contrast with the amine cleavages of the Hoffman and Von Braun reactions[2] in which the piperidine ring is opened.

Although some tertiary amines are cleaved by acid chlorides[3] at elevated temperatures[4] or when special favorable intramolecular conformations[5] are possible, triethyl amine was not affected by benzoyl chloride in boiling benzene. The cleavage of trialkyl amines by chloroformates may be a general reaction. However, further work is necessary to establish its limitations.

EXPERIMENTAL[6]

Stigmasteryl diethylcarbamate from diethyl amine and stigmasteryl chloroformate. Stigmasteryl chloroformate,[7] 5.0 g. (0.0105 mole) was dissolved in 100 ml. of benzene and 3 ml. of diethylamine was added. After standing a few minutes the mixture was warmed to about 50°, then allowed to stand at room temperature for 3 hr. The reaction mixture was extracted with 0.5*N* hydrochloric acid solution, and water, dried over magnesium sulfate, filtered, and concentrated to dryness, yield 5.0 g. Part of this material, 3.8 g., was dissolved in methylene chloride and filtered through a short column of Florisil. The solvent was removed from the filtrate and the residue (3.12 g.) was crystallized twice from acetone, yield 2.55 g., m.p. 146–148.5°, $[\alpha]_D$ −38° ($CHCl_3$).

Anal. Calcd. for $C_{34}H_{57}NO_2$: C, 79.78; H, 11.23. Found: C, 80.03; H, 11.09.

Stigmasteryl diethylcarbamate from stigmasteryl chloroformate and triethylamine. To a dry solution of 4.0 g. (0.0084 mole) of stigmasteryl chloroformate in 60 ml. of dry benzene was added 4 ml. of triethylamine (dried over CaH_2). After heating at reflux for 2 hr. the solution was cooled, extracted with water, dilute hydrochloric acid, and again with water, dried over magnesium sulfate, filtered, and concentrated to dryness. The residue, 3.85 g., was chromatographed through Florisil to give 3.45 g. (80% yield), m.p. 133–142° of stigmasteryl diethylcarbamate. One crystallization from acetone gave the pure carbamate identical in all respects to the material described above.

The gas produced from a similar run was collected and identified by its infrared absorption spectrum as ethyl chloride.

Ethyl diethylcarbamate.[8] A solution of 54 g. (0.5 mole) of ethyl chloroformate, 125 g. (1.25 moles) of triethylamine, and 200 ml. of dry benzene was heated at reflux for 24 hr. The gas was collected in a Dry Ice–acetone trap and identified as a mixture of carbon dioxide and ethyl chloride by infrared analysis. The ethyl chloride was purified by passing the vapors through a tube of Ascarite. The reaction solution was washed with water, dilute hydrochloric acid, and again with water, dried over magnesium sulfate, and filtered. The filtrate was distilled at atmospheric pressure until the boiling point reached about 165°. Vacuum was applied and the distillate collected was the ethyl diethylcarbamate n_D^{25} 1.4188. Infrared analysis supports the proposed structure with bands at 1692 cm.$^{-1}$, 1270 cm.$^{-1}$, and 1172 cm.$^{-1}$

Stigmasteryl piperidinylformate from stigmasteryl chloroformate and N-ethyl piperidine. This product was prepared following the second procedure described for the diethylcarbamate. From 1.0 g. (0.00211 mole) of stigmasteryl chloroformate, 1.0 g. of stigmasteryl *N*-piperidinylformate, m.p. 125–135° was obtained. It was crystallized from acetone–ethylacetate, then from isopropyl alcohol, yield 0.65 g., m.p. 137–140°, $[\alpha]_D$ −33° ($CHCl_3$).

Anal. Calcd. for $C_{35}H_{57}NO_2$: C, 80.25; H, 10.97; N, 2.67. Found: C, 80.54; H, 10.89; N, 2.69.

From N-methylpiperidine. Following the same procedure 1.0 g. of stigmasteryl chloroformate gave 1.0 g. of crude carbamate, m.p. 134–136°. One recrystallization from isopropyl alcohol gave material, m.p. 136–137°. This product is identical in all respects to the stigmasteryl piperidinylcarbamate prepared as described above.

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(6) M.p.'s were taken on a Kofler micro melting point hot stage. $[\alpha]_D$'s were determined at 22–26° at concentrations of 1–1.5 g. per 100 ml. in a 2-cm. tube.

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Nature of the So-Called Grignard Reagent Formed from *N*-Methylpyrrole[1]

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The formation of the pyrrole Grignard reagent from pyrrole and alkylmagnesium halides is well-known.[2] It might be expected that *N*-alkylpyrroles, having no—NH—group, would be inactive toward alkylmagnesium halides. However, in 1914, Hess and Wissing[3] reported the formation of 2-acyl-1-methylpyrroles on treatment of *N*-methylpyrrole with ethylmagnesium bromide and subsequent addition of an acid chloride.

Hess and Wissing[3] assumed originally that *N*-methylpyrrole formed a true Grignard reagent, as indicated in equation 1, but following a challenge

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(1) Supported in part by the Office of Ordnance Research, U. S. Army, under Contract No. DA-01-009-ORD-436.

(2) B. Oddo, *Gazz. chim. ital.*, **39**, I, 649 (1909).

(3) K. Hess and F. Wissing, *Ber.*, **47**, 1416 (1914).

by Oddo[4] they were forced to revise their conclusions. Hess observed that no ethane was evolved until the reaction mixture (which consisted of *N*-methylpyrrole, ethylmagnesium bromide, and acid halide) was decomposed with water.[5] To explain this phenomenon and the acylation which took place, Hess invoked the existence of an unstable tertiary amine-Grignard reagent complex which somehow reacts with the acid chloride only in the presence of water to form the 2-acyl-1-methylpyrrole and ethane.[5]

Our interest in pyrrole chemistry attracted our attention to the somewhat labored interpretation of this reaction.[5,6] The fact that carbonation[3,5] of the mixture of *N*-methylpyrrole and ethylmagnesium bromide does not result in the formation of *N*-methylpyrrole carboxylic acid[7] and the observation[5] that *ethane is not evolved until the mixture is decomposed with water* suggested that the reaction was not due to interaction of *N*-methylpyrrole with the Grignard reagent but that the 2-acyl-*N*-methylpyrrole was formed as the result of a Friedel-Crafts type acylation catalyzed by magnesium bromide, the latter arising out of equilibrium (2).[8]

$$2CH_3CH_2MgBr \rightleftharpoons (CH_3CH_2)_2Mg + MgBr_2 \quad (2)$$

Indeed, when a mixture of *N*-methylpyrrole and magnesium bromide in ether was treated with acetyl chloride a vigorous reaction ensued and 2-acetyl-*N*-methylpyrrole was isolated in about the same yield as when acetyl chloride was added to a mixture of *N*-methylpyrrole and ethylmagnesium bromide under the conditions of Hess and Wissing.[3] No acylation was observed when ether solutions of *N*-methylpyrrole and acetyl chloride were mixed in the absence of magnesium bromide or Grignard reagent.

It is considered that these experiments fully substantiate the hypothesis that the reaction of the so-called *N*-methylpyrrole Grignard reagent with acid chlorides is in reality an acylation of *N*-methylpyrrole catalyzed by magnesium bromide.[9]

EXPERIMENTAL

To a solution of 8 g. (0.1 mole) of *N*-methylpyrrole in 25 ml. of anhydrous ether was added 10 ml. of a solution of magnesium bromide in ether.[10] There was no evidence of a reaction. Addition of 8 g. of acetyl chloride in 20 ml. of chilled ether to the ice-cold mixture resulted in a vigorous reaction and immediate separation of a yellow precipitate. The product was decomposed with ice water and steam-distilled. The distillate was neutralized with sodium carbonate and extracted thoroughly with ether. The ether was dried and distilled giving 3.8 g. (31%) of a fraction boiling at 85–95° (22 mm.). Redistillation gave 3.2 g. of 2-acetyl-1-methylpyrrole, b.p. 88–93° (22 mm.), lit. 75–76° (15 mm.),[3] 88–91° (21 mm.).[9]

Reaction of *N*-methylpyrrole with ethylmagnesium bromide and acetyl chloride[3] gave a 25% yield of redistilled 2-acetyl-1-methylpyrrole.

A solution of 4 g. of *N*-methylpyrrole in 15 ml. of cold anhydrous ether was mixed with 4 g. of acetyl chloride in 15 ml. of cold anhydrous ether. There was no evidence of a reaction. Upon decomposition with ice water and working up in the usual manner, there was recovered 3.3 g. of *N*-methylpyrrole.

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(4) B. Oddo, *Ber.*, **47**, (1914). See also F. Runge, *Organometallverbindungen*, Wissenschaftliche Verlagsgesellschaft, Stuttgart, 1932, p. 223.

(5) K. Hess, *Ber.*, **48**, 1969 (1915).

(6) M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, Inc., N. Y., 1954, p. 80.

(7) Two of the illustrations given on p. 80 of ref. 6 (the reaction of the so-called *N*-methylpyrrole Grignard reagent with ethyl chloroformate and halogen) represent work not actually recorded in the literature.

(8) The author is indebted to Professor A. C. Cope who pointed out this possibility at a symposium "The Chemistry of High Nitrogen Compounds," sponsored by the Office of Ordnance Research, U. S. Army, and held at Duke University, March 28–29, 1956.

(9) A recent paper by H. J. Anderson, *Can. J. Chem.*, **35**, 20 (1957), has demonstrated that boron trifluoride etherate is also a useful acylating catalyst for *N*-methylpyrrole.

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Preparation of 3-Dehydroreserpic Acid Lactone and Its Conversion to Reserpic Acid Lactone

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The reaction of the yohimbine alkaloids with mercuric acetate has been summarized recently by Weisenborn[1] and Wenkert.[2] Concurrently the authors had also studied and utilized this reaction to obtain compounds of this class with a double bond in the 3:4 position. It was hoped that reduction of such dehydro derivatives would afford the naturally occurring epiallo bases. The present paper describes the results of this study.

The dehydrogenation proceeded normally by removal of two hydrogens in the case of yohimbane, yohimbine, and isoreserpine, giving good agreement with published results.[1,2] Similarly, dehydrogenation occurred with reserpine, deserpidine, reserpic acid lactone, and isoreserpic acid lactone while heating at reflux in 10% acetic acid. Contrary to the published work,[1] compounds in the epiallo series were dehydrogenated under these slightly more vigorous conditions. A possible explanation for this discrepancy can be found in the

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