solution containing 0.2 mole of *p*-thiocresylmagnesium iodide was refluxed for 12 hours. After the product had been treated in the customary manner, 10 g. or a 20.3% yield of di-*p*-tolyl disulfide was separated from 38 g. of unaltered phenyl *p*-toluenesulfonate by extraction with petroleum ether.

Di-*p*-Tolyl Disulfoxide and *p*-Thiocresylmagnesium Iodide.—A mixture of 2.2 g. or 0.008 mole of di-*p*-tolyl disulfoxide with an ether-toluene solution containing 0.008 mole of *p*-thiocresylmagnesium iodide was refluxed for eight hours. The mixture was treated in a manner identical with that from the reaction between phenyl *p*-toluenesulfonate and *p*-thiocresylmagnesium iodide: yield of di-*p*-tolyl disulfide, 1.2 g., or 61%.

Di-*p*-Tolyl Disulfoxide and Hydrogen Peroxide.[20]—To a solution of 2 g. of di-*p*-tolyl disulfoxide in a mixture of acetic anhydride and acetic acid was added 3 g. of 30% hydrogen peroxide. The acetic anhydride was in excess of that required to react with the water in the peroxide solution, and sufficient acetic acid was added to keep the disulfoxide in solution. After the mixture had stood for two days at room temperature, crystals began to form and these had increased slightly in quantity at the end of six days. They were separated by decantation, and a mixed-melting-point determination with the known di-*p*-tolyl disulfone showed no depression.

These results were duplicated in an experiment made under similar conditions.

When 5 g. of the disulfoxide was allowed to stand for two weeks at room temperature with 6 g. of water, 40 g. of acetic anhydride and sufficient acetic acid to keep the compound in solution, no change was noted. Practically all (over 90%) of the disulfoxide was recovered by pouring the solution into water.

Summary

The reactions of the so-called disulfoxides with organomagnesium halides and hydrogen peroxide show that the thiosulfonic ester structure is to be preferred to the disulfoxide and the anhydride formulas.

AMES, IOWA

[CONTRIBUTION FROM THE LABORATORY OF THE J. B. WILLIAMS COMPANY]

A METHOD FOR THE PREPARATION OF PRIMARY ACETYLENIC ALCOHOLS

BY HERBERT H. GUEST

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The only method described in the literature for the preparation of alcohols of the type $R.C\vdots C.CH_2OH$ is that of Moureu and Desmots[1] which depends upon the action of dry trioxymethylene on the sodium derivatives of the acetylenes. This method, according to the authors' own testimony, is very unsatisfactory, yielding only a small percentage of the desired product and producing as a by-product a high-boiling alcohol of the formula $C_{16}H_{26}O$.

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acid and RMgX compounds it was found desirable to use a higher temperature than that used with alkyl esters. A preliminary report of this work has already been made, (Ref. 4 c) and the final report will be contained in a paper to be published shortly.

[20] The experiments under this heading were performed by Chester E. Adams.

[1] Moureu and Desmots, *Bull. soc. chim.*, [3] **27**, 360 (1902).

The action of trioxymethylene upon Grignard reagents has not proved to be an easy and general method for obtaining primary alcohols, according to the testimony of West and Gilman.[2]

The action of gaseous formaldehyde upon Grignard reagents has been utilized in a few cases for the preparation of primary alcohols[3] and a very complete description of this method has been published by Wood and Scarf[4] who have prepared secondary butyl carbinol and secondary amyl carbinol in excellent yield.

This paper describes an extension of the use of gaseous formaldehyde to the preparation of acetylenic alcohols and contrasts the difference in reactivity to formaldehyde between an acetylene (heptine) sodium derivative and the corresponding Grignard derivative. Whereas the former gave only a small percentage of the desired alcohol, the latter reacted almost quantitatively. In neither case was the formation of a high-boiling by-product observed.

In a previous communication the writer[5] called attention to the fact that alcohols of the type R.C:C.C(OH)R′.R″ where R′ and R″ may be alkyl groups or hydrogen, have a more pleasant odor than the corresponding saturated alcohols, thus making a second exception to Delange's rule that the triple bond in a molecule is productive of unpleasant odors. Thus, for example, the octinol prepared by the method herein described has a much pleasanter odor than octanol. Also phenylpropargyl alcohol,[1] prepared in the same manner, has a strong lilac odor, much pleasanter than that of phenylpropyl alcohol. The effect of a triple bond upon the odor of a molecule thus is not necessarily deleterious, as has so often been stated by writers on this subject.

Experimental Part

The Preparation of Heptine.—Lewinsohn[6] has described a method for the preparation of heptine from 1,1-dichloroheptane involving the isolation of the intermediate product heptylidene chloride and the subsequent action upon the latter of sodium amide. The writer was unable to confirm the statement of Lewinsohn that boiling aqueous potassium hydroxide removes one molecule of hydrogen chloride from 1,1-dichloroheptane to give 1-chloroheptene (1-$CH_3(CH_2)_4CH{:}CHCl$). Thus, dichloroheptane was boiled for three hours with an equal weight of 50% aqueous solution of potassium hydroxide while the mixture was mechanically agitated. On attempting to distil the resulting oil, nothing came over below 170°. Even further heating did not bring about the desired result. When the reaction mixture was heated to boiling, however, with twice the calculated amount of potassium hydroxide dissolved in 4 to 5 volumes of alcohol for eight to ten hours, heptylidene chloride was obtained in 60% yield.

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[2] West and Gilman, "Organomagnesium Compounds in Synthetic Chemistry," National Research Council Series, **1922.**

[3] Grüttner and Krause, *Ber.*, **49,** 610 (1916). Ziegler, *Ber.*, **54,** 737; **55,** 3406 (1922).

[4] Wood and Scarf, *J. Soc. Chem. Ind.*, **42,** 13T (Jan., 1923).

[5] Guest, This Journal, **45,** 1804 (1923).

[6] Lewinsohn, *Perfumery Essent. Oil Record,* **14,** 291 (1923).

More recently Bourguel[7] has published a shorter method for preparing heptine which depends upon the action of sodium amide in toluene or xylene suspension upon 1,1-dichloroheptane. This author states that he obtained no *iso*heptine by this method; however, he based his conclusion upon the fact that his reaction product boiled at 99° to 100.5°, claiming that *iso*heptine boils at 112°. The writer finds that the reaction product, which distilled between 99° and 105°, on analysis by Hill and Tyson's method[8] consisted of a mixture of 70% normal heptine and 30% *iso*heptine. Moreover, *iso*heptine was prepared from *iso*heptene which had a similar boiling range.

The use of sodium amide for the elimination of hydrogen halides has greatly simplified the preparation of heptine and given a method whereby satisfactory yields may be obtained. Yields of 60 to 70% were obtained by the writer.

The Preparation of Octinol-1, $CH_3(CH_2)_4C⋮C.CH_2OH$.—To the solution which resulted from the interaction of 37 g. of ethyl bromide, 8 g. of magnesium turnings, and 200 g. of ether was added 33 g. of heptine mixture, containing 70% of heptine as shown by analysis. After standing at room temperature for one hour, the mixture was warmed gently until ethane ceased to be evolved. The flask was then immersed in a freezing mixture and a gentle stream of mixed formaldehyde and nitrogen gases was led through the contained liquid for four hours. The reaction product was allowed to stand in a cold place overnight, after which it was gradually poured onto cracked ice. Dil. sulfuric acid was then added, the ethereal layer separated, washed thoroughly and dried over potassium carbonate. After removal of the ether the residual oil was fractionated under diminished pressure. Thus there was obtained 25 g. of oil distilling at 99–104° (12 mm.). The residue of oil boiling above 104° was 4 g. The alcohol thus obtained had the same characteristics as the octinol described by Moureu. It is intensely sweet. The yield corresponds to 83%.

To a suspension of 6 g. of powdered sodium amide in 35 cc. of ether was added 15 g. of heptine. The reaction was completed by heating on a steam-bath under a reflux condenser. After this material had cooled in a freezing mixture, a mixture of formaldehyde and nitrogen gases was led into the reaction flask for 15 hours, and the product then treated as in the previous experiment; yield, 3.5 g. of octinal, or only 18%.

Preparation of Phenyl-propiolic Alcohol, $C_6H_5C⋮C.CH_2OH$.—To a solution of ethylmagnesium bromide, prepared from 15 g. of ethyl bromide, 2.8 g. of magnesium and 100 cc. of ether, was added 12 g. of phenyl-acetylene in 50 cc. of ether. Into this reaction mixture was passed mixed nitrogen and formaldehyde gases at a low temperature for four hours. The product of the reaction was treated as previously described; yield, 4 g. of phenyl-propargyl alcohol; b. p., 140° (12 mm.).

Summary

Acetylenic alcohols of the type $R.C⋮C.CH_2OH$ can be readily prepared by

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[7] Bourguel, *Compt. rend.*, **176**, 751 (1923); **177**, 823 (1923).

[8] Privately communicated before publication. To be published later.

the action of formaldehyde vapor upon the magnesium bromide derivatives of the corresponding acetylenes.

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

ORTHO-CRESOL-TETRACHLOROPHTHALEIN, SOME OF ITS DERIVATIVES, AND ISO-ORTHO-CRESOL-TETRACHLOROPHTHALEIN

BY W. R. ORNDORFF AND M. S. PATEL[1]

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Ortho-cresol-tetrachlorophthalein was first made in this Laboratory by E. L. Arnold[2] from tetrachlorophthalic acid and *o*-cresol, using stannic chloride as the condensing agent. For making larger quantities of the phthalein, fuming sulfuric acid proved to be a better condensing agent. A mixture of 100 g. of *pure* crystallized tetrachlorophthalic acid and 200 g. of *pure* *o*-cresol was heated until water ceased to be evolved and all the acid was converted into the anhydride; 55 cc. of 15% fuming sulfuric acid was then added and the mixture heated at 140° for ten hours. Water was added and the unused *o*-cresol removed by distillation in steam. The residue was boiled repeatedly with water to remove soluble products, the crude phthalein dissolved in 5% sodium hydroxide solution, the solution filtered to remove dimethyl tetrachlorofluoran and the filtrate acidified; 135 g. of the crude phthalein was obtained, an 84% yield. The phthalein was crystallized from methanol, the solution being decolorized with boneblack. After recrystallization from methanol it was analyzed.

Anal. Subs., 0.1607, 0.1239, 0.1437: AgCl, 0.1890, 0.1476, 0.1705. Calcd. for $C_{22}H_{14}O_4Cl_4$: Cl, 29.32. Found: 29.10, 29.47, 29.35.

The chemical and physical properties of *o*-cresol-tetrachlorophthalein were found to be the same as those given by Arnold.[2]

ITS DIACETATE was made by the method given by Arnold.[2] It was crystallized from methanol until it was colorless; m. p., 207–208°.

Anal. Subs., 0.2849, 0.2750: AgCl, 0.2857, 0.2769. Calcd. for $C_{22}H_{12}O_2Cl_4(OCOCH_3)_2$: Cl, 24.97. Found: 24.81, 24.91.

THE DIBENZOATE was made by heating the pure phthalein with benzoyl chloride. It was crystallized from ethanol until it was colorless; m. p., 198–200°.

Anal. Subs., 0.2015, 0.2056: 11.70, 11.90 cc. of 0.1 *N* $AgNO_3$. Calcd. for $C_{22}H_{12}O_2Cl_4(OCOC_6H_5)_2$: Cl, 20.49. Found: 20.59, 20.53.

The dibenzoate is readily soluble in benzene, toluene, xylene, acetone and ethyl acetate. It is less soluble in methanol, ethanol and ether.

Dibromo-*o*-cresol-tetrachlorophthalein.—Ten g. of pure *o*-cresol-tetrachlorophthalein was dissolved in 500 cc. of absolute alcohol and 9 g.

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[1] From a dissertation presented by M. S. Patel in partial fulfilment of the requirements for the degree of Master of Science.

[2] Arnold, THIS JOURNAL, **46**, 489 (1924).