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

Derivatives of Sulfenic Acids. XXIV. Stereochemical Studies of Certain β-Chloroalkyl Aryl Sulfides[1]

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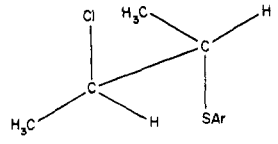
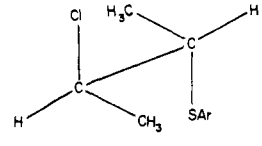
Solvolyses of the diastereomeric pairs of products formed from 2,4-dinitrobenzenesulfenyl chloride (I) or 2-nitro-4-carboxybenzenesulfenyl chloride (II) and the *cis*- and *trans*-2-butenes, respectively, gave 90–99% of the corresponding diastereomeric pairs of acetates. Similarly, acetolysis of the adduct of I to cyclohexene gave 92% of the corresponding acetate (2-acetoxycyclohexyl 2′,4′-dinitrophenyl sulfide), which was also obtained by adding 2,4-dinitrobenzenesulfenyl acetate, VII, (the first example of this class of substance) to cyclohexene. The acetolyses of the isomeric adducts of I to propylene (*i.e.*, 2-chloropropyl 2′,4′-dinitrophenyl sulfide and 1-methyl-2-chloroethyl 2′,4′-dinitrophenyl sulfide) gave the identical mixture of 2,4-dinitrophenylthiopropyl acetates. These results and data from other studies, strongly suggest that the additions of I, II and VII to the above olefins are *trans*, and that the solvolyses of the cited β-chloroalkyl 2,4-dinitrophenyl sulfides involve participation by sulfur of the neighboring arylthio group.

In a previous paper,[3] it was shown that the additions of several sulfenyl halides to the *cis*- and *trans*-2-butenes are stereospecific and it was suggested that the reactions occur in a *trans* manner, yielding racemate pairs, one enantiomer of each of which is represented by A and B. The purpose of



(A)

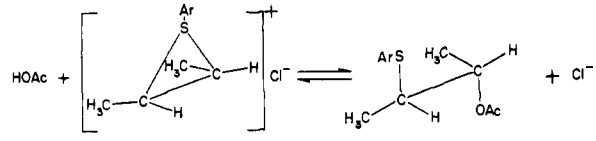


(B)

the present study was to test whether the addition is, indeed, *trans* and to investigate whether neighboring group participation, through sulfur, occurs when the sulfur atom is attached to complex radicals as 2,4-dinitrophenyl and 2-nitro-4-carboxyphenyl. The latter question was of particular importance to a related study[4] concerning the solvolyses of the diastereomeric adducts of 2,4-dinitrobenzenesulfenyl chloride (I) to the *cis*- and *trans*-2-phenyl-2-butenes, but it also has general interest—since the effects of highly electronegative substituents, as nitro and carboxyl, in the aryl groups of A and B, on the participation behavior of the sulfur atom has not been previously studied.

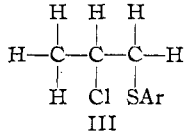
The ability of certain sulfur moieties to participate as neighboring groups has been ably demonstrated by Bartlett and Swain[5] in a kinetic study of the hydrolysis of mustard gas and "mustard chlorohydrin"; other workers[6] have also concluded, appropriately, that such participation can occur in β-chloro sulfides and related compounds. Winstein and Grunwald,[7] through their analysis of "driving forces" in participation behavior, have similarly shown that the sulfur atom of "mustard chlorohydrin" lends powerful assistance in the solvolysis of the chloride. The presence of nitro or carboxyl groups in the 2- and 4-positions of the phenyl ring should, however, have a significant effect on the electronic character of the sulfur atom in position 1, and hence on its ability to participate, *via* a cyclic sulfonium ion, in solvolysis reactions. In the absence of quantitative data on such effects, the *a priori* prediction of whether sulfur in A or B (with aryl groups as mentioned above) participates in the solvolyses could therefore not be made with assurance. The present study reports the qualitative experiments which are necessary before proceeding to a full kinetic evaluation of the solvolyses of molecules as A and B.

Table I summarizes the acetolyses of a series of β-chloroalkyl aryl sulfides. Compounds 1 and 2, and 3 and 4, represent respective diastereomeric racemate pairs, obtained by adding I or 2-nitro-4-carboxybenzenesulfenyl chloride (II) to the *cis*- and *trans*-2-butenes. Each of these four substances was converted in excellent yield to its corresponding racemic acetate. These solvolyses are therefore highly stereospecific and must involve a cyclic sulfonium ion (C) as an intermediate, or an S_N2[8] solvolysis of each racemic chloride.

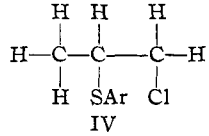


(C)

If sulfur participates in the above manner, acetolysis of the distinctly different positional isomers, III and IV (Ar = 2,4-dinitrophenyl), obtained by



III



IV

adding I to propylene,[9] should yield, as was found, the identical acetate mixture. The small difference in yield recorded in Table I is ascribed to the use of a smaller sample of the less easily available isomer, IV, than of III, for the experiments. The identity of the products was assured by their melting ranges, non-depression of the melting range on admixture,

(1) This study was carried out, in part, under sponsorship of the Office of Ordnance Research, Contract DA-04-495-Ord. 306.

(2) Atomic Energy Commission Predoctoral Fellow, University of Southern California.

(3) N. Kharasch and A. J. Havlik, THIS JOURNAL, **75**, 3734 (1953).

(4) N. Kharasch, A. J. Havlik and W. R. Brasen, in preparation.

(5) P. D. Bartlett and C. G. Swain, *ibid.*, **71**, 1406 (1949).

(6) *Cf.*, *e.g.*, R. C. Fuson, C. C. Price and D. M. Burness, *J. Org. Chem.*, **11**, 477 (1946); and W. H. Stein, S. Moore and M. Bergmann, *ibid.*, 664 (1946).

(7) S. Winstein and E. Grunwald, THIS JOURNAL, **70**, 828 (1948).

(8) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1954.

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

TABLE I

ACETOLYSES OF SOME β-CHLOROALKYL 2,4-DINITROPHENYL SULFIDES[a]

Cpd. no.	β-Chloroalkyl 2,4-dinitrophenyl sulfide	Acetolysis reagent	M.p.[b] of acetate, °C.	Yield, %	Formula of acetate	Analyses, % Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
1	1-Methyl-2-chloropropyl 2′,4′-dinitrophenyl sulfide (*threo*)	HOAc/NAOAc	121–122	90	$C_{12}H_{14}N_2O_6S$[c]	45.85	4.99	8.92	45.85	4.77	9.14
		HOAc	121.5–122.5	95							
2	1-Methyl-2-chloropropyl 2′,4′-dinitrophenyl sulfide (*erythro*)	HOAc/NaOAc	98–99	98	$C_{12}H_{14}N_2O_6S$[d]	45.85	4.99	8.92	45.55	4.20	9.07
		HOAc	97.5	97							
3	1-Methyl-2-chloropropyl 2′-nitro-4′-carboxyphenyl sulfide (*threo*)	HOAc/NaOAc	143–144	90[e]	$C_{13}H_{16}NO_6S$	49.83	4.83	4.77	50.11	5.00	4.61
		HOAc	143.5–144.5	90							
4	1-Methyl-2-chloropropyl 2′-nitro-4′-carboxyphenyl sulfide (*erythro*)[k]	HOAc/NaOAc	126–126.5	96[g]	$C_{13}H_{16}NO_6S$[f]	49.83	4.83	4.47	49.87	5.05	4.55
		HOAc	127–128	99							
5	*trans*-2-Chlorocyclohexyl 1-(2′,4′-dinitrophenylthio) sulfide	HOAc/NaOAc	81.5–82.5	92	$C_{14}H_{16}N_2O_6S$[g]	49.40	4.74		49.69	4.81	
6	2-Chloropropyl 2′,4′-dinitrophenyl sulfide[h]	HOAc/NaOAc	50–53	81	$C_{11}H_{12}N_2O_6S$	44.00	4.03	9.33	44.22	3.95	9.57
7	1-Methyl-2-chloroethyl 2,4′-dinitrophenyl sulfide[i]	HOAc/NaOAc	50–53	74	$C_{11}H_{12}N_2O_6S$[j]	44.00	4.03	9.33			9.18

[a] For the preparation of these products, *cf.* N. Kharasch and C. M. Buess, THIS JOURNAL, **71**, 2724 (1949); N. Kharasch and A. J. Havlik, *ibid.*, **75**, 3734 (1953); A. J. Havlik and N. Kharasch, *ibid.*, **77**, 1150 (1955); or part of this paper. In those cases where configurations are assigned, the assignment was made on the basis of a stereospecific, *trans* addition of the sulfenyl halide to the olefin. [b] The melting points were taken on a Fisher–Johns block. The values reported are for the analytical samples; but the products, as obtained directly from the reaction mixtures, melted, generally, within 1 to 3° of the recorded values. For the acetates obtained from compounds 1 to 5, either by treatment with acetic sodium acetate mixtures, or acetic acid alone, no depression of the melting points was noted on admixture. This observation was made for each of the acetates, obtained in these two ways. In a number of the products, identity was also checked by infrared traces; *cf.* footnote *k*. [c] *Anal.* Calcd.: S, 10.20. Found: S, 10.39. [d] *Anal.* Calcd.: S, 10.20. Found: S, 10.00. [e] Since the sodium salts of the acetates are the original products when sodium acetate is used in the acetolysis medium, the yields stated are based on the weights of the salts obtained. The melting points, however, are for the free acids obtained by hydrolyzing the salts with excess boiling water; *cf.* Experimental. [f] This analysis is for the product obtained with HOAc–NaOAc for the acetolysis. The product obtained using acetic acid alone gave: C, 49.72; H, 5.00; N, 4.56. [g] This same product (m.p., m.m.p., infrared spectra and separate analysis) was also obtained (66%) by adding 2,4-dinitrobenzenesulfenyl acetate to cyclohexene. *Cf.* Exptl. [h] This is the low-melting (74–76°) isomer, formed by adding I to propylene (*cf.*, THIS JOURNAL, 71, 2724 (1949)). *Anal.* Calcd. for $C_9H_9N_2O_4SCl$: C, 39.06; H, 3.28; Cl, 12.81. Found: C, 39.27; H, 2.98; Cl, 12.96. [i] The chlorine analysis for this higher-melting (106.5–108°) isomer (compare footnote *h*) was 12.68. Calcd. 12.81. [j] Identity of the acetate mixture from 6 and 7 was demonstrated by non-depression of the m.p. on admixture and identical infrared traces. The infrared traces of the β-chloro sulfides (cpds. 6 and 7) showed distinct differences. The dry acetic acid was prepared by refluxing glacial acid with excess acetic anhydride and distilling through a four-foot column, packed with glass helices. [k] Ultraviolet spectra of compounds 1–4, inclusive, as well as of the corresponding acetates revealed a distinct tendency for the compounds derived from *trans*-2-butene to show maxima at longer wave lengths than those of the corresponding isomer from *cis*-2-butene. These results and the infrared spectra will be reported in a subsequent publication.

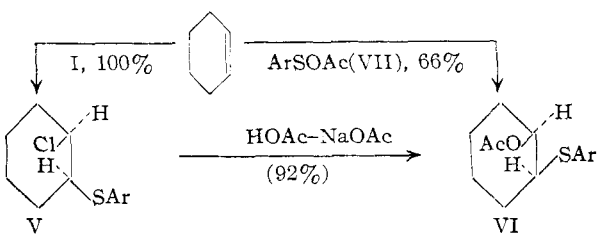
elementary analyses and infrared spectra. Acetic acid was chosen for the solvolyses, for it is known[10,11] to be an effective reagent for solvolytic reactions involving participation by neighboring groups.

The formation of the identical product mixture from III or IV (Ar = 2,4-dinitrophenyl) is strong evidence that the acetolyses of compounds 6 and 7, and the related acetolyses of Table I, involve participation by sulfur, and we would therefore formulate the reactions as proceeding through an intermediate as C. This conclusion is also supported by the evidence gained from the stereospecificities of the acetolyses (as found in the present study), considered in conjunction with the kinetic results of Baddeley and Bennett.[12] These workers found that the hydrolysis of a series of β-chloroalkyl aryl sulfides, in aqueous acetone, with more than 50% water, followed first order kinetics and that the SN1 processes were facilitated by electron releasing Ar groups (*e.g.*, *p*-tolyl). In contrast, the reactions of the same β-chloroalkyl aryl sulfides with iodide ions were second order (first order with respect to each of the reactants), and the rates were clearly depressed by electron-releasing groups, such as *p*-nitrophenyl or 2,4-dinitrophenyl). Projection of the results of Baddeley and Bennett on the hydrolyses of the β-chloroalkyl aryl sulfides in acetone–water solvent, to acetic acid solvent would exclude the SN2-type reaction as an explanation for the stereospecific acetolyses which we have found. Although Baddeley and Bennett did not interpret their results in terms of an intermediate cyclic ion, it now seems quite likely (similarly as in the present study) that such an intermediate is involved in the hydrolyses they carried out. The postulation of such a cyclic intermediate is, of course, predicted on the *fundamenta lassumption* that the corresponding free carbonium ion would be unable to retain its configuration.

In the present work, the possibility that a prior (or some actual) participation by oxygen of an *o*-nitro group occurs[13] is not completely ruled out. Further work on the precise hydrolytic rates of III and IV, and of the acetates corresponding to these isomers, may help to clarify this question of prior participation. However, since it is desirable first to determine the general nature of the participation, kinetics studies on the cyclohexene adducts of Table I have been undertaken. In the absence of complicating factors, first order solvolyses would be expected and the relative effectiveness of various ArS groups may be ascertained by comparing an appropriate series of the β-chloroalkyl aryl sulfides.

(10) E. Grunwald and S. Winstein, THIS JOURNAL, **70**, 846 (1948).
(11) C. G. Swain and W. P. Langsdorf, *ibid.*, **73**, 2813 (1951).
(12) G. Baddeley and G. M. Bennett, *J. Chem. Soc.*, 261 (1933).
(13) *Cf.* D. J. Cram and M. J. Hatch, THIS JOURNAL, **75**, 33, 38 (1953). Participation by other complex groups is discussed by S. Winstein and R. Boschan, *ibid.*, **72**, 4669 (1950).

To establish whether addition of the sulfenyl halide is *cis* or *trans*, the following evidence was collected: (a) V, the cyclohexene adduct of I, was converted in 92% yield to the corresponding acetate VI; and (b) the same acetate was also obtained (66% yield) by adding 2,4-dinitrobenzenesulfenyl acetate, VII, to the olefin. The identity of I from either route was established by melting points, mixture-melting points, infrared spectra and separate elemental analyses. These results can be suitably explained by stating that the additions of I and VII to cyclohexene occur in a *trans* manner; and that acetolysis of the adduct of I to cyclohexene (compound V) proceeds with retention of configuration, involving participation by sulfur. Alternatively, if *cis* addition of I is assumed, then it is necessary that VII adds to yield the *trans* product and that acetolysis of V proceeds by an SN2 process, without participation by the –SAr group. This alternate set of circumstances seems entirely unlikely, for one would expect both I and VII to add to cyclohexene in the same fashion. Finally, *cis* addition of I to cyclohexene would give a β-chloroalkyl aryl sulfide which should lead—by an unassisted SN1 process—to an acetate mixture which would contain mostly the inverted form,[14] and hence would be different from the acetate obtainable by *cis* addition of VII to cyclohexene. The practically quantitative conversion of V to VI speaks strongly against the latter suggested explanation.



The *trans* structure for V is also necessary, in view of the finding that solvolysis occurs with participation, since the stereochemistry of the cyclohexane ring[15] requires the Cl– and –SAr groups to be *trans* for participation to occur.[16] The recent work of Goering,[17] and Cristol[18] and Truce[19] and their co-workers, on the additions of benzenesulfenyl chloride and *p*-toluenesulfenyl chloride to cyclohexene,[17] norbornylene[18] and acetylene[19] also led these workers to conclude (on the basis of stereochemical evidence other than that used in our case) that the additions were *trans*. Such reports lend support to our present and earlier suggestions that the additions of sulfenyl halides to olefins[3] and acetylenes[20] must be *trans*, in analogy to the ionic addition of bromine to olefins.[21,22]

Brief comment on 2,4-dinitrobenzenesulfenyl acetate is in order. This compound VII is the first example of a new class of sulfenyl derivatives, although the corresponding selenenyl acetate is known[23] and the additions of 1-anthraquinoneselenenyl acetate and 4-methoxy-1-anthraquinoneselenenyl acetate to cyclohexene and styrene have been reported recently, for the first time.[24] The sulfenyl acetate was synthesized by a modification of the procedure of Buess,[25] who was the first to prepare this substance, and who called attention to its explosive character. Since the product was not fully characterized in the earlier work,[25] this was now done, by elementary analysis, determination of equivalent weight (*via* iodometric titration, using the procedure of Kharasch and Wald[26]) and determination of the infrared spectrum to establish the presence of the carbonyl group. In the present work, however, no explosions were incurred during the analysis of the sample (compare ref. 25), nor was any other difficulty found in handling the sulfenyl acetate. The addition of the sulfenyl acetate (VII) to cyclohexene was carried out in ethylene chloride as solvent, and required—in contrast to the addition of I—an extended period to complete the reaction.

Acknowledgment.—We are indebted to the Atomic Energy Commission and the Office of Ordnance Research for support of this study, to Dr. M. M. Wald for assistance in the iodometric analysis of 2,4-dinitrobenzenesulfenyl acetate and to Mr. W. J. Schenck for the elementary analyses.

Experimental

Acetolyses of the β-Chloroalkyl 2,4-Dinitrophenyl Sulfides (Compounds 1 to 7 of Table I).—The major experimental data are summarized in Table I. The following are typical procedures used to solvolyze the sulfides and to isolate the products.

(a) *threo*-1-Methyl-2-acetoxypropyl 2′,4′-Dinitrophenyl Sulfide from *threo*-1-Methyl-2-chloropropyl 2′,4′-Dinitrophenyl Sulfide.—To 5.7 g. (0.0196 mole) of the β-chloro

(14) E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 83.

(15) O. Hassel, *Quart. Revs.*, **VII**, 221 (1953).

(16) The importance of the *trans* location of Cl– and –SAr is shown by the recent study of Relyea, Larsen and Goering [Abstracts of the Meeting of the American Chemical Society, Cincinnati, Ohio, April 3, 1955], who found that the rate of solvolysis of V, Ar = phenyl, in 80% ethanol solutions, was at least one thousand times as great as that of the corresponding *cis* isomer.

(17) H. L. Goering, private communication, April, 1955.

(18) S. J. Cristol and G. D. Brindell, Paper presented before the Organic Division, American Chemical Society Meeting, April 3, 1955; Cincinnati, Ohio.

(19) W. C. Truce, private communication, July, 1955.

(20) N. Kharasch and S. J. Assony, THIS JOURNAL, **75**, 1081 (1953).

(21) For a discussion of the analogy of the addition of I to olefins, compared to the addition of bromine and based on relative rates of additions, see D. R. Hogg and N. Kharasch, following paper of this series.

(22) We are aware that another way in which the questions posed in this paper could be answered would be to study the kinetics of the acetolysis of resolved A and B (Ar = 2-nitro-4-carboxyphenyl). If addition was *trans*, and an intermediate as C involved in the solvolyses, only A should lose its optical activity completely, and, in the absence of complicated solvolysis kinetics—at a rate equal to the titrimetric rate of release of chloride ion. If, however, addition of II were *cis* (leading to the *erythro*-type compound from *cis*-2-butene), the opposite effects would be found. An inherent difficulty in this approach is the possibility (encountered in studies of related β-chloro sulfides) that a reversible elimination of hydrogen chloride may occur, so that, in effect, a symmetrical intermediate (the vinyl sulfide) could be encountered in the solvolysis of both A and B (Ar = 2-nitro-4-carboxyphenyl), thereby vitiating any conclusions to be drawn from the approach suggested above. Besides this, some complexities were revealed in the initial studies of the kinetics of the acetolyses of compounds as A and B (Ar = 2-nitro-4-carboxyphenyl). While these are of interest for their own sake, and will be published separately, these factors led us to abandon, for the present, this alternate approach—in favor of the one recorded in this paper.

(23) O. Behaghel and W. Muller, *Ber.*, **68**, 1540 (1935).

(24) W. Jenny, *Helv. Chim. Acta*, **36**, 1278 (1953).

(25) C. M. Buess, Doctoral Dissertation, University of Southern California, (1949).

(26) N. Kharasch and M. M. Wald, *Anal. Chem.*, **27**, 996 (1955).

sulfide (*cf.* ref. 3 for its preparation), was added 170 ml. dry acetic acid (*cf.* footnote *j*, Table I) and the mixture was refluxed *ca.* 42 hr., cooled to room temperature and poured on 400 g. of ice. The precipitated acetate was collected and dried at 80° for 12 hr.; wt. 5.8 g. (95% yield); m.p. 118–120°. Recrystallization from dry carbon tetrachloride raised the m.p. to 121.5–122.5°, and the m.p. was not changed by drying at 84° and 1 mm. mercury pressure for 6 hr. A mixture of this product and the original β-chloro sulfide (cpd. 1, Table I; m.p. 128–129°) melted at 100–106°. The difference between the racemic acetate, here obtained, and the one from the similar acetolyses of compound 2 (adduct of 2,4-dinitrobenzenesulfenyl chloride to *trans*-2-butene) was shown by the differences in melting points and by the infrared traces. The latter revealed distinct differences in the 9.5 μ region. The spectra were taken on saturated solutions of the acetates in carbon tetrachloride, using a Perkin–Elmer double-beam instrument.

The identical product was also obtained from 3.0 g. (0.0103 mole) of compound 1, by refluxing with 200 ml. of dry acetic acid and 3.0 g. (0.0365 mole) of sodium acetate, pouring on 300 g. of ice and drying 12 hr. at 80°; 2.9 g. (90% yield); m.p. 121–122°, and giving no depression on admixture with the racemic acetate obtained, above, by using acetic acid alone for the acetolysis.

(b) ***erythro*-1-Methyl-2-acetoxypropyl 4′-Carboxy-2′-nitrophenyl Sulfide from *erythro*-1-Methyl-2-chloropropyl 4′-Carboxy-2′-nitrophenyl Sulfide.**—The β-chloro sulfide (cpd. 4, Table I), 4.0 g. (0.0128 mole) was refluxed *ca.* 12 hr. with 60 ml. of dry acetic acid. The mixture was taken to dryness (aspirator, water-bath) and the residue dried (72 hr., at room temp. and 1 mm. mercury pressure); wt. 4.3 g.; *ca.* 100% yield. The crude crystals melted at 123–126°. They were dissolved in *ca.* 40 ml. of methanol and precipitated by adding an equal volume of water. After two such purifications, yellow crystals, m.p. 124–125°, were obtained. When dried at 118° and 1 mm. mercury pressure for 12 hr., the m.p. rose to 127–128°. The analysis is given in Table I.

The same product, as just above, was obtained by refluxing for 3.33 hr. 5.0 g. (0.0173 mole) of compound 4, Table I, and 2.84 g. (0.0345 mole) of sodium acetate in 200 ml. of dry acetic acid. After heating about half an hour, white crystals (probably sodium chloride) were noted. After the full period of heating, the mixture was filtered and the filtrate taken to dryness, giving a yellow, crystalline residue, m.p. 190–200°, and weighing 5.6 g. (96% yield, calcd. as the sodium salt of the acetolysis product (*i.e.*, the sodium salt of 1-methyl-2-acetoxypropyl 4′-carboxy-2′-nitrophenyl sulfide)). The material was quite soluble in methanol. Hydrolysis of the salt in excess of hot water gave a substance which, after drying 24 hr. at 85°, melted at 126.0–126.5° and gave no depression on admixture with the acetate obtained by using acetic acid alone as the acetolysis reagent. The infrared and ultraviolet spectra of this product, as well as of the other reactants and products of Table I, were determined but will be published separately; *cf.* footnote *k*, Table I.

(c) **Acetolyses of the Isomeric Adducts of 2,4-Dinitrobenzenesulfenyl Chloride to Propylene.**—To 2.80 g. of cpd. 6 (Table I) was added 130 ml. of dry acetic acid and 3.0 g. of sodium acetate. The mixture was refluxed *ca.* 90 hr. The precipitated sodium chloride was removed and the filtrate taken to dryness. The residue was extracted with 80 ml. of hot carbon tetrachloride and the extract was cooled and diluted with ligroin (b.p. 35–57°) until the solution became opaque. Cooling and scratching precipitated a white powder, from which the analytical sample (Table I) was prepared by repetition of the above process. The product melted at 51.5–53.5°, but was not obtained in good yield in this trial experiment, because of mechanical losses.

Repetition, using 0.75 g. of cpd. 6 and 75 ml. of dry acetic acid, at reflux for 120 hr., gave 0.66 g. (81%) of the acetate, m.p. 50–53°. The acetolysis is quite slow, as evidenced by nearly complete recovery of the β-chloro sulfide, and no isolation of the desired product, if refluxing was stopped after 17.5 hr.

To 0.50 g. of cpd. 7, Table I, was added 1.0 g. of sodium acetate and 50 ml. of dry acetic acid. The mixture was refluxed 120 hr., evaporated to dryness, extracted with 20 ml. of boiling carbon tetrachloride, and to the extract was added 100 ml. of ligroin (b.p. 35–57°). The white, powdery crystals melted at 50–53° and weighed 0.40 g. (74%). A mixture of this product and the acetolysis product of compound 5 gave no depression on admixture (m.p. 50–52.5°). The infrared spectra of Nujol mulls of the acetylated derivatives of 5 and 6 were identical.

2,4-Dinitrobenzenesulfenyl Acetate.—To 35.2 g. (0.43 mole) of freshly fused sodium acetate was added 10.0 g. (0.043 mole) of 2,4-dinitrobenzenesulfenyl chloride (I) and 300 ml. of dry benzene. The flask was stoppered, shaken mechanically for 22 hr. and the sodium chloride and unreacted sodium acetate collected and washed (into the major filtrate) with 500 ml. of dry ethylene chloride. Concentration of the filtrate at room temperature using an aspirator, gave a residue which did not melt, but which darkened to an orange solid at 85–90°. To this crude residue was added 500 ml. of dry benzene and the insoluble portion removed by filtration. Concentration of the benzene filtrate gave a residue consisting entirely of yellow needles. On heating, these turned orange at 93–105°, then red, and finally black on further heating. No appreciable melting could be observed, even when the sample was heated to 300°. However, at 250–300°, a colorless crystalline sublimate (unidentified) was observed above the black residue.

Anal. Calcd. for $C_8H_6N_2O_6S$: C, 37.21; H, 2.34; N, 10.85. Found: C, 37.42; H, 2.53; N, 11.00.

The product gave a negative Beilstein test, indicating absence of chlorine. Iodometric titration,[26] using sodium iodide in acetic acid, gave values of 260 ± 5 (calcd. for VII, 260) based on the equivalents of iodine liberated per mole of VII.

Another preparation, using 35.2 g. (0.43 mole) of freshly fused sodium acetate, 5.0 g. (0.022 mole) of I and 300 ml. of benzene, was carried out in a flask which was shielded to exclude light by shaking 41 hr. This gave 3.3 g. (60%) of yellow needles, which tested negatively for chlorine (Beilstein test) and decomposed at *ca.* 90–130°. The 3.3 g. does not represent the total weight of the residue, since only the material of needle-like structure was collected. No explosions were noted with the product during analyses, or at any other time (*cf.* discussion and reference 25).

Addition of 2,4-Dinitrobenzenesulfenyl Acetate to Cyclohexene.—To 4.0 g. (0.0155 mole) of VII was added 100 ml. of dry ethylene chloride and 10 ml. of pure cyclohexene. The mixture was immersed in a thermostat, at 50°, for 16 days. Solvent and excess cyclohexene were then removed (air stream) and the residue dried, by pumping (10 mm.) at room temperature. An attempt to purify the product by dissolving in hot carbon tetrachloride, cooling and adding ligroin (b.p. 35–37°) to reprecipitate the material, was not successful. However, chromatography of the reaction mixture on a column of alumina (20 × 2.5 cm.), using dry carbon tetrachloride as the solvent, and eluting with benzene, gave a green eluate, which—after concentrating to an oily residue—yielded a greenish-yellow solid, when ligroin (b.p. 35–57°) was added. This weighed 3.5 g. (66% yield) and melted at 82–83°.

Anal. Calcd. for $C_{14}H_{16}N_2O_6S$: C, 49.40; H, 4.76; N, 8.23; S, 9.43. Found: C, 49.64; H, 4.60; N, 8.50; S, 9.43.

A mixture of the above product and VI (obtained *via* V) showed no depression. The infrared spectra of these substances also exhibited no observable difference and both gave characteristic absorptions for a carbonyl group (*cf.* footnote *k*, Table I).

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