Aromatic Substitution. Part XXV.[1] Reaction of 3-Picoline with Some Substituted Phenyl-lithium Derivatives

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A study of the reactions of *o*-tolyl-, *o*-ethylphenyl-, and *p*-methoxyphenyl-lithium with 3-picoline has shown that the substituent has little effect upon the ratio of the 2,3- and 2,5-isomers formed. *o*-Tolyl-lithium gave, in addition, some 3-methyl-5-*o*-tolylpyridine, and 3-methyl-1,2,5,6-tetrahydro-2-*o*-tolylpyridine could be isolated under certain conditions. The latter arises by disproportionation of the intermediate σ-complex while the former probably results from the attack of this σ-complex by *o*-tolyl-lithium. An attempt to reduce 3-methyl-2-*o*-tolylpyridine to the tetrahydro-derivative with lithium aluminium hydride and aluminium chloride was unsuccessful.

In an earlier paper,[2] it was confirmed[3] that whereas the reaction of methyl-lithium with 3-picoline (I) gave 2,3- and 2,5-lutidine in the ratio 84·5 : 15·6, the corresponding reaction of (I) with isopropyl-lithium gave a 2,3- : 2,5-isomer ratio of 20·5 : 79·5. Part of this reversal of the relative orientation was ascribed to the bulk of the tetrameric (or hexameric) isopropyl-lithium.[2,3] With phenyl-lithium and 3-picoline the 2,3- : 2,5-isomer ratio is 95 : 5.[4] The importance of steric effects in the reactions of *o*-tolyl-, *o*-ethylphenyl-, and *p*-methoxyphenyl-lithium with 3-picoline have now been studied.

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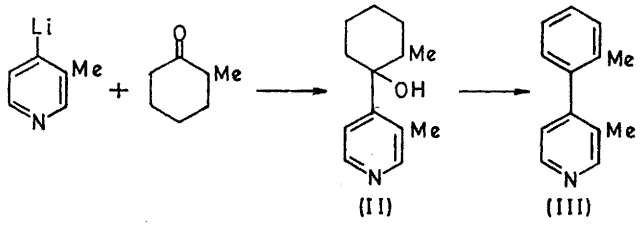
[1] Part XXIV, R. A. Abramovitch and A. R. Vinutha, *J. Chem. Soc.* (*C*), 1969, 2104.

[2] R. A. Abramovitch and G. A. Poulton, *J. Chem. Soc.* (*B*), 1969, 901.

[3] H. C. Brown, M. S. Howie, and H. E. Podall, personal communication; M. S. Howie, Ph.D. Thesis, Purdue University, 1961.

Introduction of an *o*-methyl group into the aryllithium should result in destabilisation of the corresponding anion, with a resulting decrease in selectivity and increase in reactivity. Any attractive interaction between the 3-methyl group in the pyridine and the attacking nucleophile[4,5] should decrease as should the amount of substitution at C-2 (hence the 2,3- : 2,5- ratio should also decrease). The introduction of the *o*-methyl group in the attacking species should also have an adverse steric effect upon substitution at C-2 and again a decrease in the 2,3- : 2,5- ratio should result.

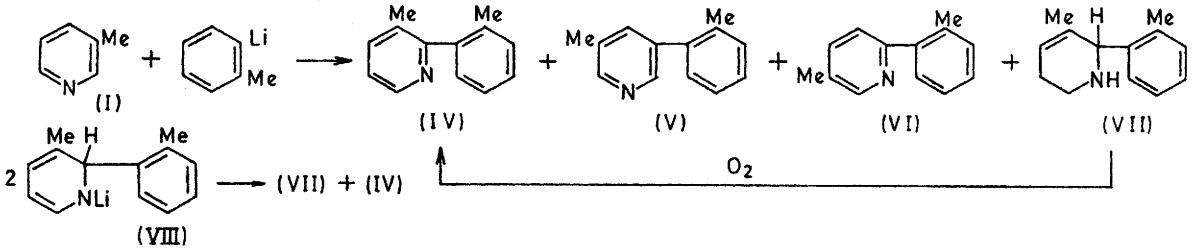
The reaction of *o*-tolyl-lithium with (I) was more complex than expected and the nature and yields of products depended on the reaction conditions. All the possible ring substitution products were synthesised by unambiguous routes. 3-Methyl-4-pyridyl-lithium and 2-methylcyclohexanone gave 4-(1-hydroxy-2-methylcyclohexyl)-3-methylpyridine (II) which was dehydrated and dehydrogenated with sulphuric acid in acetic acid[6] to give 3-methyl-4-*o*-tolylpyridine (III). 3-Methyl-



(II) (III)

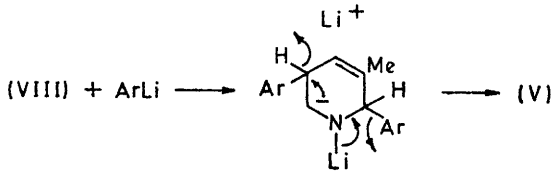
2-*o*-tolyl- (IV), 3-methyl-5-*o*-tolyl- (V), and 5-methyl-2-*o*-tolyl-pyridine (VI) were similarly prepared from the corresponding bromo-3-picolines.

Reaction of *o*-tolyl-lithium with an excess of 3-picoline in boiling ether followed by oxidation with oxygen gave 3-methyl-2-*o*-tolyl- and 5-methyl-2-*o*-tolyl-pyridine in the ratio 96 : 4 (overall yield 51—68% based on *o*-tolyl-lithium). At 110° (toluene) the reaction also gave the 3,5-isomer (V), the isomer ratio being 2,3- : 2,5- : 3,5- = 90·6 : 3·6 : 5·8. In no reaction was 3-methyl-4-*o*-tolylpyridine detected. If 3-picoline was not present in excess, 3-methyl-1,2,5,6-tetrahydro-2-*o*-tolylpyridine (VII) was an additional product.



Increased quantities of this were obtained upon reaction of equimolar amounts of 3-picoline and *o*-tolyl-lithium in boiling ether with omission of the oxidation step. The structure of this product was assigned on the following evidence. It had a molecular formula $C_{13}H_{17}N$ and $\lambda_{max.}$ 265 mμ which does not correspond to the known absorptions of dihydropyridines.[7] The n.m.r. spectrum (in CCl_4) was quite characteristic: a 4H singlet at τ 2·98 due to C_6H_4, a 1H singlet at τ 4·35 due to 4-H (C*H*=C), a 1H singlet at τ 5·62 due to 2-H (N·C*H*·Ar benzylic proton), a 2H multiplet centred at τ 7·20 due to 6-H (CH_2·N·), a 3-H singlet at τ 7·62 ($ArCH_3$), a 2H broad multiplet at τ 7·92 due to 5-H (CH_2·CH:), and a broad 4H singlet at τ 8·61 (N*H* + :C·CH_3) which reduces to a 3H singlet at τ 8·58 upon addition of D_2O. Exposure to atmospheric oxygen leads to the rapid oxidation of (VII) to (IV) but the compound can be stored under nitrogen. The tetrahydro-derivative (VII) undoubtedly arises[7] from the disproportionation of the intermediate[8] σ-complex (VIII). Until recently[8-10] this[11] was the only *direct* evidence for the intervention of such σ-complexes in the reactions of organolithium compounds with simple pyridine derivatives.

The formation of 3-methyl-5-*o*-tolylpyridine (V) could be explained by assuming a nucleophilic attack by *o*-tolyl-lithium at C-5 of (VIII) followed by a reversal of the initial addition leading to (VIII) and aromatisation. This is a modification of the mechanism suggested[12] for the formation of 2,5-diphenylpyridine from pyridine and phenylcalcium iodide.[13] If this is so, (V) is formed at the expense of (IV), and the ratio of attack by *o*-tolyl-lithium on 3-picoline at the 2- and the 6-positions is 96·4 : 3·6, which is very similar to that obtained earlier in boiling ether and then oxygen when (V) and (VII) were not observed.



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[11] R. A. Abramovitch and G. A. Poulton, *Chem. Comm.*, 1967, 274.
[12] R. A. Abramovitch and J. G. Saha, *Adv. Heterocyclic Chem.*, 1966, **6**, 229.
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The reaction of *o*-ethylphenyl-lithium with 3-picoline was not studied as extensively. Only one product, 2-*o*-ethylphenyl-3-methylpyridine, which constituted 97% of the product, was positively identified. Three other minor components were also observed on gas chromatography but the peaks were insufficiently resolved to permit collection of the individual compounds. The minimum 2,3- : 2,5- ratio of isomers in this reaction is, therefore, 97 : 3.

Two isomeric products were formed in the reaction of *p*-methoxyphenyl-lithium with 3-picoline and their structures were assigned on the basis of microanalyses and their i.r. and n.m.r. spectra. The major product exhibited a 1H doublet at τ 1·66 ($J_{5,6}$ 4·6 c./sec. 6-H), a 3H multiplet at τ 2·61 ($J_{4,5}$ 7·0 c./sec., 4-H) and 2H of C_6H_4), a 1H quartet at τ 3·04 ($J_{4,5}$ 6·8 c./sec., $J_{5,6}$ 4·5 c./sec., 5-H), a 2H doublet at τ 3·18 (J 8·0 c./sec.) (2H of C_6H_4), a 3H singlet at τ 6·24 (·OCH_3), and a 3H singlet at τ 7·69 (ArCH_3). The minor isomer exhibited a 1H singlet at τ 1·69 (6-H), a 2H doublet at τ 2·17 (J 8·7 c./sec., 2H of C_6H_4), a 2H multiplet at τ 2·66 (4-H and 5-H), a 2H doublet at τ 3·17 (J 8·5 c./sec., 2H of C_6H_4), a 3H singlet at τ 6·25 (OCH_3), and a 3H singlet at τ 7·73 (CH_3). The major isomer was therefore 2-*p*-methoxyphenyl-3-methylpyridine and the minor one 2-*p*-methoxyphenyl-5-methylpyridine. The 2,3- : 2,5-isomer ratio was 94·4 : 5·6.

It is clear that neither the *o*-methyl nor the *o*-ethyl substituent exerts any appreciable steric effect since the isomer ratio is virtually identical to that obtained with phenyl-lithium itself. This result is understandable if the geometry of the transition state leading to the formation of the intermediate σ-complex resembles that of the ground state so that the attacking nucleophile is perpendicular to the plane of the pyridine ring and the developing bond is still very long. Only large steric effects would then be felt.[4,12] The *p*-methoxy-substituent in the aryl-lithium also has little or no effect upon the isomer ratio. On the basis of its inductive effect [$\sigma_I = 0{\cdot}25$ (ref. 14)] one might expect increased stabilisation of the anion and increased selectivity, which is not observed. It has similarly been found that base-catalysed exchange of the *para*-proton in anisole is slower than in benzene ($F_p = 0{\cdot}5$) [15] so that it appears that the $+M$ effect of the OMe group is operating here and neutralising the $-I$ effect.

EXPERIMENTAL

4-(1-*Hydroxy*-2-*methylcyclohexyl*)-3-*methylpyridine*.— n-Butyl-lithium [from lithium (0·22 g.) and n-butyl bromide (2·1 g.)] was treated with 4-bromo-3-methylpyridine [16] (4·3 g.) at −68 to −72°; after the mixture had been stirred for 15 min. 2-methylcyclohexanone (2·5 g.) was added. After a further 15 min. the solution was allowed to come to room temperature and was then poured onto ice. The mixture was extracted with ether and the extracts were washed with dilute acid; the acid extracts were basified and then re-extracted with ether. The ether layer was dried ($MgSO_4$) and evaporated to give the *alcohol* (2·6 g., 52%), b.p. 55—60°/0·05 mm., m.p. 105—106° [from light petroleum (b.p. 60—80°)] (Found: C, 76·2; H, 9·4; N, 6·9. $C_{13}H_{19}NO$ requires C, 76·05; H, 9·3; N, 6·8%); $\nu_{max.}$ (KBr disc) 3650, 1588, 1430, 1398, 1335, 1290, 1250, 1190, 1168, 1130, 1108, 1070, 988, 953, 880, 812, 745, and 639 cm.$^{-1}$; τ(CCl_4) 1·95 (2H, d, $J_{5,6}$ 5·0 c./sec., 2- and 6-H), 2·68 (1H, d, $J_{5,6}$ 5·0 c./sec., 5-H), 6·08 (1H, s, OH), 7·52 (3H, s, CH_3), 8·33 (9H, m), 9·34 (3H, d, J 6·6 c./sec., CH·CH_3); the *picrate* (from water) had m.p. 163—164°.

3-*Methyl*-4-o-*tolylpyridine*.—The above alcohol (2 g.), concentrated sulphuric acid (2 ml.), and glacial acetic acid (8 ml.) were boiled under reflux for 3 hr. The acetic acid was distilled off and the residue was diluted, basified, and extracted with ether. The dried (KOH) ether extract was evaporated and the dark yellow liquid residue (1·7 g.) was boiled with sulphuric and acetic acid again. The same work up gave 3-*methyl*-4-o-*tolylpyridine* (0·22 g.), b.p. 89°/0·2 mm. (Found: C, 85·55; H, 7·3; N, 7·9. $C_{13}H_{13}N$ requires C, 85·2; H, 7·15; N, 7·6; $\nu_{max.}$ (liquid film) (main peaks only): 1586, 1472, 1440, 1398, 1377, 830, 756, 746, 721, and 621 cm.$^{-1}$; τ(CCl_4) 1·61 (1H, s, 2-H), 1·66 (1H, d, $J_{5,6}$ 5 c./sec., 6-H), 2·85 (4H, m, C_6H_4), 3·09 (1H, d, $J_{5,6}$ 5 c./sec., 5-H), 8·0 (6H, s, $2CH_3$); the *picrate* (from water) had m.p. 165—166° (Found: C, 55·5; H, 3·7; N, 13·3. $C_{13}H_{13}N,C_6H_3N_3O_7$ requires C, 55·3; H, 3·9; N, 13·6%).

3-*Methyl*-2-o-*tolylpyridine*.—This was prepared in a similar manner from 2-(1-hydroxy-2-methylcyclohexyl)-3-methylpyridine.[1] It had $\nu_{max.}$ (film) (main peaks): 1587, 1570, 1450, 1023, 783, 750, and 722 cm.$^{-1}$; τ(CCl_4) 1·4 (1H, q, $J_{5,6}$ 5 c./sec., 6-H); 2·3 (1H, d, 4-H), 7·94 (6H, s, $2CH_3$), 2·80—3·12 (complex m, 5-H and C_6H_4); the *picrate* (from benzene) had m.p. 135—136° (Found: C, 55·4; H, 3·9. $C_{13}H_{13}N,C_6H_3N_3O_7$ requires C, 55·3; H, 3·9%).

5-(1-*Hydroxy*-2-*methylcyclohexyl*)-3-*methylpyridine*.—This was prepared (61%) in a manner similar to the 4-isomer above from 5-bromo-3-methylpyridine;[16] the *alcohol* had b.p. 136°/0·24 mm., m.p. 130·5—131·5° [from light petroleum (b.p. 60—80°)] (Found: C, 75·9; H, 9·3; N, 6·7%); $\nu_{max.}$ (KBr disc) 3255, 1573, 1418, 1370, 1336, 1265, 1250, 1209, 1170, 1131, 1108, 1079, 988, 968, 849, 784, and 709 cm.$^{-1}$ τ(CCl_4) 1·82br (2H, s, 2- and 6-H), 2·52 (1H, s, 4-H), 7·30 (1H, s, OH), 7·70 (3H, s, ArCH_3), 8·34 (9H, m), 9·39 (3H, d, J 6·0 c./sec., ·CH·CH_3); the *picrate* (from water) had m.p. 135—136°.

3-*Methyl*-5-o-*tolylpyridine*.—Prepared by dehydration of the above alcohol the *product* (28%) had b.p. 87—87·5°/0·2 mm. (Found: C, 85·45; H, 4·8; N, 8·2%); $\nu_{max.}$ (film) (main peaks) 1590, 1562, 1490, 1450, 1415, 1376, 1023, 872, 790, 752, 715, 690, and 621 cm.$^{-1}$ τ(CCl_4) 1·73 (2H, s, 2- and 6-H), 2·87 (5H, m, 4-H and C_6H_4), 7·68 and 7·75 (both 3H s, $2CH_3$); the *picrate* (from water) had m.p. 147·5—148·5° (Found: C, 55·2; H, 4·0; N, 13·6. $C_{13}H_{13}N,C_6H_3N_3O_7$ requires C, 55·3; H, 3·9; N, 13·6%).

2-(1-*Hydroxy*-2-*methylcyclohexyl*)-5-*methylpyridine*.—Prepared as for the 4-isomer above from 2-bromo-5-methylpyridine this *alcohol* (62%) had b.p. 152°/12 mm., m.p. 57·5—59° [from light petroleum (b.p. 60—80°)] (Found: C, 76·2; H, 9·3; N, 6·9%); $\nu_{max.}$ (KBr disc) 3400, 1600, 1568, 1480, 1442, 1390, 1324, 1140, 1026, 992, 886, 820, and 648 cm.$^{-1}$; τ(CCl_4) 1·80 (1H, d, $J_{4,6}$ 1·1 c./sec., H_6),

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[15] A. I. Shatenshtein, *Adv. Phys. Org. Chem.*, 1963, **1**, 155.
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2·62 (1H, q, $J_{4,6}$ 1·1 c./sec. and $J_{3,4}$ 8·2 c./sec., 4-H), 2·90 (1H, d, $J_{3,4}$ 8·2 c./sec., 3-H), 5·30 (1H, s, OH), 7·70 (3H, s, ArCH_3). 8·41 (9H, m), 9·55 (3H, d, J 5·8 c./sec., ·CH·CH_3); the *picrate* (from water) had m.p. 146—146·5°.

5-*Methyl*-2-o-*tolylpyridine*.—Prepared from the alcohol as above the *product* had b.p. 96°/0·25 mm. (Found: C, 85·25; H, 7·0; N, 7·7%); $\nu_{max.}$ (film) (main peaks): 1590, 1550, 1486, 1450, 1370, 827, 762, 739, and 716 cm.$^{-1}$ τ(CCl_4) 1·83 (1H, s, 6-H), 2·67 (1H, q, $J_{4,6}$ 2·0 c./sec., and $J_{3,4}$ 8·0 c./sec., 4-H), 2·85 (4H, m, C_6H_4), 2·95 (1H, m, 3-H), 7·69 (3H, s, CH_3), 7·86 (3H, s, CH_3); the *picrate* (from water) had m.p. 150°.

Reaction of o-*Tolyl-lithium with* 3-*Picoline*.—(a) 1 : 1 *Molar ratio*. 3-Picoline (0·41 mole) stirred in dry ether (150 ml.) under oxygen-free nitrogen was treated dropwise with *o*-tolyl-lithium (0·41 mole in dry ether) at such a rate that boiling under gentle reflux was maintained. The mixture was boiled under reflux for a further hour and then cooled; oxygen was then bubbled through the mixture to give a white precipitate. Water was added to the mixture which was then basified and extracted repeatedly with ether. The ether layer was extracted with dilute hydrochloric acid, and the acid extracts were basified and re-extracted with ether. The dried (KOH) ether extract was concentrated and the products were analysed by g.l.c. on a 10 ft. × $\frac{3}{8}$ in. column packed with 25% Apiezon L on Gas Chrom P at 231° with a helium inlet pressure of 18 lb./sq. in. The products were separated initially by collecting the major and minor isomers separately, followed by rechromatography of each fraction. The order of elution of products was: 3-methyl-2-*o*-tolylpyridine (12·8 min.), 3-methyl-1,2,5,6-tetrahydro-2-*o*-tolylpyridine (see below) (13·5 min.), 5-methyl-3-*o*-tolylpyridine (18·8 min.), and 5-methyl-2-*o*-tolylpyridine (20·4 min.). No 3-methyl-4-*o*-tolypyridine (14·2 min.) was detected. The compounds were identified by comparison of their i.r. and n.m.r. spectra with those of authentic compounds.

(b) *Excess of* 3-*picoline*. Reaction of *o*-tolyl-lithium (0·192 moles) and 3-picoline (0·384 moles) in dry ether as above and analysis of the reaction mixture after complete oxidation with oxygen gave only 3-methyl-2-*o*-tolylpyridine and 5-methyl-2-*o*-tolylpyridine in the ratio of 96 : 4; overall yield 51—68%.

Alternatively, *o*-tolyl-lithium (0·0072 mole) and 3-picoline (4·0 g., 0·043 mole) were boiled in ether and the ether was then replaced by toluene; the solution was then boiled under reflux for 1 hr. Water was added to the mixture which was then worked up. Analysis was effected on an 8 ft. × $\frac{3}{16}$ in. column packed with 25% Apiezon L on Chromosorb W (100—120 mesh) at 150° and with a helium flow-rate of 110 ml./min. with 3-cyclohexylpyridine as internal standard. The 2,3-, 2,5-, and 3,5-isomers were found to be in the ratio 90·6 : 3·6 : 5·8 (average of 6 runs).

(c) *Isolation of* 3-*Methyl*-2-o-*tolyl*-1,2,5,6-*tetrahydropyridine*.—3-Picoline (9·3 g., 0·01 mole) and *o*-tolyl-lithium (0·01 mole) were heated and stirred together in dry ether under dry, oxygen-free nitrogen for 1 hr. following the completion of the addition. The mixture was cooled and treated carefully with water; it was then basified and extracted with ether. The extracts were dried (KOH) and evaporated; the residue was chromatographed on a column of alumina (19 × 3 cm.). Elution with light petroleum (b.p. 40—60°) (300 ml.) gave the methyl-*o*-tolylpyridines. Further elution with this solvent (300 ml.) gave 3-*methyl*-2-o-*tolyl*-1,2,5,6-*tetrahydropyridine* as an oil which could be stored under nitrogen or purified directly for analysis by preparative g.l.c. (Found: C, 83·4; H, 8·7; N, 7·9. $C_{13}H_{17}N$ requires C, 83·4; H, 9·15; N, 7·5%). Upon exposure to air for 24 hr. this is transformed quantitatively into 3-methyl-2-*o*-tolylpyridine.

Reaction of o-*Ethylphenyl-lithium with* 3-*Picoline*.—*o*-Ethylphenyl-lithium (0·085 mole) in dry ether (100 ml.) was added dropwise to a solution of 3-picoline (21 g., 0·226 mole) in dry ether (90 ml.) and the reaction was carried out as under (a) above. Analysis was effected on a 6 ft. × $\frac{1}{4}$ in. column of 25% Apiezon N on Celite 545 at 225° and with a helium inlet pressure of 26 lb./sq. in. Four peaks were observed. The first, the major one, was well-resolved from the other very minor peaks which could not be resolved from each other. The major compound was collected as a liquid, b.p. 109—110°/0·47 mm. (52·5% overall yield). This was 2-o-*ethylphenyl*-3-*methylpyridine*; $\nu_{max.}$ (film) (main peaks) 1590, 1575, 1450, 1190, 1120, 1070, 1025, 790, and 750 cm.$^{-1}$; τ(CCl_4) 1·4 (1H, q, $J_{5,6}$ 5 c./sec., 6-H), 2·3 (1H, d, 4-H); *picrate* (from benzene), m.p. 103—104° (Found: C, 56·2; H, 4·3. $C_{14}H_{15}N$,$C_6H_3N_3O_7$ requires C, 56·3; H, 4·3%).

Reaction of p-*Methoxyphenyl-lithium with* 3-*Picoline*.—The reaction of 3-picoline (4·0 g., 0·043 mole) and *p*-methoxyphenyl-lithium (0·0072 mole) was carried out in dry ether as above. Analysis was carried out on a 4 ft. × $\frac{1}{4}$ in. column packed with Tween 20 (20%) on Anakrom AB-S (60—70 mesh) at 200° and with a helium flow rate of 50 ml./min. Vanillin was used as the internal standard for the quantitative analysis. The peak with emergence time 20·2 min. was due to 2-p-*methoxyphenyl*-3-*methylpyridine*, b.p. 124—125°/0·7 mm. (Found: C, 78·5; H, 6·7; N, 7·4. $C_{13}H_{13}NO$ requires C, 78·4; H, 6·6; N, 7·0%). $\nu_{max.}$ (film) (main peaks) 1601, 1517, 1505, 1440, 1415, 1288, 1238, 1167, 1015, 825, and 780 cm.$^{-1}$; the *picrate* (from water) had m.p. 158—159°. The second peak, emergence time 28·5 min., was due to 2-p-*methoxyphenyl*-5-*methylpyridine*, m.p. 56·5—57° [from light petroleum (b.p. 60—80°)] (Found: C, 78·5; H, 6·65; N, 6·9%); $\nu_{max.}$ (KBr disc) (main peaks) 1600, 1589, 1575, 1505, 1465, 1264, 1240, 1168, 1010, 815, 804, and 743 cm.$^{-1}$; the *picrate* (from water) had m.p. 187—188°. The 2,3- : 2,5-isomer ratio was 94·4 : 5·6 (mean of 6 runs).

Attempted Synthesis of 3-*Methyl*-2-o-*tolyl*-1,2,5,6-*tetrahydropyridine*.—The procedure used was that reported by Ferles [17] for the reduction of pyridines to tetrahydropyridines. 3-Methyl-2-*o*-tolylpyridine (1 g.) in dry ether (10 ml.) was added to a mixture of lithium aluminium hydride (0·6 g.) in ether (30 ml.) and anhydrous aluminium chloride (0·68 g.) in ether (25 ml.). The mixture was either worked up immediately or was boiled under reflux for 6 hr. before being hydrolysed, basified, and extracted. In neither case could any desired product be detected by g.l.c. and mainly starting material was recovered.

This work was carried out during the tenure by C. S. G. (1961—1962) and G. A. P. (1966—1967) of National Research Council Studentships and with the financial support of the N.R.C. whom we thank.

[9/1031 *Received, June 17th,* 1969]

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