109. *Synthetical Applications of Activated Metal Catalysts. Part VIII.* The Action of Degassed Raney Nickel on Quinoline and Some of its Derivatives.*

By W. H. F. Sasse.

The action of W7-J degassed Raney nickel on quinoline produces, *inter alia*, indole, 3-methylindole, carbazole, aniline, *o*-toluidine, 1,2,3,4-tetrahydroquinoline, 2-methylquinoline, 2,2′-biquinolyl, and an aliphatic hydrocarbon of unknown structure. The reactions with methylquinolines are similarly complex. All quinolines examined gave 2,2′-biquinolyls; the best yield was obtained from 4-methylquinoline, while traces of 2,2′-biquinolyls were isolated from quinolines with methyl groups in the 2-position.

In an earlier paper[1] in this series the formation of 2,2′-biquinolyl from quinoline under the influence of degassed Raney nickel was described. Later, indole was isolated from

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* Part VII, *J.*, 1959, 3046.

[1] Badger and Sasse, *J.*, 1956, 616.

the same reaction.[2] The formation of these products has now been studied in greater detail, and the reaction between W7-J nickel and several methylquinolines has been examined.

Most experiments were carried out by refluxing the bases over the catalyst at atmospheric pressure, but in some cases lower reaction temperatures were attained by using reduced pressure. Preliminary work had shown that, within minutes from the beginning of refluxing, indoles could be detected in the mixture by means of *p*-dimethylaminobenzaldehyde.

The neutral products were separated quantitatively from the bases by counter-current distribution between dilute acid and ether. These neutral fractions were separated by chromatography on alumina to give indole, 3-methylindole, carbazole, and a hydrocarbon, m. p. 59—60°, which could not be identified. The hydrocarbon did not react with bromine or potassium permanganate and its infrared spectrum showed strong absorption at frequencies corresponding to C–H stretching and deformation vibrations in methyl and methylene groups. It was isolated in all the experiments, and in spite of slight variations in the melting points of samples of different origins the infrared spectra and composition of these materials were identical and corresponded to those of a polymethylene. The detection and separation of the indoles were assisted by chromatography on acetylated paper, and the composition of the mixtures of indole and 3-methylindole was estimated either by examination of the C–H stretching and deformation regions of the infrared spectra or by gas–liquid partition chromatography. 2-Methylindole was not found although it could readily be detected in standard mixtures. The combined yields of indole and 3-methylindole are shown in the Table, the percentage content of 3-methylindole being indicated in parentheses. The yield of these products was increased by prolonged heating at higher temperatures (see Table). The quinoline bases with methyl groups in the hetero-ring did not give rise to any indoles other than indole and 3-methylindole. However, the weights of the indole fractions isolated from these experiments were much smaller and the ratio indole : 3-methylindole was reversed. With 7-methylquinoline an intermediate yield of indoles was observed, 6-methylindole being the major product.

The absence of 2-methylindole in these reaction mixtures disagrees with the findings of Padoa and Carughi,[3] who reported the formation of 2-methylindole in the reaction between quinoline, hydrogen, and reduced nickel at 260—280°. However, the reported properties of their indole are compatible with those of a mixture of indole with some 3-methylindole. Repetition of this work seems necessary as Padoa and Scagliarini reported that under similar conditions 1,2,3,4-tetrahydroquinoline gave 3-methylindole.[4] After the detection of aniline (from 1,2,3,4-tetrahydroquinoline) and *o*-toluidine (from quinoline) Padoa suggested a pathway for these changes which involved fission of the hetero-ring of quinoline to give an *o*-alkylaniline which was then to undergo ring closure to form 2-methylindole. Depending on the mode of fission in the first step, different alkylanilines would be expected which could form either 3-methylindole or its 2-isomer. Dehydrocyclisation of *o*-alkylanilines is known to occur at temperatures above 400°,[5] and Padoa and Carrasco showed that indole was formed when *N*-methyl-*o*-toluidine is passed over reduced nickel at 300—330°.[6] Although aniline and *o*-toluidine were detected during the present study (see below), it seems difficult to explain in terms of Padoa's mechanism the simultaneous formation of indole and 3-methylindole, and the absence of 2-methylindole in all experiments, without additional hypotheses, the discussion of which is to be postponed until current work is complete.

Traces of carbazole and aniline were formed from all quinolines examined, except from

[2] Sargeson and Sasse, *Proc. Chem. Soc.*, 1958, 150.

[3] Padoa and Carughi, *Atti Reale Accad. Lincei, Rend.*, 1906, **15**, I, 113.

[4] Padoa and Scagliarini, *ibid.*, 1908, **17**, 730.

[5] Baeyer and Caro, *Ber.*, 1877, **10**, 692; Hansch and Helmkamp, *J. Amer. Chem. Soc.*, 1951, **73**, 3080; Lesiak, *Roczniki Chem.*, 1957, **31**, 1057 (*Chem. Abs.*, 1958, **52**, 8120).

[6] Padoa and Carrasco, *Atti Reale Accad. Lincei, Rend.*, 1906, **15**, 701.

7-methylquinoline or from quinoline at 110°. 3-Methylquinoline yielded about ten times more carbazole than did any of the other quinolines studied. Partially hydrogenated carbazole, aniline, and *o*-toluidine are known to be formed during the hydrogenolysis of quinoline at elevated temperatures and pressures,[7] and it is suggested that the traces of these compounds found during the present work were formed in this way. The absence of *o*-toluidine in the reactions with 4-methylquinoline and 2,4-dimethylquinoline points towards fission of the 1,2- and 3,4-bonds in the hetero-ring of the quinolines. Fission at the 1,2- and 4,9-bonds would lead to an intermediate (I) that could either react with hydrogen to give aniline, or, less frequently, undergo recombination to form a 2,2′-diaminobiphenyl derivative, which in turn could eliminate ammonia to produce carbazole. As no phenazine was detected, these reactions must occur while the nitrogen atoms are attached to the catalyst.

Yields (*g.*) *in reaction between some quinolines and* W7-J *Raney nickel* (*from* 125 *g. of* 1 : 1 *aluminium–nickel*).

Base	Time (hr.)	Temp.	Biaryl	Indoles	$[CH_2]_x$	Carbazole	Other bases [a]
Quinoline	140	235°	2·0	4·85 (25%) [b]	0·30	0·03	2-Me, H_4, NH_2Ph, Tol.
,, ...	42	110	8·5	1·75 (20%)	0·01 [b]	0	2-Me, H_4, Tol.
,, [c]	50	235	2·5	4·08 (12%) [b]	0·10	0·03	—
,, [c]	12	110	5·1	—	—	—	—
2-Methylquinoline	46	246	0·30	0·20 (80%) [b]	0·04	0·01	Quinoline, NH_2Ph, Tol., NHEtPh
3-Methylquinoline	19	260	1·2	0·15 (60%) [b]	0·10	0·30	NH_2Ph, Tol., 2 bases
4-Methylquinoline	50	262	8·1	0·1 (80%) [b]	0·10	0·05	Aniline, 5 bases
4-Methylquinoline [c] ...	31	140	20·4	—	—	—	—
7-Methylquinoline [c] ...	46	257	2·3	1·77 (15%) [d]	0·01	0	—
2,4-Dimethylquinoline	50	265	0·6	0·14 (65%) [b]	0·014	0·03	Quinoline, 4-Me

[a] 2-Me, 4-Me = 2- or 4-methylquinoline; H_4 = 1,2,3,4-tetrahydroquinoline; see exptl. section for yields. [b] % of 3-methylindole (within ±5%) in the mixture as determined by gas–liquid partition chromatography and infrared spectra. [c] Not all products formed in the reaction were isolated. [d] Yield of 6-methylindole and 3,6-dimethylindole, with the percentage of the latter in parentheses (determined by gas–liquid partition chromatography).

It is not certain whether the hydrogenolysis of the quinolines proceeds *via* the 1,2,3,4-tetrahydroquinoline derivatives. So far, traces of 1,2,3,4-tetrahydroquinoline were isolated only from the experiments with quinoline. The major basic product formed in these reactions was 2-methylquinoline. This finding agrees with the observation that some α-picoline is formed during the hydrogenation of pyridine over Raney nickel.[8] However, the situation is complicated by the formation of quinoline from 2-methylquinoline (see below). The origin of the new methyl group is as yet obscure. Methylation by free radicals seems unlikely as no other methylated products were discovered. An alternative source may be found in a reaction between the catalyst and 2,2′-biquinolyl. Prolonged heating of quinoline with the catalyst at temperatures near 235° led to progressively lower yields of 2,2′-biquinolyl, indicating that the biaryl was further changed by the catalyst. Even in boiling xylene (140°), 2,2′-biquinolyl slowly reacted with W7-J nickel to give small quantities of indole, 3-methylindole, and quinoline. A second base was identified by paper and gas–liquid partition chromatography as 2-methylquinoline, but derivatives have not been prepared. These results suggest that the formation of 2,2′-biquinolyl from quinoline and W7-J nickel is reversible, and that the quinoline produced from the biaryl reacts further with the catalyst. As far as the formation of 2-methylquinoline is concerned, a sequence of reactions may be envisaged leading from 2,2′-biquinolyl to 2-methylquinoline and indole, presumably *via* a derivative of *o*-ethylaniline.

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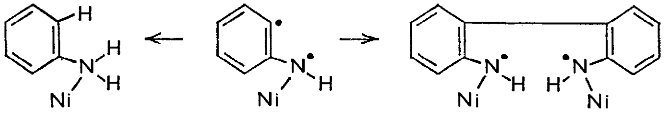
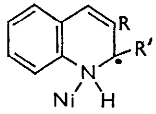
[7] Rapoport, *J. Appl. Chem. U.S.S.R.*, 1936, **9**, 1456 (*Chem. Abs.*, 1937, **31**, 2216); Eru, Sakhnovskaya, and Pychko, *J. Gen. Chem. U.S.S.R.*, 1938, **8**, 1563 (*Chem. Abs.*, 1939, **33**, 4595).

[8] Jones and Lindsey, *J.*, 1952, 3261.

All quinolines examined formed 2,2'-biaryls, the structures of which were confirmed either by comparison with authentic specimens or by the formation of coloured cuprous chelate compounds. The biaryl obtained from 3-methylquinoline did not form such a derivative, but 3,3'-dimethyl-2,2'-biquinolyl should not be capable of chelate formation for steric reasons. Like quinoline, 4-methylquinoline gave more biaryl when the reaction was carried out under reduced pressure. The observed differences in the yields of the 2,2'-biaryls agree with the mechanism proposed earlier.[1] The introduction of a methyl group into quinoline increases the basicity and thus facilitates chemisorption. With the exception of 2- and 3-methylquinoline, the yields obtained vary with the strengths of the bases.[9] With 3-methylquinoline, steric interaction between the methyl groups would make combination of the intermediate (II) more difficult. The effect would be more pronounced with the 2-isomer (III) where the methyl group would also interfere with the chemisorption of the base. Traces of 2,2'-biquinolyl, together with some quinoline, were formed from 2-methylquinoline only after prolonged heating.[1] As the concentration of quinoline in the reaction mixture is small, it seems unlikely that the biaryl is derived from the quinoline; instead the quinoline could be formed by the reaction between 2,2'-biquinolyl and the catalyst. Alternatively, the reaction between the intermediate (III) and hydrogen may lead to quinoline. Similarly, 2,4-dimethylquinoline gave some 4,4'-dimethyl-2,2'-biquinolyl.



(I)



(II) R = Me, R' = H
(III) R = H, R' = Me

Prolonged heating of quinoline over W7-J nickel at atmospheric pressure produced increasing amounts of tars from which a base $C_{17}H_{22}N_2$ was isolated. Its properties were similar to those of 2-2'-indolylquinoline which was prepared by the action of polyphosphoric acid on the phenylhydrazone of 2-acetylquinoline. Comparison of the spectra of these compounds suggested that the new base is an indolylquinoline, possibly the 2-3'-indolylquinoline.

EXPERIMENTAL

Detection and Determination of Indoles.—(*a*) *p*-Dimethylaminobenzaldehyde, dissolved in an excess of 6N-hydrochloric acid, was used to detect indoles[10] and carbazole in the presence of large quantities of quinolines. With this reagent a red colour was obtained within 10 min. of the beginning of the reaction between nickel and quinoline.

(*b*) Indoles were detected and characterised by chromatography on acetylated paper. The papers were prepared according to Spotswood[11] but more sulphuric acid (0·8 g. of 92% acid per l. of acetic anhydride) was used. The solvent system ethanol–toluene–water (80 : 25 : 5) was satisfactory for development by descent. The indoles were detected by exposure of the papers to iodine vapour. The R_F values obtained varied with different batches of papers, and standards were run simultaneously with unknown samples; typical values are: indole 0·35; 2-methylindole 0·40; 3-methylindole 0·40. A more highly acetylated paper resulted when the acetylation was continued for 8 hr., and larger differences in the R_F values were observed: indole 0·31; 2-methylindole 0·42; 3-methylindole 0·50.

(*c*) The approximate composition of the mixtures of indole and 3-methylindole was determined either by gas–liquid partition chromatography (see below) or by examination of the C–H stretching and deformation frequencies in the infrared spectrum (calcium fluoride prism) in carbon tetrachloride.

[9] Brown, McDaniel, and Häfliger in Braude and Nachod, "Determination of Organic Structures," Academic Press Inc., New York, 1955, p. 602.

[10] Chernoff, *Ind. Eng. Chem., Analyt.*, 1940, **12**, 273.

[11] Spotswood, *J. Chromatog.*, 1959, **2**, 90.

Gas–Liquid Partition Chromatography.—A Griffin V.P.C. apparatus Mk. II was used with 4 ft. column packed with " Celite " [40—80 mesh, coated with 20% (wt.) of Apiezon L]. With a flow rate of one l. per hr. of nitrogen, an inlet pressure of 330 mm., and an outlet pressure of 97 mm., the following retention times (min.) were observed at 202°: quinoline 5·23; 2-methylquinoline 6·87; 3-methylquinoline 8·85; 4-methylquinoline 9·65; 2,4-dimethylquinoline 12·10; 7-methylquinoline, 8·43; 1,2,3,4-tetrahydroquinoline 6·95; *o*-toluidine 2·35; aniline 1·53; indole 6·00; 2-methylindole 9·20; 3-methylindole 9·0; 1-methylindole 5·55.

By comparison of the areas under the peaks the approximate compositions of several mixtures were obtained. Wherever possible the method was checked with standard mixtures.

Paper Chromatography of the Basic Reaction Products.—The hydrochlorides were placed on Whatman paper No. 1 and developed by descent, with the solvent butan-1-ol–concentrated hydrochloric acid–water (80 : 20 : 60). After drying, the papers were exposed to iodine vapour. The R_F values obtained in this way varied slightly and standard samples were run simultaneously whenever unknown mixtures were examined. However, the sequence of the R_F values remained unchanged and is exemplified by the following series: quinoline 0·51; 2-methylquinoline 0·59; 3-methylquinoline 0·66; 4-methylquinoline 0·55; 7-methylquinoline 0·63; 2,4-dimethylquinoline 0·60; 1,2,3,4-tetrahydroquinoline 0·78; *o*-toluidine 0·80; aniline 0·75; phenazine 0·90; 2,2′-indolylquinoline 0·77; 2,2′-biquinolyl 0·63.

Starting Materials.—Quinoline [12] (n_D^{21} 1·6262), 2-methylquinoline [13] (n_D^{25} 1·6092), and 2,4-dimethylquinoline [14] (n_D^{21} 1·6070) were prepared by standard methods and purified by fractional distillation and by crystallisation of their hexachlorozincates. 7-Methylquinoline (B.D.H.) (n_D^{24} 1·6142) and 4-methylquinoline (B.D.H.) (n_D^{25} 1·6070) were purified similarly. 3-Methylquinoline (m. p. 16·5—17·5°; n_D^{25} 1·6069; picrate, m. p. 187—188°) was best prepared from 3-methylquinoline-4-carboxylic acid [15] by using Kaslow and Buchner's method [16] for preparation of 3-phenylquinoline; Willimot and Simpson's procedure [17] produced an inferior product in low yield.

All bases were found to be homogeneous on gas–liquid partition chromatography and paper chromatography.

Catalyst.—The catalyst was prepared as described in Part VII. Unless otherwise stated, 125 g. of alloy were used in each experiment.

2-2′-Indolylquinoline.—2-Acetylquinoline phenylhydrazone [18] (1 g.) was heated under stirring with polyphosphoric acid (10 c.c., 80% of P_2O_5) to 210° during 15 min. After decomposition with water and basification with ammonia solution, the product was purified by chromatography in benzene on alumina. After crystallisation from benzene–light petroleum (b. p. 40—70°), 2-2′-*indolylquinoline* (0·45 g.) formed colourless needles with a light yellow tinge, m. p. 190—191·5° (Found: C, 83·8; H, 5·2; N, 11·1. $C_{17}H_{12}N_2$ requires C, 83·5; H, 4·95; N. 11·5%): it gave no colour with *p*-dimethylaminobenzaldehyde. Its infrared spectrum showed an intense band at 3459 ± 2 cm.$^{-1}$. Its ultraviolet spectrum in 95% ethanol showed maxima (log ε values) at 244 (5·40), 292 (5·11), 320 (4·19), and 360 mμ (5·40), and minima at 234 (5·34), 266 (4·77), 298 (5·08), and 330 mμ (5·09). The hydrochloride of this compound was orange and only sparingly soluble in cold aqueous hydrochloric acid.

Quinoline.—(*a*) Quinoline (100 c.c.) was refluxed over the catalyst for 140 hr. Most of the black product was decanted and the remainder removed from the catalyst by repeated extraction, first with boiling benzene and then with boiling ethanol. After removal of the solvents the combined parts were separated into a neutral and a basic fraction in a Craig countercurrent apparatus (30 tubes, of 100 c.c. each) with 2N-hydrochloric acid as the stationary phase and ether (5 l.) as the transfer phase.

The neutral fraction was chromatographed on alumina (350 g.) in light petroleum (b. p. <40°). Elution with this solvent (500 c.c.) yielded (i) a colourless waxy *substance* (0·40 g.). Crystallisation from ethanol gave colourless crystals (0·30 g.), m. p. 59—60° {Found: C, 85·35; H, 14·6; *C*-Me, 0·4%; *M* (cryoscopic in naphthalene), 580. $[CH_2]_x$ requires C, 85·6; H, 14·4%}, $\nu_{max.}$ (s) 2959, 2924, 2824, 2853, 1466, and 1460 cm.$^{-1}$.

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[12] Clarke and Davis, *Org. Synth.*, 1932, Coll. Vol. I, p. 466.

[13] Vogel, " Elementary Practical Organic Chemistry," Longmans, Green, London, 1957, Part I, p. 320.

[14] Vaughan, *Org. Synth.*, 1948, **28**, 49.

[15] Ornstein, *Ber.*, 1907, **40**, 1088.

[16] Kaslow and Buchner, *J. Org. Chem.*, 1958, **23**, 271.

[17] Willimot and Simpson, *J.*, 1926, 2807.

[18] Kaufmann, Dändliker, and Burkhardt, *Ber.*, 1913, **46**, 2929.

Elution was continued with light petroleum (b. p. 40—60°) and fractions which gave a red colour with *p*-dimethylaminobenzaldehyde were examined by paper chromatography, appropriate fractions being combined. In this way were obtained (ii) 3-methylindole (0·40 g.), plates, m. p. 93° [from light petroleum (b. p. 40—60°)] [picrate, m. p. 170—171° (lit., m. p. 171°); trinitrobenzene complex, m. p. 185° (lit., m. p. 185°)] (all three compounds were identified by comparison with authentic specimens), (iii) a colourless solid (3·95 g.), m. p. 40—48°, paper chromatography (acetylated paper) of which showed the presence of indole and 3-methylindole, the infrared spectrum indicating an 8 : 2 ratio indole : 3-methylindole, and (iv) indole (0·40 g.), m. p. 50—51° [picrate, m. p. 175° (lit., m. p. 175°); trinitrobenzene complex, m. p. 187° (lit., m. p. 187°) (identical with authentic specimens)].

Further elution with light petroleum, b. p. 60—90°, yielded more indole (0·10 g.) and fraction (v) light brown plates (0·06 g.). Crystallisation from ethanol–water gave colourless plates (0·03 g.), m. p. 238° alone and mixed with carbazole [Found: C, 86·3; H, 5·5; N, 8·3%; *M* (cryoscopic in camphor), 152. Calc. for $C_{12}H_9N$: C, 86·0; H, 5·4; N, 8·4%; *M*, 167]. The picrate separated from xylene in red needles, m. p. 185° (lit., m. p. 185°), alone and mixed with an authentic specimen.

After completion of the countercurrent distribution the aqueous phases were combined, basified, and extracted with ether. Distillation gave a yellow liquid (65 c.c.), b. p. 103—125°/25 mm., and a black residue (9 g.). Paper chromatography showed that the latter contained at least five components. By repeated chromatography on alumina in benzene, pure 2,2′-biquinolyl (2 g.) was obtained. Somewhat more strongly adsorbed on alumina was a *substance*, m. p. 190—191·5° (1 g.), needles from benzene [Found: C, 83·9; H, 4·8; N, 11·2; active H, 0·47%; *M* (cryoscopic in camphor), 249. $C_{17}H_{12}N_2$ requires C, 83·6; H, 4·95; N, 11·5; active H, 0·41%; *M*, 244]. This base formed a yellowish-green hydrochloride which fluoresced strongly in ultraviolet light and was moderately soluble in aqueous hydrochloric acid. It did not give a colour with *p*-dimethylaminobenzaldehyde in hydrochloric acid. It had $\nu_{\text{max.}}$ at 3483 ± 2 (s) cm.$^{-1}$ and $\lambda_{\text{max.}}$ (in 95% EtOH) (log ε) at 228 (4·38), 277 (4·07), and 358 mμ (3·92), $\lambda_{\text{min.}}$ 248 (3·89) and 324 mμ (3·49).

Part of the distillate (60 c.c.) was distilled through a jacketed column (2 × 60 cm.) filled with single-turn glass helices. A reflux ratio of 1 : 10 was used to collect the fractions (i), b. p. 105—116°/25 mm. (3·8 c.c.), (ii) b. p. 116—117°/25 mm. (5 c.c.), (iii) b. p. 118°/25 mm. (8 c.c.), (iv) b. p. 118°/25 mm. (10 c.c.), and (v) b. p. 118°/25 mm. (21 c.c.). These fractions and the residue from the distillation (10 c.c.) were examined by paper chromatography and by gas–liquid partition chromatography. Fraction (i) contained quinoline (52%), aniline (45%), and *o*-toluidine (2·6%). Fraction (ii) contained quinoline (86%) and *o*-toluidine (13%). Fractions (iii) and (iv) consisted of quinoline. In fraction (v) quinoline (>95%) and traces of 2-methylquinoline and 1,2,3,4-tetrahydroquinoline were present. The last two compounds could not be resolved by vapour-phase chromatography and appeared as one component (2—4%); however, they were readily identified on paper. Similarly, the residue of the distillation contained quinoline (40%), and a mixture (60%) of 2-methylquinoline and 1,2,3,4-tetrahydroquinoline. The last compound (3%) was separated and characterised as the toluene-*p*-sulphonyl derivative, m. p. 96° (lit., m. p. 95°), needles from ethanol (Found: C, 66·7; H, 5·9; O, 11·4; S, 10·9. Calc. for $C_{16}H_{17}O_2NS$: C, 66·9; H, 6·0; O, 11·1; S, 11·2%). The remaining tertiary amines were fractionally distilled; the last fraction obtained in this way showed all the infrared bands of 2-methylquinoline (liquid film, sodium chloride prism). Its picrate, m. p. 190°, crystallised in yellow needles from benzene; the mixture with authentic 2-methylquinoline picrate melted at 194°, while pure 2-methylquinoline picrate melted at 195° (lit., m. p. 195°). Heating it with phthalic anhydride gave quinophthalone,[19] yellow needles (from acetic acid), m. p. and mixed m. p. 240° (Found: C, 79·1; H, 4·1; N, 5·1. Calc. for $C_{18}H_{11}O_2N$: C, 79·1; H, 4·1; N, 5·1%).

(*b*) Quinoline (132 c.c.) was refluxed over the catalyst for 42 hr. at 18 mm. The product was treated with ethanol to separate 2,2′-biquinolyl (7 g.; m. p. 190—192°). After removal of the alcohol the filtrate was worked up as described above. From the neutral fraction were isolated paraffin (0·01 g., largely liquid), and a mixture (1·75 g.) of indole (80%) and 3-methylindole. Pure carbazole could not be isolated. After distillation of the basic fraction (100 c.c.; b. p. 110—125°/25 mm.) 2,2′-biquinolyl (1·5 g.) was separated from the residue (4·5 g.) by chromatography. After fractional distillation of the liquid part, followed by gas–liquid

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[19] Eibner and Lange, *Annalen*, 1901, **315**, 303.

partition chromatography, the presence of a mixture of 2-methylquinoline and 1,2,3,4-tetrahydroquinoline (about 5%) was revealed. Paper chromatography showed the presence of traces of a base with the R_F value of *o*-toluidine.

(*c*) Quinoline (150 c.c.) was refluxed over the catalyst for 50 hr. The following products were isolated: paraffin (0·100 g.), mixture (4·08 g.) of indole and 3-methylindole (10—15%), carbazole (0·025 g.), and 2,2′-biquinolyl (2·5 g.).

(*d*) Quinoline (132 c.c.) was refluxed over the catalyst at 18 mm. for 12 hr. All products boiling up to 125°/25 mm. were removed by distillation. 2,2′-Biquinolyl (5·1 g.) was isolated from the residue.

2-*Methylquinoline.*—2-Methylquinoline (100 c.c.) was refluxed over the catalyst for 46 hr. and the resulting mixture was worked up as described for quinoline. The neutral fraction yielded carbazole (0·01 g.), a mixture (0·20 g.) of indole and 3-methylindole (about 80%), and paraffinic material, m. p. 57—58° (0·044 g., after crystallisation from ethanol) (Found: C, 85·3; H, 14·6. Calc. for $[CH_2]_x$: C, 85·6; H, 14·4%). The infrared spectrum of the paraffin was identical with that of the compound obtained from quinoline and a mixed m. p. showed no depression. 2,2′-Biquinolyl (0·300 g.) was separated from the basic fraction, and aniline, *o*-toluidine, *N*-ethylaniline, and quinoline were identified by paper and gas–liquid partition chromatography. An unidentified base (retention time 5·65 min.; conditions as above) could not be removed by means of toluene-*p*-sulphonyl chloride.

3-*Methylquinoline.*—3-Methylquinoline (90 c.c.) was refluxed over the catalyst for 19 hr. The product was black and strongly adsorbed by the nickel. From the neutral fraction carbazole (0·300 g.) and paraffin (0·100 g.; m. p. 55—60°) were separated by chromatography. In the intermediate fractions (0·150 g.) indole and 3-methylindole were identified by paper and gas–liquid partition chromatography and by their picrates, which were compared with authentic samples by means of their infrared spectra (sodium chloride prism, Nujol). Neither compound was obtained pure, but no evidence for the presence of 2- or 1-methylindole was found. A 4 : 6 ratio of indole : 3-methylindole was inferred from the gas–liquid chromatogram. Distillation of the basic fraction gave a liquid (60 c.c.; b. p. 110—138°/22 mm.) and a residue (7·5 g.). The latter was repeatedly chromatographed on alumina, first in benzene, then in light petroleum (b. p. 60—90°). Elution with light petroleum (b. p. 60—90°) gave 3,3′-*dimethyl*-2,2′-*biquinolyl* (?) (Found: C, 84·4; H, 5·7; N, 9·8. $C_{20}H_{16}N_2$ requires C, 84·5; H, 5·7; N, 9·85%), needles, m. p. 143—144° (1·2 g.), which gave no colour with cuprous ions. Aniline and *o*-toluidine were identified in the liquid products. Two bases with retention times of 4·65 and 8·05 min. did not react with toluene-*p*-sulphonyl chloride.

4-*Methylquinoline.*—4-Methylquinoline (120 c.c.) was refluxed over the catalyst for 50 hr. Extraction from the catalyst and removal of the solvent gave needles (5·8 g.) (from benzene), m. p. 278—280°, of 4,4′-*dimethyl*-2,2′-*biquinolyl* (Found: C, 84·6; H, 5·55; N, 9·6%), were obtained; they gave a deep purple colour with cuprous ions in aqueous acetic acid. The neutral fraction gave paraffin (0·100 g.), m. p. 50—55°, carbazole (0·05 g.), and a mixture (0·100 g.) of indole and 3-methylindole (80%). Distillation of the basic fraction gave a pale yellow liquid (100 c.c.; b. p. 110—141°/25 mm.) and a residue (9 g.). Chromatography of the latter in benzene yielded 4,4′-dimethyl-2,2′-biquinolyl (2·3 g.). At least six bases were detected in the liquid fraction by paper and gas–liquid partition chromatography, but only aniline was identified.

(*b*) 4-Methylquinoline (100 c.c.) was refluxed over the catalyst for 31 hr. at 22 mm. The nickel was filtered off while the mixture was still hot. On cooling of the filtrate, 4,4′-dimethyl-2,2′-biquinolyl separated in needles (11 g.), m. p. 275—276°. After distillation of the liquid products (65 c.c.) more biaryl (5·1 g.; m. p. 273—275°) was obtained from the residue by washing with benzene. Incomplete extraction (Soxhlet) (24 hr.) of the nickel with benzene yielded another crop of the biaryl (4·3 g.; m. p. 277—279°). The distillate gave positive tests for indoles.

2,4-*Dimethylquinoline.*—2,4-Dimethylquinoline (100 c.c.) was refluxed over the catalyst for 50 hr. and worked up as described for quinoline. From the neutral fraction were isolated paraffin (0·022 g.; after crystallisation 0·014 g., m. p. 56—57°), carbazole (0·030 g.), and a mixture (0·142 g.) of indole and 3-methylindole (65%). Distillation of the basic fraction gave a liquid (75 c.c.; b. p. 110—146°/25 mm.) and a residue (11 g.). From the latter 4,4′-dimethyl-2,2′-biquinolyl (0·610 g.; m. p. and mixed m. p. 277—279°) was separated by chromatography in benzene on alumina. Benzene and chloroform eluted dark brown amorphous solids which did not crystallise. In the liquid fraction three bases were detected, none of which boiled below quinoline. Peaks corresponding to quinoline and 4-methylquinoline occurred in the gas–liquid chromatogram, but the R_F values of these bases were too close to allow their unambiguous identification.

7-*Methylquinoline*.—7-Methylquinoline (90 c.c.) was refluxed over the catalyst for 46 hr., and worked up as described for quinoline. The neutral fraction gave paraffin (0·05 g.; m. p. 56—57°) and a mixture of indoles (1·77 g.). Chromatography on alumina gave 3,6-dimethylindole (0·08 g.), m. p. 89—92° (lit.,[20] m. p. 90—93°), whose picrate, m. p. 158° (decomp.) (lit.,[20] 163—164°), crystallised from benzene as dark red needles (Found: C, 51·3; H, 3·9; N, 15·0. Calc. for $C_{16}H_{14}O_7N_4$: C, 51·5; H, 3·8; N, 15·0%). The next fraction (0·6 g.), a liquid, contained 3,6-dimethylindole (28%) (retention time 12·45 min.; conditions as described), and 6-methylindole (retention time 8·30 min.); later fractions (1·1 g.) contained only 6-methylindole [picrate, m. p. 160—161° (lit.,[21] m. p. 152°, 161·5°) (Found: C, 49·8; H, 3·4; N, 15·3; O, 31·3. Calc. for $C_{15}H_{12}O_7N_4$: C, 50·0; H, 3·4; N, 15·5; O, 31·1%)]. From the basic fraction was isolated 7,7′-*dimethyl*-2,2′-*biquinolyl* (8·3 g.), needles (from toluene), m. p. 288° (Found: C, 84·8; H, 5·9; N, 9·4%), forming a purple chelate compound with cuprous ions in acetic acid.

2,2′-*Biquinolyl*.—2,2′-Biquinolyl (5 g.) was refluxed in xylene (90 c.c.) for 4 days. After addition of more boiling xylene (100 c.c.) the catalyst was filtered off and repeatedly extracted with hot xylene. The combined filtrate and washings yielded crude 2,2′-biquinolyl (4·25 g.), m. p. 185—190°. The residue from this crystallisation was separated into a neutral and a basic fraction. Paper chromatography showed the presence of 3-methylindole and of less indole; only 3-methylindole was obtained crystalline (0·005 g.; m. p. 93—94°). Traces of wax which did not react with *p*-dimethylaminobenzaldehyde were also present. The basic fraction (0·075 g.) was mainly quinoline (picrate, R_F value, and retention time). A second base (5%) had the R_F value and retention time of 2-methylquinoline.

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