Summary

1. A convenient method is described for the preparation of γ-iodopropyl chloride in considerable quantity.

2. Its reactions with sodium cyanide and the sodium derivatives of ethyl malonate, ethyl phenylmalonate and phenylacetonitrile have been studied.

3. The following acids have been prepared: α-phenyladipic, α-phenylpimelic, α-phenylundecane-α,α'-dicarboxylic, α-ethyl-α'-phenylpimelic (both forms) and 1-phenylcyclobutane-1-carboxylic acid.

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Reactions of Triphenylmethylmagnesium Bromide. II

BY W. E. BACHMANN AND R. F. COCKERILL

In a previous paper it was shown that triphenylmethylmagnesium bromide reacts with aromatic ketones and with benzils[1] in an unusual manner. The MgBr group of the Grignard reagent adds to the oxygen atom of the C=O group of the ketone but the triphenylmethyl group does not join to the carbon atom; instead, it remains free as the radical. On the other hand, the Grignard reagent reacts normally with carbon dioxide[2] and gives a nearly quantitative yield of triphenylacetic acid; likewise it couples in normal fashion with diarylmethyl halides[3] and gives penta-arylethanes. We have now investigated the reactions of triphenylmethylmagnesium bromide with a variety of reagents in order to ascertain the extent of its irregular behavior and in order to determine the practical application of the Grignard reagent in introducing the triphenylmethyl group into molecules.

Reaction with Oxygen and with Sulfur.—Contrary to the statement of Schmidlin[4] and of others[5] that the Grignard reagent is converted readily into triphenylmethyl peroxide by the oxygen of the air, only a small amount of triphenylmethyl peroxide is formed when air is passed through a solution of the Grignard reagent; the chief product is the salt of triphenylcarbinol $(C_6H_5)_3COMgBr$ when the reaction is carried out at room temperature or at the boiling point of the solution.

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[1] Bachmann, THIS JOURNAL, **53**, 2758 (1931).

[2] Gomberg and Bachmann, *ibid.*, **52**, 2455 (1930); see also Schmidlin, *Ber.*, **39**, 634 (1906) and Gilman and Zoellner, THIS JOURNAL, **51**, 3493 (1929).

[3] Bachmann, *ibid.*, **55**, 2135 (1933).

[4] Schmidlin, "Das Triphenylmethyl," Ferdinand Enke, Stuttgart, 1914, p. 127.

[5] Kinney and Mayhue [THIS JOURNAL, **53**, 193 (1931)] report an almost quantitative yield of triphenylmethyl peroxide but they give no experimental details. Gilman and Fothergill [*ibid.*, **51**, 3152 (1929)] intimate a similar reaction and offer it as support for the dissociation of the Grignard reagent but give no details. Our results make it appear unlikely that there is any appreciable dissociation of the Grignard reagent into triphenylmethyl and magnesious halide as has been postulated by these investigators.

Sulfur was found to react rapidly with the Grignard reagent and crystals of the salt of triphenyl thiocarbinol $(C_6H_5)_3CSMgBr$ precipitate from the solution. This reaction offers a convenient method for preparing triarylthiocarbinols.

Reaction with Mercuric Bromide.—The reaction between mercuric bromide and excess of triphenylmethylmagnesium bromide does not give bis(triphenylmethyl) mercury; instead, reduction of the salt occurs and mercury and triphenylmethyl are formed.[6] This reaction corresponds to the reduction of aromatic ketones by triphenylmethylmagnesium bromide.

Coupling Reactions.—Triphenylmethylmagnesium bromide has been found to couple with alkyl halides and with a number of other halogen compounds. With ethyl bromide and *n*-propyl bromide some triphenylmethane and olefin are produced in addition to triphenylpropane and triphenylbutane; with *tert*-butyl bromide this reducing reaction is the principal one. Normal addition of the reagent occurs with phenyl benzoate and with phenyl isothiocyanate.

Experimental

In all of the reactions a mixture of 16.2 g. (0.05 gram mole) of triphenylbromomethane and 1.3 g. of magnesium ribbon in 25 cc. of ether and 50 cc. of benzene was refluxed for five to ten hours in an atmosphere of nitrogen. The solution of the Grignard reagent was cooled slightly, separated from excess of magnesium by filtration through a small piece of cotton, chilled and treated with a reagent. When the reaction was com-

TABLE I

REACTIONS OF TRIPHENYLMETHYLMAGNESIUM BROMIDE

Reagent added		Time for reaction, hours,			Yield,	
Name	Amount, g.	Cold	Hot	Principal product	g.	%
Methyl iodide[a]	10		4	$(C_6H_5)_3CCH_3$	12.7	98
Methyl iodide[b]	10		4	$(C_6H_5)_3CCH_3$	12.0	93
Ethyl bromide[a]	10		12	$(C_6H_5)_3CCH_2CH_3$	10	73
n-Propyl bromide[a]	10		20	$(C_6H_5)_3CCH_2CH_2CH_3$	6	41
tert-Butyl bromide[c]	10	15 +	2	$(C_6H_5)_3CH$	9	73
Allyl bromide[d]	10		6	$(C_6H_5)_3CCH_2CH{=}CH_2$	12.6	88
Benzyl chloride[a]	10		3	$(C_6H_5)_3CCH_2C_6H_5$	15.1	90
Chloromethylcarbonate	7	15 +	0.5	$(C_6H_5)_3CCOOCH_3$	10	66
Chloroethylcarbonate[c]	7	15 +	0.5	$(C_6H_5)_3CCOOC_2H_5$	11.5	72
Chloromethyl ether[c]	8		3	$(C_6H_5)_3CCH_2OCH_3$	10	70
Mercuric bromide[e]	7.2		1	$(C_6H_5)_3C$	9.5	98
Sulfur[f]	1.7		0.2	$(C_6H_5)_3CSH$	9.7	70
Phenyl benzoate[g]	10		1.5	$(C_6H_5)_3CCOC_6H_5$	8	46
Phenyl isothiocyanate[c]	10	12 +	1	$(C_6H_5)_3CCSNHC_6H_5$	13.2	70

[a] These compounds were found to be identical with samples of the compounds prepared for the first time by Gomberg and Cone [*Ber.*, **39**, 1463 (1906)] by the action of

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[6] Hellerman and Newman, THIS JOURNAL, **54**, 2863, footnote 16 (1932), state that in the reaction between triphenylmethylmagnesium bromide and mercuric bromide reduction of the salt occurred and triphenylbromomethane was one of the products. We are endeavoring to determine the reason for the different results.

Grignard reagents on triphenylchloromethane. We used the methods of purification employed by those investigators.

[b] In this experiment the Grignard reagent was prepared in presence of air; a mercury trap prevented free circulation of air into the apparatus during the preparation of the reagent and the reaction with methyl iodide.

[c] Similar products were obtained by Schlenk and Bergmann [*Ann.*, **464**, 10 (1928)] with triphenylmethyl sodium; the yields of the products were not reported.

[d] The allyl bromide reacted rapidly and a large amount of magnesium bromide precipitated from the solution in a short time. The product 4,4,4-triphenylbutene-1 was obtained in large colorless needles by recrystallization from *n*-propyl alcohol in which the compound is readily soluble hot but little soluble cold; m. p. 69.5–70.5°. The compound is only slightly soluble in methyl alcohol, readily soluble in ligroin and very soluble in benzene.

Anal. Calcd. for $C_{22}H_{20}$: C, 92.9; H, 7.1. Found: C, 92.6; H, 7.1. *Molecular weight.* Calcd.: 284. Found (in boiling benzene): 279.

A solution of triphenylbutene in acetic acid rapidly absorbed one mole of hydrogen in the presence of platinum black and gave a 90% yield of 1,1,1-triphenylbutane; the latter product was identical with the compound obtained by the action of triphenylmethylmagnesium bromide on *n*-propyl bromide.

[e] Mercury precipitated shortly after addition of the mercuric bromide to the Grignard reagent. After hydrolysis air was passed through the ether-benzene solution in order to oxidize the triphenylmethyl to triphenylmethyl peroxide. The amount of triphenylmethyl was calculated on the basis that pure triphenylmethyl gives an 85% yield of peroxide.

[f] The salt $(C_6H_5)_3CSMgBr$ crystallized from the solution soon after the addition of sulfur to the Grignard reagent. After twelve minutes of refluxing the mixture was cooled and the salt was filtered off and hydrolyzed by a solution of ammonium chloride. The triphenylthiocarbinol was recrystallized by dissolving it in a small amount of hot chloroform and treating the chloroform solution with an equal volume of alcohol.

[g] Addition of phenyl benzoate to the Grignard reagent gave an intensely red solution. After hydrolysis the ether–benzene solution was extracted with sodium hydroxide solution; acidification of the alkaline extract gave phenol.

plete the mixture was hydrolyzed. The essential data concerning the reactions are presented in Table I.

Oxidation of Triphenylmethylmagnesium Bromide.—Dry air, free from carbon dioxide, was bubbled through a filtered solution of triphenylmethylmagnesium bromide prepared from 16.2 g. of bromide; during the addition the mixture was kept at 20–25°. After a short time crystals of the bromomagnesium salt of triphenylcarbinol precipitated. After six hours the solution was hydrolyzed with dilute acid. The triphenylmethyl peroxide was filtered off; weight, 1.2 g. (10%). The filtrate was evaporated and the residue was recrystallized twice from carbon tetrachloride and once from acetic acid; weight of triphenylcarbinol, 7.0 g. (54%). Similar results were obtained when air was passed through the boiling solution for eight hours.

Summary

A study has been made of the behavior of triphenylmethylmagnesium bromide with a variety of reagents.

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