Comparative Behaviour of σ-Complexes in Phenylation of 4-Methylpyridine by Benzoyl Peroxide in Refluxing Benzene

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Isotope effects have been determined for the phenylation of [2-^{2}H]- and [3-^{2}H]-4-methylpyridine by benzoyl peroxide in refluxing benzene. The primary deuterium isotope effect k_H/k_D for hydrogen abstraction from the σ-complex at the 3-position in 4-methylpyridine is 3.7 whereas at the 2-position $k_H/k_D = 1$. In the presence of nitrobenzene there is no isotope scrambling and it is therefore suggested that isomer distributions obtained from product analyses resulting from benzoyl peroxide decomposition in the presence of nitrobenzene reflect the true measure of relative rates at which the isomeric σ-complexes are formed initially. We have tried to understand the different behaviours of σ-complexes at position 2 and 3 in 4-methylpyridine.

In a previous paper [1] it was shown that in the homolytic arylation of 4-methylpyridine by benzoyl peroxide the reactivities of the two nuclear positions of 4-methylpyridine towards attack by phenyl radicals depend on the benzoyl peroxide concentration used. Evidence has been presented [1] that side reactions can be selective and that the σ-complexes at the 2- and 3-positions in 4-methylpyridine have different oxidation rates. We now report studies of the phenylation of deuteriated 4-methylpyridines which shed light on the behaviour of the σ-complexes and on the bond dissociation energy of the C–H and C–D bonds at the tetrahedral carbon in these complexes.

The σ-complexes resulting from the attack of 4-methylpyridine and benzene by phenyl radicals can undergo four different reactions as shown in Scheme 1.

$$Ar^1H + Ph\cdot \longrightarrow [Ar^1HPh\cdot] \quad (1)$$
$$[Ar^1H\ Ph\cdot] + \text{oxid. agent} \longrightarrow Ar^1Ph \quad (2)$$
$$[Ar^1H\ Ph\cdot] + [Ar^2H\ Ph\cdot] \longrightarrow Ar^1Ph + Ar^2Ph\ H_2 \quad (3)$$
$$[Ar^1H\ Ph\cdot] + [Ar^2H\ Ph\cdot] \longrightarrow Ph\cdot Ar^1H{-}Ar^2HPh \quad (4)$$
$$[Ar^1H\ Ph\cdot] \longrightarrow Ar^1H + Ph\cdot \quad (5)$$

Scheme 1

As reaction (2) is common to substitution reactions with diverse radical sources and is very often the only one [2] which gives arylated products, it is considered as the main one. The other three are regarded as side reactions although they may play a prominent part at very low initial peroxide concentration.[3] However reaction (5) seems unlikely since it has been shown [4] that in the pyrolysis of bi-(4-phenylcyclohexa-2,5-dienyl) in oxygen-free chlorobenzene at 170° biphenyl and 1,4-dihydrobiphenyl are formed in good yield whereas only a trace of *o*-chlorobiphenyl could be detected.

It is obvious that the ratio of the main reaction to the side reactions has to be the same for all the σ-complexes involved in order to obtain valid isomer distributions and partial rate factors, *i.e.* each σ-complex is converted randomly into biaryl or side-products. This ratio is related to the bond dissociation energy of the C–H bond at the tetrahedral carbon in the σ-complex and depends on the concentration of oxidising agent. Therefore there are two ways to modify the relative importance of reactions (2)—(5). First, one hydrogen atom can be substituted by deuterium. This substitution is assumed to increase the bond strength and for the corresponding σ-complex side reactions may be enhanced, in particular reaction (4) at the expense of reaction (2), whereas the behaviour of the other σ-complexes is not altered. Secondly, an efficient oxidising agent such as nitro- or nitroso-benzene [5] can be added. The rate of reaction (2) would be drastically increased for all the σ-complexes and reactions (3)—(5) would be of minor importance if not totally suppressed.

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[2] G. H. Williams and D. H. Hey, *Adv. Free Radical Chem.*, 1967, **2**, 47.
[3] D. F. Detar, R. A. J. Long, J. Rendleman, J. Bradley, and P. Duncan, *J. Amer. Chem. Soc.*, 1967, **89**, 4051.
[4] D. J. Atkinson, M. J. Perkins, and P. Ward, *J. Chem. Soc.* (*C*), 1971, 3240.
[5] G. R. Chalfont, D. H. Hey, K. S. Y. Liang, and M. J. Perkins, *J. Chem. Soc.* (*B*), 1971, 233.

Accordingly in order to compare the behaviour of the σ-complex at the 2-position in 4-methylpyridine (σ_2-complex) with that of the σ_3-complex the phenylation of [2-^{2}H]- and [3-^{2}H]-4-methylpyridine has been studied. Reactions were carried out with and without oxidising agent.

RESULTS AND DISCUSSION

Table 1 lists the isotopic composition of phenylated [3-^{2}H]-4-methylpyridine from phenylation of [3-^{2}H]-4-methylpyridine by benzoyl peroxide in refluxing benzene for 48 h. Experiments were carried out under nitrogen, with and without nitrobenzene but the molar ratio of benzoyl peroxide to [3-^{2}H]-4-methylpyridine and the [3-^{2}H]-4-methylpyridine concentration were kept the same in both cases.

TABLE 1

Isotopic distribution of phenylated [3-^{2}H]-4-methylpyridine formed by thermal decomposition of benzoyl peroxide at 80° for 48 h

Experimental conditions	Pyridine		Isotopic distribution [c] $^2H_0$	$^2H_1$	$^2H_2$
Benzoyl peroxide alone [a]	[3-^{2}H]-4-Me	Obs [d]	5.1	93.4	1.5
	2-Ph, 4-Me	Calc [e]	5.1	93.4	1.5
		Obs [f]	6.1	91.6	2.3
	3 Ph, 4-Me	Calc [e]	51.8	47.45	0.75
		Obs [f]	26.2	71.8	2
Benzoyl peroxide–nitrobenzene [b]	[3-^{2}H]-4-Me	Obs [d]	3.6	92.4	4.1
	2-Ph, 4-Me	Calc [e]	3.6	92.4	4.1
		Obs [f]	4.7	93.7	1.6
	3-Ph, 4-Me	Calc [e]	49.8	48.25	2.05
		Obs [f]	49	49	2

[a] Reaction carried out in refluxing benzene under nitrogen for 48 h with benzoyl peroxide : [3-^{2}H]-4-methylpyridine molar ratio of 0.05. [b] Reaction carried out in benzene (100 ml)–nitrobenzene (1 g) at 80° under nitrogen for 48 h with benzoyl peroxide : [3-^{2}H]-4-methylpyridine molar ratio of 0.05. [c] Determined by mass spectrometry at reduced ionizing voltage, the values have been corrected for ^{13}C isotope contributions. [d] Initial isotopic distribution (%). [e] Statistically calculated with the assumption that there is no isotope scrambling. [f] Isotopic distribution determined on samples purified by g.l.c. after one decomposition of benzoyl peroxide. [g] The scalar error on isotopic compositions is ±0.5%.

From Table 1 it appears that in the absence of nitrobenzene [5-^{2}H]-4-methyl-3-phenylpyridine is richer in deuterium than expected from a statistical calculation made with the assumption that there is no isotopic scrambling. The observed isotopic composition of 4-methyl-3-phenylpyridine* shows that the σ_3-complex with deuterium at the tetrahedral carbon (σ_{3D}-complex) is less prone to yield the phenyl derivative (and more prone to yield side products) than the σ_3-complex with hydrogen at the tetrahedral carbon (σ_{3H}-complex).

* The magnitude of the observed product isotope effect is too large to result only from a secondary isotope effect.[6]

† It has been shown [7] that the apparent product isotope effect in biphenyl obtained from [^{2}H]benzene and benzoyl peroxide is higher when biphenyl is carefully separated from dihydrobiphenyl than when dihydrobiphenyl is allowed to be air oxidized to biphenyl. We carried out reactions under nitrogen but no 4-methyl-3-phenyldihydropyridine could be observed and no 4-methyl-3-phenylpiperidine could be obtained by hydrogenation. However the results obtained in the case of [2-^{2}H]-4-methylpyridine show that 4-methyl-3-phenyldihydropyridines are formed according to reaction (3).

Assuming that 4-methyl-3-phenylpyridine results only from reaction (2) an apparent isotope effect has been calculated from the deuterium analysis by making the assumption of infinitesimal conversion, *i.e.* no change of substrate composition during reaction; this is justified by the high 4-methylpyridine:peroxide molar ratio. This calculation gives an apparent isotope effect of 3.7; however the isotope effect in reaction (2) is probably greater than that since the dehydrogenation of 4-methyl-3-phenyldihydropyridines resulting from reaction (3) can also give 4-methyl-3-phenylpyridine.† The result is that the ratio k_H/k_D for hydrogen and deuterium abstraction from the σ_3-complex is not accurately known but the magnitude of this ratio can only be consistent with considerable C–H bond breaking in the rate-determining step for 4-methyl-3-phenylpyridine formation.

On the contrary, as shown in Table 1, there is no isotope scrambling when nitrobenzene is added since the observed isotopic composition of 4-methyl-3-phenylpyridine is identical with the statistically calculated composition. Thus in the presence of nitrobenzene no diversion of the σ_{3D}-complex to side products occurs and the isotopic composition of 4-methyl-3-phenylpyridine gives the true measure of the relative rates at which the σ_{3D}- and σ_{3H}-complexes are formed by the initial attack of phenyl radicals. Extending this argument to the phenylation of heterocyclic compounds generally we suggest that the isomer distributions obtained from analyses of products resulting from benzoyl peroxide decomposition in the presence of nitrobenzene reflect the true measure of relative rates at which the isomeric σ-complexes are initially formed.

Table 2 gives the isotopic composition of phenylated 4-methylpyridine from the phenylation of [2-^{2}H]-4-methylpyridine by benzoyl peroxide in refluxing benzene without nitrobenzene. Note that the observed isotopic composition of 4-methyl-3-phenylpyridine differs notably from the statistically calculated composition whereas for the 2-phenyl derivative both compositions are identical.

TABLE 2

Isotopic composition of phenylated [2-^{2}H]-4-methylpyridine formed by thermal decomposition of benzoyl peroxide at 80° for 48 h

Pyridine		Isotopic composition [a] $^2H_0$	$^2H_1$	$^2H_2$
[2-^{2}H] 4-Me	Obs [b]	3	93.5	3.5
[6-^{2}H]-2-Ph, 4-Me	Calc [c]	49.75	48.45	1.7
	Obs [d]	49.7	49.1	1.2
[2-^{2}H]-3-Ph, 4-Me	Calc [c]	3	93.5	3.5
	Obs [d]	10.5	88	1.5

[a] Determined by mass spectrometry at reduced ionizing voltage; the values have been corrected for ^{13}C isotope contributions. [b] Initial isotopic composition. [c] Statistically calculated with the assumption that there is no isotope scrambling. [d] Isotopic compositions determined on samples purified by g.l.c.

[6] A. Fry, *Chem. Soc. Rev.*, 1972, **1**, 163.
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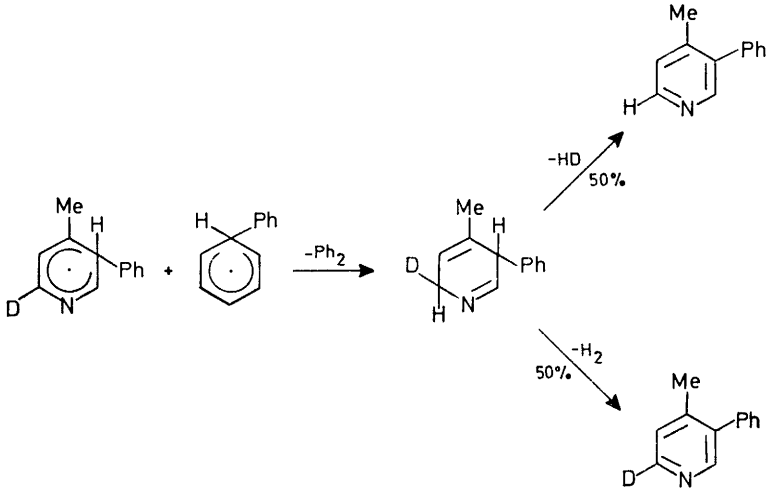
Since the 2-position is not involved during the formation of the σ_3-complex and during hydrogen abstraction [reactions (1) and (2)], the fact that 4-methyl-3-phenylpyridine is poorer in deuterium than the substrate must be due to side reactions. This deuterium loss at the 2-position can be explained by the formation of 4-methyl-3-phenyldihydropyridines according to reaction (3) structure (II). Therefore if it is supposed that dimers from the σ_2-complex give 4-methyl-2-phenylpyridine quantitatively, then the σ_2-complex has structure (II), structures (I) and (III) being of minor importance.† However the isolation of 2-phenyl-5-triphenylmethylpyridine [8] from the phenylation of pyridine with phenylazotriphenylmethane does not support this hypothesis.

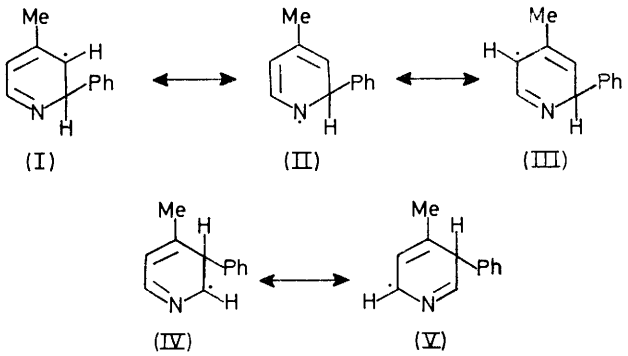


SCHEME 2

which are further dehydrogenated to 4-methyl-3-phenylpyridine as shown in Scheme 2. A calculation shows* that dihydroderivatives are responsible for 30% of the total amount of 4-methyl-3-phenylpyridine formed in the phenylation reaction. Thus as pointed out before the true isotope effect in the hydrogen abstraction from the σ_3-complex is certainly higher than 3.7.

On the contrary it appears from Table 2 that for the same conditions, *i.e.* without nitrobenzene no isotope effect is observed in the formation of 4-methyl-2-phenylpyridine. Thus either the σ_2-complex does not undergo side reactions or the by-products from the σ_2-complex are not stable under the conditions of the reactions and give quantitatively 4-methyl-2-phenylpyridine. It is reasonable to assume that dihydro-derivatives resulting from reaction (3) are easily dehydrogenated as has been observed in the case of the σ_3-complex, but it is not easy to explain why dimers from a cyclohexadienyl radical and a σ_2-complex should behave differently from dimers resulting from coupling of a cyclohexadienyl radical with a σ_3-complex. According to Scheme 3 since structures (I) and (III)—(V) are very similar, the main difference between the two σ-complexes appears to be

An alternative proposal is to assume that the σ_2-complex does not undergo side reactions, implying that the oxidation reaction of the σ_2-complex is much faster than



SCHEME 3

the disproportionation and dimerisation reactions. These three reactions have approximately the same rate for the σ_3-complex. Therefore the oxidation rate of the σ_2-complex should be higher than that of the σ_3-complex,

* From the observed isotopic composition of the 4-methyl-3-phenylpyridine it is possible to calculate the amount of 4-methyl-3-phenyldihydropyridines formed. It is assumed that the numbers of σ_3-complexes with the deuterium atom at the 2- and 6-positions are equal, that both σ_3-complexes give 2,3- and 3,6-dihydro-derivatives in the same ratio, and that there is no isotope effect upon dehydrogenation to 4-methyl-3-phenylpyridine. Then the quantity of 4-methyl-3-phenylpyridine resulting from the dihydro-compounds is: $10.5 - 3/100 \times 2 \times 2 \times 100 = 30\%$. If the third assumption was not true, *i.e.* if there is an isotope effect upon dehydrogenation then this percentage would be higher.

† Since hydrogenation does not modify the yields of 4-methyl-(phenyl)pyridines, it is assumed that dimers are dehydrogenated to biphenylyl-4-methyl(phenyl)pyridines under the reaction conditions as 4-methyl-3-phenyldihydropyridines are dehydrogenated to 4-methyl-3-phenylpyridine. According to this assumption and as shown in Scheme 4 dimers from structures (I) and (III) can give respectively 3- and 5-biphenylyl-4-methyl-2-phenylpyridine whereas the dimer from structure (II) cannot produce a similar derivative. Therefore in order to explain that the σ_2-complex gives quantitatively 4-methyl-2-phenylpyridine structure (II) is postulated for this complex.

[8] R. Grashey and R. Huisgen, *Chem. Ber.*, 1959, **92**, 2641.

i.e. the C–H bond strength at the 2-position in 4-methylpyridine should be smaller than that at the 3-position. It is obvious that a study of the side products obtained would not give definite information. However it appeared that such a study should confirm the absence of side products from the σ_2-complex and permit measurements of the amount of σ_3-complex diverted to side products. Table 3 lists the yields of the products from phenylation of 4-methylpyridine in refluxing benzene with benzoyl peroxide under various conditions. Every yield was measured by g.l.c. on hydrogenated and unhydrogenated reaction mixtures. Note that in any case the yields in 4-methyl(phenyl)pyridines remain unchanged upon hydrogenation whereas in the absence of nitrobenzene the biphenyl yield measured on unhydrogenated reaction mixtures is 50% higher than that obtained upon hydrogenation.

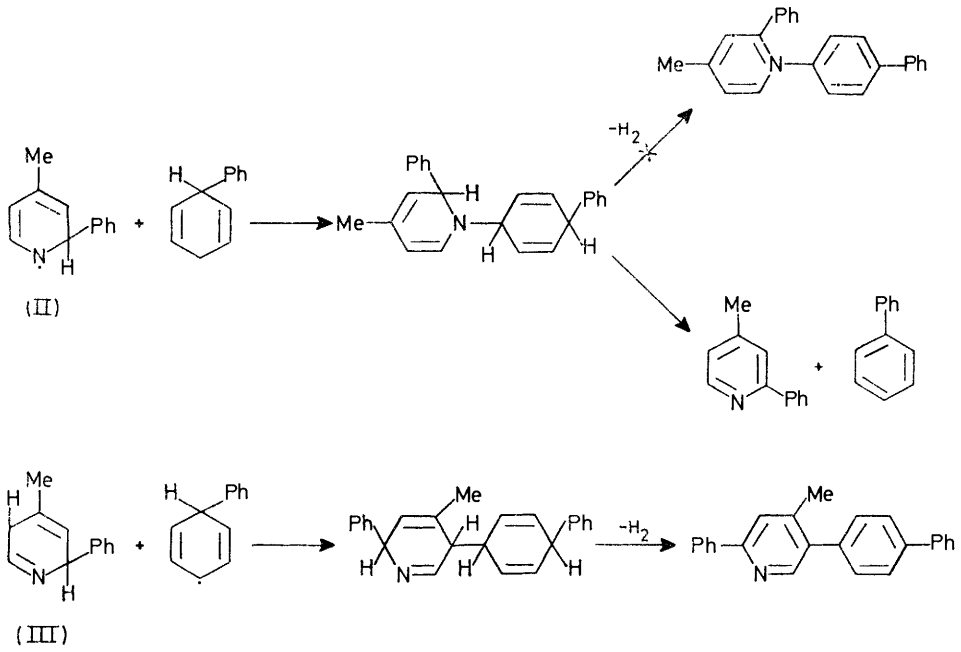
Since the variation of the biphenyl yield results from thermolysis of the tetrahydroquaterphenyls in the injection port * the fact that hydrogenation does not modify the yields of 4-methyl(phenyl)pyridines shows that the reaction mixture does not contain dimers from the σ_2- or σ_3-complexes. However this result does not imply that reaction (4) does not occur since the dimers from the σ_2- and σ_3-complexes could be dehydrogenated under the reaction conditions, as are the 4-methyl-3-phenyldihydropyridines, since methyl(phenyl)piperidines are not observed upon hydrogenation, whereas the isotopic study showed that they are formed. In order to test this possibility the most likely product† which would result from the reaction of a σ_3-complex with a cyclo-

TABLE 3

Yields of products from the phenylation of 4-methylpyridine in refluxing benzene with benzoyl peroxide under various conditions

Experimental conditions		Yields in mole per mole of peroxide				
		Biphenyl	$C_{12}H_{12}$ 1,4-Dihydro-triphenyl	Phenyl-cyclohexane	4-Me, 2-PhC_5H_3N	4-Me, 3-PhC_5H_3N
Under N_2	*a*	0.45	0.057		0.037	0.026
	b	0.31		0.034	0.037	0.026
Under N_2, $PhNO_2$ added	*a*	0.65	Trace		0.032	0.038
	b	0.67		Trace	0.032	0.038
In air	*a*	0.515			0.029 5	0.023
In air, $PhNO_2$ added	*a*	0.61			0.031 5	0.038

[a] Yields measured in unhydrogenated reaction mixtures. [b] Yields measured in hydrogenated reaction mixtures.



SCHEME 4

* In an exhaustive study [3] of the thermal decomposition of benzoyl peroxide in benzene, it has been shown that tetrahydroquaterphenyls disproportionate at 170° and can be analysed by g.l.c. as dodecahydroquaterphenyls resulting from the hydrogenation of the reaction mixture. For 0.05M initial peroxide concentration the yields of biphenyl and tetrahydroquaterphenyls amount to 0.36 and 0.32, respectively mole per mole of peroxide; therefore the thermolysis of tetrahydroquaterphenyls accounts for the variation in biphenyl yield.

† The molar ratio of 4-methylpyridine to benzene is 20, the total rate ratio in the phenylation of 4-methylpyridine is *ca.* 1, therefore reactions of σ_3- or σ_2-complexes with cyclohexdienyl radicals are more likely than coupling of σ_2- and σ_3-complexes. Moreover it has been shown in the phenylation of benzene [3] that *p,p'*-quaterphenyl represents 56% of the quaterphenyl fraction.

hexadienyl radical, *i.e.* 6-biphenylyl-4-methyl-3-phenylpyridine has been prepared but so far this compound has not been identified in the reaction mixture. Nevertheless it appears from Table 3 that the amount of σ_3-complex diverted to side products when the reaction is carried out under nitrogen is at least 30% since the addition of nitrobenzene results in a 50% increase of the yield in 4-methyl-3-phenylpyridine.

As expected the biphenyl yield remains unchanged upon hydrogenation when the reaction is carried out in the presence of nitrobenzene; however this yield is lower than that obtained from the decomposition in benzene–nitrobenzene (100 : 1 v/v) which has been reported as 81% under similar conditions.[5] This observation is probably due to the fact that in pyridine derivatives a second decomposition mechanism of benzoyl peroxide competes with homolysis.[9] The observed decrease in 4-methyl-2-phenylpyridine in the presence of nitrobenzene requires some comment since the yields of arylated products are usually enhanced by the addition of oxidising agents. As shown earlier no isotope effect is observed in the formation of 4-methyl-2-phenylpyrine, *i.e.* no σ_2-complexes are diverted to side products and therefore the addition of nitrobenzene cannot increase the yield of 4-methyl-2-phenylpyridine. Moreover when phenylation of benzene is carried out in the presence of various additives,[5] some consumption of phenyl and benzoyloxyl radicals by these additives occurs so the highest yield of biphenyl does not exceed 90%. Therefore the observed decrease in 4-methyl-2-phenylpyridine yield when nitrobenzene is added could be attributed to the consumption of phenyl and benzoyloxyl radicals by the additive. It is also interesting to note that when the reaction is carried out in air the yield of 4-methyl-2-phenylpyridine is lower than under nitrogen; moreover this yield decreases dramatically under oxygen. Therefore oxygen can oxidize the σ-complexes but it scavenges the phenyl radicals and yields of arylated products are low. This conflicts with the work of Eberhardt and Eliel [10] but is in accord with other results.[11,12]

From the apparent isotope effect for hydrogen abstraction from the phenylcyclohexadienyl radical, 6.6, the σ_2- 1.0, and the σ_3-complex, 3.7, it appears that in phenylation of 4-methylpyridine by benzoyl peroxide in refluxing benzene the various σ-complexes are not converted randomly into phenyl derivatives and by-products. Moreover in the presence of nitrobenzene the yields of biphenyl, 2-phenyl-, and 3-phenyl-4-methylpyridines are not increased by the same factors. Therefore no significance can be ascribed to the isomer distributions and to the partial rate factors obtained with benzoyl peroxide alone. We suggest that the high side-reaction selectivity observed in the case of 4-methylpyridine results from the ability of σ-complex dimers to undergo further reactions under the reaction conditions. In particular dimers from the σ_3-complex are possibly dehydrogenated to biphenylyl-4-methyl(phenyl)pyridines which are not thermolysed to phenyl derivatives in the injection port of the gas chromatograph employed in the analyses as happens to coupling products from σ-complexes.* Further study on the by-products is needed to confirm this. However, we think that the side-reaction selectivity observed in the case of 4-methylpyridine is not exceptional and that an efficient oxidising agent should be added to benzoyl peroxide.

EXPERIMENTAL

Starting Materials.—[2-^{2}H]-4-*Methylpyridine.* This was prepared from deuterium oxide and 4-methyl-2-pyridyllithium obtained by the reaction [13,14] of n-butyl-lithium with 2-bromo-4-methylpyridine [15]. The crude product was purified by g.l.c. giving [2-^{2}H]-4-methylpyridine (32%). The isotopic purity (established from low voltage mass spectra) was $^2H_0$ 3, $^2H_1$ 93.5, $^2H_2$ 3.5%.† The position of deuterium incorporation was checked from the n.m.r. spectrum.

[3-^{2}H]-4-*Methylpyridine.* This was prepared similarly from 3-bromo-4-methylpyridine.[17] The isotopic purities of samples from two different runs were (i) $^2H_0$ 5.1, $^2H_1$ 93.4, $^2H_2$ 1.5% and (ii) $^2H_0$ 3.6, $^2H_1$ 92.4, $^2H_2$ 4.1%

General Procedure for Phenylation of Monodeuteriated 4-Methylpyridines with Benzoyl Peroxide.—A solution of monodeuteriated 4-methylpyridine (1.88 g, 20 mmol) in thiophen-free, sodium-dry benzene (20 ml) was refluxed and oxygen-free nitrogen was bubbled through the mixture during 3 h at the rate of 20 ml mm^{-1}. Benzoyl peroxide (0.242 g, 1 mmol) was then added and the reaction allowed to proceed during 48 h while the nitrogen stream was maintained at the same rate. The mixture was cooled, poured into a saturated aqueous solution of $NaHCO_3$ (100 ml), and extracted with ether (3 × 50 ml). After drying (Na_2SO_4) ether was removed and the 4-methyl-(phenyl)pyridines were isolated from the concentrated solution by preparative g.l.c. as pure components. The

* Given that dihydro-derivatives and σ-complex dimers should be totally thermolysed into phenyl derivatives in the injection port whereas they are stable under the reaction conditions. An apparently normal isomer distribution should be obtained in the g.l.c. analysis even if side reactions were selective. Therefore in order to test the side-reaction selectivity it is better to use another method for the analysis or to hydrogenate the reaction mixture before analysis.

† Since n-butyl-lithium is used to metallate 2- and 4-picoline [16] the formation of dideuteriated 4-methylpyridine is ascribed to this reaction. It is assumed that n-butyl-lithium can metallate 4-methyl-2-pyridyl-lithium which upon hydrolysis with two moles of deuterium oxide gives [2-^{2}H]-4-deuteriomethylpyridine, whereas hydrolysis with one mole of water and one mole of deuterium oxide can afford either [2-^{2}H]-4-methylpyridine or 4-deuteriomethylpyridine. A statistical calculation shows that the later compound represents <0.2% of the [2-^{2}H]-4-methylpyridine sample.

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conditions were: column 6 ft × 1/4 in packed with 4% KOH and 5% asphalt on 45—60 mesh Chromosorb G regular, helium flow rate 60 ml min^{-1}, isothermal at 200°. The isotopic distribution of each 4-methyl(phenyl)pyridine was determined from the ratio of the parent peak intensities of $C_{12}H_{11}N$(*M* 169), $C_{12}H_{10}DN$(*M* 170), and $C_{12}H_9D_2N$(*M* 171). It had been checked that the parent ion was the only mass peak in the 11 eV spectrum of 2- and 3-phenyl-4-methylpyridine.

Reaction in the Presence of Nitrobenzene.—The same procedure was used except that nitrobenzene (0.200 g, 1.62 mmol) was added to the 4-methylpyridine solution in benzene prior to refluxing.

Hydrogenation of Reaction Mixtures.—The procedure described [18] in the case of the decomposition of benzoyl peroxide in benzene was used.

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