

The Decomposition Kinetics of Benzoyl Peroxide in Pyridine and in Pyridine-Benzene

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The decomposition kinetics of benzoyl peroxide in pyridine and in pyridine-benzene have been studied in the presence and absence of an inhibitor. We observed that pyridine could induce the decomposition of benzoyl peroxide, the reaction of which was first-order with respect to the peroxide and pyridine, respectively, to give pyridine *N*-oxide and benzoic anhydride. We demonstrated that pyridine cation radicals are not formed in the reaction. The unusual decrease of the first-order rate constant for the decomposition of benzoyl peroxide in pyridine with the increase of the initial concentration is ascribed to a decomposition induced by the dihydro- and tetrahydro-pyridines which predominates at low initial concentrations.

It is well known that the overall decomposition kinetics of benzoyl peroxide (BPO) in solution^{1,2} are the sum of spontaneous cleavage and radical-induced decomposition. The disappearance of BPO can be expressed by equation (1) where $-d[P]/dt$ represents the decomposition rate of BPO, k_1 the specific rate constant of the spontaneous cleavage reaction which is first-order with respect to the peroxide concentration, and k_i the specific

$$-d[P]/dt = k_1 [P] + k_i [P]^x \quad (1)$$

rate constant of the radical-induced decomposition which is dependent on the x th order of the peroxide concentration. The large variation of the overall rates of BPO decomposition in various solvents³ mainly arises from drastic variations of k_i , whereas k_1 remains nearly the same in the solvents studied.⁴ However in the presence of nucleophiles, such as sulphides,⁵ a third decomposition pathway competes with homolysis. In the thermal decomposition of BPO in pyridine⁶ and methylpyridines⁷ this third type of decomposition has been postulated in order to rationalize the formation of pyridine *N*-oxide and the high yield of benzoic acid. Therefore we assumed that in the presence of pyridine the rate equation should have form (2) where k_2 represents the specific rate

$$-d[P]/dt = k_1 [P] + k_i [P]^x + k_2 [P][Pyr]^y \quad (2)$$

constant of the pyridine-induced decomposition and y the order of the pyridine concentration. Our purpose was to determine the rate constants k_1 , k_i , and k_2 and to evaluate the relative importance of these pathways in an endeavour to assign a mechanism to the pyridine-induced decomposition. We therefore measured the rate of disappearance of BPO at various initial concentrations of the peroxide in pyridine-benzene in the presence and absence of radical traps. Since BPO decomposition could be accelerated by the addition of stable radicals,^{8,9} benzoyloxy radical scavengers, such as galvinoxyl, should be avoided. We therefore chose *N*-(*t*-butyl)- α -phenylnitron (PBN) as the inhibitor, as it is known that phenyl and benzoyloxy radicals are readily trapped by this compound.¹⁰

RESULTS AND DISCUSSION

Decomposition of PBO in Benzene.—In order to establish the experimental procedure as well as the PBN

trapping efficiency, we first studied the kinetics of BPO decomposition in benzene at 80 °C. In this solvent the radical-induced reaction is three-halves order in peroxide concentration [*i.e.* $x = 3/2$ in equation (1)] leading to equation (3).¹¹ The rate constants k_1 and k_i can be

$$-d[P]/dt = k_1 [P] + k_i [P]^{3/2} \quad (3)$$

deduced from equation (4) where k_t stands for the ob-

$$k_t = k_1 + k_i [P]_0^{1/2} \quad (4)$$

served first-order rate constant and $[P]_0$ for the initial peroxide concentration (Table 1). A plot of k_t against

TABLE 1

Rate constants for the decomposition of benzoyl peroxide (BPO) in benzene at 80 °C

| $10^2 [P]_0/M^{-1}$ | 4.63 | 9.7 | 14.5 | 18 | 22.8 |
|---------------------|------|------|------|------|------|
| $10^5 k_t/s^{-1} *$ | 4.22 | 4.72 | 5.06 | 5.18 | 5.25 |

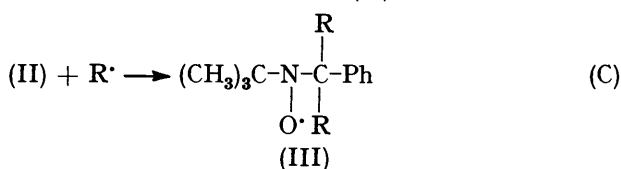
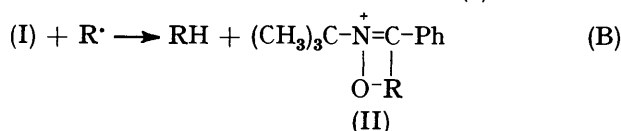
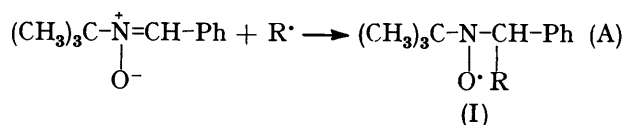
* All data are an average result of three independent runs.

$[P]_0^{1/2}$ gave rate constants $k_1 = 4.0 \times 10^{-5} s^{-1}$ and $k_i = 3.1 \times 10^{-5} mol^{-1/2} l^{1/2} s^{-1}$. These results are in accord with those reported in the literature.†

In the presence of PBN, the second term in equation (4) disappeared due to scavenging and indeed the BPO decomposition obeyed strictly first-order kinetics with rate constant $k_t = k_1 = 3.9 \times 10^{-5} s^{-1}$ which is identical to that obtained for the uninhibited decomposition ($4.0 \times 10^{-5} s^{-1}$), within experimental error. Furthermore, since we did not detect any biphenyl by g.l.c. analysis of the decomposition products, benzoyloxy and phenyl radicals must have been cleanly trapped by PBN and the radical-induced decomposition suppressed. As only 0.52 mole of PBN was consumed per mole of BPO decomposed, we used e.s.r. spectroscopic analysis to monitor the trapping pattern of PBN during decomposition. At the beginning of the decomposition the e.s.r. spectrum consisted of a triplet of doublets as expected for nitroxide radicals derived from the addition of benzoyloxy and phenyl radicals to PBN. But, when the decomposition was near completion, a triplet (a_N 15 G)

† In the presence of styrene, Swain³ reported k_1 $4.5 \times 10^{-5} s^{-1}$. Furthermore taking the results of Gill and Williams¹² at 78 °C and the activation energy recommended by Janzen *et al.*⁹ we calculated a value of $2.5 \times 10^{-5} s^{-1}$. Gill and Williams¹² also reported $k_i = 3.7 \times 10^{-5} l^{1/2} mol^{-1/2} s^{-1}$.

was observed. Such a hyperfine splitting pattern indicated the absence of a β -hydrogen in the second nitroxide, to which structure (III) might be assigned. These observations can be explained by the sequence of reactions (A)–(C).



This suggestion does not contradict Janzen's report¹⁰ that PBN trapping can be used to monitor benzoyloxy and phenyl radicals produced from BPO decomposition as a function of time since Janzen ran the reaction at low conversion of BPO for which products (II) and (III) would not be formed. A coupled dimer of nitroxide (I) seems unlikely since it has been recently shown¹³ that rate constants for bimolecular coupling of such spin adducts are smaller than the rate constants of these spin adducts with radicals. Such a reaction sequence has been reported in the case of atom reactions.¹⁴ As the spin adduct (III) could also trap another radical, one molecule of PBN could in theory scavenge four radicals. Therefore, although the consumption of PBN per mole of BPO was low, we concluded that both benzoyloxy and phenyl radicals were totally trapped.

Decomposition of BPO in Mixed Solvents of Pyridine-Benzene.—In order to eliminate the radical-induced decomposition, the kinetic measurements were carried out in the presence of PBN. In such a case rate equation (2) becomes (5). Assuming that the pyridine-induced

$$-d[\text{P}]/dt = k_1[\text{P}] + k_2[\text{P}][\text{Pyr}]^y \quad (5)$$

decomposition is first-order in peroxide and pyridine concentrations, by analogy with the decomposition of peroxide by amines,¹⁵ the rate constants k_1 and k_2 can be deduced from equation (6) where k_1 is the observed

$$k_1 = k_1 + k_2[\text{Pyr}]_0 \quad (6)$$

first-order rate constant in the presence of inhibitor and $[\text{Pyr}]_0$ the initial concentration of pyridine. A plot of k_1 (Table 2) against $[\text{Pyr}]_0$ affords a straight line* for concentrations up to 4M (Figure). At higher concentrations the plot curves upward and this can be attributed to the effects of the dielectric constant of the solution. The rate constant of the bimolecular reaction of BPO and pyridine derived from the slope is $k_2 = 2 \times 10^{-6}$

$1 \text{ mol}^{-1} \text{ s}^{-1}$; in neat pyridine ($[\text{Pyr}] = 12.43\text{M}$) it rises to $6.4 \times 10^{-6} 1 \text{ mol}^{-1} \text{ s}^{-1}$.

These bimolecular kinetics are expected for both mechanisms postulated to rationalize the data for the

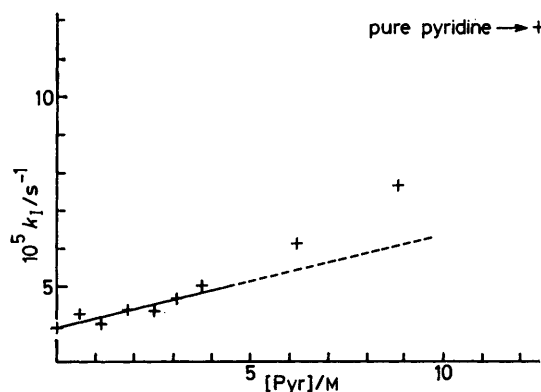
TABLE 2

Rate constants for the decomposition of benzoyl peroxide (BPO) in pyridine-benzene mixtures at $80 \pm 0.1^\circ \text{C}$ with $[\text{P}]_0 = 10^{-3}\text{M}$

| [Pyr]/M | $10^5 k_1/\text{s}^{-1}$ ^a | $10^5 k_2/\text{l mol}^{-1} \text{s}^{-1}$ ^b | $10^5 k_1/\text{s}^{-1}$ ^c | $10^6 k_1/[\text{P}]^y/\text{s}^{-1}$ ^d |
|--|---------------------------------------|---|---------------------------------------|--|
| 0 (pure C ₆ H ₆) | 3.9 | | 4.72 | 8.2 |
| 0.62 | 4.25 | 0.56 | 5.06 | 8.1 |
| 1.24 | 4.01 | 0.09 | 5.55 | 15.4 |
| 1.86 | 4.38 | 0.26 | 6.76 | 23.8 |
| 2.49 | 4.34 | 0.18 | 7.40 | 30.6 |
| 3.11 | 4.69 | 0.25 | 8.3 | 36.1 |
| 3.73 | 5.02 | 0.30 | 9.23 | 42.1 |
| 6.22 | 6.13 | 0.36 | | |
| 8.70 | 7.64 | 0.43 | 23.23 | 231.5 |
| 12.43 (pure Pyr) | 11.89 | 0.64 | 50.20 | 383.1 |

^a Observed first-order rate constant in the presence of inhibitor; $[\text{PBN}]_0 10^{-3}\text{M}$. ^b Second-order rate constant for the induced decomposition of BPO by pyridine. ^c Observed first-order rate constant without inhibitor. ^d Apparent first-order rate constant for the radical-induced decomposition of BPO.

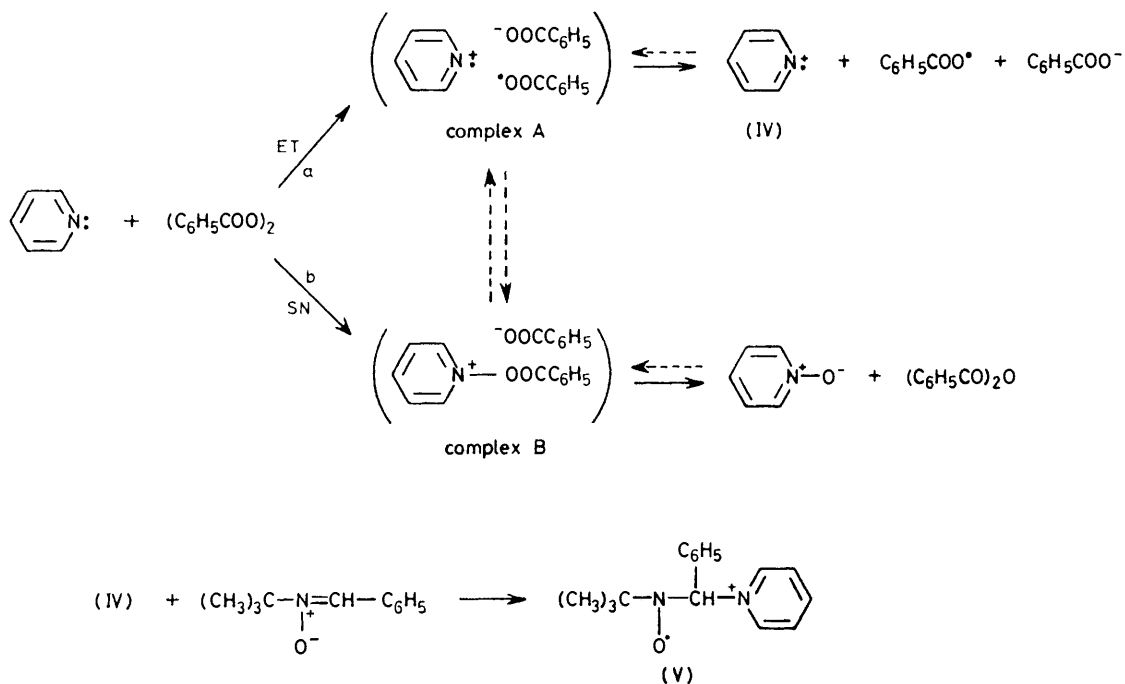
decomposition of peroxides in the presence of nucleophiles as in Scheme 1,^{16,17} *i.e.* one-electron transfer from the nucleophile (path a) and nucleophilic attack on an oxygen atom of the peroxide by pyridine (path b). As we have not found any compound which could arise

FIGURE Plot of k_1 against $[\text{Pyr}]$

from the pyridinium cation radical (IV), the intermediacy of such a radical is doubtful. The following experiments also support our argument. We have generated the pyridinium radical (IV), by the oxidation of pyridine with peroxydisulphate, in the presence of PBN and

* Note that the percentage of BPO decomposed in the pyridine-induced decomposition is low, *e.g.* it is 10% at a pyridine concentration of 1.86M, then the error in the determination of the pseudo-first-order rate constant k_1 results in a larger error for the determination of the rate constant k_2 . With a more reactive heterocycle, the accuracy of the k_2 determination is far better and there must be a second-order reaction as shown by the results obtained with 4-methylpyridine [$k_2 = 9.8 \times 10^{-6} 1 \text{ mol}^{-1} \text{ s}^{-1}$, $r = 0.997$ (S. Vidal, unpublished results)].

observed the e.s.r. signal of nitroxide (V) *i.e.* a 1 : 1 : 1 triplet of 1 : 2 : 2 : 1 quartets.¹⁸ E.s.r. analysis of samples during the BPO decomposition in the presence of PBN did not reveal an unusual nitroxide spectrum. Since (IV) could attack pyridine to give pyridylpyridinium salts which could be degraded by the Zincke method to aminopyridines, the reaction mixture left after a kinetic run in the presence of PBN was subjected to Zincke



SCHEME 1

degradation.¹⁹ As we did not detect any aminopyridines by g.l.c. analysis of the resulting mixture, pyridylpyridinium salts were not formed. Finally, bipyridyls which could arise from the radical substitution of pyridine were also not detected. On the other hand the formation of pyridine *N*-oxide and benzoic anhydride can be regarded as good evidence in favour of path b. In the absence of PBN, the yield of benzoic anhydride was 0.23 mole per mole of peroxide, in good agreement with the theoretical yield deduced from the rate constants k_2 and k_t in neat pyridine (theoretical yield = $k_2[\text{Pyr}]/k_t$). Therefore our data on the induced decomposition of BPO by pyridine are better rationalized by the SN than by the ET mechanism. However the ET mechanism cannot be totally discounted since complex A may be rapidly transformed into complex B.¹⁷

In the absence of inhibitor, a third decomposition path may also occur in addition to the two already investigated. The observed first-order rate constant in the absence of inhibitor k_t is then the sum of three terms as shown in equation (7). A combination of equations (6) and (7) gives equation (8) from which the importance of the radical-induced decomposition can be determined. From the kinetic data (Table 2) it appears that $k_i[\text{P}]_0^{x-1}$

increases rapidly as the pyridine concentration increases. If we assume, in analogy with the proposal^{12,20} that the major induced decomposition pathway in benzene arises from the oxidation of the phenylcyclohexadienyl radicals, the present observation suggests that the σ -complexes

from pyridine are more prone to attack the peroxide linkage than are the σ -complexes from benzene.

Decomposition of BPO in Pyridine.—The decomposition rate of BPO in substituted benzenes^{12,21} has been reported to be either insensitive to the initial peroxide concentration $[\text{P}]_0$ or to increase as this concentration increases. On the other hand, in the similar decomposition of BPO in pyridine the first-order rate constant decreases as $[\text{P}]_0$ increases (Table 3). Two possible

TABLE 3

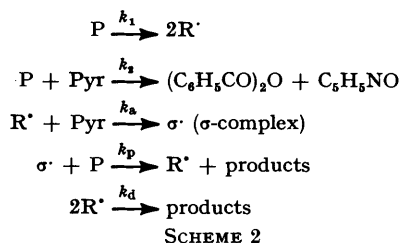
Rate constants for the decomposition of BPO in pyridine at various initial BPO concentrations $[\text{P}]_0$

| | | | | | | |
|--|-------|-------|-------|-------|-------|-------|
| $[\text{P}]_0/\text{M}$ | 0.187 | 0.141 | 0.096 | 0.067 | 0.05 | 0.024 |
| $10^4 k_t/\text{s}^{-1}$ | 3.86 | 4.44 | 5.02 | 5.7 | 6.2 | 8.01 |
| $[\text{P}]_0^{-1/2}/1^{1/2} \text{ mol}^{-1/2}$ | 2.31 | 2.66 | 3.23 | 3.86 | 4.47 | 6.46 |
| $10^4 k_1/\text{s}^{-1}$ | 1.2 | | 1.2 | | 1.08 | |
| $[\text{P}]_0/\text{M}$ | 0.183 | | 0.087 | | 0.049 | |

explanations can be envisaged for this unusual observation. First, one can postulate that the order x of the radical-induced decomposition with respect to BPO is smaller than 1. Alternatively, it could be suggested that in addition to radicals, other non-radical species might also induce BPO decomposition. As such, in order to

fit the experimental results, the BPO concentration has to be related to the concentration of the compounds responsible for induced decomposition in such a way that the lower the former, the higher is the latter.

The first postulate was tested by a plot of k_t from Table 3 against $[P]_0^{-1/2}$, giving a straight line (r 0.99); this indicates that the radical-induced decomposition should be dependent on a half-order in peroxide concentration, the rate constant of the radical-induced decomposition deduced from the slope is $k_t = 9.7 \times 10^{-5} \text{ mol}^{1/2} \text{ l}^{-1/2} \text{ s}^{-1}$. The half-order necessitates that the induced decomposition process and the termination process have the stoichiometry shown in Scheme 2. In this simplified



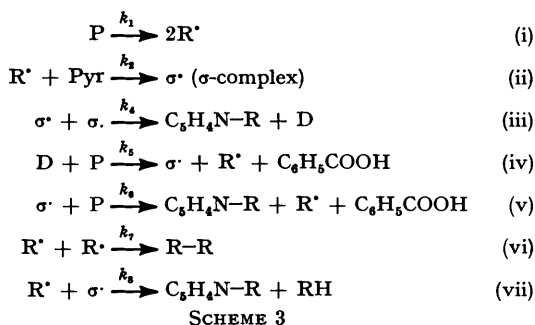
mechanism P stands for the undecomposed BPO and R^* for benzoyloxyl and phenyl radicals.

Applying steady-state treatment to the mechanism shown in Scheme 2, equation (9) is obtained. The calcu-

$$k_t = [\text{Pyr}]_0 k_a (k_1/k_d)^{1/2} \quad (9)$$

lated value from equation (9) for k_t , $1 \text{ mol}^{1/2} \text{ l}^{-1/2} \text{ s}^{-1}$,* is four orders of magnitude higher than the actual value of k_t , $9.7 \times 10^{-5} \text{ mol}^{1/2} \text{ l}^{-1/2} \text{ s}^{-1}$. Such a discrepancy rules out a radical-induced reaction being half-order in peroxide concentration.

Thus the second assumption is more likely. We propose that another species responsible for the decomposition arises from the disproportionation of the σ -complexes, *i.e.* dihydropyridines as shown in Scheme 3. In Scheme 3 D stands for dihydropyridines.



Several facts support this assumption. (i) Contrary to a report for benzene,²³ dihydro-derivatives are not observed at the end of the reaction. Since dihydrophenylpyridines can be thermally decomposed into phenyl- and tetrahydrophenyl-pyridines we also looked for the latter compounds but we did not find any.

* From the value of k_a in ref. 22, our value of k_1 , and assuming that the termination reaction is diffusion controlled.

However, the formation of dihydrophenylpyridines must be postulated to rationalize the results of the phenylation of [2-²H]- and [3-²H]-4-methylpyridine by BPO.²⁴ Therefore the dihydrophenylpyridines initially formed have to be oxidised.

(ii) It has been reported that dihydropyridine derivatives are oxidised by BPO at room temperature.²⁵ We prepared an ethereal solution of 1,2-dihydro-2-phenylpyridine using the method published by Giam *et al.*²⁶ This compound reacts readily with BPO at room temperature and the rate constant is estimated as $10 \text{ l mol}^{-1} \text{ s}^{-1}$ from the half-life of BPO in benzene solution. Thus, dihydrophenylpyridine concentrations as low as 10^{-5} M would justify the magnitude of the induced decomposition.

(iii) It has been shown²³ that in the reaction of BPO with benzene termination at low $[P]_0$ occurs largely by interaction of pairs of cyclohexadienyl radicals giving rise to dihydrobiphenyls and tetrahydroquaterphenyls; we assume that the same should hold for decomposition in pyridine. Thus at very low $[P]_0$, the reaction should be almost entirely accommodated by the processes (i)–(iv), whereas at high $[P]_0$ the process (vi) should predominate with processes (iii) and (iv) being of minor importance. Therefore as $[P]_0$ increases, the yield of phenylpyridines should increase whereas the yield of σ -complex dimers (which one would expect to be formed together with the disproportionation products by reaction of two σ -complexes) should decrease. As shown in Table 4,

TABLE 4

Variation in yield of σ -complex dimers in the phenylation of 4-methylpyridine–benzene mixtures with initial BPO concentration $[P]_0$

| $10^3 [P]_0/\text{M}$ dimer ^a | 8.4 | 5.9 | 4.5 | 2.4 |
|---|------|------|------|------|
| 2- and 3-Ph-4-MeC ₆ H ₃ N | 0.15 | 0.23 | 0.27 | 0.38 |

^a This ratio has been deduced from the variation in isomer percentages with initial BPO concentration⁷ since this variation results from the selective removal of the 3-position σ -complex by the dimer formation.

the variation in yield of σ -complex dimers in the phenylation of 4-methylpyridine–benzene mixtures with initial BPO concentration, $[P]_0$, are consistent with this assumption.† Therefore as $[P]_0$ increases the decomposition induced by the dihydro- and tetrahydro-phenylpyridines decreases, providing an explanation for the unusual variation of the pseudo-first-order rate constant in pyridine with change in $[P]_0$.

† In pure pyridine the coupling reactions of the three σ -complexes might give rise to many bisdihydrophenylbipyridyl isomers and stereoisomers. Even after dehydrogenation, the reaction mixture might remain complex and the accuracy of the yield measured might be low. We chose to study the decomposition in 4-methylpyridine–benzene solutions since the product analysis should be less difficult and therefore more accurate than in pyridine. In addition to the tetrahydroquaterphenyls and the quaterphenyls, we only observed two dimers, namely 2-(*p*-biphenyl)-4-methyl-3-phenyl- and 2-(*p*-biphenyl)-4-methyl-5-phenyl-pyridine which resulted from the coupling of the σ -complex at the 3-position with the phenylcyclohexadienyl radical.²⁷ A benzene:4-methylpyridine ratio of 6:1 (or higher) prevents coupling of two 4-methylpyridine σ -complexes.

Note that radical traps scavenge not only the benzoyloxy and phenyl radicals but also the σ -complexes formed under these conditions. Therefore, dihydropyridine-induced decomposition is suppressed and consequently the reaction may be taken as a radical-induced decomposition.

EXPERIMENTAL

Starting Materials.—Pyridine and principally 4-methylpyridine may contain traces of amine. Because of the high reactivity of amines with BPO,²⁸ they must be removed. For pyridine BPO (12 g) was decomposed in 1 l which was then distilled over a spinning band column. In order to obtain good reproducibility of the kinetic results, this procedure was repeated. Pyridine *N*-oxide was identified by comparison of its i.r. spectrum and its retention time in g.l.c. with that of an authentic sample. Benzoic anhydride could not be isolated from the reaction mixture; however g.l.c. comparison and co-injection with an authentic sample showed its presence. Furthermore, on addition of water, it disappeared to give benzoic acid. Yields were measured by g.l.c. analysis with 1,2-di-4-pyridylethylene as internal standard (column 3 ft \times 1/8 in packed with 5% SE 30 on 80–100 mesh Chromosorb W; isothermal at 180 °C).

2-(p-Biphenyl)-4-methyl-3-phenylpyridine and 2-(p-Biphenyl)-4-methyl-5-phenylpyridine.—A solution of biphenyl-lithium (27 mmol) in ether (80 ml) was added at room temperature to a solution of 4-methyl-3-phenylpyridine²⁹ (2.5 g, 15 mmol) in toluene (100 ml). The mixture was cooled to 40 °C and water (20 ml) was added. The ethereal extract was dried (Na_2SO_4), the toluene distilled, and the residue poured into *n*-hydrochloric acid (200 ml). The ethereal extract gave *p*-quarterphenyl (0.15 g, 0.5 mmol). The aqueous solution was basified and extracted with chloroform. The residue was chromatographed over silica gel with light petroleum–chloroform (1 : 1 v/v) as eluant. *2-(p-Biphenyl)-4-methyl-5-phenylpyridine* was eluted first. The two isomers were distinguished by ¹H n.m.r. spectroscopy, the 6-H of the *2-(p-biphenyl)-4-methyl-3-phenylpyridine* is coupled with the 5-H ($J^{5,6}$ 4 Hz) whereas the 6-H signal of the other isomer appeared as a singlet ($J^{3,6} < 0.5$ Hz). *2-(p-Biphenyl)-4-methyl-5-phenylpyridine* (Found: C, 89.6; H, 6.0; N, 4.4. $\text{C}_{24}\text{H}_{19}\text{N}$ requires C, 89.7; H, 5.9; N, 4.35%) had ν_{max} (KBr) 3 030, 3 000, 1 600, 1 480, 1 450, 1 000, 885, 840, 765, 760, 725, 705, and 695 cm^{-1} ; $\delta(\text{CDCl}_3)$ 2.35 (3 H, s, CH_3), 7.1–7.65 (13 H, m, aromatic H), 8.05, 7.95 (2 H, 2'- and 6'-H of biphenyl), and 8.4 (1 H, s, 6-H); m/e 321 (100%, M^+), 320 (14, $M^+ - \text{H}$), 244, 243, 215, 202, 178, 177, 167, 166, 165, 153, 152, 151, 141, 140, 139, 128, 127, 126, and 115. *2-(p-Biphenyl)-4-methyl-3-phenylpyridine* (Found: C, 89.5; H, 6.0; N, 4.5%), ν_{max} (KBr) 3 040, 3 010, 2 940, 2 905, 1 580, 1 560, 1 475, 1 455, 1 430, 1 395, 1 008, 845, 765, 730, 700, and 595 cm^{-1} ; $\delta(\text{CDCl}_3)$ 2.15 (3 H, s, CH_3), 7.05–7.6 (15 H, m, aromatic), and 8.45 (1 H, d, J 4 Hz, 6-H); m/e 321 (58%, M^+), 320 (100, $M^+ - \text{H}$), 304, 244, 160, 153, 151, 139, 126, and 115.

1,2-Dihydro-2-phenylpyridine—An ethereal solution of this compound was prepared according to the procedure described by Giam *et al.*²⁶ by hydrolysis of the corresponding *N*-lithio-2-phenyl-1,2-dihydropyridine³⁰ with an excess of water which was removed by addition of anhydrous sodium sulphate.

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