tion, since water and resin are the only products. No intermediate aldehyde is formed. (b) The reaction, when carried on at a temperature at which both reactants are liquid, goes very rapidly at the start, evolving heat and is apparently about one-half complete within one minute of mixing. (c) As the reaction proceeds under isothermal conditions, the free acidity decreases, and the percentage esterification and the flow point increase. (d) The properties and appearance of the resinous products are similar except that the phenomenon of gelation possessed by the product of the glycerol–phthalic anhydride reaction is not possessed by the product of the ethylene glycol–phthalic anhydride reaction.

2. The glycol–phthalic anhydride reaction is dissimilar to the glycerol–phthalic anhydride reaction in that: (a) gelation of the resinous product does not take place at any temperature at which the reaction is carried out. The product remains fusible and soluble. (b) The reaction may be carried practically to completion, because gelation does not interfere with its normal course.

SCHENECTADY, NEW YORK

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF WASHINGTON]

SOME NEW DERIVATIVES OF DIPHENYLCARBAMINE CHLORIDE

BY THEODORE W. EVANS[1] AND WILLIAM M. DEHN

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Recently the probable –OM rather than the –NM linking in salts of cyclic imides was shown. Since the reactions of metallic sodium on aniline and acetanilide are remarkably different, it was thought that the constitution of sodium acetanilide is $C_6H_5{-}N{=}CONaCH_3$, rather than $C_6H_5{-}N{-}NaCOCH_3$. When this salt is treated with RI, etc., the R or other group is known to be linked to nitrogen; however, this linking can result from either of the two forms of the salt, from the –NNa form by direct substitution and from the –ONa form by initial addition, followed by a splitting off of sodium chloride, as indicated in the equation

$$C_6H_5N{=}CONaCH_3 + RI \longrightarrow C_6H_5NRICONaCH_3 \longrightarrow C_6H_5NRCOCH_3 + NaI$$

Since diphenylcarbamine chloride[2] reacted with many bases to yield additive compounds, it was anticipated that it would react with this salt to give some indication of addition. This was found to be the case.

When the sodium salt of acetanilide is suspended in toluene, treated with its equivalent of diphenylcarbamine chloride dissolved in toluene,

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[1] The material presented in this paper is part of a thesis submitted by Theodore W. Evans, du Pont fellow for 1929–1930, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1930.

[2] Platt and Dehn, THIS JOURNAL, 37, 2122 (1915).

and the mixture is heated gently, a clear solution is obtained.[3] Since the original salt is insoluble in toluene, this clear solution must contain a solute other than the original salt or sodium chloride, which latter is precipitated from the clear solution by boiling or by merely permitting it to stand. After filtering, etc., the acetyltriphenylurea was obtained.

Similar evidence of the formation of an intermediate additive compound was obtained with the sodium salt of acetyl-*p*-phenetidine and diphenylcarbamine chloride in toluene solution.

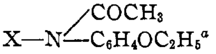
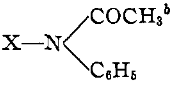
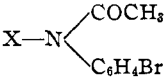
Other condensations were studied. Whereas piperidine reacts exothermically with diphenylcarbamine chloride, pyrrole could be condensed with the latter only by employing its potassium salt. The diphenylthiocarbamic esters, Ph_2NCOSR, formed from the mercaptans, constitute a new type of compound.

Experimental

The methods studied to produce condensation products were three. (A) Equivalents of the compound studied and diphenylcarbamine chloride

Table I

Derivatives of Diphenylcarbamine Chloride

Compound used	Method	Formula $X = Ph_2NCO-$	Crystd. from	Crystal form	M. p., °C.	Nitrogen Calcd.	Nitrogen Found
Na acetyl phenetidine	C	 $X—N\begin{cases}COCH_3\\C_6H_4OC_2H_5{}^{a}\end{cases}$	Alcohol	Prisms	131	7.49	7.27
Na acetanilide	C	 $X—N\begin{cases}COCH_3{}^{b}\\C_6H_5\end{cases}$	Alcohol	Prisms	144	8.48	8.38
Na *p*-Br-acetanilide	C	 $X—N\begin{cases}COCH_3\\C_6H_4Br\end{cases}$	Alcohol	Prisms	137	6.84	6.95
K pyrrole	C	$X—NC_4H_4$	Alcohol	Needles	117	10.68	10.76
Piperidine	B	$X—NC_5H_5$	Ether	Prisms	110	10.18	9.66
Sodium	B	$(X)_2$	Toluene	Prisms	187	7.14	7.41
o-Cl-aniline	B	$X—NH—C_6H_5Cl$	Toluene	Prisms	115	8.68	8.37
m-Cl-aniline	B	$X—NH—C_6H_4Cl$	Toluene	Needles	129	8.68	8.23
p-Cl-aniline	B	$X—NH—C_6H_4Cl^{c}$	Toluene	Plates	169	S	S
Na ethylmercaptan	C	$X—S—C_2H_5$	Toluene	Leaflets	108	12.46	12.07
Na benzyl mercaptan	C	$X—S—CH_2—C_6H_5$	Toluene–ether	Needles	125	10.04	9.55
Na *p*-thiocresol	C	$X—S—C_6H_4CH_3$	Toluene	Plates	180–182	10.04	9.79

[a] Calcd.: C, 73.77; H, 5.92. Found: C, 74.03; H, 6.10. [b] Calcd.: C, 76.33; H, 5.49. Found: C, 76.13; H, 5.53. [c] Calcd.: Cl, 10.99. Found: Cl, 11.38.

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[3] For a somewhat similar case involving acetoacetic ester see Michael, *Ber.*, **38**, 3217 (1905); this was claimed to be due to colloidal sodium chloride by Paal, *ibid.*, **39**, 1436 (1906). Our case seems to be essentially different from Michael's in that the sodium chloride is much more readily precipitated, and when once precipitated it does not redissolve; also, similar solutions are not obtained with metallic salts where addition should not be expected, *e. g.*, with the sodium salts of the mercaptans.

were melted together. (B) They were boiled for several hours in toluene. (C) The sodium salt of the compound to be condensed was heated with with diphenylcarbamine chloride in toluene solution. Upon filtering and evaporation of the toluene solution, the product usually crystallized out; otherwise, ether was added and the solution cooled with ice. The products were purified by recrystallization.

Diphenyl-*p*-phenetylacetylurea was prepared by method (C) and also by direct acetylation of diphenyl-*p*-phenetylurea.

Summary

1. Diphenylcarbamine chloride reacts with the sodium salt of acetanilide to give first an additive compound. This indicates that the salt possesses the enol structure.

2. A number of new derivatives of diphenylcarbamine chloride have been prepared.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF WASHINGTON]

ORGANIC OXIDATIONS BY IODIC ACID

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This acid has been used only rarely, exclusively in acid solutions and almost entirely for producing color effects.[2]

We have found that iodic acid can be applied in neutral solution, as, for example, its characteristic effect on amidol; in acid solutions, with most amines and phenols; in alkaline solutions, with mercaptans, thioureas and benzoin. Because it has no effect on alcohols, most alkaloids,[3] gluco-

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[1] The material presented in this paper is from part of a thesis submitted by Theodore W. Evans, du Pont fellow for 1929–1930, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1930.

[2] For a voluminous bibliography on the color tests for morphine, see Merck's "Reagenzien Verzeichnis," **1924**. For Strychnine, see Selmi, *Ber.*, **11**, 1692 (1902). For emetine, Peroni, *Boll. chim. farm.*, 273 (1907). The naphthols, Vincent, "Merck's Report," 1902, p. 59. Guaiacol, Guerine, *J. pharm. chim.*, 173 (1903). Adrenalin, Frankel and Allers, *Biochem. Z.*, **18**, 40 (1904); Ewins, *J. Physiol.*, No. 4, 110 (1910); Bayer, *Biochem. Z.*, **20**, 183 (1906); Krauss, *ibid.*, **22**, 131 (1908). Since iodic acid gives color tests with creatinine and uric acid [Vitali, *L'Orosi*, **21**, 73 (1898)], the following tests for components of urine by iodic acid are doubtful: glucose, Jaworowski, *Chem. Z.*, 269 (1907); *Z. anal. chem.*, **42**, 463 (1907); bile pigments, Copranica, *ibid.*, **22**, 626 (1883); acetoacetic acid, Riegler, *Pharm.-Ztg.*, **1902**, 249. Aniline was oxidized to aniline black, Ostrogovich and Silbermann, *Bul. chim. soc. Roman stiinte*, **16**, 128 (1913).

[3] Warneke, *Arch. Pharm.*, **226**, 281 (1888), oxidized wrightine to oxywrightine by iodic acid; this product by means of other oxidizing agents has been attempted in vain.