[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

MIGRATION OF THE CARBAMYL RADICAL IN 2-AMINOPHENOL DERIVATIVES

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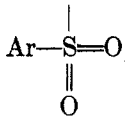
When two different acyl radicals derived from carboxylic acids are introduced into an *ortho*-aminophenol, only one mixed diacyl derivative can generally be obtained, regardless of the order of introduction of these groups; and in this product the heavier and more acidic acyl is usually found attached to nitrogen. To account for these facts, migration of acyl from nitrogen to oxygen must occur in one of these reactions (1). This rearrangement takes place most frequently during acylation, but in some instances it occurs when the diacyl derivative is partially hydrolyzed (2).

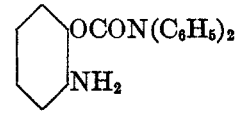
If one of the acyls is derived from a sulfonic acid and has the composition



Ar—S═O, isomeric mixed diacyl derivatives are obtained when the groups

are introduced in different orders and no rearrangement takes place (3), which shows that the migration in question depends, to some extent, on the composition and structure of the acyls. On this account, it was of much interest to test acylating agents other than those previously studied. In this report, results obtained by the use of certain derivatives of carbamic acid will be given.

Herzog (4) noted that diphenylcarbamyl chloride reacts readily with phenols to give high yields of solid derivatives that crystallize well, and hence is a suitable reagent for use in identification of such hydroxy compounds. Of particular interest is his statement concerning the behavior of this reagent with 2-aminophenol. Here he isolated a product that melted at 177°, and for which complete analysis indicated that only one position had been acylated. Without further proof he assumed that acyl was attached to oxygen and that the product had the structure shown below.



Previous to this time, Lellmann and Bonhöffer (5) reduced the 2-nitrophenyl ester of diphenylcarbamic acid, m.p., 112–114°, and obtained a compound that melted at 189–191°, which gave satisfactory analysis for carbon and hydrogen, and to which they, also, assigned the structure given above. But the previous work of Böttcher (6) and the later work of Ransom (7) proved that reduction of 2-nitrophenyl benzoate and 2-nitrophenyl ethyl carbonate gave phenolic compounds that were identified as 2-benzoylaminophenol and 2-hydroxyphenylurethane, respectively. This clearly indicates that the 2-aminophenyl-O-esters, which are the first reduction-products in such cases, are not stable, and that they readily rearrange to the isomeric N-acyl derivatives.[1] It is also interesting to note that the latter may suffer further change. Moore (8), working in this laboratory, found that reduction of the methyl, ethyl, *n*-propyl, and *n*-butyl 2-nitro-4-bromo-5-methylphenyl carbonates gave the 2-amino compounds which, under the usual laboratory conditions, promptly rearranged to the isomeric 2-hydroxyphenylurethanes as had previously

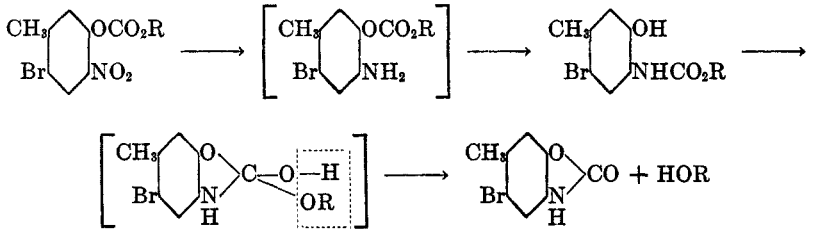
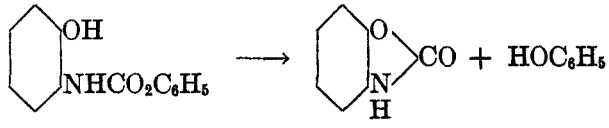


FIGURE I

been shown by Ransom for 2-nitrophenyl ethyl carbonate, and by Stieglitz and Upson (9) for the methyl ester. In addition, Moore found that under similar conditions portions of the urethanes containing the ethyl, propyl, and butyl radicals lost the elements of the related alcohols and suffered ring closure to give the corresponding benzoxazolone as shown in Figure I. The latter change is of the same type as that observed by Raiford and Inman (10), who found that when the N-carboaryloxy derivatives of *o*-aminophenol and its substitution-products are dissolved in caustic alkali solution they are converted into benzoxazolone, and a phenol is liberated. In some instances the change takes place slowly when the product is stored at room temperature (11), as indicated.



[1] Ransom (7, p. 43) found that under special conditions he was able to isolate 2-aminophenyl ethyl carbonate and to observe its rearrangement directly.

As a proof of the structure of their product, Lellmann and Bonhöffer state that when it was heated eight to ten hours at 190° it decomposed into benzoxazolone and diphenylamine. But the observations cited above show that benzoxazolone ring formation may easily occur when acyl is bound to nitrogen and the hydroxyl group is exposed, consequently the interpretations of Herzog, and of Lellmann and Bönhoffer are questioned.

To test this point, the work of the last named authors was repeated. 2-Nitrophenol was converted into the diphenylcarbamic ester, and the product was found to have the melting point 113–114°, and other physical properties reported by them. Reduction of this ester gave a compound that likewise melted at the point recorded for their supposed amino com-

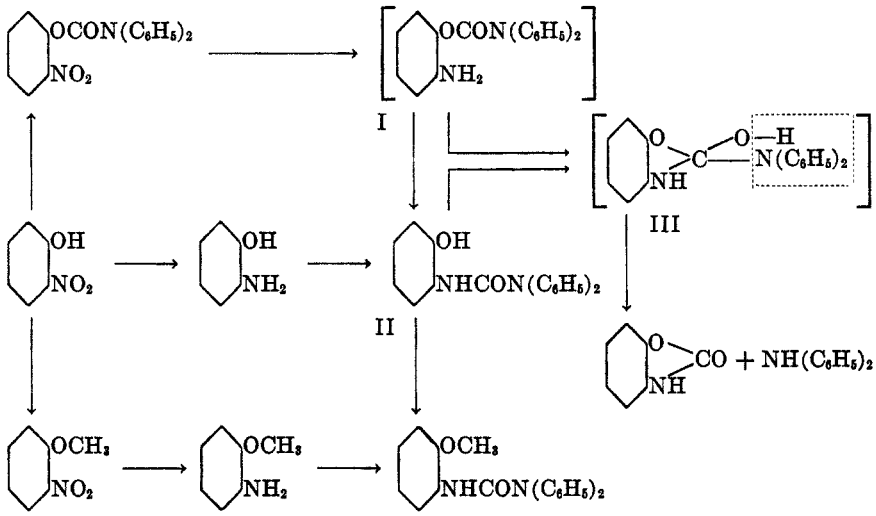


FIGURE II

pound, but whose chemical behavior was not in agreement with the structure they assigned. The substance was soluble in cold dilute solution of caustic alkali, and from this solution acids precipitated it in unchanged form, which indicates a phenol. The presence of the hydroxyl group was further indicated by the fact that the product in question was obtained by the direct action of diphenylcarbamyl chloride on 2-aminophenol, and also by the fact that treatment of it with diazomethane gave the same methyl ether as that obtained by interaction of *o*-anisidine with diphenylcarbamyl chloride, all of which supports structure II rather than I (see Figure II). In addition, the closure of the benzoxazolone ring may have taken place through the intermediate III, but it is probable that the latter could have been formed quite as readily from II as from I. Finally, when the compound melting at 190–191° was refluxed with 2 *N* alcoholic potash,

it was converted into benzoxazolone and diphenylamine, both of which were identified by mixed melting point determinations with authentic samples. Diphenylamine was obtained in nearly quantitative amount. Analogous results were obtained by the use of halogen substitution-products of 2-nitrophenol.

Diacyl derivatives containing the diphenylcarbamyl radical. In view of the facts stated above, it was of much interest to test the behavior of the diphenylcarbamyl radical in the formation of mixed diacyl derivatives of *o*-aminophenol. It was found that when a warm 1,4-dioxane solution of diphenylcarbamyl chloride was added to a warm solution of 2-acetylaminophenol (III, Figure III) in a mixture of pyridine and dioxane, a product (IV) was obtained that contained both the expected acyl radicals.

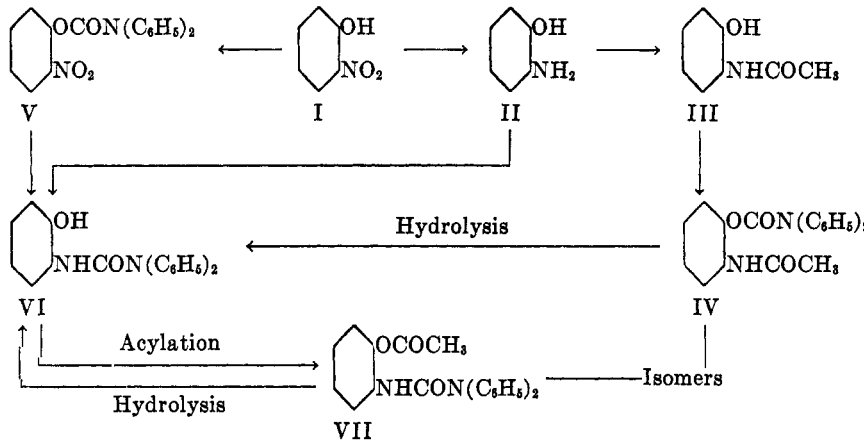


FIGURE III

Hydrolysis of this compound with alcoholic potash caused the loss of acetyl and gave an almost quantitative yield of product (VI), which had previously been obtained by the reduction of 2-nitrophenyl diphenylcarbamate, and in this case was also prepared by the direct action of diphenylcarbamyl chloride on *o*-aminophenol. During the hydrolysis of (IV) the diphenylcarbamyl radical must have migrated from oxygen to nitrogen. These relations are shown in Figure III for one pair of acyls with *o*-aminophenol. Similar results were obtained when acetyl was replaced by benzoyl, and also when the 4-bromo substitution-product of 2-aminophenol was used as the free base.

As noted above, when the 2-nitrophenyl ester of diphenylcarbamic acid was reduced, the resulting amino compound rearranged at once to the isomeric carbamylaminophenol. This made it a matter of interest to test the behavior of an ester containing an acyl of somewhat different com-

position. Accordingly, 2-nitrophenyl methylphenylcarbamate, first obtained by Lellmann and Benz (12), was prepared. When this compound was reduced by hydrochloric acid solution of stannous chloride (13), as used by Raiford and Colbert with 3-nitro-4-hydroxydiphenyl, no solid separated as it did with the diphenylcarbamic ester. With the latter, reduction was followed by rearrangement, consequently this difference in behavior suggested that in the compound in question migration of acyl may not have occurred and that the product might contain an exposed amino group as indicated by the formula used by Lellmann and Benz, who offered no proof of structure. Repetition of the experiment with a larger quantity of starting material gave the same result.

The presence of an exposed amino radical was indicated by the behavior toward nitrous acid. One portion of the solution thus obtained evolved nitrogen when it was warmed, and a second was coupled with β-naphthol to give a deep red precipitate of azo dye. To test this view further the compound in question was converted into the 4-tolylsulfonyl derivative and the product formed was compared with that obtained when 2-aminophenyl 4-tolylsulfonate was treated with methylphenylcarbamyl chloride. It was found that the resulting compounds had different melting points and that they gave different products when hydrolyzed.[2]

The failure of 2-aminophenyl methylphenylcarbamate to rearrange immediately in the reaction-mixture in which it was formed made it a matter of much interest to study the action of the related acid chloride on an *ortho*-aminophenol. In this case it was found that treatment of 2-aminophenol with one molecular proportion of methylphenylcarbamyl chloride in the presence of dimethylaniline, heating the mixture nearly to the boiling point for a few moments on the steam-bath, and then allowing it to stand overnight, gave an 84% yield of a monoacylated compound.[3] This substance was soluble in caustic alkali solution and from this liquid it was precipitated unchanged by acids. It was identified as 2-methylphenylcarbamylaminophenol. When the acylation was carried out in

[2] It had previously been shown by Raiford and Shelton, and others whose work was cited by them (3), that when the N-sulfonyl and O-sulfonyl derivatives of *ortho*-aminophenol were converted into diacylated compounds by introduction of other acyl radicals, isomers were always obtained in the cases thus far examined. Likewise, when these products were hydrolyzed the sulfonyl radical was found on nitrogen in every case in which it had been attached there in the starting material, while in those instances where it had been bound to oxygen in the starting material it was lost by hydrolysis and the other acyl was found on nitrogen. No rearrangement took place either during acylation or hydrolysis.

[3] In a previous trial in which the reaction-mixture was heated for several hours over the steam-bath about 80% of the aminophenol was converted into benzoxazolone.

the presence of pyridine instead of dimethylaniline, a mixture of 2-methylphenylcarbamylaminophenol and 2-aminophenyl methylphenylcarbam-

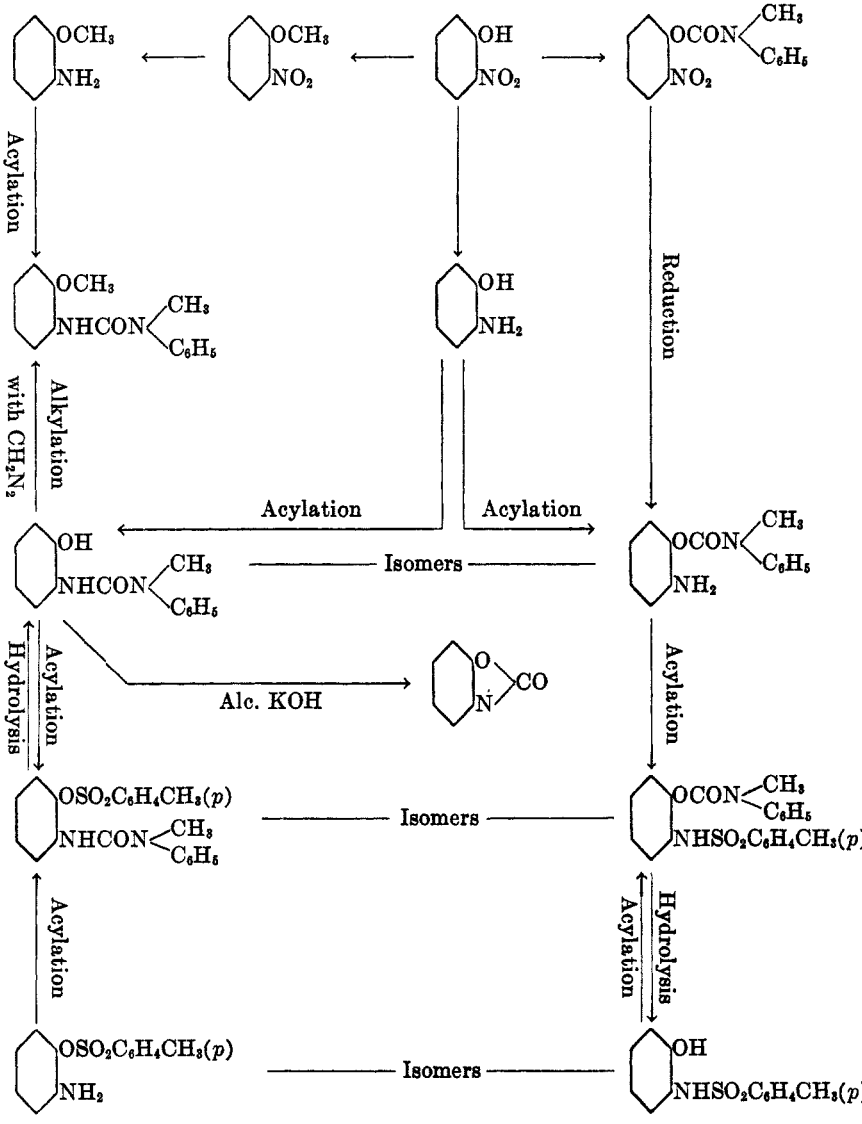


FIGURE IV

ate was obtained, in the proportions of 60% and 35%, respectively. Their relations are shown in Figure IV.

EXPERIMENTAL

The carbamyl chlorides. The diphenylcarbamyl chloride was Eastman's best grade and was used without further purification. Methylphenylcarbamyl chloride was first prepared by Michler and Zimmermann's (14) method, but a poor yield was obtained. The general procedure described by Shriner and Cox (15) was more satisfactory. Three hundred cubic centimeters of ethyl acetate was saturated with phosgene and into this warm liquid, while the gas bubbled through continuously, a solution of 153 g. of freshly distilled methylaniline in 600 cc. of ethyl acetate was introduced rather rapidly. Phosgene was allowed to run through for five minutes longer, the solvent was distilled until the contents of the flask showed a temperature of 140–150°, then the residue was allowed to cool and crystallize. Recrystallization of the pale brown material from ligroin (65–70°) gave large, nearly colorless rhombohedra that melted at 87–88°. The yield was 92%. The previous workers reported 88°, but recorded no yield.

2-Diphenylcarbamylaminophenol. Five grams of 2-nitrophenyl diphenylcarbamate[4] was reduced by stannous chloride as described by Raiford and Colbert (13), and the oil that separated when the reaction-mixture was diluted with several volumes of dilute hydrochloric acid stiffened into a plastic mass on standing. Repeated crystallization of this material from methanol gave nearly colorless needles that melted at 190–191°. This substance was found to be identical with the product obtained by the action of diphenylcarbamyl chloride on 2-aminophenol, and also with that produced by hydrolysis of 2-acetylaminophenyl diphenylcarbamate (see Figure III).

2-Diphenylcarbamylaminophenyl methyl ether. One gram of the above-described phenol was dissolved in 8 cc. of acetone, and an excess of diazomethane (16) dissolved in dry ether was added. The vessel was closed with a stopper bearing a capillary tube, it was held in an ice-bath for two and one-half hours, the solvent was evaporated, and the remaining solid was extracted with a small portion of ether to remove starting material. Crystallization of the residue from alcohol gave colorless plates that melted at 106–107° and that did not depress the melting point of the compound obtained by treatment of *o*-anisidine with diphenylcarbamyl chloride.

Anal. Calc'd for $C_{20}H_{18}N_2O_2$: N, 8.80. Found: N, 8.85.

2-Nitro-4-bromophenyl diphenylcarbamate. Ten and nine-tenths grams of the required nitrophenol was treated with diphenylcarbamyl chloride as previously noted. The yield was almost quantitative. The product was repeatedly crystallized from alcohol, from which it separated in nearly colorless needles that melted at 137–138°. Korczynski and Grzybowski (17), who previously prepared it, recorded no yield but reported 129–130° as the melting point. When exposed to bright light the product became deep purple in color.

Anal. Calc'd for $C_{19}H_{13}BrN_2O_4$: Br, 19.36. Found: Br, 19.30.

Reduction of the above compound was brought about by treatment of a hot 1,4-

[4] This was prepared in 95% yield from equimolecular proportions of *o*-nitrophenol and diphenylcarbamyl chloride by a modification of Fischer's method [*Ber.*, **53**, 1625 (1920)]. A dry chloroform solution of the acid chloride was added to a pyridine solution of the nitrophenol, the mixture was warmed on the steam-bath for a few minutes and allowed to stand for twenty-four hours. Chloroform was distilled and the residue was poured into dilute hydrochloric acid. Repeated crystallization of the product from alcohol gave nearly colorless needles that melted at 113–114°, and agreed in properties with the compound isolated by Lellmann and Bonhöffer (5).

dioxane solution of it with a hydrochloric acid solution of stannous chloride as indicated above. After the rearranged product, 2-diphenylcarbamylamino-4-bromophenol, had been removed, the purple filtrate was diluted with water until precipitation was complete. The solid obtained, which represented about one-third of the reduction-product, was highly colored and obviously impure. Crystallization from benzene, which involved considerable loss, gave fine, nearly colorless needles that melted at 216–218°, and which did not depress the melting point of an authentic sample of 4-bromobenzoxazolone, m.p. 215° (18).

2-Diphenylcarbamylamino-4-bromophenyl methyl ether. Three-tenths gram of the above N-acyl derivative was dissolved in a few cc. of chloroform in a test tube and treated with diazomethane. Recrystallization of the product from carbon tetrachloride gave brownish rhombohedra that melted at 155–156°. This compound did not depress the melting point of the product, m.p. 155–156°, especially prepared for this comparison by the action of diphenylcarbamyl chloride on 2-amino-4-bromophenyl methyl ether.

Anal. Calc'd for $C_{20}H_{17}BrN_2O_2$: Br, 20.15. Found: Br, 20.14.

The analytical data and other properties for a number of *o*-aminophenol derivatives containing the diphenylcarbamyl radical are given in Table I.

2-Nitrophenyl methylphenylcarbamate. A pyridine solution of 23.4 g. of 2-nitrophenol was treated with a chloroform solution of 30 g. of methylphenylcarbamyl chloride, and the reaction-mixture was worked up as previously noted. Crystallization of the product from alcohol gave slightly yellowish needles that melted at 111–112°. The yield of purified material was 95%. Lellmann and Benz (12), who first prepared this compound from the potassium salt of the nitrophenol, reported the melting point 110°, but recorded no yield. Reduction of this compound with a hydrochloric acid solution of stannous chloride gave 2-aminophenyl methylphenylcarbamate, m.p. 105–106°, which was identified as indicated above. The previous authors recorded 103° but gave no proof of structure.

Action of methylphenylcarbamyl chloride on 2-aminophenol. To a warm solution of 10.9 g. of 2-aminophenol and 25 cc. of dimethylaniline in 20 cc. of 1,4-dioxane was added 17 g. of the acid chloride in 90 cc. of dioxane, the mixture was warmed nearly to the boiling point for a few minutes, and then set aside. A viscous, oily phase separated. The mixture was shaken vigorously at frequent intervals for about two hours, and allowed to stand overnight. Considerable solid was formed in this way. The mixture was then poured into about 600 cc. of dilute hydrochloric acid, the whole was shaken well, and the solid collected. Crystallization from alcohol gave nearly colorless needles that melted at 171–172°, and which were identified as 2-methylphenylcarbamylaminophenol (Table II).

Methylphenylcarbamylaminophenyl methyl ether. One gram of the product just described, in acetone solution, was treated with an excess of ether solution of diazomethane. The product was dissolved in ether, the liquid was shaken with 5% solution of sodium hydroxide, then with water. Evaporation of ether from the remaining liquid gave nearly colorless transparent crystals that melted at 77–78°. They did not depress the melting point of the product, m.p. 77–78°, obtained by action of methylphenylcarbamyl chloride on *o*-anisidine.

Anal. Calc'd for $C_{15}H_{16}N_2O_2$: N, 10.93. Found: N, 10.77.

Acylation of 2-aminophenol with methylphenylcarbamylchloride in the presence of pyridine. Ten and nine-tenths grams of 2-aminophenol was dissolved by warming in 20 cc. of pyridine. Seventeen grams of the acid chloride was dissolved in about 30 cc. of pyridine, but very soon crystals of pyridine-acyl-halide complex began to separate and in a few minutes the mixture had set to a solid mass of crystals. These

TABLE I

DIACYL DERIVATIVES OF *ortho*-AMINOPHENOLS

(a) 2-Aminophenol; (b) 2-amino-4-bromophenol

POSITION OF ACYL	YIELD %[a]	SOLVENT	CRYSTAL FORM	M.P., °C.	FORMULA	ANALYSES			
						Halogen		Nitrogen	
						Calc'd	Found	Calc'd	Found
(a)									
N-acetyl-O-diphenylcarbamyl	95	Alcohol	Pale brown prisms	150–153[b]	$C_{21}H_{18}N_2O_3$			8.09	8.07
N-diphenylcarbamyl-O-acetyl	82	Alcohol	Nearly colorless granules	119–121	$C_{21}H_{18}N_2O_3$			8.09	8.20
N-diphenylcarbamyl-O-diphenylcarbamyl	60	Benzene-ligroin[c]	Colorless needles	184–185	$C_{32}H_{25}N_3O_3$			8.41	8.21
N-diphenylcarbamyl[d]	76	Methanol	Colorless needles	190–191	$C_{19}H_{16}N_2O_2$			9.21	9.09
N-benzoyl-O-diphenylcarbamyl	98	Alcohol	Colorless prisms	153–154	$C_{26}H_{20}N_2O_3$			6.86	7.07
N-diphenylcarbamyl-O-benzoyl	76	Chloroform and alcohol[e]	Colorless cubes	210–212	$C_{26}H_{20}N_2O_3$			6.86	6.87
(b)									
N-acetyl-O-diphenylcarbamyl	80	Benzene	Colorless needles	176–178	$C_{21}H_{17}BrN_2O_3$	18.82	18.75		

N-diphenylcarbamyl-O-acetyl	70	Alcohol	Colorless hexagonal plates	117–118	$C_{21}H_{17}BrN_2O_3$	18.82	18.90		
N-diphenylcarbamyl[h]	40	Methanol-ethanol[f]	Colorless needles	199[g]	$C_{19}H_{15}BrN_2O_2$	20.88	20.87		
N-diphenylcarbamyl-O-diphenylcarbamyl	64	Ethanol-butanol	Colorless needles	198[g]	$C_{32}H_{24}BrN_3O_3$	13.84	13.85		

[a] These values represent purified materials.

[b] Though this product softened at 145° and melted over a range of three degrees, analysis for nitrogen indicated that it was nearly pure.

[c] The hot saturated benzene solution was diluted with an equal volume of ligroin and allowed to cool.

[d] Monoacyl derivative; this product was also obtained by slowly adding a dioxane solution of diphenylcarbamyl chloride and dimethylaniline to a hot dioxane solution of 2-aminophenol with stirring and continued heating on a steam-bath. The product was proved to be identical with that obtained by reduction of 2-nitrophenyl diphenylcarbamate, previously prepared by Lellmann and Bonhöffer (5) and erroneously reported by them to be 2-aminophenyl diphenylcarbamate.

[e] Hot chloroform solution was slowly diluted under reflux with several volumes of alcohol.

[f] The purple-colored filtrate was diluted with water until no more solid separated, the mixture was stirred well, allowed to settle and the solid collected and dried. Crystallization from benzene gave nearly colorless needles that melted at 216–218°, and which did not depress the melting point of 4-bromobenzoxazolone, m.p., 215°, obtained by Raiford and Inman (18).

[g] A mixture of these showed a melting range of 169–180°.

[h] Monoacyl derivative.

TABLE II

DIACYL DERIVATIVES OF *o*-AMINOPHENOL CONTAINING THE METHYLPHENYLCARBAMYL RADICAL

POSITION OF ACYL	YIELD %[a]	SOLVENT	CRYSTAL FORM	M.P., °C.	FORMULA	ANALYSES			
						Sulfur		Nitrogen	
						Calc'd	Found	Calc'd	Found
N-(4-Tolylsulfonyl)-O-methylphenylcarbamyl[b]	89	Alcohol (75%)	Nearly colorless granules	125–126	$C_{21}H_{20}N_2O_4S$	8.08	8.22		
N-Methylphenylcarbamyl-O-(4-tolylsulfonyl)	80	Alcohol	Pale brown masses	111–112	$C_{21}H_{20}N_2O_4S$			7.07	7.07
2-Aminophenyl methylphenylcarbamate	41	Alcohol	Pale brown needles	105–106	$C_{14}H_{14}N_2O_2$			11.57	11.60
2-Methylphenylcarbamylaminophenol[d]	53	Alcohol	Nearly colorless needles	171–172[c]	$C_{14}H_{14}N_2O_2$			11.57	11.60

[a] These values refer to purified materials.

[b] Hydrolysis of this product with alcoholic potash gave an 88% yield of an alkali-soluble product that melted at 138–139°, and which did not depress the melting point of 2-(4-tolylsulfonylamino) phenol previously obtained by Bell (*J. Chem. Soc.*, **1930**, 1984) and specially prepared for this comparison.

[c] This value was obtained by rapid heating. Melting occurred at 150° in six minutes, and at 135° in thirty minutes.

[d] Monoacyl derivative.

were disintegrated with a rod, 20 cc. of dioxane was added, the resulting suspension was mixed with the aminophenol solution, the whole was warmed over the steam-bath until solution occurred, and it was then set aside for twenty-four hours. When the mixture was poured into 350 cc. of water containing an excess of hydrochloric acid a reddish solid separated. The yield was 60%. Crystallization of this product from alcohol[5] gave nearly colorless needles of m.p. 171–172°, which were identical with 2-methylphenylcarbamylaminophenol described above.

When the filtrate left after removal of the above product was made alkaline with sodium hydroxide, a brownish colored solid precipitated in a yield of 35%. Repeated crystallization of this from alcohol gave pale brown needles of m.p. 105–106°, which were identified as 2-aminophenyl methylphenylcarbamate, previously obtained by reduction of the corresponding nitro compound. Analytical data and other properties for a number of derivatives containing the methylphenylcarbamyl radical and prepared by standard methods are given in Table II.

SUMMARY

Reduction of 2-nitrophenyl diphenylcarbamate and its substitution-products caused migration of the diphenylcarbamyl radical from oxygen to nitrogen to give the corresponding 2-carbamylaminophenol. The structures of these compounds were established by preparing them by the direct action of the acid chloride on the required 2-aminophenols, and also by showing that the methyl ethers prepared by the action of diazomethane on the carbamylaminophenols were identical with the products obtained by treatment of the related anisidines with the required carbamyl chloride.

In the reduction of the related 2-nitrophenyl methylphenylcarbamate, the *o*-aminophenyl derivative was obtained. This product was also prepared by treatment of 2-aminophenol with methylphenylcarbamyl chloride, but in this reaction the isomeric 2-methylphenylcarbamylaminophenol was also formed.

Partial hydrolysis of a mixed diacyl derivative containing either of these carbamyl radicals attached to oxygen, and another acyl of composition R(Ph)CO bound to nitrogen, caused loss of the latter acyl and migration of the former to nitrogen. As in many other examples, the heavier acyl was ultimately found on nitrogen. When the second acyl had the composition $Ar—\overset{|}{\underset{\|}{S}}(=O)=O$ no migration was observed.

2-Methylphenylcarbamylaminophenol and 2-diphenylcarbamylaminophenol are readily decomposed by alcoholic potash to give benzoxazolone.

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[5] In subsequent experiments it was found that this product may be more conveniently purified to nearly as high a degree by repeated treatment of its caustic alkali solution with an acid.

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