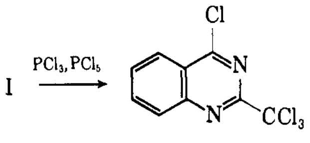
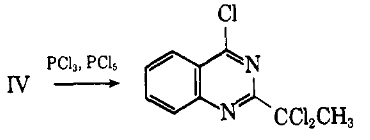
The n.m.r. spectrum of Dehoff's tetrachlorinated methyl compound clearly showed that *only aromatic protons* were present (τ 1.64–2.42). Accordingly, structure II has been revised to 2-(trichloromethyl)-4-chloroquinazoline (VI).



VI

In our hands, the chlorination of 2-ethyl-4-quinazolone did not proceed as reported by Bogert and May. Utilizing a variety of reaction conditions, we have been unable to isolate any of the tetrachlorinated material reported by Bogert and May. Chlorination of IV by the same procedure that was employed for the conversion of I to VI resulted in the formation of a low yield of a *trichloro compound* (VII). The n.m.r. spectrum of this compound showed the presence of a singlet at τ 7.29 (3 H) and an aromatic multiplet at τ 1.50–2.42 (4 H). On the basis of the n.m.r. spectrum, nuclear chlorination is ruled out and the structure of the trichloro compound is most likely 2-(1,1-dichloroethyl)-4-chloroquinazoline (VII).



VII

Experimental

Melting points were determined on a Mel-Temp apparatus and are uncorrected. Analyses are by Mr. Kenneth Fleisher and his staff of the Sterling–Winthrop Research Institute. N.m.r. spectra were run in deuteriochloroform on a Varian A-60 spectrometer using tetramethylsilane as the internal standard.

2-Trichloromethyl-4-chloroquinazoline (VI).—The procedure of Dehoff[2] was followed with a few modifications. A sealed tube containing 2.0 g. (0.0125 mole) of 2-methyl-4-quinazolone,[6] 6.25 g. of PCl_5, and 5.00 g. of PCl_3 was heated behind a safety screen at 170° for 4 hr. The tube was cooled to Dry Ice–acetone temperature and cautiously opened. The volatile phosphorus halides were removed at steam-bath temperature *in vacuo*. The residue was stirred with 50 ml. of warm 6 *N* NaOH and filtered. The insoluble material was dissolved in ethanol, decolorized with charcoal, and reprecipitated with water to give 1.31 g. (37%) of VI, m.p. 114–116°. Recrystallization from dilute ethanol gave white crystals, m.p. 121–123°, lit.[2] m.p. 125°.

Anal. Calcd. for $C_9H_4Cl_4N_2$: C, 38.33; H, 1.43; N, 9.94. Found: C, 38.43; H, 1.78; N, 10.07.

2-(1,1-Dichloroethyl)-4-chloroquinazoline (VII).—By employing the same procedure described above, the chlorination of 2-ethyl-4-quinazolone yielded 26% of crude VII, m.p. 86–89°. Recrystallization from dilute ethanol gave white needles, m.p. 96–96.5°.

Anal. Calcd. for $C_{10}H_7Cl_3N_2$: C, 45.92; H, 2.70; Cl, 40.67; N, 10.71. Found: C, 46.01; H, 3.03; Cl, 40.89; N, 10.57.

Acknowledgment.—We thank the National Science Foundation for an Undergraduate Research Participation Grant and the Research Foundation of the State University of New York for a Grant-in-Aid. We also wish to thank Mr. Kenneth Fleisher and his staff of the Sterling–Winthrop Research Institute for the analytical results and Miss Katherine Martini of Sterling–Winthrop for the n.m.r. determinations.

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(6) A. Buzas and C. Hoffmann, *Bull. soc. chim. France*, 1889 (1959).

Convenient Preparations of α-Halo Sulfones and Their Use in the Synthesis of Deuterated Olefins, the Desulfurization of Alkyl Sulfones, and the Homologization of Olefins

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During a study of the mechanism of the alkaline degradation of α-haloalkyl sulfones (Ramberg–Bäcklund reaction)[1] convenient synthetic methods were developed for a variety of α-halo sulfones. The reactions used in the syntheses and the halo sulfones themselves have a chemical utility which would seem worthy of further attention. Procedures are given in this brief paper for the preparation of several α-chloro, α-bromo, and α-iodo sulfones and for the use of these sulfones as part of three broader chemical schemes: (1) the synthesis of olefins deuterated at the double bond, (2) the desulfurization of alkyl sulfones, and (3) the homologization of olefins.

Synthesis of α-Halo Sulfones.—A simplified procedure has been developed for the oxidation of α-halo sulfides to sulfones by using a dried solution of 40% commercial peracetic acid in methylene chloride.[2,2a] Very high yields were obtained when the starting sulfides were pure. Details are given in the Experimental section.

A different technique was employed for α-bromo and α-iodo sulfones. Dialkyl sulfones in benzene solution were treated with 1 mole of commercial butyllithium. The resulting slurry of the α-lithium salt was then halogenolyzed in the cold with either bromine or iodine. While yields were not extremely good and while the products were contaminated with some impurities, the simplicity of the reaction and the ready availability of the starting materials justify its use. Details are given in the Experimental section.

Synthesis of Deuterated Olefins.—The Ramberg–Bäcklund reaction of α-halo sulfones is shown schematically (see p. 1314, top of col. 1).

In the course of our mechanistic studies of this reaction,[1] it was found that the hydrogens α to the sulfonyl group exchange with the basic medium much more rapidly than the olefinic product is formed. In

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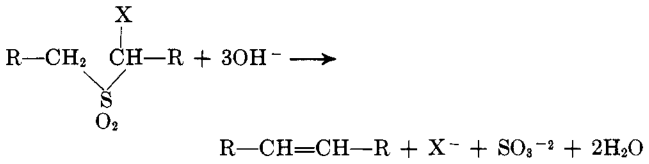
(1) Reported in communication form: N. P. Neureiter and F. G. Bordwell, *J. Am. Chem. Soc.*, **85**, 1209 (1963).

(2) Previously reported methods employed perbenzoic acid, monoperphthalic acid, or peracetic acid alone: see (a) H. Böhme, *Ber.*, **70**, 379 (1937); (b) L. Ramberg and B. Bäcklund, *Arkiv Kemi, Mineral. Geol.*, **13A**, No. 27 (1940); (c) F. G. Bordwell and G. D. Cooper, *J. Am. Chem. Soc.*, **73**, 5184 (1951).

(2a) Note Added in Proof.—Since this work was completed, *m*-chloroperbenzoic acid has become commercially available. This material in chloroform solution is a particularly convenient reagent for anhydrous oxidation of sulfides to sulfones. Its use has been reported by L. A. Paquette, *J. Am. Chem. Soc.*, **86**, 4085, 4089, 4383 (1964), in transformations analogous to several in the present report.

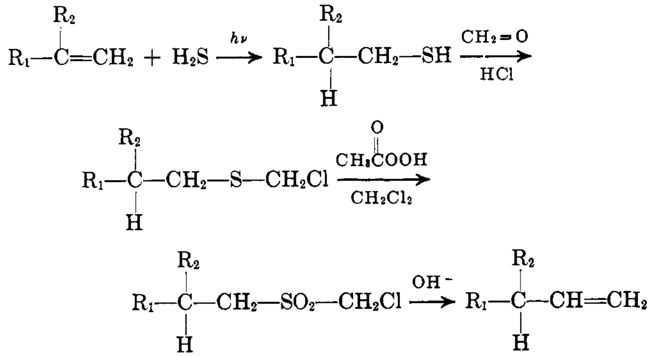


$$R{-}CH_2\underset{\substack{S\\O_2}}{\;}\overset{X}{CH}{-}R + 3OH^- \longrightarrow R{-}CH{=}CH{-}R + X^- + SO_3^{-2} + 2H_2O$$

an environment of deuterium oxide with a sodium deuterioxide catalyst, essentially complete equilibrium is established prior to C–C bond formation and SO_2 elimination. This fact permits very convenient preparation of samples of olefins highly deuterated at the double bond. The reaction has been used to prepare small laboratory samples of propene-1,1,2-d_3, 2-butene-2,3-d_2, 3-methyl-1-butene-1,1,2-d_3, 2-methyl-1-butene-1,1-d_2, and 3-methyl-1-pentene-1,1,2-d_3.

Desulfurization of Alkyl Sulfones.—For purposes of degradative analysis the removal of SO_2 from an alkyl sulfone with retention of the carbon skeleton may be desirable. Utilizing commercial butyllithium to remove one of the α-hydrogens, treating the lithium salt with iodine, and treatment of the crude product with aqueous alkali conveniently effect the desulfurization. In this way di-*n*-propyl sulfone was converted within a few hours to an over-all yield of 47% of 3-hexene, while di-*n*-butyl sulfone gave a 40% over-all yield of 4-octene.[3]

Homologization of Olefins.—A facile preparation of chloromethyl alkyl sulfides from alkyl mercaptans and formaldehyde has been reported.[4,5] Simple peracetic acid oxidation gives the sulfones. Combination of these reactions with the free radical addition of hydrogen sulfide[6] or thiolacetic acid[7] to an olefin to give a mercaptan provides a convenient means of homologizing an olefin. In particular, we have used this sequence for preparation of samples of 3-methyl-1-pentene from 2-methyl-1-butene, and of deuterated 2-methyl-1-butene from 2-butene.



$$R_1{-}\overset{R_2}{C}{=}CH_2 + H_2S \xrightarrow{h\nu} R_1{-}\overset{R_2}{\underset{H}{C}}{-}CH_2{-}SH \xrightarrow[HCl]{CH_2{=}O}$$

$$R_1{-}\overset{R_2}{\underset{H}{C}}{-}CH_2{-}S{-}CH_2Cl \xrightarrow[CH_2Cl_2]{CH_3\overset{O}{C}OOH}$$

$$R_1{-}\overset{R_2}{\underset{H}{C}}{-}CH_2{-}SO_2{-}CH_2Cl \xrightarrow{OH^-} R_1{-}\overset{R_2}{\underset{H}{C}}{-}CH{=}CH_2$$

Since the sequence can be carried out with crude reaction products (except that the mercaptan should be distilled), the necessary laboratory time is quite short. If the mercaptans are commercially available, the first step of the series becomes superfluous. By replacement of the paraformaldehyde with acetaldehyde or higher aldehydes, olefins with internal double bonds can be prepared. While the yields appear to decrease as higher aldehydes are used, two syntheses of sulfones leading to 2-pentene were carried out. Certainly, alternative syntheses of the α-halo sulfides could also be utilized. Monochlorination of alkyl sulfides by sulfuryl chloride or chlorine has been successful.[4,8]

Experimental[9]

Preparation of α-Chloro Sulfides.—The method was adapted from Böhme, *et al.*,[4] using molar equivalents of mercaptan and formaldehyde (as polyoxymethylene, trioxane did not give a satisfactory reaction). When hydrogen chloride uptake was complete, an excess of calcium chloride was added, and the mixture was tumbled at −10° on a Rinco evaporator with gradually decreasing pressure until water and hydrogen chloride removal appeared complete. At the end methylene chloride was added, partially exhausted *in vacuo* to remove final traces of hydrogen chloride, and the solution was filtered. To facilitate the oxidation to the sulfone, the sulfides were frequently vacuum distilled; however, the crude product could be oxidized with final purification at the sulfone stage. When higher monomeric aldehydes were used, the aldehyde was added dropwise to the stirred mercaptan through which hydrogen chloride was passed. In such cases it was important to keep the temperature low (−15° or below) to minimize side reactions. The following chloro sulfides were prepared: α-chloroethyl *n*-propyl sulfide (paraldehyde and *n*-propyl mercaptan), α-chloropropyl ethyl sulfide (propionaldehyde, added dropwise, and ethyl mercaptan), α-chloromethyl *sec*-butyl sulfide (polyoxymethylene and *sec*-butyl mercaptan), and α-chloromethyl isopentyl sulfide (polyoxymethylene and isopentyl mercaptan), which were not distilled, and α-chloromethyl isobutyl sulfide (polyoxymethylene and isobutyl mercaptan), b.p. 64–72° (22 mm.), 43% yield, and α-chloromethyl ethyl sulfide (polyoxymethylene and ethyl mercaptan), b.p. 66–70° (80–85 mm.),[10] 42% yield (some mechanical loss).

The α-chloroethyl ethyl sulfide was prepared by the method of Bordwell and Pitt[8] by chlorination of ethyl sulfide with sulfuryl chloride. A higher yield was obtained in pentane than in methylene chloride solution.

Oxidation of Sulfides to Sulfones.—Commercial peracetic acid (Becco 40% in acetic acid) was diluted with 3–4 vol. of methylene chloride. The upper aqueous layer was removed, and the remaining solution was dried overnight in the cold over sodium sulfate. Reaction with potassium iodide and thiosulfate titration usually showed a peracid titer of 1.1–1.4 *M*. To ensure sufficient oxidant for complete conversion to the sulfone, between 2.2 and 2.6 moles of peracid were used per mole of chlorosulfide. With a pure, distilled chloro sulfide, only a small excess was needed. For the nondistilled sulfides, a larger excess was desirable. The peracid solution was vigorously stirred in a creased three-neck flask which was cooled to −25° in a Dry Ice–alcohol bath, while the chloro sulfide dissolved in methylene chloride was added as rapidly as possible keeping the temperature of the mixture below −10°. As soon as addition was complete, the mixture was allowed to warm to room temperature and then gently refluxed for about 1 hr. It was found that when a crude chloro sulfide was used, there was an exothermic reaction which took place as the solution warmed to room temperature. It was not dangerous at any time, but caution should be observed during the warming operation. After refluxing, the solution was cooled to room temperature and the excess of peracetic acid was destroyed by adding portions of solid sodium sulfite or sodium bisulfite to the stirred solution. When no further temperature rise occurred on addition of the bisulfite, and when a potassium iodide test for peroxide was negative, the mixture was filtered, the solvent was removed *in vacuo* on a Rinco evaporator, and the residue was distilled through a short Vigreux column. When the chloro sulfide was pure, the sulfone product was nearly pure. When a crude sulfide was oxidized, there was always a high-boiling residue which decomposed somewhat during the distillation.

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[3] The olefins were mixtures of *cis* and *trans* isomers. A detailed discussion of the stereochemistry of this reaction will be presented in a later paper.

[4] H. Böhme, H. Fischer, and R. Frank, *Ann.*, **563**, 54 (1949).

[5] L. A. Walter, L. H. Goodson, and R. H. Fosbinder, *J. Am. Chem. Soc.*, **67**, 657 (1945).

[6] See H. L. Goering, D. I. Relyea, and D. W. Larsen, *ibid.*, **78**, 348 (1956).

[7] See F. G. Bordwell and W. A. Hewett, *ibid.*, **79**, 3493 (1957).

[8] F. G. Bordwell and B. M. Pitt, *ibid.*, **77**, 572 (1955).

[9] Boiling points are uncorrected. Combustion analyses were by Earl Bowers of the Humble Oil and Refining Co.

[10] H. Böhme [*Ber.*, **69**, 1610 (1936)] gives b.p. 128–131° for the sulfide and b.p. 128° (14 mm.) for the sulfone.

For chloro sulfides with chlorine on secondary carbon atoms, about 10% (by volume) of acetic anhydride was also added to the dried methylene chloride solution after cooling, and prior to sulfide addition, for purposes of final water removal. After vigorous stirring for about 0.5 hr. at −10 to −25°, the sulfide was added as above. It is not known if this additional attempt to create anhydrous conditions is necessary. If the methylene chloride solution is thoroughly dried with sodium sulfate, the additional precaution may well be superfluous. The work-up is somewhat complicated by presence of the acetic anhydride, and the possible formation of acetyl peroxide which must be completely destroyed before product distillation. Where acetic anhydride was used, the oxidizing mixture was stirred at room temperature for 24 hr. without refluxing. This is likely an unnecessary precaution.

Sulfones were usually purified by distillation, although in some cases the crude products were treated with base to give the olefins directly. Often it was difficult to remove small amounts of evil-smelling impurities from the sulfones by distillation. However, the materials could be recrystallized at −78° from ethanol, ethanol–petroleum ether, or ether–petroleum ether mixtures. Sulfones were prepared from all the sulfides that are described above.

α-Chloroethyl ethyl sulfone, b.p. 64–65° (0.5 mm.), $n^{25}\text{D}$ 1.4703, 69% yield (based on sulfide), was recrystallized from ether–petroleum ether at −78°. Ramberg and Bäcklund[2] give m.p. 19.8°, $n^{20}\text{D}$ 1.4723.

α-Chloroethyl *n*-propyl sulfone, b.p. 73–77° (0.3 mm), $n^{26}\text{D}$ 1.4670, was recrystallized from ether–petroleum ether at −78° in 50% yield (based on original mercaptan).

Anal. Calcd. for $C_5H_{11}ClO_2S$: C, 35.19; H, 6.50. Found: C, 35.21; H, 6.57.

α-Chloropropyl ethyl sulfone, b.p. 85° (0.65 mm), $n^{26}\text{D}$ 1.4700, was recrystallized from ether–petroleum ether and then ethanol at −78°, in 30% yield (based on mercaptan).

Anal. Calcd. for $C_5H_{11}ClO_2S$: C, 35.19; H, 6.50. Found: C, 35.31; H, 6.52.

Chloromethyl isobutyl sulfone had b.p. 92° (0.65 mm.), $n^{25.9}\text{D}$ 1.4686, crude yield 99% (based on sulfide).

Chloromethyl ethyl sulfone[10] had b.p. 78–80° (0.4 mm.), $n^{25.6}\text{D}$ 1.4757, crude yield 100% (based on sulfide).

Chloromethyl *sec*-butyl sulfone had b.p. 85–88° (0.5 mm.), $n^{25.3}\text{D}$ 1.4755, 39% yield (based on mercaptan).

Chloromethyl isopentyl sulfone had b.p. 98° (0.4 mm.), $n^{25}\text{D}$ 1.4710, 65% yield (based on mercaptan).

Where no analytical data are given, product identity was verified by reaction with base to give the expected olefin. The olefins were analyzed by vapor phase chromatography.[11]

Conversion of sulfones to olefins was effected simply by gentle refluxing of the sulfone with a solution of 2–3 *N* sodium or potassium hydroxide. Low-boiling olefinic products were collected in a Dry Ice or liquid nitrogen trap connected by a delivery tube to a condenser atop the reaction flask. Usually a slow nitrogen sweep was used to carry over the product. Heavier olefins were collected by boiling the solution vigorously enough to effect a steam distillation through a short Vigreux column simultaneous with the decomposition. The product was then separated from the water layer and dried.

In a typical deuterated olefin synthesis, sodium metal (40 g.-atoms) was dissolved in 20 ml. of deuterium oxide (99.5% min.; 2200 mmoles of deuterium) under nitrogen. The sulfone (10 mmoles) was added at room temperature, and the mixture was stirred vigorously for about 1 hr. at 65–70°. The temperature was slowly raised until gentle boiling commenced and continued until reaction was complete. The long reaction time is used to permit maximum equilibration prior to elimination. The deuterium content of the product can be no greater than the equilibrium concentration in the solution, which in the present case is about 98%. Actual values obtained were closer to 97% of the available olefinic hydrogens deuterated. By carrying out the equilibration in two steps or varying preliminary equilibration conditions further, this value might be improved upon, although such exhaustive studies were not made in the course of this work.

Analyses of Deuterated Olefins.—The olefinic products were assayed for chemical purity by vapor phase chromatography[11] and for deuterium content by a mass spectrometric technique.[12] Mass spectra of the samples were run at a series of ionizing voltages between 13 and 7.5 v. The relative parent peak intensities were assumed equal to the relative concentrations. The ionizing voltage was decreased in 1-v. steps until at two successive voltages the ratios of the three parent peaks (corresponding to the mono-, di-, and trideuterated molecules) to each other remained constant. This was assumed to indicate the absence of serious fragmentation of the molecules. Success of the analysis rests on the further assumption that the sensitivity of the three molecules is the same. This technique did not appear to be satisfactory with propene-d_3. Even at the lowest practical ionizing voltage there appeared to be some fragmentation occurring, probably resulting in a low value for the extent of deuteration. The analyses of various deuterated olefins prepared as above were 1-propene, >85% d_3, total yield 50%; 3-methyl-1-butene, 90.7% d_3, 9.3% d_2, 0.0 ± 0.4% d_1, total yield 75% (In a second run the partially equilibrated sulfone was recovered by removal of the deuterium oxide *in vacuo* and then treated anew with sodium deuterioxide. This "double exchange" gave 93.3% d_3, 6.7% d_2, 0.0 ± 0.6% d_1. The product was contaminated with small amounts of 2-methyl-1-butene and 1-pentene arising from impurities in the isobutyl mercaptan.); 2-methyl-1-butene, 93.5% d_3, 6.5% d_2, 0.0 ± 0.5% d_1, total yield 66%; 3-methyl-1-pentene, 91.7% d_3, 8.3% d_2, 0.0 ± 0.5% d_1, total yield 82%.

Halogenation of Alkyl Sulfones.—This method was used with ethyl, propyl, and butyl sulfones. No prolonged experimentation was done to optimize conditions. To the vigorously stirred solution of sulfone (0.04 mole) in dry benzene (about 150 ml.) was added through a serum cap at room temperature over a few minutes under nitrogen a commercial solution of butyllithium (0.04 mole of 15% solution in hexane, Foote Mineral Co., Johnsonville, Tenn.). The white slurry was stirred for 0.5 hr., refluxed for 3 min., cooled, and then poured gradually into a rapidly stirred solution of bromine or iodine (20% molar excess) dissolved in benzene and cooled in an ice bath. As soon as addition was complete, the mixture was allowed to warm to room temperature, then heated to 50° for 5 min., cooled, and shaken with sodium bisulfite solution until colorless and then with water. The combined aqueous extracts were extracted with chloroform to recover any dissolved sulfone (not necessary with heavier sulfones), and the chloroform extract was added to the benzene layer. After drying (sodium sulfate) and concentration the crude product was either distilled, recrystallized, or treated directly with base to give the olefin. Iodination in general seemed to give higher yields than bromination. The products were always somewhat impure, but since impurities such as unreacted starting materials did not interfere with the conversion to olefin, no special efforts at purification were made. Conversion of alkyl sulfones to olefins was effected through the crude iodo sulfones to the extents of 40% dibutyl sulfone, 47% dipropyl sulfone, and 50% ethyl sulfone. The hexenes and octenes isolated directly from the steam distillate were subjected to v.p.c. analysis and shown to be mixtures of *cis* and *trans* isomers.[4] A few per cent of a contaminating peak eluting much later than the olefins was also present. It was not identified although its odor suggested an aldehyde.

The bromoethyl ethyl sulfone was distilled through a short Vigreux column giving several cuts, the last of which had b.p. 84–86° (0.75 mm), $n^{25}\text{D}$ 1.5000, and which analyzed about 78% pure by n.m.r. The principal contaminant was diethyl sulfone (at least 16%).

The iodoethyl ethyl sulfone gave a cut with b.p. 112–114° (0.9 mm.), $n^{25}\text{D}$ 1.5487, which had a reddish color arising from by-product decomposition during distillation and which analyzed 90–95% pure by n.m.r. It contained a small amount of diethyl sulfone. The iodinated hexyl and butyl sulfones were not distilled but used in the crude state.

Addition of Hydrogen Sulfide to Olefins.—The procedure described by Goering, *et al.*,[6] was used. While any of a variety of intense light sources may be used, a large excess of hydrogen sulfide is necessary to minimize organic sulfide formation by reaction of the initially formed mercaptan with unreacted olefin.

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(11) The author is indebted to W. C. Jones and associates of the Humble Oil and Refining Co. for the olefin analyses. Columns and procedures were those developed in the Humble laboratories for routine olefin analyses.

(12) The author is indebted to T. Aczel, E. Lumpkin, and associates of the Esso Research and Engineering Co. for developing and carrying out these analyses.

Acknowledgment.—The author is grateful to the Humble Oil and Refining Company for permission to publish these results.

A New Selective Desulfurization Method[1]

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The catalysis exhibited by nickel salts on the hydrolysis of sodium borohydride was described by Schlesinger and co-workers[2] in 1953. The black material resulting from the reaction of nickel salts with sodium borohydride is believed to be nickel boride, Ni_2B,[2,3] and has been reported[3,4] to be a selective hydrogenation catalyst nearly as active as Raney nickel.

The first use of nickel boride as a desulfurization reagent was reported[5] in 1963 when it was found possible, by varying the amount of nickel boride, to replace one or both sulfur atoms of a mercaptole by hydrogen. With this apparent selectivity a further study of nickel boride as a desulfurization reagent was in order.

The use of nickel boride for desulfurization has now been extended and it has been shown to be an effective reagent for desulfurization of mercaptans, sulfides, and sulfoxides in yields nearly comparable to Raney nickel (Table I). The utility of nickel boride as a desulfurization reagent for disulfides is diminished by the formation of the corresponding sulfide as a by-product. Furthermore, the lack of desulfurization activity toward sulfones by nickel boride indicates a high degree of selectivity when compared with Raney nickel, which is known to cleave many simple sulfones in high yield.[6] To determine the extent of this selectivity, *p*-phenylsulfonylphenyl *p*-tolyl sulfide was treated with both nickel boride and Raney nickel. As expected, the Raney nickel treatment produced high yields of both benzene and toluene, whereas the nickel boride treatment produced high yields of toluene and phenyl sulfone.

TABLE I

DESULFURIZATION WITH RANEY NICKEL AND NICKEL BORIDE

Compd.	% yield of toluene[a] Nickel boride	Raney nickel
p-Toluenethiol	60	91
p-Tolyl disulfide	37[b]	85
p-Tolyl sulfide	72	86
p-Tolyl sulfoxide	80	100
p-Tolyl sulfone	0	88
p-Phenylsulfonylphenyl *p*-tolyl sulfide	84[c,d]	91[e]

[a] Percentages were determined by vapor phase chromatographic analysis on a 12-ft. column packed with di-*n*-decyl phthalate on Chromasorb W. [b] *p*-Tolyl sulfide (5.7% of theoretical) was isolated and identified by melting point. [c] Phenyl sulfone (91% of theoretical) was isolated and identified by melting point and mixture melting point with an authentic sample. [d] There was no detectible amount of benzene by vapor phase chromatographic analysis. [e] Benzene (100% of theoretical) was observed by vapor phase chromatographic analysis.

Despite the fact that the yields of desulfurization products are lower when nickel boride is used than when Raney nickel is used, nickel boride does have significant advantages over Raney nickel as a desulfurization reagent. First of all, nickel boride can be used to remove selectively only a single sulfur atom of a mercaptole or to remove selectively mercapto, sulfide, and sulfoxide groups without disturbing sulfone groups which may be present. Second, since nickel boride is more easily prepared, the necessity for a tedious preparation of Raney nickel is eliminated. Third, nickel boride is completely nonpyrophoric[3] and is less hazardous than Raney nickel. Fourth, since the nickel boride is generated from easily handled materials, the exact amounts can be determined, in contrast to Raney nickel which cannot be weighed accurately because the pyrophoric solid must be kept wet.

In summary, a selective new desulfurization method using nickel boride has been developed, which is safer and in many instances more convenient than desulfurization with Raney nickel.

Experimental[7]

A Generalized Procedure for Desulfurization Using Nickel Boride.—In a flask fitted with an addition funnel, a stirrer, and a condenser was placed the organic sulfur compound, 10 mole equiv. of nickelous chloride hexahydrate, and ethanol solvent. After the system had been swept with a stream of nitrogen for 15 min., an aqueous solution of 30 mole equiv. of sodium borohydride was added dropwise, while the reaction mixture was being cooled in an ice bath. The evolved hydrogen was passed through a vapor trap cooled in a Dry Ice bath. After addition was complete, the reaction mixture was refluxed for 7 hr. and distilled until the distillate showed no trace of toluene by vapor phase chromatographic analysis. The distillation residue was filtered and washed with acetone to remove any remaining organic material. The acetone solution was evaporated and the residual organic material was identified.

A Generalized Procedure for Desulfurization Using Raney Nickel.—In a flask, fitted with a stirrer and reflux condenser, was placed the organic sulfur compound (2.0 g.), W2 Raney nickel[8] (7 level teaspoons or approximately 21 g. of nickel), and ethanol (100 ml.). This mixture was refluxed 7 hr. and then water (50 ml.) was added. The mixture was distilled until the distillate failed to show the presence of toluene by vapor phase chromatographic analysis.

Preparation of *p*-Phenylsulfonylphenyl *p*-Tolyl Sulfide.[9]—A mixture of *p*-bromophenyl phenyl sulfone (29.7 g., 0.1 mole), cuprous *p*-tolylmercaptide (18.65 g., 0.1 mole), quinoline (84 ml.), and dry pyridine (2 ml.) was refluxed 36 hr. with stirring. The reaction mixture was poured slowly into a mixture of cracked ice and concentrated hydrochloric acid and allowed to stand for 2 hr. This mixture was filtered and both residue and filtrate were washed several times with chloroform. The chloroform washings were combined and treated twice with charcoal. After evaporation of the chloroform, the residue was recrystallized from absolute ethanol to give *p*-phenylsulfonylphenyl *p*-tolyl sulfide (50% yield), m.p. 107–110°.

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(1) Abstracted fron the Ph.D. Thesis of F. M. Perry, Purdue University, 1965.

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