# 1059. *Alkylation of Substituted Methylpyridines.*

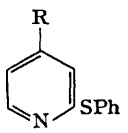
By D. E. Ames and B. T. Warren.

The alkylation of methylpyridines containing a substituent group (benzyloxy-, phenylthio-, and diethylaminocarbonyl-) is described. Primary amides are formed by ammonolysis during condensation reactions involving *NN*-dialkyl-amides in liquid ammonia. Ammonolysis is catalysed by sodamide or sodio-picolines but only occurs to a very small extent in condensation of an alkyl halide with the sodio-derivative of *NN*-dimethyl-ω-alkynamide.

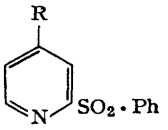
Extension of the side-chain of methylpyridines by alkylation of an alkali-metal derivative has been widely used to prepare higher alkylpyridines,[1] but few examples of alkylation of compounds containing a nuclear functional group have been described. 2-Hydroxymethyl-5-methylpyridine gives an *O*-ether rather than a *C*-alkyl derivative on alkylation.[2] Clemo and his collaborators[3] failed to obtain the corresponding acid by treatment of 2-methoxy-6-methylpyridine with phenyl-lithium and carbon dioxide, but alkylations of alkoxy-methylpyridines[4] and of 5-nitro-2-picoline[5] have been described. Tetramethylene dibromide has been condensed with some benzyloxy- and methoxy-methylpyridines but 3-benzyloxy-6- and 2-benzyloxy-5-methylpyridines failed to give the expected products.[6]

Alkylation of benzyloxy-methylpyridines has now been further examined. In preliminary experiments, 2-benzyloxy-4-methylpyridine was added to potassamide in liquid ammonia and then treated with benzyl bromide to give 2-benzyloxy-4-phenethylpyridine in 14% yield. Undecyl bromide gave 2-benzyloxy-4-dodecylpyridine (34%) and a trace of 4-dodecyl-2-pyridone (apparently formed by pyrolysis during distillation). 2-Benzyloxy-5-dodecyl-pyridine was obtained similarly. Alkylation with hexyl bromide proved more convenient, as the products could be isolated by fractional distillation without decomposition; 2-benzyloxy-3-, -4-, -5-, and -6-methylpyridines were all alkylated successfully but 4-benzyloxy-2-methylpyridine could not be condensed with hexyl bromide, presumably owing to its insolubility in liquid ammonia.

4-Methyl-2-phenylthiopyridine (I; R = Me) was similarly alkylated with hexyl bromide but the product (I; R = n-$C_7H_{15}$) could not be purified completely, though it gave the corresponding sulphone (II; R = n-$C_7H_{15}$) on oxidation with potassium permanganate. Alkylation of the sulphone (II; R = Me) with hexyl bromide in the presence of potassamide, however, failed to give any alkylation product.



(I)



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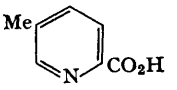

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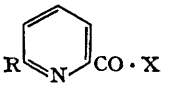


(IV)

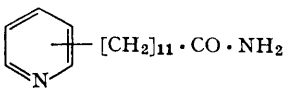
Hardegger and his co-workers[7] have recently described the alkylation of 5-methylpicolinic acid (III) with allyl chloride in the presence of potassamide, but we were unable to alkylate 6-methylpicolinic acid (IV; R = Me, X = OH) with either hexyl or undecyl bromides under

[1] *E.g.*, H. C. Brown and W. A. Murphey, *J. Amer. Chem. Soc.*, 1951, **73**, 3308.
[2] H. Gilman and S. M. Spatz, *J. Org. Chem.*, 1951, **16**, 1485.
[3] G. R. Clemo, B. W. Fox, and R. Raper, *J.*, 1954, 2693.
[4] L. Marion and W. F. Cockburn, *J. Amer. Chem. Soc.*, 1949, **71**, 3402; T. R. Govindachari, N. S. Narasimhan, and S. Rajadurai, *J.*, 1957, 560.
[5] W. Gruber and K. Schlögl, *Monatsh.*, 1950, **81**, 473.
[6] D. E. Ames and J. L. Archibald, *J.*, 1962, 1475.
[7] K. Steiner, U. Graf, and E. Hardegger, *Helv. Chim. Acta*, 1963, **46**, 690.

similar conditions. The dialkyl-amide has been used as a protecting group for an acid function in the synthesis of long-chain acetylenic acids,[8] and alkylation of the amide (IV; R = Me, X = $NEt_2$) was therefore examined. Condensation with hexyl bromide gave the amide (IV; R = n-$C_7H_{15}$, X = $NEt_2$), and with undecyl bromide gave crude amide which was hydrolysed under forcing conditions to the acid (IV; R = n-$C_{12}H_{25}$, X = OH), isolated as the acid potassium salt.

The analogous condensation of 11-bromo-*NN*-dimethylundecanamide with the sodio-derivative of 2-, 3-, and 4-picolines was next examined. In each case, the high-melting primary amide (V) was isolated, evidently owing to ammonolysis of the substituted amide. These structures (V) were confirmed by the spectra (bands at 3400 and 3200 cm.$^{-1}$) and by hydrolysis of the 4-isomer to the corresponding acid.

The ammonolysis of esters to give amides is well known[9] but there appear to be few examples of ammonolysis of substituted amides.[10] Ammonolysis of *NN*-dimethyl-amides was not observed during the preceding condensations, or in the synthesis of acetylenic dimethyl-amides,[8] although the reduction of *NN*-dimethylnonadec-10-ynamide (VI) with sodium in liquid ammonia to give *trans*-nonadec-10-enamide (VII) involved simultaneous ammonolysis.[11] The preparation of amide (VI) by condensation of octyl bromide with the



(V)

$C_8H_{17}\cdot C{\equiv}C\cdot[CH_2]_8\cdot CO\cdot NMe_2$ (VI)

$C_8H_{17}\cdot CH{=}CH\cdot[CH_2]_8\cdot CO\cdot NH_2$ (VII)
*trans*

sodio-derivative of *NN*-dimethylundec-10-ynamide was therefore repeated. The physical properties of the product were in agreement with those reported[11] but when the oil was kept for a week a trace (1%) of the primary amide crystallised out and was isolated. In another experiment, *NN*-dimethylundec-10-ynamide was treated with 5 mol. of sodamide in liquid ammonia; the primary amide, undec-10-ynamide, was then isolated in 51% yield.

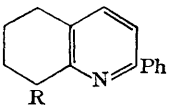
These experiments indicate that ammonolysis of *NN*-dialkyl-amides may occur extensively when catalysed by sodamide or a sodio-picoline but that it only occurs to a very small extent in condensation of alkyl halide with the sodio-derivative of an ω-acetylenic dimethyl-amide. This ammonolysis does not reduce the efficiency of this synthesis of acetylenic acids since both amides give the required acid on hydrolysis.

Alkylation of 4-picoline *N*-oxide with tetramethylene dibromide in presence of sodamide and liquid ammonia to give 1,6-di-4′-pyridylhexane *NN*′-dioxide in low yield has been described.[6] We have now alkylated 2-picoline *N*-oxide with hexyl bromide to obtain 2-heptylpyridine *N*-oxide (17%). Similar alkylation of 4-picoline *N*-oxide gave unsatisfactory results, but, with dodecyl bromide, 4-tridecylpyridine *N*-oxide[12] was obtained in low yield. 3-Picoline *N*-oxide, however, could not be alkylated with either hexyl or undecyl bromide. Thus, the alkylation of picoline *N*-oxides does not appear to be of any preparative value.

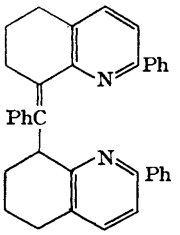
Finally, some condensation reactions of 5,6,7,8-tetrahydro-quinolines and -isoquinolines were examined. Conversion of 5,6,7,8-tetrahydro-2-phenylquinoline (VIII; R = H) into the lithio-derivative with phenyl-lithium and addition of methyl benzoate gave the olefin (IX) by dehydration of the intermediate carbinol. The potassium derivative of the base (VIII; R = H), prepared in liquid ammonia, however, gave ketone (VIII; R = CO·Ph) on treatment with methyl benzoate. The infrared spectrum showed an intense band at 1680 cm.$^{-1}$ indicating that, in the solid state, the compound exists as the ketone rather than the

[8] D. E. Ames and P. J. Islip, *J.*, 1961, 4409.
[9] L. F. Audrieth and J. Kleinberg, *J. Org. Chem.*, 1938, **3**, 312.
[10] K. N. Lerman and N. I. Gavrilov, *J. Gen. Chem.* (*U.S.S.R.*), 1941, **11**, 127; W. C. Fernelius and G. B. Bowman, *Chem. Rev.*, 1940, **26**, 32; cf. T. Kaufmann and J. Sobel, *Angew. Chem.*, 1963, **75**, 1177.
[11] D. E. Ames and P. J. Islip, *J.*, 1961, 351.
[12] D. E. Ames and T. F. Grey, U.S.P., 2,995,562/1961.

alternative enol form (cf. phenacylpyridines[13]). From each of these reactions only one product could be isolated, presumably corresponding to the greater reactivity of α- than β-picoline (*i.e.*, at the 8- rather than the 5-position). Alkylation of the base (VIII; R = H) with hexyl bromide gave 8-hexyl-5,6,7,8-tetrahydro-2-phenylquinoline (VIII; R = n-$C_6H_{13}$).




(VIII)




(IX)

Similarly, 5,6,7,8-tetrahydroquinoline gave the 8-hexyl derivative, and condensation of 5,6,7,8-tetrahydroisoquinoline with undecyl bromide gave 5,6,7,8-tetrahydro-5-undecylisoquinoline.

## Experimental

Infrared spectra of solids were determined as Nujol mulls, and of liquids as liquid films.

*2-Benzyloxy-3-methylpyridine.*—Potassium hydroxide (14·4 g.), benzyl alcohol (46 g.), and xylene (40 c.c.) were refluxed until no more water could be collected in a phase separator. 2-Bromo-3-methylpyridine[14] (29 g.) was added and the mixture was refluxed for 3 hr. (bath 190°); addition of water, isolation with benzene, and distillation gave the *base* (29·5 g.), b. p. 79—80°/0·1 mm., $n_D^{22}$ 1·5649 (Found: C, 78·9; H, 6·9; N, 6·7. $C_{13}H_{13}NO$ requires C, 78·4; H, 6·6; N, 7·0%).

*2-Benzyloxy-4-heptylpyridine.*—2-Benzyloxy-4-methylpyridine (20 g.) was added to potassamide (from potassium, 3·9 g.) in liquid ammonia (about 400 c.c.). The green-brown solution was stirred under reflux for 1 hr., and hexyl bromide (14·9 g.) was added, the mixture being stirred under reflux for 2 hr. more. After evaporation of the ammonia, water was added and the mixture was extracted with ether. The ethereal solution was extracted with 6N-hydrochloric acid; basification, isolation with ether, and fractional distillation gave *2-benzyloxy-4-heptylpyridine* (11·9 g., 47%), b. p. 140—145°/0·3 mm., $n_D^{26}$ 1·5314 (Found: C, 80·3; H,8·5; N, 4·9. $C_{19}H_{25}NO$ requires C, 80·5; H, 8·9; N, 4·9%).

The following compounds were prepared similarly: *2-benzyloxy-6-heptylpyridine* (47%), b. p. 120—130°/0·5 mm., $n_D^{26}$ 1·5292 (Found: C, 80·1; H, 8·4; N, 5·4%); *2-benzyloxy-4-phenethylpyridine* (14%), b. p. 184—186°/0·15 mm., $n_D^{22}$ 1·5870 (Found: C, 83·5; H, 6·9; N, 4·5. $C_{20}H_{19}NO$ requires C, 83·0; H, 6·6; N, 4·8%).

Similar condensation of 2-benzyloxy-4-methylpyridine with undecyl bromide gave oil, b. p. 194—201°/0·1 mm. On cooling, *4-dodecyl-2-pyridone*, needles, m. p. 88—89° [from light petroleum (b. p. 80—100°)] separated (Found: C, 77·1; H, 11·3; N, 5·7. $C_{17}H_{29}NO$ requires C, 77·5; H, 11·1; H, 5·3%). The remaining oil, in ether, was washed with 2N-sodium hydroxide; evaporation and distillation gave *2-benzyloxy-4-dodecylpyridine* (34%), b. p. 182—190°/0·15 mm., $n_D^{21}$ 1·5194 (Found: C, 81·4; H, 10·1; N, 3·9. $C_{24}H_{35}NO$ requires C, 81·5; H, 10·0; N, 4·0%).

The following were also prepared similarly, but the methylpyridine was stirred for 3 hr. with potassamide before addition of alkyl halide: *2-benzyloxy-5-heptylpyridine* (22%), b. p. 142—146°/0·35 mm., $n_D^{22}$ 1·5325 (Found: C, 80·1; H, 9·4; N, 4·9%); *2-benzyloxy-3-heptylpyridine* (14%), b. p. 148—150°/0·3 mm., $n_D^{21}$ 1·5324 (Found: C, 80·5; H, 9·5; N, 4·8%); *2-benzyloxy-5-dodecylpyridine* (22%), b. p. 190—194°/0·4 mm., $n_D^{21}$ 1·5147 (Found: C, 81·8; H, 10·1; N, 4·0%).

*4-Methyl-2-phenylthiopyridine.*—Thiophenol (16·5 g.) was added to sodium methoxide (from sodium, 3·45 g.) in methanol (60 c.c.). Solvent was removed by distillation, 2-bromo-4-methylpyridine (25·8 g.) in 2-butoxyethanol (25 c.c.) was added, and the mixture was boiled under

[13] R. F. Branch, A. H. Beckett, and D. B. Cowell, *Tetrahedron*, 1963, **19**, 401.
[14] J. H. Boyer and R. F. Reinisch, *J. Amer. Chem. Soc.*, 1960, **82**, 2218.

reflux for 3 hr. Addition of water and isolation with ether gave *4-methyl-2-phenylthiopyridine* (27·5 g.), b. p. 132—136°/0·25 mm., $n_D^{18}$ 1·6263 (Found: C, 72·0; H, 5·1; N, 6·9; S, 16·2. $C_{12}H_{11}NS$ requires C, 71·6; H, 5·5; N, 7·0; S, 15·9%).

*4-Heptyl-2-phenylthiopyridine.*—The methyl compound (20 g.) was alkylated in the manner described, using potassium (3·9 g) in ammonia (350 c.c.) and hexyl bromide (17 g.). The *product* (14·3 g.) had b. p. 176—180°/0·5 mm. (Found: C, 74·6; H, 8·3; N, 5·4; S, 13·4. $C_{18}H_{23}NS$ requires C, 75·8; H, 8·1; N, 4·9; S, 11·2%) but could not be purified further by distillation. A portion (2·8 g.) in acetic acid (16 c.c.) was treated with potassium permanganate solution (150 c.c.; 3%); the solution was decolourised with sulphur dioxide and filtered. Repeated recrystallisation from ethanol (charcoal) gave *4-heptyl-2-phenylsulphonylpyridine* (0·8 g.), m. p. 68—70° (Found: C, 68·3; H, 7·1; N, 4·1. $C_{18}H_{23}NSO_2$ requires C, 68·1; H, 7·3; N, 4·4%).

*Oxidation of 4-Methyl-2-phenylthiopyridine.*—(*a*) Oxidation of the sulphide (7·3 g.) with potassium permanganate as in the preceding experiment gave *4-methyl-2-phenylsulphonylpyridine* (4·95 g.), plates, m. p. 118—120° (Found: C, 61·7; H, 4·7; N, 5·8; S, 13·6. $C_{12}H_{11}NO_2S$ requires C, 61·8; H, 4·8; N, 6·0; S, 13·7%). This could not be alkylated with hexyl bromide in the presence of potassamide.

(*b*) Hydrogen peroxide (5 c.c.; 30%) was added to the sulphide (8 g.) in formic acid (75 c.c.; 90%). After the initial exothermic reaction had subsided, the mixture was stirred at 35—40° while more hydrogen peroxide (25 c.c.) was added during 45 min., and for a further 4 hr. the solution was poured into ice–water; collection and recrystallisation of the precipitate gave the sulphone (3·6 g.), m. p. 116—119°. Basification of the aqueous filtrate yielded *4-methyl-2-phenylsulphonylpyridine N-oxide* (1·0 g.), m. p. 180—182° (from ethanol) (Found: C, 57·8; H, 4·3; N, 5·5; S, 13·0. $C_{12}H_{11}NO_3S$ requires C, 57·8; H, 4·5; N, 5·6; S, 12·9%).

NN-*Diethyl-6-methylpicolinamide.*—A mixture of 6-methylpicolinic acid (10 g.) and thionyl chloride (15 c.c.) was left at room temperature for 12 hr. After removal of the excess of thionyl chloride by distillation under reduced pressure, the residual solid was stirred with diethylamine (24 g.) at 0°. Water was added and the mixture was extracted with ethyl acetate; the extracts were washed with sodium hydrogen carbonate solution and water and distilled, to give the *amide* (8·8 g.), b. p. 112—116°/0·5 mm., which formed needles, m. p. 45·5—47° [from light petroleum (b. p. 40—60°)] (Found: C, 68·6; H, 8·2; N, 14·7. $C_{11}H_{16}N_2O$ requires C, 68·7; H, 8·4; N, 14·6%).

*Alkylation of* NN-*Diethyl-6-methylpicolinamide.*—(*a*) The amide (12 g.) in tetrahydrofuran (35 c.c.) was added to potassamide (from potassium, 2·4 g.) in liquid ammonia (500 c.c.). After 2 hr., hexyl bromide (9·3 g.) was added to the deep red solution. Isolation as described gave NN-*diethyl-6-heptylpicolinamide* (4·6 g.), b. p. 129—130°/0·06 mm., $n_D^{22}$ 1·5002 (Found: C, 74·4; H, 10·4; N, 10·2. $C_{17}H_{28}N_2O$ requires C, 73·9; H, 10·2; N, 10·1%).

(*b*) The amide (17 g.) was condensed similarly with undecyl bromide to give crude product (7·1 g.), b. p. 190—200°/0·4 mm. This (5·7 g.), potassium hydroxide (4 g.), water (5 c.c.), and 2-methoxyethanol (20 c.c.) were refluxed for 22 hr.; the solution was poured into water and acidified with acetic acid. Recrystallisation from ethanol gave the acid potassium *salt* of 6-dodecylpicolinic acid, m. p. 117—118° (Found: C, 69·1; H, 9·3; N, 4·6. $C_{18}H_{29}NO_2$,$C_{18}H_{28}NO_2K$ requires C, 69·6; H, 9·3; N, 4·5%).

NN-*Dimethyl-11-bromoundecanamide.*—11-Bromoundecanoic acid (10 g.) was warmed at 50° with thionyl chloride (5 c.c.) for 4 hr. After removal of excess of thionyl chloride by distillation under reduced pressure, the acid chloride was taken up in ether and ethereal dimethylamine was added until the mixture was just alkaline. The mixture was washed with water, 2N-hydrochloric acid, and water, dried ($MgSO_4$), and evaporated under reduced pressure (bath below 40°). The *amide* (7·1 g.) had m. p. 56·5—57·5° [from light petroleum (b. p. 40—60°)] (Found, C, 53·7; H, 9·0; Br, 26·7; N, 4·7. $C_{13}H_{26}BrNO$ requires C, 53·4; H, 9·0; Br, 27·3, N, 4·8%).

*12-4′-Pyridyldodecanamide.*—Sodamide (from sodium, 5 g.) in ammonia (500 c.c.) was treated with 4-picoline (10 g.), and after 1 hr. the bromo-amide (6·3 g.) in tetrahydrofuran (30 c.c.) was added dropwise. When the solvent had evaporated, water was added and the mixture was extracted with ether. Evaporation and recrystallisation from acetone gave crude product (4·1 g.), m. p. *ca.* 120°. Repeated recrystallisation from acetone gave the *amide*, m. p. 135·5—136° [bands at 3380 and 3120 ($NH_2$) and 1670 $cm.^{-1}$ ($CO{\cdot}NH_2$)] (Found: C, 73·8; H, 10·1; N, 10·2. $C_{17}H_{28}N_2O$ requires C, 73·9; H, 10·2; N, 10·1%). Similarly prepared were: *12-3′-pyridyldodecanamide*, m. p. 93—96° (from benzene) (Found: C, 73·7; H, 10·4; N, 10·0%); *12-2′-pyridyldodecanamide*, m. p. 92—94° (from benzene) (Found: C, 74·2; H, 10·2; N, 9·5%).

12-4′-*Pyridyldodecanoic Acid.*—Crude amide (3·3 g.) in 2-methoxyethanol (50 c.c.) and potassium hydroxide (5 g.) in water (5 c.c.) were refluxed for 10 hr. The hot solution was acidified with acetic acid, cooled, and filtered. Recrystallisation from light petroleum (b. p. 100—120°) containing a little acetic acid gave the *acid* (1·0 g), needles, m. p. 130—131·5° (Found: C, 73·4; H, 9·9; N, 5·3. $C_{17}H_{27}NO_2$ requires C, 73·6; H, 9·8; N, 5·1%).

*Nonadec-10-ynamide.*—*NN*-Dimethylnonadec-10-ynamide (1·55 g.) was prepared as described.[11] After 1 week at room temperature, a little solid had separated; this was collected and washed with light petroleum (b. p. 40—60°). The *amide* (25 mg.) had m. p. 74—77° [bands at 3400 and 3200 ($NH_2$) and 1650 cm.$^{-1}$ ($CO{\cdot}NH_2$)] (Found: C, 77·1; H, 11·8; N, 4·3. $C_{19}H_{35}NO$ requires C, 77·8; H, 12·0; N, 4·8%).

*Ammonolysis of* NN-*Dimethylundec-10-ynamide.*—The amide (3·3 g.) in tetrahydrofuran (20 c.c.) was added to sodamide (from sodium, 1·89 g.) in ammonia (250 c.c.), and the mixture was refluxed for 4 hr. When the ammonia had evaporated, ethanol and water were added. Isolation with ether and recrystallisation from benzene gave undec-10-ynamide (1·4 g.), m. p. and mixed[15] m. p. 97—98·5°.

*Alkylation of Picoline* N-*Oxides.*—(*a*) 2-Picoline *N*-oxide (12 g.) in tetrahydrofuran (40 c.c.) was added to sodamide (from sodium, 2·44 g.) in ammonia (500 c.c.). After 2 hr. under reflux, hexyl bromide (18·3 g.) was added and the deep red solution rapidly turned black. After ammonia had evaporated, potassium carbonate solution (100 c.c.; 25%) was added. Extraction with chloroform and distillation gave 2-*heptylpyridine* N-*oxide* (3·1 g.), b. p. 120—130°/0·1 mm. (Found: C, 75·0; H, 10·2; N, 7·0. $C_{12}H_{19}NO$ requires C, 74·6; H, 9·9; N, 7·3%). The *picrate* had m. p. 77—78° (from ether) (Found: C, 51·6; H, 5·3; N, 13·5. $C_{18}H_{22}N_4O_8$ requires C, 51·2; H, 5·3; N, 13·3%). The same *N*-oxide (identical infrared structure) and picrate (mixed m. p.) were obtained by oxidation of 2-heptylpyridine with perbenzoic acid (cf. Ames and Grey[12]).

(*b*) 4-Picoline *N*-oxide (8·5 g.) was similarly condensed with dodecyl bromide, to give 4-tridecylpyridine *N*-oxide (0·8 g.), isolated with chloroform and recrystallised from light petroleum (b. p. 60—80°). It had m. p. and mixed[12] m. p. 61—62°.

*Reactions of* 5,6,7,8-*Tetrahydro-2-phenylquinoline.*—(*a*) The base[16] (6·3 g.) was added to phenyl-lithium (from lithium, 0·42 g.) in ether (200 c.c.). After 15 min. methyl benzoate (4·1 g.) in ether was added dropwise to the stirred solution. Water was added and the product isolated with ether. Recrystallisation from benzene–light petroleum (b. p. 60—80°) gave 5,6,7,8-*tetrahydro-2-phenyl*-8-[α-(5,6,7,8-*tetrahydro-2-phenyl-8-quinolylidene*)*benzyl*]*quinoline* (IX) (0·95 g.), m. p. 162·5—163·5° (Found: C, 87·8; H, 6·6; N, 5·6. $C_{37}H_{32}N_2$ requires C, 88·1; H, 6·4; N, 5·6%).

(*b*) 5,6,7,8-Tetrahydro-2-phenylquinoline (21 g.) was added to potassamide (from potassium, 3·9 g.) in ammonia (450 c.c.). After 45 min., methyl benzoate (6·8 g.) in ether (20 c.c.) was added during 10 min. and the mixture was worked up as described. Low-boiling materials were removed by distillation at 0·15 mm. (bath 200°). Trituration of the residue with ether gave material of m. p. 120—140°; this, in benzene (150 c.c.), was applied to an 8-in. column of alumina, and elution with benzene–ether (1:1) gave 8-*benzoyl*-5,6,7,8-*tetrahydro-2-phenylquinoline* (0·5 g.), m. p. 150—151° (from acetone) (Found: C, 84·4; H, 6·3; N, 4·8. $C_{22}H_{19}NO$ requires C, 84·3; H, 6·1; N, 4·5%).

(*c*) Condensation of the base (10·5 g.) with hexyl bromide under similar conditions to those in (*b*) gave 8-*hexyl*-5,6,7,8-*tetrahydro-2-phenylquinoline* (6·2 g.), b. p. 179—181°/0·5 mm. (Found: C, 85·8; H, 9·4; N, 4·7. $C_{21}H_{27}N$ requires C, 86·0; H, 9·3; N, 4·8%).

8-*Hexyl*-5,6,7,8-*tetrahydroquinoline*, prepared similarly, had b. p. 99—100°/0·1 mm., $n_D^{21}$ 1·5122 (Found: C, 83·1; H, 10·7; N, 6·4. $C_{15}H_{23}N$ requires C, 82·9; H, 10·7; N, 6·5%).

5,6,7,8-Tetrahydroisoquinoline[17] was similarly alkylated with undecyl bromide; treatment of the crude product (b. p. 180—200°/2 mm.) with ethereal picric acid gave 5,6,7,8-*tetrahydro*-5-*undecylisoquinoline picrate*, m. p. 119—121° (from ethanol) (Found: C, 60·4; H, 7·1; N, 10·9. $C_{24}H_{36}N_4O_7$ requires C, 60·5; H, 7·0; N, 10·9%).

We are indebted to Dr. J. F. McGhie for helpful discussions, and to the Governors of this College for the award of a Research Assistantship to one of us (B. T. W.).

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MANRESA ROAD, LONDON, S.W.3. [*Received, September 10th,* 1964.]

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