Anal.[7] Calcd. for $C_{14}H_{28}O_2N_2$: N, 10.92. Found: N, 10.64.

This amide is soluble in water.

N,N,N',N'-Tetramethylsebacamide crystallized from a mixture of low- and high-boiling petroleum ether. It formed glistening white plates which melted at 87–88° and were soluble in water and organic solvents.

Anal. Calcd. for $C_{14}H_{28}O_2N_2$: C, 65.57; H, 11.00; N, 10.89. Found: C, 65.21; H, 10.48; N, 10.91.

The amide formed a hygroscopic crystalline salt on treatment with dry hydrogen chloride; m. p. 122–126°. Chloroplatinic acid gave an orange-colored solid melting at 156.5–158°—presumably the chloroplatinate—which, like the hydrochloride, was difficult to purify. The **chloroaurate** crystallized from dilute alcohol in yellow plates melting at 158–158.5°.

Anal. Calcd. for $C_{14}H_{29}O_2N_2AuCl_4$: C, 28.18; H, 4.90; Au, 33.07. Found: C, 28.17; H, 4.91; Au, 32.94.

N,N,N',N'-Tetraethylsebacamide did not solidify and was not very soluble in water. However, it dissolved readily in 10% hydrochloric acid and was reprecipitated from this solution by the addition of excess sodium hydroxide. The hydrochloride melted at about 0° and the chloroplatinate at 148.5–150°. The amide was identified by conversion to the **chloroaurate**. The latter was purified by repeated recrystallization from aqueous alcohol. It formed flaky yellow crystals melting at 130–131°.

Anal. Calcd. for $C_{18}H_{37}O_2N_2Cl_4Au$: C, 33.01; H, 5.71; Au, 30.22. Found: C, 32.76; H, 5.58; Au, 30.18.

N,N,N',N'-Tetraethylazelamide resembled tetraethylsebacamide with respect to solubility in water, acids and bases. Likewise it failed to crystallize. The hydrochloride was an oil and the chloroplatinate a solid melting at 140–142°. A more satisfactory derivative was the **chloroaurate**. It separated from dilute alcohol as yellow crystals melting at 136.5–137°.

Anal. Calcd. for $C_{17}H_{35}O_2N_2Cl_4Au$: C, 31.93; H, 5.53; Au, 30.84. Found: C, 32.01; H, 5.48; Au, 30.75.

(7) The analyses in this paper are microanalyses and were carried out by Mr. C. W. Beazley, Mr. L. G. Fauble and Miss Mary S. Kreger.

THE NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS RECEIVED NOVEMBER 7, 1940

p-(*p*-Aminophenyl)-benzenesulfonamide and Derivatives

BY I. F. HALVERSTADT AND W. D. KUMLER

In view of the recent publication[1] by Van Meter, Bianculli and Lowy on the above subject it seems desirable to give an account of work we have completed on these compounds.

Before the above article appeared we had prepared *p*-(*p*-acetaminophenyl)-benzene sulfonyl chloride I, *p*-(*p*-acetaminophenyl)-benzenesulfonamide II and *p*-(*p*-aminophenyl)-benzenesulfonamide III and had sent the last two compounds together with *p*-(*p*-nitrophenyl)-benzenesulfonamide to Dr. L. A. Sweet of Parke, Davis and Company for pharmacological evaluation.

(1) Van Meter, Bianculli and Lowy, THIS JOURNAL, **62**, 3146 (1940)

The compounds were prepared by the same series of reactions as described by the above authors and the yields were about the same except in case of the *p*-(*p*-aminophenyl)-benzenesulfonamide which was obtained in 85% yield compared with the reported yield of about 60%. Different methods of purification were used and the observed melting or decomposition points are higher than those reported. All melting points are corrected.

The crude damp I was dissolved in acetone, neutralized with sodium bicarbonate, filtered and the filtrate concentrated to precipitate yellow crystals of the compound.

These crystals were extracted with ether using a Soxhlet apparatus and the product thus obtained from the ether did not melt on heating, but sintered at 180° and slowly decomposed at higher temperatures.

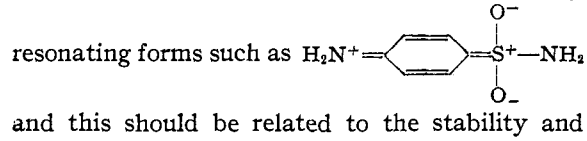
Gelatinous II was boiled with water, filtered, triturated with acetone, filtered, and recrystallized from 50% dioxane–water as white crystals, m. p. 295.0–296.5° with some decomposition.

To make III, pure II was refluxed with 12% hydrochloric acid, cooled with neutralizing to *p*H 6, filtered and washed. The precipitate was dissolved in acetone, decolorized with Norit and the solution concentrated at room temperature to give white, fine crystals of m. p. 259–260° and 266–267° with slight decomposition. The double m. p. is observed only if the rate of heating is slow in order to promote crystal formation in the molten compound at the first m. p.

To prove the position of the sulfonamide group *p*-(*p*-nitrophenyl)-benzenesulfonamide m. p. 225.5–227.0° was prepared by the method of Gabriel and Dambergris.[2] The nitro compound was then reduced to the amino compound with tin and a 10% solution of hydrochloric acid in 70% ethanol. The compound gave the same melting point as III and the same mixed melting point with III.

These compounds are part of a series we are making to investigate the effect of substituting different nuclei with the same resonance type as benzene, between the amino and sulfonamide groups.

A current theory in regard to the action of sulfanilamide is that the active agent is an oxidized form of the compound. The ease of oxidation would be correlated with the contribution made by resonating forms such as



and this should be related to the stability and consequently the reduction potentials of the corresponding *p*-quinones. An examination of such potentials suggested to us the preparation of the

(2) Gabriel and Dambergris, *Ber.*, **13**, 1408 (1880).

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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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

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

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

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

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

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

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

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.

(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).

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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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