of a portion of the above hydrogenated adduct (24.3 g.) in a flask equipped with a heated 6-in. distillation head attached to a cold trap gave 9.1 g., vinylcyclohexane (98% yield). The ultraviolet spectrum of the solid (14.9 g., ∽100% recovery) remaining in the flask indicated it to be 104 ± 5% anthracene melting at ∼ 218° (m.p. of an authentic sample was 217–218°).

The pyrolysis proceeds rather slowly below 300° but smoothly and rapidly at temperatures ≥ 330°.

Distillation of the liquid product gave pure vinylcyclohexane; b.p. 125.7–126°, n^{20}_D 1.4458, d_4^{20} 0.80178. Lit.,[3] b.p. 127°, $n^{20.0}_D$ 1.4462, d_4^{20} 0.8012.

Pyrolysis of semicrystalline adduct I. The second crop of adduct I obtained above was pyrolyzed without hydrogenation to give a 70–80% recovery of 4-vinylcyclohexene-1 and ≤ 15% of C_9–C_{16} hydrocarbons. A near quantitative recovery of anthracene was obtained.

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The Reaction between 2-Bromobenzamide and Benzylmagnesium Chloride[1]

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In attempting to synthesize α-phenyl-2-bromoacetophenone by the reaction of excess benzylmagnesium chloride with 2-bromobenzamide,[3] it was surprisingly found that the product was α-phenylacetophenone (desoxybenzoin), the bromine having been removed. A study of the reaction was undertaken to determine conditions for removal of the halogen and whether it indeed could be retained.

The most important variable appeared to be the ratio of benzylmagnesium choride to 2-bromobenzamide and, accordingly, a series of experiments was carried out in which this ratio was varied from 1:1 to 13.8:1 (see Table I).

The data show that with a ratio of Grignard to amide of from 1:1 to 3:1, the products are the starting amide, 2-bromobenzamide, the corresponding acid, 2-bromobenzoic acid, or the magnesium salt of the latter. With a ratio of 4:1 the desired product, α-phenyl-2-bromoacetophenone, was obtained in good yield. However, with a large excess of Grignard dehalogenation took place.

The dehalogenation is most readily understood as a metal-halogen exchange reaction. Although metal-halogen exchange reactions have been postulated from organomagnesium compounds for some time,[4] none seems to have been reported for compounds containing active hydrogen. A possible equation for the reaction based on the evidence in Table I is as follows:

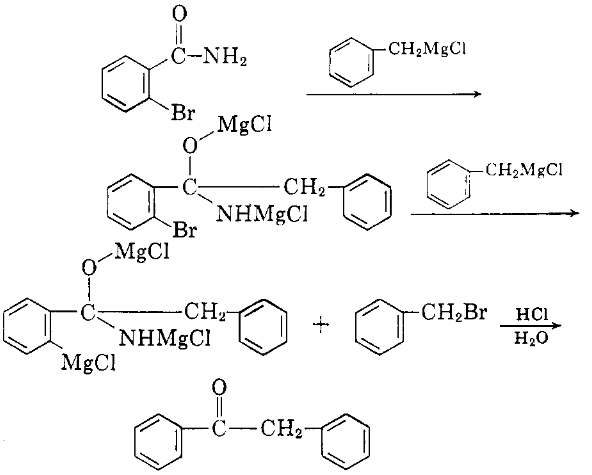

TABLE I

PRODUCTS OF THE REACTION BETWEEN 2-BROMOBENZAMIDE AND BENZYLMAGNESIUM CHLORIDE

Grignard Reagent, Moles[a]	Ratio Grignard: Amide	Products	Yield, %
0.042	1:1	2-Bromobenzamide	89.3
0.084	2:1	2-Bromobenzamide	64.3
		2-Bromobenzoic acid	16.7
		Magnesium 2-bromobenzoate	14.0
0.125	3:1	2-Bromobenzamide	19.0
		2-Bromobenzoic acid	29.8
		Magnesium 2-bromobenzoate	39.7
0.168	4:1	α-Phenyl-2-bromoacetophenone	77.1
0.368	9:1	α-Phenylacetophenone	83.9
0.580	13.8:1	α-Phenylacetophenone	81.6

[a] The yield of Grignard reagent was not determined in each case, but estimated from the quantities of benzyl chloride taken. In standard runs 92 ± 2% yield of benzylmagnesium chloride was obtained.

It is of interest that 2-chlorobenzamide was not found to undergo any exchange with benzylmagnesium chloride.[3] This is in accord with the facts known for metal-halogen exchange reactions with organolithium compounds,[5] namely, that chlorine atoms are less reactive than bromine atoms.

EXPERIMENTAL

A general procedure was followed. To the Grignard reagent prepared in ether from the stated quantities (see Table I) of benzyl chloride and sublimed magnesium was added with stirring the stated quantity of 2-bromobenzamide (m.p. 154.5–156.5°). Reflux with stirring was maintained for 2

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(1) Submitted to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of doctor of philosophy, 1956.

(2) To whom inquiries should be addressed.

(3) For analogous reactions see E. I. Shapiro and E. I. Becker, *J. Am. Chem. Soc.*, **75**, 4769 (1953).

(4) E. Urion, *Compt. rend.*, **198**, 1244 (1934).

(5) R. G. Jones, *Org. Reactions*, **VI**, 339 (1951).

days. The reaction mixture was then hydrolyzed with a mixture of ice and 10% sulfuric acid.

1. Grignard: amide ratio less than 4:1. The solid material which was insoluble in both the aqueous and organic phases was filtered and heated in 10 ml. of sulfuric acid on a water bath until it dissolved. The solution was cooled to room temperature, added to 90 ml. of water, and the mixture filtered. The solid did not depress the melting point of authentic *o*-bromobenzoic acid. The acidic filtrate was tested for magnesium ions as magnesium ammonium phosphate and gave a positive test.

The aqueous-organic filtrate, after removal of the magnesium *o*-bromobenzoate, was separated, discarding the aqueous layer, and extracted with 10% sodium carbonate solution and finally 5% sodium hydroxide solution. Acidification of the alkaline extracts with 1:1 hydrochloric acid gave a precipitate which did not depress the melting point of authentic *o*-bromobenzoic acid.

The organic layer was dried over anhydrous sodium sulfate and distilled to give *o*-bromobenzamide, b.p. 158–161° (12 mm.).

2. Grignard: amide ratio 4:1. The organic layer from the hydrolysis step was separated, extracted with 10% sodium carbonate solution, and then with 5% sodium hydroxide. The combined alkaline layers were acidified with 1:1 hydrochloric acid, but no precipitate formed.

The organic layer was washed with water, dried over anhydrous sodium sulfate, and vacuum distilled to yield α-phenyl-2-bromoacetophenone as a yellow oil, b.p. 203–206° (2 mm.).

3. Grignard: amide ratio greater than 4:1. The organic layer from the hydrolysis step was separated, extracted with 10% sodium carbonate solution, and then with 5% sodium hydroxide. The combined layers were acidified with 1:1 hydrochloric acid, but no precipitate appeared.

The organic layer was washed with water, dried over anhydrous sodium sulfate, and vacuum distilled to give α-phenylacetophenone, b.p. 176–178° (12 mm.).

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Aminohydrins from Aziridine

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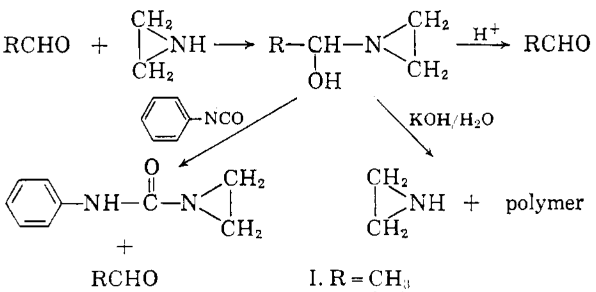
Aminohydrins, $R_2C(OH)NR_2$, are unknown generally except as certain reactive intermediates from the addition of aldehydes to amines. The products from the reaction of secondary amines and carbonyl compounds usually are water and enamines or alkylidenediamines.[1] The secondary heterocyclic amine aziridine reacting in the cold with carbonyl compounds yields addition products containing oxygen[2] which have been formulated as aminohydrins[3] without adequate proof of structure. The comparable reaction under prolonged reflux in ether solution opens the aziridine ring and gives 2-oxazolidines.[4] Kostyanovskii has reported from the reaction of aziridine and formaldehyde the formation of two products: aziridinemethanol and methylenebisaziridine.[5]

We have prepared stable addition products of aziridine and acetaldehyde, propionaldehyde, and butyraldehyde. Infrared spectra along with other physical properties indicate that these addition products are stable aminohydrins, 1-aziridine-1-alkanols, $RCH(OH)N(CH_2)_2$. The infrared spectra of all three products exhibited similarities and showed a strong hydroxyl absorption band at 3.1 μ which nearly obscured the strong aziridine C—H stretching band at 3.25 μ. The strong C—O stretching band at 9.0 μ is evidence of secondary hydroxyl groups. Intact aziridine rings were indicated by the strong bands at 3.25 μ, strong symmetric ring breathing deformations at 8.0 μ, and additional aziridine ring deformations in the 11.8- and 12.2-μ region.[6]

1-Aziridine-1-ethanol (I) from aziridine and acetaldehyde was sufficiently pure after distillation for characterization (Table I). It was soluble in ethyl ether, ethanol, and water, but insoluble in petroleum ether. 1-Aziridine-1-propanol (II) and 1-aziridine-1-butanol (III) were soluble in the same solvents and in petroleum ether. The latter two products after distillation were believed to contain some of the corresponding 1,1-alkylidenebisaziridines (1 to 4%), and were purified further by recrystallization from petroleum ether at −20° (Table I). 1-Aziridine-1-butanol treated with 2,4-dinitrophenylhydrazine reagent gave a 93% yield of butyraldehyde 2,4-dinitrophenylhydrazone.

1-Aziridine-1-ethanol did not react with ammonia either in ethyl ether or aqueous solution. Warming with aqueous potassium hydroxide under reduced pressure returned aziridine in 50% yield. Reaction with phenyl isocyanate in ethyl ether solution gave the unsymmetrical urea derivative (IV) rather than the urethan. The aziridine aminohydrins have remained stable and clear for several weeks at room temperature in the presence of a little calcium hy-



IV

I. $R = CH_3$
II. $R = C_2H_5$
III. $R = C_3H_7$

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(1) C. Mannich and H. Davidsen, *Ber.* **69,** 2106 (1936); N. J. Leonard, *J. Org. Chem.,* 21, 1187 (1956); M. E. Herr and F. W. Heyl, *J. Am. Chem. Soc.,* **75,** 5927 (1953); A. J. Birch, R. Jaeger, and R. Robinson, *J. Chem. Soc.,* (1945) 582.

(2) A. Dornow and W. Schacht, *Chem. Ber.,* **82,** 464 (194).

(3) Houben-Weyl, "Methoden Der Organischen Chemie," Vierte Auflage Stickstoff Verbindungen II/III, Georg Thieme Verlag, Stuttgart (Germany), 1958, p. 245.

(4) J. B. Doughty, C. L. Lazzell, and A. R. Collett, *J. Am. Chem. Soc.,* **72,** 2866 (1950).

(5) R. G. Kostyanovskii, *Doklady Akad. Nauk S.S.S.R.,* **135,** 853 (1960); *Chem. Abstr.* **55,** 12380a (1961).

(6) The authors express appreciation to H. L. Spell for the infrared spectra and aziridine band assignments.