of this kind. Certain regularities in the surface tension behavior of these solutions were pointed out, and a discussion given of the various hypotheses which have been advanced to explain such types of behavior.

The interfacial tensions between benzene and solutions of sodium alkyl sulfonates showed changes with time, a phenomenon which has not been previously reported.

Conductivity measurements made on solutions of the sodium alkyl sulfonates showed that the conductivity of these substances is analogous to that of the potassium soaps.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF COLORADO]

The Action of Chloral on β-Phenylethylmagnesium Bromide, γ-Phenylpropylmagnesium Bromide and δ-Phenylbutylmagnesium Bromide

BY PAUL M. DEAN AND WENDELL I. WOLF

Secondary alcohols containing the trichloromethyl group have been prepared by several investigators[1,2,3,4] through the addition of chloral to the corresponding Grignard reagent. Since such carbinols are readily formed from alkyl- and arylmagnesium halides as well as from benzylmagnesium chloride, one would anticipate the formation of analogous compounds from phenyl substituted alkylmagnesium halides. However, numerous attempts, in this Laboratory, to prepare secondary alcohols from chloral and β-phenylethylmagnesium bromide, γ-phenylpropylmagnesium bromide, and δ-phenylbutylmagnesium bromide have failed. In all cases, such by-products as trichloroethanol, styrene or its homologs and 1,4-diphenylbutane or its homologs were obtained. No secondary alcohol could be separated from the reaction mixture by the methods employed. Since no reference to the action of the three Grignard reagents, named above, on the unsubstituted aldehydes has been found in the literature, it is planned to investigate this point in the near future.

Procedure

Action of Chloral on β-Phenylethylmagnesium Bromide.—To the cooled Grignard reagent prepared from a 0.25-mole portion of β-phenylethyl bromide dissolved in 200 cc. of ether was added a solution of 0.25 mole of chloral dissolved in 50 cc. of ether. After refluxing for one hour the gray solid was filtered and washed with ether.

(a) **Examination of the Solid.**—The solid was hydrolyzed with water and the solution cleared with hydrochloric acid. A heavy oil separated which was extracted with ether, washed with sodium bisulfite solution, then with sodium carbonate, and dried over sodium sulfate. After removal of the ether the residue was distilled under diminished pressure. Nearly all distilled at 67–68° at 25 mm. pressure. This liquid was shown to be trichloroethanol through the preparation of the phenyl urethan, the *p*-nitrobenzoate and the urethan from α-naphthyl isocyanate. The last named new derivative was prepared by heating the trichloroethanol with α-naphthyl isocyanate for two hours at 120–135°. The white solid crystallized from ligroin melted at 120°; melting point of product from authentic trichloromethanol 119°; mixed melting point 120°.

Anal. Calcd. for $C_{13}H_{10}NO_2Cl_3$: Cl, 33.43; H, 4.40. Found: Cl, 33.90; N, 4.56.

(b) **Examination of the Ether Filtrate.**—The filtrate was hydrolyzed and washed in the same manner as the solid residue above. The following products were obtained on fractional distillation: some trichloroethanol, styrene, 1,4-diphenylbutane, some unidentified material. To facilitate the separation of styrene from the mixture, the dried ether solution was treated with a slight excess of bromine in diffused light, and washed with sodium bisulfite and carbonate solution. The dried ether was distilled off and the residue fractionated under diminished pressure. This procedure was followed in all of the experiments except the one in which the styrene was identified. The results are summarized in Table I.

TABLE I

Products recovered	Yield in grams				
Experiment	1	2	3	4	5
CCl_3CH_2OH from solid	10	14	14	14	14
CCl_3CH_2OH from filtrate	2	2	2	2	1
$C_6H_5CH{=}CH_2$	6	..	..	..	..
$C_6H_5CHBrCH_2Br$	10	29	30	35	34
$C_6H_5CH_2CH_2CH_2CH_2C_6H_5$	2	..	1	1	1
$C_6H_5CH_2CH_2Br$	2	1	2	1	2

Action of Chloral on γ-Phenylpropylmagnesium Bromide.—Similarly to the foregoing case γ-phenylpropylmagnesium bromide treated with chloral yielded a solid and filtrate which hydrolyzed separately gave from the solid trichloroethanol, and from the liquid, trichloroethanol, allylbenzene, 1,6-diphenylhexane and a small amount of unidentified material. The allylbenzene was identified

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(1) Henry, *Compt. rend.*, **138**, 204 (1904).

(2) Savariau, *ibid.*, **146**, 297 (1908).

(3) J. W. Howard, THIS JOURNAL, **48**, 774 (1926).

(4) J. W. Howard, *ibid.*, **49**, 1068 (1927).

through its conversion first to the dibromide, followed by its conversion to cinnamyl tribromide.[5]

In all experiments except one, the ether solution was treated with bromine before fractionation in order to facilitate the removal of allylbenzene. The results of the various trials are summarized in Table II.

TABLE II

Products recovered	Yield in grams				
Experiment	1	2	3	4	5
CCl_3CH_2OH from solid	11	15	15	12	6
CCl_3CH_2OH from filtrate	5	..	3	..	7
$C_6H_5CH_2CH{=}CH_2$	..	12	..	..	..
$C_6H_5CH_2CHBrCH_2Br$	30	8	23	24	25
$C_6H_5CH_2CH_2CH_2CH_2CH_2CH_2C_6H_5$	7	5	3	5	3

TABLE III

Products recovered	Yield in grams		
Experiment	1	2	3
CCl_3CH_2OH from solid	13	16	12
CCl_3CH_2OH from filtrate	4	2	4
$C_6H_5CH_2CH_2CHBrCH_2Br$	33	34	29
$C_6H_5(CH_2)_8C_6H_5$	3	3	3

Action of Chloral on δ-Phenylbutylmagnesium Bromide.—In these experiments the usual procedure described above was followed except that no attempt was made to separate the 4-phenylbutene-1 formed in the reaction. In all cases this was identified as the dibromide. The results are given in Table III.

Summary

1. β - Phenylethylmagnesium bromide, γ - phenylpropylmagnesium bromide and δ-phenylbutylmagnesium bromide reacted with chloral to give trichloroethanol, unsaturated hydrocarbons and coupling products.

2. No secondary alcohols containing the trichloromethyl group were obtained under the conditions of these experiments.

BOULDER, COLORADO RECEIVED NOVEMBER 18, 1935

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[5] Ch. Prévost, *Bull. soc. chim.*, [4] 49, 1376 (1931).

[CONTRIBUTION FROM THE NEW YORK STATE COLLEGE OF FORESTRY AND DEPARTMENT OF RADIOLOGY, SYRACUSE UNIVERSITY]

x-Ray Studies of Reactions of Cellulose in Non-Aqueous Systems. I. Interaction of Cellulose and Liquid Ammonia[1]

BY A. J. BARRY, F. C. PETERSON AND A. J. KING

In the course of preliminary studies on the swelling of cellulose in non-aqueous systems, it was found that when ramie fiber is immersed in anhydrous liquid ammonia, a swelling occurs which, according to the type of subsequent treatment, results ultimately in one of two different structures as revealed by x-ray diagrams.

One of the structures seems to be analogous to the three similar products found by Trogus and Hess[2] in their treatment of cellulose with hydrazine, ethylenediamine and tetramethylenediamine.

The second structure which was obtained bears a striking similarity to that of hydrate cellulose. The sharpness of the x-ray diagram in either case indicates a crystalline structure as well defined as exists in the original cellulose used.

For the investigations, the cellulose used was ramie pretreated by digesting for one hour in 1% sodium hydroxide solution at 100°, washing with water, dilute acetic acid, and finally again with water, then drying for five to six hours at 105°. The diffraction pattern of the purified ramie agreed well with the data for normal cellulose.

Prior to treatment with liquid ammonia the fibers were wrapped into small tight bundles on small spring wire frames so that the samples were under a slight tension during treatment. In all cases, the presence of water was precluded by drying for an additional two hours just before treatment with liquid ammonia. The racked samples were placed in a reaction flask which was part of a closed system and pure, dry ammonia gas was condensed in the flask by cooling with carbon dioxide ice in acetone. Enough ammonia was condensed so that, as it evaporated under atmospheric pressure, the samples were covered with liquid ammonia for five to ten hours. The fibers during this treatment showed a perceptible swelling. Immediately after all the ammonia had vaporized, the bundles were coated with paraffin oil and subjected immediately to x-ray examination. The ammonia content of the material at this stage determined gravimetrically, indicated roughly 1 mole of ammonia to 1 mole of cellulose ($C_6H_{10}O_5$).

For a source of x-rays, a Müller tube with a

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[1] Presented before the Cellulose Division of the A. C. S. at the New York Meeting, April 25, 1935.

[2] C. Trogus and K. Hess, *Z. physik. Chem.*, B14, 387–95 (1931).