[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

# Thermal Degradation of Alkyl N-Phenylcarbamates

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Ethyl carbanilate yielded chiefly phenyl isocyanate and alcohol when heated at 200° under reduced pressure. At 250° and atmospheric pressure α-methylbenzyl carbanilate gave major amounts of aniline, α-methylbenzyl aniline, styrene and carbon dioxide. Kinetic and chemical data supported an initial intramolecular decomposition followed by amine displacement reactions. Under the same conditions benzyl carbanilate yielded chiefly aniline, benzylaniline, dibenzylaniline and carbon dioxide. Kinetic studies confirmed the probable importance of attack by amines at the α-carbon of the alcoholic constituent of the carbamate.

Few detailed studies have been made of the products resulting from purely thermal degradation of carbamates. It is well known that the N-monosubstituted carbamates decompose on heating to give the isocyanate and alcohol to some extent[2,3] at high temperatures the carbamate appears to be in equilibrium with the isocyanate and alcohol. A few such carbamates have yielded additional products.[4,5] The purpose of the present work was to make a study of the nature, amounts and mechanism of formation of the products from heating alkyl N-phenylcarbamates of the formula $C_6H_5NHCOOR$, where R is $C_2H_5$, $CH(CH_3)C_6H_5$ and $CH_2C_6H_5$.

## Results and Discussion

**Ethyl Carbanilate.**—The thermal degradation of ethyl carbanilate was originally studied by Métayer,[2] who concluded that this ester appears to distil unchanged because the dissociation products, phenyl isocyanate and alcohol, readily recombine. The present work confirmed Métayer's observation that at atmospheric pressure the distillate consisted largely of the carbanilate. Minor amounts of carbon dioxide and of diphenylurea were formed. Prolonged heating at 230–260° increased the carbon dioxide somewhat and gave triphenyl isocyanurate. Only by conducting the degradation at about 200° and under reduced pressure, sufficiently low to vaporize the alcohol but high enough to retain the isocyanate, was it possible to separate these products. Under these conditions (Table I), there was isolated over 90 mole % of the theoretical alcohol and 60–75 mole % of the isocyanate (based on the carbanilate degraded). Thus the equilibrium of reaction 1 was continuously shifted to the right.

$$C_6H_5NHCOOR \rightleftarrows C_6H_5NCO + ROH \qquad (1)$$

**α-Methylbenzyl Carbanilate.**—The literature states[3a,4] that carbamate esters of secondary and tertiary alcohols may decompose according to equation 2 if the alcohol has a β-hydrogen. The products have been clearly described, however, only in the case of N-benzyl cholesteryl carbamate.[4]

$$C_6H_5NHCOOCH(CH_3)R \longrightarrow C_6H_5NH_2 + CO_2 + RCH{=}CH_2 \qquad (2)$$

Hence, a study was made of the thermal degradation of α-methylbenzyl carbanilate. After this ester was degraded at 230–260° (bath 270–304°) to an average of 92% completion (based on the combined yields of the carbonyl constituents, carbon dioxide and 1,3-diphenylurea), the mean quantities of isolated products were 85% carbon dioxide, 40% styrene, 35% aniline, 24% α-methylbenzylaniline, 7% diphenylurea and 3% α-methylbenzyl alcohol (Table II). The formation of large amounts of carbon dioxide, olefin and amines is in strong contrast to the results from ethyl carbanilate and indicates that reactions giving the products of equation 2 must be prominent in the case of α-methylbenzyl carbanilate.

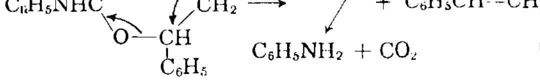
The secondary amine, α-methylbenzylaniline could arise from reaction 3a and the diphenylurea could come from phenyl isocyanate and aniline by reaction 4.

$$C_6H_5NHCOOCH(CH_3)C_6H_5 \longrightarrow C_6H_5NHCH(CH_3)C_6H_5 + CO_2 \qquad (3a)$$

$$C_6H_5NCO + C_6H_5NH_2 \rightleftarrows (C_6H_5NH)_2CO \qquad (4)$$

The small amount of α-methylbenzyl alcohol produced indicates that reaction 1 occurred to a certain extent. There is evidence that reaction 1 which is the source of phenyl isocyanate, may have been more important in the earlier than in the later stages of the degradation. When the degradation was carried to only 30% completion, as in run 1 of Table II, the observed yield of diphenylurea was 70 times as great as that from run 2, where the degradation was almost complete[6] (as shown by 96% carbon dioxide evolution).

Reaction 2 may be expected to proceed by an intramolecular cyclic mechanism, as suggested for the thermal degradation of many esters[7–9] including chloesteryl carbamate.[4] To find out



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whether the degradation of olefin-forming carbamates takes place by such an intramolecular path, kinetic studies were made on ethyl carbazole-9-carboxylate, a carbamate known[5] to give a single set of products

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[1] From the Ph.D. thesis (1958) of George C. Wright, Armstrong Cork Co. Research Fellow, 1955–1957.

[2] M. Métayer, *Bull. soc. chim. France*, 802 (1951).

[3] (a) O. Bayer, *Angew. Chem.*, **A59**, 257 (1947); (b) S. Petersen, *Ann.*, **562**, 205 (1949).

[4] A. F. McKay and G. R. Vavasour, *Can. J. Chem.*, **31**, 688 (1953).

[5] M. A. Fletcher, M. W. Lakin and S. G. P. Plant, *J. Chem. Soc.*, 3898 (1953).

[6] Although total recovery of products was poor at 180–220° (run 2 of Table II), the yields of carbon dioxide and diphenylurea are believed to be reliable.

[7] C. D. Hurd and F. H. Blunck, THIS JOURNAL, **60**, 2419 (1938).

[8] G. L. O'Connor and H. R. Nace, *ibid.*, **74**, 5454 (1952).

[9] A. T. Blades, *Can. J. Chem.*, **32**, 366 (1954).

TABLE I

PRODUCTS FROM ETHYL CARBANILATE

| Time, min. | Bath temp., °C. | Press., mm. | Products, mole % EC[a] used[b] EtOH | PhNCO | $CO_2$ | Other | EC recov. | Total recov.[c] |
|---|---|---|---|---|---|---|---|---|
| 331[d] | 190–230 | 760 | | | 3.9 | 2.3[e] | 30 | 36 |
| 45 | 294–305 | 760 | | | 1.8 | 3.1[e] | 79 | 85 |
| 212 | 284–293[i] | 760 | 23 | | 6.9 | 13[f] | | |
| 375 | 187–198 | 62–120 | 92[h] | 60[h] | | | 56 | 87 |
| 187 | 190–215 | 100 | 91[h] | 72[h] | | 2.7[g] | 56 | 90 |
| 220 | 191–196 | 81 | 92[h] | 75[h] | | | 70 | 96 |

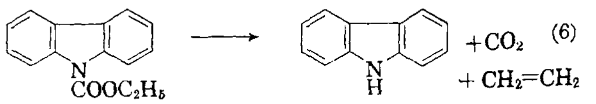
[a] Ethyl carbanilate. [b] Sample 6–10 g. [c] % by weight. [d] Preceded by 66 min. from 70–190°. [e] Diphenylurea. [f] Triphenyl isocyanurate. [g] Ethyl α,γ-diphenylallophanate. [h] Mole % of EC degraded. [i] Temp. of reactn. mixture, 230–260°.

TABLE II

YIELDS OF PRODUCTS[a] FROM α-METHYLBENZYL CARBANILATE (MBC)

| MBC used, g. | Bath temp., °C. | Time, min. | $CO_2$ | Styrene | Aniline | α-Me-benzyl-aniline | Di-phenyl-urea | α-Me benzyl alc. | Total recov., wt. % |
|---|---|---|---|---|---|---|---|---|---|
| 8.72[b] | 190–198 | 420 | | | 28 | | 35 | | 88 |
| 1.14 | 180–220 | 445 | 96 | | 16 | | 0.5 | | 24 |
| 23.1[c] | 290–304 | 45 | | 24 | 31 | | 19 | 15 | 55 |
| 7.29 | 295–304 | 44 | | 41 | 48 | 10 | 3.0 | | 47 |
| 18.0 | 292–300 | 180 | | 45 | 38 | 20 | 8.2 | 4.7 | 74 |
| 20.0 | 290–300 | 180 | | 42 | 34 | 24 | 8.8 | 3.1 | 75 |
| 19.1 | 290–300 | 180 | 75 | 40 | 35 | 28 | 7.1 | 1.3 | 74 |
| 19.6 | 290–300 | 180 | 81 | 33 | 26 | 22 | 4.8 | 1.2 | 62 |
| 6.0 | 270–290[d] | 1081 | 99 | | | | 0.6 | | |
| Mean values[e] at 300°: | | | 85 ± 9 | 40[f] ± 3 | 35 ± 5 | 24[g] ± 2 | 7 ± 4 | 3[f] ± 1 | |

[a] Mole % of MBC degraded. [b] MBC recov., 6.11 g., shows 30% degraded. [c] MBC recov., 3.8 g.; 84% degraded. [d] Temp. of react. mixture 230–260°. [e] Excluding Runs 1 and 2. [f] Excluding run 3. [g] Excluding run 4.



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By measuring the rate of evolution of carbon dioxide at 293–318°, it was shown that the decomposition of ethyl carbazole-9-carboxylate followed first-order kinetics to at least 50% completion (Fig. 1). From three determinations at 293° the average rate constant was (18.6 ± 0.4) $10^{-4}$ $\text{min.}^{-1}$ and the order of the reaction 0.9 ± 0.1. The activation energy, determined from reactions carried on at 271, 293 and 318°, was 31.6 kcal. per mole. An approximate entropy of activation at 271° was calculated to be −16 e.u. These data are similar to results obtained from the degradation of other olefin-forming compounds, including xanthates,[8] alkyl acetates[9] and alkyl vinyl ethers.[10] In all cases the reactions were unimolecular, the activation energies were of the same order of magnitude and the entropies of activation were negative. These facts support the probability that ethyl carbazole-9-carboxylate undergoes decomposition by the same path as the other esters, and that a cyclic transition state is involved. Such a four-center decomposition[11] is also in accord with the fact that neither benzoic acid nor N,N,dibenzylaniline catalyzed the rate of degradation of ethyl carbazole-9-carboxylate.

When the kinetics of the decomposition of α-methylbenzyl carbanilate were measured at 185° by carbon dioxide evolution, the reaction was found to be first order to approximately 10% and then the rate increased markedly. It is reasonable to suppose that the initial decomposition (reaction 2) proceeds by an intramoledular path, by analogy to the ethyl carbazole-9-carboxylate, but that then a product of the reaction reacts further with the carbanilate. It is proposed that aniline, produced in reaction 2, attacks the carbanilate by a nucleophilic displacement on carbon, giving α-methylbenzylaniline as is shown beyond in equation 3b. Thus the secondary amine would be produced chiefly by 3b rather than 3a. Reaction 3b is

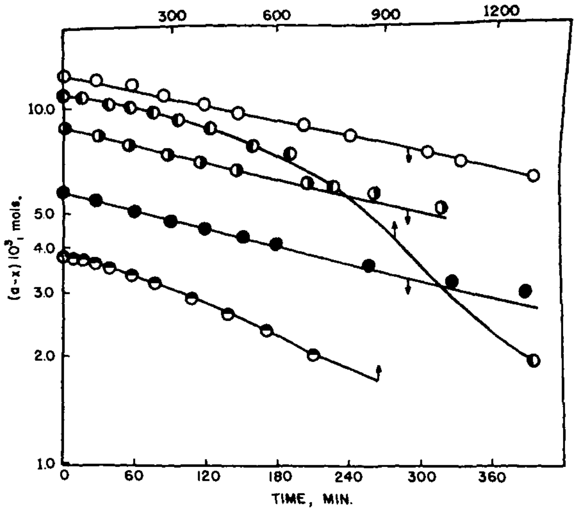

Fig. 1.—First-order plots of the degradation of ethyl carbazole-9-carboxylate; $a$, initial moles of carbamate; $x$, moles $CO_2$: ○, 293°, $a = 0.0122$; ◑, 294°, $a = 0.00876$; ●, 293°, $a = 0.00578$. First-order plots of the degradation of α-methylbenzyl carbanilate at 185°: ◐, $a = 0.0108$; ⊖, $a = 0.00382$.

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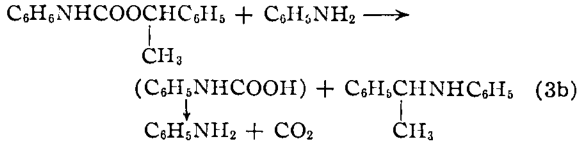
(10) A. T. Blades, *J. Chem. Soc.*, **31**, 418 (1953).

(11) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 453.



$$C_6H_6NHCOOCH(CH_3)C_6H_5 + C_6H_5NH_2 \longrightarrow (C_6H_5NHCOOH) + C_6H_5CH(CH_3)NHC_6H_5 \quad (3b)$$
$$(C_6H_5NHCOOH) \downarrow C_6H_5NH_2 + CO_2$$

analogous to the reported[5] decarboxylation of carbazole-9-carboxylate with α-naphthylamine, giving a 95% yield of carbazole.

To test the correctness of reaction 3b, α-methylbenzyl carbanilate was heated at 214–237° with excess *p*-toluidine. The isolated products were 31 mole % of α-methylbenzyl-*p*-toluidine, 56 mole % carbon dioxide, 51 mole % aniline, 37 mole % *sym*-di-*p*-tolylurea, 9 mole % α-methylbenzyl alcohol and 1% N-phenyl-N′-*p*-tolylurea. The formation of significant quantities of α-methylbenzyl-*p*-toluidine, together with carbon dioxide and aniline, is strong evidence that the amine displacement reaction 3b is reasonable.

The relatively high yield of *sym*-di-*p*-tolylurea rather than of N-phenyl-N′-*p*-tolylurea may be explained by combination of phenyl isocyanate (from reaction 1) with *p*-toluidine to give N-phenyl-N′-*p*-tolylurea, which could dissociate[12] to form *p*-tolyl isocyanate. Reaction of the latter substance with *p*-toluidine would yield the *sym*-di-*p*-tolylurea.

Further confirmation of the correctness of reaction 3b was obtained by heating α-methylbenzyl carbanilate with excess aniline (with bath at 290–300°), when the products contained a larger amount of α-methylbenzylaniline (31 mole %) than from the degradation of the carbamate alone (24 mole %, Table II). Other products from this degradation in the presence of excess aniline were 46 mole % carbon dioxide, 46 mole % *sym*-diphenylurea and α-methylbenzyl alcohol (shown by qualitative test); 79% of the aniline added was recovered.

Thus the evidence supports reactions 1, 2, 3b and 4 as routes for the formation of the observed degradation products of α-methylbenzyl carbanilate. A series of other tests was done to throw light on alternative paths to these products. The possibility of reaction of aniline with styrene to form α-methylbenzylaniline was investigated by heating the two reactants for 8 hours under degradation temperatures. The secondary amine was not produced. The formation of styrene by thermal degradation of α-methylbenzyl alcohol alone was tried by refluxing the alcohol for 44 minutes using a bath at 295–305°. No styrene resulted. The formation of diphenylurea did not occur when the α-methylbenzyl carbanilate was heated with a 100% excess of aniline for 90 min. at 162–165°. The possibility of this aminolysis reaction at higher temperatures is not excluded, however.

**Benzyl Carbanilate**—The thermal degradation of benzyl carbanilate was studied by Mukaiyama and co-workers,[13,14] who used a temperature of 160° and primary amines as solvents. It was concluded that the carbamate initially dissociated into the isocyanate and the alcohol in a rate-determining step and that the isocyanate and amine rapidly formed the stable urea.

In the current work benzyl carbanilate was studied at higher temperatures. At approximately 250° the degradation products consisted of 93% carbon dioxide, 34% aniline, 25% benzylaniline, 21% dibenzylaniline and 1.5% diphenylurea. At 300° the distribution of products was similar (Table III). The formation of both secondary and tertiary amines is notable. The products are analogous to those resulting from methyl carbanilate,[15] which gave carbon dioxide, aniline, methylaniline and dimethylaniline at 260° in the presence of calcium oxide.

TABLE III

PRODUCTS[a] FROM BENZYL CARBANILATE

| BC,[b] g. | Bath temp., °C. | Time, hr. | $CO_2$ | Aniline | Benzylaniline | Dibenzylaniline | Diphenylurea |
|---|---|---|---|---|---|---|---|
| 50.6 | 285–300 | 10.0 | 94 | 29 | 31 | 15 | 1.4[c] |
| 47.0 | 245–255 | 30.3 | 93 | 34 | 25 | 21 | 1.5[d] |
| 40.2 | 245–260 | 7.3 | 30 | | | 5.3 | 15 |
| 7.6[e] | 250–253 | 26.4 | 95[f] | 39 | 97[h] | 17 | 0 |
| 7.6[g] | 245–254 | 24.0 | 89[f] | 81 | 63[h] | 23 | 0 |

[a] Mole % of BC sample. [b] Benzyl carbanilate. [c] Also 0.1 mole % benzyl alcohol. [d] Recovery of carbonyl, nitrogenous and alcoholic constituents was 94, 83 and 68%. [e] With 100 mole % added benzylaniline. [f] Estimated; reaction stopped when $CO_2$ evolution less than 6 mg. per hour. [g] With 300 mole % added benzylaniline. [h] Recovery, based on initial benzylaniline.

The products of degradation of benzyl carbanilate can be explained by the following reactions, in addition to reactions 1 and 4, which are common to all the degradations

$$C_6H_5NHCOOCH_2C_6H_5 \longrightarrow C_6H_5NHCH_2C_6H_5 + CO_2 \quad (7)$$

$$C_6H_5NHCOOCH_2C_6H_5 + C_6H_5NHCH_2C_6H_5 \longrightarrow C_6H_5NH_2 + CO_2 + C_6H_5N(CH_2C_6H_5)_2 \quad (8)$$

$$C_6H_5NHCOOCH_2C_6H_5 + C_6H_5NH_2 \longrightarrow C_6H_6NH_2 + CO_2 + C_6H_5NHCH_2C_6H_5 \quad (9)$$

Reactions 8 and 9 are amine displacements on carbon, analogous to reaction 3b.

Since benzyl carbanilate gave an almost quantitative yield of carbon dioxide, the rate of formation of carbon dioxide was studied to test the plausibility of these reactions. It was found (Fig. 2) that the initial rate of formation of carbon dioxide was slow and first order to approximately 10% completion, and that then the rate increased with time. Further evidence in support of the series of reactions 7, 8 and 9 was the acceleration caused by addition of either benzylaniline or aniline.

At 250° the addition of 10, 50 and 300 mole % of benzylaniline to benzyl carbanilate increased the initial rate by factors of approximately 5–10, 38 and 80 times the rate in the absence of added amine (Table IV). Plots of these reactions (Fig. 3) as pseudo first order (in carbanilate) gave straight lines to 10% completion when 50% benzylaniline was added and to 65% completion with 300% benzylaniline. When plotted as second-order reactions (depending on both carbanilate and benzylaniline), straight lines resulted to 15% completion with 50% added benzylaniline and to 55% com-

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[12] T. L. Davis and K. C. Blanchard, THIS JOURNAL, **45**, 1816 (1923).

[13] T. Mukaiyama and Y. Hoshino, *ibid.*, **78**, 1946 (1956).

[14] T. Mukaiyama and M. Iwanami, *ibid.*, **79**, 73 (1957).

[15] E. Nölting, *Ber.*, **21**, 3154 (1888).

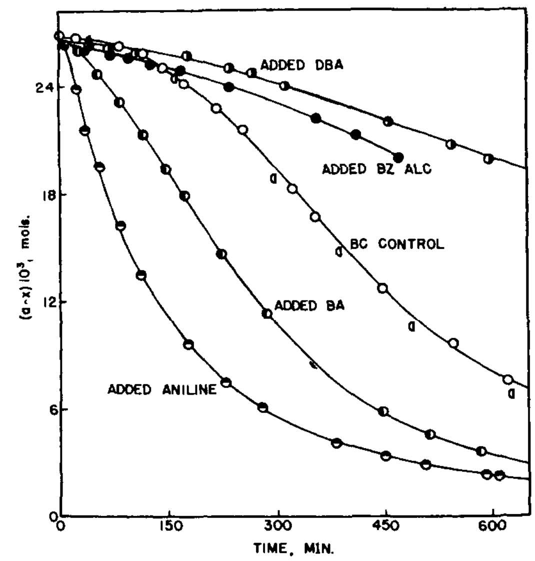

Fig. 2.—Effects of products on the rate of degradation of benzyl carbanilate (BC) at 250°: ○ and ◖, duplicate runs with no addition to the BC; ◑, addition of 50 mole % of dibenzylaniline; ●, 55 mole % of benzyl alcohol; ◐, 50 mole % of benzylaniline; ⊖, 51 mole % of aniline.

pletion with 300% benzylaniline. These kinetics are indicative of an S$_N$2 mechanism for reaction 8.

The rate of degradation of benzyl carbanilate with added aniline was also studied. The addition of 51% aniline afforded pseudo first-order kinetics to 70% completion and second-order kinetics to less than 2% completion. These data support reaction 9, since aniline is both a reactant and a product. Moreover, the reaction is rapid, initially 8 times as fast with added aniline as with added benzylaniline.

Several pieces of evidence indicate that dibenzylaniline was used up or that aniline was formed by some reaction in addition to reactions 8 and 9. In the absence of excess aniline the mole % of aniline formed should be the same as that of dibenzylaniline, from reaction 8, but the former was found to be 13% greater. Moreover, with a 3:1 ratio of benzylaniline to carbanilate, the yield of aniline increased from 34% (in the absence of added benzylaniline) to 81%, but the yield of dibenzylaniline did not increase appreciably. The fact that 63% of the benzyl aniline used was recovered indicates that one mole (37% × 3) of the aniline reacted for every mole of the carbanilate. Additional basic material was present in an intractable oil. It is conceivable that this might contain another amine formed by disproportionation of a quaternary ammonium salt[16] resulting from the action of dibenzylaniline on the carbanilate.

Further information about the nature of the degradation reactions was obtained from the yields of carbon dioxide and of diphenylurea. Over-all data at 250° are in Table IV, and data from the early stages (up to 20% degradation) are in Table V.

Since the yield of aniline (less than 2% based on the yield of carbon dioxide, over the 100-minute period) was apparently insufficient to react with the anticipated phenyl isocyanate (5 to 20%) by reaction 4, known amounts of aniline were added to the degraded benzyl carbanilate, followed by rapid cooling. The control run in the absence of added aniline gave 1.4% carbon dioxide and 1.1% diphenylurea; apparently the greater portion of the free isocyanate reacted with the alcohol as the reaction mixture was cooled. In the presence of added aniline the yield of diphenylurea varied only slightly (average 16 ± 1.6 mole %) when the time of heating was changed from 0 to 95 minutes, and the excess aniline from 23 to 39%.

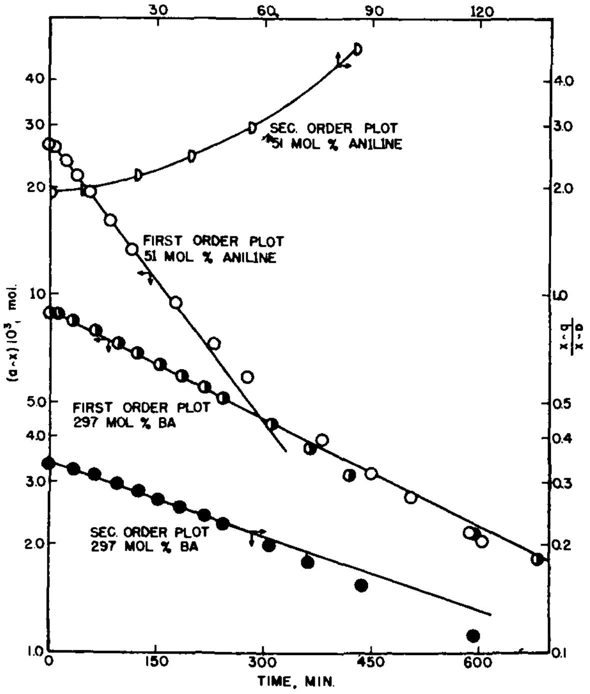

Fig. 3.—First- and second-order plots of the degradation of benzyl carbanilate with amines at about 250°: ○ and ◖, 51 mole % added aniline; ◑ and ●, 297 mole % added benzylaniline (BA).

TABLE IV

RATES AND CARBONYL PRODUCTS OF DEGRADATION OF BENZYL CARBANILATE WITH ADDED SUBSTANCES

| Reagent added[a] Name | Mole % | Temp., °C. | Period studied, hr. | Half-life, hr. | Products, mole % CO$_2$ | $(C_6H_5NH)_2CO$ |
|---|---|---|---|---|---|---|
| None | | 248–252 | 26.0 | 7.1 | 93 | 0 |
| None | | 248–251 | 22.3 | 6.9 | 95 | 0 |
| DBA[b] | 50.0 | 248–251 | 32.3 | 18.0 | 74 | 5.2 |
| B. alc.[c] | 55.7 | 248–250 | 7.8 | 14.2[d] | 25 | 1.2 |
| BA[e] | 10.3 | 240–243 | 29.7 | 10.0 | 88 | 1.2 |
| BA | 10.1 | 248–252 | 22.5 | 6.1 | 91 | 0.4 |
| BA | 12.8 | 247–250 | 5.7 | | 50 | 11 |
| BA | 50.0 | 248–252 | 25.5 | 4.4 | 99 | 0 |
| BA | 297 | 248–252 | 24.5 | 5.6 | 89 | 0 |
| BA | 500 | 248–251 | 10.8 | 6.0 | | |
| A[f] | 11.1 | 248–251 | 7.8 | 5.7 | 68 | 7.9 |
| A[f] | 51.2 | 248–250 | 10.1 | 1.9 | 92 | 4.6 |

[a] To benzyl carbanilate, 6.00-g. sample, except for runs 3, 9 and 10, 2-g. sample. [b] Dibenzylaniline. [c] Benzyl alcohol. [d] By extrapolation of rate curve. [e] Benzylaniline. [f] Aniline.

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[16] H. E. Snyder, E. L. Eliel and R. E. Carnahan, THIS JOURNAL, 72, 2959 (1950).

TABLE V

DETERMINATION OF PHENYL ISOCYANATE[a] FROM DEGRADATION OF BENZYL CARBANILATE TO 20% COMPLETION AT 250°

| Time,[b] min. | Aniline added,[c] mole % | $CO_2$ | Diphenylurea |
|---|---|---|---|
| 100 | 0 | 1.42 | 1.1[e] |
| 20[d] | 25.5 | 3.87 | 15.5 |
| 95 | 24.2 | 1.72 | 14.3 |
| 95 | 39.4 | 1.68 | 18.6[f] |
| 7 | 23.4 | | 13.4[f] |

[a] As diphenylurea by addition of aniline to 6.00 g. of benzyl carbanilate. [b] Time at 250 ± 2° and time to reach 250° (5 to 6 min.). [c] Added at 250° to quench the reaction; time of addition 2 to 7 min., followed by quick cooling. [d] Heated with aniline from 25 to 250° as well as 20 min. at 250°. [e] Recov. benzyl carbanilate, 98%. [f] Recov. carbanilate, 82–84%.

These data support the idea that the yield of diphenylurea was determined by the rapidly established equilibrium reactions 1 and 4 rather than by the possible aminolysis reaction 10

$$C_6H_5NHCOOCH_2C_6H_5 + C_6H_5NH_2 \longrightarrow (C_6H_5NH)_2CO + C_6H_5CH_2OH \quad (10)$$

If aminolysis had occurred, the yield of diphenylurea would have increased to a greater extent by increase in aniline concentration and in the time of heating.

The available data at 250° (Tables IV and V) show that the yield of diphenylurea decreased as the yield of carbon dioxide increased. Thus the diphenylurea (rapidly formed in the early stages of the degradation) gradually disappeared as carbon dioxide and related products ultimately accounted for all the carbamate. These observations, which apply to both benzyl carbanilate and α-methylbenzyl carbanilate, are reasonably explained through the reversible reactions 1 and 4.

Evidence of a carbodiimide intermediate in the degradation of biscarbamates was given in recent work.[17] If this were present in the degradation of benzyl carbanilate, the following reactions could account for the formation of benzylaniline

$$2C_6H_5NCO \longrightarrow C_6H_5N{=}C{=}NC_6H_5 + CO_2 \quad (11)$$

$$C_6H_5N{=}C{=}NC_6H_5 + 2C_6H_5CH_2OH \longrightarrow 2C_6H_5NHCH_2C_6H_5 + CO_2 \quad (12)$$

Accordingly, a mixture of 0.02 mole of diphenyl carbodiimide and 0.04 mole of benzyl alcohol was heated at about 250° for 7.8 hours. The products included 68 mole % of carbon dioxide, 3.7 mole % of benzylaniline and 0.62 mole % of dibenzylaniline. The small amount of amines suggests that this is not a major path in the degradation of benzyl carbanilate, but it might provide the benzylaniline for starting reaction 8.

## Conclusions

Ethyl carbanilate is decomposed at 200° and 60–100 mm. pressure to yield chiefly the alcohol and phenyl isocyanate.

α-Methylbenzyl carbanilate, when heated at about 250°, yields major amounts of carbon dioxide, styrene, aniline and α-methylbenzylaniline. The kinetic and chemical data support an intramolecular degradation of the carbanilate followed by attack of aniline at the secondary carbon atom.

Similar amine displacements on carbon can account for the formation of major amounts of aniline, benzylaniline and dibenzylaniline in the degradation of benzyl carbanilate at 250°. In this case the evidence indicates that the following series of changes may occur: (a) The benzyl carbanilate rapidly dissociates (to about 15%), giving an equilibrium mixture with benzyl alcohol and phenyl isocyanate. (b) The isocyanate forms diphenyl carbodiimide and carbon dioxide at a slow rate.[18] (c) The carbodiimide and benzyl alcohol react relatively fast ($t_{1/2} \approx 1.5$ hr.) yielding benzylaniline and carbon dioxide. (d) Benzylaniline and benzyl carbanilate react less rapidly ($t_{1/2} \approx 4.4$ hr.) to give aniline, carbon dioxide and dibenzylaniline. (e) Aniline and benzyl carbanilate react relatively fast ($t_{1/2} \approx$ 1.9 hr.) to give aniline, carbon dioxide and benzylaniline. The equilibrium reactions 1 and 4 are gradually shifted to the left as the carbanilate is depleted by other reactions, primarily 8 and 9. For the over-all degradation of benzyl carbanilate at 250° the half-life period is approximately 7 hours.

**Acknowledgment**.—The authors are indebted to the Armstrong Cork Co. for a fellowship in support of this investigation and to Drs. L. H. Dunlap and J. A. Parker for helpful discussions.

## Experimental

**General Procedure for Degradations.**—Samples were placed in a Claisen flask with Vigreux side-arm arranged for passage of a stream of dry nitrogen. The flask was lowered into a preheated bath of Wood metal. The liquid products were collected in successive traps cooled by water and Dry Ice. Carbon dioxide was caught in weighed Ascarite tubes. In subsequent separations, the identity of all solids was checked by mixed melting-points with authentic specimens.

**Ethyl Carbanilate.**—Ethanol, collected in the Dry Ice trap, was separated by distillation from traces of carbanilate and diphenylurea. The diphenylurea in the trap and in the pot was separated by extraction of the more soluble carbanilate with ether. Triphenyl isocyanurate was precipitated from 1:1 ether–petroleum ether containing 1% ethanol. Phenyl isocyanate was determined by allowing the pot and trap contents to stand overnight with water, then separating the diphenylurea as above. The allophanate was obtained from ether extracts containing unreacted carbanilate.

**α-Methylbenzyl Carbanilate.**—The nitrogen stream was oxygen-free as well as dry, and the Claisen column was air-cooled to promote refluxing during the period of the reaction. In a typical separation of products (from the 18.0-g. run), the reaction mixture was distilled at 42–175° at 1 atm. The distillate was dissolved in chloroform and treated with 3% bromine in chloroform at 0.5° to give a precipitate of 2,4,6-tribromoaniline hydrobromide (0.57 g., m.p. 194–196°). From the filtrate was obtained 4.35 g. of α,β-dibromostyrene, m.p. 68–70°. The undistilled residue was treated with 1:2.5 ether–petroleum ether to precipitate a mixture, separable by benzene into 1.23 g. of diphenylurea and 1.0 g. of polystyrene, precipitated by methanol. The ether–petroleum ether filtrate on distillation yielded fraction A, b.p. 58–70° at 12 mm.; B, b.p. 45–130° at 7 mm.; and C, 130–142° at 7 mm. Fraction A, dissolved in benzene and treated with dry hydrogen chloride, yielded a precipitate of 3.01 g. of aniline hydrochloride, m.p. 194–195°. The filtrate, after removal of solvent, yielded 0.26 g. of an oil, identified as α-methylbenzyl alcohol by preparation of its α-naphthyl carbamate derivative. Fraction B, treated in the same way as fraction A, gave a further 0.39 g. of aniline hydrochloride and 0.2 g. of α-chloroethylbenzene, b.p. 194–195°. Frac-

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(17) E. Dyer and G. E. Newborn, THIS JOURNAL, **80**, 5495 (1958).

(18) R. Stollé, *Ber.*, **41**, 1125 (1908).

tion C yielded 3.56 g. of α-methylbenzylaniline hydrochloride, m.p. 178–179°, neut. equiv. 233.

**α-Methylbenzyl Carbanilate with Added *p*-Toluidine.**—A mixture of 0.054 mole of α-methylbenzyl carbanilate and 0.27 mole of *p*-toluidine was refluxed at 215–237° for 12 hr. Products were separated by solvent treatments, fractionation and formation of hydrochlorides and picrates. Identifications were made by mixed melting points and neutral equivalents.

**Benzyl Carbanilate.**—The Claisen flask was replaced by a round-bottom flask with water condenser. Products were separated by use of 1:1 ether–petroleum ether to remove diphenylurea, followed by fractionation under reduced pressure and solvent treatment to separate aniline from the secondary and tertiary amines. Benzylaniline was obtained both as a solid, m.p. 37–39°, and as its hydrochloride from benzene, m.p. 208–210°. The separation of dibenzylaniline, m.p. 67–69°, was aided by column chromatography on alumina from petroleum ether solution.

Certain other possible routes to the secondary and tertiary amines resulting from degradation of benzyl carbanilate were eliminated as major paths by control experiments. When a mixture of 0.055 mole of benzylaniline and 0.043 mole of benzyl alcohol was heated at 238–246° for 36 hr., only 3.7% of dibenzylaniline was obtained; 88% of the benzylaniline was recovered. Disproportionation among the amines was shown to be not extensive by heating a mixture of 0.0335 mole of benzylaniline and 0.0334 mole of dibenzylaniline for 23.5 hr. at 248–255°; 91% of the dibenzylaniline was recovered.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MISSOURI]

# Substituted Styrenes. IV. The Reaction of the Vinylanisoles with *p*-Nitrobenzenediazonium Chloride in Pyridine[1,2]

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The reactions of *o*- and *p*-vinylanisole with *p*-nitrobenzenediazonium chloride in pyridine gave 4-nitrobenzyl-2′-methoxyphenylcarbinol (6.5%) and 4-nitro-4′-methoxystilbene (12%), respectively. Similar reactions could not be effected using *m*-vinylanisole. The reaction of *p*-vinylanisole with other diazonium chlorides proved to be a new and novel method for preparing substituted stilbenes which would be difficult to prepare by conventional procedures. By the method described, 4-cyano- and 4-acetyl-4′-methoxystilbene were obtained in 41 and 19% yields, respectively.

Earlier studies in this series[3,4] have demonstrated the electrophilic character of the vinyl groups in *o*- and *p*-nitrostyrene and recent work on the syntheses and spectra of the vinylphenols[5] included attempts to prove, by chemical means, pronounced nucleophilic character of the vinyl groups in *o*- and *p*-vinylphenol. However, the ease of polymerization of the vinylphenols hindered the initial efforts of the latter study and clear differences have yet to be demonstrated chemically for the vinyl groups in these compounds.

The vinylanisoles represent another class of styrenes with an electron-releasing nuclear substituent and, for these compounds, enhanced nucleophilic character would again be expected for the vinyl groups when situated *ortho* or *para* to the methoxy group. Pronounced reactivity for these vinylanisoles was indicated from the evidence of several earlier reports. Thus, Schmidle and Mansfield[6] found that *p*-vinylanisole, formaldehyde and morpholine, under mild conditions, gave 4-anisyl-2-(4-morpholinyl)-ethylcarbinol and *p*-vinylanisole, formaldehyde and dimethylamine, refluxed in acetic acid, gave N,N-dimethyl-4-methoxycinnamylamine. Also, Shamshurin[7] obtained 1-(acetomercurimethyl) - 2,6 - dimethoxyphenylcarbinol from the reaction of 2,6-dimethoxystyrene and mercuric acetate in water, and Ainley and Robinson[8] prepared anisaldehyde 2,4-dinitrophenylhydrazone from *p*-vinylanisole and 2,4-dinitrobenzenediazonium sulfate in ethanol. In the latter reaction formaldehyde was eliminated. *p*-Nitrobenzenediazonium sulfate, dissolved in glacial acetic acid or suspended in alcohol, also was reported to attack the *n*-propenyl side chain of anethole, isosafrole, isoapiole and isoeugenol with the formation of the corresponding substituted benzaldehyde *p*-nitrophenylhydrazones and acetaldehyde.[9,10]

All these examples may be classified as electrophilic substitution or addition reactions. The influence of the *o*- or *p*-methoxy group must certainly be of importance in these reactions since styrene fails to give a sharply defined crystalline compound with 2,4-dinitrobenzenediazonium sulfate,[8] a very powerful electrophilic reagent.

It was the intent in this study, therefore, to investigate differences in the reactions of isomeric vinylanisoles with a common reagent. Reaction conditions were selected to give a minimum of side reactions. *p*-Nitrobenzenediazonium chloride was chosen for the reagent because it has been demonstrated that anisole[11] will not react with this reagent. This would obviate the possibility of a reaction on the aromatic nucleus and restrict reactions, if any, to the side chain. Preliminary reactions of *p*-vinylanisole with *p*-nitrobenzenediazonium chloride in acetic acid gave only dark tars and pyridine was used in subsequent reactions

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[1] Abstracted from a portion of a thesis submitted by H. E. H. to the Graduate School of the University of Missouri in partial fulfillment of the requirements for the Ph.D. degree.

[2] Presented at the 132nd Meeting of the American Chemical Society, New York, N. Y., September 17, 1957.

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[4] W. J. Dale and G. Buell, *J. Org. Chem.*, **21**, 45 (1956).

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[9] A. Quilico and M. Freri, *Gazz. chim. ital.*, **58**, 380 (1928); *C. A.*, **23**, 597 (1929).

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