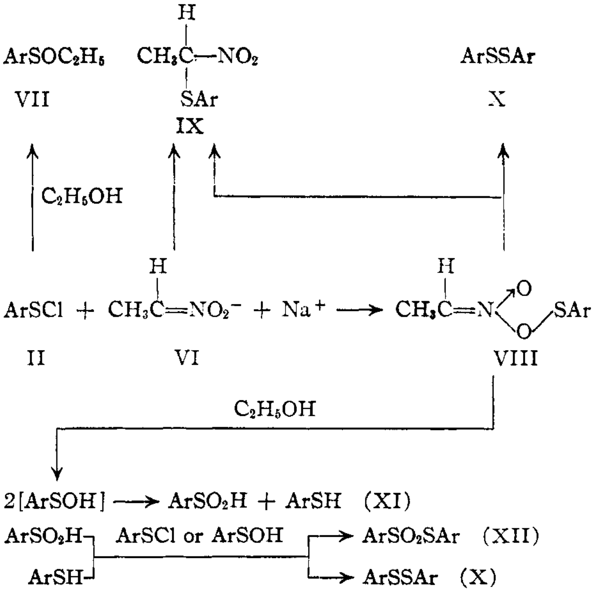
While IA was obtained by the general method of reference 1, *via* 2,4-dinitrobenzenesulfenyl chloride (II) and the sodium salt of 1-nitrobutane, in 75% yield, the syntheses of IB and IC were not realized—for under conditions which had proved suitable for all the previously-known α-nitro sulfides,[1] the reactions of 4-chlorobenzenesulfenyl chloride (III) and 2,4-dichlorobenzenesulfenyl chloride (IV) led to alternate products. Thus, from III, there resulted 53% pure 4-chlorophenyl 4′-chlorobenzenethiolsulfonate; and in the reaction with IV, bis-(2,4-dichlorophenyl) disulfide (61%) and 1-chloro-1-nitropropane (45%) were obtained. The latter product was characterized by conversion to *p*-tolyl 1-nitropropyl sulfone by reaction with sodium *p*-toluenesulfinate.

The reaction of III with the sodium salt of 1-nitropropane was carried out under rigorously anhydrous conditions, and under nitrogen, suggesting that the nitroalkane salt is required to form the thiolsulfonate ester. Since all other α-nitro sulfides heretofore prepared were stable under the conditions employed for reaction of III, and also because it is difficult to visualize a reasonable route for transforming IB to 4-chlorophenyl 4′-chlorobenzenethiolsulfonate, we consider that the intermediate formation of IB in the reaction of III with the sodium salt of 1-nitropropane is unlikely. The possible occurrence of an intermediate such as V suggests itself, however, for this could conceivably decompose to 4-chlorobenzenesulfinic acid, which—in turn—could lead to the thiolsulfonate ester.[2]



V

The unusual behaviors of III and IV, above, recalled a previous observation made in this Laboratory,[3] that if absolute alcohol were substituted for ether or benzene, as solvent in the reactions of certain sulfenyl halides with salts of nitroalkanes, considerable quantities of thiolsulfonate esters and disulfides resulted at the expense of the yields of the desired α-nitro sulfides. A reinvestigation of these observations for the case of reaction of II with the sodium salt of nitroethane confirmed the former experiments, and the conclusion[3] that the thiolsulfonate ester and increased yields of disulfides may result by alcoholysis of the intermediate 2,4-dinitrobenzenesulfenic ethanenitronic anhydride (VIII). The possible courses of the reaction are illustrated in the following scheme (Ar = 2,4-dinitrophenyl), and substantiated, in part, in the notations: (1) The "normal" reaction of II and VI, in absolute ether, gave 60–70% crude yields (50–



---

[1] N. Kharasch and J. L. Cameron, THIS JOURNAL, **73**, 3864 (1951); **75**, 1077 (1953).

[2] Formation of 4-chlorophenyl 4′-chlorobenzenethiolsulfonate from 4-chlorobenzenesulfinic acid was observed by Otto, *Ann.*, **145**, 323 (1868), and such products have frequently been found in reactions which involve the decompositions of sulfinic acids. *Cf.*, *e.g.*, W. E. Truce and A. M. Murphy, *Chem. Revs.*, **48**, 69 (1951). The decompositions are presumed to involve the intermediate formation of sulfenic acids (RSOH).

[3] N. Kharasch and J. L. Cameron, unpublished work.

56%, pure) of IX and 15–21% X, in accord with our earlier study.[1] (2) Reaction of equimolar amounts of II and VI, with absolute alcohol instead of ether as solvent, yielded 38–40% of X, 14–24% of XII and a small amount of XI. While some of IX may also have been present, it was not found. Thus, alcohol effects a fundamental change in the final products—an effect which cannot be explained by reaction of IX with alcohol, for IX does not change by treatment with alcohol. (3) Reaction of equimolar amounts of II, VI and absolute alcohol—in excess absolute ether as solvent—gave 52% of IX, 19% X and indications of XI (typical red color of the sodium salt of 2,4-dinitrothiophenol, never observed in the reaction in the absence of alcohol). (4) Reaction of II, with absolute alcohol, at reflux, gave the ethyl ester (VII), 95%. At 0°, a mixture of VII and unchanged II was obtained. Thus, reaction of II with alcohol directly cannot be responsible for the alternate products of section 2. (5) Eighty per cent. of VII was recovered from an attempted reaction with VI, simulating conditions of reaction of II with VI, as in part 2. The alternate products of part 2 were not found, showing that VII is not the precursor of the thiosulfonate ester (XII) and thiol (XI), nor of additional X, as found in section 2. (6) Under conditions simulating reaction of II with VI, in part 2, X was recovered in 98% yield. Thus, the disulfide X does not appear to be the precursor of the alternate products of section 2. (7) 2,4-Dinitrobenzenesulfenyl chloride is stable thermally under the conditions of the reaction effected with VI. Thus, X does not stem from thermal decomposition of II. Nitroethane and II also failed to react, 94% of II being recovered after refluxing equimolar amounts for three hours in carbon tetrachloride solution.

The suggestion of intermediates such as V and VIII in the reactions of sulfenyl halides with nitroalkane salts also finds support, by analogy, from the extensive studies of the alkylation of nitroparaffin salts, in which O-alkylation has been well substantiated[4]; and while formation of X, XI and XII *via* the postulated intermediate sulfenic acid is by no means well understood, the occurrence of similar products in scores of related cases where unstable sulfenic acids are suspected as intermediates,[5] lends support to the suggestion that such an intermediate may be involved in the present study. The alcoholysis of anhydride VIII also appears to be a reasonable expectation.

In those cases in which product IX was found, its formation by direct reaction of II with VI, without involving VIII, has not been ruled out; but we are inclined to believe that its formation *via* intermediate VIII is more likely. Also, since some disulfide formation has generally been observed in the reactions of sulfenyl halides with the sodium salts of nitroalkanes (*cf.*, *e.g.*, footnotes *d* and *h* of Table I, ref. 1) it may be that disulfide X is formed as an attendant product in the conversion of VIII to IX. In this connection, the formation of bis-(2,4-dichlorophenyl) disulfide and 1-chloro-1-nitropropane in the reaction of IV with the sodium salt of 1-nitropropane is of considerable interest, for the result implies that IV can act in the capacity of a chlorinating agent, thereby suggesting still another route to the disulfide fraction, possibly

$$\mathrm{ArSCl + RCH{=}NO_2Na \longrightarrow RCH(Cl){-}NO_2 + ArSNa}$$
$$\text{and } \mathrm{ArSNa + ArSCl \longrightarrow ArSSAr + NaCl}$$

The decided differences observed in the course of the reactions of II, III and IV with the nitroalkane salts, led us to seek whether such differences might also be found in other reactions of these sulfenyl halides. Perhaps of greatest interest was the finding that III reacted rapidly with absolute methanol at room temperature to give 80–90% yields of bis-(4-chlorophenyl) disulfide, in sharp contrast with the high conversion of II to the methyl ester, isolated in 88% yield, by refluxing with methanol. The sulfenyl chloride, IV, likewise reacted with absolute methanol at room temperature to give bis-(2,4-dichlorophenyl) disulfide as the only isolated product, but the reaction was far less rapid in this case, and the yield of isolated disulfide was lower (30%). The products from hydrolysis of III were mainly the corresponding thiolsulfonate ester, and some disulfide, whereas IV hydrolyzed to give bis-(2,4-dichlorophenyl) disulfide as the major product.[6]

Compounds II, III and IV all react smoothly with cyclohexene to give corresponding 1:1 adducts, but the reactions with III and IV were decidedly faster than was reaction with II. On oxidation, the adducts of III and IV led to the corresponding sulfones, whereas the adduct of II led to 2-chlorocyclohexyl 2′,4′-dinitrophenyl sulfoxide. The conversions of III and IV to the corresponding disulfides by reactions, respectively, with 4-chlorothiophenol and 2,4-dichlorothiophenol, and the characterization of 2,4-dichlorothiophenol by reaction with 2,4-dinitrochlorobenzene are also recorded. The yields in these conversions were satisfactory, but exact percentages were not determined.

Acknowledgment.—The support of this work by a grant from Commercial Solvents Corporation is gratefully acknowledged. We are also indebted to the Fulbright Commission for travel aid extended to one of us (M.B.S.) as a visiting scholar from the United Kingdom.

Experimental[7]

2,4-Dinitrophenyl 1′-Nitrobutyl Sulfide, IA.—The sodium salt of 1-nitrobutane was prepared from 3.78 g. (0.07 mole) of C.P. sodium methoxide and 14.5 g. (0.14 mole) of 1-nitrobutane (b.p. 149–151°), in 75 ml. of dry ethanol. This was precipitated and washed with dry ether, dried 14 hr. over calcium chloride at 20 mm., and added—with stirring and exclusion of moisture—to 14.0 g. (0.0625 mole) of II, in 250 ml. of ether, in a 3-neck flask maintained at 0°. After complete addition, the mixture was stirred at room temperature for 30 min. and then at reflux for 30 min.

---

[4] *Cf.*, *e.g.*, the papers of H. B. Hass and M. L. Bender, THIS JOURNAL, **71**, 1787, 3482 (1949).

[5] *Cf.*, *e.g.*, N. Kharasch, S. J. Potempa and H. L. Wehrmeister, *Chem. Revs.*, **39**, 269 (1946).

[6] A description of the hydrolysis of II is deferred to a later paper of this series (N. Kharasch, W. King and T. C. Bruice, study in progress). *Cf.* also, Experimental for description of a second product, of unestablished structure, isolated in the hydrolysis of IV.

[7] The microanalyses were performed by Mr. J. V. Pirie and Dr. A. Elek. Melting points are not corrected.

The solid was collected, and the residue, after removal of adhering solvent, was continuously extracted in a Soxhlet thimble with 100 ml. of absolute methanol. After removing the methanol from the extract, the oily residue was dissolved in a minimum of dry methanol and refrigerated, giving 13.7 g. (75%) of product; yellow needles, m.p. 122–123° after recrystallization from methanol. Traces of moisture greatly impeded the crystallization.

Anal. Calcd. for $C_{10}H_{11}O_6N_3S$: C, 39.86; H, 3.68. Found: C, 39.62; H, 3.54.

Dry dioxane was also used as solvent in this preparation, with essentially the same results. IA was difficulty soluble in 10% aqueous sodium hydroxide and could be recovered (m.p. and m.m.p.) by acidifying with glacial acetic acid. Attempted conversion to a sulfone, however, by the method below (for the 1-nitropropyl analog) was not successful. The product isolated was strongly acidic and corresponded in m.p. to 2,4-dinitrobenzenesulfonic acid trihydrate, m.p. 108°.[8] Attempts to oxidize IA with potassium permanganate in glacial acetic acid, at room temperature, gave only recovered IA.

2,4-Dinitrophenyl 1'-Nitropropyl Sulfone.—This was prepared in 72% yield by heating the corresponding sulfide[1] with excess peracetic acid solution,[9] at 50° for 5 hr., and diluting with water; m.p., after recrystallizing from methanol, 140–141°.

Anal. Calcd. for $C_9H_9O_8N_3S$: C, 33.86; H, 2.84; N, 13.16. Found: C, 33.96; H, 3.02; N, 13.48.

Synthesis and Reactions of 4-Chlorobenzenesulfenyl Chloride (III).—III was obtained in near quantitative yield, by adding 4-chlorothiophenol (14.0 g.) to dry carbon tetrachloride (350 ml.), at 0°, presaturated with dried chlorine gas, and continuing passage of chlorine, with stirring, for 3 hr.; red fuming liquid, b.p. 86–90° (5 mm.), which may be stored unchanged for days in a well-sealed container.[10]

In moist air, III, 0.11 g., changed to a yellow solid (0.10 g.). After triturating this twice with 1-ml. portions of Skellysolve A, this melted at 134–135°, and at 136–137° after recrystallization from benzene–Skellysolve C mixture.

Anal. Calcd. for $C_{12}H_8O_2Cl_2S_2$: C, 45.14; H, 2.53. Found: C, 45.14; H, 2.54.

This product corresponds to the 4-chlorophenyl 4-chlorobenzenethiosulfonate of Bulmer and Mann,[11] m.p. 137–138°.

Hydrolysis of III (0.49 g.) with 6 ml. of water at room temperature gave an oil which solidified when let stand 2 days. The solid (0.28 g.), m.p. 50–95°, was separated by 8 recrystallizations (methanol, micro-beaker technique) into a small amount of the known bis-(4-chlorophenyl) disulfide (see below), and a major fraction of the more soluble thiolsulfonate ester. Mixtures with the authentic products gave no m.p. depressions.

Conversion of III to 2-chlorocyclohexyl 4-chlorophenyl sulfone was effected by addition of III to cyclohexene, in dry ethylene chloride, evaporating the solvent, and oxidizing the residual oil with potassium permanganate; white crystals, m.p. 75–76° (recrystallized from ethanol–benzene mixture).

Anal. Calcd. for $C_{12}H_{14}O_2Cl_2S$: C, 49.17; H, 4.78. Found: C, 49.13; H, 4.85.

Reaction of III with pure, absolute methanol gave 90% yields of pure bis-(4-chlorophenyl) disulfide, m.p. 72–73°. The identical product (m.p. and m.m.p.) was obtained in 85% yield, *via* III and 4-chlorothiophenol; white leaflets from methanol.[12]

Reaction of III with the sodium salt of 1-nitropropane was carried out as follows. The sodium salt (0.69 g., 0.0062 mole) was added to III (0.87 g., 0.0048 mole) in dry ether (30 ml.). Moisture and air were excluded by drying traps and use of a pure nitrogen atmosphere. Reaction was completed by refluxing 20 min., and the mixture diluted with 50 ml. of dry ether and filtered rapidly to remove sodium chloride. Evaporation of the filtrate left a white solid (0.77 g.) which was recrystallized from a mixture of benzene–Skellysolve B to give 0.41 g. of product, m.p. 133–135°, which did not depress the melting point of 4-chlorophenyl 4'-chlorobenzenethiolsulfonate[11] on admixture; yield 53%, based on sulfenyl chloride. A larger scale run (using 11.5 g. of III) gave essentially the same results, but after separation of the thiolsulfonate ester there also remained a small amount of viscous, dark red oil, which decomposed extensively on attempted distillation *in vacuo*. None of the desired IB was found.

Synthesis and Reactions of 2,4-Dichlorobenzenesulfenyl Chloride (IV).—2,4-Dichlorothiophenol was best prepared by reduction of 2,4-dichlorobenzenesulfonyl chloride,[13] using zinc and sulfuric acid[14]; white needles, melting at room temperature.[15] The thiol was characterized by conversion to 2,4-dichlorophenyl 2',4'-dinitrophenyl sulfide (bright-yellow prisms from methanol; m.p. 133–133.5°) *via* reaction of the thiol and 2,4-dinitrochlorobenzene, by the method of Bost, *et al.*[16]

Anal. Calcd. for $C_{12}H_6O_4Cl_2N_2S$: C, 41.75; H, 1.75; N, 8.12. Found: C, 41.91; H, 1.63; N, 8.40.

The thiophenol was also converted to 2,4-dichlorophenyl 2',4'-dinitrophenyl disulfide (m.p. 139–140°) by reaction with a slight molar deficiency of II, in warm, dry ethylene chloride solution. The pale-yellow derivative was recrystallized from glacial acetic acid.

Anal. Calcd. for $C_{12}H_6O_4Cl_2N_2S_2$: C, 38.20; H, 1.60; N, 7.43. Found: C, 38.14; H, 1.60; N, 7.41.

Chlorination of 10.8 g. of the thiophenol (*cf.* the corresponding preparation of III) gave a red, fuming liquid (11.6 g., 90% yield, b.p. 94–96° (4 mm.)). The sulfenyl chloride was not analyzed, but was converted to bis-(2,4-dichlorophenyl) disulfide, m.p. 82–83° (75% yield) by reaction with 2,4-dichlorothiophenol. The product corresponds to the one of Baddeley and Bennett,[15] who prepared it by an alternate route. Addition of IV to cyclohexene occurred rapidly, in ethylene chloride solution, giving an oil; and oxidation of the latter, with potassium permanganate in aqueous acetic acid, gave a white, crystaline solid, m.p. 109–110°, whose analysis, while somewhat high, was in fair agreement for 2-chlorocyclohexyl 2',4'-dichlorophenyl sulfone.

Anal. Calcd. for $C_{12}H_{13}O_2Cl_3S$: C, 43.98; H, 4.00. Found: C, 44.31; H, 4.60.

The sulfenyl chloride (IV) could be kept for days in a tightly-sealed container but, on exposure to moist air, the red color faded and a mixture of white solids resulted. Fractionation, by crystallization from methanol, led mainly to bis-(2,4-dichlorophenyl) disulfide (m.p. 82–83°, and undepressed on admixture with authentic product) and a lesser proportion of an unidentified, white, crystalline solid, m.p. 193–193.5°, which gave the following analysis: C, 41.34, 41.50; H, 1.90, 204 (on two separate samples). While this analysis does not agree for the possibly expected product, 2,4-dichlorophenyl 2',4'-dichlorobenzenethiolsulfonate ($C_{12}H_6O_2Cl_4S_2$) requiring C, 37.11; H, 1.55, it was nevertheless found that the identical product (m.p. and m.m.p.) resulted *via* 2,4-dichlorobenzenesulfonyl chloride and potassium ethyl xanthate, following the procedure of Bulmer and Mann[11] for obtaining the analogous 4-chlorophenyl 4'-chlorobenzenethiolsulfonate.

Reaction of IV with dry methanol was slow, compared to III, unchanged IV remaining after two days. The precipitated solid was collected and shown to be bis-(2,4-dichlorophenyl) disulfide; m.p. and m.m.p. with authentic disulfide. The recovery of disulfide was 30%, based on IV.

The reaction of IV with the sodium salt of 1-nitropropane

---

[8] J. Elgersma, *Rec. trav. chim.*, **48**, 757 (1929).

[9] M. W. C. Smit, *ibid.*, **49**, 675 (1930).

[10] E. Gebauer-Fülnegg, THIS JOURNAL, **49**, 2270 (1927), reported this compound, in unstated yield, b.p. 94° (6 mm.). The 4-chlorothiophenol was prepared, in the present study, by the general method of Leuckart, *J. prakt. Chem.*, [2] **41**, 173 (1890); compare also Tarbell and Fukushima, *Org. Syntheses*, **27**, 81 (1947). On one occasion, considerable of the fairly volatile thiophenol was lost while being dried in a desiccator at 20 mm.

[11] G. Bulmer and F. G. Mann, *J. Chem. Soc.*, 680 (1945).

[12] P. deSmet, *Natuurs. Tijdschrift*, **15**, 215 (1933); *C. A.*, **28**, 3065 (1934), gives m.p. 71–71.5° for this disulfide.

[13] E. Huntress and F. Carten, THIS JOURNAL, **62**, 511 (1940).

[14] R. Adams and C. S. Marvel, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 504.

[15] G. Baddeley and G. M. Bennett, *J. Chem. Soc.*, 46 (1933), give m.p. 20° for the thiol, prepared *via* 2,4-dichloroaniline and potassium ethyl xanthate. Our yield by this procedure was only 15%, whereas the alternate procedure gave 60%, based on crude 2,4-dichlorobenzenesulfonyl chloride.

[16] R. W. Bost, J. C. Turner and R. D. Norton, THIS JOURNAL, **54**, 1986 (1932).

was carried out by the general method for synthesis of α-nitro sulfides.[1] To 17.8 g. of distilled IV, in 500 ml. of dry ether at room temperature, was added a slight molar excess of the sodium salt. The mixture was stirred for 40 min., at which time a negative starch–iodide test showed absence of unreacted IV. The mixture was filtered, ether was stripped off through a short Schneider column, and the residue distilled at 3 mm., trapping 8.7 g. of volatile material (product A) in the cold trap; and leaving a residual red oil. The latter was taken up in 1:1 mixture of carbon tetrachloride and ethyl acetate, and passed through a 55 × 2 cm. column of alumina. Working up the eluents gave 8.2 g. of bis-(2,4-dichlorophenyl) disulfide (51% yield); m.p. and m.m.p. with authentic disulfide (81–82°). Concentration of the final eluents from the column gave 1.7 g. of a nitrogen-containing oil which could not be purified by distillation or further chromatography. Fractionation of the volatile product A led to 4.8 g. of material, which on basis of b.p., odor and refractive index appeared to be 1-chloro-1-nitropropane. In confirmation of this, both the product from A and authentic 1-chloro-1-nitropropane were converted to the identical derivative (m.p. and m.m.p.), by reaction with sodium *p*-toluenesulfinate dihydrate, following the procedure used for the analogous reaction with 1-chloro-1-nitroethane.[1] From 3.1 g. of redistilled A, there was obtained 2.0 g. of 1-nitropropyl *p*-tolyl sulfone, m.p. 68–69°, after crystallizing from aqueous methanol.

Anal. Calcd. for $C_{10}H_{13}O_4NS$: C, 49.37; H, 5.39. Found: C, 49.44; H, 5.37.

The Effect of Alcohol on the Reaction of 2,4-Dinitrobenzenesulfenyl Chloride (II) with the Sodium Salt of 1-Nitroethane. a.—Yields of IX of 60–70% crude (50–56% pure) were obtained in the "normal" reaction of II and the sodium salt, in absolute ether, substantiating the earlier results.[1]

b.—Reactions of II with ethanol and methanol were carried out as follows. II (5.97 g., m.p. 95–96°) was stirred vigorously with 100 ml. of dry ethanol,[17] at 0°, for 35 min. The alcohol was pumped off (30 min.) and the residue fractionally crystallized from carbon tetrachloride—giving 75% recovered II and 21% of VII, which melted at 120–121°, and did not depress the m.p. of authentic VII (m.p. 122–123°).[18] In accord with earlier work,[18] reaction of II with refluxing dry ethanol (or methanol) led only to VII (or the methyl ester) in 95 and 88% yields, respectively.

c.—The thermal stability of II under the conditions of the reaction with nitroalkane salts has been observed repeatedly in this Laboratory. There is no reaction between II and dry ether at room temperature or reflux. Refluxing II (1.32 g., 0.0056 mole) with nitroethane (0.40 ml., 0.0056 mole) in 25 ml. of dry carbon tetrachloride for 3 hr. also gave no reaction—94% of II (1.24 g.) being recovered by evaporating the solution.

d.—The results of an attempted reaction of X with the sodium salt of nitroethane were as follows. X (132 mg., 0.0045 mole) was added to a suspension of the sodium salt of nitroethane in dry ethanol (20 ml.), prepared from sodium (0.115 g., 0.005 atom) and nitroethane (0.37 ml., 0.005 mole). The mixture was stirred vigorously at 0° and, after 40 min., filtered and washed with 50% acetic acid (4 × 5 ml.), then with acetone. The dried product (129 mg.) corresponded to unchanged disulfide (X), 98% recovery.

e.—Ethyl 2,4-dinitrobenzenesulfenate (VII) did not interact with the sodium salt of nitroethane. Sodium (0.05 g., 0.0021 atom) was dissolved in 5 ml. of dry ethanol[17] and 5 ml. of nitroethane was added. To the stirred suspension, at 0°, was added 0.491 g., 0.002 mole, of VII. The mixture was stirred 40 min., filtered and washed with cold, dry ethanol until the washings were colorless. Evaporation of the combined ethanol solutions gave 0.412 g. of unchanged VII (m.p. and m.m.p. 121–122°). Further concentration gave 0.031 g. more, m.p. 120–122°. Total recovery of VII was 0.443 g. (90%).

f.—The reaction of II with the sodium salt of nitroethane, in alcohol as solvent, was carried out as follows. Sodium (0.57 g., 0.025 atom) was dissolved in absolute alcohol (100 ml.), the solution was cooled to 0° and nitroethane (1.65 ml., 0.023 mole) was added dropwise. Stirring of the suspension was continued for 10 min., the ice-bath removed, and 5.86 g. (0.025 mole) of II was added during 20 min. The mixture became deep red initially, and the final color was orange. After stirring 10 min. more, the mixture was filtered, and the residue washed with boiling benzene, then with water, leaving the insoluble, yellow crystalline disulfide X (melting above 250° dec.); dry weight, 2.16 g. (40%) based on II. The benzene washings were added to the above filtrate, and the combined solutions evaporated by an airstream. The product which accumulated during evaporation was collected periodically; and, when further concentration yielded oils, additional solid product was obtained by diluting with ether. By fractional crystallizations of the precipitated fractions, a total of 1.18 g. of crude 2,4-dinitrophenyl 2′,4′-dinitrobenzenethiolsulfonate was obtained (m.p. 100–130°); and recrystallization of this gave a product melting at 126–126.5° (and giving a strong m.p. depression with VII, m.p. 122–123°).

Anal. Calcd. for $C_{12}H_6O_{10}N_4S_2$ (the thiolsulfonate ester): C, 33.49; H, 1.41. Found: C, 33.60; H, 1.73.

The presence of 2,4-dinitrothiophenol in the reaction mixture was shown by repeating the above-type reaction (using 0.028 mole of the sodium salt of nitroethane, 100 ml. of dry alcohol and 0.025 mole of II). The latter was added during ten minutes; and as soon as addition was completed, a 3-ml. portion of the mixture was removed and tested as follows. (1) The red color was discharged by adding aqueous hydrochloric acid, and regenerated with base. (2) Reaction of the test portion of the reaction mixture with a solution of II in ethylene chloride led to bis-(2,4-dinitrophenyl) disulfide (X); and reaction with IV gave 2,4-dichlorophenyl 2′,4′-dinitrophenyl disulfide (m.p. 139–140°), from glacial acetic acid, and not depressing the m.p. of the same disulfide, prepared unambiguously *via* IV and authentic 2,4-dinitrothiophenol. Chromatographic purification of the above disulfide (as obtained by addition of IV to the reaction mixture) was accomplished, using alumina and mixtures of benzene–Skellysolve B as eluents. Some bis-(2,4-dichlorophenyl) disulfide, m.p. and m.m.p. 82–83°, was also noted as a product in this reaction, and was eluted from the column more readily than the higher-melting, unsymmetrical disulfide.

After removal of the above test portions, the remaining reaction mixture was stirred for 30 min., then filtered. The residue was washed with hot benzene, and proved to be X (1.42 g.), while the concentrated filtrate yielded 0.73 g. of XII (m.p. 124–126° from hot glacial acetic acid). Chromatography of the oily residue on alumina, using methanol as eluent gave only 70 mg. more of XII (total yield of XII, 14%). None of the α-nitro sulfide, IX, could be found.

Repetition of the above reaction of II with the sodium salt of nitroethane, using also one equivalent of alcohol, in dry ether as solvent, gave 52% of IX and 19% of X. The distinct color of the reaction mixture (not observed in the absence of alcohol) was indicative of the sodium salt of XI.

2-Chlorocyclohexyl 2′,4′-Dinitrophenyl Sulfoxide.—This was obtained by oxidation of 2-chlorocyclohexyl 2′,4′-dinitrophenyl sulfide,[19] m.p. 116–117°, using potassium permanganate in aqueous acetic acid at room temperature. The product was recrystallized from alcohol, and melted with decomposition at 173°.

Anal. Calcd. for $C_{12}H_{13}O_5ClN_2S$: C, 43.30; H, 3.90. Found: C, 43.18; H, 3.84.

LOS ANGELES, CALIFORNIA

---

[17] "Dry ethanol" in the above reactions refers to alcohol dried by the method of E. L. Smith, *J. Chem. Soc.*, 1288 (1927), as modified by R. H. Manske, THIS JOURNAL, **53**, 1106 (1931).

[18] N. Kharasch, D. P. McQuarrie and C. M. Buess, *ibid.*, **75**, 2658 (1953).

[19] N. Kharasch and C. M. Buess, THIS JOURNAL, **71**, 2724 (1949).