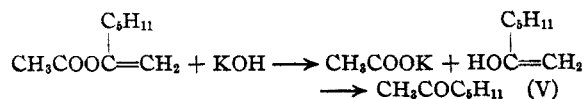


m. p. 122–123° and (3) acetic acid. The reaction may be formulated as follows



Reactions of α -Amylvinyl Acetate.—This compound (IV) dissolved in carbon tetrachloride adds bromine very readily to form an unstable bromide with distinct lachrymatory properties. It dissolves completely in cold concentrated sulfuric acid and is not reprecipitated by careful dilution with cold water. Ammonolysis of the ester (IV) yields acetamide and amyl methyl ketone (V).

This work is being continued in order to complete several

homologous series of these ketals and esters, and to investigate their reactions and properties.

Summary

1. Alkyl acetylenes react with methyl alcohol and glycol in the presence of boron fluoride and mercuric oxide to form good yields of ketals.

2. Alkyl acetylenes react with acetic acid in a similar manner to form α -alkylvinyl esters, some ketone being formed as a by-product.

3. Hydrolysis of these ketals and esters yields ketones in high yields.

NOTRE DAME, INDIANA

RECEIVED NOVEMBER 20, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE RICE INSTITUTE]

Synthesis of Some Halogenated Thiophenols

BY R. C. DOSSER AND G. HOLMES RICHTER

Hammet and his co-workers¹ have observed that thiocresol not only accelerates the rate of healing of wounds of long standing, but also exerts a bacteriostatic action not shown by other compounds commonly used as tissue proliferants. It is well known that the introduction of chlorine into phenols increases their antiseptic properties, hence the chlorinated thiophenols should possess a specific interest. The synthesis of a number of compounds of this type not previously described in the literature is here reported. Their biological properties will be described elsewhere.

The method of synthesis employed in each case was to sulfonate the suitable aromatic amine by the baking process; after which the aminosulfonic acid was put through a Sandmeyer reaction in which the amino group was replaced by chlorine. The chlorosulfonic acids were usually isolated as the sodium salts, which were treated with phosphorus pentachloride. The resulting chlorosulfonyl chlorides were then reduced with hydrochloric acid and zinc in benzene suspension. A portion of the chlorosulfonyl chloride was usually converted into the corresponding sulfonamide. The mercury salts were prepared by treating an alcoholic solution with mercuric chloride. The disulfides were prepared by exposing an ammoniacal solution of the thiol to air for several hours.

Experimental

1. **6-Chloro-1-methyl-3-thiolbenzene.**—*o*-Toluidine was used as the starting material. The chlorosulfonyl chloride melted at 64°. The final product was isolated by distillation; b. p. 122–123° at 26 mm.; d_4^{20} 1.2217; n_D^{20} 1.5967.

Anal. Calcd. for $\text{C}_7\text{H}_7\text{SCl}$: S, 20.22. Found: S, 20.17.

2. **Mercury Salt of 6-Chloro-1-methyl-3-thiolbenzene.**—The product recrystallized from alcohol and dried over phosphorus pentoxide melted at 193–194°.

Anal. Calcd. for $\text{C}_7\text{H}_7\text{Cl}_2\text{S}_2\text{Hg}$: C, 32.57; H, 2.34. Found: C, 32.50; H, 2.57.

3. **Disulfide of 6-Chloro-1-methyl-3-thiolbenzene.**—The product was purified by recrystallization from alcohol, m. p. 65°.

Anal. Calcd. for $\text{C}_{14}\text{H}_{12}\text{Cl}_2\text{S}_2$: C, 53.31; H, 3.83. Found: C, 52.70; H, 3.62.

4. **2-Chloro-1,3-dimethyl-5-thiolbenzene.**—The starting material was 1,3-dimethyl-2-aminobenzene. The chlorosulfonyl chloride recrystallized from ligroin melted at 121°. The sulfonamide, recrystallized from alcohol, melted at 205°. The final product purified by distillation boiled at 141–142° at 29 mm.; d_4^{20} 1.1906; n_D^{20} 1.5911.

Anal. Calcd. for $\text{C}_8\text{H}_9\text{ClS}$: S, 18.58. Found: S, 18.62.

5. **The Mercury Salt of 2-Chloro-1,3-dimethyl-5-thiolbenzene.**—The product recrystallized from alcohol melted at 240–245° (dec.).

Anal. Calcd. for $\text{C}_8\text{H}_9\text{Cl}_2\text{SHg}$: C, 23.55; H, 1.98. Found: C, 23.32; H, 2.30.

6. **Disulfide of 2-Chloro-1,3-dimethyl-5-thiolbenzene.**—The product separates out from alcohol as needles with a slight yellowish cast, m. p. 124–125°.

Anal. Calcd. for $\text{C}_{16}\text{H}_{16}\text{Cl}_2\text{S}_2$: C, 55.95; H, 4.69. Found: C, 56.08; H, 4.63.

(1) "Synthetic Organic Chemicals," Eastman Kodak Publication, Vol. III, No. 5, 1930; *J. Exptl. Med.*, **60**, 445 (1929); *Proc. Soc. Exptl. Biol. Med.*, **27**, 20 (1929).

7. **5-Chloro-1,4-dimethyl-2-thiolbenzene.**—The starting material was 2-amino-1,4-dimethylbenzene. All attempts to sulfonate this material were unsatisfactory. The amine was acylated with acetic anhydride and sulfonated according to the directions of Junghahn.² The acetyl group was removed by refluxing for three hours with concentrated hydrochloric acid. The reactions from this stage on were identical with those in the previous cases. The chlorosulfonyl chloride melted at 49–49.5°; the sulfonamide at 189–190°. It was possible to recrystallize the product from benzene if the solution was placed in a desiccator filled with paraffin shavings; the melting point was 92.5°.

Anal. Calcd. for C_8H_9ClS : S, 18.57. Found: S, 18.67.

8. **Disulfide of 5-Chloro-1,4-dimethyl-2-thiolbenzene.**—The product was recrystallized from a chloroform–alcohol mixture (1:2) and melted at 103°.

Anal. Calcd. for $C_{16}H_{18}Cl_2S_2$: C, 55.95; H, 4.69. Found: C, 56.15; H, 4.68.

9. **2-Chloro-1-thionaphthalene.**—The starting material was 2-amino-1-naphthalene sulfonic acid. The final product recrystallized from alcohol melted at 66.5°.

(2) Junghahn, *Ber.*, **33**, 1364 (1900).

Anal. Calcd. for $C_{10}H_7SCl$: S, 16.47. Found: S, 16.58.

10. **Disulfide of 2-Chloro-1-thionaphthalene.**—After several recrystallizations from a chloroform–alcohol mixture (1:2) the product melted at 134°.

Anal. Calcd. for $C_{20}H_{12}Cl_2S_2$: C, 62.01; H, 3.12. Found: C, 62.08; H, 3.12.

11. **4-Chloro-1-thionaphthalene.**—The starting material was 1-naphthylamine-4-sulfonic acid. The product was purified by dissolving it in dilute alkali, clarifying the solution with kieselguhr, and precipitating it with dilute hydrochloric acid, melting point 51°.

12. **The Disulfide of 4-Chloro-1-thionaphthalene.**—Very easily formed; recrystallized from alcohol, it melted at 124–125°.

Anal. Calcd. for $C_{20}H_{12}Cl_2S_2$: C, 62.01; H, 3.12. Found: C, 62.00; H, 3.17.

Summary

Several new halogenated thiophenols and naphthols were prepared which are interesting because of a possible therapeutic application.

HOUSTON, TEXAS

RECEIVED DECEMBER 1, 1933

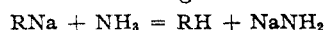
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

The Reduction of Phenylated Olefins with Alkali Metals in Liquid Ammonia Solution

BY CHARLES BUSHNELL WOOSTER AND JOHN F. RYAN¹

The present investigation was undertaken to obtain further information regarding the nature of the reactions which may occur between alkali metals and phenylated olefins in liquid ammonia at its boiling point. The compounds studied were styrene, stilbene, unsymmetrical diphenylethylene, triphenylethylene, tetraphenylethylene, 1,1-diphenylpropylene, 1,1,3,3-tetraphenylpropylene and tetraphenylallene; the general results may be summarized briefly as follows.

In no case did the alkali metal attack the phenyl groups, but it was found possible, under suitable conditions, to saturate the double bonds in the side chains of every hydrocarbon and to obtain the corresponding phenylated paraffins after decomposition of the intermediate organo-alkali compounds with ammonium chloride. In some cases the double bonds were partially or completely saturated with hydrogen before the addition of ammonium chloride due to ammonolysis of the intermediate organo-alkali compounds.



(1) Metcalf Fellow in Chemistry at Brown University.

The occurrence and extent of the ammonolysis may in general be predicted on the basis of the benzohydril rule;² that is, the alkali metal atoms were replaced with hydrogen except when they were present in the grouping $(C_6H_5)_2C(M)$ —(M = alkali metal), as may be seen by inspection of Table I giving the reaction products obtained with *excess* sodium.

TABLE I
THE ACTION OF SODIUM ON PHENYLATED OLEFINS IN LIQUID AMMONIA

No.	Olefin	Products
I	$C_6H_5CH=CH_2$	$C_6H_5C_2H_5$ and styrene polymers
II	$C_6H_5CH=CHC_6H_5$	$C_6H_5CH_2CH_2C_6H_5$
III	$(C_6H_5)_2C=CH_2$	$(C_6H_5)_2CNaCH_3$ and $(C_6H_5)_2CNaCH_2CH_2CNa(C_6H_5)_2$
IV	$(C_6H_5)_2C=CHC_6H_5$	$(C_6H_5)_2CNaCH_2C_6H_5$
V	$(C_6H_5)_2C=C(C_6H_5)_2$	$(C_6H_5)_2CNaCNa(C_6H_5)_2$ and $(C_6H_5)_2CHNa$ or $(C_6H_5)_2CNa?$
VI	$(C_6H_5)_2C=CHCH_3$	$(C_6H_5)_2CNaCH_2CH_3$
VII	$(C_6H_5)_2C=CHCH(C_6H_5)_2$	$(C_6H_5)_2CNaCH_2CH(C_6H_5)_2$
VIII	$(C_6H_5)_2C=C=C(C_6H_5)_2$	$(C_6H_5)_2CNaCH_2CNa(C_6H_5)_2$

The alkali metals also reacted with some of the phenylated olefins in other ways, including

(2) (a) Wooster and Mitchell, *THIS JOURNAL*, **52**, 688 (1930);
(b) Wooster and Ryan, *ibid.*, **54**, 2419 (1932).