

nitrogen atmosphere had been maintained; thereafter, the reaction products were handled in air without special precautions. The ether layer was mixed with 150 cc. of water and the ether removed at reduced pressure. A white precipitate of aminoethyl ester separated as the ether distilled. This material, after drying in a vacuum desiccator melted at 128–135° and weighed 19.9 g. (83%). The first crystallization from toluene gave a 96% recovery of ester melting at 139.5–141°, and the second recrystallization an 80% recovery of ester (over-all yield of purified material, 64%), m.p. 141–142°; neutralization equivalent, determined by titration with standard hydrochloric acid, 242; calcd. for $C_{15}H_{13}BON$, 239.

To prove the presence of the benzyl group in the molecule a 0.539-g. sample of the ester was oxidized with 2.5 g. of potassium permanganate in 50 cc. of water made alkaline with potassium hydroxide. After the initial exothermic reaction, an additional 2.5 g. of permanganate was added and the mixture warmed on a steam bath for 15 min. It was then cooled, decolorized with ethylene glycol, acidified, cleared of manganese dioxide with sodium hydrogen sulfite, and extracted with ether. The mixture of acids isolated from the ether was separated by sublimation to give benzoic acid (sublimate) m.p. 121–122°, 0.217 g. (80%); and benzenboronic acid (residue) as the oxide, m.p. (193–197°), 0.079 g. (29%).

In another degradation 1.00 g. of ester was shaken with 3*N* hydrochloric acid and ether for several seconds to effect hydrolysis. The ether layer was evaporated on a steam bath to leave an oil which was warmed with 10 cc. of 5% potassium hydroxide solution. Air was passed through the solution for an hour then the mixture separated into neutral and organic acid products. From the acid portion was obtained 0.358 g. (70%) of benzenboronic acid (m.p. 222–223°), proving the presence of a phenyl-boron linkage in the aminoethyl ester; and from the neutral fraction was isolated, following treatment with 3,5-dinitrobenzoyl chloride, 0.08 g. of benzyl 3,5-dinitrobenzoate, m.p. 111–113° (undepressed on mixture with an authentic sample).

Aminoethyl butylphenylborinate. By the procedure described for the benzyl compound 13.8 g. (71%) of aminoethyl butylphenylborinate m.p. 104–107°, was obtained from 0.103 mole of dibutyl benzenboronate and 0.103 mole of *n*-butylmagnesium bromide. One recrystallization from toluene-hexane raised the melting point to 106–107° (12.2 g., 60% yield), and a subsequent recrystallization raised the melting point to 108–108.5°. As expected, aromatic C—H absorption was weak in the infrared whereas aliphatic C—H absorption was strong.

Anal. Calcd. for $C_{12}H_{20}BON$; C, 70.26; H, 9.83; N, 6.83; neut. equiv., 205. Found: C, 69.97; H, 9.42; N, 7.18; neut. equiv., 206 (C, H, and N analyses by H. Beck).

Mercuric chloride in ethanol cleaved 1.241 g. of the aminoethyl ester in ethanol to give 1.8 g. (95%) of phenylmercuric chloride. In another experiment, 0.92 g. of ester was hydrolyzed with hydrochloric acid, the reaction products taken up in ether and the ether evaporated. Sufficient oxidation had occurred that 0.2 g. (37%) of benzenboronic acid could be isolated from the residue.

Aminoethyl 1-methylheptylphenylborinate. By the above procedure 23.5 g. of crude ester, m.p. 85–92°, was isolated from a reaction of 0.090 mole of dibutyl benzenboronate with 0.090 mole of 1-methylheptylmagnesium bromide. Recrystallization from hexane that contained a small amount of benzene yielded 12.83 g. (55%) of the aminoethyl ester, m.p. 93–95°, neut. equiv. 258; calcd. for $C_{18}H_{28}BON$, 261. Acid hydrolysis of the aminoethyl ester in the presence of air yielded, as in the case of the butylphenylborinate, benzenboronic acid, 0.153 g. (64%). The ease of oxidation of this mixed borinic acid points up the value of ethanolamine as a tool for working with this class of compounds.

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Acetylation of Amides with Ketene

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Although it has been demonstrated by several workers that amides can be acetylated with ketene, the number of such examples is rather limited. Rice and co-workers¹ prepared *N*-phenyldiacetamide by passing ketene into acetanilide at 140°. They suggested that *N*-acetylbenzamide was formed similarly from benzamide at 180° but that it decomposed into benzonitrile as the reaction progressed. Later, Padgham and Polya² isolated *N*-acetylbenzamide and diacetamide by passing ketene into molten benzamide and acetamide, respectively. The use of sulfuric acid as a catalyst in the formation of *N*-phenyldiacetamide from ketene and molten acetanilide was reported by Smirnova³ and others.

In this present study seven amides, namely: acrylamide, methacrylamide, cyanoacetamide, *p*-toluamide, formamide, acetamide, and benzamide, have been successfully acetylated by ketene. Of these, the first four were treated with ketene for the first time. These reactions were carried out in a suitable solvent and in some cases in the presence of catalytic amounts of sulfuric acid. When sulfuric acid was used it was necessary to wash it from the reaction mixture as soon as possible after the reaction was completed. Continued contact with the catalyst in most instances caused decomposition of the acetylated product with a proportional decrease in yield. Monoacetyl derivatives were formed with the exception that formamide yielded *N*-formyldiacetamide. This triacylated ammonia is crystalline, a fact of interest in connection with Smirnova's³ statement that triacetylammonia is a liquid. *N*-Acetylacrylamide and *N*-acetylmethacrylamide, prepared in the present study, are two additional new compounds reported for the first time, and their melting points are recorded. The melting point of cyanoacetamide is also recorded, as well as that of *N*-formyldiacetamide. The carbon, hydrogen, and nitrogen content of the latter is also reported in support of its identity.

EXPERIMENTAL

The ketene used was generated by the pyrolysis of acetone using the lamp previously described.⁴ The amides were each individually placed in the gas absorption apparatus designed

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TABLE I
 KETENE ACETYLATION PRODUCTS OF AMIDES

Amide	Solvent	Catalyst	M.P., °C.		Mol. Wt.		N %		Recryst. Solvent
			Obs.	Lit.	Found	Calcd.	Found	Calcd.	
Acetamide	Ligroin	H ₂ SO ₄	79	78-79 ^a	100	101	Acetone
Acrylamide	Ether	CuSO ₄	200	12.3	12.4	Insol.
Benzamide	Benzene	H ₂ SO ₄	114	115 ^b	162	163	Ethanol
Formamide ^c	Ether + ethanol	H ₂ SO ₄	107	...	130	129	10.5	10.8	Water
Methacrylamide	Ether	None	Dec. at 300	11.1	11.0	Ether
<i>p</i> -Toluamide	Benzene	H ₂ SO ₄	145	147 ^d	179	177	Acetone-H ₂ O
Cyanoacetamide	Benzene	H ₂ SO ₄	115	...	126	126	22.0	22.2	Acetone

^a W. Hentschel, *Ber.*, **23**, 2394 (1890). ^b C. E. Colby and F. D. Dodge, *Am. Chem. J.*, **13**, 1 (1891). ^c Product isolated was diacetyl formamide. *Anal.* Calcd. for C₆H₇NO₃: C, 46.5; H, 5.42. Found: C, 47.2% and H 5.50%. ^d G. Glock, *Ber.*, **21**, 2650 (1888).

by Bolstad and Dunbar,⁵ together with a suitable solvent, and an acetylation catalyst⁸ or a polymerization⁶ inhibitor in one instance.

A typical acetylation is that of benzamide, which is described in detail. Exceptions to this procedure for other amides will be noted. A suspension of 3.6 g. (0.03 mole) benzamide and two drops of concentrated sulfuric acid in 70 ml. of benzene was agitated with a magnetic stirrer at room temperature while 0.03 mole of ketene was passed through the suspension. Care was taken to avoid any appreciable excess of ketene. The resulting product was soluble in the solvent. At the end of the run the solution was washed with 25-ml. portions of water until the washings were neutral to litmus, and the solvent was then allowed to evaporate at room temperature. The resulting product was recrystallized from a minimum amount of 95% ethanol. Yields were essentially quantitative except for mechanical loss in handling and recrystallizing the product. The molecular weights were determined by the Rast method⁷ using camphor as the solvent. The nitrogen content was determined by the micro-Kjeldahl method.⁸ Physical constants and other significant data are recorded in Table I.

Concentrated sulfuric acid proved to be a satisfactory catalyst for most of these acetylations. The unsaturated amides, however, when acetylated in the presence of sulfuric acid, formed gelatinous polymeric products. Methacrylamide was acetylated satisfactorily without any catalyst, but acrylamide had to be stabilized with copper sulfate. When acetamide was acetylated in hot ligroin it formed an oily insoluble product that was isolated with a separatory funnel, solidified at -5°, and was recrystallized from acetone. The diacetamide, contrary to most of the reaction products, was relatively stable at elevated temperatures.

Formamide was so insoluble in most inert organic solvents as to make acetylation nearly impossible even when the suspension was vigorously agitated. However, when the formamide was dissolved in an equal volume of ethanol, the resulting mixture was then found to be soluble in ether and the same could then be successfully acetylated. For this preparation 1.35 g. of formamide was, therefore, dissolved in 3 ml. of 95% ethanol and 70 ml. of anhydrous ether was then added. Ketene was then passed into the solution until two equivalents had been provided on the assumption that the ethanol would react with an equal amount of ketene. However, at the end of this period, the ketene was being ab-

sorbed so completely and readily that a third equivalent was provided. The crystalline product was isolated by permitting the solvent to evaporate at room temperature, and adding water to the remaining liquid. According to Smirnova and co-workers,³ the literature regarding acetylated amides is "erroneous and contradictory." They report that triacetyl-ammonia is a liquid at room temperature and leave the reader with the impression that this is the case with all similarly trisubstituted ammonias. It has been found, however, that treatment of formamide with excess ketene yielded a solid product with a molecular weight of 130 corresponding to the diacetyl derivative and a nitrogen content of 10.5%, also corresponding to the diacetyl derivative. Their conclusion is supported only by a nitrogen determination while this study reports not only the nitrogen percentage, but percentages of carbon and hydrogen, as well as molecular weight.

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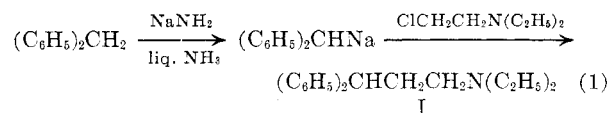
Alkylations of Alkali Diphenylmethides with β -Diethylaminoethyl Chloride and Ethylene Oxide¹

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Sodium diphenylmethide prepared from diphenylmethane and sodium amide in liquid ammonia has recently² been alkylated with alkyl halides in this medium to form hydrocarbons of the type (C₆H₅)₂CHR, where R is an alkyl group or a phenyl-substituted alkyl group.

This reagent has now been alkylated similarly with β -diethylaminoethyl chloride to form tertiary amine I in 83% yield (Equation 1).



(1) Supported by the Duke University Research Council.

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