the presence of 1 *M* sodium methoxide in anhydrous methanol. The reaction solution was neutralized with anhydrous methanolic hydrochloric acid, and the resulting sodium chloride removed by centrifugation. The supernatant liquid was evaporated to a small volume and chromatographed directly on the DEGS column. The resulting chromatogram showed the presence of both peak A and peak B. The area of peak A represented 41.8% of the mixture.

(b) Methyl 2,4-dimethylheptanoate was heated under reflux for 21 hr. in the presence of 1 *M* sodium methoxide in anhydrous methanol. The infrared spectrum of the resulting ester, as a pure liquid or in carbon tetrachloride was essentially identical with the spectrum of untreated methyl 2,4-dimethylheptanoate. Chromatography on the DEGS column showed the presence of peaks A and B. The area of peak A had decreased to 41.8% of the mixture.

(c) An approximately 10% aqueous solution of sodium 2,4-dimethylheptanoate was heated 18 hr. in a sealed tube at 115°. The free acid was isolated and esterified with diazomethane. Separation of the ester on the DEGS column showed that peak A had increased to 56.2% of the total mixture of components A and B.

Discussion

The synthesis of 2,4-dimethylheptanoic acid was accomplished in a straightforward manner. The fact that its methyl ester was separated by gas chromatography into two almost equal components (A and B) suggested that diastereoisomers had been resolved. The possible presence of impurities such as methyl 4-methylheptanoate, methyl propionate, and free 2,4-dimethylheptanoic acid was eliminated by comparison of the retention volumes of components A and B with those of the authentic reference compounds.

A and B were shown to be diastereoisomers by the fact that the infrared spectrum of A was essentially identical to the infrared spectrum of methyl 2,4-dimethylheptanoate, that A was epimerized to a mixture of A and B, that the relative quantities of A and B were changed by epimerization, and that the infrared spectrum of the epimerized mixture was the same as that of the original methyl 2,4-dimethylheptanoate.

Addition of Selenium and Sulfur Tetrachlorides to Alkenes and Alkynes

REED F. RILEY, J. FLATO,[1] AND D. BENGELS

Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn 1, New York

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Preparation of organic selenides and their dihalides by addition of selenium halides to an unsaturated linkage is interesting in that it produces compounds having a reactive halogen on the *beta* carbon atom.[2,5] This note describes further work on addition to olefinic linkages and an extension of the reaction to acetylenic compounds.

Although the reaction of selenium tetrachloride with unsaturated linkages to produce selenium dichlorides is quite general, our results show that a selenide is produced with acrylonitrile. Subsequent chlorination of this selenide yields the expected selenium dichloride which reverts to the selenide on recrystallization from acrylonitrile. As the latter is not chlorinated with particular ease,[6] the presence of the nitrile group *beta* to the selenium atom must exert a labilizing influence on the selenium-chlorine linkage in this compound. Thus, selenides are to be expected whenever the selenium-chloride linkage is labilized and/or the unsaturated starting material is easily and rapidly chlorinated. In an attempt to isolate the dichloride from the addition reaction, the stoichiometric amount of acrylonitrile was reacted with selenium tetrachloride in ether. This leads to a highly colored solution, typical of solutions of alkylselenium trihalides (an almost certain intermediate of the addition reaction), from which no solid product could be obtained. This suggests that excess alkene is needed to force the reaction towards completion.

Lack of addition of selenium tetrachloride to *trans*-stilbene, even at temperatures substantially above those required for the other additions to occur, is probably due to the well documented π-electron delocalization of the carbon double bond in this type of compound. Addition occurs with diphenylacetylene, but subsequent cyclization takes place. This reaction will be reported in a separate place in the near future.

As the nearly quantitative reaction between sulfur tetrachloride and cyclohexene occurs more rapidly and at temperatures substantially lower than reported for the analogous reaction using sulfur dichloride,[7] the tetrachloride is a more active addition reagent than the dichloride. It is also a more active chlorinating agent, however, and it was found impossible to separate the sulfides from other reaction products without nearly total decomposition of the desired product in the other cases studied (see Experimental). All attempts to isolate bisorgano sulfur dichlorides of cyclohexene and hexene by separating the products from impurities at Dry Ice temperature resulted in failure.

Experimental

Sulfur and Selenium Tetrahalides.—The selenium compound was prepared by condensing dried tank chlorine onto elementary repurified selenium in a flask protected from atmospheric moisture and warming to room temperature while simultaneously passing through a slow stream of nitrogen. The sulfur compound was prepared in the same

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[1] Abstracted in part from the B.S. thesis (1961) of J. Flato.

[2] H. Brintzinger, K. Pfannstiel, and H. Vogel, *Z. anorg. allgem. Chem.*, **256**, 75 (1948).

[3] H. L. Riley and N. A. C. Friend, *J. Chem. Soc.*, 2342 (1932).

[4] H. Funk and W. Weiss, *J. prakt. Chem.*, **1**, 33 (1954).

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[7] H. W. Moll, U. S. Patent 2,472,755 (1949); *Chem. Abstr.*, **43**, 6358 (1949).

TABLE I

Substance	M.p.	Yield	Calcd.	Found
2-Chloropentyl selenoxide	103–104°	93%	C, 39.20; H, 6.54	C[a], 37.55; H, 6.54
2-Chlorohexyl selenoxide	103–104°	94%	C, 43.13; H, 7.19	C[a], 41.60; H, 7.43
2-Chloro-2-phenylethenyl selenoxide	142–143°	89%	C, 51.99; H, 3.24	C, 51.63; H, 3.16
2-Chloro-2-phenylethyl selenoxide	91–91.5°	82%	C, 51.40; H, 4.29	C, 51.43; H, 4.53

[a] See ref. 12.

way except that excess chlorine was removed at −78°. Yields are essentially 100%.

Bis-2-chloropentylselenium Dichloride.—1-Pentene, 7 g. (1 mole), was added dropwise over a period of 15 min. to 22.1 g. (0.1 mole) of selenium tetrachloride cooled to −78°. The flask was gradually warmed to room temperature and the solvent stripped off leaving a crystalline solid. Recrystallization from pentene yielded a white solid melting at 74–75°. The recrystallized yield was 52%.

Anal.[8] Calcd. for $C_{10}H_{20}Cl_4Se$: C, 33.64; H, 5.55; Cl, 39.31; Se, 21.83. Found: C, 34.07; H, 5.72; Cl, 39.18; Se, 21.85.

Bis-2-chlorohexylselenium Dichloride.—1-Hexene, 84 g. (1 mole), was added dropwise over a period of 15 min. to 22.1 g. (0.1 mole) of selenium tetrachloride cooled to 78°. The flask was gradually warmed to room temperature and the solvent stripping off leaving an oil. The oil crystallized after standing overnight at −30° and was recrystallized from pentane, yielding a white solid melting at 45–46° (lit.[5] 42–43°). The recrystallized yield was 86%.

Anal. Calcd. for $C_{12}H_{24}Cl_4Se$: C, 37.01; H, 6.18; Cl, 36.50; Se, 19.80. Found: C, 37.31; H, 6.32; Cl, 36.04; Se, 19.90.

Bis-2-chlorocyclohexylselenium Dichloride.—Cyclohexene, 82 g. (1.0 mole), was added dropwise over a period of 15 min. to 22.1 g. (0.1 mole) of selenium tetrachloride cooled to −78°. The flask was gradually warmed to room temperature, the solid filtered off, and recrystallized from benzene. Recrystallization gave a white solid melting at 141–142° (lit.[4] 144°) in 74% yield.

Anal. Calcd. for $C_{12}H_{20}Cl_4Se$: C, 37.52; H, 5.22; Cl, 36.90; Se, 20.56. Found: C, 37.64; H, 5.39; Cl, 36.40; Se, 20.57.

Bis-2-chloro-2-phenylethylselenium Dichloride.—Styrene, 26 g. (0.25 mole), was dissolved in 100 ml. of ether and the solution added dropwise to 22.1 g. (0.1 mole) of selenium tetrachloride at room temperature yielding a dark red solution. Vacuum evaporation of solvent and excess styrene gave a solid which, after recrystallization from ether, melted at 100–101° (lit.[5] 91°). The recrystallized yield was 83%.

Anal. Calcd. for $C_{16}H_{16}Cl_4Se$: C, 44.70; H, 3.73; Cl, 33.11; Se, 18.35. Found: C, 44.68; H, 3.96; Cl, 33.59; Se, 18.12.

2-Chloro-2-cyanoethyl Selenide.—Acrylonitrile, 80 g. (1.5 moles), was added dropwise over 15 min. to 22.1 g. (0.1 mole) of selenium tetrachloride at room temperature. The color became dark red and considerable heat was evolved, but on standing for 0.75 hr. the color changed again to light yellow. Evaporation of solvent and excess reactant yielded an oil which solidified on trituration with ether. Recrystallization from ether gave a white solid melting at 94–94.5° in 77% yield. Infrared analysis showed a nitrile peak at 2280 cm.$^{-1}$. The reaction was repeated in ether using a 2:1 olefin to halide ratio, but on evaporation of solvent only an intractable oil resulted.

Anal. Calcd. for $C_6H_6N_2Cl_2Se$: C, 29.72; H, 2.49; Cl, 29.35; Se, 32.62. Found: C, 29.17; H, 2.65; Se, 32.70. Mol. Wt. Calc: 256. Found: 258.[9]

Bis-2-chloro-2-cyanoethylselenium Dichloride.—Chlorine was bubbled through an ethereal solution of 10 g. of 2-chloro-2-cyanoethyl selenide held at room temperature until material ceased separating from solution. The filtrate was then chilled and the precipitate filtered and recrystallized from ether yielding a white solid in over 90% yield which melted at 71–72°. The compound is unstable and slowly yields a mixture of chlorine and hydrogen chloride at room temperature. When dissolved in acrylonitrile, the dichloride loses its halogen to give an almost quantitative yield of 2-chloro-2-cyanoethyl selenide (ident. by m.p.).

Anal. Calcd. for $C_6H_6N_2Cl_4Se$: Cl, 43.67; Se, 24.16. Found: Cl, 42.10; Se, 25.30.

Bis-2-chloroethenylselenium Dichloride.—Acetylene, 7.8 g. (0.3 mole), was bubbled into a cooled (−45°) ether slurry of selenium tetrachloride made from 100 ml. of ether and 22.1 g. (0.1 mole) of selenium tetrachloride with slow stirring. The dark yellow solution was stirred 1 hr., warmed to room temperature, and vacuum evaporated. The resulting solid was recrystallized from ether yielding a white solid in 9% yield, melting at 95–96° (lit.[4] 104–105°). A =C—H absorption was found in the infrared at 3100 cm^{-1}.

Anal. Calcd. for $C_4H_4Cl_4Se$: C, 17.69; H, 1.46; Cl, 52.00; Se, 28.93. Found: C, 18.97; H, 1.58; Cl, 52.13; Se, 29.60.

Bis-2-chloro-2-phenylethenylselenium Dichloride.—Phenylacetylene, 25.5 g. (0.25 mole), was dissolved in 100 ml. of ether and the solution added dropwise over 30 minutes to 22.1 g (0.1 mole) of selenium tetrachloride at room temperature. As the halide dissolved, the solution became dark red subsequently lightening to pale yellow on standing. Overnight chilling at −78° produced a solid which, when recrystallized from ether, melted at 89–90°. The yield of white solid was 73%. A =C—H absorption was found in the infrared spectrum at 3100 cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{12}Cl_4Se$: C, 45.60; H, 2.82; Cl, 33.34; Se, 18.50. Found: C, 46.39; H, 2.97; Cl, 32.78; Se, 18.10.

2-Chlorohexylsulfide.—1-Hexene, 18.5 g. (0.22 mole), dissolved in 100 ml. of ether was added dropwise to 17.4 g. (0.1 mole) of sulfur tetrachloride at −78°. Removal of the solvent and excess reactant yielded a yellow solid which gave on recrystallization from petroleum ether a 12% yield of yellow solid melting at 52° (lit.[10] 46–50°).

Anal. Calcd. for $C_{12}H_{24}Cl_2S$: Cl, 25.62; S, 11.81. Found: Cl, 25.34; S, 11.68.

2-Chlorocyclohexyl Sulfide.—Cyclohexene, 16.4 g. (0.2 mole), dissolved in 100 ml. of ether was added dropwise to 17.4 g. (0.1 mole) of sulfur tetrachloride cooled to −78°. A white solid immediately formed which was filtered off and recrystallized from ether. The recrystallized product melts at 72–73° (lit.[7] 72–73.5°) and is formed in 84% yield.

Anal. Calcd. for $C_{12}H_{20}Cl_2S$: Cl, 26.63; S, 11.98. Found: Cl, 25.61,; 27.23; S, 12.00.

Other Alkenes with Sulfur and Selenium Tetrachlorides.—Pentene, styrene, acrylonitrile, 1,2-dicyanoethylene, and phenylacetylene reacted (−78°) in various mole ratios with sulfur tetrachloride in ether and pentane solvents. Reaction occurred at the low temperature, but in each case evaporation of solvent left an oil which was intractable in our hands. Butadiene and selenium tetrachloride in ether behaved similarly. *trans*-Stilbene on the other hand would

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[8] All carbon, hydrogen, and chlorine analyses were done by the Schwarzkopf Microanalytical Laboratories, Woodside, New York. Selenium analyses were done gravimetrically after decomposing the compound with fuming nitric acid and precipitating the elementary selenium with sulfur dioxide.

[9] Molecular weights were measured by the vapor pressure equilibrium method.

[10] Ger. Patent 846,397 (1952); *Chem. Abstr.*, **50**, 7847 (1956).

not react with selenium tetrachloride even on extended refluxing in benzene.

Selenoxide Preparations.—All selenoxides were prepared by the same procedure. A slurry made from several grams of the selenium dichloride and 100 ml. of water was stirred for 2 hr. at room temperature. The resulting material was recrystallized from acetone yielding a white solid. The results are shown in Table I. Stirring for longer periods (up to 2 days) did not result in hydrolysis of the chlorine-chlorine linkages as is reported by Smedsland[11] for bis-2-chloroethylselenium dichloride.

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(11) T. Smedsland, *Finska Kemistamfundets Medd.*, **41**, 13 (1932); *Chem. Abstr.*, **26**, 5905 (1932).

(12) Too low a combustion temperature was used resulting in the low carbon results observed.

Potassium *p*-Phenylazophenoxide as a Reagent for the Identification of Organic Halogen Compounds

E. O. WOOLFOLK, ELWOOD DONALDSON,[1]
AND MUERL PAYNE[1]

Chemistry Department, Central State College, Wilberforce, Ohio

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The literature records many reagents which have been suggested for the identification of alkyl halides.[2,3] No one of these is entirely satisfactory, either because of difficulty in preparation or because their application is not general. It has been suggested[4] that thiourea and *p*-bromobenzenesulfon-*p*-anisidide appear to be the most generally useful reagents. However, the *S*-alkyl isothioureas have to be isolated as picrates or styphnates and the *n*-alkyl-*p*-bromobenzenesulfon-*p*-anisidides have low melting points. More recently it has been stated[3] that the best method for making derivatives of alkyl halides was their conversion into the corresponding Grignard reagents and the reaction of these with phenyl-, *p*-tolyl-, or α-naphthyl isocyanate to give the anilides, toluides, or α-naphthalides. However, this is a rather lengthy experimental procedure for preparing derivatives, and its application is limited only to organic halogen compounds which form Grignard reagents.

Among the many other derivatives suggested for the identification of alkyl halides are the *p*-alkoxybenzoic acids,[5] alkyl triiodophenyl ethers,[6] alkyl β-naphthyl ethers,[7] *p*-alkoxydiphenylamines,[8] alkyl 2,4-dinitrophenyl sulfides,[9] alkyl 6-nitro-2-mercaptobenzothiazolyl sulfides,[10] and *S*-alkylmercaptosuccinic acids.[11] In terms of suitability, each of these derivatives has certain limitations, except the alkyl 2,4-dinitrophenyl sulfides, which appear to have general applicability. The preparation of the *p*-alkoxybenzoic acids involves a lengthy experimental procedure, and the alkyl triiodophenyl ethers, *p*-alkoxydiphenylamines, and alkyl 6-nitrobenzothiazolyl sulfides are low melting derivatives. The alkyl β-naphthyl ethers usually were separated as oils and had to be isolated as picrates. The usefulness of *S*-alkylmercaptosuccinic acids has been demonstrated only for alkyl bromides which require long reaction times (four to twenty-four hours) for preparing derivatives.

We wish to report the use of *p*-phenylazophenol as a reagent for the identification and chromatographic separation of organic halogen compounds. Similarly, Hurd and coworkers[12,13] have reported the use of *p*-phenylazophenol as a reagent for the preparation and chromatographic separation of *p*-phenylazophenyl polyacetylglycosides. In several instances,[14–16] the reaction of an alkyl halide with *p*-phenylazophenol under alkaline conditions to form an ether has been reported.

The potassium salt of *p*-phenylazophenol (m.p. 155–156°) reacted readily with organic halogen compounds in dimethylformamide or dimethoxyethane to form crystalline *p*-phenylazophenyl ethers in good yields. In a few cases of these derivatives similar melting points were obtained; however, a mixture melting point showed a marked depression in all such cases.

Of fifty halides investigated, all the primary and secondary halides reacted, in many instances with only mixing and no heating. The reagent also reacted with straight- and branched-chain halogen esters, halohydrins, halo ketones, halo ethers, and chloroformates. Good yields of the derivatives of the chloroformates were obtained only by allowing their reaction mixtures to stand for sixteen hours at room temperature. The vicinal halide, 1,2-dibromoethane, gave constant melting point material (196.0–198.0°); however, analytical results indicated that this material was a mixture of the mono- and diderivatives. A well defined

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(1) This paper is based on work presented by Elwood Donaldson and Muerl Payne in partial fulfillment of requirements for an undergraduate research course offered in the Department of Chemistry of Central State College.

(2) A comprehensive review of the reagents, which have been suggested for the identification of alkyl halides, has been published by Hopkins and Williams Research Staff, "Organic Reagents for Organic Analysis," 2nd ed., Chemical Publishing Co., Inc., Brooklyn, New York, 1950, pp. 32–33.

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