(recrystallization from aqueous methanol did not change the melting point); λ_{max} 279 mμ (MeOH, aqueous HCl), 273 (MeOH, aqueous NaOH).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.15; H, 7.92. Found: C, 74.06; H, 8.06.

Registry No.—**1**, 21297-55-2; **2**, 21297-56-3; **3**, 21297-57-4; **4**, 21297-58-5; **5**, 21297-59-6; **6**, 21297-60-9; **7**, 21297-61-0.

Raney Nickel Desulfurization of Cyclooctyl Mercaptan and Cyclooctyl Sulfide

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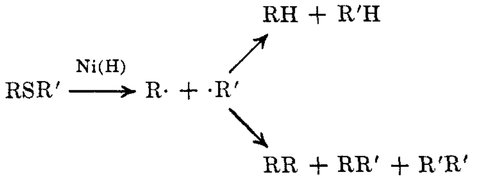
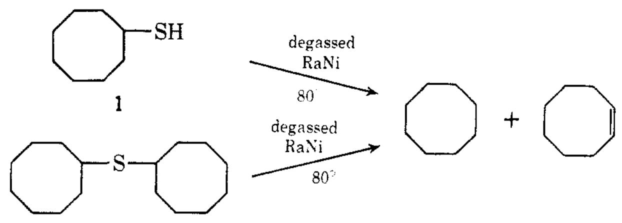
It has been suggested that the Raney nickel desulfurization of an organic mercaptan or sulfide proceeds through a free-radical intermediate which is subsequently hydrogenated or recombines to form a coupled product.[3-7] The following equation illustrates the process by which such reactions are believed to take place.[8]



In view of our interest in the free-radical reactions of medium sized ring compounds,[9] we undertook a brief study of the desulfurization of cyclooctyl mercaptan and cyclooctyl sulfide. If a cycloalkyl mercaptan or sulfide of this type is desulfurized with degassed Raney nickel with the subsequent formation of cycloalkyl radicals, one would expect these radicals to undergo characteristic disproportionation and coupling reactions rather than being hydrogenolyzed to a hydrocarbon.

For this study, cyclooctyl mercaptan (**1**) was prepared in 43% yield by the reaction of cyclooctyl bromide with thiourea followed by basic hydrolysis of the intermediate isothiouronium salt. Cyclooctyl sulfide (**2**) was prepared in 41% yield by the reaction of sodium sulfide nonahydrate with cyclooctyl bromide. The desulfurization reactions were carried out by refluxing a benzene solution of mercaptan or sulfide with a tenfold excess of degassed Raney nickel for time intervals up to 48 hr. The desulfurization of cyclooctyl mercaptan gave a 80–85% yield of a product mixture containing only cyclooctane and *cis*-cyclooctene. The relative amounts of these products varied over a wide range depending on the length of time the Raney nickel was degassed. Generally, the product mixture contained about 80% cyclooctane and 20% *cis*-cyclooctene. However, if the Raney nickel was vigorously degassed for periods of 24 hr or more, the yield of *cis*-cyclooctene approached 80% whereas the yield of cyclooctane dropped to 20%. The desulfurization of cyclooctyl sulfide proceeded very slowly and always gave back on the order of 70% unchanged starting material. From the sulfide which did decompose there was obtained a 71% hydrocarbon yield which consisted principally of *cis*-cyclooctene. No bicyclooctyl could be isolated from desulfurization of either **1** or **2**, lending some doubt as to whether these particular desulfurizations proceed through a conventional free-radical intermediate under the experimental conditions employed. In addition, the relative amounts of cyclooctane and *cis*-cyclooctene which are formed in these desulfurizations indicate that disproportionation of cyclooctyl radicals is not an important reaction pathway. The cyclooctane formed in these desulfurizations does not arise by hydrogenation of *cis*-cyclooctene since a sample of *cis*-cyclooctene was unaffected when refluxed with degassed Raney nickel in benzene. Cyclooctane is apparently formed by partial hydrogenolysis of the mercaptan or sulfide and is dependent on the amount of hydrogen bound to the surface of the degassed Raney nickel. The formation of *cis*-cyclooctene, however, is presumably due to elimination of the elements of hydrogen sulfide from cyclooctyl mercaptan or elimination of a mercaptan moiety from cyclooctyl sulfide.



1

2

Because of the highly complex nature of metallic surfaces, it is difficult to postulate an exact mechanism for these elimination reactions. In the case of a Raney nickel catalyst, a further complicating factor is the presence of substantial amounts of basic oxides.[10] One possible explanation would involve coordination of the sulfur with a metal surface followed by a homolytic weakening of the carbon–sulfur bond. Hydrogenolysis of the carbon–sulfur bond would yield cyclooctane as expected. Abstraction of a hydrogen atom on the 2 position of the ring at the metal surface, together with complete homolytic cleavage of the carbon–sulfur bond, would yield *cis*-cyclooctene. Further work on the desulfurization of alkyl mercaptans and sulfides would be useful to better understand the nature of this reaction.

Experimental Section

Boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses. Gas chromatography was carried out with 190 × 0.8 cm Pyrex columns containing 25–30% by weight liquid stationary phase on 60–80 or 80–100 mesh Johns-Manville Chromosorb. Samples were eluted with helium gas at 15 psi and detected by use of a thermal conductivity cell.

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Cyclooctyl Mercaptan (1).—The general procedure of Urquhart, Gates, and Connor[11] was used to prepare this compound. To a solution of 15.2 g of thiourea in 150 ml of absolute ethanol was added 38.2 g of cyclooctyl bromide and the resulting solution was refluxed for 48 hr. To the cooled solution was then added 120 ml of 10% sodium hydroxide solution and the mixture was refluxed for an additional 2 hr. The mercaptan layer was separated and the neutralized aqueous layer extracted with three 100-ml portions of benzene and the benzene extracts were dried over sodium sulfate. The benzene was removed by distillation through a Vigreux column under reduced pressure and the product was distilled through a semimicro column yielding 12.44 g (43%) of crude mercaptan, bp 31–34° (0.35 mm), $n^{24}\mathrm{D}$ 1.4822–1.5034. A portion of this product was chromatographed on Merck activity II acid-washed alumina and eluted with petroleum ether (bp 35–60°) to yield pure cyclooctyl mercaptan. Further elution with petroleum ether yielded a fraction shown to be cyclooctyl ethyl ether by comparison of its infrared spectrum with that of an authentic spectrum. This ether usually contaminated the crude reaction product to the extent of about 10%. The pure mercaptan had bp 98–99° (20 mm), $n^{25}\mathrm{D}$ 1.5076–1.5078. Its infrared spectrum had the characteristic mercaptan absorption[12] at 2540 cm^{-1}.

Anal. Calcd for $C_8H_{16}S$: C, 66.63; H, 11.18; S, 22.19. Found: C, 66.86; H, 11.17; S, 21.66.

Cyclooctyl Sulfide (2).—The method of Bost and Conn[13] was used in the preparation of this compound. To a solution of 6 g of sodium sulfide nonahydrate in 50 ml of absolute ethanol was added 9.6 g of cyclooctyl bromide and the resulting solution was refluxed for 20 hr. The solution was then cooled and 50 ml of water was added. The sulfide layer was separated, the aqueous layer was extracted with five 20-ml portions of petroleum ether, and the combined extracts were dried over sodium sulfate. After removal of the petroleum ether under reduced pressure with a rotary concentrator, the crude product was distilled through a semimicro column. A total of 2.6 g (41%) of product, bp 126–127° (0.25 mm), $n^{25}\mathrm{D}$ 1.5250–1.5286, was obtained. An analytical sample of cyclooctyl sulfide had bp 126–127° (0.25 mm), $n^{25}\mathrm{D}$ 1.5255.

Anal. Calcd for $C_{16}H_{30}S$: C, 75.53; H, 11.89; S, 12.58. Found: C, 75.22; H, 11.90; S, 12.58.

Preparation of Degassed Raney Nickel.—The procedure used was adapted from a similar one used by Hauptmann.[4] Commercial W-2 Raney nickel (Raney Catalyst Co., Chattanooga, Tenn.) was thoroughly washed with large portions of distilled water, ethanol, and finally reagent benzene. The wet Raney nickel was transferred to a Carius tube and the excess benzene was removed under reduced pressure. A 1500-G permanent magnet surrounding the outside of the Carius tube held the powdered nickel in place. The system was then evacuated to 1–2-mm pressure and heated to 150°. Heating was continued for at least 8 hr, after which the system was cooled and the vacuum was slowly released under nitrogen pressure. The degassed nickel was then poured into an empty reaction flask under nitrogen and a benzene solution of mercaptan or sulfide was added.

Desulfurization of Cyclooctyl Mercaptan.—A 1.10-g sample of cyclooctyl mercaptan dissolved in 35 ml of dry benzene was refluxed for 49 hr with about 10 g of degassed Raney nickel. The benzene solution was then decanted from the nickel and the nickel was carefully transferred to a Soxhlet extraction apparatus and continuously extracted with pentane for 96 hr. The pentane extracts and benzene solution were then combined and the benzene and pentane were removed by distillation. Distillation of the product mixture at 25–40° (10 mm.) yielded 698 mg (82%) of a mixture consisting of approximately 80% cyclooctane and 20% *cis*-cyclooctene. The small amount of residue contained no bicyclooctyl as determined by gc analysis on a silicon grease column heated to 230°.

Desulfurization of Cyclooctyl Sulfide.—A 1.10-g sample of cyclooctyl sulfide dissolved in 35 ml of dry benzene was refluxed with about 10 g of degassed Raney nickel for 48 hr. Separation of the reaction products was accomplished using the procedure described in the desulfurization of cyclooctyl mercaptan. Distillation of the product mixture at 25–40° (10 mm) yielded 200 mg (71% based on recovered sulfide) of a mixture of 7% cyclooctane and 93% *cis*-cyclooctene as determined by gc using an NMPN column at 30°. Chromatography of the high boiling residue on 20 g of Merck activity II acid-washed alumina and elution with pentane yielded 688 mg of a colorless oil. This material was shown to be unreacted cyclooctyl sulfide by the use of infrared and gas chromatographic techniques (silicon gum rubber at 300°). No other product could be isolated from the column chromatogram.

Registry No.—**1,** 20628-54-0; **2,** 20628-55-1.

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The Reaction of N-Sulfinylamines and N-Sulfinylsulfonamides with Carbonyl Chloride. A New Synthesis of Isocyanates

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The direct phosgenation of amine salts to isocyanates is well known; however, long reaction times are required because of the poor solubility of amine salts in organic solvents.[1] The facile reaction of amines and sulfonamides with thionyl chloride[2] provides a method of protection of the amino group, and the generated N-sulfinyl derivatives are easily soluble in organic solvents. Subsequent phosgenation could produce the corresponding isocyanate with regeneration of thionyl chloride. The over-all reaction is shown below (eq 1, 2).

$$\mathrm{RNH_2 + SOCl_2 \longrightarrow RN{=}S{=}O + 2\ HCl} \qquad (1)$$

$$\mathrm{RN{=}S{=}O + COCl_2 \longrightarrow RN{=}C{=}O + SOCl_2} \qquad (2)$$

When carbonyl chloride is added to N-sulfinylaniline (N-thionylaniline) in *o*-dichlorobenzene at 180°, no reaction occurs. In contrast, facile conversion could be achieved in refluxing benzene (80°), provided that a catalytic amount of pyridine or N,N-dimethylformamide is added to the reaction mixture. The reaction is general, and aliphatic and aromatic amines as well as aromatic sulfonamides can be converted to the corresponding isocyanates (see Table I).

TABLE I[a]

CONVERSION OF N-SULFINYLAMINES AND N-SULFINYLSULFONAMIDES TO ISOCYANATES

$$\mathrm{RN{=}S{=}O + COCl_2 \longrightarrow RN{=}C{=}O + SOCl_2}$$

Registry no.	R	Scale, mol	Time,[b] min	Yield,[c] %	Bp, °C (mm)
103-71-9	C_6H_5	0.03	85	60	55–57 (16)
4083-64-1	4-$CH_3C_6H_4SO_2$	0.03	90	62	90–92 (0.5)
622-58-2	4-$CH_3C_6H_4$	0.03	120	67	88 (17)
104-12-1	4-ClC_6H_4	0.03	45	75	87 (8.5)
5416-93-3	4-$CH_3OC_6H_4$	0.03	300	73	102 (6.5)
3173-53-3	C_6H_{11}	0.035	630	61	76 (17)

[a] An amount of 5% (by weight) of pyridine was used as the catalyst. [b] The flow rate of carbonyl chloride was approximately 145 ml/min. [c] The yields are not optimal. Losses in distillation were encountered because of the small-scale experiments.

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[1] W. Siefken, *Ann.*, **562**, 75 (1949).

[2] G. Kresze and W. Wucherpfennig in "Newer Methods of Preparative Organic Chemistry," Vol. V, Academic Press, New York, N. Y., 1968, p 113–115.