TABLE III

4-METHYL-6-ALKYLTETRAHYDRO-2-PYRONES

Alkyl	B.P. (°C./mm.)	n_D	Yield, %	Analyses: Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
n-Butyl[a]	114/4	1.4517					
Isobutyl	110/5	1.4484	40	70.55	70.22	10.67	10.73
Isoamyl	89/1	1.4509	26	71.69	71.66	10.94	10.76
n-Hexyl	89/1	1.4545	50	72.68	72.90	11.18	11.05

[a] See R. H. Wiley and H. G. Ellert, *J. Am. Chem. Soc.*, **79**, 2266 (1957).

TABLE IV

INFRARED ABSORPTION MAXIMA OF 4-METHYL-6-ALKYL-2-PYRONES AND THEIR 3-BROMO AND TETRAHYDRO DERIVATIVES[a]

6-Alkyl Group	C═O Stretching	C═C Stretching		C—O Stretching Region			C—H Out of Plane Deformation
2-Pyrones:							
Methyl	1736s	1645m	1565s	1227w	1147w	1130w	846m
n-Butyl	1730s	1637m	1567s	1222w	1142w	1125w	846m
Isobutyl	1736s	1639m	1562s	1225w	1145w		842m
2′-Methylpropenyl	1730s	1642m	1536s	1228w	1179w	1159w	840m
Amyl	1730s	1634m	1567s	1218w	1140w	1124w	845w
Isoamyl	1730s	1634m	1560s	1219w	1143w	1126w	846w
Hexyl	1736s	1647m	1567s	1222w	1147w	1130w	847m
2′,6′-Dimethylheptyl	1736s	1745m	1567s	1225w	1149w	1126w	844m
3-Bromo-2-pyrones:							
Methyl	1712s	1645m	1536w	—	1185m	—	846m
n-Butyl	1730s	1639m	1531w	—	1168w	—	—
1′,2′-Dibromo-2′-methyl	1724s	1631m	1531w	—	1186w	—	836w
n-Hexyl	1718s	1637m	1529w	—	1165w	—	—
Tetrahydro-2-pyrones:							
Methyl	1733s	—	—	1235s	1181m	1138w	—
n-Butyl	1736s	—	—	1236m	1170w		
Isobutyl	1739s	—	—	1235s	1168w	1147w	—
Isoamyl	1736s	—	—	1233s	1161w	—	—
n-Hexyl	1739s	—	—	1240s	1161w	—	—

[a] In cm.$^{-1}$ s, strong; m, medium; w, weak.

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Cleavage of Trialkylamines by Chloroformates

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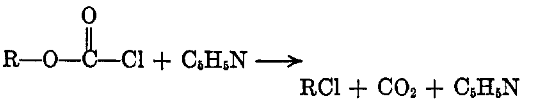
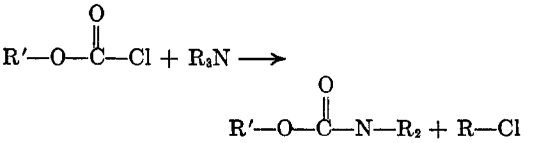
Girrard and Schild[1] have reported that chloroformates react with pyridine and quinoline to give an alkyl chloride, carbon dioxide, and the free base (Equation 1). It has been found in this laboratory that chloroformates will cleave trialkyl amines in boiling benzene to give the alkyl chloride and a carbamate (Equation 2). Both reactions take place with ethyl chloroformate and triethyl amine since carbon dioxide, ethyl chloride, and ethyl diethylcarbamate were produced. However, stigmasteryl chloroformate and triethyl amine react as in Equation 2 exclusively.



$$R—O—\overset{O}{\overset{\|}{C}}—Cl + C_6H_5N \longrightarrow RCl + CO_2 + C_5H_5N \quad (1)$$



$$R'—O—\overset{O}{\overset{\|}{C}}—Cl + R_3N \longrightarrow R'—O—\overset{O}{\overset{\|}{C}}—N—R_2 + R—Cl \quad (2)$$

Stigmasteryl chloroformate cleaved both *N*-ethyl and *N*-methyl piperidine to give stigmasteryl *N*-piperidinylformate. These reactions are in

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[1] W. Girrard and F. Schild, *Chemistry & Industry*, 1232 (1954).

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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(2) J. Schmidt and H. G. Rule, *A Text Book of Organic Chemistry*, Revised by N. Campbell, 5th Edition, Gurney and Jackson, London, 1947, p. 703.

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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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(8) J. v. Braun, *Ber.*, **36**, 2286 (1903).

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

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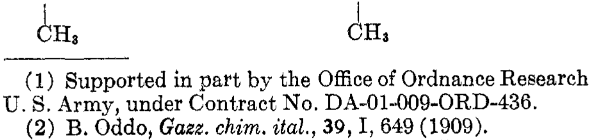
The formation of the pyrrole Grignard reagent from pyrrole and alkylmagnesium halides is well-known.[2] It might be expected that *N*-alkylpyrroles, having no—NH—group, would be inactive toward alkylmagnesium halides. However, in 1914, Hess and Wissing[3] reported the formation of 2-acyl-1-methylpyrroles 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).