Tetrahedron. Vol. 25, pp. 4797 to 4807. Pergamon Press 1969. Printed in Great Britain

KINETICS AND MECHANISM OF THE NITRIC ACID OXIDATION OF DESOXYBENZOIN[2]

Y. OGATA and H. TEZUKA

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku,
Nagoya, Japan

(*Received in Japan* 9 *May* 1969; *Received in the UK for publication* 10 *July* 1969)

Abstract—Oxidation of desoxybenzoin with 1M HNO_3 at 60° in 40% dioxan gives benzoin (25%), benzil (12%) and degradation products (benzoic and *p*-nitrobenzoic acids and benzaldehyde) (62%), while in 70% acetic acid, benzoin (46%), benzil (11%) and the degradation products (41%) are produced. Benzil and benzoic acids are probably formed directly from desoxybenzoin, since both benzoin and benzil are stable under these conditions. The oxidation rate of *p*-nitrobenzyl phenyl ketone to benzoic acids is expressed as: $k[H_3O^+]_H[ArCH_2COPh]$. A scheme involving acid-catalysed enolization of desoxybenzoin is suggested and discussed on the basis of the kinetics and the oxidation behaviour of assumed intermediates.

NITRIC acid oxidation of aromatic ketones produces benzoic acids or furoxanes etc.[2,3] The mechanism involves the nitrosation of the substrate, but it is obscure whether the nitrosation occurs via H-atom abstraction or an attack on the nitrosonium ion.[4]

The present paper deals with the nitric acid oxidation of desoxybenzoin. We found that H-atom abstraction did not occur even in desoxybenzoin containing benzylic hydrogen. Desoxybenzoin was easily oxidized with 1M HNO_3 containing a small amount of nitrous acid (ca. 0·005M) at 60°, a temperature lower than that for other benzyl compounds (90°)[5] to afford benzoin and benzil together with C—C bond fission products, i.e., benzoic and *p*-nitrobenzoic acids and benzaldehyde.

$$PhCH_2COPh \rightarrow PhCH(OH)COPh + PhCOCOPh + PhCO_2H + p\text{-}NO_2C_6H_4CO_2H + PhCHO$$

Possible mechanisms are discussed.

RESULTS AND DISCUSSIONS

Products. Desoxybenzoin (ca. 0·030M) was treated with 1–2M HNO_3 containing 0·005M HNO_2 in both aqueous acetic acid and aqueous dioxan at 60° for 8 hr. The chloroform extract of the reaction mixture was washed with aqueous sodium hydroxide, and then both layers were analyzed independently by GLC. Benzoin, benzil, benzoic and *p*-nitrobenzoic acids and benzaldehyde were identified.

The following observations suggest that benzoic acid is not formed via benzoin, benzil, or benzaldehyde and that benzil is not formed via benzoin. (i) Benzoin is stable, although desoxybenzoin was oxidized almost completely under these conditions. (ii) Benzil is also stable. (iii) Benzaldehyde was unchanged under these conditions, although it is often susceptible to oxidation. The yields are shown in

Table 1, where it is taken into account that two moles of benzoic acids or benzaldehyde are formed from one mole of reactant, desoxybenzoin. The yield of *p*-nitrobenzoic acid is low (ca. 20% of benzoic acids). The yields of benzaldehyde is very low. The C—C bond fission takes place more readily in aqueous dioxan than in aqueous acetic acid.

TABLE 1. YIELDS OF PRODUCTS IN THE NITRIC ACID OXIDATION OF DESOXYBENZOIN AT 60°
Initial conc.: $[NaNO_2]$ = 0·005 M, $[PhCH_2COPh]$ = 0·032 M

$[HNO_3]$ (M)	Benzoin (%)	Benzil (%)	Benzoin + Benzil (%)	(ArCOOH + PhCHO)/2 (%)	[PhCHO]/[ArCOOH] × 100
1·0[a]	25	12	37	62	9
1·0[b]	28	12	40	60	10
1·0[c]	47	11	58	42	20
2·0[c]	47	12	59	40	20
1·0[c]	17	45[e]	59	36	—
1·0	5·0[d]	49[e]	54	—	—
3·0	8·7[d]	43[e]	52	—	—
4·0	7·7[d]	45[e]	52	—	—

[a] In 40% dioxan.
[b] In 60% dioxan.
[c] In 70% acetic acid.
[d] In 50% acetic acid.
[e] The reaction at 90°.

Benzoin is slowly oxidized to benzil at 90°, but a higher temperature and acidic solvent do not increase the yields of benzoin and benzil from desoxybenzoin (Table 1). The yields of benzoin and benzil increase with decreasing content of water in the solvent acetic acid and with decreasing polarity of the solvent (Table 2). Here, the total yield was below 100%, since the yield of benzaldehyde was not estimated.

TABLE 2. POLAR EFFECT OF SOLVENT ON PRODUCTS IN THE NITRIC ACID OXIDATION OF DESOXYBENZOIN IN AQUEOUS ACETIC ACID AT 60°

Initial conc.: $[HNO_3]$ = 1·0 M, $[NaNO_2]$ = 0·005 M, $[PhCH_2COPh]$ = 0·030 M

AcOH (%)	Benzoin (%)	Benzil (%)	Benzoin + Benzil (%)	$PhCO_2H$ + p-$C_6H_4CO_2H$ (%)
40	31	10	41	49
50	42	13	55	35
70	45	14	59	34

The reaction of substituted desoxybenzoin. The yield of the C—C bond fission products, i.e., benzoic acids, is higher in aqueous dioxan than in aqueous acetic acid (Table 3). Table 3 shows that the C—C bond fission occurs more readily if the benzyl phenyl ketone has an electron-attracting group.

TABLE 3. YIELDS OF BENZOIC ACIDS IN THE NITRIC ACID OXIDATION OF SUBSTITUTED BENZYL PHENYL KETONES IN VARIOUS SOLVENTS AT 60°.[a]

$$p\text{-X-}C_6H_4CH_2COC_6H_5 \rightarrow p\text{-X-}C_6H_4COOH + C_6H_5COOH$$

Solvent	Substituent X	Yield (%) p-X-C_6H_4COOH	C_6H_5COOH
70% AcOH	CH_3	26	54
70% AcOH	Cl	38	65
70% AcOH	NO_2	56	86
40% dioxan	CH_3	42	63
60% dioxan	Cl	61	72
60% dioxan	NO_2	81	87

[a] Initial conc.: $[HNO_3] = 1{\cdot}0$ M, $[NaNO_2] = 0{\cdot}005$ M, $[ArCH_2COPh] = 0{\cdot}028$ M

Kinetics of the nitric acid oxidation of p-nitrobenzyl phenyl ketone. The rate of the nitric acid oxidation of p-nitrobenzyl phenyl ketone was followed by the spectrophotometric estimation of benzoic acid in 70% acetic acid (30 vol % water–70 vol % acetic acid) at 60°. The reaction did not start in pure nitric acid, but only after a small amount of nitrous acid was added, but the rate was not influenced by nitrous acid concentration as shown in Table 4. The oxidation of p-nitrobenzyl phenyl ketone with excess nitric acid was first-order with the substrate, and was independent of the concentrations of nitric and nitrous acids as shown in Tables 4 and 5, where the rate constants are compared at constant acidity. Therefore, the rate is expressed as:

$$v = k[ArCH_2COPh]$$

TABLE 4. EFFECT OF NITROUS ACID CONCENTRATION IN THE NITRIC ACID OXIDATION OF p-NITROBENZYL PHENYL KETONE IN 70% ACETIC ACID AT 60°

Initial conc.: $[HNO_3] = 1{\cdot}0$ M, $[ArCH_2COPh] = 0{\cdot}024$ M

$[NaNO_2]$ (M)	Induction period (hr)	$10^4\,k(\text{sec}^{-1})$
None	>5	—
0·005	—	1·48
0·010	—	1·45
0·015	—	1·43

The rate is enhanced by the acidity of the solution, but the plot of log k vs H_0 (acidity function) does not give a straight line. Hammett *et al.* observed the proportionarity of the first-order rate constant with $[H_3O^+]$ but not h_0 for halogenation of acetophenones.[6] Also, in the present reaction, the first-order rate constant is proportional to $[H_3O^+]$, i.e. the plot of log k vs log $[HNO_3 + H_2SO_4]$ gave a straight line with a slope of ca. 0·8 (Fig. 1).

The rates for the oxidation of substituted benzyl phenyl ketones were measured in 70% acetic acid at 60°. The observed first-order rate constants, 10^4k sec^{-1}, were 1·48 for p-NO_2, 0·65 for p-Cl, 0·28 for p-CH_3. The order, p-NO_2 > p-Cl > p-CH_3, is consistent with that for enolization of desoxybenzoins.[7]

TABLE 5. EFFECT OF INITIAL CONCENTRATION OF NITRIC ACID AND *p*-NITROBENZYL PHENYL KETONE ON THE RATE CONSTANTS FOR THE NITRIC ACID OXIDATION OF *p*-NITROBENZYL PHENYL KETONE IN 70% ACETIC ACID AT 60°

Initial conc.: $[NaNO_2] = 0{\cdot}005$ M

$[HNO_3]$ (M)	$[ArCH_2COPh]$ (M)	$10^4 k(sec^{-1})$
1·0	0·050	1·59
1·0	0·031	1·48
1·0	0·028	1·61
0·2[a]	0·030	1·28[b]
0·4[a]	0·030	1·32[b]
0·6[a]	0·029	1·31[b]
0·8[a]	0·028	1·40[b]
1·0[a]	0·030	1·32[b]

[a] In the presence of 0·2 M sulfuric acid.

[b] The corrected values at a definite acidity of $[HNO_3 + H_2SO_4] = 1$ M.

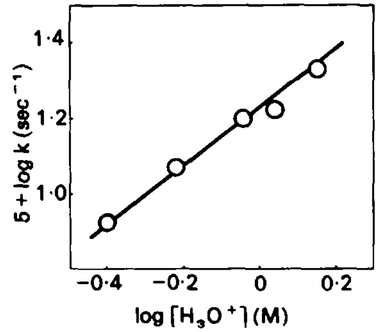
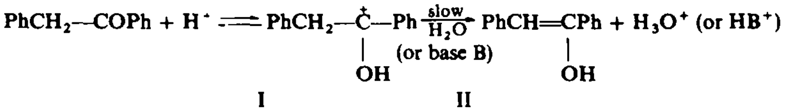


FIG. 1. Plot of log *k* vs. $[HNO_3 + H_2SO_4]$ for the nitric acid oxidation of *p*-nitrobenzyl phenyl ketone in 70% acetic acid at 60°.
Initial conc.: $[HNO_3] = 0{\cdot}40$ M, $[NaNO_2] = 0{\cdot}005$ M, $[p\text{-}NO_2C_6H_4CH_2COPh] = 0{\cdot}030$ M.

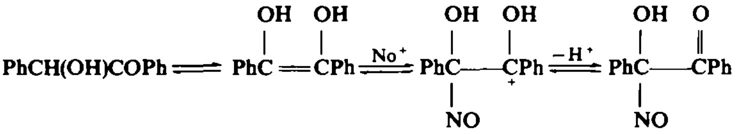
Mechanism. The mechanism for the nitric acid oxidation of desoxybenzoin seems to involve two parallel pathways leading to benzoic acids and benzoin. Neither pathway involves H-atom abstraction, since benzoin, more susceptible to H-atom abstraction, is stable under the conditions.

The kinetic results suggest the intervention of the acid-catalysed rate-determining enolization of desoxybenzoin (Eq. 1) in view of the following facts. (i) The rate is first-order in *p*-nitrobenzyl phenyl ketone and is independent of nitric and nitrous acids. (ii) The rate is proportional to $[H_3O^+]$ rather than h_0. (iii) An electron-attracting group accelerates the reaction.[7]



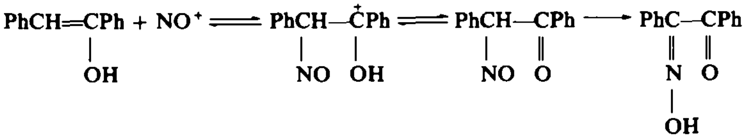
$$PhCH_2{-}COPh + H^+ \rightleftharpoons \underset{\substack{|\\ OH\\ \text{I}}}{PhCH_2{-}\overset{+}{C}{-}Ph} \xrightarrow[H_2O\ \text{(or base B)}]{\text{slow}} \underset{\substack{|\\ OH\\ \text{II}}}{PhCH{=}CPh} + H_3O^+ \text{ (or } HB^+\text{)} \qquad (1)$$

Here, simultaneous attacks of NO^+ and NO_2 on enol II are not conceivable, since more enolizable benzoin[8] is inactive under the same conditions, i.e., if the enol II reacts with NO_2, enol of benzoin should react with NO_2 to give benzil. The fact is explained by assuming that NO^+ is much more reactive than NO_2. The reaction of benzoin with NO^+ should reach the following unimportant equilibrium rapidly and then subsequently reaction is not expected, because the enolization of the product is impossible.



$$\text{PhCH(OH)COPh} \rightleftharpoons \text{PhC(OH)=C(OH)Ph} \xrightleftharpoons{\text{No}^+} \text{PhC(OH)(NO)—}\overset{+}{\text{C}}\text{(OH)Ph} \xrightleftharpoons{-\text{H}^+} \text{PhC(OH)(NO)—C(=O)Ph} \qquad (2)$$

On the other hand, dezoxybenzoin can react with NO^+ to form benzilmonoxime (V), similarly to the nitrous acid oxidation of aliphatic ketones.[4]



$$\underset{\text{II}}{\text{PhCH=C(OH)Ph}} + \text{NO}^+ \rightleftharpoons \underset{\text{III}}{\text{PhCH(NO)—}\overset{+}{\text{C}}\text{(OH)Ph}} \rightleftharpoons \underset{\text{IV}}{\text{PhCH(NO)—C(=O)Ph}} \longrightarrow \underset{\text{V}}{\text{PhC(=NOH)—C(=O)Ph}} \qquad (3)$$

II III IV V

Our observations described in the following are consistent with the above assumptions.

The reaction of desoxybenzoin with N_2O_4. Desoxybenzoin or benzoin was treated with ca. 0·09M N_2O_4 in glacial acetic acid at room temperature. The results are shown in Table 6. In a polar solvent such as acetic acid, N_2O_4 should dissociate as shown below.[9]

$$2\,NO_2 \rightleftharpoons N_2O_4 \rightleftharpoons NO^+ + NO_3^- \qquad (4)$$

TABLE 6. THE PRODUCTS OF THE REACTION OF DESOXYBENZOIN AND BENZOIN WITH N_2O_4 IN GLACIAL ACETIC ACID AT ROOM TEMPERATURE[a]

Substrate	Reaction time (hr)	Product
$PhCH_2COPh$	45	None
$PhCH_2COPh$[b]	46	PhCOCOPh
PhCH(OH)COPh	46	None
PhCH(OH)COPh[b]	45	None
PhC(=NOH)COPh[b]	72	PhCOCOPh

[a] Initial conc.: [substrate] = 0·050 M, $[N_2O_4]$ = ca. 0·09 M.

[b] 0·1 ml (corresponding to 0·036 M) H_2SO_4 was added.

In the absence of strong acid, the oxidation reaction does not occur, probably because the substrate (desoxybenzoin) is not enolized. In the presence of strong acid, desoxybenzoin was slowly transformed to benzil (73% after 46 hr), while benzoin remained unchanged. The results suggest the conversion of desoxybenzoin to benzilmonoxime (V), which forms benzil by hydrolysis as shown in Eq. 3. Benzilmonoxime gave a quantitative yield of benzil under similar conditions. Hence, benzilmonoxime was probably hydrolysed during the extraction procedure after the reaction. Both benzoin and desoxybenzoin remained unchanged in the same reaction in ether. N_2O_4 in ether dissociates only to nitrogen dioxide.[10]

A. *A pathway to benzoic acids.* Benzilmonoxime (V) was easily oxidized with 1M HNO_3 at 60° in 70% acetic acid to benzoic and *p*-nitrobenzoic acids in a molar ratio of 8:2. This molar ratio is comparable to that observed in nitric acid oxidation of desoxybenzoin. Although the nitration mechanism for the present reaction is still obscure, it certainly involves benzilmonoxime.

Benzilmonoxime does not give benzoic acids in glacial acetic acid in the presence of N_2O_4, but it is slowly transformed to benzoic and *p*-nitrobenzoic acids in aqueous (10% water) acetic acid (Fig. 2).

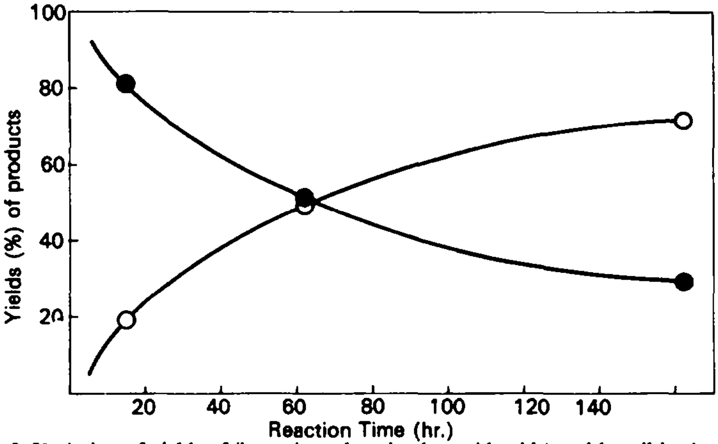
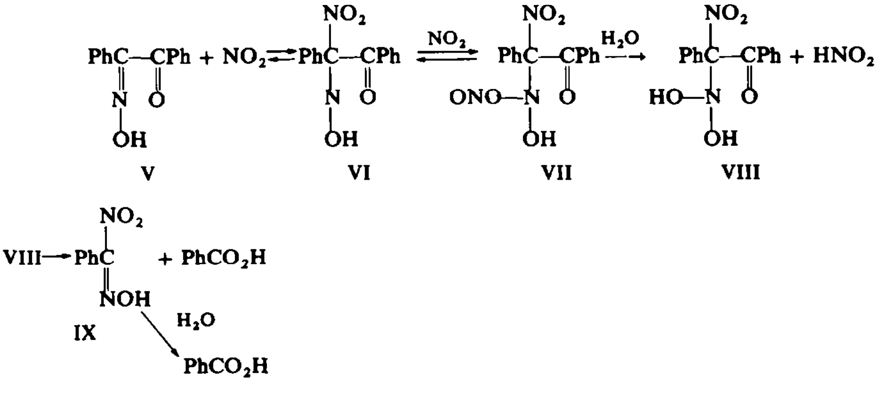


FIG. 2. Variation of yields of (benzoic and *p*-nitrobenzoid acids) and benzil in the reaction of benzilmonoxime (V) with N_2O_4 in 90% acetic acid at room temperature.
Initial conc.: $[H_2SO_4] = 0{\cdot}036$ M, $[PhC(=NOH)COPh] = 0{\cdot}018$ M,
$[N_2O_4] =$ ca. $0{\cdot}09$ M.
○($PhCO_2H + p\text{-}NO_2C_6H_4CO_2H$), ● PhCOCOPh.

Benzoic acid may be formed as follows:

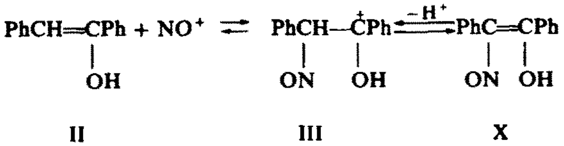


$$\underset{\mathrm{V}}{\mathrm{PhC(=NOH)\text{—}C(=O)Ph}} + \mathrm{NO_2} \rightleftharpoons \underset{\mathrm{VI}}{\mathrm{PhC(NO_2)(NOH)\text{—}C(=O)Ph}} \underset{}{\overset{\mathrm{NO_2}}{\rightleftharpoons}} \underset{\mathrm{VII}}{\mathrm{PhC(NO_2)(N(ONO)OH)\text{—}C(=O)Ph}} \xrightarrow{\mathrm{H_2O}} \underset{\mathrm{VIII}}{\mathrm{PhC(NO_2)(N(OH)OH)\text{—}C(=O)Ph}} + \mathrm{HNO_2}$$

$$\mathrm{VIII} \rightarrow \underset{\mathrm{IX}}{\mathrm{PhC(NO_2)\text{=}NOH}} + \mathrm{PhCO_2H} \qquad \mathrm{IX} \xrightarrow{\mathrm{H_2O}} \mathrm{PhCO_2H} \tag{5}$$

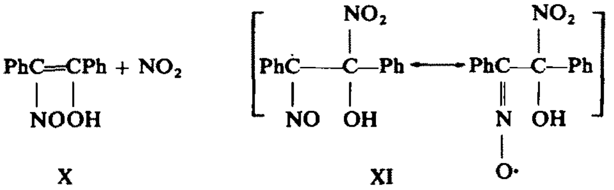
This scheme involves an intermediate (IX) analogous to 6-nitro-6-hydroxyiminohexanoic acid suggested in the nitric acid oxidation of cyclohexanone.[11, 12]

B. *A pathway to benzoin.* In the nitric acid oxidation of desoxybenzoin, an appreciable amount of benzoin is formed besides the benzoic acids. Benzoin was not formed from benzilmonoxime (V), and H-atom abstraction from desoxybenzoin with NO_2 is also impossible as described before. Hence, a probable preliminary step is as follows.

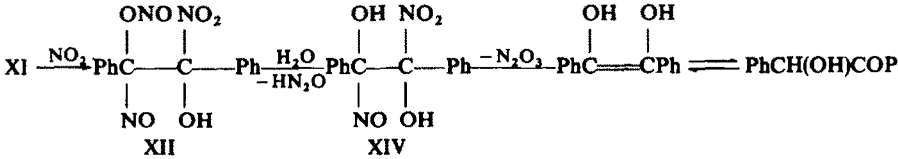


$$\underset{\text{II}}{\text{PhCH}{=}\underset{\text{OH}}{\underset{|}{\text{C}}}\text{Ph}} + \text{NO}^+ \rightleftharpoons \underset{\text{III}}{\text{Ph}\underset{\text{ON}}{\underset{|}{\text{CH}}}{-}\underset{\text{OH}}{\underset{|}{\overset{+}{\text{C}}}}\text{Ph}} \xrightleftharpoons{-\text{H}^+} \underset{\text{X}}{\text{Ph}\underset{\text{ON}}{\underset{|}{\text{C}}}{=}\underset{\text{OH}}{\underset{|}{\text{C}}}\text{Ph}} \qquad (6)$$

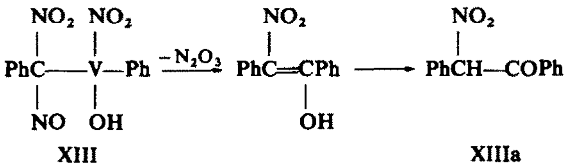
Intermediate III may give X besides IV (Eq. 3). X may give XI in view of the favourable attack of NO_2 to give the more resonance-stabilized structure.



$$\underset{\text{X}}{\text{Ph}\underset{\text{NO}}{\underset{|}{\text{C}}}{=}\underset{\text{OH}}{\underset{|}{\text{C}}}\text{Ph}} + \text{NO}_2 \quad \underset{\text{XI}}{\left[\text{Ph}\underset{\text{NO}}{\underset{|}{\dot{\text{C}}}}{-}\underset{\text{OH}}{\underset{|}{\overset{\overset{\text{NO}_2}{|}}{\text{C}}}}{-}\text{Ph} \longleftrightarrow \text{Ph}\underset{\underset{\underset{\text{O}\cdot}{|}}{\text{N}}}{\underset{\|}{\text{C}}}{-}\underset{\text{OH}}{\underset{|}{\overset{\overset{\text{NO}_2}{|}}{\text{C}}}}{-}\text{Ph}\right]} \qquad (7a)$$



$$\text{XI} \xrightarrow{\text{NO}_2} \underset{\text{XII}}{\text{Ph}\underset{\text{NO}}{\underset{|}{\overset{\overset{\text{ONO}}{|}}{\text{C}}}}{-}\underset{\text{OH}}{\underset{|}{\overset{\overset{\text{NO}_2}{|}}{\text{C}}}}{-}\text{Ph}} \xrightarrow[-\text{HN}_2\text{O}]{\text{H}_2\text{O}} \underset{\text{XIV}}{\text{Ph}\underset{\text{NO}}{\underset{|}{\overset{\overset{\text{OH}}{|}}{\text{C}}}}{-}\underset{\text{OH}}{\underset{|}{\overset{\overset{\text{NO}_2}{|}}{\text{C}}}}{-}\text{Ph}} \xrightarrow{-\text{N}_2\text{O}_3} \text{Ph}\overset{\overset{\text{OH}}{|}}{\text{C}}{=}\overset{\overset{\text{OH}}{|}}{\text{C}}\text{Ph} \rightleftharpoons \text{PhCH(OH)COPh} \qquad (7b)$$



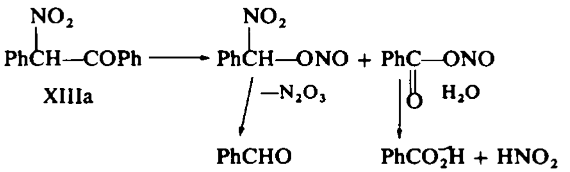
$$\underset{\text{XIII}}{\text{Ph}\underset{\text{NO}}{\underset{|}{\overset{\overset{\text{NO}_2}{|}}{\text{C}}}}{-}\underset{\text{OH}}{\underset{|}{\overset{\overset{\text{NO}_2}{|}}{\text{V}}}}{-}\text{Ph}} \xrightarrow{-\text{N}_2\text{O}_3} \text{Ph}\overset{\overset{\text{NO}_2}{|}}{\text{C}}{=}\underset{\text{OH}}{\underset{|}{\text{C}}}\text{Ph} \longrightarrow \underset{\text{XIIIa}}{\text{Ph}\overset{\overset{\text{NO}_2}{|}}{\text{CH}}{-}\text{COPh}} \qquad (7c)$$

XII can readily be hydrolysed to XIV.[13] Nitrogen trioxide may be eliminated from XIV to form the enol of benzoin, since the bulky nitroso compound is decomposed easily.[14] It is explained in terms of intermediate X why benzoin does not form benzil, while desoxybenzoin gives benzoin (Eq. 2).

C. *A pathway to benzil.* Hydrolysis of benzilmonoxime (V) leads to benzil. The yield of benzil in the nitric acid oxidation in aqueous acetic acid is nearly equal to that in aqueous dioxan in spite of a decrease in the yield of benzoic acids (Table 1). This is due either to the faster hydrolysis than oxidation of V in aqueous acetic acid or to the presence of another pathway to give benzil alone. However, oximes may be more easily oxidized in aqueous acetic acid than in aqueous dioxan as exemplified by benzaldoxime under these conditions. ($[PhCO_2H]/[PhCHO]$ is 5 in 70% AcOH and 0 in 40% dioxan). Hence, benzil may be formed from both V and XIIIa,[15] and the total yield remains nearly constant in spite of variation in the total yield of benzoic acids.

$$\text{V} \xrightarrow{\text{H}_3\text{O}^+} \text{PhCOCOPh} \xleftarrow{\text{H}_3\text{O}^+} \text{XIIIa}$$

The possible source of benzaldehyde is α-nitrodesoxybenzoin (XIIIa), which is known to form degradation products at higher temperature.[16] The higher yield of benzaldehyde in aqueous acetic acid than in aqueous dioxan (Table 1) is explicable by assuming pathways of Eqs. 6 and 7c, and intermediary XIIIa.

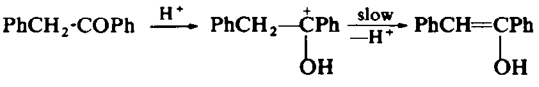


$$\underset{\text{XIIIa}}{\overset{NO_2}{PhCH}\text{—}COPh} \longrightarrow \overset{NO_2}{PhCH}\text{—}ONO + PhC(=O)\text{—}ONO;\quad PhCH(NO_2)\text{—}ONO \xrightarrow{-N_2O_3} PhCHO;\quad PhC(=O)\text{—}ONO \xrightarrow{H_2O} PhCO_2H + HNO_2 \qquad (8)$$

These facts suggest an overall mechanism for the nitric acid oxidation of desoxybenzoin.

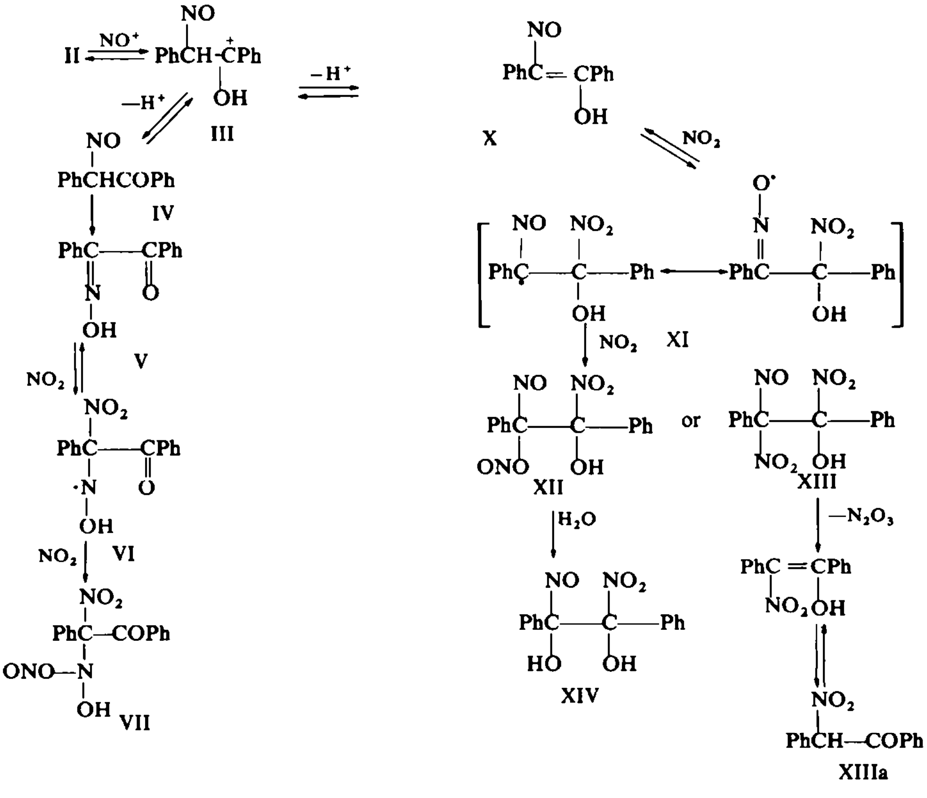
$$HNO_3 + HNO_2 \rightleftharpoons N_2O_4 + H_2O \qquad (9)$$

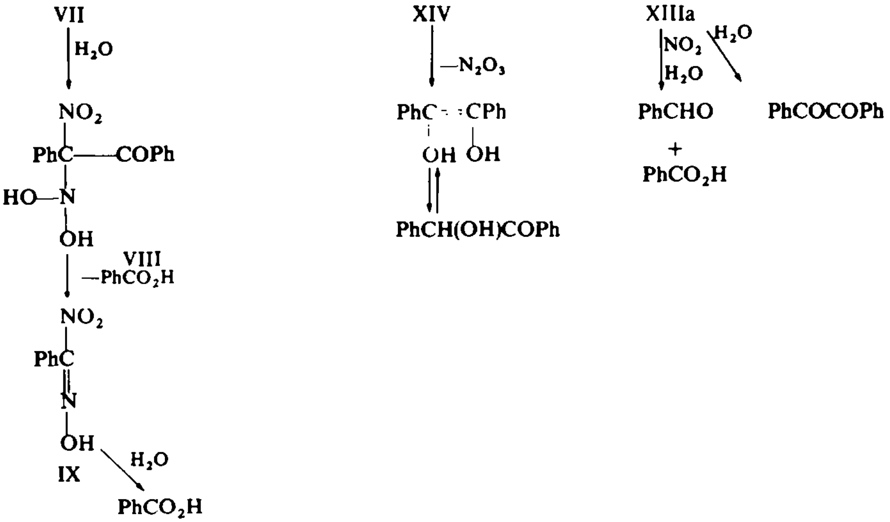
$$2NO_2 \rightleftharpoons N_2O_4 \rightleftharpoons NO^+ + NO_3^- \qquad (4)$$



$$PhCH_2\text{-}COPh \xrightarrow{H^+} \underset{\text{I}}{PhCH_2\text{—}\overset{+}{C}Ph(OH)} \xrightarrow[-H^+]{slow} \underset{\text{II}}{PhCH{=}CPh(OH)}$$

I II





Intermediate III leads to IV and X. Since V did not give benzoin, the isomerization of IV to V may be irreversible. The hydrolysis of (VII → VIII) or (XII → XIV) is probably involved in this scheme, since both desoxybenzoin and benzilmonoxime (V) gave neither benzoin nor benzoic acids in the absence of water.

The solvent effect on the products distribution is explained as follows. The yield of benzoin is lower in a more polar (more aqueous) solvent (Table 2), probably because the carbonyl group of IV (keto type) is more solvated than X (enol type), and the equilibrium between IV and X shifts to the left and the concentration of X (enol type) decreases in more polar solvents as has been reported.[17] In aqueous dioxan, in spite of its lower polarity, the yield of benzoin is lower and it varies little in both 40 and 60% dioxan (Table 1). The pathway to benzoic acids is unfavourable in terms of the equilibrium between IV and X, as the solvent changes to less polar, i.e., from 40 to 60% dioxan, but the solvation of NO_2 with dioxan should make NO_2 less reactive in the reaction of X with it. Hence, the effect of the solvation on the equilibrium (IV $\rightleftharpoons$ X) and the effect of the solvation on NO_2 are compensated and thus little change of yield of benzoin is observed by changing solvent polarity in aqueous dioxan.

An electron-attracting group favours benzoic acid formation (Table 3), but the substituent effect on the equilibrium between IV and X, and on their reaction is still obscure.

EXPERIMENTAL

Materials. Desoxybenzoins were prepared by the Friedel–Crafts reaction of the corresponding acid chlorides with benzene,[18] except *p*-nitrobenzyl phenyl ketone which was prepared by nitration of desoxybenzoin.[19] Desoxybenzoin, m.p. 56°, lit.[20] 56°; *p*-methylbenzyl phenyl ketone, m.p. 95°, lit.[20] 95·5°; *p*-chlorobenzyl phenyl ketone, m.p. 136–137°, lit.[20] 136·5°; *p*-nitrobenzyl phenyl ketone, m.p. 145°, lit.[20] 144°. Benzoin, m.p. 136–137°, lit.[21] 137°; benzil, m.p. 96·5°, lit.[21] 95°; benzoic acid, m.p. 122° lit.[21] 122·4°; *p*-methylbenzoic acid, m.p. 181° lit.[21] 179–181 ; *p*-chlorobenzoic acid, m.p. 242 , lit.[21] 243°; *p*-nitrobenzoic acid, m.p. 240·5°, lit.[21] 242·4°. Nitrogen dioxide was prepared by thermal decomposition of dinitrogen pentoxide and stored as a soln of CCl_4.[22] β-Benzilmonoxime was prepared by the reaction of benzil with hydroxylamine sulfate, m.p. 108°, lit.[18] 113–114°.

The reaction of desoxybenzoin with 1M nitric acid in aqueous media

Identification of products. 40–60% dioxan, or 40–70% AcOH containing 1M HNO_3 and 0·03M desoxybenzoin was thermostated. The reaction was initiated by adding 0·005M $NaNO_2$ aq. After 8 hr, the reaction mixture was extracted with $CHCl_3$, and the extract was washed with NaOH aq. The aqueous layer was acidified with HCl, and the ppt was esterified with MeOH, and it was analysed qualitatively with GLC furnished with a flame ionization detector operated with a 2 m × 3 mm column packed with Apiezon grease L 15% on Celite 545 of 80–100 mesh using N_2 flow rate of 20–30 ml/min. The peaks were identical with those of authentic methyl benzoate and methyl *p*-nitrobenzoate. The carboxylic acids formed in the nitric acid oxidation of desoxybenzoin were also identified by comparison of IR spectra with that from authentic samples.

The chloroform layer was dried over Na_2SO_4, and benzaldehyde and benzoin (or benzil) were detected by GLC. Benzoin was not separable from benzil. On evaporation of $CHCl_3$, benzoin was obtained, m.p. 134°, lit.[21] 137°, and the IR spectrum was identical with that of the authentic sample. Benzil was detected from the mother liquor by UV spectrum (260 mμ) and GLC analysis.

The quantitative analysis. Benzoic acids were measured as follows. The $CHCl_3$ extract was washed with NaOH aq and after the aqueous layer was acidified, benzoic acids were extracted with ether. The extract was washed with sat NaCl aq, diluted with MeOH and the content of benzoic acids was measured UV spectrophotometrically by means of simultaneous equation at 229 and 264 mμ for *p*-nitro- and at 225 and 245 mμ for *p*-chloro- and *p*-methylbenzyl phenyl ketones. The molar absorbances with wavelength (mμ) of benzoic acids in MeOH are as follows; p-NO_2, λ_{max} 264 mμ (log ε 4·04); *p*-Cl, λ_{max} 236 mμ (log ε 4·20); H, λ_{max} 228 mμ (log ε 4·04); p-CH_3, λ_{max} 236 μ (log ε 4·13).

After washing of the $CHCl_3$ extract with NaOH aq, and then dilution with MeOH containing a small amount of acid, benzoin and benzil were estimated by means of the UV absorbances at 235 and 270 mμ. The molar absorbances are as follows: benzil, λ_{max} 260 mμ (log ε 4·25); benzoin, λ_{max} 247 mμ (log ε 4·08). Benzaldehyde was estimated by GLC using chlorobenzene as an internal standard.

The reaction of desoxybenzoin with dinitrogen tetroxide. Desoxybenzoin was dissolved in organic solvents, e.g., ether or glacial acetic acid, and if necessary, 0·1 ml H_2SO_4 was added. A CCl_4 soln of N_2O_4 was added and the mixture kept at room temp. The mixture was treated with NaOH aq, and both organic and aqueous layers were measured by GLC and UV spectrophotometry as described above.

Kinetic procedure. A mixture of the proper amount of HNO_3, substituted benzyl phenyl ketone and 70% AcOH as solvent was thermostated at 60°. The reaction was initiated by addition of 0·005M $NaNO_2$ aq. The reaction mixture was taken out at appropriate intervals of time, and benzoic acid was estimated by means of UV as shown above.

REFERENCES

[1] Contribution No. 133.

[2] [a] A. W. Ralston and S. T. Bauer, *J. Org. Chem.* **5**, 165 (1940);
[b] R. C. Franklin, U.S. 2,742,499 (1956); *Chem. Abstr.* **51**, 1280 (1957).

[3] H. R. Snyder and N. E. Boyer, *J. Am. Chem. Soc.* **77**, 4233 (1955).

[4] [a] K. Singer and P. A. Vamplew, *J. Chem. Soc.* 3052 (1957);
[b] R. Stewart, *Oxidation Mechanisms* p. 111. Benjamin, New York (1964).

[5] [a] Y. Ogata, Y. Sawaki, F. Matsunaga and H. Tezuka, *Tetrahedron* **22**, 2655 (1966);
[b] Y. Ogata and Y. Sawaki, *J. Am. Chem. Soc.* **88**, 5832 (1966).

[6] [a] M. A. Paul and L. P. Hammett, *Ibid.* **58**, 2182 (1936);
[b] L. Zucker and L. P. Hammett, *Ibid.* **61**, 2791 (1939).

[7] E. J. Corey and J. P. Schaefer, *Ibid.* **82**, 918 (1960).

[8] K. Ichikawa and Y. Takeuchi, *Nippon Kagaku Zasshi* **79**, 1060 (1958).

[9] P. Gray and A. D. Yoffe, *Chem. Rev.* **55**, 1069 (1955).

[10] H. Shechter and F. Conrad, *J. Am. Chem. Soc.* **75**, 5610 (1953).

[11] H. C. Godt and J. F. Quinn, *Ibid.* **78**, 1461 (1956).

[12] W. J. Van Asselt and D. W. Van Krevelen, *Rec. Trav. Chim.* **82**, 51 (1963).

[13] [a] A. D. Allen, *J. Chem. Soc.* 1968 (1954);
[b] N. Levy and C. W. Scaife, *Ibid.* 1093 (1946).

[14] W. Schlenk, L. Mair and C. Bornhardt, *Ber. Dtsch. Chem. Ges.* **44**, 1169 (1911).

[15] R. B. Cundall and A. W. Locke, *J. Chem. Soc.* (B) 98 (1968).

[16] J. Meisenheimer and E. Mahler, *Liebigs Ann.* **508**, 185 (1934); *Chem. Abstr.* **28**, 1690 (1934).

[17] G. W. Wheland, *Advanced Organic Chemistry*, p. 663. Wiley, New York (1960).

[18] C. F. H. Allen and W. E. Barker, *Organic Syntheses* Coll. Vol. 2; p. 156. Wiley, New York (1950).

[19] G. Wagner, *Ber. Dtsch. Chem. Ges.* **11**, 1937 (1878).

[20] A. Fischer, B. A. Grigor, J. Packer and J. Vaughan, *J. Am. Chem. Soc.* **83**, 4208 (1961).

[21] *The Merck Index*, Merck & Co., New York (1960).

[22] A. Pedler and F. H. Pollard, *Inorganic Syntheses* Vol. 5; p. 87. McGraw-Hill, New York (1957).

[23] K. Auwers and V. Meyer, *Ber. Dtsch. Chem. Ges.* **22**, 537 (1889).