was then heated in a 75° bath for 48 hr. A second mixture was irradiated for 48 hr. using an ultraviolet lamp. The following isolation procedure was used on the mixture which had been irradiated. A similar procedure was used for the peroxide-catalyzed reaction product, with like results. Distillation gave, in addition to solvent and unchanged triphenylgermane, 3.0 g. of a solid, b.p. 175–180° at 0.06 mm., which, after recrystallization from a mixture of 150 ml. of absolute ethanol and 50 ml. of isopropyl ether, melted at approximately 150–190°. This latter mixture was lixiviated with hot 80% aqueous ethanol and cooled. The crystals which were deposited melted at 147.0–149.5°, and a mixture with triphenylcyclohexylgermane (m.p. 143–146°) melted at 146.5–148.5°. The infrared absorption spectra confirmed the identity of the two samples. Another portion of the crude solid (m.p. 150–190°) was recrystallized twice from heptane and once from benzene-heptane mixture. The product, which melted at 228–232°, when mixed with authentic tetraphenylgermane (m.p. 232–234°), melted at 231–233°.

Reaction of triphenylgermane with 1,1-diphenylethylene and peroxide. The benzoyl peroxide initiation procedure used with cyclohexene was employed with the substitution of 1.1 ml. (0.0063 mole) of freshly distilled 1,1-diphenylethylene (b.p. 136–140° at 12 mm.) for the cyclohexene. The mixture was heated for 48 hr., and the unchanged triphenylgermane was distilled leaving behind a yellow oil which could not be crystallized with or without the aid of solvents. The oil appeared to be an olefin polymer. The desired product, triphenyl-2,2-diphenylethylgermane, or an isomer, which has been prepared by the addition[11] of triphenylgermylpotassium to 1,1-diphenylethylene, is a readily crystallizable solid which melts at 99.0–99.5°.

Preparation of triphenyl-1-octyltin from triphenyltin chloride and 1-octylmagnesium bromide. 1-Octylmagnesium bromide was prepared from 1.22 g. (0.05 g. atom) of magnesium and 9.7 g. (0.05 mole) of 1-bromooctane in ether. To the filtered Grignard solution was added dropwise a solution of 7.2 g. (0.02 mole) of triphenyltin chloride[12] in ether. The mixture was refluxed for 2 hr. and then was hydrolyzed by the addition of 125 ml. of cold water. The ether layer was separated and dried over magnesium sulfate. Removal of the solvent left a yellow liquid which was crystallized from 150 ml. of ethanol. The yield was 6.3 g. (68%) of crystals which melted at 54.0–54.6°. Another recrystallization raised the melting point to 54.3–55.0°.

Anal. Calcd. for $C_{26}H_{32}Sn$: Sn, 25.6. Found: Sn, 25.8, 26.0.

Reaction of triphenyltin hydride and 1-octene with benzoyl peroxide, ultraviolet or phenylazotriphenylmethane initiation. Three experiments were run using the three sources of radical initiation. In a typical run 23.8 g. (0.068 mole) of triphenyltin hydride,[13] 1.7 ml. (0.01 mole) of 1-octene, 25 ml. of petroleum ether (b.p. 60–70°), and 0.3 g. of benzoyl peroxide were heated to 75° for 24 hr. Another run used ultraviolet irradiation for 4 days at about room temperature in place of the benzoyl peroxide and heat. The third run used 0.3 g. of phenylazotriphenylmethane[14] at room temperature in the dark. In all three cases a white solid was deposited as the reaction progressed. A solution of triphenyltin hydride in petroleum ether remained clear for 2 days when kept in the dark. The white solid was collected by filtration and extracted with hot ethanol. No dissolved material could be isolated from the ethanol, although triphenyl-1-octyltin is very soluble in the hot solvent. Recrystallization of the white solid from chloroform gave crystals melting at 226.0–228.5°. A mixture with authentic tetraphenyltin (m.p. 228.0–228.5°) melted at 226.5–228.5°.

Solvent was distilled from the filtrate from which the tetraphenyltin had originally been isolated. During the distillation the residue changed to a dark gray solid mass, apparently due to disproportionation. Extraction of the solid with hot ethanol failed to dissolve any material suggestive of triphenyl-1-octyltin. The gray solid dissolved in chloroform except for a small amount of black powder which dissolved in hydrochloric acid and appeared to be metallic tin.

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[Contribution from the Department of Chemistry, Iowa State College]

Stability of an Ether Solution of Methylmagnesium Iodide

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Incidental to studies concerned with the stability of some organometallic compounds, it has been observed that an ether solution of methylmagnesium iodide contained in a sealed glass container is essentially unchanged after a period of twenty years.

In connection with studies on the general reactions of organometallic compounds, the stability of Grignard reagents has long been of interest. Previous work in this laboratory[1] indicated that the normalities of diethyl ether solutions of various Grignard reagents, as determined by acid titration,[2] remained essentially unchanged for four months. It was necessary to adequately protect the Gri-

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gnard reagent solutions from the air, but parallel experiments with ethylmagnesium bromide in the light and in the dark indicated that daylight had little effect on the stability of the solutions. Solutions of methylmagnesium iodide are widely used in analytical methods based on the Tschugaeff-Zerewitinoff[3] analysis for active hydrogen, and as a result their stability has been subjected to some study. A solution of methylmagnesium iodide in di-*n*-amyl ether is reported to be "stable for a month or more."[4] When a diisoamyl ether solution of methylmagnesium iodide, prepared for use in an apparatus designed for analysis with Grignard reagents, was analyzed "immediately after its preparation and after it had remained in its receptacle, exposed to the light for months," the composition of the solution was found to be invariable.[5a] In connection with the stability of solutions of organometallic compounds in general, it is of interest to compare the above reported stability of methylmagnesium iodide in various solvents with the stability of methyllithium. Methyllithium in diethyl ether and in di-*n*-butyl ether[6] has been shown to enjoy certain advantages over methylmagnesium halides in the Tschugaeff-Zerewitinoff analysis, partly because of its stability and partly because of the greater solubility of some —OLi compounds over —OMgX compounds. In studies on a modification of the Tschugaeff-Zerewitinoff determination,[7] a di-*n*-butyl ether solution of methyllithium was stored in a Grignard machine[5b] and the normality of the solution, as determined by gas analysis, was found to have decreased only from 0.777 to 0.764 during four months. The above evidence indicates that a di-*n*-butyl ether solution of methyllithium is sufficiently stable for use as a valuable supplement to solutions of methylmagnesium iodide in carrying out Tschugaeff-Zerewitinoff analyses.

We are reporting further evidence of the stability of methylmagnesium iodide obtained recently when a sealed Carius tube containing 50 ml. of a diethyl ether solution of about $2N$ methylmagnesium iodide was opened after remaining sealed for twenty years. The normality of the solution was determined by both acid titration and gas analysis[2] and was found to be essentially the same as when the solution was first placed in the tube. The results of the gas and acid titration analyses are listed in Table I. Of particular significance is the fact that the normality values found by the two different methods of analysis are in close agreement. It has been shown[2] that the normality values obtained by acid titration normally run slightly higher than those obtained by gas analysis, due probably to the presence of basic magnesium compounds formed by means other than hydrolysis of the Grignard reagent such as ether cleavage and the reaction of the Grignard reagent with traces of water and/or oxygen. Any cleavage of the diethyl ether by the methylmagnesium iodide which might have occurred during the twenty years of storage would have been evidenced by an abnormal difference between the normality values found by acid titration and those found by gas analysis. The average difference was found to be 2.6%, well below the reported average difference of 3.9%.[2]

TABLE I

COMPARISON OF THE NORMALITY VALUES OF AN ETHER SOLUTION OF METHYLMAGNESIUM IODIDE AS DETERMINED BY ACID TITRATION AND BY GAS ANALYSIS

Sample No.	Volume of Sample (ml.)	Method of Analysis	Normality Found	Variation from Mean Titration Normality (%)[a]
1	2.66	Titration	2.295	−0.1[b]
2	2.66	Titration	2.301	+0.1
3	2.66	Titration	2.328	+1.3
4	2.56	Titration	2.267	−1.4
Mean	—	Titration	2.298	—
5	1.66	Gas	2.287	−0.5
6	1.16	Gas	2.164	−6.2
7	1.26	Gas	2.264	−1.5
Mean	—	Gas	2.239	−2.6

[a] Calculated as per cent of the normality found. [b] + and − indicate higher and lower percentage respectively.

Positive identification of the material as a solution of methylmagnesium iodide was made by preparing acet-α-naphthalide[8] and methylmercuric iodide[9] and checking their properties against those of authentic specimens.

A Color Test I,[10] which was taken immediately after opening the sealed tube, was strongly positive.

It would not be unreasonable to expect variations with other Grignard reagents and variations with other solvents. For example, it is known that methylmetallic compounds may differ appreciably from others.[6,11,12]

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EXPERIMENTAL

The volume of the solution contained in the sealed Carius tube (50 ml.) and the total volume of the tube (140 ml.) were determined by measuring an equivalent volume of water in a tube of comparable size. The volume of the diethyl ether solution of methylmagnesium iodide had not decreased appreciably during the twenty years of storage as the level of the top of the solution prior to opening the tube was even with the top of a blank label which had been placed on the tube to mark the initial volume. The tube had been wrapped in a towel and kept in a shatter-proof container throughout the twenty years it had remained sealed. There was no detectable rush of gas when the tube was opened after having been cooled for 4 hr. in an ice bath. By working promptly in an inert atmosphere according to the usual techniques employed when handling reactive organometallic compounds, all quantitative determinations were completed within 8 hr. after opening the tube. The samples used were removed by a pipette of previously determined volume which had been drawn out long enough to easily reach the solution in the tube and small enough to readily pass through the constricted neck of the tube.

The analytical procedures were essentially those reported earlier from this laboratory,[2] the chief difference being in the size of the sample used. The sulfuric acid in the gas wash bottle used in the gas analysis was replaced with fresh acid between the analyses of samples 6 and 7.

Acet-α-naphthalide (m.p. 159.5-160°) was prepared by the procedure previously reported from this laboratory,[8] and methylmercuric iodide (m.p. 146-147°) was prepared by the procedure of Marvel, Gauerke, and Hill.[9] A mixed melting point of a sample of each derivative with its respective authentic specimen was not depressed.

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

Addition of Organometallic Reagents to α,β-Unsaturated Amides

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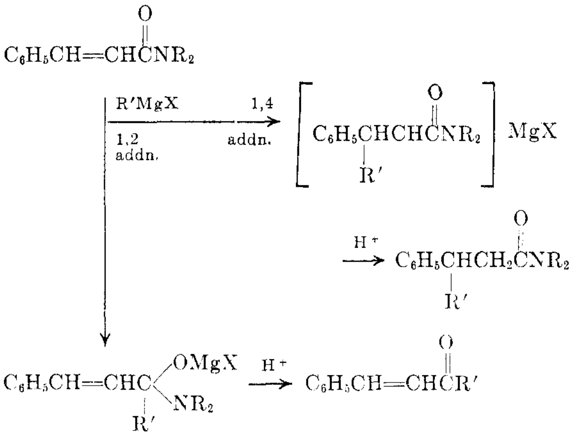
Phenyllithium adds *via* conjugate addition to *N*,*N*-dicyclohexylcinnamamide with no evidence of 1,2 addition, but adds 1,2 to *N*,*N*-dimethylcinnamamide.

N,*N*-Disubstituted α,β-unsaturated amides add phenyl and ethyl Grignard reagents by conjugate addition despite wide variations in the substituents. In contrast, methylmagnesium iodide yields some 1,2 addition and some unchanged starting material. The latter appears to involve a complex which regenerates the amide on hydrolysis. Enolization does not occur to an important extent in the formation of this intermediate.

An organometallic reagent may add to an unsaturated amide by normal addition to form an unsaturated ketone or by conjugate addition to form a saturated amide.



The reaction of phenylmagnesium bromide with *N*-ethylcinnamanilide was reported by Kohler and Heritage[3] to yield conjugate addition products. The investigation was extended by Maxim and Ioanid[4] to the condensation of several cinnamanilides with ethyl- and phenylmagnesium bromides and with methylmagnesium iodide.

In the present work, it was desired to determine the effect of wider variations in the structure of the amide on the course of the condensation. As the study progressed and the conjugate nature of the addition of the Grignard reagents was confirmed, the addition of phenyllithium to α,β-unsaturated amides became a further object of investigation.

The extent of 1,2 addition was found by comparison of the ultraviolet absorption spectrum of the products with a standard curve of the ketone produced. The extent of conjugate addition was determined by isolation of the saturated amide. The results of these and previously reported experiments are summarized in Table I. They illustrate a marked tendency of the unsaturated amides to undergo conjugate addition somewhat like that shown by the unsaturated ketones. For example, the reaction of phenylmagnesium bromide with *N*,*N*-dimethylcinnamamide yields 93% 1,4 addition[5] while isopropyl styryl ketone, which is almost identical sterically, yields 88% of the conjugate addition product.[6] However, the analogy is not

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