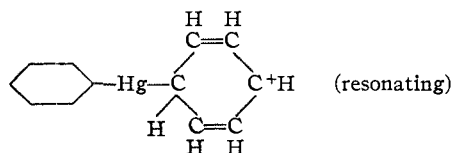


Conclusions

It is evident from our studies that the mechanism of cleavage of diphenylmercury by formic and acetic acids involves an attack of the acid upon the mercurial. Our results are consistent with the formulation of the first intermediate in the reaction as follows¹¹



It thus becomes possible to utilize the large variety of known aromatic mercurials for the purpose of studying the mechanism of aromatic substitution.

In spite of the general applicability of this mechanism, the kinetics of the cleavage reaction are not second order when followed through changes in concentration of each reagent. Further study will be necessary to determine whether or not molecular association constitutes the reason for the variation of the rate constant with changes in concentration.

One of us (M.A.N.) wishes to acknowledge a grant-in-aid from Hynson, Westcott and Dunning Research Fund.

Summary

1. The cleavage of diphenylmercury in diox-

(11) See Branch and Calvin, "Theory of Organic Chemistry," Prentice-Hall, New York, 1941, p. 473.

ane with formic and acetic acids has been followed dilatometrically.

2. The velocity constants are independent of the concentration of peroxide or of chloride ion at the saturation value in the reaction mixture.

3. The addition of water has little effect on the rate of cleavage.

4. The rate constant is increased by increasing acid strength.

5. The rate of the reaction is dependent upon the concentration of diphenylmercury. Within a single experiment, the rate constant does not drift with exhaustion of the reagent. In spite of this, the rate constant is dependent upon the initial concentration of diphenylmercury, decreasing concentration causing an increase in the rate constant.

6. The relation between the preceding observation and the possibility of molecular association of the diphenylmercury is discussed.

7. The rate of the reaction is dependent upon the concentration of the acid employed. The rate constant varies with the concentration of the acid, increasing with increasing concentration.

8. Two hypotheses are advanced to account for the variation of rate constant with acid concentration. The first assumes the formation of a polymolecular acid complex. The second assumes association between acid and solvent.

9. It is concluded that aromatic mercurials may be utilized to study the mechanism of aromatic substitution.

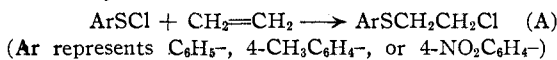
BALTIMORE 18, MARYLAND RECEIVED DECEMBER 11, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

Arylsulfenyl Chlorides. I. Addition to Unsaturated Compounds¹

BY ROBERT A. TURNER² AND RALPH CONNOR³

The arylsulfenyl halides, ArSX, discovered by Zincke,⁴ were reinvestigated by Lecher and his collaborators.⁵ Lecher and Stöcklin⁶ demonstrated that an arylsulfenyl chloride would react with ethylene



The yields of aryl β-chloroethyl sulfides varied from 60 to 80%. The investigations to be de-

(1) This paper is abstracted from the dissertation of Robert A. Turner presented to the Graduate School of the University of Pennsylvania in June, 1943, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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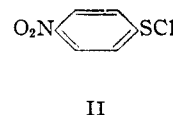
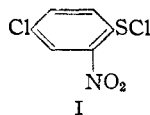
(4) Zincke, *Ann.*, **391**, 55; 57 (1912).

(5) The literature of arylsulfenyl chlorides is reviewed in a recent article by Kharasch, Potempa and Wehrmeister, *Chem. Rev.*, **39**, 269-332 (1946).

(6) Lecher and Stöcklin, *Ber.*, **58**, 414 (1925).

scribed here were undertaken in order to examine the generality of the addition of arylsulfenyl chlorides to unsaturated compounds.⁷

The arylsulfenyl chlorides chosen for use were 2-nitro-4-chlorophenylsulfenyl chloride (I) and 4-nitrophenylsulfenyl chloride (II). Of these, I



is the more stable and may be stored indefinitely. On the other hand, II can be stored only a few

(7) The work reported in this paper was completed in the spring of 1943, but war-time conditions have prevented earlier publication. Recently, Fuson, *et al.* [Fuson, Price, Bauman, Bullitt, Hatchard and Maynert, *J. Org. Chem.*, **11**, 469 (1946); Fuson, Price and Burness, *ibid.*, **11**, 475 (1946)] have reported the results of their work on the Levinstein process (for the synthesis of mustard gas) which includes a study of the addition of 2-chloroethylsulfenyl chloride to olefins.

hours: it fumes in moist air and cannot be isolated free of the disulfide from which it is prepared. Because of these properties II was not isolated before being used in the addition experiments: instead, its solution in chloroform was used directly. Because of the greater reactivity of II it seemed safe to assume that if an unsaturated compound reacted with I, it would surely react with II; and that if an unsaturated compound did not react with II, it would not react with I. Our findings have confirmed these assumptions.

The results of the experiments on the addition of I and II to olefins are summarized in Table I.

TABLE I
ADDITION OF SULFENYL CHLORIDES TO OLEFINS

Olefin	Yield on addition of I, %	II, % ^a
Cyclopentene	94	33
Cyclohexene	100	40
1,2-Dichloroethylene	0	0
1,1-Diphenylethylene	70	x
<i>i</i> -Butylene	96	x
Pentene-2	70	x
Stilbene	0	40
Styrene	91	x

^a 0 indicates no yield. x indicates that the reaction was not tried.

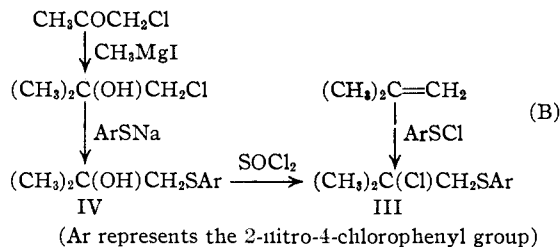
The chlorides I and II reacted vigorously with ordinary olefins. However, vicinal halogen atoms (1,2-dichloroethylene) decreased the reactivity of the double bond, and no reaction took place. When the double bond was conjugated with a carbonyl, carboxyl, or cyano group, no reaction occurred despite repeated attempts to induce addition.

Among the olefins stilbene was a special case, for while it failed to react with I, it reacted readily with II. Moreover, the primary product of addition, 1-(4-nitrophenylthio)-2-chloro-1,2-diphenylethane, was unstable and immediately decomposed with evolution of hydrogen chloride to give 4-nitrophenylthio-stilbene.

Besides the experiments on addition, unsuccessful attempts were made to effect reaction between the sulfenyl chlorides (I and II) and cyclopropane.

The direction of addition, which in the case of an unsymmetrical olefin is of prime importance, was proved in the case of isobutylene. When isobutylene was allowed to react with I, 1-(2-nitro-4-chlorophenylthio)-2-methyl-2-chloropropane (III) was formed, which was then prepared by an independent synthesis (B). Thus, during the addition of the sulfenyl chloride to the double bond of isobutylene the chlorine atom became linked to the less hydrogenated carbon atom.⁸

(8) This direction of addition of a sulfenyl chloride is confirmed by the results obtained by Fuson, Price, and Burness, ref. 7, in a study of the reaction of 2-chloroethylsulfenyl chloride with propylene.



The validity of the proof of the structure of III rests on the certainty of the structure of the chlorohydrin IV. The common syntheses of chlorohydrins lead usually to mixtures of isomers, and often, if the isomers are separable, investigators disagree in their assignment of structure to one isomer or the other. The Grignard synthesis leads to a single chlorohydrin, and the preparation of IV from chloroacetone and methylmagnesium iodide removes any doubt of its structure.

The Grignard synthesis was found, however, to be not of general application, for repeated attempts to prepare 1,1-diphenyl-2-chloroethanol by a Grignard synthesis failed. This result is in accord with those obtained by Huston, Jackson, and Spero,⁹ who have made a study of the Grignard synthesis.

Experimental

2,5-Dichloronitrobenzene.¹⁰—Into a 3 liter flask equipped with a mercury-sealed stirrer, a reflux condenser, and an addition tube fitted with a thermometer and a dropping funnel, were introduced 1 kg. (6.80 moles) of 1,4-dichlorobenzene and 600 cc. of concentrated sulfuric acid. One hundred cubic centimeters of concentrated nitric acid was added with stirring, followed by 375 cc. more at such a rate that the temperature remained below 110°. When all the nitric acid had been added, the mixture was stirred and heated at 105–115° for seven hours. The upper layer was decanted while it was still warm into a large pan containing 2 kg. of cracked ice. When the product had solidified, it was broken up, washed with sodium carbonate solution, filtered and dried. It weighed 1250 g. (96%) and melted at 52–54°; reported, 53–54°¹¹ and 54.6°.¹²

bis-(2-Nitro-4-chlorophenyl) disulfide was prepared from 2,5-dichloronitrobenzene and sodium disulfide by the method of Bogert and Stull.¹³ The product was washed with warm acetic acid; yield 60–65%; m. p. 207–218°; reported,¹⁴ 212–218°.

bis-(4-Nitrophenyl) disulfide was prepared from 4-nitrochlorobenzene by the method of Bogert and Stull.¹³ After one recrystallization from glacial acetic acid the product was obtained in yield of 56%; m. p. 178°, reported¹⁵ 181°.

2-Nitro-4-chlorophenylsulfenyl chloride (I) was prepared by chlorination of bis-(2-nitro-4-chlorophenyl) disulfide in chloroform by the method of Zincke and Bauemer¹⁴ in 80–85% yield; m. p. 97.5–98° (yellow needles); reported,¹⁴ 98°.

4-Nitrophenylsulfenyl Chloride, II.—In a filter flask containing 60 cc. of dry chloroform was suspended 7.70 g. (0.025 mole) of bis-(4-nitrophenyl) disulfide. Chlorine

- (9) Huston, Jackson and Spero, *THIS JOURNAL*, **63**, 1459 (1941).
 (10) Procedures for the preparation of this compound which were found in the literature were unsatisfactory.
 (11) Ganopol'skii, *Org. Chem. Ind. U.S.S.R.*, **1**, 342 (1936); *C. A.*, **30**, 6347 (1936).
 (12) Crauw, *Rec. trav. chim.*, **50**, 753 (1931).
 (13) "Organic Syntheses," Coll. Vol. I, p. 220 (2nd ed.).
 (14) Zincke and Bauemer, *Ann.*, **416**, 86 (1918).
 (15) Zincke and Lenhardt, *Ann.*, **400**, 1 (1913).

was bubbled through the suspension with exclusion of moisture. When all of the disulfide had dissolved, dry air was sucked through the solution for twenty minutes. The solution was filtered directly into the apparatus in which it was to be used.

Addition of 2-Nitro-4-chlorophenylsulfenyl Chloride to Olefins

1-(2-Nitro-4-chlorophenylthio)-2-chlorocyclopentane (V).—To 16.8 g. (0.075 mole) of I, dissolved in 50 cc. of dry chloroform was added 7.0 g. (0.010 mole) of cold cyclopentene. The solution immediately became warm. It was heated under reflux for four hours and then evaporated to dryness. The residue (20.6 g., m. p. 53–55°) was recrystallized from ethanol-ether; yield, 16.0 g. of yellow crystals (73%); m. p. 58.8–60.0° (cor.).

Anal. Calcd. for $C_{11}H_{11}O_2SNCl_2$: N, 4.78; mol. wt., 292. Found: N, 4.52; mol. wt., 291.

1-(2-Nitro-4-chlorophenylthio)-2-chlorocyclohexane.—This compound was prepared in the same way as V; yield, 100%. The pure compound consisted of yellow crystals; yield, 71%; m. p. 79.2–79.6° (cor.).

Anal. Calcd. for $C_{12}H_{13}O_2SNCl_2$: N, 4.57; S, 10.47. Found: N, 4.33; S, 10.22.

1-(2-Nitro-4-chlorophenylthio)-2-methyl-2-chloropropane (III).—*i*-Butylene was generated by very slow addition of a solution of 5 cc. of concentrated sulfuric acid in 5 cc. of water to 30 g. (0.40 mole) of boiling tertiary butyl alcohol. The isobutylene was passed through tubes of calcium chloride and of soda-lime into a stirred solution of 22.4 g. (0.10 mole) of I in 70 cc. of dry chloroform (previously warmed to 50°) at such a rate that the temperature of the solution remained at 40°. Evaporation of the solvent left 27.0 g. (96.4%) of yellow crystals which melted at 75–79°. After two recrystallizations from ethanol the melting point became constant at 79.4–80.2° (cor.).

Anal. Calcd. for $C_{10}H_{11}O_2SNCl_2$: N, 5.00; mol. wt., 280. Found: N, 4.91; mol. wt., 292.

Product from Styrene.—The addition product from I and styrene, prepared in the same way as V, was obtained in yield of 91%; m. p. 57–63°. After three recrystallizations from benzene-petroleum ether the yellow crystals melted at 62.4–62.8° (cor.).

Anal. Calcd. for $C_{11}H_{11}O_2NSCl_2$: N, 4.27. Found: N, 4.08.

Product from Pentene-2.—The addition product from I and pentene-2¹⁶ prepared in the way described for V was difficult to purify. After several recrystallizations from petrol ether, a pure sample (yellow crystals) was obtained; m. p. 93.0–93.6° (cor.).

Anal. Calcd. for $C_{11}H_{13}O_2SNCl_2$: N, 4.76. Found: N, 4.40.

Product from 1,1-Diphenylethylene.—The addition product from I and 1,1-diphenylethylene, prepared in the way described for V, except that the reflux period was eleven hours, crystallized when the reaction mixture was concentrated and ethanol was added; yield, 76%; m. p. 92–95°. After two recrystallizations from benzene-methanol the product was obtained in the form of red crystals, m. p. 102.8–103.4° (cor.).

Anal. Calcd. for $C_{20}H_{15}O_2SNCl_2$: N, 3.47; S, 7.93. Found: N, 3.58; S, 8.07.

Addition of 4-Nitrophenylsulfenyl Chloride to Olefins

1-(4-Nitrophenylthio)-2-chlorocyclohexane.—To a solution of II in chloroform, prepared as described above and chilled in an ice-bath, was added a cold solution of 4.10 g. (0.05 mole) of cyclohexene in 50 cc. of chloroform. The solution was left overnight; next day most of the solvent was distilled. The product crystallized in the cold. Two recrystallizations from methanol gave 4.10 g. (30%) of yellow crystals; m. p. 65.6–65.8° (cor.).

(16) "Organic Syntheses," Coll. Vol. I, p. 430 (2nd ed.).

Anal. Calcd. for $C_{12}H_{14}O_2SNCl$: S, 11.80; mol. wt., 272. Found: S, 11.93; mol. wt., 278.

1-(4-Nitrophenylthio)-2-chlorocyclopentane.—This compound was prepared in the same way as 1-(4-nitrophenylthio)-2-chlorocyclohexane, except that the reaction mixture was heated under reflux for two hours before distillation of the solvent. The residue was crystallized from alcohol-ether after filtration of insoluble matter. The product was obtained in the form of light yellow crystals in 33% yield; m. p. 41–43°. A recrystallization afforded a sample of m. p. 49.8–50.6° (cor.).

Anal. Calcd. for $C_{11}H_{12}O_2SNCl$: N, 5.44; mol. wt., 258. Found: N, 5.35; mol. wt., 259.

(4-Nitrophenylthio)-stilbene.—When 9.0 g. (0.05 mole) of stilbene was added to a solution of II in chloroform, the mixture became warm. After it had cooled somewhat, it was heated under reflux, when hydrogen chloride was evolved. After the evolution had ceased, the solvent was allowed to distil. The residue was dissolved in hot 95% ethanol; the solution was filtered to free it of insoluble matter and then concentrated. The crystallize which formed in the cold was recrystallized twice from ethanol. The product weighed 5.0 g. (30%); m. p. 106.4–108.0° (cor.). A test for halogen was negative.

Anal. Calcd. for $C_{20}H_{15}O_2SN$: S, 9.62; mol. wt., 333. Found: S, 9.63; mol. wt., 341.

Alternative Synthesis of III

2-Methyl-2-chloropropanol-1.—Attempts to prepare this chlorohydrin from ethyl chloroacetate and methylmagnesium iodide failed. Its synthesis was accomplished with chloroacetone.

Methylmagnesium iodide was prepared in the usual fashion from 15 g. (0.62 mole) of magnesium turnings, and a solution of 45 g. (0.49 mole) of chloroacetone in 100 cc. of ether was added slowly. The product was decomposed with saturated aqueous ammonium chloride solution. The reddish-brown ether solution was washed with dilute sodium thiosulfate until the color no longer diminished, when the solution was light yellow. The solution, dried over sodium sulfate, was distilled, first at atmospheric pressure, and finally at 20 mm. The clear distillate was decolorized and dried as before, and redistilled at atmospheric pressure. As soon as heat was applied, the distillate rapidly darkened. When most of the product had passed over, dark fumes were evolved, and the distillation was interrupted at once. A fraction weighing 8.0 g. (15%) distilled at 126–128° (uncor.); reported¹⁷ 126–128°.

2-Nitro-4-chlorothiophenol.—This compound was prepared from bis-(2-nitro-4-chlorophenyl) disulfide and alkaline dextrose solution, according to the method Claasz¹⁸ in yield of 55%; m. p. 117°; reported¹⁹ 122°.

1-(2-Nitro-4-chlorophenylthio)-2-methyl-2-hydroxypropane.—Eighteen grams (0.10 mole) of 2-nitro-4-chlorothiophenol was dissolved in a solution of 5 g. (0.12 mole) of sodium hydroxide in 100 cc. of water. The solution was mixed with a solution of 8.0 g. (0.08 mole) of 2-methyl-2-chloropropanol-1 and stirred at 60–70° for forty-five minutes. A dark oil separated which became crystalline overnight. The supernatant liquor was decanted and extracted with ether three times. The dark crystals were dissolved in the combined ether extracts, and the ether solution, dried over sodium sulfate, was evaporated. The residue melted at 50°. After recrystallization from aqueous methanol the product weighed 11 g. (57%) and melted at 82–89°. After two further recrystallizations the melting point was 89.8–90.4°.

Anal. Calcd. for $C_{10}H_{12}O_3SNCl$: N, 5.35. Found: N, 5.17.

1-(2-Nitro-4-chlorophenylthio)-2-methyl-2-chloropropane.—Five grams of 1-(2-nitro-4-chlorophenylthio)-2-

(17) Michael and Leighton, *Ber.*, **39**, 2789 (1906).

(18) Claasz, *Ber.*, **45**, 2427 (1912); Lecher and Simon, *ibid.*, **55**, 2423 (1922).

(19) Blankensma, *Rec. trav. chim.*, **20**, 339 (1901).

methyl-2-hydroxypropane dissolved in 60 cc. of chloroform was treated with 4.0 g. of thionyl chloride, and the solution was boiled under reflux for four hours. After distillation of the solvent, the residue was boiled with alcohol. A considerable quantity of insoluble substance, identified as bis-(2-nitro-4-chlorophenyl) disulfide, was removed by filtration. The concentrated filtrate was again freed of insoluble matter and left in the cold. It yielded crystals of m. p. 76–79° which, after two recrystallizations from ethanol, melted at 79–80°. The melting point of a mixture of this substance and the product from the addition of I to *i*-butylene (III) was undepressed.

Other Experiments

The following compounds could not be induced to react with either I or II: *trans*-dichloroethylene, phenanthrene, mesityl oxide, ethyl maleate, ethyl fumarate, benzalacetophenone, acrylonitrile, and cyclopropane. In several cases when I was employed, most of it was recovered.

1,1-Diphenyl-2-chloroethanol could not be prepared by the Grignard synthesis, reported by Klages and Kessler.²⁰

(20) Klages and Kessler, *Ber.*, **39**, 1754 (1906).

Summary

The addition of arylsulfenyl chlorides to olefins has been studied. The yields in favorable cases were nearly quantitative, but were greatly diminished or null in cases of olefins having electronegative substituents (such as phenyl or halogen) adjacent to the double bond. The arylsulfenyl chlorides did not add to double bonds conjugated with a carbonyl or nitrile group.

It was demonstrated that when arylsulfenyl chloride added to the double bond of isobutylene, the chlorine atom became linked to the less hydrogenated carbon atom while the sulfur atom became linked to the more hydrogenated carbon atom.

SUMMIT, NEW JERSEY
PHILADELPHIA, PENNSYLVANIA

RECEIVED DECEMBER 12, 1946

[CONTRIBUTION FROM SOCONY-VACUUM LABORATORIES (A DIVISION OF SOCONY-VACUUM OIL CO., INC.) RESEARCH AND DEVELOPMENT DEPARTMENT]

Acylation Studies in the Thiophene and Furan Series. II. Zinc Chloride Catalyst

BY HOWARD D. HARTOUGH AND ALVIN I. KOSAK¹

The authors have previously reported that iodine and hydriodic acid catalyze the acylation of thiophene and furan with acid anhydrides and halides.²

Zinc chloride and zinc bromide have been found to be effective catalysts for the acylation of thiophene if employed in amounts ranging from 0.01 to 0.03 mole per mole of acylating agent. Yields as high as 87% of 2-acetylthiophene and 95% of 2-benzoylthiophene have been obtained from the respective acid anhydrides with an excess of thiophene using 0.03 mole of fused zinc chloride as catalyst. Higher concentration of catalyst caused decomposition of the 2-acetylthiophene. In two otherwise identical experiments yields of 11 and 78% of 2-acetylthiophene were obtained from reaction mixtures wherein 0.5 mole of zinc chloride was used and the reaction time varied from two hours to five minutes. Continued heating after the initial heat of reaction caused thiophene ring rupture with evolution of hydrogen sulfide and formation of unidentified tars. Zinc fluoride failed to catalyze this reaction. Aluminum chloride, ferric chloride, mercuric chloride and stannic chloride failed to promote acylation of thiophene with acetic anhydride when employed in amounts of 0.01 mole per mole of anhydride.

Furan also is acylated with acetic anhydride in a similar manner giving a 66% yield of 2-acetylfuran. The preferred reaction temperature is much lower, 0–20°, since two otherwise similar

runs at 0–20° and 30–60° give yields of 66 and 40%, respectively, of 2-acetylfuran.

2-Acetylthiophene can be further acylated with acetic anhydride in the presence of zinc chloride to give about a 6% yield of 2,5-diacetylthiophene. Diacylation of the thiophene nucleus has previously been observed by v. Schweinitz³ who reported that the acetylation of octylthiophene yielded some octyldiacetothienone. Attempts to improve the yield above 6% have not been successful.

The use of aliphatic and aromatic anhydrides is preferred to the corresponding acyl chlorides since higher yields are obtained with the anhydrides.

Attempts to acylate aromatic hydrocarbons under the conditions described herein have not been successful.

Zinc chloride is well known as a catalyst for the acylation of phenol and resorcinol,⁴ but equimolar amounts of catalyst are required. The singular action of zinc chloride as a catalyst in this reaction indicates that it does not undergo complex formation with acyl halides and acid anhydrides in the same manner as aluminum chloride.⁵

Experimental

2-Acetylthiophene.—To 168 g. (2 moles) of thiophene and 107 g. (1 mole) of 95% acetic anhydride was added 4.0 g. (0.03 mole) of fused zinc chloride, previously pow-

(3) v. Schweinitz, *Ber.*, **19**, 646 (1886).

(4) Nencki, *et al.*, *J. prakt. Chem.*, [2] **23**, 147–546 (1881); Ward, *J. Chem. Soc.*, **119**, 852 (1921).

(5) Groggins, Nagel and Stirton, *Ind. Eng. Chem.*, **26**, 1317 (1934).

(1) Present address: Department of Chemistry, Ohio State University, Columbus, Ohio.

(2) Hartough and Kosak, *THIS JOURNAL*, **68**, 2639 (1946).