amino sulfonamide compounds corresponding to diphenoquinone, 2,6-naphthoquinone and the phenanthrene quinones for pharmacological and dipole moment studies. Such studies are now in progress in this Laboratory.

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RECEIVED NOVEMBER 18, 1940

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## Reactions of Atoms and Free Radicals in Solution. III. The Introduction of a Mercaptan Group into Cyclohexane

BY M. S. KHARASCH AND KENNETH EBERLY[1]

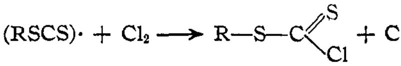
In previous articles from this Laboratory, it has been postulated that substitution reactions of aliphatic hydrocarbons (bromination,[2] chlorination,[3] sulfonation,[4] carboxylation,[5] etc.) proceed through the intermediate formation of atoms or free radicals. It appeared reasonable that under certain conditions useful synthetic reactions might be obtained by employing these. Specifically, it seemed probable that if cyclohexane were mixed with a large quantity of carbon disulfide and chlorine gas introduced slowly in the illuminated mixture, the following sequence of reactions would take place

$$Cl_2 \xrightarrow{h\nu} 2Cl\cdot \qquad (1)$$

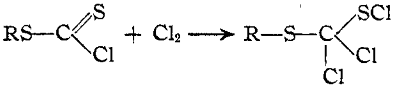
$$RH + Cl\cdot \longrightarrow R\cdot + HCl \qquad (2)$$

$$R\cdot + CS_2 \longrightarrow (RSCS)\cdot \qquad (3)$$

$$R\cdot + Cl_2 \longrightarrow RCl + Cl\cdot \qquad (4)$$



$$(RSCS)\cdot + Cl_2 \longrightarrow R{-}S{-}C(=S)Cl + Cl\cdot \qquad (5)$$



$$RS{-}C(=S)Cl + Cl_2 \longrightarrow R{-}S{-}C(SCl)(Cl)Cl \qquad (6)$$

These expectations were fully realized. When a mixture of one gram molecular equivalent of carbon disulfide and of cyclohexane (and a few drops of pyridine) was illuminated (1000 watt Mazda), and chlorine passed slowly into the solution, an energetic reaction took place. The temperature of the reaction mixture was controlled by external cooling, and by the rate of introduction of the chlorine. An effort was made to keep this temperature below 40°, and it was found necessary to use about five hours for the introduction of 30 g. of chlorine.

The reaction mixture was then transferred to an all-glass distillation apparatus and the carbon disulfide, cyclohexane, cyclohexyl chloride, and the perchloromethyl mercaptan removed at reduced pressure. At no time was the temperature of the mixture allowed to rise above 80°, since violent decomposition of the condensation product occurs at 90–100°. The last traces of volatile materials were removed by maintaining the mixture for two hours at 80° under a pressure of 4 mm. A clear light yellow non-distillable oil was thus obtained (30 g.).

Because of the impossibility of distilling this material at even low pressures ($10^{-4}$ mm.), the analytical results in various experiments did not agree as well as they probably would have if this material could have been purified. Thus, the chlorine content of various lots of the oil varied from 39 to 43%, and the sulfur content from 24 to 25%. In view of the fact that cyclohexyl dithiochlorocarbonate contains only 18.22% chlorine and 32.94% sulfur, the oil obviously is not that substance. However, if further chlorination of that substance is assumed (as in 6) to cyclohexyl dithiotrichlorocarbonate (Cl, 40.05%; S, 24.14%), then the analytical data are good enough for an oil which cannot be purified by distillation.

To prove that the postulated cyclohexyl dithiotrichlorocarbonate actually contains a cyclohexyl residue attached to sulfur, the oil was heated with alcoholic potassium hydroxide (2.5 times the calculated amount). The oil (30 g.) was added slowly (two hours) to the hot solution and the reaction brought to completion by heating for three hours longer. The alcohol was removed *in vacuo*, and water added to the residue. Upon acidification with hydrochloric acid, a dark, vile smelling oil separated. This oil was extracted with ether, and the ether extract dried over sodium sulfate. Upon distillation of the ether an oil remained. This oil was distilled and the fraction which boiled at 157–162° was collected. This fraction contained sulfur and no chlorine.

*Anal.* Calcd. for $C_6H_{12}S$: S, 27.60. Found: S, 27.16.

The recorded boiling point of cyclohexyl mercaptan is 158–161°.

The identity of the cyclohexyl mercaptan thus prepared was further confirmed by treating it with mercuric chloride and by the analysis of the cyclohexyl mercaptomercuric chloride.

*Anal.* Calcd. for $C_6H_{11}SHgCl$: Hg, 57.1. Found: Hg, 56.6.

The series of reactions cited prove conclusively that a mercaptan group can be introduced directly into cyclohexane.

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RECEIVED NOVEMBER 20, 1940

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## Application of the Gibbs Adsorption Equation to Solutions of Paraffin-Chain Salts

BY F. A. LONG AND G. C. NUTTING

The validity of the application of the Gibbs adsorption equation to aqueous solutions of

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[1] The authors wish to express their appreciation to the du Pont Company for support which made this work possible.

[2] For references, see Kharasch, Fineman and Mayo, THIS JOURNAL, **61**, 2139 (1939).

[3] For references, see Kharasch and Brown, *ibid.*, **61**, 2142 (1939).

[4] Kharasch and Read, *ibid.*, **61**, 3089 (1939).

[5] Kharasch and Brown, *ibid.*, **62**, 454 (1940).