743. *The Mechanism of the Schmidt Reaction with* o-*Benzoylbenzoic Acid.*

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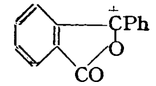
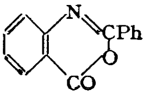
The interaction of *o*-benzoylbenzoic acid with hydrazoic and sulphuric acids yields 6-oxo-2-phenyl-4 : 5-benz-1 : 3-oxazine (II); *N*-benzoylanthranilic acid (Badger, Howard, and Simons, *J.*, 1952, 2849) arises from a subsequent hydrolysis. A mechanism for the reaction is proposed in which the oxazine is formed by ring-expansion from the cyclic cation (I).

(I)

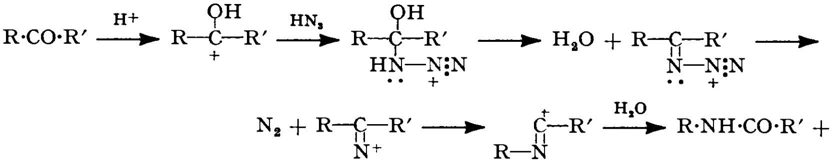




(II)

2-*p*-Toluoylbenzoic acid, by a similar reaction, yields 6-oxo-2-*p*-tolyl-4 : 5-benz-1 : 3-oxazine.

Badger, Howard, and Simons (*J.*, 1952, 2849) have allowed *o*-benzoylbenzoic acid in solution in trichloroacetic acid, and also in chloroform, to react with hydrazoic acid in the presence of sulphuric acid: the reaction mixtures were finally poured into water. From the reaction in trichloroacetic acid there was obtained *N*-benzoylanthranilic acid (91%); reaction in chloroform gave this acid and 6-oxo-2-phenyl-4 : 5-benz-1 : 3-oxazine (II) in 31% and 67% yield respectively. These authors envisage the reaction as that of a substituted benzophenone, and have adopted (and slightly modified) a mechanism which Smith and his co-workers (*J. Amer. Chem. Soc.*, 1948, **70**, 320; 1950, **72**, 2503, 3718) have proposed for ketones:



$$\mathrm{R{\cdot}CO{\cdot}R'} \xrightarrow{\mathrm{H^+}} \mathrm{R{-}\overset{OH}{\underset{+}{C}}{-}R'} \xrightarrow{\mathrm{HN_3}} \mathrm{R{-}\overset{OH}{\underset{H\ddot{N}-N{:}\overset{}{N}^{+}}{C}}{-}R'} \longrightarrow \mathrm{H_2O} + \mathrm{R{-}\underset{\ddot{N}-N{:}N^{+}}{\overset{}{C}}{-}R'} \longrightarrow$$

$$\mathrm{N_2} + \mathrm{R{-}\underset{N^+}{C}{-}R'} \longrightarrow \mathrm{\underset{R-N}{\overset{+}{C}}{-}R'} \xrightarrow{\mathrm{H_2O}} \mathrm{R{\cdot}NH{\cdot}CO{\cdot}R'} + \mathrm{H^+} \quad . \quad (1)$$

($R = o\text{-}C_6H_4{\cdot}CO_2H$, $R' = Ph$.)

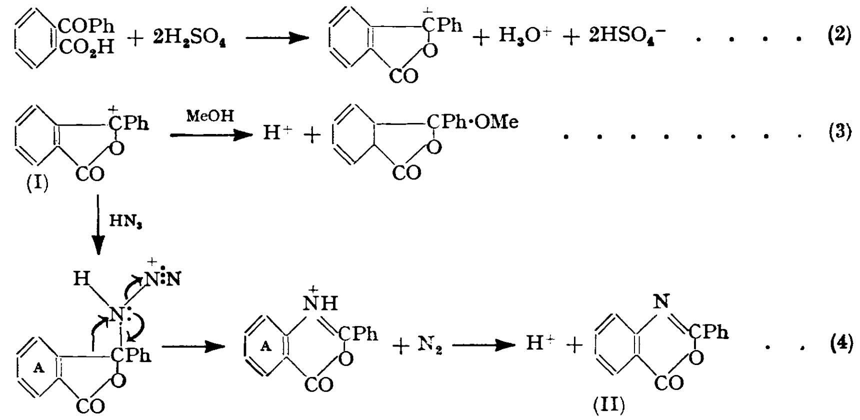
We have repeated the reaction using the trichloroacetic acid method of Badger *et al.*, and obtained *N*-benzoylanthranilic acid (78%); by a modified procedure using chloroform as solvent the oxazine was obtained in 80% yield. The following facts relating to the reaction have been ascertained:

The oxazine, when its solution in trichloroacetic–sulphuric acid is diluted with water, becomes largely hydrolysed to *N*-benzoylanthranilic acid. If the acid solution is diluted with chloroform and the mixture shaken with cold water, the oxazine can be recovered nearly quantitatively and, when the acidic solution from the Schmidt reaction in trichloroacetic acid is similarly treated, the oxazine (91%) is obtained. The oxazine is thus the actual product of the interaction of *o*-benzoylbenzoic acid with hydrazoic–sulphuric acid in both trichloroacetic acid and chloroform.

N-Benzoylanthranilic acid, in either chloroform or trichloroacetic acid, undergoes ring closure when treated with sulphuric acid, as in the Schmidt reaction procedure; the oxazine can be isolated in good yield from the former solvent, and also from the latter provided that chloroform is added as a diluent.

Newman, Kuivila, and Garrett (*ibid.*, 1945, **67**, 704) have found that *o*-benzoylbenzoic acid in solution in sulphuric acid has a van't Hoff *i* factor of 3·8, in agreement with ionisation according to equation (2), which requires $i = 4$. Further evidence for the cyclic structure of the cation is provided by the observation (Newman, *ibid.*, 1942, **64**, 2324) that considerable methyl *pseudo*-*o*-benzoylbenzoate is formed (reaction 3) when a solution of *o*-benzoylbenzoic acid in sulphuric acid is poured into methanol.

It is now suggested that 6-oxo-2-phenyl-4 : 5-benz-1 : 3-oxazine arises from the interaction of the cation (I) with hydrazoic acid, followed by a ring-expansion (4), closely analagous to that occurring during the formation of phenanthridine by the reaction of hydrazoic–sulphuric acid with fluoren-9-ol (Arcus and Mesley, *J.*, 1953, 178). The four electrons initially present as the A–CPh bond and the nitrogen lone-pair appear finally as the A–$\overset{+}{\text{N}}$H bond and the π-electrons of the $\overset{+}{\text{N}}$H═CPh bond.



It has been found (above) that *N*-benzoylanthranilic acid is converted into the oxazine under the conditions of the Schmidt reaction in either chloroform or trichloroacetic acid, whence the possibility cannot be excluded that reaction proceeds by mechanism (1), followed by ring closure of the acid. However, in view of the evidence of Newman *et al.* for the cyclic structure of the cation, it is concluded that mechanism (3) (which results directly in the oxazine) is the more probable.

The migratory aptitudes shown by different groups during the Schmidt reaction of ketones have been studied by Badger and Smith and their co-workers (*locc. cit.*) and by Westland and McEwen (*J. Amer. Chem. Soc.*, 1952, **74**, 6141); mechanism (4) implies that the migratory aptitude of the *o*-carboxyphenyl group cannot properly be compared with the aptitudes of groups which do not interact with the carbonyl group.

2-*p*-Toluoylbenzoic acid (in solution in chloroform) reacted with hydrazoic–sulphuric acid to yield 6-oxo-2-*p*-tolyl-4 : 5-benz-1 : 3-oxazine.

EXPERIMENTAL

The Schmidt Reaction.—*o-Benzoylbenzoic acid.* Badger, Howard, and Simons (*loc. cit.*) refer to their procedure with trichloroacetic acid as method *B*, and to that with chloroform as method *A*; these designations have been retained.

o-Benzoylbenzoic acid (4·52 g.) yielded, by method *B*, *N*-benzoylanthranilic acid (3·75 g., 78%), m. p. 176—178°. This reaction was repeated, but the acidic solution was poured into chloroform (200 ml.). The chloroform solution was washed with water and with aqueous sodium hydrogen carbonate, dried (Na_2SO_4), and evaporated. 6-Oxo-2-phenyl-4 : 5-benz-1 : 3-oxazine (4·05 g., 91%), m. p. 120°, was obtained; after recrystallisation from ethanol, it (2·8 g.) had m. p. 123°.

o-Benzoylbenzoic acid (4·52 g.), subjected to the Schmidt reaction by the method (*A'*) described below for 2-*p*-toluoylbenzoic acid, yielded 6-oxo-2-phenyl-4 : 5-benz-1 : 3-oxazine (3·55 g., 80%), m. p. 122·5° (Found: C, 75·5; H, 4·4; N, 6·3. Calc. for $C_{14}H_9O_2N$: C, 75·3; H, 4·1; N, 6·3%).

Hydrolysis and Ring Closure.—(*a*) 6-Oxo-2-phenyl-4 : 5-benz-1 : 3-oxazine (3·05 g.) gave, by method *B* (sodium azide omitted), *N*-benzoylanthranilic acid (3·05 g., 93%), m. p. 177°.

(*b*) *N*-Benzoylanthranilic acid (2·25 g.) yielded, by method *A'* (sodium azide omitted), 6-oxo-2-phenyl-4 : 5-benz-1 : 3-oxazine (1·85 g., 89%), m. p. 123°.

(*c*) The oxazine (0·30 g.) was heated with trichloroacetic acid (2·0 g.) and sulphuric acid (0·8 ml.) for 1 min. to 50° and the solution was poured into water. The precipitate was filtered off, washed, and dried; it yielded *N*-benzoylanthranilic acid (0·26 g., 80%), m. p. 177°. A similar experiment, but with heating for 4 hr. at 50°, gave *N*-benzoylanthranilic acid (0·20 g., 62%), m. p. 178°. The oxazine was recovered unchanged after it had been kept overnight in a refrigerator together with the diluted mixed acids, a process which forms part of procedure *B*.

(*d*) A solution of the oxazine, prepared and heated as in (*c*), was poured into chloroform (25 ml.). From the chloroform solution, treated as described for the Schmidt reaction, the oxazine (0·25 g., 83%) was recovered. From a similar experiment, but with heating for 4 hr. at 50°, the oxazine (0·28 g., 93%), m. p. 121°, was recovered.

(*e*) *N*-Benzoylanthranilic acid (0·50 g.), trichloroacetic acid (4·0 g.), and sulphuric acid (0·75 ml.) were heated to 50°; the solution was treated as in (*d*). 6-Oxo-2-phenyl-4 : 5-benz-1 : 3-oxazine (0·38 g., 82%), m. p. 121°, was obtained.

2-p-*Toluoylbenzoic Acid.*—Sulphuric acid (98%; 15 ml.) was added dropwise to a stirred mixture of sodium azide (2·6 g.) and chloroform (15 ml.) at 0°. A solution of 2-*p*-toluoylbenzoic acid (4·8 g.) in chloroform (15 ml.) was added at 30° during 1 hr.; stirring was continued for 2 hr. at this temperature and the mixture was then poured into cold water (250 ml.). The chloroform layer was separated, washed with aqueous sodium carbonate and with water, dried (Na_2SO_4), and evaporated; the product, on recrystallisation from ethanol, yielded 6-oxo-2-*p*-tolyl-4 : 5-benz-1 : 3-oxazine (4·15 g., 88%), m. p. 155° (Found: C, 76·1; H, 4·7; N, 6·1. Calc. for $C_{15}H_{11}O_2N$: C, 76·0; H, 4·7; N, 5·9%). Zentmeyer and Wagner (*J. Org. Chem.*, 1949, **14**, 967), who prepared this compound by heating *N*-toluoylanthranilic acid with acetic anhydride, record m. p. 154·5°.

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