[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MAINE]

Methanesulfenyl Chloride. III. The Reactions with Methanol and Methyl Sulfite[1]

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Received September 20, 1961

Methanesulfenyl chloride (I) has been reported previously to react with methanol forming methyl chloride, methyl disulfide (IV), and methyl methanethiolsulfonate (V) through the intermediate formation of methyl methanesulfenate (II) and methyl methanethiolsulfinate (III), followed by disproportionation of the latter. Further study of the reaction has revealed that methanesulfinyl chloride (VI), methyl methanesulfinate (VII), and methanesulfonyl chloride (X) are also products of the reaction. The formation of these additional compounds is explained by assuming that I reacts with III to form VI, which then reacts with methanol to form VII, which, in turn, is attacked by I in two ways, forming VI and X as end products.

Methyl sulfite, a mild alkoxylating agent, reacts with I to form most of the same products that result from the reaction of I with methanol. The sequence of reactions by which these are formed appears to be very similar to that followed in the methanol reaction.

The reaction with methanol. Sulfenyl chlorides may be considered as the acid chloride derivatives of sulfenic acids. Some representatives of the class, such as trichloromethanesulfenyl chloride, readily form esters[3] in keeping with their acid chloride character. In a previous paper from this laboratory,[4] however, it was pointed out that methanesulfenyl chloride (I), when it reacts with methanol, does not yield the expected methyl methanesulfenate (II) but rather gives a mixture of products in which methyl chloride, methyl disulfide, and methyl methanethiolsulfonate have been identified.

As this reaction of I with methanol seemed to afford a relatively simple means to form methyl methanethiolsulfonate, a study was begun in an effort to extend the reaction to other sulfenyl chlorides and other alcohols. Difficulties arose, however, in that the yields of thiolsulfonates were variable and, on distilling the reaction mixtures, intermediate fractions containing chlorine were obtained which could not be accounted for by the reaction sequence previously advanced.

Qualitative tests on the intermediate fractions indicated that they contained sulfinyl and sulfonyl chlorides. Later, the infrared spectrum of one fraction showed an absorption band of 1010 cm.$^{-1}$ strongly suggesting the presence of methyl methanesulfinate. These facts, together with others found in later experiments, convinced us that the sequence of reactions was more involved than previously supposed and followed the path outlined in Figure 1. The complexity of the reaction, we believe, results from the electrophilic character of I which causes it to react not only with the initial reactant, methanol, but also successively with intermediate products having unshared electron pairs.

One can hardly doubt that methyl methanesulfenate (II) is the first product of the reaction in view of the stable sulfenate esters formed by analogous reactions.[3] The formation of methyl methanethiolsulfinate (III), likewise, seems a logical next step in the reaction sequence for the reasons previously advanced.[4]

The disproportionation of III into methyl disulfide (IV) and methyl methanethiolsulfonate (V) under conditions somewhat different than those employed in this study has been reported.[5,6] Attempts in our laboratory to prepare III by the conventional method[7] have yielded only trace amounts, but we have treated the more easily prepared ethyl ethanethiolsulfinate with anhydrous hydrogen chloride at −35° and have found that it readily disporportionates into ethyl disulfide and ethyl ethanethiolsulfonate. Hydrogen chloride appears to be a catalyst for the disproportionation of compounds of this type. In a recent study of the reaction of I with ethylene oxide,[8] 2-chloroethyl methanethiolsulfinate was postulated as an intermediate, but in the absence of hydrogen chloride there was no evidence of disproportionation.

In addition to its tendency to disproportionate, III might be expected to be susceptible to electrophilic attack on sulfur by I with the production of methyl disulfide (IV) and methanesulfinyl chloride (VI). Because we could not obtain III in sufficient quantity to test this reaction the higher homolog, ethyl ethanethiolsulfinate, was treated with ethanesulfenyl chloride and formed a constant-boiling

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

[2] National Defense Education Act Fellow, 1960–1961.

[3] G. Sosnovsky, *J. Chem. Soc.*, 3139 (1956).

[4] I. B. Douglass, *J. Org. Chem.*, **24**, 2004 (1959), paper I of this series.

[5] H. J. Backer and H. Kloosterziel, *Rec. trav. chim.*, **73**, 129 (1954).

[6] F. Ostermayer and D. S. Tarbell, *J. Am. Chem. Soc.*, **82**, 3752 (1960).

[7] La V. D. Small, N. H. Bailey, and C. J. Cavallito, *J. Am. Chem. Soc.*, **69**, 1710 (1947).

[8] I. B. Douglass and J. A. Douville, *J. Org. Chem.*, **25**, 2221 (1960), paper II of this series.

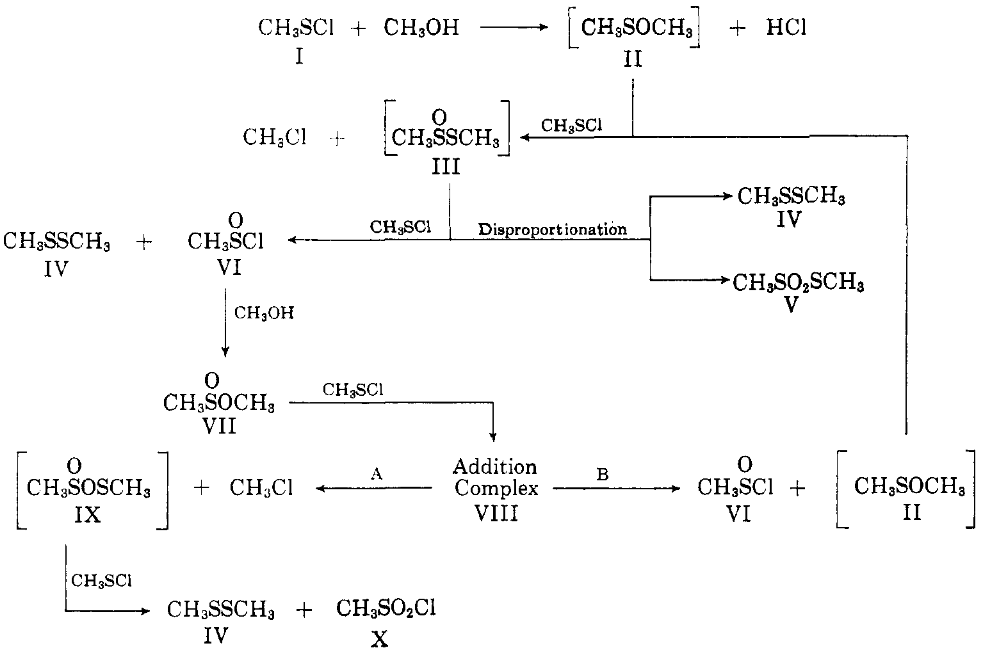

Figure 1

mixture of ethanesulfinyl chloride and ethyl disulfide.

The formation of VI in the reaction of I with methanol was confirmed by carrying out an experiment in which the proportion of reactants and the order of addition were so chosen that the sequence of reactions would end with free VI in the mixture. The addition of 0.2 mole of methanol to 0.6 mole of I gave a mixture from which was isolated 0.085 mole of the sulfinyl chloride VI.

Methanol readily reacts with VI to form methyl methanesulfinate (VII), hence the continued addition of methanol to a mixture in which VI was being formed would be expected to product VII. When 0.44 mole of methanol was added to 0.6 mole of I, a mixture was obtained from which was isolated 0.06 mole of methyl methanesulfinate (VII) in relatively pure condition. In all experiments the mixture of closely related compounds proved difficult to separate using a 15-in. Vigreux column. The instability of the compounds in the mixture, however, made the use of a more efficient column impractical. Identification of individual components was nevertheless readily accomplished by means of their infrared spectra, even though the fractions contained small amounts of impurities.

The positive identification of VII as one product of the reaction served to suggest the manner in which methanesulfonyl chloride (X), had been formed. In a previous paper[4] it was reported that I reacts with ethyl ethanesulfinate to form ethanesulfonyl chloride, methyl disulfide, and ethyl chloride. In the present study when pure VII was treated with I, methyl chloride, methyl disulfide (IV), methyl methanethiolsulfonate (V), methanesulfonyl chloride (X), and methanesulfinyl chloride (VI) were isolated, with VI being found in greater amount than X. These results suggested that the reaction between I and sulfinate esters not only occurs in the manner previously reported[4] (path A in Figure 1) but also by another pathway, indicated as B in Figure 1. Work is currently in progress which may shed light on the factors influencing the two pathways the reaction may take.

The reaction with methyl sulfite.[9] As sulfenyl chlorides are known to attack trialkyl phosphates with the formation of alkyl chlorides and thiophosphate esters,[10,11] it seemed possible that methanesulfenyl chloride might react with methyl sulfite, which is analogous to phosphite ester in that the central atom has an unshared electron pair, to form dimethyl thiosulfate, $CH_3SSO_2OCH_3$.

The reaction was attempted, but no product with the properties expected of dimethyl thiosulfate was found. It was then thought possible that the thiolsulfate ester had been destroyed through further reaction with I to form methyl disulfide and methyl chlorosulfonate, $ClSO_3CH_3$, in accordance with the previously established ability of I to react with thiol esters.[4] Methyl disulfide was readily detected among the products of the reaction, but all efforts to identify methyl chlorosulfonate were fruitless.

When the reaction was carried out in such a manner that volatile products could be collected in a

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[9] The senior author wishes to acknowledge the assistance of undergraduate students Norman O. Farrar and Lorraine L. Stubbs.

[10] E. E. Gilbert and C. J. McGough, U. S. Patents 2,690,450 and 2,690,451, September 28, 1954.

[11] D. C. Morrison, *J. Am. Chem. Soc.*, **77**, 181 (1955) and *J. Org. Chem.*, 21, 705 (1956).

Dry Ice trap, methyl chloride and sulfur dioxide were found in amounts which accounted for more than 80% of the sulfite ester consumed. It was then postulated that methyl chlorosulfonate might react with I in some way to form the products observed. A subsequent experiment, however, established that when I and methyl chlorosulfonate were brought together under the conditions previously employed, they reacted to form an unidentified solid in a manner unlike anything observed in the original reaction.

Herbrandson and others[12] have pointed out that esters of sulfurous acid behave as mild alkoxylating agents. This suggested the possibility that I and methyl sulfite might react to form methyl methanesulfenate (II) and methyl chlorosulfinate, CH_3OSOCl. As II is the same compound postulated as the initial product of the reaction between I and methanol, it would be expected to undergo further reaction with I and start a series of successive reactions in the same manner as proposed in Figure 1.

This idea initiated a search for the products shown in Figure 1. By varying the proportions of I and methyl sulfite and by carefully distilling the reaction mixtures, methanesulfinyl chloride (VI), methyl methanesulfinate (VII), and methanesulfonyl chloride (X) were isolated. The formation of methanesulfonyl chloride (IX) was easily explained, as work reported above had clearly demonstrated that it is formed when I reacts with methyl methanesulfinate (VII). The formation of VII, however, could only be explained by assuming that some of the original methyl sulfite had reacted with the methanesulfinyl chloride (VI) formed. A separate experiment demonstrated that this reaction takes place readily.

The fact that methyl methanethiolsulfonate (V in Figure 1) was not observed among the products of the reaction between I and methyl sulfite seemed unusual, as Figure 1 shows it as a disproportionation product of methyl methanethiolsulfinate (III). The explanation seems to lie in the fact that the disporportionation of thiolsulfinate esters is catalyzed by hydrogen chloride, none of which was produced in the reaction under discussion.

The idea that methyl chlorosulfinate might be a product of the initial reaction and might give rise to the sulfur dioxide observed was abandoned when a sample of this compound was prepared and found to be stable under the condition of the experiment. It also showed no tendency to react with I. These observations suggest that the initial addition complex formed when I and methyl sulfite react decomposes in such a way as to form methyl chloride and sulfur dioxide directly.

EXPERIMENTAL

Methanesulfenyl chloride was prepared by the method previously described.[4,8]

Reaction procedure. In the reaction with methanol the compound to be treated, either I or methanol, was placed in a 3-neck flask fitted with stirrer, dropping funnel, and outlet tube leading through a cold trap to a system for absorbing hydrogen chloride. The flask was surrounded by a bath cooled by Dry Ice to −20° or −30°. The reagent to be added, either methanol or I, was then run in slowly with constant stirring. When all had been added, the reaction mixture was allowed to warm slowly to room temperature with continued stirring, after which it was warmed briefly to 60° to facilitate escape of volatile products.

The liquid products were distilled at reduced pressure through a 15-in. Vigreux column. The contents of the cold trap, after being washed with alkali, dried, and recondensed was identified as methyl chloride by boiling point, molecular weight, infrared spectrum, and the formation of methylmercury chloride by means of the Grignard reagent. The isolation of methyl disulfide (IV) and methyl methanethiolsulfonate (V) from the reaction has already been described.[4]

Isolation of methanesulfinyl chloride VI *and methanesulfonyl chloride* X. The addition of 6.4 g. (0.2 mole) of methanol to 49.5 g. (0.6 mole) of I in the manner described resulted in a mixture from which were isolated 8.3 g. (0.085 mole) of VI and 1.1 g. (0.01 mole) of X. VI was identified by its boiling point, refractive index, and comparison of its infrared spectrum with that of an authentic sample.[13] It was further characterized by hydrolysis and reaction of its alkaline solution with benzyl chloride to form methyl benzyl sulfone, which melted at 125–126°, and unchanged when mixed with an authentic sample.

The small sample of X was isolated from a fraction boiling 52–56° (15 mm.) by washing with cold water to destroy any sulfinyl chloride and drying the remaining oil with magnesium sulfate. The product had an infrared spectrum identical to that of an authentic sample[14] and reacted with *p*-toluidine to form methanesulfon-*p*-toluidide which melted at 103–104° and unchanged when mixed with an authentic sample.

Isolation of methyl methanesulfinate (VII). The addition of 14.0 g. (0.44 mole) of methanol to 49.5 g. (0.6 mole) of I in the manner described gave a mixture from which, in addition to the products already mentioned, there was isolated 5.6 g. (0.06 mole) of VII. This product boiled at 54° (27 mm.) and had an infrared spectrum identical with that of a specially prepared and purified sample of methyl methanesulfinate.[15].

Methyl methanesulfinate. Methanesulfinyl chloride, 0.5 mole, and methanol, 0.55 mole, were mixed at 0° and allowed to stand in an ice bath for 2 hr. or longer. The mixture was then distilled at reduced pressure and yielded 33 g. (70%) of product boiling at 64–65° (49 mm.) Prepared in this way the compound always showed a positive Beilstein test for halogen and marked acidity. Treatment with anhydrous pyridine and careful fractionation through a 1-m. packed column gave a chlorine-free product boiling at 48° (23 mm.) and having n^{25}_D 1.4366, d^0_4 1.1785, and d^{25}_4 1.1498. The infrared spectrum showed strong absorption bands at 700, 946, 982, 1010, and 1132 cm.$^{-1}$ and weaker bands at 670, 800, 1305, 1415, and 1460 cm.$^{-1}$. The band at 1010 cm.$^{-1}$ seems to be the most useful part of the infra-

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[12] H. F. Herbrandson, R. T. Dickerson, Jr., and J. Weinstein, *J. Am. Chem. Soc.*, **78**, 2576 (1956).

[13] Sadtler Standard Spectra, Infrared Spectrogram #12506.

[14] Sadtler Standard Spectra, Infrared Spectrogram #13515.

[15] Although methyl methanesulfinate has been patented for use in a spinning solution of polyvinyl chloride, its properties are not recorded. *Cf.* E. Heisenberg and J. Kleine, U. S. Patent **2,617,777**; *Chem. Abstr.*, **47**, 4625 (1953).

red spectrum in identifying this compound as a component of mixtures with related substances.

Anal. Calcd. for $C_2H_6O_2S$: C, 25.5; H, 6.43; S, 34.07. Found: C, 25.63, 25.75; H, 6.06, 6.37; S, 33.0, 33.4.

Disproportionation of ethyl ethanethiolsulfinate. Ethyl ethanethiolsulfinate,[7] $C_2H_5SOSC_2H_5$ (6.9 g., 0.05 mole), was cooled to −35° and saturated with anhydrous hydrogen chloride. The reaction mixture was then warmed to room temperature and evacuated with a water pump to remove the hydrogen chloride. Distillation yielded 2.6 g. (0.021 mole) of ethyl disulfide and 3.2 g. (0.021 mole) of ethyl ethanethiolsulfonate, $C_2H_5SO_2SC_2H_5$. Both products had infrared spectra identical to those of authentic samples.

The reaction of ethanesulfenyl chloride with ethyl ethanethiosulfinate. Ethyl ethanethiolsulfinate (6.9 g., 0.05 mole) was added slowly with stirring to ethanesulfenyl chloride (4.8 g., 0.05 mole) which had been cooled to −60°. Stirring was continued while the mixture warmed to room temperature and was continued for 1.5 hr. Distillation of the mixture yielded 8.3 g. of a single fraction boiling at 45° (25 mm.) and having $n^{25}\text{D}$ 1.5017. A synthetic mixture of equimolar quantities of ethyl disulfide and ethanesulfinyl chloride boiled at 60.6° (30 mm.) and had $n^{25}\text{D}$ 1.5018. The infrared spectra of the distillate from the experiment and the synthetic mixture were identical.

The constant-boiling mixture from the experiment was diluted with ether and extracted with cold saturated sodium bicarbonate solution to hydrolyse the sulfinyl chloride present. Boiling this alkaline solution with benzyl chloride yielded a small quantity of white solid melting 81.5–82.5°. A mixture with pure ethyl benzyl sulfone melted at 84–85°, the reported melting point of the pure compound. The infrared spectra of the solid from the experiment and pure ethyl benzyl sulfone were identical with strong absorption bands at 1310, 1282, 1260, 1168, 1158, 1120, 895, 810, and 715 cm.$^{-1}$ and with numerous weaker bands.

The ether solution remaining from the alkaline extraction, after being dried over sodium sulfate and distilled, yielded 0.9 g. of pure ethyl disulfide which was identified by its infrared spectrum.

Reaction of I *with* VII. Methyl methanesulfinate (18.8 g., 0.20 mole) was added slowly and with stirring to I (33.0 g., 0.40 mole) in the manner described above without evidence of immediate reaction. The reaction mixture was slowly warmed to 60° with constant stirring and held there for 3 hr. until the color had faded to pale yellow. Volatile products were collected in a cold trap. Evaporation, washing, and recondensation of this fraction yielded 5.8 g. (0.11 mole) of methyl chloride which was identified by its infrared spectrum and by the formation of methylmercury chloride which melted at 171–173° in a sealed tube and unchanged when mixed with an authentic sample.

Distillation of the reaction mixture yielded 11.8 g. (0.125 mole) of methyl disulfide (IV), 9.4 g. (0.096 mole) of methanesulfinyl chloride (VI), 8.1 g. 0.071 mole) of methanesulfonyl chloride (X), and 2.8 g. (0.022 mole) of methyl methanethiolsulfonate (V). All products had infrared spectra identical to authentic samples except the sample of VI. The spectrum of this fraction showed all the strong absorption bands of pure VI and two weaker bands at 700 and 1010 cm.$^{-1}$, which were readily accounted for as coming from unchanged VII present as an impurity.

The fraction believed to be VI reacted vigorously with sodium bicarbonate solution. On boiling the resulting solution with benzyl chloride, methyl benzyl sulfone was formed which melted at 124–126° and unchanged when mixed with an authentic sample.

The reaction of I *with methyl sulfite.* Methanesulfenyl chloride was freshly prepared in a 500 ml. 3-neck flask fitted with mechanical stirrer and attached to a cold trap. After cooling the reaction flask to the temperature of Dry Ice, freshly distilled methyl sulfite, also cooled to Dry-Ice temperature, was added. The mixture was then allowed to warm slowly to 0° and the flask was packed in ice and allowed to stand for 12 to 24 hr.

After standing in ice the mixture was slowly warmed to 60° with vigorous stirring until no more volatile material was driven over into the cold trap. Without further treatment the mixture was then distilled at reduced pressure through a 15-in. Vigreux column. Sharp fractionation could not be achieved, but fractions boiling over relatively narrow temperature ranges, after redistillation, were readily identified by comparing their infrared spectra with those of authentic compounds.

Recovery and identification of methyl chloride and sulfur dioxide. The material collecting in the cold trap was redistilled and then allowed to bubble through sodium hydroxide solution. The unabsorbed gas, after being dried and recondensed, was identified as methyl chloride in the manner previously described. In one experiment 81% of the methyl groups originally present in the methyl sulfite were recovered as methyl chloride. The portion of the cold trap contents absorbed in the alkaline wash was first recognized as sulfur dioxide by its odor and identified by its oxidation to sulfate ion by a solution of iodine. The yield of sulfur dioxide was estimated by weighing the amount of material condensed in the cold trap both before and after the alkaline wash and also by titration of the alkaline wash solution with standard iodine solution. The moles of sulfur dioxide thus determined in some experiments amounted to nearly 100% of the sulfur originally present in the methyl sulfite used.

Identification of methyl disulfide (IV). In an early experiment 38.4 g. (0.466 mole) of I was treated with 25.6 g. (0.233 mole) of methyl sulfite in the manner described. An attempt was made to distil the crude reaction mixture through a 1.0-m. column packed with glass helices using bromobenzene as a chaser. The only product obtained, before decomposition set in, was 12.0 g. (0.13 mole) of methyl disulfide boiling at 109° and, after washing with sodium hydroxide and drying, having $n^{25}\text{D}$ 1.5228. These properties were identical to the purified methyl disulfide originally used to prepare I.

Identification of methanesulfinyl chloride VI *and methanesulfonyl chloride* (X). When 62 g. (0.75 mole of I was treated with 27.5 g. (0.25 mole) of methyl sulfite in the manner described, there was obtained a 6.9 g. fraction having an infrared spectrum identical to that of methanesulfinyl chloride.[13] This fraction reacted vigorously with cold water and when its alkaline solution was boiled with benzyl chloride, a solid was formed which melted unchanged at 125° when mixed with an authentic sample of methyl benzyl sulfone.

Fractions boiling over the range 53–70° (30 mm.) were treated with cold water to decompose any sulfinyl chloride present and were then dried. The oil recovered had an infrared spectrum identical with that of an authentic sample of methanesulfonyl chloride. The sample was treated with *p*-toluidine and formed methanesulfon-*p*-toluidide melting at 103–104° both alone and when mixed with a pure sample.

Identification of methyl methanesulfinate (VII). The reaction of 49.5 g. (0.6 mole) of I with 44 g. (0.4 mole) of methyl sulfite yielded 5.5 g. of a fraction boiling 55–58° (35 mm.). All the major infrared absorption bands of this fraction were identical to the strong bands of methyl methanesulfinate. One weak absorption band of the fraction at 1207 cm.$^{-1}$ was not found in the spectrum of pure VII but was readily accounted for as coming from a small amount of unreacted methyl sulfite present as an impurity.

Reaction of methanesulfinyl chloride VI *with methyl sulfite.* Using the same equipment described above, 22 g. (0.2 mole) of methyl sulfite and 19.7 g. (0.2 mole) of VI were mixed at Dry-Ice temperature and let stand at 0° overnight. The mixture was then allowed to stand at room temperature several hours after which it was heated with stirring at 50° for a total of 13 hr. and finally distilled at reduced pressure. There was obtained 15.6 g. (88% yield) of colorless liquid boiling 57–60° (37 mm.) and having an infrared spectrum identical to that of pure methyl methanesulfinate (VII). The methyl chloride collected accounted for 67% of the chlorine in the sulfinyl chloride used and the sulfur dioxide, after oxidation to sulfate ion and precipitation as barium sulfate, corresponded to 87% of the sulfur present in the methyl sulfite.

Reaction of I *with methyl chlorosulfonate.* Methyl chlorosulfonate, $ClSO_3CH_3$ (26.1 g., 0.2 mole), was mixed with 16.5 g. (0.2 mole) of I at low temperature and the mixture was allowed to stand at ice temperature overnight. The next morning the entire reaction mixture had solidified. About 25 ml. of methylene chloride was added, but the solid did not dissolve. The mixture was heated until the solid melted (above 60°) and an attempt was made to distil it at reduced pressure. No recognizable product was obtained and the experiment was discontinued because the results indicated that methyl chlorosulfonate was not an intermediate product in the reaction under investigation.

Attempted reaction of I *with methyl chlorosulfinate.* To 33 g. (0.4 mole) of I, 46 g. (0.4 mole) of methyl chlorosulfinate, $ClSO_2CH_3$, was added at Dry-Ice temperature without evidence of reaction. The mixture was allowed to warm to room temperature and stand for several hours without any diminution of the red color of I and without the evolution of any volatile material into the cold trap. The experiment was discontinued as the failure to decolorize I seemed to indicate that methyl chlorosulfinate was not an intermediate in the reaction between I and methyl sulfite.

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Free-Radical Phosphonation of Aromatic Compounds

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Received September 25, 1961

Free phosphonyl radicals, generated from diethyl phosphite and *t*-butyl peroxide, react with polycyclic aromatic and heterocyclic compounds to give phosphonic acid derivatives in good yields. This novel reaction has been studied with naphthalene, anthracene, phenanthrene, dibenzofuran, and carbazole. Anthracene and phenanthrene give mainly the 9-isomer; the others give isomer mixtures. Ferrocene and pyridine are not phosphonated by this procedure. Diethyl isobutylphosphonate, a by-product of these reactions, is probably formed through an intermediate from diethyl phosphite and *t*-butoxy radical.

Although aromatic reactions of phenyl radicals have been known since 1895,[1] free-radical aromatic substitutions were not recognized until twenty-five years ago.[2] The substituting radical has usually been alkyl, aryl, or acyl.[3] Substitution in the aromatic ring by an inorganic radical, free phosphonyl, has only recently been announced.[4]

This novel reaction may prove useful for synthesis of surface-active agents, pesticides, and plasticizers. Its scope has been explored by treating diethyl phosphite and *t*-butyl peroxide with four aromatic and three heterocyclic compounds. In two cases, pure phosphonic acids were isolated by hydrolysis of their esters; in the others, mixtures of isomers were not separated. A by-product, diethyl isobutylphosphonate, has been noted in these reactions; to shed light on how it formed, diethyl phosphite was treated separately with *t*-butyl peroxide, *t*-butyl alcohol, and isobutylene; in the last two reactions, catalytic amounts of *t*-butyl peroxide were used.

EXPERIMENTAL

Diethyl phosphite was purchased from Virginia-Carolina; *t*-butyl peroxide, *t*-butyl alcohol, isobutylene, the three arenes, dibenzofuran, and carbazole were from Matheson Coleman & Bell or from Eastman. Ferrocene was from Ethyl. The dibenzofuran and ferrocene were recrystallized before use; the other materials were used as purchased.

In all experiments, a slight excess over 0.5 mole of *t*-butyl peroxide was used per mole of aromatic compound. Enough diethyl phosphite—at least equimolar with aromatic—was added to dissolve all the aromatic. To keep reaction temperatures at 130–150°, low-boiling products were allowed to escape by refluxing under a condenser containing stationary water.

Phosphonation of naphthalene. A mixture of 50 g. (0.4 mole) of naphthalene, 51.2 g. (0.4 mole) of diethyl phosphite, and 37.5 ml. (0.2 mole) of *t*-butyl peroxide was refluxed 8 hr. Volatile material was collected in two traps, one cooled with ice and water, one with Dry Ice and acetone. Uncondensed gas was passed into a bulb for analysis by mass spectrometry.

To remove unchanged starting material and partially hydrolyzed products, the reaction mixture was diluted with 200 ml. of ether, washed twice with 500 ml. of cold water, and extracted once with 250 ml. of 5% potassium hydroxide. Evaporation and steam distillation of the ether solution recovered 26 g. of the original naphthalene.

As the residue was neutral, no hydrolysis had occurred during the steam distillation. It was extracted three times with 200-ml. portions of ether; the ether solution was dried over sodium sulfate and evaporated. Distilling the residue *in vacuo* gave an 8-g. viscous, colorless fraction; b.p. 163–172° (0.4 mm.); n^{20}_D 1.5671.

Anal. Calcd. for diethyl naphthalenephoshonate, $C_{14}H_{17}PO_3$: C, 63.6; H, 6.4; P, 11.7; mol. wt. 264. Found: C, 63.3; H, 6.1; P, 11.3; mol. wt. 264.

Molecular weight was determined by mass spectrometry. The spectrum showed that small amounts of materials

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[1] O. Kühling, *Ber.*, **28**, 41 (1895); E. Bamberger, *ibid.*, **28**, 403 (1895).

[2] D. H. Hey and W. A. Waters, *Chem. Revs.*, **21**, 169 (1937).

[3] O. C. Dermer and M. T. Edmison, *ibid.*, **57**, 77 (1957); D. R. Augood and G. H. Williams, *ibid.*, **57**, 123 (1957).

[4] E. K. Fields and R. J. Rolih, *Chem. and Ind.*, 999 (1960).