322. *Reactions of Organic Azides. Part VI.* The Interaction of 2-Acylbenzoic Acids and Alkylidenephthalides with Hydrazoic and Sulphuric Acids.*

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2-Acylbenzoic acids and alkylidenephthalides react with hydrazoic and sulphuric acids to yield, principally, 2-substituted 6-oxo-4 : 5-benz-1 : 3-oxazines; where the substituent is aryl, the oxazine is the isolated product under the conditions employed; where it is alkyl or aralkyl, the hydrolysis product, an *N*-acylanthranilic acid, is obtained. The mechanisms of this reaction, and of a subsidiary rearrangement, are discussed.

IT has been shown (Part II,[1] and earlier observations by Badger, Howard, and Simons [2]) that the Schmidt reaction with 2-benzoylbenzoic acid proceeds as follows: reaction of the keto-acid (I; R = Ph) with sulphuric acid gives a cyclic cation (II) which combines with hydrazoic acid, yielding the protonated azide (III); the latter rearranges and undergoes ring-expansion to form the proton-adduct (VI) of 6-oxo-2-phenyl-4 : 5-benz-1 : 3-oxazine; addition of water (in the presence of chloroform as a protective solvent against hydrolysis) yields the benzoxazine (IV).

Seven 2-acylbenzoic acids (I; R representing groups of different electronic character, and size) have been subjected to the Schmidt reaction under standardised conditions in order to ascertain whether there is a relation between the nature of R and (*a*) the rate of oxazine formation and (*b*) the extent of rearrangement in the direction which leads, not to the oxazine, but (ultimately) to the amine $R\cdot NH_2$. The results obtained are shown in the Table.

The reaction of 2-acylbenzoic acids and alkylidenephthalides with hydrazoic and sulphuric acids.

Benzoic acid	Principal product	Yield (%)	Amine	Yield (%)
	6-Oxo-4 : 5-benz-1 : 3-oxazine :			
2-*p*-Methoxybenzoyl-	2-*p*-Methoxyphenyl-	75	—	—
2-*p*-Chlorobenzoyl-	2-*p*-Chlorophenyl-	84	*p*-Chloroaniline	3
2-*m*-Nitrobenzoyl-	2-*m*-Nitrophenyl-	87	*m*-Nitroaniline	4
2-Mesitoyl-	2-Mesityl-	29	*	—
2-α-Naphthoyl-	2-α-Naphthyl-	51	α-Naphthylamine	7
	Anthranilic acid :			
2-Phenylacetyl-	*N*-Phenylacetyl-	85	—	—
2-Butyryl-	*N*-Butyryl-	77	Propylamine	5
Benzylidenephthalide	*N*-Phenylacetyl-	62	—	—
Propylidenephthalide	*N*-Butyryl-	69	Propylamine	5

* *N*-Mesitylphthalamidic acid (14%) isolated.

6-Oxo-2-phenyl- and -2-*p*-tolyl-4 : 5-benz-1 : 3-ozaxine have been obtained [1] in 80 and 88% yield, respectively, by a procedure almost identical with that of the present work. It is apparent from these results, together with those of the Table, that (apart from the reaction of 2-mesitoylbenzoic acid) the presence of groups of markedly different electronic

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* Part V, *J.*, 1956, 1498.

[1] Arcus and Coombs, *J.*, 1953, 3698.

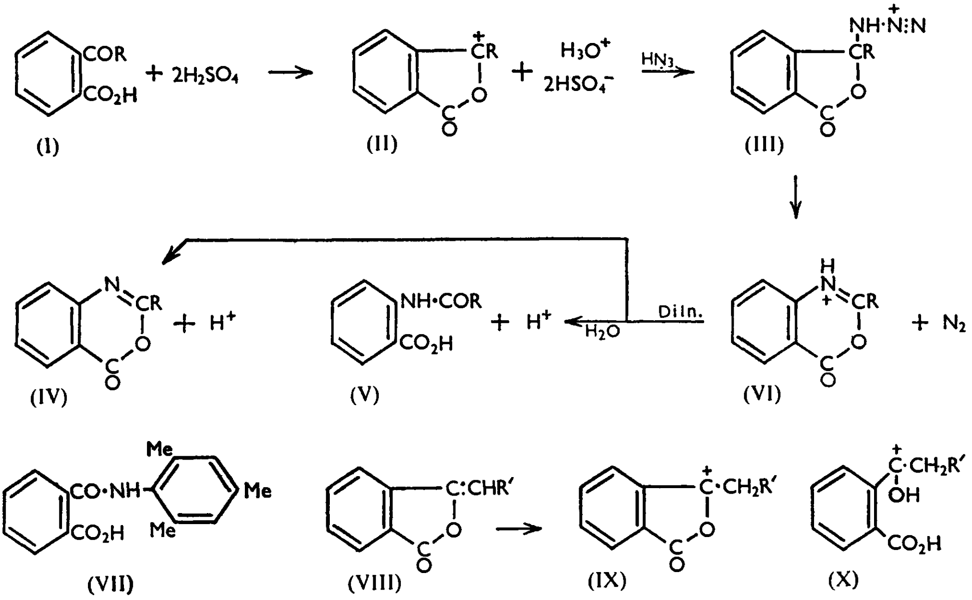
[2] Badger, Howard, and Simons, *J.*, 1952, 2849.

character (*p*-Me, *p*-MeO, *p*-Cl, *m*-NO_2) in the benzoyl group has little effect on the course of the reaction, the oxazine being isolated in 75—88% yield. The yield of oxazine from 2-α-naphthoylbenzoic acid was somewhat lower; that from 2-mesitoylbenzoic acid was comparatively small, and, unlike any other, this reaction yielded an appreciable amount of the phthalamidic acid (VII). 2-Phenylacetyl- and 2-butyryl-benzoic acid gave the *N*-acylanthranilic acids in yields which lie in the range of those of the phenyl-oxazines, above.

p-Chloro- and *m*-nitro-aniline, α-naphthylamine, and propylamine were characterised; the largest yield was that of α-naphthylamine, 7%.

By the use of procedures different from that of the present work, Badger *et al.*[2] have isolated the oxazine and *N*-α-naphthoylanthranilic acid, depending on the conditions, from the Schmidt reaction with 2-α-naphthoylbenzoic acid, and Smith[3] has obtained *N*-acetylanthranilic acid from the reaction with 2-acetylbenzoic acid.

Mechanism.—The cyclic cation (IX), which is formed from 2-phenylacetyl- and 2-butyryl-benzoic acid by the process (I) ⟶ (II), may also be formed by the protonation of the olefins benzylidene- and propylidene-phthalide (VIII); these compounds reacted similarly to the 2-acylbenzoic acids, giving the *N*-acylanthranilic acids in somewhat lower yields. That reaction succeeds with these olefins is considered to support the mechanism of reaction *via* the cyclic cation (IX), since the ion (X), derived from the protonation of the 2-acylbenzoic acid regarded simply as a ketone, could only arise by the hydration, as well as protonation, of the alkylidenephthalides, a process unlikely to occur in concentrated sulphuric acid.



Formation of N*-acylanthranilic acids.* The isolation of the N-acylanthranilic acid as end-product from the reaction when R is alkyl or aralkyl (see Table) is attributed to hydrolysis of the initially formed oxazine at the point where the chloroform–sulphuric acid reaction mixture is diluted with water. 2-Benzyl-6-oxo- and 6-oxo-2-propyl-4 : 5-benz-1 : 3-oxazine were prepared by ring closure of the corresponding *N*-acylanthranilic acids; each was then subjected to the conditions of the Schmidt reaction, but without sodium azide: hydrolysis occurred, and 97 and 88% yields, respectively, of the *N*-acylanthranilic acid were isolated.

The marked difference in ease of hydrolysis of 2-alkyl- and 2-aryl-oxobenzoxazines has

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[3] Smith, *J. Amer. Chem. Soc.*, 1954, **76**, 431.

been noted by Zentmeyer and Wagner [4] and is demonstrated by the following observations. 2-Benzyl, 2-propyl, and 2-*p*-chlorophenyl derivatives of 6-oxo-4 : 5-benz-1 : 3-oxazines were heated for 30 min. with 80% acetic acid and with 80% ethanol: from the 2-benzyl-oxazine 94 and 88% of phenylacetylanthranilic acid was isolated, and from the 2-propyl-oxazine 90 and 95% of butyrylanthranilic acid; of the *p*-chlorophenyloxazine 73 and 96% were recovered, 13% of chlorobenzoylanthranilic acid being isolated from the treatment with aqueous acetic acid.

Intermediates, and the " non-oxazine " rearrangement. It had been supposed that there might be a partition of the various products, or their precursors, in the above reactions, between the chloroform and the sulphuric acid layer. Accordingly, the following procedure was applied to the reactions with 2-*p*-chlorobenzoyl-, 2-mesitoyl-, and 2-butyrylbenzoic acid, compounds which yield as main end-products respectively oxazine, oxazine and phthalamidic acid, and *N*-acylanthranilic acid: the chloroform layer was separated at the end of the reaction, but before the addition of ice, and evaporated; in each instance it contained no solute. All the products at this stage of the above reactions are therefore present in the sulphuric acid layer, presumably as their hydrogen sulphates.

In completion of the above reactions, the separated sulphuric acid layers were added to ice; essentially the same products as those of the Table were obtained, except that the absence of chloroform as a diluent led to certain secondary reactions. The reaction with 2-*p*-chlorobenzoylbenzoic acid gave *N*-*p*-chlorobenzoylanthranilic acid together with a much reduced yield of the oxazine, a result ascribed to the hydrolysis of the oxazine, the occurrence of which, on dilution of a sulphuric acid solution of this compound, was directly confirmed. The analogous products have been obtained [1] from the Schmidt reaction with 2-benzoylbenzoic acid on dilution in the presence or absence of chloroform. The yield of 2-mesityl-6-oxo-4 : 5-benz-1 : 3-oxazine (26%) is close to that (see Table) obtained in the presence of chloroform, and no hydrolysis product was encountered; the greater resistance of this oxazine is attributed to protection of the site of hydrolysis by the *o*-methyl groups of the mesityl substituent. In one instance *N*-mesitylphthalamidic acid (22%) was obtained, but in two cases it had become cyclised to *N*-mesitylphthalimide (20%), the occurrence or absence of conversion of the phthalamidic acid into the phthalimide depending, apparently, on small variations in experimental conditions. From 2-butyrylbenzoic acid there was obtained *N*-butyrylanthranilic acid in nearly the same yield as recorded in the Table.

The mechanisms of formation of the amines and the phthalamidic acid of the Table are not completely understood; the following two points are relevant.

The extent of rearrangement with migration of the group R is seen to be greatest in the two examples (mesityl and α-naphthyl) in which R has the greatest bulk in the neighbourhood of the keto-carbon atom.

It appeared possible that the amine $R{\cdot}NH_2$ is formed by hydrolysis of the corresponding phthalamidic acid. Accordingly, *N*-*m*-nitrophenylphthalamidic acid was subjected to the conditions of the Schmidt reaction: *m*-nitroaniline (29%) was isolated, the remaining phthalamidic acid being partly recovered (39%), and in part isolated as the phthalimide. Hydrolysis of the phthalamidic acid is, therefore, too slow to account satisfactorily for the presence of the amine.

From the present and earlier results [1] it is concluded, with regard to the reaction of 2-acylbenzoic acids and alkylidenephthalides with hydrazoic and sulphuric acids, that: (*a*) The greater part of the reaction takes the following course: the protonated azide (III), formed by addition of hydrazoic acid to the cyclic cation (II), rearranges as shown to (VI); the benzoxazine is the isolated product of reaction if (i) R is aryl and (ii) chloroform is present as a protective solvent during dilution with water; in other circumstances the hydrolysis product of the oxazine, the *N*-acylanthranilic acid, is obtained. (*b*) Where $R = C_6H_4X$, the electronic character of the substituent X has little effect on the course of the reaction. (*c*) Migration of R is appreciable only when this group has exceptional bulk in the neighbourhood of the carbonyl-carbon atom.

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[4] Zentmeyer and Wagner, *J. Org. Chem.*, 1949, **14**, 967.

EXPERIMENTAL

M. p.s are corrected.

Phthalic anhydride (30 g.), anisole (22 ml.), and aluminium chloride (60 g.) yielded, by Lin Che Kin's procedure,[5] 2-*p*-methoxybenzoylbenzoic acid (37 g.), m. p. 136—138°; after recrystallisation from ethanol and from toluene it (26 g.) had m. p. 145·5—146°. Lin Che Kin records m. p. 145°.

Phthalic anhydride (30 g.), chlorobenzene (122 ml.), and aluminium chloride (64 g.), on reaction according to Groggins and Newton,[6] gave 2-*p*-chlorobenzoylbenzoic acid (45 g.), m. p. 147°; on recrystallisation from benzene it (38 g.) had m. p. 150·5—151°. These authors record m. p. 147·5°.

2-Benzoylbenzoic acid (11·3 g.), on nitration according to Basler,[7] gave a product (13·8 g.) having m. p. 136—150°. This material was recrystallised from acetic acid, then dissolved in alkali, and the solution treated with charcoal and acidified; the product, thrice recrystallised from ethanol, yielded 2-*m*-nitrobenzoylbenzoic acid (2·90 g.), m. p. 189—189·5° (Basler records m. p. 186—187°).

Phthalic anhydride (15 g.), mesitylene (15 ml.), and aluminium chloride (30 g.), on reaction in *sym*-tetrachloroethane (75 ml.) by the method indicated by Newman and McCleary,[8] yielded 2-mesitoylbenzoic acid (24 g.), m. p. 215°; on recrystallisation from aqueous ethanol it (20 g.) had m. p. 214—214·5°. These authors record m. p. 214—216°.

Phthalic anhydride (100 g.), naphthalene (130 g.), and aluminium chloride (208 g.) gave, by Heller and Schulke's method,[9] a product (165 g.), m. p. 137—150°, which was rubbed with and filtered from cold acetic acid, then recrystallised from toluene and twice from ethanol; it yielded 2-α-naphthoylbenzoic acid (50 g.), m. p. 175·5—176°. Heller and Schulke record m. p. 173°.

Benzylidenephthalide[10] (31·3 g.; m. p. 100—100·5°) was heated with a solution of potassium hydroxide (30 g.) in water (100 ml.). The cooled solution was poured into a solution of sulphuric acid (40 ml.) in water (250 ml.); the product was collected and dissolved in aqueous sodium hydrogen carbonate. This solution was acidified with dilute hydrochloric acid until a faint permanent precipitate appeared; the whole was then extracted with chloroform (4 × 30 ml.). Excess of acid was added to the solution, and the product was collected, ground, washed and dried; it (32·0 g.), m. p. 72·5—73·5°, was twice recrystallised from ethanol–water (60 : 40) and yielded 2-phenylacetylbenzoic acid monohydrate (24·2 g.), m. p. 74·5—75° (Found: equiv., 259. Calc. for $C_{14}H_{11}O\cdot CO_2H,H_2O$: equiv., 258). Gabriel and Michael[11] record m. p. 74—75° for the monohydrate.

From phthalic anhydride (58·5 g.), butyric anhydride (125 g.), and sodium acetate (32·5 g.) there was prepared, by the procedure of Ullyot, Taylor, and Dawson,[12] propylidenephthalide (41 g.), b. p. 146—149°/4 mm. It contained needles of phthalic anhydride, which was removed as follows: the material was dissolved in ethanol (40 ml.) and 0·12N-sodium hydroxide was added until, when spotted on to phenolphthalein paper, the mixture proved alkaline. By this procedure phthalic anhydride would be expected to be quantitatively converted into sodium ethyl phthalate.[13] The solution was extracted with chloroform (2 × 50 ml.), and the extract was washed, dried (Na_2SO_4), and evaporated; the product gave, on distillation, propylidenephthalide (28 g.), b. p. 149—150°/4 mm., n_D^{20} 1·5824.

Propylidenephthalide (22·9 g.) was converted by the method of Ullyot *et al.*[12] into 2-butyrylbenzoic acid (23·2 g.), m. p. 84—85°; after purification *via* solution in aqueous sodium hydrogen carbonate, and two recrystallisations from ether–light petroleum (b. p. 40—60°), it (11·7 g.) had m. p. 90·5—91° (these authors record m. p. 86—89°).

Schmidt Reactions.—The above 2-acylbenzoic acids and alkylidenephthalides were subjected to the Schmidt reaction by the following standardised procedure. The names of products are given in square brackets at the points where, when present in sufficient amount, they were isolated.

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[5] Lin Che Kin, *Ann. Chim.* (*France*), 1940, **11**, 317.
[6] Groggins and Newton, *Ind. Eng. Chem.*, 1929, **21**, 369.
[7] Basler, D.R.-P. 148,110.
[8] Newman and McCleary, *J. Amer. Chem. Soc.*, 1941, **63**, 1540.
[9] Heller and Schulke, *Ber.*, 1908, **41**, 3633.
[10] *Org. Synth.*, Coll. Vol. II, 1st. Edn., p. 61.
[11] Gabriel and Michael, *Ber.*, 1878, **11**, 1018.
[12] Ullyot, Taylor, and Dawson, *J. Amer. Chem. Soc.*, 1948, **70**, 542.
[13] Anderson and Kenyon, *ibid.*, p. 3952.

Sulphuric acid (98%; 15 ml.) was added dropwise to a stirred, ice-cooled mixture of sodium azide (2·6 g., 0·040 mole) and chloroform (15 ml.). After a further 15 min., the ice was replaced by a water-bath maintained at 30°, and the 2-acylbenzoic acid or the alkylidenephthalide (0·0200 mole), in suspension or solution in chloroform (20 ml.), was added during 1 hr.; stirring was continued for 2 hr., the mixture was then poured on ice (200 g.). The whole, together with washes of water and chloroform (25 ml.), was shaken mechanically for ½ hr., and filtered [*N*-mesitylphthalamidic acid, and the bulk of the *N*-phenylacetylanthranilic acid]. The aqueous layer was extracted with chloroform (2 × 25 ml.), and the combined chloroform solutions were twice extracted with saturated aqueous sodium hydrogen carbonate, washed with water, dried (Na_2SO_4), and the solvent distilled [benzoxazines].

The sodium hydrogen carbonate extract was acidified with dilute hydrochloric acid, and the product filtered off [*N*-phenylacetyl- and *N*-butyryl-anthranilic acid].

The acidic aqueous solution was concentrated by distillation, filtered, brought to pH 10 with sodium hydroxide solution, and extracted with ether (2 × 50, 2 × 25 ml.). The extract was dried (Na_2SO_4), and the ether distilled [amines].

2-*p*-Methoxybenzoylbenzoic acid [(i), (ii) 5·12 g.)] yielded 2-*p-methoxyphenyl*-6-*oxo*-4 : 5-*benz*-1 : 3-*oxazine* [(i) 3·68, (ii) 3·87 g., from ethanol], needles, m. p. 157·5—158°, which had m. p. 158·5° after further recrystallisation (Found: C, 71·0; H, 4·45; N, 5·7. $C_{15}H_{11}O_3N$ requires C, 71·4; H, 4·4; N, 5·55%).

2-*p*-Chlorobenzoylbenzoic acid [(i), (ii) 5·21 g.] gave 2-*p*-chlorophenyl-6-oxo-4 : 5-benz-1 : 3-oxazine [(i) 4·31, (ii) 4·35 g., from *n*-butanol], m. p. 191° (Found: N, 5·55; Cl, 14·1. Calc. for $C_{14}H_8O_2NCl$: N, 5·45; Cl, 13·75%). Zentmeyer and Wagner[4] record m. p. 190°. There was also isolated an aromatic amine [(i) 0·07, (ii) 0·06 g.] having m. p. 62·5—63·5°, and m. p. 63—66° when mixed with *p*-chloroaniline of m. p. 70—71°; its benzoyl derivative, recrystallised from aqueous ethanol, had m. p. 192—193° alone and when mixed with *N*-benzoyl-*p*-chloroaniline of m. p. 194—194·5°.

2-*m*-Nitrobenzoylbenzoic acid [(i), (ii) 5·42 g.] yielded 2-*m*-nitrophenyl-6-oxo-4 : 5-benz-1 : 3-oxazine [(i) 4·61, (ii) 4·73 g., from *n*-butanol], m. p. 169·5—170° (Bogert, Gortner, and Amend[14] record m. p. 167—168°) (Found: N, 10·5. Calc. for $C_{14}H_8O_4N_2$: N, 10·45%). There was also isolated *m*-nitroaniline [(i) 0·11, (ii) 0·09 g.], having m. p. 113—114° alone and when mixed with an authentic specimen; its benzoyl derivative had m. p. 158° alone and when mixed with authentic *N*-benzoyl-*m*-nitroaniline.

2-Mesitoylbenzoic acid [(i), (ii) 5·36 g.] gave 2-*mesityl*-6-*oxo*-4 : 5-*benz*-1 : 3-*oxazine* [(i) 1·66, (ii) 1·39 g., from ethanol], m. p. 138—139°, which after two recrystallisations formed pale yellow plates, m. p. 142° (Found: C, 76·65; H, 5·7; N, 5·55. $C_{17}H_{15}O_2N$ requires C, 76·95; H, 5·7; N, 5·3%). There was also obtained N-*mesitylphthalamidic acid* [(i) 0·64 g., from ethanol; (ii) 1·01 g. from dioxan], m. p. 191·5—193° (decomp.) (the m. p. varied with the rate of heating) (Found: C, 72·5; H, 6·25; N, 5·3%; equiv., 282. $C_{16}H_{16}ON{\cdot}CO_2H$ requires C, 72·05; H, 6·05; N, 4·95%; equiv., 283). It (0·1 g.) was heated under reflux for ½ hr. with glacial acetic acid (1·3 ml.); to the cold solution water was added, the whole was warmed, and on cooling there separated needles of *N*-mesitylphthalimide having m. p. 180·5°, unaltered by recrystallisation from aqueous acetic acid and by admixture with an authentic specimen of the same m. p.

2-α-Naphthoylbenzoic acid [(i), (ii), (iii) 5·52 g.] yielded 2-α-naphthyl-6-oxo-4 : 5-benz-1 : 3-oxazine [(i) 2·51, (ii) 3·08, (iii) 2·78 g.], m. p. 137—138°; after recrystallisation, with charcoal treatment, from ethanol, it formed golden needles, m. p. 138° (Found: N, 5·1. Calc. for $C_{18}H_{11}O_2N$: N, 5·15%). Badger *et al.*[2] record m. p. 134°. There was also isolated a base [(i) 0·20, (ii) 0·15, (iii) 0·23 g.] which yielded a benzoyl derivative having m. p. 159·5° alone, and m. p. 161·5—162° when mixed with benzo-α-naphthalide of m. p. 162—162·5°.

Benzylidenephthalide [(i), (ii) 4·44 g.] and 2-phenylacetylbenzoic acid [(iii), (iv) 5·16 g.] both gave *N*-phenylacetylanthranilic acid [(i) 2·64, (ii) 2·11, (iii) 4·07, (iv) 3·86 g., from ethanol–water (1 : 1)], m. p. 186—189·5°; after further recrystallisation it had m. p. 189·5—190° (Diesbach *et al.*[15] record m. p. 188°) (Found: C, 70·35; H, 5·05; N, 5·6%; equiv., 255. Calc. for $C_{14}H_{12}ON{\cdot}CO_2H$: C, 70·5; H, 5·15; N, 5·5%; equiv., 255). The chloroform solutions from these experiments yielded a non-homogeneous material [(i) 0·23, (iii) 0·33, (iv)0·64 g.] which may have contained the oxazine since, by the following ring-opening procedure,[1] it gave *N*-phenylacetylanthranilic acid. The material was heated at 50° for 1 min. with trichloroacetic acid (2 g.) and sulphuric acid (0·8 ml.); the solution was poured into water, and the precipitate was

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[14] Bogert, Gortner, and Amend, *J. Amer. Chem. Soc.*, 1911, **33**, 952.

[15] Diesbach, Gross, and Tschannen, *Helv. Chim. Acta*, 1951, **34**, 1050.

recrystallised from aqueous ethanol. The specimens of *N*-phenylacetylanthranilic acid so obtained [(i) 0·10, (iii) 0·11, (iv) 0·40 g.] had m. p.s 182·5—187° and m. p.s 186—189° when mixed with the acid above.

Propylidenephthalide [(i), (ii) 3·48 g.] and 2-butyrylbenzoic acid [(iii), (iv) 3·84 g.] both gave *N*-butyrylanthranilic acid [(i) 2·89, (ii) 2·76, (iii) 3·24, (iv) 3·11 g.], m. p. 117·5—118·5°; after recrystallisation from ethanol–water (1 : 1) it had m. p. 118·5—119° (Found: equiv., 209. Calc. for $C_{10}H_{12}ON{\cdot}CO_2H$: equiv., 207). Pictet and Du Parc[16] record m. p. 117°. In these experiments the acidic aqueous solution was concentrated, made alkaline, and distilled in steam; aqueous sodium hydroxide was added to the distillate which was then shaken with benzoyl chloride (0·7 ml.) and thrice extracted with ether. The latter yielded specimens of *N*-propylbenzamide [(i) 0·15, (ii) 0·19, (iii) 0·11, (iv) 0·25 g.] which, after recrystallisation from benzene–light petroleum (b. p. 60—80°), had m. p.s in the range 77—83° alone and when mixed with an authentic specimen of m. p. 83°.

N-Phenylacetylanthranilic acid (5·0 g.) and acetic anhydride (15 ml.) were heated under reflux for 30 min.; after distillation of acetic acid and acetic anhydride, finally under reduced pressure, the product was recrystallised from anhydrous methanol; it yielded *2-benzyl-6-oxo-4 : 5-benz-1 : 3-oxazine* (3·35 g.), needles, m. p. 90·5° (Found: C, 75·8; H, 4·8; N, 5·75. $C_{15}H_{11}O_2N$ requires C, 75·9; H, 4·65; N, 5·9%). This oxazine (1·18 g., 0·0050 mole) was subjected to the Schmidt reaction procedure on $\frac{1}{4}$ scale (sodium azide omitted), and gave *N*-phenylacetylanthranilic acid (1·23 g.), m. p. 182°; after recrystallisation from aqueous ethanol it (0·96 g.) had m. p. 187·5—188° alone and when mixed with an authentic specimen.

The oxazine (0·80 g.) was heated on a steam-bath with acetic acid–water (4 : 1; 8 ml.) for 30 min. On cooling, there separated *N*-phenylacetylanthranilic acid (0·81 g.), m. p. and mixed m. p. 188°. A similar experiment with ethanol–water (4 : 1) gave this acid (0·76 g.) having m. p. and mixed m. p. 188·5—189°.

N-Butyrylanthranilic acid, on being heated with acetic anhydride according to Zentmeyer and Wagner,[4] was converted into 6-oxo-2-propyl-4 : 5-benz-1 : 3-oxazine, which after two recrystallisations from methanol had m. p. 58·5° (the above authors record m. p. 59—60°). This oxazine (0·95 g., 0·0050 mole) was subjected to the Schmidt procedure on $\frac{1}{4}$ scale (sodium azide omitted); there was obtained *N*-butyrylanthranilic acid (0·91 g.) having m. p. 113·5° and mixed m. p. 115°.

This oxazine (0·95 g.) was treated as above with aqueous acetic acid (9·5 ml.). No solid separated from the cold solution, but addition of water gave a precipitate of *N*-butyrylanthranilic acid (0·96 g.) which had m. p. and mixed m. p. 116°. The oxazine (0·80 g.) was heated as above with aqueous ethanol (8 ml.); the cold solution was thrice extracted with chloroform, which yielded *N*-butyrylanthranilic acid (0·82 g.) m. p. 112° and mixed m. p. 114·5—115°.

2-*p*-Chlorophenyl-6-oxo-4 : 5-benz-1 : 3-oxazine (1·00 g.) was treated as above with aqueous acetic acid (10 ml.). After cooling, the mixture was filtered, yielding a product (0·92 g.), m. p. 177—182°, which was dissolved in chloroform (30 ml.); the solution was twice extracted with aqueous sodium hydrogen carbonate, washed with water, and dried. It yielded the oxazine (0·73 g.), m. p. and mixed m. p. 188·5°. From the sodium hydrogen carbonate solution a solid (m. p. > 300°) separated which on treatment with dilute hydrochloric acid gave a product (0·14 g.) having m. p. 207° (Zentmeyer and Wagner[4] record m. p. 204—205° for *N*-*p*-chlorobenzoylanthranilic acid).

This oxazine (1·00 g.) was heated as above with aqueous ethanol (10 ml.); it (0·96 g.) was recovered, having m. p. and mixed m. p. 189·5°.

Three Schmidt reactions were carried out by the procedure above, except that, at the end of the reaction, the chloroform and the sulphuric acid layers were separated. The latter was washed with chloroform (2 × 25 ml.), and the combined chloroform solutions were filtered and evaporated; in each instance they gave no residue. The sulphuric acid layer was poured on ice.

(1) 2-*p*-Chlorobenzoylbenzoic acid yielded material (5·30 g.), m. p. 182—184°, which was stirred with chloroform (150 ml.); the latter was filtered, twice washed with aqueous sodium hydrogen carbonate, dried, and evaporated; it gave a product (0·36 g.) which on recrystallisation from ethanol yielded 2-*p*-chlorophenyl-6-oxo-4 : 5-benz-1 : 3-oxazine (0·23 g.), m. p. 189·5°. The chloroform-insoluble material (4·18 g.) and that obtained on acidification of the sodium hydrogen carbonate solution (0·56 g.) after two recrystallisations from aqueous ethanol gave *N*-*p*-chlorobenzoylanthranilic acid (3·46 g.), m. p. 207·5°.

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[16] Pictet and Du Parc, *Ber.*, 1887, **20**, 3421.

2-*p*-Chlorophenyl-6-oxo-4 : 5-benz-1 : 3-oxazine (2·00 g.) was dissolved in sulphuric acid (6 ml.), and the solution was kept at 30° for 30 min., and then poured on ice; the solid which separated was recrystallised from aqueous ethanol, yielding *N*-*p*-chlorobenzoylanthranilic acid (1·68 g.), m. p. 207·5°.

(2) The diluted sulphuric acid layer from the reaction with 2-mesitoylbenzoic acid [(i)—(iii) 2·68 g., 0·0100 mole] was shaken with chloroform (50 ml.), and the whole was filtered. The chloroform solution was separated, washed with aqueous sodium hydrogen carbonate, and with water, and dried. It yielded 2-mesityl-6-oxo-4 : 5-benz-1 : 3-oxazine [(i) 0·77, (ii) 0·60, (iii) 0·70 g., from ethanol], m. p. 134—136° and, on further recrystallisation, m. p. 139°, mixed m. p. 139·5—140°. The material which was insoluble in dilute sulphuric acid and in chloroform was recrystallised from aqueous dioxan; in two experiments it yielded *N*-mesitylphthalimide [(i) 0·61, (iii) 0·45 g.] having m. p. 178—179°, and on further recrystallisation m. p. 180° alone and when mixed with an authentic specimen of the same m. p.; in (ii) it gave *N*-mesitylphthalamidic acid (0·62 g.), m. p. 191·5—192·5° (decomp.) raised by further recrystallisation to 193·5—194° (decomp.).

(3) 2-Butyrylbenzoic acid yielded *N*-butyrylanthranilic acid (3·19 g.), m. p. 115°.

N-*m*-Nitrophenylphthalamidic acid [(i), (ii) 0·36 g., m.p. 206·5° (decomp.); Meyer and Lüders [17] record m. p. 201° (decomp.)], sulphuric acid (98%, 15 ml.), and chloroform (35 ml.) were stirred for 2 hr. at 30°, and the mixture was then treated as in the Schmidt procedure. The following were obtained. Insoluble in chloroform and dilute sulphuric acid : unchanged *N*-*m*-nitrophenylphthalamidic acid [(i), (ii) 0·14 g.], m. p. 206° (decomp.). From chloroform : material [(i) 0·11, (ii) 0·10 g.] which, on crystallisation from ethanol, yielded *N*-*m*-nitrophenylphthalimide, m. p. 246° and m. p. 246·5° when mixed with an authentic specimen of m. p. 246·5—247°. From the acidic aqueous solution : *m*-nitroaniline [(i), (ii) 0·04 g.], m. p. 107—111°, and, on recrystallisation from water, m. p. and mixed m. p. 111·5—112°.

Thanks are expressed to the Governing Body of Battersea Polytechnic for an Edward Tate and Holl Scholarship (to R. E. M.), and to the Government Grants Committee of the Royal Society and Imperial Chemical Industries Limited for grants.

Battersea Polytechnic, London, S.W.11. [*Received, November 8th,* 1955.]

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[17] Meyer and Lüders, *Annalen*, 1918, **415**, 48.