Dr. N. Kharasch, gave m.p. 75–78°. The mixed melting point was 75–76°.

4-Amino-2,2-dimethylvaleric Acid Hydrochloride.—Two grams of II and 20 ml. of concentrated hydrochloric acid were heated under reflux for 24 hours. The solution was decolorized and evaporated to dryness *in vacuo*. The product was washed with acetone and recrystallized several times from ethanol and acetone to give 1.5 g., m.p. 156–157°, lit.[4] m.p. 164°.

Anal. Calcd. for $C_7H_{16}ClNO_2$: C, 46.28; H, 8.88. Found: C, 46.12; H, 8.54.

The pyrrolidone was regenerated easily by neutralization of the hydrochloride.

2,2-Dimethyl-4-pentenamide (III).—The corresponding nitrile was prepared in 61% yield by alkylation of lithium isobutyronitrile with allyl chloride according to Ziegler.[10] The nitrile was hydrolyzed by heating 5 g. under reflux for 6 hours with a solution of 15 g. of potassium hydroxide in 100 ml. of ethylene glycol and 5 ml. of water. After the addition of 100 ml. of saturated salt solution and 20 ml. of concentrated hydrochloric acid, the solution was extracted with methylene chloride. Distillation gave 5.3 g. (90%) of the acid, b.p. 104–108° (20 mm.). The amide, m.p. 80–81°, prepared from the acid *via* the acid chloride sublimes readily at 70° (20 mm.) to give large sheets which are invisibly thin and show strong interference colors.

Anal. Calcd. for $C_7H_{13}NO$: C, 66.10; H, 10.30; N, 11.02. Found: C, 66.40; H, 10.35; N, 10.94.

A solution of 2 g. of III in 15 ml. of toluene was added (vigorous ammonia evolution) to 0.031 mole of sodamide in 20 ml. of toluene. After heating under reflux for 4 hours, the solution was cooled, treated with 5 ml. of acetic acid and extracted with saturated salt solution. The toluene solution was evaporated to small volume and decolorized. The addition of petroleum pentane and chilling gave 1.5 g. (75%) of II, m.p. 90–91°. The m.p. of a mixture with authentic material was undepressed.

Alternatively, 1.00 g. of III in 5 ml. of hot ligroin, b.p. 115–135°, was added to 0.38 g. of sodium hydride in 5 ml. of ligroin at 80°. After the vigorous hydrogen evolution subsided, the mixture was heated under reflux for 1 hour, during which time a gummy sodium salt went into solution, leaving about one-half of the original sodium hydride on the bottom. The mixture was cooled and decomposed by the portionwise addition of 1 ml. of acetic acid. The mixture was filtered and heated to boiling to codistil traces of acetic acid. Cooling deposited 0.72 g. (72%) of II.

N-Benzyl-2,2-dimethyl-4-pentenamide.—A solution of 2,2-dimethyl-4-pentenoyl chloride (from 2.56 g. of the acid and 4 ml. of thionyl chloride) in 5 ml. of ether was added portionwise to a solution of 10 ml. of benzylamine and 20 ml. of water maintained in an ice-bath. The product, 3.5 g. (81%), was recrystallized from petroleum hexane and again from 70% methanol giving 3.2 g. of material, m.p. 55–56°. Sublimation at the water-pump (100°) raised the m.p. to 56–57°.

Anal. Calcd. for $C_{14}H_{19}NO$: C, 77.38; H, 8.81. Found: C, 77.50; H, 8.71.

Treatment with sodium hydride in either ligroin or toluene according to the procedure for 2,2-dimethyl-4-pentenamide gave the sodium salt as a gum. The benzyl amide was recovered unchanged to the extent of 77%. No other product was isolated.

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(10) K. Ziegler and H. Ohlinger, *Ann.*, **495**, 84 (1932).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

The Beckmann Rearrangement of the Oximes of Alkyl Phenyl Ketones[1,2]

BY RONALD F. BROWN, NORMAN M. VAN GULICK AND GEORGE H. SCHMID

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The rearrangement of the oximes of pivalophenone and of 5-phenoxy-2,2-dimethylvalerophenone in alkaline solution with benzenesulfonyl chloride results in alkyl group migration, in contrast to aryl migration with hydrogen chloride in acetic acid. Aceto-, propio- and isobutyrophenoximes (both *syn*- and *anti*-forms of the last) behave normally with phosphorus pentachloride or with benzenesulfonyl chloride, but the *syn*- and *anti*-isobutyrophenoxime react alike with hydrogen chloride in acetic acid. The sensitivity of the acyl derivatives of *t*-carbinamines to cleavage by acids is noted.

While attempting to prepare the hydrobromide of 4-bromo-1,1-dimethylbutylamine,[3] a synthetic route which involved the rearrangement of the oxime of 5-phenoxy-2,2-dimethylvalerophenone appeared to be of utility if the alkyl group migrated instead of the phenyl. It had been reported that pivalophenoxime (I), a model compound, gave benzonitrile exclusively upon treatment with phosphorus pentachloride, but that treatment with a solution of hydrogen chloride in acetic acid gave pivalanilide.[4] In spite of these discouraging facts, pivalophenoxime was prepared and subjected to rearrangement under various conditions. The rearrangement with phosphorus pentachloride, even under the mildest conditions, led to the exclusive formation of benzonitrile, and the rearrangement with hydrogen chloride in acetic acid to give pivalanilide was confirmed also. It seemed possible that the benzenesulfonyl chloride method of rearranging oximes[5] might produce the desired result, since the rearrangement occurs in an alkaline environment. The rearrangement was carried out in the usual manner, the unstable benzenesulfonyl ester rearranged *in situ*, giving N-*t*-butylbenzamide in 72% yield. The rearrangement under these conditions followed two competing paths since the odor of benzonitrile was evident at the end of the reaction.

Because of the success of the model rearrangement, 2,2-dimethyl-5-phenoxyvalerophenone was prepared and the crude liquid ketone was converted into the oxime directly. Rearrangement of the oxime produced an 84% yield of N-benzoyl-1,1-dimethyl-4-phenoxybutylamine. This amide proved extremely resistant to basic hydrolysis. After treatment with sodium butoxide in refluxing butanol, the amine was obtained in only 25% yield, 47% of the amide being recovered unchanged. Potassium hydroxide in boiling ethylene glycol like-

(1) Abstracted in part from the Ph.D. Dissertation of N. M. van Gulick, 1953.

(2) Generously supported in part by the Office of Naval Research under Contract No. Nonr-723(00).

(3) R. F. Brown and N. M. van Gulick, THIS JOURNAL, **77**, 1079 (1955).

(4) G. Schroeter, *Ber.*, **44**, 1201 (1911).

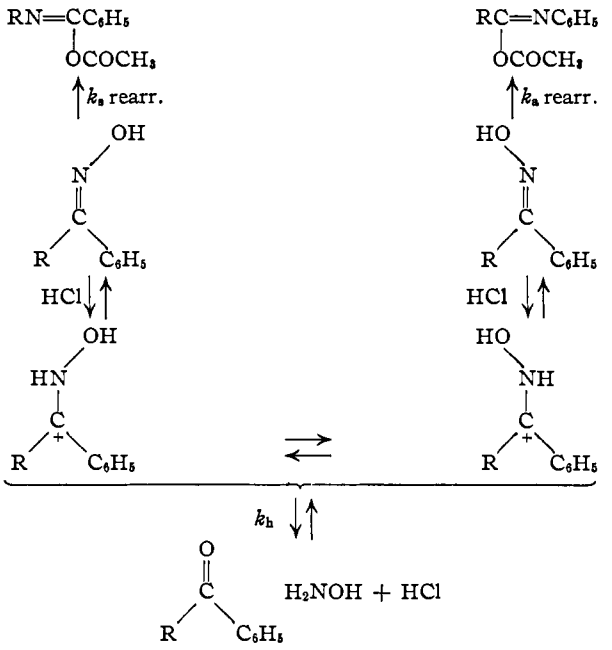
(5) H. Wege, *ibid.*, **24**, 3537 (1891); A. Werner and A. Piguet, *ibid.*, **37**, 4295 (1904); and see P. Oxley and W. F. Short, *J. Chem. Soc.*, 1514 (1948), for recent work.

wise failed to afford complete conversion, giving only 18% of the amine. The latter conditions were drastic enough to cleave the ether linkage as well, since phenol was detected in the product. Acid hydrolysis, using hydrobromic acid, was attempted in the hope that simultaneous cleavage of the amide and ether functions would lead directly to the required bromo amine salt. However, the products observed were phenol, benzoic acid, ammonium bromide and a neutral oil containing bromine, and this synthesis was abandoned.

In order to elucidate the nature of the hydrolysis, both *t*-butylamine and N-*t*-butylbenzamide were subjected to acid hydrolysis under the same conditions. It was found that although the former compound was inert to scission, the latter compound cleaved rapidly to give *t*-butyl bromide, benzoic acid and ammonium bromide. The reaction probably follows a path similar to that proposed by Cohen and Schneider[6] for the alcoholysis of *t*-butyl esters. Although there are reports[7] in the literature concerning the instability of certain amines, this paper seems to be the first to call attention to the facile cleavage of acyl derivatives of *t*-alkylamines. It is now clear why Ritter and Kalish[8] used only basic conditions for the hydrolysis of N-*t*-alkylformamides in their elegant synthesis of *t*-alkylamines.

To gather additional information on the problem of the rearrangement of I, acetophenoxime (II), propiophenoxime (III) and the *syn*-phenyl (IVs) and *anti*-phenyl (IVa) forms of isobutyrophenoxime[9] were prepared and subjected to rearrangement under various conditions. With phosphorus pentachloride in ether or with benzenesulfonyl chloride, II, III and IVa each gave rise to phenyl migration, and IVs yielded N-isopropylbenzamide in good yield. These results, and the lack of much (if any) isomerization during the reactions, leads to an assignment of *syn*-phenyl for the configuration of I. That phosphorus pentachloride causes the loss of the elements of *t*-butyl alcohol is consistent with this configuration if the elimination is *trans*. It is also logical that the oximes should be *anti*-phenyl until the neighboring alkyl group increases in size to isopropyl, for which both forms exist, and go over to the single form again with the *t*-butyl group and become *syn*-phenyl. Models do not give a clear answer to this question, although the *syn*-phenyl form of I is slightly favored.

The use of hydrogen chloride in acetic acid, which with I gave pivalanilide in good yield, must involve a preliminary isomerization.[10] This was confirmed when IVa and IVs under identical treatment gave rise to similar amounts of isobutyranilide. N-Isopropylbenzamide may have been present, but none could be isolated. The major product in both instances was isobutyrophenone. Thus, solvolysis and isomerization under this condition compete favorably with rearrangement. A possible schematic mechanism involves the mobile equilibrium between



the *syn*- and *anti*-phenyl structures, the specific rate of solvolysis (k_h), and the specific rates of rearrangement (k_s and k_a). If R is *t*-butyl, k_h would be small because of the difficulty of adding the fourth group to the central carbon. The equilibrium between *syn* and *anti* would be over toward the former. But with $k_a > k_s$, the phenyl shift will predominate if the *syn* may isomerize readily to the *anti*-phenyl configuration. It is reasonable to postulate $k_a > k_s$ since the comparison is essentially that of the intrinsic migratory aptitudes of phenyl and *t*-butyl. Although it is generally assumed that aryl migrates in preference to alkyl,[11] there is little evidence in the literature on which to evaluate the series Me, Et, *i*-Pr, *t*-Bu in relation to each other. Nybergh has shown that Et > Me by 4:1 in the rearrangement of *sym*-diethyldimethylethylene glycol.[12] But further substitution of methyl should bring strong steric effects into play so that *i*-Pr and, certainly, *t*-Bu should be less effective as migrants with or without concurrent displacement of an anion. It seems safe to postulate $k_a > k_s >> k_h$ for the pivalophenoxime case.

With IVa and IVs (R = *i*-Pr), k_h should be relatively larger than for I, and if the rate of equilibration of the two forms exceeds both k_a and k_s, then with k_a again greater than k_s phenyl migration will be favored. So $k_h > k_a > k_s$ seems reasonable to explain the results obtained.

There remains the problem of reconciling the results with phosphorus pentachloride and with benzenesulfonyl chloride. In the former case, the combination of hydrogen chloride and ether is less effective as a solvolytic medium, and, moreover, the dissociation of the oxime chlorophosphate is presumably so rapid that equilibration is relatively

(6) S. G. Cohen and A. Schneider, THIS JOURNAL, **63**, 3382 (1941).

(7) M. S. Kharasch and L. B. Howard, *ibid.*, **56**, 1370 (1934), found triphenylmethylamine to be cleaved by dilute hydrochloric acid at 100° although *t*-butylamine was unaffected; see also W. J. Hickenbottom, *ibid.*, **56**, 1820 (1934).

(8) J. J. Ritter and J. Kalish, *ibid.*, **70**, 4048 (1948).

(9) H. M. Kissman and J. Williams, *ibid.*, **72**, 5323 (1950).

(10) For example see G. W. Wheland, "Advanced Organic Chemistry," Second Ed., John Wiley and Sons, Inc., New York, N. Y., p. 345.

(11) Reference 10, pp. 494–519.

(12) B. Nybergh, *Ber.*, **55**, 1960 (1922).

slow. With I, the positive ion left loses the readily dissociable *t*-butyl ion, leaving the nitrile. With IVs, the isopropyl group does not dissociate and is forced to migrate. Under alkaline conditions, the oxime benzenesulfonate dissociates easily with concomitant migration of the group *anti* to the leaving group. With *t*-butyl *anti*, because of low migratory aptitude, some elimination still occurs as shown by the presence of benzonitrile. Protonation of the oxime is impossible in the alkaline environment and isomerization does not occur. With II and III no problems arise since they, as *anti*-phenyl structures, are in the correct configuration to allow the superior migratory phenyl to operate under all conditions.

Experimental[13]

Acetophenone, propiophenone and isobutyrophenone were Eastman products. Pivalophenone was prepared according to Willemart[14] in 44% yield. The oximes were prepared in the usual fashion. IV was separated into *syn*- and *anti*-phenyl forms as described by Kissman and Williams.[9] Attempts to isolate other forms of I by similar techniques failed. Acetanilide, propionanilide, isobutyranilide and pivalanilide were prepared from aniline, the corresponding acid chloride and pyridine. N-Isopropyl- and N-*t*-butylbenzamide were prepared from benzoyl chloride and the corresponding amine. All m.p.'s checked the literature values.

Rearrangements with **phosphorus pentachloride** were done by a modification of the procedure of Drake.[15] To 1.00 g. of an oxime dissolved in 5 ml. of dry ether held at 0° was added in small portions over a 20-minute period a solution of 1.10 to 1.60 g. (5% molar excess) of phosphorus pentachloride in 10 ml. of dry benzene. After the addition, the mixture was allowed to come to room temperature. After standing for at least an hour, the mixture was poured over ice, neutralized with dilute sodium hydroxide and extracted with three 25- to 50-ml. portions of ether. The ethereal solutions were combined, dried over sodium sulfate and the product isolated by concentration, crystallization or distillation as appropriate. II gave acetanilide, crude 73%, pure 65%; III gave propionanilide in similar yields; IVa gave isobutyranilide, pure 53%; IVs gave N-isopropylbenzamide, pure 72%. I gave benzonitrile, b.p. 75° (18 mm.), only.

Rearrangements with **benzenesulfonyl chloride** were carried out by heating under reflux for 4 hours a solution of 1.00 g. of an oxime, 1.10 to 1.40 g. (5% molar excess) of benzenesulfonyl chloride and 0.40 to 0.60 g. of sodium hydroxide in 5 ml. of water and 20 ml. of acetone. Water, 50 ml., was added, and most of the acetone removed at the aspirator. When cool, the mixture was extracted with ether and the products isolated as described previously. II gave acetanilide, crude 80%, pure 72%; III gave propionanilide (violent initial reaction), similar yields; IVa gave isobutyranilide, pure 65%; IVs gave N-isopropylbenzamide, pure 28% (accidental loss); compound I gave N-*t*-butylbenzamide, crude, 76%, pure 65%.

Shorter reaction times (1 or 2 hr.) with IVa or IVs gave a crude product, m.p. 92–94°, which was a mixture. Recrystallization from ether produced no purification. An attempted quantitative alkaline hydrolysis failed in complete recovery of products but showed unreacted oxime to be the major constituent. Thus 0.1917 g. (1.177 mmoles) of the product from IVs was heated under reflux with 20 ml. of 10% sodium hydroxide solution for three hours, and steam distilled. Bromine water was added to the distillate until no further reaction occurred. The tribromoaniline was collected, dried and weighed (negligible amount). The residue from the steam distillation after being cooled was extracted with three 15-ml. portions of ether. The ethereal solution was evaporated and the residual oxime dried and weighed; 0.0590 g. (0.362 mmole). The aqueous layer was heated to remove dissolved ether, cooled and acidified to give benzoic acid, 0.0230 g. (0.188 mmole); total recovery 47%. The product from IVa, 0.4060 g. (2.490 mmoles), treated similarly gave 0.2193 g. (0.666 mmole) of tribromoaniline, 0.1246 g. (0.764 mmole) of oxime and 0.0067 g. (0.055 mmole) of benzoic acid; total recovery 60%.

The ultraviolet absorption curves of the products could be duplicated by synthetic mixtures of only two components made up as calculated from the original curves of the 92–94° products. This as well as the hydrolytic work indicated that isomerization was almost negligible.

Rearrangements with **hydrogen chloride** were carried out by bubbling hydrogen chloride for 15 min. through a solution of about 1.0 g. of the oxime in 15 ml. of acetic acid. The mixture was allowed to stand overnight, heated to boiling for 5 minutes, poured over ice and worked up. Compound I, 1.00 g., gave 0.94 g. of crude product, m.p. 118–141°. One crystallization from petroleum heptane yielded needles, m.p. 117–124°; mixed with pivalanilide, m.p. 118–122°; mixed with N-*t*-butylbenzamide, m.p. 95–104°. IVa or IVs gave oils which were extracted from the ice–water mixture with chloroform. The chloroform solutions were dried and evaporated to yellow oils with the odor of isobutyrophenone; IVa, 1.00 g., gave 0.70 g., and IVs, 0.88 g., gave 0.54 g. Trituration of the oils with petroleum pentane yielded crude crystalline products which on recrystallization from petroleum hexane gave nearly pure material; from IVa, 0.132 g. crude, 0.067 g. pure, m.p. 99–101°; from IVs, 0.147 g. crude, 0.074 g., pure, m.p. 100–102°; a mixture of the two gave m.p. 100–102°; mixed with N-isopropylbenzamide, m.p. 81–83°; mixed with isobutyranilide, m.p. 103–104°. The petroleum pentane solutions were evaporated, and the resulting oils treated with 2,4-dinitrophenylhydrazine. The dinitrophenylhydrazones (90% yield crude, 70% after recrystallization), m.p. 158–160°, obtained were mixed with authentic isobutyrophenone dinitrophenylhydrazone of m.p. 160–161°, to give m.p. 159–160°.

2,2-Dimethyl-5-phenoxyvalerophenone.—To an ammonia slurry of sodamide from 11.5 g. of sodium was added 500 ml. of toluene, followed by the dropwise addition of 111 g. of isobutyrophenone. The ammonia was evaporated and the suspension heated under reflux for 1 hour. After cooling, 107.5 g. of 3-phenoxypropyl bromide in 40 ml. of toluene was added over a 1-hour period with stirring. After the addition, the mixture was kept at room temperature for 1 hour, heated on the steam-bath for 18 hours, and then heated under reflux for 18 hours. At this point, the mixture was only slightly basic. After the addition of 200 ml. of water, the organic layer was separated and washed several times with dilute hydrochloric acid, followed by water. After removal of solvents and isobutyrophenone at the aspirator, the solution was distilled at 2 mm. The product, a yellow oil, was collected continuously over the range 70–200° (major fraction 142–162°). The distillate contained *ca.* 0.5 g. of crystals, which were acidic and proved to be benzoic acid (m.p. and mixed m.p.). The crude phenone was not further purified, but was converted directly to the oxime.

2,2-Dimethyl-5-phenoxyvalerophenone Oxime.—The entire quantity of the crude phenone was dissolved in 500 ml. of 95% ethanol. A solution of 21 g. of hydroxylamine hydrochloride and 41 g. of sodium acetate trihydrate in 50 ml. of water was added and the solution was allowed to cool. The bright yellow crystals were collected and washed with petroleum pentane which removed a yellow tar, leaving colorless crystals. The tar was oximated again to give 6 g. more of oxime. The oxime was recrystallized once from carbon tetrachloride and again from 100% ethanol. The product weighed 56.7 g. (38% from isobutyrophenone). The melting point dropped from 131–132° to 129–130° with the purification.

Anal. Calcd. for $C_{19}H_{23}NO_2$: C, 76.73; H, 7.79. Found: C, 76.68; H, 7.78.

An unsuccessful attempt was made to regenerate the pure phenone by transoximation. Thus, 10.00 g. of oxime was dissolved in 250 ml. of acetone (100 equivalents) and 25 ml. of water and 5 ml. of acetic acid were added. After a 24-hour reflux period, water was added and 9.27 g. of the unchanged oxime was collected.

The phenone was successfully regenerated as follows: A solution of 9.22 g. of the oxime and 30 ml. of 2 *N* hydro-

(13) All m.p.'s and b.p.'s are uncorrected. Analyses by Mr. W. J. Schenck of this department.

(14) A. Willemart, *Bull. soc. chim.*, [5] **2**, 867 (1935).

(15) N. L. Drake, G. M. Kline and W. G. Rose, THIS JOURNAL, **56**, 2076 (1934).

chloric acid (2 equivalents) in 200 ml. of 2-propanol was heated under reflux for 6 hours. Water was added, the unchanged oxime (2.70 g.) was removed, and the solution was partitioned between water and petroleum pentane. After removal of the solvent, the remaining oil was distilled to give 5.77 g., b.p. 154–166° (2 mm.). Thus, the hydrolysis was 71% complete and the yield was 93%. The yellowish phenone partially solidified upon standing (low melting crystals), but was at least 90% pure since 1 g. gave 0.9 g. of oxime of m.p. 129–130°. The mixed m.p. with the original oxime was undepressed.

N-Benzoyl-1,1-dimethyl-4-phenoxybutylamine.—Ten grams of 2,2-dimethyl-5-phenoxyvalerophenone oxime was added to a solution of 50 ml. of acetone and 25 ml. of water containing 5.0 g. of sodium hydroxide. A solution of 5 ml. of benzenesulfonyl chloride in 5 ml. of acetone was added over a 5-minute period with stirring. The mixture was then heated to 45° and stirred at that temperature for 2 hours. The mixture was neutralized with acetic acid, and 100 ml. of water was added. The crystals were collected and recrystallized twice from aqueous methanol to give 8.42 g. (84%) of product, m.p. 91–92°.

Anal. Calcd. for $C_{19}H_{23}NO_2$: C, 76.73; H, 7.79. Found: C, 76.82; H, 7.98.

A solution of 1.5 g. of the amide and 20 equivalents of sodium 1-butoxide in 50 ml. of absolute 1-butanol was heated under reflux for 6 hours. Water (2 ml.) was added and heating continued for 1 hour. Water was added and the butanol distilled. The remaining mixture was extracted with ether. The alkaline solution was acidified, precipitating benzoic acid, identified by m.p. and mixed m.p. The ether solution was extracted with dilute hydrochloric acid and the ether evaporated to give a solid which was recrystallized from chloroform and petroleum pentane to give 0.7 g. of unchanged amide (identified by m.p. and mixed m.p.). The acidic extract was evaporated to dryness and the residue recrystallized once from chloroform and ethyl acetate and again from ethylene chloride to give 0.3 g. of 1,1-dimethyl-4-phenoxybutylamine hydrochloride, m.p. 173–174°.

Anal. Calcd. for $C_{12}H_{20}ClNO$: C, 62.73; H, 8.77; N, 6.10. Found: C, 62.70; H, 8.96; N, 6.00.

Another basic hydrolysis was run in which a mixture of 1.0 g. of amide, 5 g. of potassium hydroxide, 5 ml. of water and 45 ml. of ethylene glycol was heated under reflux for 22 hours. The mixture was then acidified with 15 ml. of concentrated hydrochloric acid. The benzoic acid and silica were removed by filtration and the filtrate was extracted with ether to remove phenol and the remainder of the benzoic acid. The phenol was identified as the tribromo derivative. The aqueous solution was evaporated to dryness *in vacuo* and the residue was extracted with acetone to remove traces of glycol. Recrystallization from chloroform–acetone afforded 0.14 g. (18%) of the amine salt (m.p. and mixed m.p.). No amide was recovered from any of the fractions.

An acid hydrolysis was conducted by heating a solution of 2.97 g. of the amide in 10 ml. of concentrated hydrobromic acid under reflux for 6 hours. More concentrated hydrobromic acid (10 ml.) was added and the solution then was distilled slowly from an oil-bath (145–155°) for 3 hours. Water was added to the residue and after decolorizing to remove a small amount of tar, the solution was evaporated to dryness. The solid (0.8 g.) was inferred to be ammonium bromide by m.p. > 300°, insolubility in chloroform and evolution of ammoniacal gas upon dissolving in base. The distillate was diluted with water and extracted with ether. The ethereal extract was extracted with sodium bicarbonate to remove benzoic acid and with sodium hydroxide to remove phenol. The ether was then evaporated, giving a small quantity of an oil with a strong pleasant smell. Sodium fusion indicated bromine, but no nitrogen. The oil could not be induced to crystallize, and was not further characterized.

Hydrolysis of N-*t*-Butylbenzamide and *t*-Butylamine.—A mixture of 1.77 g. of N-*t*-butylbenzamide and 10 ml. of concentrated hydrobromic acid was distilled from an oil-bath at 150° until 9 ml. of distillate had been collected. Almost immediately upon reaching the b.p. the originally clear solution became cloudy and separated into two phases. An oil passed over in the distillate for about 20 minutes and then stopped. Benzoic acid slowly sublimed throughout the distillation. The oil was decanted from the distillate, washed with water and dried with calcium chloride. The b.p. was determined to be 73°. The oil was more dense than water and gave an instantaneous test with silver nitrate, indicating *t*-butyl bromide, b.p. 73°. The residue (0.90 g., 92%) in the flask was ammonium bromide (insoluble in chloroform, behavior with base). It was found that *t*-butylamine was resistant to hydrolysis under identical conditions.[16] Thus, no cloudiness was noted in the distillate and the amine salt, which was quantitatively recovered, was slightly but completely soluble in chloroform.

N-*t*-Butylbenzamide charred when treated with concd. sulfuric acid at room temperature, but was partially hydrolyzed by heating a mixture of 2 g. in 8 ml. of 85% phosphoric acid with 3 drops of concentrated hydrochloric acid for 24 hours at 100°. When cooled, the upper liquid layer crystallized. The benzoic acid was collected, washed with water and dried; 0.7 g., m.p. 116–118°. Dilution of the phosphoric acid deposited unchanged amide, insoluble in sodium bicarbonate solution. A solution of 2.0 g. of the amide and 1.7 g. of sodium in 25 ml. of 1-butanol was heated under reflux for 3 hours. Water (2 ml.) was added and the heating was continued for 1 hour. Excess water was added and the butanol was removed by steam distillation. Unreacted amide (0.91 g.) was filtered off and the solution was rendered acidic. Benzoic acid was collected in the amount of 0.54 g.

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(16) M. Brander reported that *t*-butylamine hydrochloride heated for 14 hr. to 280° gave an unsaturated hydrocarbon, *Rec. trav. chim.*, **37**, 67 (1918).