avoid molecular rearrangements. It was shown that "niacet" crotonaldehyde is the *trans* isomer by comparison with *trans*-crotonaldehyde prepared by treatment with hydrogen chloride and sunlight. Both aldehydes gave only *trans*-crotonic acid on oxidation under controlled conditions, but some *cis*-crotonic acid when the temperature was not controlled.

It was concluded that the *cis*-crotonic acid reported by Kaufler[4f] was probably formed from the *trans* isomer by stereomutation during the oxidation process.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

THE REDUCING ACTION OF THE GRIGNARD REAGENT. II. COMPARISON WITH THE EASE OF REMOVAL OF HYDROGEN BROMIDE FROM ALKYL BROMIDES AND WITH THE AMOUNT OF DIALKYLMAGNESIUM IN THE GRIGNARD REAGENT

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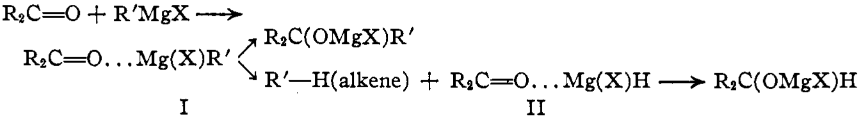
The theory proposed by Hess and Rheinboldt[1] to account for the reducing action of certain alkylmagnesium halides is that a primary addition product with the carbonyl compound is first formed and that this may either rearrange to give the normal addition product or may lose unsaturated hydrocarbon and then rearrange to give the reduction product.



$$R_2C{=}O + R'MgX \longrightarrow$$
$$\underset{\text{I}}{R_2C{=}O\ldots Mg(X)R'} \begin{cases} \nearrow R_2C(OMgX)R' \\ \searrow R'{-}H(\text{alkene}) + \underset{\text{II}}{R_2C{=}O\ldots Mg(X)H} \longrightarrow R_2C(OMgX)H \end{cases}$$

Meisenheimer[2] proposed a similar mechanism except that the postulation of the intermediate compound II is omitted.

One might predict, if Hess' formulation represents the mechanism of the reaction, that for a series of alkylmagnesium halides the relative ease with which unsaturated hydrocarbon is lost from the complex $R_2CO\ldots Mg(X)R'$ and hence the relative amount of reduction might be comparable with the relative ease with which alkenes are formed from alkyl halides. A rough evaluation of the relative ease with which pyridine reacts with alkyl bromides to form alkene and pyridine hydrobromide has been reported recently[3] and it is the purpose of this paper to present data on the amount of reduction brought about by Grignard reagents from these same alkyl

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[1] Hess and Rheinboldt, *Ber.*, **54**, 2043 (1921).

[2] Meisenheimer, *Ann.*, **442**, 180 (1925).

[3] Noller and Dinsmore, THIS JOURNAL, **54**, 1025 (1932).

bromides. At the same time data on the amount of dialkylmagnesium in the Grignard reagent will also be given.

The method of Blicke and Powers[4] for estimating the amount of reduction, which is based on the insolubility of the bromomagnesium salt of benzohydrol in ether, is probably the most satisfactory for comparing the reducing action of various reagents. Their data, however, are not sufficiently complete to compare with the data on the relative ease of formation of alkenes from alkyl bromides. We have made use of their method and extended their data taking the precautions to use filtered solutions, to use solutions of the same concentration and in definite excess, and to carry the reaction out within the narrow temperature range of 0–5°.[5]

The amount of dialkylmagnesium in the solutions was determined by a modification[6] of the method of Schlenk and Schlenk, Jr.[7] The combined data are summarized in Table I which gives the average values of at least two determinations.

The work on the reaction of alkyl bromides with pyridine[3] showed that *tert.*-butyl bromide loses hydrogen bromide about eighty times more rapidly than the secondary bromides, isopropyl and *sec.*-butyl, and these in turn about ten times more rapidly than the primary bromides, ethyl, *n*-propyl, isobutyl and *n*-butyl. On comparing this order with that given in Table I, it is readily seen that there is no observable relation between the amount of reduction and the ease with which alkenes are formed from alkyl bromides.

On the other hand, it appears that the amount of reduction increases with increasing dialkylmagnesium content of the solution. There is, however, no direct relationship between the two since the *tert.*-butyl solution causes no reduction although there is 32 equivalent per cent. of dialkylmagnesium present, the isobutyl solution causes 86% reduction although only 78% of dialkylmagnesium is present, and the isopropyl and *sec.*-butyl solutions have almost the same dialkylmagnesium content but cause 13 and 40% reduction, respectively. None of the explanations that have suggested themselves will satisfy the data obtained thus far.

Our modification[6] of the excellent method used by Schlenk and Schlenk, Jr.,[7] for determining the amount of dialkylmagnesium is by no means as exact as theirs but the greater ease of carrying out the determination and its applicability to solutions of the Grignard reagent as directly pre-

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[4] Blicke and Powers, THIS JOURNAL, **51**, 3378 (1929).

[5] The necessity for using filtered solutions and for keeping the Grignard reagent in excess have been reported in a previous paper.[6] Rheinboldt and Roleff, *J. prakt. Chem.*, **109**, 175 (1925), have shown that the amount of reduction increases with the temperature, and we have reason to believe that the amount of reduction also varies with the concentration of the Grignard reagent.

[6] Noller, THIS JOURNAL, **53**, 635 (1931).

[7] Schlenk and Schlenk, Jr., *Ber.*, **62**, 920 (1929).

pared give it certain advantages. In the two instances where a direct comparison is possible the two methods check fairly well. Thus Schlenk, Jr.,[8] finds for ethylmagnesium bromide solutions 29.5% diethylmagnesium and for *n*-propylmagnesium bromide 38% of di-*n*-propylmagnesium as compared with our values of 25.5 and 35.5%, respectively.

It appears that the generalization of Schlenk, Jr., that the amount of dialkylmagnesium increases with increasing molecular weight, must be modified to take the structure of the hydrocarbon radical into consideration. Our results for example indicate that the amount of dialkylmagnesium in the solution of *tert.*-butylmagnesium bromide is lower than that in any of the Grignard reagents including the ethyl and propyl solutions.

Experimental

Grignard Reagents.—Solutions of the alkylmagnesium bromides were prepared in the usual manner from purified alkyl bromides and filtered by pressure through a 3-mm. layer of ignited kieselguhr on a sintered glass filter. They were analyzed by titration with standard acid and then concentrated or diluted to give a concentration of approximately 1.75 *N*, after which the concentration was checked again by titration.

Reduction Procedure.—To a 300-cc. Erlenmeyer flask fitted with a 30-cc. dropping funnel and thermometer was added 25 cc. of the Grignard reagent. The solution was cooled to 0° in an ice–salt bath. The amount of benzophenone to be used was calculated for the particular Grignard reagent so that the latter was present in 10% excess, and this amount dissolved in 8 cc. of warm dry benzene. This solution was added dropwise from the separatory funnel at such a rate that the temperature remained between 0 and 5°. The contents of the flask was swirled continuously to keep the mixture well stirred.[9] When all the benzophenone had been added the contents of the flask was allowed to come to room temperature. The precipitate was filtered with suction on a 5-cm. Büchner funnel and washed carefully with three 10-cc. portions of dry benzene, care being taken not to suck air through the precipitate before the last washing. The cake was transferred to the Erlenmeyer flask, decomposed with 50 cc. of saturated ammonium chloride solution and extracted with three 50-cc. portions of ether. The combined ether extracts were evaporated in a tared 150-cc. beaker over a warm hot-plate. To prevent benzohydrol from creeping over the edge of the beaker, the ether vapors were removed by a tube attached to a water pump and extending into the center of the beaker. When practically all of the ether and benzene had been removed, the warm beaker was placed in a vacuum desiccator over phosphorus pentoxide, the desiccator evacuated and allowed to stand for two hours. The amount of benzohydrol was weighed and the percentage reduction calculated.

In checking the accuracy of the method we have determined roughly the solubility of the bromomagnesium salt of benzohydrol in ether, benzene and ether–benzene mixtures (25:8 by volume) and obtained the values 0.006, 0.007 and 0.006 g. per cc. of solution, which corresponds to 0.0038, 0.0045 and 0.0038 g. of benzohydrol. This solubility does not account for the fact that Blicke and Powers[4] recovered only 81% of the

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[8] Schlenk, Jr., *Ber.*, **64,** 734 (1931).

[9] In all cases the usual transient red color was observed. In the case of *sec.*-butylmagnesium bromide, however, the color was permanent for as long as two weeks and was not destroyed by passing air through the solution for ten minutes. The *tert.*-butylmagnesium bromide likewise gave a permanently colored solution.

benzohydrol added to a solution of ethylmagnesium bromide. On repeating their work with 7.54 g. of freshly recrystallized benzohydrol, m. p. 66–67°, under exactly the same conditions used for determining the amount of reduction, we recovered 7.24 g. or 96% of the benzohydrol, m. p. 62–66°, from the precipitate and 0.26 g. or 3.4% from the filtrate. This indicates a mechanical loss of 0.6%. The value of 0.26 g. in the filtrate checks very closely with the calculated value of 0.27 g. based on the solubility determinations. This indicates that the values for the amount of reduction are low by about 4%.

Determination of Dialkylmagnesium.—The procedure was identical with that previously reported.[6]

All data are tabulated in Table I.

TABLE I

COMPARISON OF AMOUNT OF REDUCTION WITH DIALKYLMAGNESIUM CONTENT OF THE GRIGNARD REAGENT

Alkylmagnesium bromide	Concentration, equiv. per cc.	Dialkyl-magnesium, equiv., %	Benzohydrol, %	M. p. of Benzohydrol, °C.
Tert.-butyl	0.00172	32	0[10]	
Ethyl	.00175	51	2	50–70
Isopropyl	.00165	59	13	61–63
Sec.-butyl	.00183	62	40	61–64
n-Propyl	.00179	71	58	60–63
n-Butyl	.00177	74	59	61–64
Isobutyl	.00174	78	86	62–66

Summary

1. Comparison of the amount of reduction of benzophenone by Grignard reagents from seven alkyl bromides with data on the relative ease with which alkenes are formed from these bromides shows that no relationship between the two exists.

2. The amount of reduction increases with the increasing dialkylmagnesium content of the solutions but is not proportional to the amount of dialkylmagnesium present.

3. The amount of dialkylmagnesuim present in Grignard solutions appears to be influenced more by the structure than by the molecular weight of the hydrocarbon radical.

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[10] From 7.1 g. of benzophenone there was obtained 7.1 g. of a viscous liquid distilling almost completely between 155–160° at 4 mm. Marvel and Bateman, THIS JOURNAL, **49**, 2917 (1927), give the b. p. of *tert.*-butyldiphenylcarbinol as 148–150° at 2.5 mm. This behavior of *tert.*-butylmagnesium bromide is surprising since Conant and Blatt, THIS JOURNAL, **51**, 1227 (1929), found that in general *tert.*-butylmagnesium chloride caused more reduction than either isopropyl or *n*-butylmagnesium bromide and Konovalov, Miller and Timtschenko, *Chem. Zentr.*, II, 312 (1906), have obtained 38.5% benzohydrol from the reaction of benzophenone with *tert.*-butylmagnesium bromide. We believe that these apparent discrepancies may be due to variation in the conditions under which the reaction takes place, *cf.* Note 5.