

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI]
**NEW CHLOROCARBONATES DERIVED FROM AROMATIC AND
 DIHYDROXY ALCOHOLS**

BY RALPH E. OESPER, WALTER BROKER AND WALTER A. COOK

RECEIVED JUNE 20, 1925

PUBLISHED OCTOBER 6, 1925

Phosgene forms addition compounds with certain tertiary bases, and these products react with alcohols to give chlorocarbonates. This procedure has been patented.¹ Although the patentees claim almost theoretical yields, the present writers have thoroughly tested this method on a variety of aromatic alcohols, using antipyrine, which was particularly recommended, as the base. Yields of chlorocarbonate ranging from 40 to 60% have been obtained consistently, the formation of considerable quantities of the normal carbonate being responsible for the comparatively low yield.

Chlorocarbonates are formed when a base is slowly added to a non-aqueous solution of equivalent quantities of phosgene and an alcohol. A wide variety of bases and aromatic alcohols was used in the present test of this patented procedure.² The yields invariably reach 75% or better and dialkylated anilines were found to be especially reliable. This method was found applicable to diatomic alcohols and the *bis*-chlorocar-

TABLE I
 NEW COMPOUNDS

Chlorocarbonate	B. p. °C.	% Cl		Converted into	M. p., °C.	% N	
		Calcd.	Found			Calcd.	Found
<i>o</i> -Chlorophenyl	113 (27 mm.)	37.13	36.64	Carbamate	142	8.16	8.13
<i>p</i> -Chlorophenyl	114 (20 mm.)	37.13	36.86
<i>m</i> -Nitrophenyl ^a	158 (18 mm.)	17.60	17.28
α -Naphthyl	132 (5 mm.)	17.17	17.07	Carbamate ^b	158
Ethylene (<i>bis</i>)	122 (37 mm.)	37.93	38.05	Carbamate ^c	165	18.92	19.12
Trimethylene (<i>bis</i>)	135 (41 mm.)	35.30	35.40	Carbamate	167	17.30	17.41
<i>m</i> -Phenylene (<i>bis</i>)	155 (30 mm.) m. p., 46	30.18	30.30	Carbamate ^d	194
<i>p</i> -Phenylene (<i>bis</i>)	m. p., 100	30.18	29.74	Diethyl ester ^e	100

^a *bis-m*-Nitrophenyl carbonate recovered as by-product in the form of straw-colored needles from toluene; m. p., 168.5°. Calcd. for C₁₃H₈O₇N₂: N, 9.21. Found: 8.94.

^b Gattermann, *Ann.*, **244**, 43 (1888).

^c Gattermann, *Ref. b*, p. 42, gives the melting point as 147–149°. Crystallization from various solvents gave consistently 165°.

^d *Ref. b*, p. 45.

^e Bender, *Ber.*, **13**, 697 (1880). Wallach, *Ann.*, **226**, 85 (1884).

o-Tolyl carbamate from the chlorocarbonate and ammonia. Recrystallized from alcohol; m. p., 160°. Calcd. for C₈H₉O₂N: N, 9.27. Found: 9.19.

¹ (a) Ger. pat. 117,624; 118,536; 118,537; (b) Friedländer, "Fortschritte Teerfarbenfabrikation," **6**, 1164 (1904).

² Ger. pat. 251,805; *Ref. 1 b*, 11, 82 (1915).

bonates isolated, while previous investigators found that the corresponding normal carbonates were formed when phosgene was allowed to stand in contact with ethylene glycol³ or with hydroquinone or resorcinol.⁴

Some chlorocarbonates not previously described were prepared in the course of this study and their properties are summarized in Table I. The identity of several of these was more definitely established by conversion into solid derivatives already known or by analysis of the new products.

Summary

A study has been made of the yields of chlorocarbonates derived from aromatic alcohols by two patented procedures. Chlorocarbonates not previously described have been prepared.

CINCINNATI, OHIO

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

A SEARCH IN THE DIPHENYLMETHANE SERIES FOR THE ISOMERISM CHARACTERISTIC OF CERTAIN DIPHENYL DERIVATIVES

BY C. L. BUTLER, JR.¹ WITH ROGER ADAMS

RECEIVED JUNE 26, 1925

PUBLISHED OCTOBER 6, 1925

The peculiar type of isomerism that exists in many diphenyl derivatives is most satisfactorily explained by assuming that no free rotation can occur between the two benzene rings² and that the two rings are superimposed over each other. In no other compounds in organic chemistry has such a type of isomerism been found. Since the assumption of the free rotation of atoms when attached by a single bond is the very basis of structural organic chemistry, it is somewhat disconcerting to consider the possibilities if free rotation does not take place. Even though the diphenyl isomerism seems to be specific for the single series, the reason for this specificity is not obvious. This paper describes experiments to obtain analogous isomers in the diphenylmethane series.

The peculiar isomerism of diphenyl was discovered and the Kaufler formula³ for benzidine (I) was suggested following a consideration of two important reactions of benzidine; tetrazotized benzidine reacts in such

³ Nemirowsky, *J. prakt. Chem.*, [2] **28**, 439 (1882). Vorländer, *Ann.*, **280**, 185 (1894).

⁴ Einhorn, *Ann.*, **300**, 152 (1898).

¹ This paper is an abstract of a thesis submitted by C. L. Butler, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy in chemistry at the University of Illinois.

² (a) Cain, *J. Chem. Soc.*, 101, 2298 (1912); 103, 586, 2074 (1913); 105, 1437 (1914). (b) Brady, *ibid.*, **123**, 2047 (1923). (c) Compare Turner, *Nature*, **112**, 439 (1923).

³ (a) Kaufler, *Ber.*, **40**, 3250 (1907); *Ann.*, **351**, 151 (1907). Ref. 2 a. (b) Adams, Bullock and Wilson, *THIS JOURNAL*, **45**, 521 (1923).