[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Effect of Traces of Carbon Disulfide on the Yields of Grignard Reagents[1]

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The preparations of many of the compounds needed for researches in progress in this Laboratory involve the use of Grignard reagents. Inasmuch as maximum yields are desirable it seemed worth while to investigate means of increasing the yields of Grignard reagents.

The effect of added substances and also of other factors, such as speed of addition and concentration of halide, has been studied by several workers.[3]

A decreased yield of alkyl Grignard reagent usually is accompanied by an increase in the amount of olefin which is formed, apparently by the removal of hydrogen halide from the halide molecule by the magnesium. In acid pickling baths for removal of the surface oxide from iron and steel it is customary to add small amounts of so-called inhibitors which, while they do not interfere with oxide removal, do check the action of the acid on the metal itself. Rhodes and Kuhn[4] have made a careful study of these inhibitors and find certain cyclic nitrogen compounds to be the most effective. Consequently the effect of traces of pyridine, acridine, and α-picoline on the yield of *tert*-butyl- and *tert*-amylmagnesium chlorides was studied. In no case was the yield of Grignard reagent raised appreciably by traces of the inhibitors. Larger amounts of inhibitor delayed the reactions and decreased the yields. Thus the inhibiting action extended to the formation of the Grignard reagent as well as to the formation of hydrogen by the action of magnesium.

Freundler and Damond[5] noticed in the preparation of *sec*-butylmagnesium bromide that when a certain lot of ether was used the yield of Grignard reagent was increased and the amount of olefin formed was decreased. On careful investigation they found that this particular lot of ether had a small amount of carbon disulfide present as an impurity.

This lead looked promising and has been investigated in a quantitative manner. Traces of carbon disulfide present during its preparation raise the yield of Grignard reagent from primary and secondary bromides and iodides. The increase in yield is greatest in the more concentrated halide–ether solutions (compare Tables I and II). The increase in yield is accompanied by a marked decrease in the total volume of gas evolved (Table

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(2) Submitted in partial fulfilment of the requirements for the Ph.D. degree.

(3) Tschelinzeff, *Ber.*, **38**, 3664 (1905); **39**, 773 (1906); Hepworth, *J. Chem. Soc.*, **119**, 1249 (1921); Gilman and co-workers, THIS JOURNAL, **51**, 1583 (1929); *Rec. trav. chim.*, **46**, 463 (1927); Johnson and Adkins, THIS JOURNAL, **53**, 1520 (1931).

(4) Rhodes and Kuhn, *Ind. Eng. Chem.*, **21**, 1066 (1929).

(5) Freundler and Damond, *Bull. soc. chim.*, [3] **35**, 108 (1908).

II). The exact composition of these gases, with and without carbon disulfide present, is being studied at the present time. *tert*-Butyl bromide gave erratic results. Primary, secondary and tertiary chlorides are being investigated. The chlorides appear to be rather sensitive to traces of carbon disulfide, small amounts being sufficient to completely stop the reaction. The violence of the reaction between the halide and magnesium is in all cases moderated when carbon disulfide is present.

In each case in which the Grignard reagent was prepared in the presence of a trace of carbon disulfide the yield of product prepared from the reagent and the carbonyl compound was higher, based not only on halide, *but also on Grignard reagent,* than when the reagent was prepared in the absence of carbon disulfide (see Table II). This phenomenon is being studied further with the purpose of investigating the effect of traces of carbon disulfide on the reducing, coupling and enolizing action of the Grignard reagent.

In all cases in which carbon disulfide was present the solution became jet black, due to the presence of a small amount of very finely divided black solid, the nature of which has not been investigated.

Other workers in this Laboratory have fully confirmed our results.

Experimental

The results are listed in Tables I and II. Only a few details need be noted. In the larger runs, it was found advisable to start the reaction with a small amount of a concentrated solution (about 1:1) of halide in *pure* ether because the carbon disulfide, while it raises the yield, retards the start of the reaction. The carbon disulfide is then added to the remainder of the halide–ether solution, once reaction is started.

TABLE I

Halide	Ratio CS_2 to ether by vol.	Yield of RMgX, % CS_2 present	No CS_2 present
Isopropyl bromide	1:500	No reaction	82.5
	1:1000	87.9	
	1:2500	81.5	65.1
	1:2500	84.3	74.0
	1:4000	88.3	
Isobutyl bromide	1:4000	86.8	81.7
	1:4000	88.5	83.2
sec-Butyl bromide	1:4000	84.8	78.2
Capryl bromide	1:600	No reaction	67.0
	1:4000	71.2	66.0
sec-Butyl chloride	1:600	No reaction	87.2
	1:4000	79.6[a]	87.3
tert-Butyl bromide[b]	1:4000	40.6	38.9
	1:4000	44.5	43.3

[a] Reaction hard to start and did not proceed smoothly.

[b] Further experiments with *tert*-butyl bromide gave erratic results with poor checks.

TABLE II (LARGER RUNS)

ISOPROPYL BROMIDE; PREPARATION OF METHYL ISOPROPYL CARBINOL

Size of runs, 0.75 mole. Vol. of ether used, 250 cc. 0.1 cc. of CS_2 used in each run in which CS_2 was present.

	CS_2 present			No CS_2	
Yield of RMgX, %	89.6	97.0	89.3	64.4	56.5
Gas evolved, liters	2.9	1.1	0.7	4.7	6.9
Yield of carbinol, %					
Based on halide	48.0	61.7		29.3	20.0
Based on Grignard		63.4			34.0

n-PROPYL BROMIDE: PREPARATION OF METHYLETHYL-*n*-PROPYLCARBINOL FROM *n*-PROPYLMAGNESIUM BROMIDE AND METHYL ETHYL KETONE

Size of runs, 2.0 moles. Volume of ether used, 500 cc.

	0.25 cc. CS_2	0.4 cc. CS_2	No CS_2
Yield of RMgX, %	88.3	88.2	65.5
Gas evolved, liters	3.7	4.6	11.8
Yield of carbinol, %			
Based on halide	70.5	69.0	51.5
Based on RMgX	80.0	78.2	65.5

ISOPROPYL IODIDE

Size of runs, 0.25 mole. Volume of ether used, 90 cc.

	0.1 cc. CS_2	No CS_2
Yield of RMgX, %	79.0	56.0

It appears from the results with *n*-propyl bromide (Table II) that only a trace of carbon disulfide is necessary. There was very little difference in the yield of *n*-propylmagnesium bromide when 0.25 cc. and 0.4 cc. of carbon disulfide was present.

The reactions in Table I were carried out using 0.05 mole of halide and 30 cc. of ether in each.

The reactions were carried out in all-glass apparatus, two reactions being carried out at once, one with and one without carbon disulfide. The reactions given in Table II were carried out with larger amounts as indicated.

Summary

1. "Pickling" inhibitors do not increase the yield of Grignard reagents.

2. Traces of carbon disulfide raise the yield in the preparation of the Grignard reagents from several aliphatic primary and secondary bromides and isopropyl iodide. Chlorides are being studied at the present time.

3. The increase in yield is accompanied by a decrease in the volume of gas evolved during the preparation of the Grignard reagent.

4. Preliminary experiments indicate that the yield of product prepared from the Grignard reagent and a carbonyl compound is higher, based on Grignard reagent, when the reagent was prepared in the presence of a trace of carbon disulfide. This work is being continued.

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