[Contribution from the George Herbert Jones Laboratory, the University of Chicago]

REACTIONS OF ATOMS AND FREE RADICALS IN SOLUTION. XXXII. REACTION OF FREE BENZOYL RADICALS WITH PYRIDINE IN THE PRESENCE OF BENZALDEHYDE (PRELIMINARY PAPER)

M. S. KHARASCH, DANIEL SCHWARTZ, MARKUS ZIMMERMANN, and W. NUDENBERG

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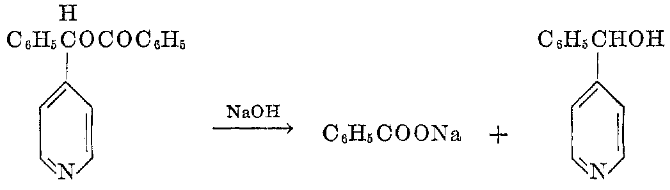
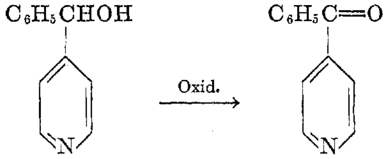
It is well-established that heating benzaldehyde with *tert*-butyl peroxide (1) or acetyl peroxide (2) gives rise to a mixture of *meso* and racemic forms of hydrobenzoin dibenzoate and some unidentified oil. However, when to a mixture of benzaldehyde (1.2 moles) and pyridine (1 mole) heated to 141°, *tert*-butyl peroxide (0.3 mole) dissolved in benzaldehyde (0.4 mole), is slowly added, only a small amount of hydrobenzoin dibenzoate is obtained. The reaction product is an equimolecular mixture of basic material (**A**), and a neutral material (**B**). A small amount of benzoic acid is also formed in the reaction. The basic material (**A**) was shown to be 4-(α-benzoxybenzyl)pyridine by analyses and conversion to 4-benzoylpyridine.



(Compound **A**)

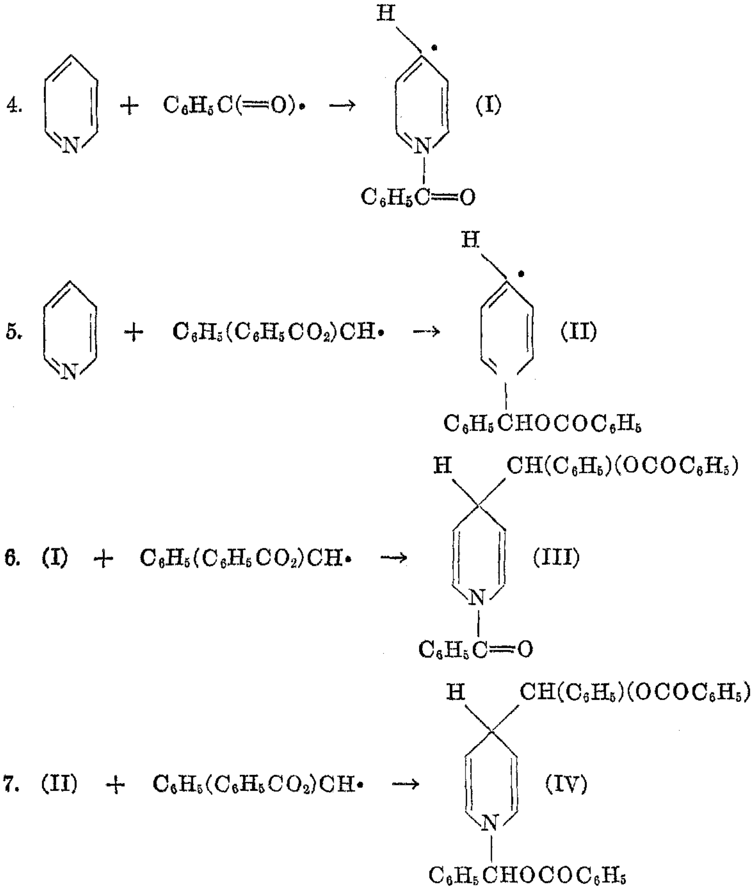


The structure of Compound **B** (neutral material) is as yet unknown. When hydrolyzed with base, Compound **B** gave benzoic acid (*ca.* 67%), phenyl-4-pyridylcarbinol (21%) and a neutral material (14%) which could not be crystallized.

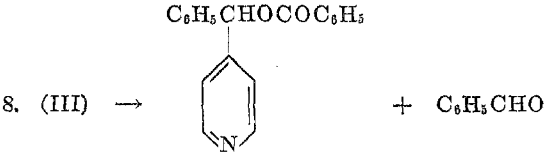
DISCUSSION

Because the structure of Compound **B** is as yet unknown, it is difficult to formulate a reaction mechanism to account for the formation of Compounds **A** and **B**. However, the hydrolysis of Compound **B** to give about 67% benzoic acid and phenyl-4-pyridylcarbinol (hydrolysis product of Compound **A**) suggests that perhaps Compound **B** (Compound III or Compound IV, below) is the precursor of Compound **A**. Of the many ways whereby the formation of these products could be formulated, we prefer, at this time, the reaction scheme indicated below:

1. $[(CH_3)_3CO]_2 \xrightarrow{\Delta} 2(CH_3)_3CO\cdot$
2. $C_6H_5CHO + (CH_3)_3CO\cdot \rightarrow (CH_3)_3COH$ (or $CH_4 + CH_3COCH_3$) $+ C_6H_5C(=O)\cdot$
3. $C_6H_5C(=O)\cdot + C_6H_5CHO \rightarrow C_6H_5(C_6H_5CO_2)CH\cdot$



Compounds III and IV could break down thermally.



(Compound **A**)

9. (IV) → Compound **A** + $C_6H_5CH_2OCOC_6H_5$

Alternatively Compound **A** could be formed by oxidation of the γ-hydrogen atom of the pyridine molecule of either Compound III or of Compound IV.

We hope to elucidate this mechanism (as well as reactions of the free benzoyl radical with other heterocyclic systems) in a subsequent publication.

EXPERIMENTAL

Reaction of benzaldehyde with pyridine in the presence of tert-butyl peroxide. A mixture of benzaldehyde (1.2 moles) and pyridine (1 mole) (mixture A) was placed in a three-necked flask fitted with a dropping-funnel, an efficient stirrer, a thermometer, and a Vigreux column equipped with a fractionation take-off. The outlet of the column was connected to a Dry-Ice trap, and a vessel for collection of the gas generated in the reaction. The air in the apparatus was displaced by nitrogen gas, and the flask was immersed in an oil-bath maintained at 141°. To this mixture a solution of *tert*-butyl peroxide (0.3 mole) in benzaldehyde (0.4 mole) (mixture B) was slowly added through a dropping-funnel. At the end of 1.5 hours, the temperature in the flask started to drop. The *tert*-butyl alcohol formed in the reaction was then removed through the column. More mixture B was then added until a drop in temperature was noted, and the procedure described above repeated. (The yield of the final product depends on the care exercised in decomposing the *tert*-butyl peroxide without loss of the material during the removal of the *tert*-butyl alcohol, and the length of time of heating the reaction mixture. Thus, in an experiment in which 0.31 mole of *tert*-butyl peroxide was consumed, the yield, after removal of the unchanged pyridine and benzaldehyde at reduced pressure, was 30 g. (In another experiment, consuming 0.62 mole of *tert*-butyl peroxide, 102 g. of material was obtained.)[1] During the decomposition of the *tert*-butyl peroxide, small amounts of methane (*ca.* 10% on the basis of the peroxide used) and acetone are formed in addition to the *tert*-butyl alcohol.

The material obtained after removal of the volatile compounds (30 g.) is a dark-red oil.

The oil, after extraction of benzoic acid (0.2 g.), can be separated into a basic fraction (**A**) and a neutral fraction (**B**) by (*a*) extraction of the solution of the oil in ether with 2 *N* hydrochloric acid; (*b*) preparation of a chromatogram on alumina. The basic compound (**A**), by either procedure of separation, amounts to about 40–50% of the total product formed in the reaction.

Compound **A**, when isolated by extraction with acid, may be obtained in pure condition by crystallization from hexane, or, still better, by a chromatogram on alumina. When ether is used as the eluent it is obtained in the form of a white crystalline compound. After a single crystallization from *n*-hexane the compound melts sharply at 87–88°.

Proof of structure of Compound **A** [*4-(α-benzoxybenzyl)pyridine*]. (*a*) The analytical data are consistent with the formulation of Compound **A** as 4-(α-benzoxybenzyl)pyridine.

Anal. Calc'd for $C_{19}H_{15}NO_2$: C, 78.87; H, 5.23; N, 4.84; Mol. Wt., 289.

Found: C, 78.8; H, 5.24; N, 5.0; Mol. Wt., 285.

A solution of Compound **A** in alcohol gives an immediate precipitate with an alcoholic solution of picric acid. The picrate (m.p. 157.5°) is rather insoluble in alcohol and changes color when exposed to light.

(*b*) *Hydrolysis of compound* **A**. Compound **A** (0.5 g.) was dissolved in 25 ml. of alcohol. A solution of sodium hydroxide (3 g.) in 25 ml. of water was then added, and the mixture was heated for four hours. Alcohol was removed at reduced pressure, and the remaining solution was extracted twice with ether. Upon evaporation of the combined ether extracts an oil was obtained. Upon standing in an evacuated desiccator the oil was converted to a solid crystalline material (0.3 g.). The material melted, before crystallization, at 124°. The melting point of phenyl-4-pyridylcarbinol reported in the literature is 126°.

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[1] In this experiment about 0.5 g. of *meso* and racemic forms of hydrobenzoin dibenzoate was obtained.

The alkaline solution was acidified and extracted four times with ether. The ether extracts were combined, dried, and evaporated. The residue (0.19 g.) was a solid melting at 122°; it did not depress the melting point of an authentic sample of benzoic acid.

(*c*) *Oxidation of phenyl-4-pyridylcarbinol.* The material obtained from the hydrolysis of Compound **A**, presumably phenyl-4-pyridylcarbinol (0.26 g.) was suspended in water, and potassium permanganate was added to it. The mixture was heated on a water-bath to 70° for three hours, and then for 30 minutes at 100°. The mixture was then extracted with benzene. Upon concentration of the benzene solution a crystalline material (m. 72°) separated (0.25 g.). It formed a picrate which melted at 160°. The melting points are the same as those recorded in the literature for 4-benzoylpyridine and its picrate.

Examination of neutral fraction (**B**). The neutral fraction (**B**), obtained after removal of the basic material with acid, is an oil which could not be crystallized. When chromatogrammed on alumina, benzene eluted a small amount (*ca.* 1.5%) of meso-hydrobenzoin dibenzoate (m.p. 247°). A mixture of ether and alcohol (2%) eluted a light oil, which had a mol. wt. of about 490 and which gave the following values on analyses: C, 77.4; H, 5.8. It made little difference whether the original oil or the oil obtained from the chromatogram was hydrolyzed with alkali in alcohol. The reaction mixture when worked up gave the following materials: benzoic acid (67%); Compound **A** (21%) and a neutral material (14%). The neutral material again could not be crystallized and appeared not to contain nitrogen (sodium fusion).

SUMMARY

1. Benzaldehyde and pyridine react when heated (140°) with *tert*-butyl peroxide to give a mixture of a base, a neutral material, and a very small amount of hydrobenzoin dibenzoate.

2. The basic material, which constitutes about 50% of the reaction mixture was shown to be 4-(α-benzoxybenzyl)pyridine.

3. The neutral fraction upon hydrolysis with alkali gave benzoic acid (67%) phenyl-4-pyridylcarbinol (21%), and an unidentified neutral material (14%).

4. A mechanism to account for the formation of these products is tentatively suggested.

CHICAGO 37, ILLINOIS

REFERENCES

(1) RUST, SEUBOLD, AND VAUGHAN, *J. Am. Chem. Soc.*, **70**, 3258 (1948).
(2) KHARASCH AND MCBAY, unpublished work.