distilling. It analyzed 62.52, 62.08% of chlorine and 13.39, 13.51% of sulfur, as compared with theoretical values of 62.77 and 14.19, respectively. $\alpha,\alpha,\beta,\beta,\beta,\beta'$-Hexachlorodiethyl sulfide boils at 131–132° (4.5 mm.) or 159.5–160° (15 mm.). Mann and Pope[3] give 160–161° (15 mm.) for the same compound.

Anal. Calcd. for $C_4H_4SCl_6$: Cl, 71.67; S, 10.80. Found: Cl, 70.88, 70.85; S, 11.05, 10.93.

This compound, since it contains no hydrogen in the chlorinated ethyl group, is stable and distils unchanged. Further chlorination under the conditions employed by us leads to a complete breaking up of the molecule with the formation of chlorinated hydrocarbons. This was also observed by Mann and Pope.

Summary

1. Practically all of the compounds theoretically possible on treating β,β-dichloro-ethyl sulfide with chlorine have been isolated and identified.
2. With one exception, all chlorinated derivatives below the hexachloro are unstable, splitting out hydrogen chloride on distillation with formation of unsaturated compounds. The exception, $\alpha,\beta,\beta,\beta'$-tetrachlorodiethyl sulfide, may be distilled, but breaks up like the others on refluxing.
3. None of these compounds is vesicant.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY]

ACYL DERIVATIVES OF ORTHO-AMINOPHENOL. III

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Previous work published from this Laboratory[1] has shown that, "when *o*-aminophenol is acylated with the structural isomers, *n*-carbopropoxy and *iso*carbopropoxy groups, irrespective of their original positions, a partial rearrangement occurs. When the corresponding compounds with the *n*- and *iso*butoxy groups are made, their behavior is somewhat different. While the butyl carbonate of *iso*butyl-*o*-hydroxycarbanilate rearranges partially, giving a mixture of the two isomers, *iso*butyl carbonate of butyl *o*-hydroxycarbanilate was not found to change." In view of the behavior of these isomers against each other in the acylating of *o*-aminophenol it became of interest to us to investigate the behavior of such structural isomers against an aliphatic group and also against an aromatic group. The following pairs of groups were used:

$—CO_2C_4H_9(n)$ and $—CO_2C_5H_{11}(iso)$; $—CO_2C_4H_9(iso)$ and $—CO_2C_5H_{11}(iso)$;
$—CO_2C_3H_7(n)$ and $—COC_6H_5$; $—CO_2C_3H_7(iso)$ and $—COC_6H_5$

Iso-amyl-*o*-hydroxycarbanilate was acylated with *n*-butylchloro-carbonate and a stable diacyl obtained which yielded *iso*-amyl-*o*-hydroxycarbanilate on saponification. When *n*-butyl-*o*-hydroxycarbanilate was

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[1] Nelson and Aitkenhead, THIS JOURNAL, **48**, 1680 (1926).

acylated with *iso*-amylchlorocarbonate the same diacyl was obtained as above and the saponification product was *iso*-amyl-*o*-hydroxycarbanilate. The *n*-carbobutoxy group in the second diacyl had migrated from the nitrogen to the oxygen during the preparation of the compound.

When *iso*-amyl-*o*-hydroxycarbanilate was acylated with *iso*-butylchlorocarbonate a stable diacyl was obtained which yielded *iso*-amyl-*o*-hydroxycarbanilate on saponification. Treatment of *iso*-butyl-*o*-hydroxycarbanilate with *iso*-amylchlorocarbonate resulted in the same diacyl as that from *iso*-amyl-*o*-hydroxycarbanilate and the saponification product was *iso*-amyl-*o*-hydroxycarbanilate. In this case the *iso*-carbobutoxy group had migrated from the nitrogen to the oxygen.

Benzoyl-*o*-aminophenol was acylated with *n*-propylchlorocarbonate and gave a diacyl which yielded benzoyl-*o*-aminophenol on saponification. When *n*-propyl-*o*-hydroxycarbanilate was acylated with benzoyl chloride the same diacyl was obtained and the saponification product was benzoyl-*o*-aminophenol. A rearrangement of the *n*-carbopropoxy from the nitrogen to the oxygen had taken place in the latter case.

When *iso*propyl-*o*-hydroxycarbanilate was acylated with benzoyl chloride a stable diacyl was obtained which yielded *iso*propyl-*o*-hydroxycarbanilate on saponification. Treatment of benzoyl-*o*-aminophenol with *iso*propylchlorocarbonate yielded the same diacyl. Saponification gave *iso*propyl-*o*-hydroxycarbanilate. The benzoyl group had migrated from the nitrogen to the oxygen.

Experimental Part

All the mono-acyls used were prepared by Groenvik's method and are described in the literature.

The diacyl derivatives of *o*-aminophenol were prepared by the Schotten-Baumann method from the mono-acyl derivatives and the acyl chlorides as follows. About 3 g. of the mono-acyl derivative was dissolved in 75 cc. of water containing 1 g. of potassium hydroxide (slightly more than the calculated amount). After solution was complete, an excess (about 2 cc.) of the acyl chloride was added. The oil which formed was extracted with

TABLE I

DIACYL DERIVATIVES

Compound	Formula	M. p., °C.	Analysis, N, % Calcd.	Analysis, N, % Found
Butylcarbonate of *iso*-amyl-*o*-hydroxycarbanilate	$C_4H_9CO_2OC_6H_4NHCO_2C_5H_{11}$	77	4.33	4.23
*iso*Butylcarbonate of *iso*-amyl-*o*-hydroxycarbanilate	$C_4H_9CO_2OC_6H_4NHCO_2C_5H_{11}$	61.5	4.33	4.38
Propylcarbonate of benzoyl-*o*-aminophenol	$C_3H_7CO_2OC_6H_4NHCOC_6H_5$	52	4.68	4.67
o - *iso*Carbopropoxyaminophenylbenzoate	$C_3H_7CO_2NHC_6H_4OCOC_6H_5$	82	4.68	4.68

ether and the ether evaporated. A brown oil remained. When this was dissolved in alcohol and poured into water, an emulsion was formed and crystallization finally took place. These crystals were purified from dilute alcohol.

The diacyls were saponified by dissolving in 10% potassium hydroxide and then acidifying with hydrochloric acid. The precipitate was purified by recrystallization from dilute alcohol. All analyses were made by the Kjeldahl method.

Summary

1. The heavier *iso*-carbopentoxy group replaces both the *n*- and the *iso*carbobutoxy from the nitrogen in diacyl derivatives of *o*-aminophenol.
2. The benzoyl group does not behave the same with the *n*-carbopropoxy and the *iso*-carbopropoxy groups in diacyl derivatives of *o*-aminophenol. In the case of the *n*-carbopropoxy derivative the benzoyl group goes to the nitrogen, but in the case of the *iso*carbopropoxy group the benzoyl group goes to oxygen.
3. New diacyl derivatives of *o*-aminophenol have been prepared and studied.

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[Contribution from the Chemical Laboratory of the University of California]

THE HYDROGEN-ETHYLENE REACTION IN THE PRESENCE OF EXCITED MERCURY ATOMS

By A. R. Olson and Charles H. Meyers

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In a former paper the authors[1] concluded from semi-quantitative evidence that ethane was formed from hydrogen and ethylene when a mixture of the latter is illuminated with ultraviolet light in the presence of mercury vapor. However, it was also known at this time that in addition to ethane other substances must be formed. The experiments about to be described were undertaken to determine the products of the reaction more definitely.

The experimental arrangement used to expose the gas to the light was the same as that described in our former paper except that the gases were kept in constant circulation.

The ethylene and hydrogen were prepared as described in our former paper. Ethane was prepared by treating an ether solution of C_2H_5MgI with dilute sulfuric acid. The ethane was dried and purified by bubbling through concentrated sulfuric acid and by means of liquid air fractionally distilled three times, the middle portion only being saved for each subsequent distillation.

In Experiment I a mixture of hydrogen at a pressure of 39 cm. and ethyl-

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[1] Olson and Meyers, This Journal, **48**, 389 (1926).