added with stirring to a mixture of 18 ml. of concentrated sulfuric acid and 37 ml. of concentrated nitric acid at room temperature. As soon as all had dissolved, the solution was poured into cracked ice. The resulting solid was filtered, washed and dried. After several fractional crystallizations from glacial acetic acid two isomers were obtained. The more abundant, less soluble one, obtained in about 40% yield, consisted of cream colored shining disks, m. p. 256° (uncor.). Oxidation by chromic acid yielded quantitatively long yellow needles of 2,7-dinitrofluorenone, m. p. 293° (uncor.): oxime, m. p. 289° (uncor.); phenylhydrazone, m. p. 259° (uncor.); semicarbazone, m. p. above 338° (uncor.). It was therefore 2,7-dinitro-9-acetaminofluorene.

Anal. Calcd. for $C_{15}H_{11}O_5N_3$: C, 57.5; H, 3.5; N, 13.4. Found[16]: C, 57.27; H, 3.76; N, 13.39.

The more soluble fraction after several recrystallizations from glacial acetic acid melted at 243° (uncor.) and consisted of cream colored needles which usually formed a roset pattern. It was shown to be 2,5-dinitro-9-acetaminofluorene by its oxidation to 2,5-dinitrofluorenone, m. p. 240° and its analysis.[16] Calculated for $C_{15}H_{11}O_5N_3$: C, 57.5; H, 3.51; N, 13.4. Found: C, 56.30; H, 3.99; N, 13.05. These acetyl derivatives are very resistant to hydrolysis, long boiling with sodium hydroxide and with dilute acids having no effect.[17] Heating with nitric acid (sp. gr. 1.42) for one hour on the steam-bath also produced no change.

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Summary

1. The unknown dinitrofluorenone, m. p. 220°, of Goldschmiedt and Schranzhofer (the xx-dinitrofluorenone of Beilstein) is in reality an impure 2,5-dinitrofluorenone.

2. Huntress and Cliff's dinitrofluorenone, m. p. 213–214°, is this same 2,5-dinitrofluorenone as is Langecker's compound, m. p. 236°.

3. Mild nitration of 9-acetaminofluorene yields two new dinitro-derivatives. The more abundant 2,7-dinitro-9-acetaminofluorene melts at 256° uncor. while the other isomer, 2,5-dinitro-9-acetaminofluorene, melts at 243° uncor.

4. Dinitration of fluorene or its derivatives seems always to yield a mixture of the 2,7- and the 2,5-dinitro derivative, the former more abundant and less soluble.

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[16] The actual analyses were performed by Dr. Carl Tiedcke of New York, N. Y.

[17] Popkin, Peretta and Selig, THIS JOURNAL, **66**, 833 (1944), have reported a similar resistance to hydrolysis in the biphenyl series.

[CONTRIBUTION FROM THE KNIGHT CHEMICAL LABORATORY, UNIVERSITY OF AKRON]

The Reaction of α,α,β-Trichlorobutyraldehyde with a Number of Grignard Reagents

BY VAUGHN W. FLOUTZ

Jocicz[1] found that phenylmagnesium bromide and α,α,β-trichlorobutyraldehyde, commonly called butyl chloral, react normally and give a good yield of the secondary alcohol. One might expect other simple Grignard reagents to react with this aldehyde in a similar manner to give corresponding alcohols. Inasmuch as a search of the literature revealed no information in this connection, the research project here reported was undertaken to investigate further the reaction of α,α,β-trichlorobutyraldehyde with typical Grignard reagents. The study was conducted with *n*-hexylmagnesium bromide, cyclohexylmagnesium bromide, β-phenylethylmagnesium bromide and benzylmagnesium chloride, and the results of reaction with butyl chloral show that with these Grignard reagents products other than the anticipated carbinols are formed. Each of the first three mentioned reagents reacts to give 2,2,3-trichlorobutanol-1, and in addition hexene-1, cyclohexene or styrene, respectively, as main products. The last mentioned, benzylmagnesium chloride, reacts with butyl chloral to yield dibenzyl as the principal product.

It is evident that in the reaction of Grignard reagents, RMgX, with butyl chloral reduction of this aldehyde to the corresponding alcohol predominates in those cases where the Grignard reagent can be oxidized by the loss of two hydrogen atoms from adjacent carbons, with the resulting formation of a carbon to carbon double bond. For phenylmagnesium bromide and benzylmagnesium chloride such an oxidation is not possible.

In order to secure data for comparison purposes the synthesis reported by Jocicz[1] was repeated, with certain changes in reaction conditions.

Experimental[2]

α,α,β-Trichlorobutyraldehyde and Phenylmagnesium Bromide.—One-fourth mole portions of reactants were used and the procedure employed for the preparation of the Grignard reagent and its reaction with the aldehyde was essentially that outlined in the section which follows. Unreacted aldehyde was recovered and weighed as the hydrate. The secondary alcohol, 2,2,3-trichloro-1-phenylbutanol-1, was obtained as a colorless, viscous liquid which distilled at 160–163° at 8 mm. Weights of substances isolated as averaged from two runs were as follows, 2,2,3-trichloro-1-phenylbutanol-1, 45 g. (71.1%); diphenyl, 1.3 g.; hydrate of unreacted aldehyde, 5 g.; undistillable residue, 2 g. These results verify those of Jocicz's experiments.

α,α,β-Trichlorobutyraldehyde and *n*-Hexylmagnesium Bromide, Cyclohexylmagnesium Bromide and β-Phenylethylmagnesium Bromide.—In the preparation of each of these Grignard reagents a 1-liter, three-necked flask fitted with a stirrer, dropping funnel and condenser was

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[1] Jocicz, *J. Russ. Phys.-Chem. Soc.*, **34**, 97 (1902).

[2] α,α,β-Trichlorobutyraldehyde (butyl chloral) was furnished through the courtesy of the Westvaco Chlorine Products Corporation.

used. 0.25 gram-atom of magnesium turnings was placed in the flask, covered with 200 ml. of anhydrous ether, and the reagent was formed by adding over a period of forty-five minutes 0.25 mole of the halide dissolved in a like volume of dry ether. After adding the halide the reaction mixture was heated to gentle refluxing for one-half hour. The reagent was cooled by immersing the reaction flask in cold water, and 0.25 mole of the aldehyde carried in a like volume of dry ether was added at a rate such that no refluxing of the solvent was evident. Following the addition of the aldehyde the reaction mixture was permitted to come to room temperature; it was then heated to reflux temperature for one-half hour. The product was hydrolyzed by pouring it into a mixture of ice and water, and cleared by the addition of cold 5% aqueous acetic acid. The ether layer was removed, washed in turn with sodium bicarbonate solution and water, and dried over anhydrous sodium sulfate.

In the case of the *n*-hexylmagnesium bromide and butyl chloral the resulting dry ether solution was subjected to distillation in order to remove the ether and the hexene-1 formed in the reaction. The major portion of the ether and hexene-1 was distilled by use of a hot water-bath; following this the residue was heated in an oil-bath to a bath temperature of 130°, and the additional distillate collected with the main portion. It was found that the quantity of hexene-1 present could be more accurately determined by its conversion to 1,2-dibromohexane; this was accomplished by adding a slight excess of bromine to the ether solution in subdued light. The ether was then removed by distillation and the residual oil was washed in turn with sodium bicarbonate solution and water. After a period of drying over anhydrous calcium chloride the product was distilled under reduced pressure to obtain the 1,2-dibromohexane, b. p. 92–93° at 18 mm. The residue from the removal of the ether and hexene-1 was distilled under diminished pressure in an atmosphere of nitrogen. Unreacted aldehyde was recovered as the crystalline hydrate. This compound was washed with cold petroleum ether and dried; m. p. 78°. A fraction which distilled at 115–120° at 45 mm. formed a crystalline mass on cooling. Recrystallization from petroleum ether gave a solid melting at 62°. This substance was further identified as 2,2,3-trichlorobutanol-1 by treatment with phosphorus pentachloride to form the tris-(β,β,γ-trichlorobutyl) phosphate,[3] m. p. 85°.

Similar to the foregoing case, cyclohexylmagnesium bromide treated with butyl chloral gave cyclohexene and 2,2,3-trichlorobutanol-1. The determination of the amount of cyclohexene formed was facilitated by converting this hydrocarbon into 1,2-dibromocyclohexane according to the procedure previously described for hexene-1. The 1,2-dibromocyclohexane distilled at 116–118° at 29 mm.

The dry ether solution resulting from the reaction of α,α,β-trichlorobutyraldehyde and β-phenylethylmagnesium bromide was subjected to distillation to remove the ether, and distillation was continued under reduced pressure in an atmosphere of nitrogen to remove the styrene produced in the reaction and the unused aldehyde. These were contained in the fraction distilling up to 100° at 45 mm. Upon adding a small amount of water to this fraction, agitating it thoroughly, and permitting it to stand for several hours the aldehyde separated as the crystalline hydrate. The hydrate was removed by filtration and the layer of filtrate which contained the styrene was separated from the water layer, dried and added to the original ether distillate. Treatment with a slight excess of bromine gave styrene dibromide. Following washing, drying and removal of ether the dibromide was obtained in a fraction distilling at 137–142° at 15 mm. which solidified on cooling. Recrystallization from ethanol gave lustrous white plates, m. p. 74°. 2,2,3-Trichlorobutanol-1 was separated by fractionation under diminished pressure from the liquid remaining after the removal of the styrene and aldehyde.

Results for the studies described in this section are summarized in Table I.

TABLE I

GRIGNARD REAGENTS

	$C_6H_{13}MgBr$		$C_6H_{11}MgBr$		$C_6H_5(CH_2)_2$-MgBr	
Experiment no.	1	2	1	2	1	2
Substances isolated. g.						
$CH_3CHClCCl_2CHO \cdot H_2O$	6	7	8.5	9	6	5
Dibromo addition product	31.5	33	26	27.5	33	32
$CH_3CHClCCl_2CH_2OH$	27	28.5	23	22.5	22.5	21.5
Tarry residue	4	2.5	4	3	6.5	7

α,α,β-Trichlorobutyraldehyde and Benzylmagnesium Chloride.—One-fourth mole quantities of reactants were used. The Grignard reagent was prepared in the manner previously described. During the addition of the butyl chloral it was observed that only approximately the first 50% gave a noticeable reaction; hence during the addition of the last one-half of the aldehyde the reaction mixture was heated to gentle refluxing. Heating was continued for one-half hour after adding the aldehyde.

The only isolable reaction product was dibenzyl, melting point from ethanol 51°, further identified through mixed melting point. It is to be noted that a considerable quantity of the aldehyde failed to react, and that a large quantity of undistillable tarry matter was produced. Weights of substances isolated, averaged from two determinations, were as follows, unreacted butyl chloral, recovered and weighed as the hydrate, 15.5 g.; dibenzyl, 13.7 g.; tarry residue, 14 g.

Summary

1. The reaction of α,α,β-trichlorobutyraldehyde with *n*-hexylmagnesium bromide, cyclohexylmagnesium bromide, β-phenylethylmagnesium bromide and benzylmagnesium chloride has been studied; the reaction with phenylmagnesium bromide has been verified.

2. Phenylmagnesium bromide reacts normally with α,α,β-trichlorobutyraldehyde and gives a good yield of the expected secondary alcohol. No secondary alcohols were detected in the reaction products from the other Grignard reagents and this aldehyde.

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[3] Norton and Noyes, *Am. Chem. J.*, **10**, 430 (1888).