the cyclic carbonate at 1812–1840 cm^{-1} on a Perkin-Elmer Model 137 spectrophotometer at selected time intervals at room temperature.

The data were plotted and the half-life of the reaction was determined. Assuming second-order kinetics, the reaction rate was calculated for several different concentrations according to the formula $t_{1/2} = 1/kc_0$ where c_0 = initial concentration. In Table III, no corrections were made for change in the amine–alcohol equilibrium with temperature.

Solvent Effects on Reaction of I with Benzyl Alcohol–Triethylamine Complex.—To 20 ml of the solvent was added 0.432 g of benzyl alcohol. The infrared spectrum of this solution was recorded from 3000 to 4000 cm^{-1}. The position of the absorbance peak for the alcohol is shown in Table IV. This solution was treated with 1.00 ml of triethylamine and warmed to 70° in a constant temperature oil bath. Then 0.292 g of I was added and the reaction was monitored by measuring the carbonyl absorbance for the cyclic carbonate at selected time intervals against the solvent blank on the Perkin-Elmer Model 137 spectrophotometer. The half-life for each reaction is given in Table IV.

Reaction of I with α-Toluenethiol (Benzyl Mercaptan).—To 15 ml of xylene at 100° was added 0.292 g of I. After dissolution, 1.0 ml of triethylamine was added, followed by the addition of 4.0 ml of a solution composed of 2.5 ml of α-toluenethiol and 18.5 ml of xylene. The reaction mixture was then placed in an oil bath at 100° and the reaction monitored by removing portions and recording the absorbance at 2000–1570 cm^{-1}.

Reaction of I with Benzylamine.—To a solution of 0.292 g of I in 20 ml of xylene at 100° was added 0.428 g of benzylamine. The reaction mixture was kept at 100° in an oil bath and the reaction monitored by recording the absorbance at 2000–1570 cm^{-1}.

Registry No.—I, 14419-73-9; benzyl alcohol, 100-51-6; α-toluenethiol, 100-53-8; benzylamine, 100-46-9.

Acknowledgment.—We are grateful to Dr. W. F. Kwolek, USDA Biometrical Services and stationed in Peoria, for his assistance for mathematical interpretation of the data.

Rearrangements of O and N Acyl and Alkoxycarbonyl Derivatives of *o*-Aminophenol

LAWRENCE H. AMUNDSEN* AND CESARE AMBROSIO[1]

Department of Chemistry, The University of Connecticut, Storrs, Connecticut 06268

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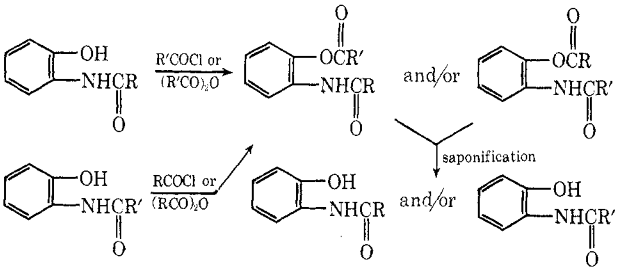
The preparation of several acyl–alkoxycarbonyl O,N derivatives of *o*-aminophenol by both orders of introduction of groups has produced only one isomer, the *N*-alkoxycarbonyl-*O*-acyl derivative, a rearrangement occurring in one of the preparations. Saponification of these derivatives is shown definitely to proceed without rearrangement. Isomeric bisalkoxycarbonyl derivatives were obtained, dependent upon the order of introduction of groups, a result contrary to most previously reported experience with compounds of this type. Furthermore, saponification of these derivatives gave no rearrangements. A mechanism is presented in an attempt to explain these data and most of the data previously reported.

Rearrangements occurring during preparation and saponification of O,N-disubstituted derivatives of *o*-aminophenol are well known (Scheme I). The extensive work involving these diacyl derivatives published by Raiford and coworkers[2] has indicated that, when two different acyl groups are introduced into an *o*-aminophenol, the same diacyl derivative usually is obtained regardless of the order of introduction. Other workers, however, have isolated isomeric pairs of diacyl derivatives.[3,4]

SCHEME I



R and R′ = alkyl or alkoxy group

Studies by Ransom[5] and by Nelson and coworkers[3,4] of derivatives containing an acyl and an alkoxycarbonyl group have shown that only one isomer results, regardless of the order of introduction of groups. Saponification of each of these derivatives has, with one exception,[6] always produced the urethane. These workers, therefore, assumed that the O,N-disubstituted compounds were *N*-alkoxycarbonyl-*O*-acyl derivatives and not the isomeric *N*-acyl-*O*-alkoxycarbonyl derivatives. This proof of structure has, however, become questionable because of the demonstration of LeRosen and Smith[7,8] in an analogous case involving acyl groups that there is a tendency to rearrange during saponification which is exactly the reverse of the tendency to rearrange during the preparation and purification of such compounds. If this is true of the partial rearrangements that they observed, it is at least possible that in the preparations of acyl–alkoxycarbonyl derivatives studied by Nelson and coworkers a complete (or nearly complete) rearrangement may have occurred during the preparation of the compounds, and a reverse rearrangement during saponification, which would have caused wrong structures to be assigned to the disubstituted products.

The theoretical considerations developed by LeRosen and Smith also can be shown to cast doubt upon the assigned structures. Their "principal of minimum charge concentration" would predict that the more stable isomer should be the one that has the more electron-releasing group on the carbonyl group that is attached

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[1] Abstracted in part from the Ph.D. Thesis of C. Ambrosio, The University of Connecticut, 1965.

[2] (a) L. C. Raiford, *J. Amer. Chem. Soc.*, **41**, 2068 (1919); (b) L. C. Raiford and J. R. Couture, *ibid.*, **46**, 2305 (1924); **44**, 1792 (1922); (c) L. C. Raiford and H. P. Lankelma, *ibid.*, **47**, 1111 (1925).

[3] C. B. Pollard and R. E. Nelson, *ibid.*, **53**, 996 (1931), and references cited therein.

[4] R. E. Nelson and H. S. Rothrock, *ibid.*, **51**, 2761 (1929), and references cited therein.

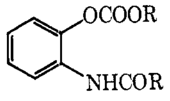
[5] J. H. Ransom, *Ber.*, **31**, 1055 (1898).

[6] R. E. Nelson, N. W. Shock, and W. H. Sowers, *J. Amer. Chem. Soc.*, **49**, 3129 (1927).

[7] A. L. LeRosen and E. D. Smith, *ibid.*, **70**, 2705 (1948).

[8] A. L. LeRosen and E. D. Smith, *ibid.*, **71**, 2815 (1949).

to oxygen and the less electron-releasing group on the carbonyl group that is attached to nitrogen. The +T effect being greater for an alkoxy group than for an alkyl group, **1** should, according to this theory, be more stable than **2**, which is the structure that was assigned to these compounds by saponification. Thus the work of LeRosen and Smith gives double reason for believing that the structures assigned to these compounds might be wrong. The present study was undertaken to check this possibility by determining the structures of the disubstituted products by some means other than hydrolysis.



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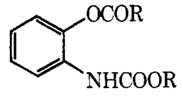


2

Nelson and coworkers[6,9] also investigated disubstituted derivatives containing two different alkoxycarbonyl groups. Usually only one compound was obtained regardless of the order of introduction of the groups. Because structures were assigned to these compounds in accordance with the products that they gave upon hydrolysis, these structures too are not necessarily reliable and also need to be reinvestigated. Although Nelson and coworkers usually reported that identical products were formed, such was not the case with the pair of groups: *n*-butoxycarbonyl and isobutoxycarbonyl. Relatively little rearrangement was indicated in this instance. Since it seems peculiar that this pair should give uniquely different results from the other closely analogous pairs studied, we selected it first for reinvestigation. Their results were largely confirmed: we find no evidence of *any* rearrangement, the two products seeming to be homogeneous and different. On the chance that the formation of isomeric products might be a more general phenomenon in this series than their results indicate, we checked another similar pair not used by them: *n*-butoxycarbonyl and *n*-pentoxycarbonyl. Here, too, isomeric products seem clearly to be formed.

We are led to suspect that Nelson's group may have been mistaken about the identity of some of their pairs of products. The paper[6] in which the products that happened to be solids are described contains almost no experimental details. The other paper[9] in which liquid products are reported gives enough detail to yield a hint of what may have happened. These compounds were distilled under vacuum at about 200°, and it was presumably on such distilled products that the hydrolyses were run. Somewhat analogous compounds containing acyl groups rather than alkoxycarbonyl groups have been shown[7] to be rearranged by heating to temperatures considerably lower than this.

LeRosen and Smith proposed that these rearrangements "are not true migrations occurring during the preparation of the mixed diacyl derivatives, but are rather isomerizations of the normally expected product caused by a catalytic effect of the reaction media used." Milder conditions, therefore, might also in other instances than the ones reported above yield the hitherto unobtainable isomer. In this connection, it is noteworthy that this has not proven to be possible, even when we used quite mild conditions in the preparation of the acylalkoxycarbonyl mixed derivatives.

LeRosen and Smith believed that these rearrangements involved general acid–base catalysis and they proposed a mechanism for the rearrangement in alcohol, the commonly used recrystallization solvent. We feel, however, that their mechanism cannot be entirely correct because it postulates no involvement of the amido hydrogen atom (a point discussed later).

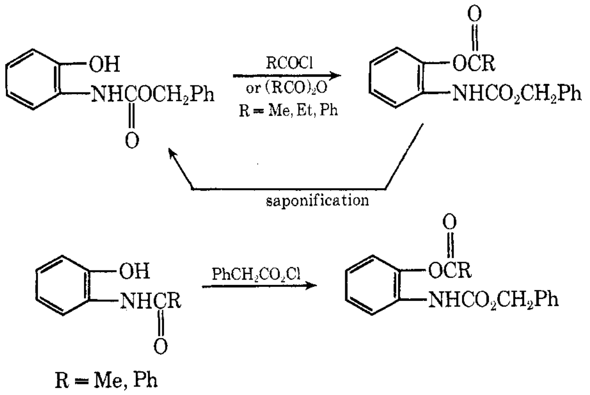
These rearrangements do not occur in a meta or a para aminophenol[10,11] nor do they occur when one of the amino hydrogen atoms is replaced with a methyl group.[12,13] This latter fact, which may possibly have been overlooked by LeRosen and Smith, is particularly important in any mechanistic considerations.

The purpose of this paper is to report our results from the preparation and saponification of some acyl–alkoxycarbonyl derivatives and bisalkoxycarbonyl derivatives of *o*-aminophenol and to present our mechanistic interpretation of the rearrangements involved. The mixed acyl–alkoxycarbonyls seemed to us particularly worthy of study because they are the type that has most consistently given rearrangements during preparation.

Results and Discussion

The reaction of several acid chlorides or anhydrides with benzyl *o*-hydroxycarbanilate produced only one disubstituted product in each case, the *N*-benzyloxycarbonyl-*O*-acyl derivative. Since determination of these structures by hydrolysis might not be reliable, they were established by infrared spectroscopy. Attempts to prepare two *N*-acyl-*O*-benzyloxycarbonyl derivatives resulted in isolation of only the rearranged *N*-benzyloxycarbonyl-*O*-acyl isomers. This result agrees with all previously published data, but it is significant that rearrangement occurred even under the relatively mild experimental conditions that we used. There seems to be an overwhelming tendency for rearrangement to occur when an alkyl chloroformate reacts with an *o*-acylaminophenol.

Saponification of these derivatives produced only the urethane, benzyl *o*-hydroxycarbanilate. Thus no rearrangement occurs in the saponification step, the structure of the disubstituted compounds being known with certainty before saponification because of the infrared spectroscopy.



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[9] R. E. Nelson and W. C. Aitkenhead, *J. Amer. Chem. Soc.*, **48**, 1680 (1926).

[10] L. C. Raiford and H. A. Iddles, *ibid.*, **45**, 469 (1923).

[11] F. Bell, *J. Chem. Soc.*, 2966 (1931).

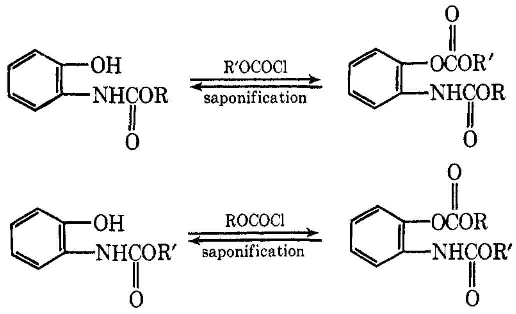
[12] J. H. Ranson, *Amer. Chem. J.*, **23**, 1 (1900).

[13] L. C. Raiford and C. D. Inman, *J. Amer. Chem. Soc.*, **56**, 1586 (1934).

LeRosen and Smith postulated on theoretical grounds that, when rearrangement occurs in the preparation of a diacyl derivative, a reverse arrangement should occur upon saponification, and they presented experimental evidence to show that this did indeed take place with the acetyl–benzoyl derivatives. We have conclusively established, nevertheless, that the acyl–alkoxycarbonyl derivatives formed in this study by rearrangement do not undergo a reverse rearrangement when saponified. This is quite likely true of all acyl–alkoxycarbonyl substitution products of *o*-aminophenol, and, if so, all structures assigned by previous workers, based as they were upon the saponification products, are in fact correct. Although the fact that these products yield only alkyl *o*-hydroxycarbanilates upon saponification is well established,[3,4] we did perform a few experiments to verify this fact. In all cases, melting points, infrared spectroscopy, and thin layer chromatography showed the products to be alkyl *o*-hydroxycarbanilates free of any detectable quantity of acylamidophenols. These measurements were made directly upon the hydrolysis products as precipitated by acid from the alkaline saponifying solutions; so it is unlikely that any significant quantity of the other possible product could have been formed without being detected. The previously published data on these acyl–alkoxycarbonyl compounds do not show conclusively that the hydrolysis products reported were the only ones formed. Yields are not given and, what is more important, it is not stated whether the melting points and mixture melting points used to establish the identity of the hydrolysis products were taken on the crude products as precipitated by acid from the saponifying solutions or were taken on products that had been purified by crystallization. The latter appears more likely, and thus one could not really rule out the possibility that both possible hydrolysis products had been formed, but we found no indication in melting points, mixture melting points, infrared spectra, or thin layer chromatograms that the possible *o*-acylaminophenol was present in any of our crude products as precipitated.

It seemed desirable also to check the reported results when two alkoxycarbonyl groups are used. Our results have failed to confirm the previous reports[6,9,14] that only one *o*-(*N*-alkoxycarbonylamino)phenyl alkyl carbonate is obtained regardless of which of the two groups is initially substituted onto the amino group. Indeed it appears that reversing the order of introducing the groups gives an entirely different product if mild conditions are used (in anhydrous ether–pyridine at room temperature); each of the two products upon saponification yields the particular N-substituted *o*-aminophenol from which it was prepared. The lack of identity of the O,N-disubstituted compounds was deduced primarily from this difference in saponification products; no interpretable differences were noted in the infrared spectra and behavior in the thin layer chromatography seemed to be identical.

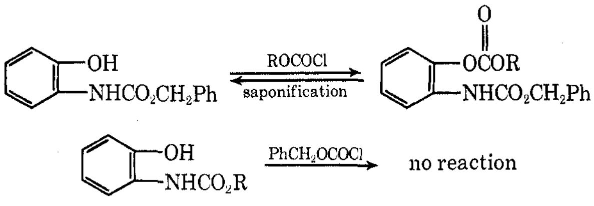
Because we have found it impossible to distinguish by infrared spectroscopy an *o*-(*N*-alkoxycarbonylamino)phenyl alkyl carbonate from its isomer in which the two different alkyl groups are interchanged, we have had to rely for assignment of structure upon the method of preparation, which would seem to be reliable in cases such as these where the two orders of introduction of the groups give clearly different products. If the two products are solids, their nonidentity is, of course, readily determinable. This is not so clear if the products are liquids, but here the fact that the two give different hydrolysis products that are relatively pure as precipitated by acid is quite conclusive.



R and R′ = *n*-Bu and *i*-Bu in one case
R and R′ = *n*-Bu and *n*-C_5H_{11} in the second case

The reaction of several alkyl chloroformates with benzyl *o*-hydroxycarbanilate produced only one *O*,*N*-bisalkoxycarbonyl derivative in each case. Saponification of each derivative produced the starting urethane, benzyl *o*-hydroxycarbanilate. This suggests that each derivative is the *N*-benzyloxycarbonyl-*O*-alkoxycarbonyl isomer.

Attempts to prepare the isomeric *N*-alkoxycarbonyl-*O*-benzyloxycarbonyl derivatives failed, the starting urethan being recovered in each case. This was not studied further and no satisfactory explanation for this lack of reactivity can be given.



R = Et, *i*-Bu, *n*-Bu

In proposing a mechanism for the rearrangement of O,N-disubstituted derivatives of *o*-aminophenol, the following factors must be considered.

(1) The amido hydrogen atom must have some role in the rearrangement, since *N*-methyl derivatives do not suffer rearrangements.

(2) Attempted preparation of certain diacyl derivatives results in the formation of an equilibrium mixture of diacyl isomers.

(3) Attempted preparation of acylalkoxycarbonyl derivatives by both orders of introduction of groups always gives the urethanecarboxylate ester as the only product.

(4) Attempted preparation of bisalkoxycarbonyl compounds can result in complete, partial, or no rearrangement. Apparently, the experimental conditions are important and can alter the course of the reaction.

(5) Since most of the preparations reported by earlier workers involved aqueous basic conditions, it seems probable that the basicity of the medium is an important factor.

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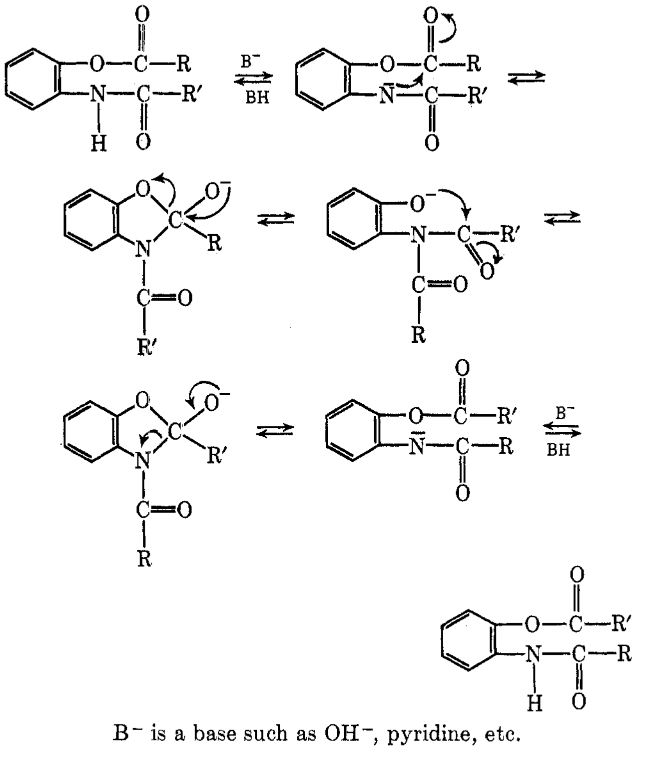
[14] J. H. Ransom and R. E. Nelson, *J. Amer. Chem. Soc.*, **36**, 390 (1914).

In Scheme II is a proposed mechanism which shows the abstraction of the amido proton. This mechanism explains the formation of an equilibrium mixture of diacyl products. Apparently a urethanecarboxylate is more thermodynamically stable than the isomeric amide carbonate, but just why this should be so is not clear. The LeRosen and Smith theory would, as we have said, seem to have predicted the reverse.

Scheme II



B^- is a base such as OH^-, pyridine, etc.

Experimental Section

The purification of *o*-aminophenol and the preparation of the following compounds have been reported:[15] benzyl *o*-hydroxycarbanilate, isobutyl *o*-hydroxycarbanilate, *o*-benzamidophenol, *o*-acetamidophenol, *o*-propionamidophenol, benzyl *o*-benzoyloxycarbanilate, benzyl *o*-acetoxycarbanilate, benzyl *o*-propionyloxycarbanilate, and *N*-benzyloxycarbonyl-*o*-aminophenyl isobutyl carbonate. All reagents were of the highest purity available commercially and were used without further purification. Infrared absorption spectra were taken on a Perkin-Elmer Model 137B Infracord. Solids were placed in the instrument as potassium bromide disks while liquids were neat. A magnetic stirrer was used in all reactions requiring constant stirring.

Alkyl *o*-Hydroxycarbanilates.—A procedure previously described for both benzyl and isobutyl *o*-hydroxycarbanilate was followed.[15]

A. *n*-Butyl *o*-Hydroxycarbanilate.—The crude product, mp 84–87°, was obtained in 43% yield. It was recrystallized from hexane–benzene, mp 86–88° (lit.[16] mp 89°).

B. Ethyl *o*-Hydroxycarbanilate.—The crude product, mp 83–87°, was obtained in 44% yield. It was recrystallized several times from dilute ethanol, mp 88–90° (lit.[16] mp 89.5°).

C. *n*-Pentyl *o*-Hydroxycarbanilate.—The crude product, mp 65–68°, was obtained in 72% yield. Two recrystallizations from pentane gave an analytical sample, mp 70–71°.

Anal. Calcd for $C_{12}H_{17}NO_3$: C, 64.57; H, 7.62. Found: C, 64.86, 65.05; H, 7.63, 7.49.

Attempted Preparation of *o*-Benzamidophenyl Benzyl Carbonate. Rearrangement to Benzyl *o*-Benzoyloxycarbanilate.—*o*-Benzamidophenol (2.1 g, 0.01 mol) was placed in a 250-ml, two-neck, round-bottom flask equipped with a drying tube and a dropping funnel. Anhydrous ether (150 ml) and 1 ml of pyridine were added, followed by the dropwise addition of a solution of 2 ml of benzyl chloroformate in 20 ml of ether, with constant stirring for 1 hr. Upon filtration of the pyridine hydrochloride and evaporation of the ether, a brown-purple semisolid resulted. A small sample was taken up in boiling hexane and upon cooling a light purple-white solid, mp 105–107.5°, 0.6 g, was obtained. An infrared spectrum was identical with that of benzyl *o*-benzoyloxycarbanilate[15] (mp 108–109°). The remainder of the crude product was dissolved in 95% ethanol and poured over crushed ice. A brown-white solid was obtained, mp 103–107°, 2.3 g.

Attempted Preparation of *o*-Acetamidophenyl Benzyl Carbonate. Rearrangement to Benzyl *o*-Acetoxycarbanilate.—A procedure identical with the one in the preceding paragraph was followed. *o*-Acetamidophenol, the starting material in this preparation, is considerably less soluble in ether; so it was used as a suspension instead of being completely dissolved. The presumed pyridine hydrochloride in this case was only partially soluble in water, and the insoluble portion (1 g) was identified as unreacted *o*-acetamidophenol. The ether solution was evaporated and a red-brown oil was obtained which was taken up in hexane and cooled. Pink-white crystals precipitated, mp 90–96°, 0.750 g (76% corrected for recovered *o*-acetamidophenol). One recrystallization from hexane gave a white solid, mp 94–96°. An infrared spectrum was identical with that of benzyl *o*-acetoxycarbanilate[15] (mp 95–96°).

Saponification of Benzyl *o*-Benzoyloxycarbanilate.—The ester (1.7364 g, 0.005 mol), which was insensitive to treatment with dilute aqueous base, was saponified by stirring mechanically at room temperature with 30 ml of 6 *N* alcoholic potassium hydroxide until all of the sample was dissolved. The resulting solution was acidified with 6 *N* hydrochloric acid. The precipitate was collected, washed, and dried, mp (without further purification) 113–116°, no depression when mixed with an authentic sample of benzyl *o*-hydroxycarbanilate, mp 116–117°. (The other possible hydrolysis product, *o*-benzamidophenol, melts at 167–168°). The yield was 1.0758 g (88.6%). That the hydrolysis product is a substantially pure sample of benzyl *o*-hydroxycarbanilate is attested to also by the fact that its infrared spectrum matches closely that of the purified authentic sample and by the complete absence of any spot corresponding to *o*-benzamidophenol on the thin layer chromatogram.

Two analogous compounds, benzyl *o*-acetoxycarbanilate and benzyl *o*-propionyloxycarbanilate, were saponified similarly except that 10 *N* aqueous sodium hydroxide was used, which caused complete hydrolysis at room temperature in about 1 hr. Again, only the benzyl *o*-hydroxycarbanilate was obtained, and the products seemed likewise to be free of *o*-acetamidophenol (mp 203–205°) and *o*-propionamidophenol (mp 78°), respectively.

***o*-(*N*-Benzyloxycarbonylamino)phenyl Ethyl Carbonate.**—Benzyl *o*-hydroxycarbanilate (1.2 g, 0.005 mol) was placed in a 100-ml, round-bottom flask equipped with a drying tube. Anhydrous ether (50 ml) and 0.5 ml of pyridine were added, followed by the addition of 0.7 ml of ethyl chloroformate with constant stirring. From time to time thin layer chromatograms were prepared (Silica Gel G; Merck, Darmstadt, Germany) and eluted with 1:1 ether–pentane. Both starting materials were present and also another substance with a higher R_f value (presumably the desired product). After 3 days, the starting urethane was absent. Upon filtration of the pyridine hydrochloride and evaporation of the ether, a pale yellow oil resulted which was taken up in pentane and cooled overnight. Fluffy white crystals precipitated, mp 50–55°, 1.5 g (94%). An infrared spectrum showed two strong, sharp carbonyl peaks, one at 1725 cm^{-1} (urethane) and one at 1750 cm^{-1} (carbonate). Five recrystallizations from pentane gave an analytically pure sample in the form of long, fluffy, white needles, mp 54–55°.

Anal. Calcd for $C_{17}H_{17}NO_5$: C, 64.75; H, 5.43. Found: C, 64.89, 65.04; H, 5.36, 5.24.

***o*-(*N*-Benzyloxycarbonylamino)phenyl *n*-Butyl Carbonate.**—The procedure followed was identical with the preceding one. Thin layer chromatograms were essentially the same as those described above, the reaction being complete after 3 days. After work-up, fluffy white needles were obtained, mp 53–55°, 1.6 g (94%). An infrared spectrum was identical with that of the ethyl carbonate described above. Five recrystallizations from pentane gave an analytical sample, mp 55–56°.

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[16] P. Chalrier, H. Najer, and R. Giudicelli, *Bull. Soc. Chim. Fr.*, 1353 (1955).

[15] L. H. Amundsen and C. Ambrosio, *J. Org. Chem.*, **31**, 731 (1966).

Anal. Calcd for $C_{19}H_{21}NO_5$: C, 66.46; H, 6.12. Found: C, 66.39, 66.24; H, 6.14, 6.08.

Saponification of *o*-*N*-Benzyloxycarbonylamino)phenyl Alkyl Carbonates.—Each *o*-(*N*-benzyloxycarbonylamino)phenyl alkyl carbonate (ethyl, *n*-butyl, isobutyl[15]) was treated with 10 *N* potassium hydroxide for about 2 hr. The basic solutions were then shaken with ether, separated, and acidified with concentrated hydrochloric acid. A white precipitate formed in each case, mp 114–116°. An infrared spectrum and a mixture melting point showed each to be benzyl *o*-hydroxycarbanilate.

Attempted Preparation of Alkyl *o*-Aminophenyl Benzyl Carbonates.—Benzyl, ethyl, *n*-butyl, and isobutyl *o*-hydroxycarbanilate were treated with benzyl chloroformate and pyridine in anhydrous ether as described in previous procedures. In each case the starting urethane was recovered, a thin layer chromatogram indicating that no reaction had occurred.

***o*-(*N*-*n*-Butoxycarbonylamino)phenyl Isobutyl Carbonate.**—A procedure identical with that for the benzyl *o*-aminophenyl alkyl carbonates, previously described, was followed. *n*-Butyl *o*-hydroxycarbanilate (1.0 g, 0.005 mol), 0.6 ml of pyridine, and 1 ml of isobutyl chloroformate were used. After the mixture was stirred overnight, a thin layer chromatogram showed the presence of product and the absence of starting urethane. After filtration of the pyridine hydrochloride and evaporation of the ether, a pale yellow liquid resulted which was taken up in pentane and cooled to −10 to −20°. Yellow-white crystals precipitated overnight which quickly melted at room temperature but slowly in a cold room (5°). The solid was quickly filtered in a cold room, yield 1.2 g (80%). The infrared spectrum was essentially identical with the spectra of the benzyl *o*-aminophenyl alkyl carbonates previously described, 1750 (carbonate) and 1725 cm^{-1} (urethane). For analysis a sample was distilled at an estimated 10^{-5} mm of mercury in a Kugelrohr.

Anal. Calcd for $C_{16}H_{23}NO_5$: C, 62.12; H, 7.49. Found: C, 61.94, 62.18; H, 7.49, 7.67.

***o*-(*N*-Isobutoxycarbonylamino)phenyl *n*-Butyl Carbonate.**—A procedure identical with the preceding one was followed (1 g of *n*-butyl *o*-hydroxycarbanilate and 1 ml of isobutyl chloroformate). After the usual work-up, a pale yellow liquid was obtained which would not crystallize. The infrared spectrum was identical with that of the isomeric *o*-(*N*-*n*-butoxycarbonylamino)phenyl isobutyl carbonate. The product weighed 1.4 g (93%). For analysis, a sample was distilled in a Kugelrohr. Saponification (described below) showed that this product and the product from the preceding reaction were not identical.

Anal. Calcd for $C_{16}H_{23}NO_5$: C, 62.12; H, 7.49. Found: C, 62.00, 62.27; H, 7.45, 7.68.

***o*-(*N*-*n*-Pentoxycarbonylamino)phenyl *n*-Butyl Carbonate.**—The procedure was the same as those previously described. *n*-Pentyl *o*-hydroxycarbanilate (1.1 g, 0.005 mol) and 0.9 ml of *n*-butyl chloroformate were used. After 3 days, a chromatogram showed the presence of one product and the absence of starting urethane. A pale yellow liquid was obtained, 1.6 g (100%). The infrared spectrum was identical with that of the other bisalkoxycarbonyl compounds previously described. For analysis a sample was distilled in a Kugelrohr.

Anal. Calcd for $C_{17}H_{25}NO_5$: C, 63.14; H, 7.79. Found: C, 63.23, 63.45; H, 7.71, 7.96.

***o*-(*N*-*n*-Butoxycarbonylamino)phenyl *n*-Pentyl Carbonate.**—The procedure followed was the same as those previously described. *n*-Butyl *o*-hydroxycarbanilate (1.0 g, 0.005 mol) and 0.9 ml of *n*-pentyl chloroformate were used. After 3 days, a thin layer chromatogram showed the presence of one product and no starting urethane. White silky needles, which melted at room temperature, were obtained in a cold room. The solid was recrystallized from pentane and dried over phosphorus pentoxide in the cold room, yield 1.8 g (81%), mp 24.5–26.2°. The infrared spectrum was identical with that of the other bisalkoxycarbonyl derivatives previously described. For analysis a sample was distilled in a Kugelrohr. Again, saponification showed this compound not to be identical with its presumed isomer.

Anal. Calcd for $C_{17}H_{25}NO_5$: C, 63.14; H, 7.79. Found: C, 62.62, 62.49; H, 7.36, 7.24.

Saponification of Bisalkoxycarbonyl Derivatives.—The saponifications were accomplished by dissolving the sample in ether and shaking the solution vigorously with an equal volume of 10 *N* potassium hydroxide. The basic layer was separated and acidified with concentrated hydrochloric acid to precipitate the product. The infrared spectra of the products were all essentially identical, each having the characteristic urethane carbonyl peak at 1725 cm^{-1}.

A. ***o*-(*N*-Isobutoxycarbonylamino)phenyl *n*-Butyl Carbonate.**—A light brown solid was obtained, mp 81–84°. One recrystallization from hexane gave white crystals, mp 84–85.5°. A mixture melting point showed this compound to be isobutyl *o*-hydroxycarbanilate (mp 86°[9]).

B. ***o*-(*N*-*n*-Butoxycarbonylamino)phenyl Isobutyl Carbonate.**—A light brown solid was obtained, mp 84–87°. One recrystallization from hexane gave white crystals, mp 87–88°. A mixture melting point showed the compound to be *n*-butyl *o*-hydroxycarbanilate (mp 89°[16]).

C. ***o*-(*N*-*n*-Pentoxycarbonylamino)phenyl *n*-Butyl Carbonate.**—A brown-white solid was obtained, mp 68–70°. A mixture melting point showed the compound to be *n*-pentyl *o*-hydroxycarbanilate (mp 70–71°).

D. ***o*-(*N*-*n*-Butoxycarbonylamino)phenyl *n*-Pentyl Carbonate.**—A light brown solid was obtained, mp 85–87°. A mixture melting point showed the compound to be *n*-butyl *o*-hydroxycarbanilate (mp 89°[16]).

Registry No.—*n*-Pentyl *o*-hydroxycarbanilate, 31020-08-3; benzyl *o*-benzoyloxycarbanilate, 5211-51-8; benzyl *o*-acetoxycarbanilate, 5211-52-9; *o*-(*N*-benzyloxycarbonylamino)phenyl ethyl carbonate, 31020-10-7; *o*-(*N*-benzyloxycarbonylamino)phenyl *n*-butyl carbonate, 31020-11-8; *o*-(*N*-benzyloxycarbonylamino)phenyl isobutyl carbonate, 5211-54-1; *o*-(*N*-*n*-butoxycarbonylamino)phenyl isobutyl carbonate, 31020-13-0; *o*-(*N*-isobutoxycarbonylamino)phenyl *n*-butyl carbonate, 31020-14-1; *o*-(*N*-*n*-pentoxycarbonylamino)phenyl *n*-butyl carbonate, 31020-15-2; *o*-(*N*-*n*-butoxycarbonylamino)phenyl *n*-pentyl carbonate, 31020-16-3.

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