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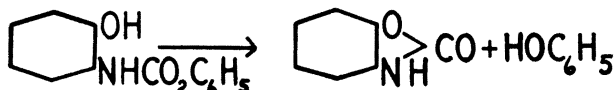
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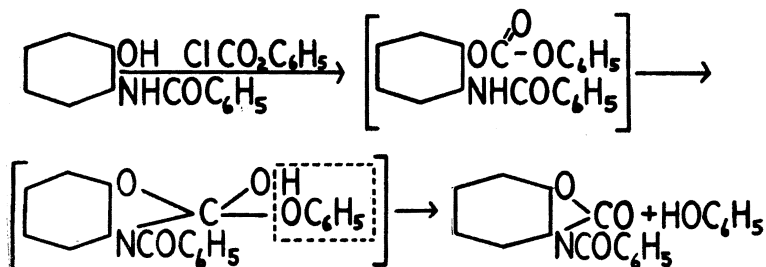
PHENYL CHLOROCARBONATE AND SUBSTITUTION PRODUCTS AS ACYLATING AGENTS

L. CHAS. RAIFORD AND J. R. DUDLEY

Hinsberg and Udranszky (1) converted 2-aminophenol into the O-benzoyl-N-benzoyl derivative by means of the Schotten-Baumann (2) reaction. Raiford and Inman (3) prepared a number of N-carboaryloxy derivatives of 2-aminophenol by following the method of Groenvik (4) who used ethyl chlorocarbonate as the only reagent. When these compounds were mixed with caustic alkali solution for the purpose of acylating them (2) they were converted into the corresponding benzoxazolones while the required phenols were



eliminated. It was further shown that warming 2-N-carboaryloxyaminophenol with pyridine and with acetic anhydride, respectively, caused ring closure, and that in the latter instance there was formed N-acetylbenzoxazolone, previously prepared in a different way by Kalckhoff (5). This tendency toward ring formation is so great that when 2-benzoylaminophenol, in caustic alkali or pyridine solution, is treated with phenyl chlorocarbonate phenol is liberated and N-benzoylbenzoxazolone is obtained in yields as high as 85%.



No diacyl derivatives of 2-aminophenol were obtained by this method.

In view of these facts it was of interest to test the behavior of aryl chlorocarbonates toward 4-aminophenol. When acylation is carried out in ether solution, using two molecular proportions of the aminophenol and one of the acyl halide, as recommended by Ransom (6), one-half the aminophenol is lost as hydrochloride, and the chief product is the N-acylaminophenol. It is to be noted, however, that this method may sometimes give a mixture of mono- and dibenzoyl derivatives (7).

Contribution from the Laboratory of Organic Chemistry at the State University of Iowa.

Proof that phenyl chlorocarbonate may be used to give good yields of relatively pure diacylated compounds of certain benzene derivatives where the functional groups involved are not in positions 1 and 2, was obtained by Raiford, Conrad and Coppock (8) who prepared the dicarbophenoxy derivatives of the isomeric phenylenediamines. La Rue (9), working in this laboratory, failed to obtain a diacyl derivative by treatment of the isomeric dihydric phenols with 4-chlorophenyl chlorocarbonate. A modification of the method she used has now made it possible to prepare the desired product from hydroquinone.

Attempts to prepare diacyl derivatives from 4-aminophenol and its substitution products by the methods previously used by Döbner (10) for hydroquinone and for p-phenylenediamine (1) gave poor results. The most suitable procedure tested in the present work was that described by Einhorn and Hollandt, (11) but even this gave low yields.

EXPERIMENTAL

Materials: 2-chloro-4-aminophenol was obtained by reduction of the required nitro compound which, in turn, was prepared as described by Kollrepp (12). The 2, 6-dichloro compound was obtained in the same way.

Phenyl chlorocarbonate and substitution products were prepared by the method briefly outlined by Oesper, Broker and Cook (13) and modified slightly by Raiford and Inman (3). These products were further characterized by conversion of them into certain ureas.

sym-Diphenylurea: Fifty grams of phenyl chlorocarbonate was added, drop by drop, to 100 g. of boiling aniline. The liquid became dark red and the mixture solidified on cooling. The solid was washed with dilute hydrochloric acid and was purified by repeated crystallization from ethanol which caused much loss of material. The yield was 29% and the product melted at 235.5°. Exkenroth (14) previously obtained this compound by heating a mixture of diphenyl carbonate and two molecular proportions of aniline for several hours in a sealed tube at 150-180°, but he recorded neither yield nor melting point. Other workers have reported values from 235 to 239°. Our product was analyzed for nitrogen.

Anal. Calc'd for $C_{13}H_{12}N_2O$: N, 13.21.

Found: N, 12.75

sym-Di-[2-chlorophenyl]-area This substance was previously obtained by different methods. Vittenet (15) boiled a mixture of diphenyl carbonate and 2 molecular proportions of 2-chloroaniline on a sand bath and obtained a compound that melted at 235-236°. No yield was recorded. Manuelli and Ricca-Rosellini (16) recorded 238° for a product prepared in 30% yield by heating a mixture of 2-chloroaniline and urethan at 200° for seven hours. In the present work 46 g. of phenyl chlorocarbonate was added, drop by drop, to 92 g. of 2-chloroaniline that had been heated to 165°. The temperature rose to 200° during the reaction, the mixture became dark red in color and

was allowed to cool and solidify. The solid was extracted with water which removed large amounts of the hydrochloride of 2-chloroaniline. Repeated crystallization of the remaining urea from ethanol gave small colorless, needles, that melted at 232°. The yield of purified material was 7%.

Anal. Calc'd for $C_{13}H_{10}Cl_2N_2O$: Cl, 25.26; N, 9.96

Found: Cl, 24.46; N, 9.96

1, 4-Di-[carbophenoxyamino]-benzene Thirty-six grams of phenyl chlorocarbonate was dropped slowly with stirring into a solution of 10 g. of p-phenylenediamine in 25 cc. of dimethylaniline, the reaction mixture was allowed to stand for two hours and was then poured into a slight excess of 5% hydrochloric acid. The solid that separated was crystallized from ethanol and was obtained in colorless plates that melted at 238.5°. The yield was 57%.

Anal. Calc'd for $C_{20}H_{16}N_2O_4$: N, 8.04

Found: N, 8.01

1, 4-Di-[carbo-4-chlorophenoxyamino]-benzene Three grams of p-phenylenediamine and 10 cc. of dimethylaniline were dissolved in 30 cc. of 1, 4-dioxane, and to this solution there was slowly added with shaking 12 g. of 4-chlorophenyl chlorocarbonate. Heat was developed and the hydrochloride of dimethylaniline separated rapidly. The mixture was heated on the steam bath for an hour and then poured into dilute hydrochloric acid. The solid that separated was crystallized from dioxane from which it separated in small colorless plates that melted at 262°. The yield was 91%.

Anal. Calc'd for $C_{20}H_{14}Cl_2N_2O_4$: Cl 17.02.

Found: Cl, 16.83

1, 4-Di-[carbo-4-chlorophenoxy]-hydroquinone Forty grams of 4-chlorophenyl chlorocarbonate was slowly added to a warm solution of 10 g. of hydroquinone and 25 cc. of dimethylaniline in 100 cc. of dioxane and the resulting red solution was heated for an hour on the steam bath. A mass of nearly colorless crystals separated during this period, the mixture was allowed to stand overnight and was then poured into 5% hydrochloric acid to precipitate the product. Crystallization from dioxane gave colorless needles that melted at 221°. A yield of 58% was obtained.

Anal. Calc'd for $C_{20}H_{12}Cl_2O_4$: Cl, 16.94.

Found: Cl, 16.83.

Acylation of aminophenols To prepare the acyl derivatives the hydrochloride of the required aminophenol was dissolved in water, though in some cases very dilute hydrochloric acid was necessary, the liquid was covered with a layer of ether, solution of ammonium carbonate was added slowly until effervescence ceased, and the mixture was extracted with ether. The extract was dried with anhydrous sodium sulfate, the solution of the aminophenol was decanted, dimethylaniline was added, then slightly more than one molecular proportion of the aryl chlorocarbonate for each radical to be acylated was slowly introduced with stirring and cooling, and the mixture was allowed to stand for two hours. Water was next added to dissolve salts, the ether solution was separated, dried, and the solvent distilled.

The residue was purified by crystallization from a suitable solvent. Analytical data and other properties for several acyl derivatives prepared as indicated are given in Table 1.

TABLE 1. Acyl Derivatives of 4-aminophenol
(1) 2-chloro-; (2) 2, 6-dichloro-

Acyl on nitrogen	Acyl on oxygen	Yield Solvent % a	Crystal Form	M. P. oC.	Formula	Analyses			
						Halogen		Nitrogen	
						Calc'd	Found	Calc'd	Found
(1) Carbo-phenoxy-	Unsubst. Acetyl-	64 Ethanol	Colorless needles	119-120	$C_{13}H_{10}ClN_3O_3$	5.31	5.45
	Acetyl-	53 Acetic acid	Colorless plates	104	$C_{15}H_{12}ClN_4O_4$	11.62	11.64
	Benzoyl-	88 Dilute dioxane	Crystalline powder	146	$C_{20}H_{14}ClN_4O_4$	9.66	9.56
	Carbo-phenoxy-	16 ^b Dilute dioxane	Fine powder	129	$C_{20}H_{14}ClN_4O_5$	9.25	9.21
(2) Carbo-phenoxy-	Unsubst.	52 Ethanol	Colorless powder	184	$C_{13}H_9Cl_2N_3O_3$	23.82	23.67
	Acetyl-	81 Ethanol	Colorless plates	132	$C_{15}H_{11}Cl_2N_4O_4$	20.88	20.79
	Benzoyl-	69 Chloroform and ligroin	Colorless powder	165	$C_{20}H_{13}Cl_2N_4O_4$	17.66	17.65

a. Figures refer to purified materials.

b. The low yield here is due to loss caused by repeated recrystallizations.

SUMMARY

Phenyl chlorocarbonate has been used to prepare a number of new O-acyl-N-acyl derivatives of 4-aminophenol and some of its halogen substitution products. The most suitable method of acylation found was that described by Einhorn and Hollandt.

COS COB,

CONN.

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