# *Action of Grignard Reagents and Dialkylcadmiums on Alkylquinolinium and Alkyl*isoquinolinium *Salts. A Relation between the Basic Strength of Anions and their Orientation in Nuclear Substitution Reactions.*

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Previous work on nuclear substitution by anions and other bases in aromatic nitro- and carbonyl compounds has been extended to alkylquinolinium and alkyl*iso*quinolinium salts. In confirmation of Freund's rule all the Grignard reagents studied gave 2-derivatives of 1-alkyl-1 : 2-dihydroquinoline and 1-derivatives of 2-alkyl-1 : 2-dihydro*iso*quinoline. Similar reactions with dialkylcadmiums gave the same results, though more slowly. The factors which lead to 2- or 4-substitution in quinoline and alkylquinolinium salts are discussed.

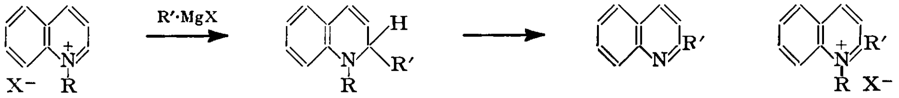
Whilst it is generally recognized that active anions and primary and secondary amines can react with aromatic systems at positions *ortho* or *para* to nitro- or carbonyl groups (Bradley, *J.*, 1937, 1091), less is known about the factors which determine whether *ortho*- or *para*-substitution will be the more important. With *meso*benzanthrone it has been shown (Bradley and Sutcliffe, *J.*, 1954, 708) that anions which are most active in forming covalent links with carbonyl-carbon, *e.g.*, $NH_2^-$ and $R^-$, enter the ring mainly *ortho* to the carbonyl group, whilst the less active ones, *e.g.*, $NPh_2^-$ and $OH^-$, enter mainly or exclusively in the *para*-position.

The present investigation is concerned with the same problem in the chemistry of quinoline. 1-Alkylquinolinium salts react with alkali hydroxides and Grignard reagents, to form 1-alkyl-1 : 2-dihydro-2-hydroxyquinolines (Hantzsch and Kalb, *Ber.*, 1899, **32**, 3109) and 1 : 2-dialkyl-1 : 2-dihydroquinolines (Freund, *Ber.*, 1904, **37**, 4666), respectively, whilst alkali cyanides afford 1-alkyl-4-cyano-1 : 4-dihydroquinolines (Kaufmann and Albertini, *Ber.*, 1909, **42**, 3776). These results accord with Bradley and Sutcliffe's work on *meso*benzanthrone, the more active $R^-$ and $OH^-$ anions substituting the quinolinium nucleus at the 2-position whilst the less active $CN^-$ anion combines with the more distant 4-position. Freund (*loc. cit.*) studied the action of methylmagnesium iodide and phenylmagnesium bromide on quinoline methiodide, and Freund and Richard (*Ber.*, 1909, **42**, 1101) studied the action of methylmagnesium iodide on quinaldine methiodide; all the products were 2-substituted 1-alkyl-1 : 2-dihydro-quinolines or -quinaldines. In the present paper a more extended study is described in which both the *N*-substituent and the Grignard reagent have been varied over a wider range with the object of establishing whether 2-substitution is invariable and independent of the size and chemical character of the reacting molecules. Freund and Bode (*ibid.*, p. 1758) showed that Grignard reagents and 2-alkyl*iso*quinolinium salts gave derivatives of 1 : 2-dihydro*iso*quinoline, and this reaction too has been investigated further. Finally, the action of dialkylcadmiums on quaternary salts derived from both quinoline and *iso*quinoline has been studied.

*The Grignard Reaction.*—The method of experiment was generally the same as that of Freund (*loc. cit.*) but it was standardized and many of the reactions were carried out in duplicate, good agreement being obtained in the results. The Grignard reagents were prepared in ether from an alkyl halide and a slight excess of magnesium, the amount of residual metal being determined and employed to calculate the maximum yields of reagent R·MgX obtained (R = Me, Et, $Pr^n$, $Bu^n$, 90—100%; $Pr^i$, $Bu^i$, 85%; $Bu^s$, 80%; $Bu^t$, 30—35%), which approximate to those reported by Gilman, Zoellner, and Dickey (*J. Amer. Chem. Soc.*, 1929, **51**, 1579) (Et 93, $Pr^n$ 92, $Bu^n$ 94, $Pr^i$ 84, $Bu^i$ 87, $Bu^s$ 78, $Bu^t$ 25%).

In carrying out a reaction 0·2 mole of a qaternary salt was added to 0·3—0·4 mole of a Grignard reagent, except in the case of *tert.*-butylmagnesium bromide where 0·2—0·3 mole of the reagent was used. The yields of 1 : 2-dialkyl-1 : 2-dihydroquinolines obtained are given in Table 1.

All the products were identified as derivatives of 1 : 2-dihydroquinoline (II) by their decomposition by heat to 2-alkylquinolines (III) (Meisenheimer *et al.*, *Ber.*, 1923, **56**, 1353; 1925, **58**, 2320). In most cases the orientation was confirmed by oxidation with iodine, a 1 : 2-dialkylquinolinium salt (IV) resulting (Kaufmann and Janini, *Ber.*, 1911, **44**, 2670). A characteristic feature of all the experiments was the rapidity of the Grignard addition reaction. With any single reagent and a series of alkylquinolinium halides the yield tended to diminish with increase in the size of the alkyl group. All the reactions proceeded to completion and the diminishing yield of isolatable product was due to the formation of emulsions which increased in stability with the size of the alkyl groups and reached a maximum with *sec.*-butyl in the series examined. All the 1 : 2-dialkyl-1 : 2-dihydroquinolines were yellow oils. There was no notable variation in the stability of the dihydro-bases and the yields of 2-alkylquinolines obtained therefrom varied little over the 25 examples examined, except with the *tert.*-butyl compounds, which gave quinoline. Again, on oxidation of the dihydro-bases by alcoholic iodine (Kaufmann and Janini, *loc. cit.*) the related 1 : 2-dialkylquinolinium halides generally resulted, but the *tert.*-butyl compounds lost the *tert.*-butyl group. Because of this the constitution of the dihydro-bases containing *tert.*-butyl groups could not be established, but they were probably 1 : 2-dihydroquinoline derivatives for they had the same order of stability at room temperature as the dihydro-bases containing unbranched alkyl groups; by contrast, the stability of 1 : 4-dihydroquinolines has been stated to be much lower. Quinoline hydriodide gave quinoline with the Grignard reagents from methyl iodide and butyl and *iso*butyl bromide.



(I) (II) (III) (IV)

TABLE 1. *Yields* (%) *of* 1 : 2-*dialkyl*-1 : 2-*dihydroquinoline from* R·MgX *and quinolinium salts.*

| Quinoline derivative | R in R·MgX | | | | | | |
|---|---|---|---|---|---|---|---|
| | Me | Et | $Pr^n$ | $Pr^i$ | $Bu^n$ | $Bu^i$ | $Bu^s$ |
| MeI | 85 | 69 | 59 | 45 | 50 | 35 | 45 |
| EtI | 75 | 64 | 55 | 42 | — | — | — |
| $Pr^nI$ | 56 | 60 | 53·5 | 42 | 50 | 22 | 44 |
| | — | — | 51 | 46·5 | 48 | 20 | 44 |
| $Pr^iI$ | 53·5 | 50 | 42 | 46·5 | 44 | 17·5 | 44 |

The main conclusion from these experiments is that methyl- to butyl-magnesium halides, irrespective of the size and shape of the alkyl group, react with alkylquinolinium salts at the 2-position, in agreement with Freund and Richard's rule.

In a parallel study with 2-alkyl*iso*quinolinium halides reaction occurred readily with all the Grignard reagents investigated, 1 : 2-dialkyl-1 : 2-dihydro*iso*quinolines resulting (see Table 2). Their stabilities at room temperature were similar to those of the corresponding quinoline derivatives. *iso*Quinoline hydriodide gave *iso*quinoline.

TABLE 2. *Yields* (%) *of* 1 : 2-*dialkyl*-1 : 2-*dihydro*iso*quinoline from* R·MgX *and* iso*quinolinium salts.*

| *iso*Quinoline derivative | R in R·MgX | | |
|---|---|---|---|
| | Me | Et | $Pr^n$ |
| MeI | 75·5 | 58 | 51 |
| EtI | 55 | 53·5 | 50 |
| $Pr^nI$ | 56 | 50 | |
| $Pr^iI$ | 53·5 | 45 | |

*Reaction of* 1-*Alkylquinolinium and* 2-*Alkyl*iso*quinolinium Salts with Dialkylcadmiums.*—The reaction of dialkylcadmiums with heterocyclic ammonium salts, which has not been studied previously, was slower than with Grignard reagents and gave more completely isolatable products. These were the same 1 : 2-dihydro-bases that were formed in the Grignard reaction, but because of the lower rate of change it was possible to use the dialkylcadmium reaction to compare the relative rates of substitution by different reagents in various quaternary salts.

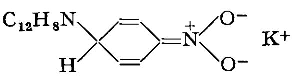
The experiments with *N*-alkyl-quinolinium and -*iso*quinolinium salts, carried out in duplicate, gave the yields shown in Table 3 (for proof of identities see p. 2777). Under standard conditions with any one dialkylcadmium the yield of dihydro-bases fell with increase in the complexity of the *N*-alkyl substituent in both the quinoline and the *iso*quinoline series. In the parallel investigation in which Grignard reagents were used it was found that steric factors did not affect the speed of the reaction or the orientation of the entering groups. For this reason it was probable that with dialkylcadmiums, too, the size and spatial form as such of the alkyl groups involved were not important factors and that the relative yields were determined by a progressive decrease in the reactivity of the nucleus and of the dialkylcadmium with increase in the complexity of the alkyl groups.

TABLE 3. *Yields* (%) *of* 1 : 2-*dialkyl*-1 : 2-*dihydroquinolines* (*duplicate experiments*) *and* 1 : 2-*dialkyl*iso*quinolines.*

| | R in $CdR_2$ | | | |
|---|---|---|---|---|
| | Me | Et | Pr | $Pr^i$ |
| *Quinoline derivative* | | | | |
| MeI | 20·1, 19·5 [a] | 15·6, 16·2 [b] | 8·6, 8·6 [c] | 8·0, 8·0 |
| EtI | 13·9, 14·5 [e] | 9·6, 10·2 [f] | 4·4, 4·4 [g] | 4·4, 4·0 [h] |
| PrI | 6·4, 7·5 [i] | 4·4, 4·4 [k] | Small [l] | Small [m] |
| $Pr^iI$ | 5·3, 5·3 [n] | 4·0, 4·4 [o] | ,, [p] | ,, [q] |
| iso*Quinoline derivative* | | | | |
| MeI | 20·8 [a] | 16·2 [b] | 9·1 [c] | 9·1 [d] |
| EtI | 14·5 [e] | 10·7 [f] | 5·0 [g] | 4·5 [h] |
| PrI | 7·0 | 4·5 [j] | Small | Small |
| $Pr^iI$ | 5·9 | 4·5 [l] | ,, | ,, |

[a–q] See p. 2777.

*General Considerations.*—The greater nuclear reactivity of the quinolinium cation, compared with that of nitrobenzene and *meso*benzanthrone, is shown by the reaction with aqueous alkali hydroxides and cyanides. On Bradley and Sutcliffe's relation the reaction of the Grignard reagent at the 2-position in a quinolinium cation and the reaction of the cyanide ion at the 4-position is to be expected because the two substituting agents differ widely in reactivity. Similarly both malononitrile and ethyl cyanoacetate react at the 4-position of methylquinolinium iodide (Leonard and Foster, *J. Amer. Chem. Soc.*, 1952, **74**, 2110), and quinaldine methiodide yields an *iso*cyanine (4-substitution) with the same quaternary salt (Mills and Wishart, *J.*, 1920, 579). In Reissert's reaction (*Ber.*, 1905, **38**, 1603) a 1-benzoylquinolinium salt and an alkali cyanide yield a 2-cyano-derivative. In this instance the reactivity of the nucleus has been augmented by the effect of the benzoyl group. The same relation is encountered also in substitutions by a given anion in a series of nuclei. Thus substitution by hydroxyl ions occurs *ortho* in the more reactive quinolinium cation and mainly *para* in the less reactive *meso*benzanthrone. Benzylmagnesium chloride reacts at the 2-position of an alkylquinolinium ion but mainly at the 4-position of pyridine, the nucleus of which is less reactive (Benkeser and Holton, *J. Amer. Chem. Soc.*, 1951, **73**, 5861). Other effects arise from special circumstances. Potassiocarbazole does not react with the quinolinium cation, although reaction takes place easily with nitrobenzene probably because the nitro-group passes into the anion of an *aci*-form with formation of an adduct (V) (Bradley and Robinson, *J.*, 1932, 1254). By contrast the product from potassiocarbazole and an alkylquinolinium salt is a dihydro-base which is incapable of stabilization as an alkali-metal derivative under the conditions employed.



(V)

## EXPERIMENTAL

iso*Quinoline* iso*propiodide*, m. p. 174° (from alcohol) (Found: N, 4·7. $C_{12}H_{14}NI$ requires N, 4·5%), resulted (120 g.) when *iso*quinoline (64·5 g.) was heated with *iso*propyl iodide (85 g.) at 100° (sealed tube) for 0·5 hr. The other quaternary salts used in the investigation were prepared by methods recorded in the literature: their purity was checked by analysis. Heating quinoline with *sec.*- or *tert.*-butyl iodide gave only quinoline hydriodide. Similarly with *iso*-

quinoline the two iodides gave only iso*quinoline hydriodide*, m. p. 194° (Found: N, 5·4; I, 48·9. $C_9H_8NI$ requires N, 5·5; I, 49·4%).

*Experiments with Potassiocarbazole.*—The reagent did not react with quinoline or *iso*quinoline under reflux during 12 hr., or with quinoline or *iso*quinoline ethiodide in quinoline or *iso*quinoline, respectively under (reflux 12 hr.), and in the absence of a solvent (200°, 3 hr.), or with 2-iodoquinoline ethiodide (120—130°, 3 hr.).

*Experiments with Sodiofluorene.*—No substitution occurred when the reagent (3·7 g.) was heated with quinoline methiodide (5·4 g.) at 150° for 3 hr., or when 1·9 g. was heated with 2-iodoquinoline ethiodide or with 1-iodo*iso*quinoline methiodide (4 g.) at 150° for 3 hr.

*Experiments with Piperidine and Morpholine.*—Heated under reflux with piperidine (10 c.c.), quinoline methiodide (4 g.) afforded piperidine hydriodide, m. p. 186° (Found: N, 6·5. Calc. for $C_5H_{12}NI$: N, 6·3%). A similar result was obtained when *iso*quinoline methiodide, 2-iodoquinoline ethiodide, and 1-iodo*iso*quinoline methiodide were heated with piperidine. Heated under reflux with morpholine, quinoline methiodide gave morpholine hydriodide, m. p. 215° (Found: N, 6·45. Calc. for $C_4H_{10}ONI$: N, 6·5%). The same salt resulted when *iso*quinoline methiodide, 2-iodoquinoline ethiodide, or 1-iodo*iso*quinoline methiodide was used.

*Experiments with Toluene-*p*-sulphinic Acid.*—There was no reaction when a solution of sodium toluene-*p*-sulphinate (1·78 g.) in water (10 c.c.) was shaken with quinoline or *iso*quinoline ethiodide (2·85 g.) in water (50 c.c.) and ether (50 c.c.).

*Experiments with Grignard Reagents.*—The reagent was prepared from magnesium (10 g.), alkyl halide (0·4 mole), and ether (250 c.c.), and the resulting solution was decanted from the excess of magnesium when the reaction was complete. The product contained 0·3—0·4 mole of alkylmagnesium halide. In the preparation of *tert.*-butylmagnesium bromide 0·6 mole of *tert.*-butyl bromide and 300 c.c. of ether were used. The yield was 0·2—0·3 mole. In carrying out a reaction the powdered quaternary salt (0·2 mole) was added to the Grignard reagent with stirring. Reaction occurred at once and when it was complete water was added slowly, then hydrochloric acid until two clear layers resulted, and finally ammonium chloride (5 g.) and sufficient ammonia to make the solution alkaline. The ether layer was separated, washed with water (2 × 50 c.c.), and dried for 2 days over solid potassium hydroxide. Evaporation of the ether gave red oils and these were distilled under reduced pressure.

*Quinoline methiodide.* (*a*) With methylmagnesium iodide the product was a greenish-yellow oil (27 g.), b. p. 70°/0·6 mm. (Found: C, 82·9; H, 8·4; N, 8·8. Calc. for $C_{11}H_{13}N$: C, 83·0; H, 8·2; N, 8·8%) (Freund and Richard, *Ber.*, 1909, **42**, 1101, state b. p. 255—260°). Heated under reflux for 8 hr., the 1 : 2-dihydro-1 : 2-dimethylquinoline (6 g.) gave a greenish-yellow oil (4 g.), b. p. 242—248°, which on redistillation gave quinaldine (3 g.), b. p. 66°/0·4 mm. The derived methiodide, m. p. 193°, did not depress the identical m. p. of quinaldine methiodide.

A solution of the dihydro-base (3 g.) and iodine (4·8 g.) in ethanol (20 c.c.) was refluxed for 15 min. and then cooled. The product which separated crystallised from alcohol, as orange needles, m. p. 193°, not depressed by mixing with quinaldine methiodide.

(*b*) In a similar experiment with ethylmagnesium bromide the yield of 2-ethyl-1 : 2-dihydro-1-methylquinoline (Found: C, 83·0, 83·5; H, 8·8, 8·8; N, 7·8, 7·8. Calc. for $C_{12}H_{15}N$: C, 83·2; H, 8·7; N, 8·1%), b. p. 76—78°/0·5 mm. (Freund and Richard, *loc. cit.*, state b. p. 265°/757 mm., 141—142°/21 mm.), was 24 g. Heating the product (6 g.) under reflux for 10 hr. and distillation gave fractions, (i) b. p. <260°, a yellow oil (4 g.), and (ii) b. p. >260°, an orange-yellow oil (1·6 g.). Redistillation of fraction (i) gave a pale green oil (3 g.), b. p. 72—78°/0·6 mm. (Found: N, 8·5. Calc. for $C_{11}H_{11}N$: N, 8·9%), identified as 2-ethylquinoline by conversion into 2-ethylquinoline methiodide (Found: I, 42·7. Calc. for $C_{12}H_{14}NI$: I, 42·5%), m. p. 166°, not depressed by the authentic compound, m. p. 168°.

On refluxing of the dihydro-base (2 g.) and iodine (2·9 g.) in ethanol (15 c.c.) for 15 min. and cooling, brown crystals, m. p. 142°, separated. Purification from ethanol gave yellow crystals (Found: I, 42·4. Calc. for $C_{12}H_{14}NI$: I, 42·5%), m. p. 168°, and not depressed when mixed with 2-ethylquinoline methiodide.

(*c*) Propylmagnesium bromide gave 22 g. of 1 : 2-dihydro-1-methyl-2-propylquinoline (Found: C, 83·6, 83·6; H, 9·1, 9·4; N, 7·5, 7·3. Calc. for $C_{13}H_{17}N$: C, 83·4; H, 9·1; N, 7·5%), b. p. 96°/0·7 mm. (von Braun and Aust, *loc. cit.*, record 168°/21 mm.; Freund and Kessler, *loc. cit.*, 268—270°; Meisenheimer and Schutze, *Ber.*, 1923, **56**, 1353, b. p. 152°/13 mm.).

Heating of the dihydro-base (5 g.) under reflux for 10 hr. followed by distillation gave as main fraction a light yellow oil, b. p. 276—280° (1·0 g.), and this on fractionation gave 2-propylquinoline (2 g.) (Found: N, 7·9. Calc. for $C_{12}H_{13}N$: N, 8·2%), b. p. 91—93°/1 mm. The methiodide had m. p. 185° (lit., 184°).

A solution of the dihydro-base (7·5 g.) and iodine (10 g.) in ethanol (30 c.c.), heated to boiling and then cooled, gave 2-propylquinoline methiodide (Found: C, 50·0; H, 5·1; N, 4·5; I, 40·4. Calc. for $C_{13}H_{16}NI$: C, 49·8; H, 5·1; N, 4·5; I, 40·6%), m. p. and mixed m. p. 185°.

(*d*) In a similar experiment with *iso*propylmagnesium bromide the yield of 1 : 2-dihydro-1-methyl-2-*iso*propylquinoline, b. p. 90/0·7 mm., was 17 g. (Found: C, 83·7, 83·2; H, 9·3, 9·4; N, 7·7, 7·3. Calc. for $C_{13}H_{17}N$: C, 83·4; H, 9·1; N, 7·5%) (Freund and Kessler, *loc. cit.*, record b. p. 268—274°). After being heated under reflux for 12 hr. the dihydro-base (6 g.) gave a yellow oil (4 g.), b. p. 274—276°, and this gave a fraction, b. p. 74—78°/0·5 mm. (Found: N, 8·4. Calc. for $C_{12}H_{13}N$: N, 8·2%). Union with methyl iodide gave 2-*iso*propylquinoline methiodide, m. p. 190° (lit., 182°). The same compound, m. p. 190°, was obtained from the dialkylcadmium reaction.

With iodine in ethanol the dihydroquinoline (3·7 g.) gave 2-*iso*propylquinoline methiodide (Found: I, 40·6. Calc. for $C_{13}H_{16}NI$: I, 40·6%), m. p. and mixed m. p. 190°.

(*e*) Butylmagnesium bromide gave 20 g. of *2-butyl-1 : 2-dihydro-1-methylquinoline*, b. p. 122°/1·5 mm. On redistillation the dihydro-base had b. p. 106—108°/1 mm. (Found: C, 83·1; H, 9·4; N, 7·1. $C_{14}H_{19}N$ requires C, 83·6; H, 9·5; N, 7·0%).

The dihydro-base (7 g.) decomposed when heated for 12 hr. under reflux. After distillation the main fraction (5 g.) was an orange oil, b. p. 274—290°, and this on redistillation gave a pale green oil, b. p. 94—98°/0·7 mm. (3·5 g.) (Found: C, 84·4; H, 8·3; N, 7·9. Calc. for $C_{13}H_{15}N$: C, 84·3; H, 8·1; N, 7·6%) [Delaby and Hiron (*Compt. rend.*, 1930, **191**, 847) record 153°/14 mm. as the b. p. of 2-butylquinoline]. The picrate had m. p. 162° (*idem, ibid.*, m. p. 162°). The *methiodide* crystallised from ethanol as a bright yellow microcrystalline powder, m. p. 175° (Found: C, 51·6; H, 5·7; N, 4·5; I, 38·7. $C_{14}H_{18}NI$ requires C, 51·4; H, 5·5; N, 4·3; I, 38·8%).

With iodine in ethanol 2-butyl-1 : 2-dihydro-1-methylquinoline (8 g.) gave *2-butylquinoline methiodide*, orange-yellow crystals [from ethanol (charcoal)], m. p. 175° (Found: I, 39·2. $C_{14}H_{18}NI$ requires I, 38·8%), identical with the product prepared from 2-butylquinoline.

(*f*) When *iso*butylmagnesium bromide was used the product was 2-*iso*butyl-1 : 2-dihydro-1-methylquinoline (14 g.) (Found: C, 83·3; H, 9·3; N, 6·6. Calc. for $C_{14}H_{19}N$: C, 83·6; H, 9·5; N, 7·0%), b. p. 98°/0·7 mm. Freund and Kessler (*loc. cit.*) and Meisenheimer, Stotz, and Bauer (*Ber.*, 1925, **58**, 2320) record b. p. 278—280° and 143—144°/12 mm. respectively.

As stated by Meisenheimer *et al.*, the dihydro-base (6 g.), after being heated under reflux for 10 hr. and subsequently distilled, gave a main fraction (2·9 g.), b. p. 274—280° (Found: N, 7·5. Calc. for $C_{13}H_{15}N$: N, 7·6%), as a pale yellow oil, and this combined with methyl iodide to form 2-*iso*butylquinoline methiodide, m. p. 184°. Refluxing with iodine in ethanol converted the dihydro-base into 2-*iso*butylquinoline methiodide. After purification from alcohol (charcoal) this formed bright yellow crystals, m. p. 184° (Found: I, 38·7. Calc. for $C_{14}H_{19}NI$: I, 38·8%), identical with the compound prepared from 2-*iso*butylquinoline.

(*g*) *sec.*-Butylmagnesium bromide afforded *2-*sec.*-butyl-1 : 2-dihydro-1-methylquinoline* (18 g.), b. p. 116°/1·5 mm., 120°/2 mm. (Found: C, 83·5; H, 9·7; N, 6·7. $C_{14}H_{19}N$ requires C, 83·6; H, 9·5; N, 7·0%). When refluxed for 11 hr. the dihydro-base (7 g.) decomposed and distillation then gave fractions, (i) a pale greenish oil, b. p. 274—280° (0·7 g.), (ii) a yellowish oil, b. p. 280—290° (3·7 g.), and (iii) an orange oil, b. p. 290—300° (9 g.). Redistillation of fraction (ii) gave a pale yellow oil (2·9 g.), b. p. 102—106°/1 mm. (Found: N, 7·3. Calc. for $C_{13}H_{15}N$: N, 7·6%), which formed a picrate, m. p. 163° (Bergstrom, *J. Amer. Chem. Soc.*, 1931, **53**, 4075, records 2-*sec.*-butylquinoline picrate, m. p. 163·5—164·5°). Heating 2-*sec.*-butylquinoline with methyl iodide afforded a dark red viscous mass which solidified after 5—6 days and then crystallised from ethanol (charcoal) as orange-yellow needles of the *methiodide*, m. p. 175° (Found: C, 51·1; H, 5·3; N, 4·2; I, 38·8. $C_{14}H_{18}NI$ requires C, 51·4; H, 5·5; N, 4·3; I, 38·8%).

When the dihydro-base was refluxed with iodine and ethanol 2-*sec.*-butylquinoline methiodide, m. p. 173°, was formed, unchanged by further crystallisations from ethanol (Found: I, 39·3. Calc. for $C_{14}H_{18}NI$: I, 38·8%). It was identical with the salt prepared from 2-*sec.*-butylquinoline.

(*h*) When *tert.*-butylmagnesium bromide was used and the product was distilled, the main fraction (24 g.) was a light yellow oil, b. p. 104°/1·5 mm. (Found: C, 83·6; H, 9·0; N, 6·9. $C_{14}H_{19}N$ requires C, 83·6; H, 9·5; N, 7·0%). Refluxed for 10 hr. *2-*tert.*-butyl-1 : 2-dihydro-1-methylquinoline* (10 g.) afforded a product from which a main fraction (5 g.) was obtained as a colourless oil, b. p. 230—240°. Redistillation gave 4·6 g., b. p. 80°/2·5 mm. The methiodide, m. p. 132° (Found: I, 46·0. Calc. for $C_{10}H_{10}NI$: I, 46·9%), did not depress the m. p. of quinoline methiodide. The picrate, yellow needles, m. p. 202° (from benzene) was identical with quinoline picrate.

The dihydro-base (4 g.) and picric acid (4·5 g.) were separately dissolved in the minimum volumes of ethanol, and the solutions were mixed. A viscous brown mass separated from the red solution. After collection and washing with cold acetone (6 × 25 c.c.) the yellow solid had m. p. 144°. Repeated crystallisation from water gave yellow slender needles of 1-*methylquinolinium picrate*, m. p. 166° (Found : N, 15·0. $C_{16}H_{12}O_7N_4$ requires N, 15·1%).

*Quinoline ethiodide.* (*a*) Methylmagnesium iodide gave 1-*ethyl*-1 : 2-*dihydro*-2-*methylquinoline* (26 g.), b. p. 88°/1 mm. (Found : C, 83·5; H, 8·5; N, 7·9. $C_{12}H_{15}N$ requires C, 83·2; H, 8·7; N, 8·1%). When heated under reflux for 10 hr. the dihydro-base (7 g.) gave as main fraction a greenish-yellow oil (4 g.), b. p. 240—250°. Redistillation afforded 3·4 g., b. p. 84—86°/1·7 mm. [methiodide, m. p. 193° (decomp.); quinaldine methiodide has m. p. 193°]. 1-Ethyl-1 : 2-dihydro-2-methylquinoline with iodine in ethanol gave quinaldine ethiodide, m. p. and mixed m. p. 239° (decomp.) (Found : I, 42·2. Calc. for $C_{12}H_{14}NI$ : I, 42·5%).

(*b*) Ethylmagnesium bromide gave 1 : 2-*diethyl*-1 : 2-*dihydroquinoline* (24 g.), b. p. 86°/0·7 mm. (Found : C, 83·4; H, 8·9; N, 7·8. $C_{13}H_{17}N$ requires C, 83·4; H, 9·1; N, 7·5%). Refluxing this for 12 hr. and fractionation gave 2-ethylquinoline (3·2 g.), b. p. 76—78°/0·5 mm. (methiodide, m. p. 168°). Dehydrogenation (30 min.) with iodine in ethanol gave 2-ethylquinoline ethiodide, m. p. and mixed m. p. 170° (Found : C, 50·2; H, 4·9; N, 4·7; I, 40·7. Calc. for $C_{13}H_{16}NI$ : C, 49·8; H, 5·1; N, 4·5; I, 40·6%).

(*c*) Propylmagnesium bromide gave 1-*ethyl*-1 : 2-*dihydro*-2-*propylquinoline* (22 g.), a golden-yellow oil, b. p. 112°/1 mm. (Found : C, 83·7; H, 9·6; N, 7·1. $C_{14}H_{19}N$ requires C, 83·6; H, 9·5; N, 7·0%). When refluxed for 8 hr. and then distilled twice, this gave 2-propylquinoline, b. p. 92°/1 mm. (methiodide, m. p. 185°). Refluxing for 30 min. with iodine in ethanol gave 2-*propylquinoline ethiodide*, m. p. 179—180° (Found : I, 39·0. $C_{14}H_{18}NI$ requires I, 38·8%).

(*d*) *iso*Propylmagnesium bromide similarly gave 1-*ethyl*-1 : 2-*dihydro*-2-iso*propylquinoline* (17 g.), b. p. 98°/0·6 mm. (Found : C, 83·3; H, 9·7; N, 7·0. $C_{14}H_{19}N$ requires C, 83·6; H, 9·5; N, 7·0%). Refluxed for 10 hr. and then distilled the dihydro-base gave 2-*iso*propylquinoline, b. p. 78°/0·5 mm. (methiodide, m. p. 190°, identical with the salt prepared from 1-methyl-1 : 2-dihydro-2-*iso*propylquinoline and alcoholic iodine, p. 2777).

(*e*) *tert.*-Butylmagnesium bromide gave tert.-*butyl*-1-*ethyl*-1 : 2-*dihydroquinoline* (26 g.), b. p. 106°/0·4 mm. (Found : C, 83·7; H, 9·6; N, 6·6. $C_{15}H_{21}N$ requires C, 83·7; H, 9·8; N, 6·5%). When 10 g. of this were refluxed for 12 hr. and the product was distilled an amber oil (4·8 g.), b. p. 232—240°, and an orange oil (1·2 g.), b. p. 240—248°, were obtained. Redistillation of the larger fraction gave quinoline (4 g.), b. p. 62°/1 mm. (picrate, m. p. 202°; methiodide, m. p. 132°; m. p.s not depressed by authentic samples). When the dihydroquinoline (8·6 g.) was refluxed for 15 min. with iodine (10 g.) in ethanol (25 c.c.) and the resulting solution was cooled a marked odour of *tert.*-butyl iodide was observed. Evaporation afforded a tar and when this was extracted with cold acetone (3 × 20 c.c.) yellow crystals remained. Purification from ethanol gave quinoline ethiodide, m. p. and mixed m. p. 156°.

*Quinoline propiodide.* (*a*) Methylmagnesium iodide gave 2-*methyl*-1 : 2-*dihydro*-1-*propylquinoline* (21 g.) as a pale greenish-yellow oil, b. p. 82°/0·4 mm. (Found : C, 83·3; H, 9·3; N, 7·2. $C_{13}H_{17}N$ requires C, 83·4; H, 9·1; N, 7·5%. When heated it gave quinaldine, and when 7·5 g. of the dihydro-base were refluxed for 15 min. with iodine (10 g.) in ethanol quinaldine propiodide resulted. This separated from ethanol as bright yellow crystals, m. p. and mixed m. p. 173° (Found : I, 40·9. Calc. for $C_{13}H_{16}NI$ : I, 40·6%).

(*b*) Ethylmagnesium bromide gave 2-*ethyl*-1 : 2-*dihydro*-1-*propylquinoline* (24 g.), b. p. 100°/0·6 mm. (Found : C, 83·3; H, 8·3; N, 7·1. $C_{14}H_{19}N$ requires C, 83·6; H, 9·5; N, 7·0%). It yielded 2-ethylquinoline when heated; with iodine in ethanol 2-*ethylquinoline propiodide* resulted, which crystallised from ethanol in orange-yellow needles, m. p. 208° (Found : I, 38·7. $C_{14}H_{18}NI$ requires I, 38·8%).

(*c*) Propylmagnesium bromide was used in two independent experiments and the products were separately isolated and analysed. In each case the main fraction, 1 : 2-*dihydro*-1 : 2-*dipropylquinoline*, was a yellow oil: (i) (23 g.) b. p. 102°/0·6 mm. (Found : C, 83·6; H, 9·8; N, 6·6%), (ii) (22 g.) b. p. 114°/1 mm. (Found : C, 83·8; H, 9·9; N, 6·4. $C_{15}H_{21}N$ requires C, 83·7; H, 9·8; N, 6·5%). Heating either preparation gave 2-propylquinoline. The dihydro-base with iodine in ethanol gave 2-*propylquinoline propiodide*, bright yellow crystals [from ethanol (charcoal)], m. p. 165—166° (Found : C, 52·8; H, 5·7; N, 4·3; I, 37·1. $C_{15}H_{20}NI$ requires C, 52·8; H, 5·9; N, 4·1; I, 37·2%).

(*d*) Two similar experiments were carried out also with *iso*propylmagnesium bromide. Each gave 1 : *2-dihydro-1-propyl-2-*iso*propylquinoline* (18 g., 20 g.), b. p. 108°/0·9 mm., 104°/0·7 mm. (Found : C, 83·5, 83·6; H, 9·8, 9·6; N, 6·6, 6·7. $C_{15}H_{21}N$ requires C, 83·7; H, 9·8; N, 6·5%).

Heating gave 2-*iso*propylquinoline, and oxidation with alcoholic iodine gave yellow 2-iso*propylquinoline propiodide*, m. p. 194° (from ethanol) (Found : I, 37·2. $C_{15}H_{20}NI$ requires I, 37·2%).

(*e*) Two experiments with butylmagnesium bromide gave *2-butyl-1 : 2-dihydro-1-propylquinoline* (23 g., 22 g.), b. p. 116°/0·7 mm., 136°/1·8 mm. (Found : C, 83·5, 83·7; H, 10·4, 9·8; N, 6·1, 6·4. $C_{16}H_{23}N$ requires C, 83·8; H, 10·0; N, 6·1%). Heating gave 2-butylquinoline. Treatment with iodine gave *2-butylquinoline propiodide*, m. p. 155—156° (from ethanol) (Found : C, 54·0; H, 6·1; N, 4·0; I, 35·4. $C_{16}H_{22}NI$ requires C, 54·1; H, 6·2; N, 3·9; I, 35·8%).

(*f*) In two similar experiments with *iso*butylmagnesium bromide 2-iso*butyl-1 : 2-dihydro-1-propylquinoline* was obtained. The main products were yellow oils (10 g., 9 g.), b. p. 104°/0·7 mm., and 100°/0·5 mm. (Found : C, 83·9, 83·9; H, 10·0, 10·1; N, 6·1, 6·1. $C_{16}H_{23}N$ requires C, 83·8; H, 10·0; N, 6·1%). When heated, each gave 2-*iso*butylquinoline, and dehydrogenation with iodine gave 2-iso*butylquinoline propiodide*, m. p. 193° (Found : C, 54·1; H, 6·0; N, 3·7; I, 35·8. $C_{16}H_{22}NI$ requires C, 54·1; H, 6·2; N, 3·9; I, 35·8%).

(*g*) Two experiments with *sec.*-butylmagnesium bromide gave 2-sec.*-butyl-1 : 2-dihydro-1-propylquinoline* (20 g., 20 g.), b. p. 128°/1·5 mm. (Found : C, 84·0, 83·9; H, 10·5, 10·4; N, 6·1, 6·1. $C_{16}H_{23}N$ requires C, 83·8; H, 10·0; N, 6·1%). It gave 2-*sec.*-butylquinoline when heated. Alcoholic iodine afforded a red tar.

(*h*) Two experiments with *tert.*-butylmagnesium bromide gave a tert.*-butyldihydro-1-propylquinoline* (28 g., 27 g.), as a yellow oil, b. p. 100°/0·5 mm. (Found : C, 84·1, 84·0; H, 10·0, 10·1; N, 5·8, 6·1. $C_{16}H_{23}N$ requires C, 83·8; H, 10·0; N, 6·1%). Heated under reflux for 12 hr., dihydro-base (11 g.) gave after redistillation quinoline (4·1 g.), b. p. 72°/2 mm. (picrate, m. p. 202°; methiodide, m. p. 132°; not depressed on admixture with authentic samples). When 9·2 g. of the dihydro-base were refluxed for 15 min. with iodine (10 g.) in ethanol (25 c.c.) the product did not crystallise on cooling, but on addition to ether (75 c.c.) a red tar was precipitated. The solvents were decanted, the residue was kept for 3 weeks and then extracted with cold acetone (3 × 20 c.c.). The solid residue, purified from alcohol, afforded orange-yellow crystals, m. p. 143° (Found : I, 42·8. Calc. for $C_{12}H_{14}NI$ : I, 42·5%), of quinoline propiodide.

*Quinoline* iso*propiodide*. (*a*) Methylmagnesium iodide gave 1 : *2-dihydro-2-methyl-*1-iso*propylquinoline*, a pale greenish-yellow oil (20 g.), b. p. 76°/0·5 mm. (Found : C, 83·7; H, 9·3; N, 7·6. $C_{13}H_{17}N$ requires C, 83·4; H, 9·1; N, 7·5%), and this on heating gave quinaldine. With iodine it gave yellow crystals, m. p. 186°, which on recrystallisation had m. p. 224° (decomp.) (Found: N, 4·7; I, 41·0. Calc. for $C_{13}H_{16}NI$: N, 4·5; I, 40·6%). According to Hamer *et al.* quinaldine *iso*propiodide has m. p. 163·5° (decomp.). The same salt, m. p. 224° (decomp.), was obtained from the dialkylcadmium reaction.

(*b*) Ethylmagnesium bromide gave *2-ethyl-1 : 2-dihydro-*1-iso*propylquinoline* (20 g.), b. p. 90°/0·6 mm. (Found : C, 83·3; H, 9·5; N, 7·2. $C_{14}H_{19}N$ requires C, 83·6; H, 9·5; N, 7·0%). Heating it gave 2-ethylquinoline. With iodine it gave *2-ethylquinoline* iso*propiodide*, m. p. 195° (Found : I, 38·9. $C_{14}H_{18}NI$ requires I, 38·8%).

(*c*) Propylmagnesium bromide gave 1 : *2-dihydro-2-propyl-*1-iso*propylquinoline* (18 g.), b. p. 106°/1 mm. (Found : C, 83·7; H, 10·1; N, 6·5. $C_{15}H_{21}N$ requires C, 83·7; H, 9·8; N, 6·5%), which afforded 2-propylquinoline on long heating. Refluxing with iodine in ethanol and then cooling gave a red oil, which partly solidified during 6 weeks; digestion with cold acetone (3 × 20 c.c.) gave a solid, which crystallised from ethanol in orange plates of *2-propylquinoline* iso*propiodide*, m. p. 174° (Found : N, 3·9. $C_{15}H_{20}NI$ requires N, 4·1%).

(*d*) Similarly, *iso*propylmagnesium bromide gave 1 : *2-dihydro-1 : 2-di*iso*propylquinoline* (20 g.), b. p. 106°/1·3 mm., 112°/1·5 mm. (Found : C, 83·8; H, 9·9; N, 6·7. $C_{15}H_{21}N$ requires C, 83·7; H, 9·8; N, 6·5%), which gave 2-*iso*propylquinoline on long heating and a tar on oxidation with alcoholic iodine.

(*e*) Butylmagnesium bromide gave *2-butyl-1 : 2-dihydro-*1-iso*propylquinoline* (20 g.), b. p. 106°/0·4 mm. (Found : C, 83·8; H, 10·1; N, 6·0. $C_{16}H_{23}N$ requires C, 83·8; H, 10·0; N, 6·1%). On long heating the dihydro-base gave 2-butylquinoline.

(*f*) *iso*Butylmagnesium bromide gave 2-iso*butyl-1 : 2-dihydro-*1-iso*propylquinoline* (8 g.), b. p. 108°/0·7 mm. (Found : C, 84·1; H, 9·9; N, 6·1%), which on long heating gave 2-*iso*butylquinoline.

(*g*) *sec.*-Butylmagnesium bromide gave 2-sec.*-butyl-1 : 2-dihydro-*1-iso*propylquinoline* (20 g.), b. p. 104°/0·4 mm. (Found : C, 83·6; H, 10·2; N, 6·4%). 2-*sec.*-Butylquinoline was formed when the dihydro-base was refluxed.

(*h*) *tert.*-Butylmagnesium bromide gave a tert.-*butyldihydro*-1-iso*propylquinoline* (24 g.), b. p. 130°/2·6 mm. (Found: C, 83·5, 83·6; H, 9·8; 10·0; N, 6·2, 6·1%). Refluxing 11 g. of the dihydro-base for 12 hours and distillation of the product gave fractions, (i) b. p. 236—240° (5 g.) and (ii) 248—260° (0·6 g.). Fraction (i) redistilled as a colourless oil, b. p. 78—80°/2·5 mm., which was identified as quinoline by conversion into the picrate and methiodide. Treatment with iodine gave an odour of *tert.*-butyl iodide and a tar which, when stirred with acetone and then crystallised therefrom (charcoal) to constant m. p., formed pale yellow needles, m. p. 98°, not depressed by quinoline *iso*propiodide.

No nuclear substitution was observed in experiments with Grignard reagents and quinoline hydriodide.

*Experiments with Quaternary Salts derived from* iso*Quinoline.*—These were carried out under the conditions used for the quinoline derivatives. The following substituted 1 : 2-dihydro-*iso*quinolines were obtained: 1 : 2-dimethyl- (24 g.), b. p. 64°/0·3 mm., 76°/1·5 mm. (Found: C, 83·1; H, 8·2; N, 8·8. Calc. for $C_{11}H_{13}N$: C, 83·0; H, 8·2; N, 8·8%) (Freund and Bode, *loc. cit.*, record b. p. 150°/20 mm.); 1-ethyl-2-methyl- (20 g.), b. p. 72°/0·6 mm. (Found: C, 83·6; H, 8·8; N, 7·8. Calc. for $C_{12}H_{15}N$: C, 83·2; H, 8·7; N, 8·1%) (Freund and Bode, *loc. cit.*, record b. p. 165°/45 mm.); 2-*methyl*-1-*propylquinoline* (19 g.), b. p. 84°/0·5 mm. (Found: C, 82·9; H, 9·2; N, 7·4. $C_{13}H_{17}N$ requires C, 83·4; H, 9·1; N, 7·5%); 2-*ethyl*-1-*methyl*- (19 g.), b. p. 74°/0·7 mm. (Found: C, 82·2; H, 9·0; N, 7·7%); 1 : 2-diethyl- (20 g.), b. p. 84°/0·5 mm. (Found: C, 82·8; H, 9·3; N, 7·4. Calc. for $C_{13}H_{17}N$: C, 83·4; H, 9·1; N, 7·5%) (Wedekind and Bandau, *Annalen*, 1913, **401**, 437, record b. p. 145—150°/15 mm.); 2-*ethyl*-1-*propyl*- (20 g.), b. p. 84°/0·3 mm. (Found: C, 83·4; H, 9·5; N, 6·8. $C_{14}H_{19}N$ requires C, 83·6; H, 9·5; N, 7·0%); 1-*methyl*-2-*propyl*- (21 g.), b. p. 100°/2 mm. (Found: C, 83·2; H, 9·3; N, 7·7%); 1-*ethyl*-2-*propyl*- (20 g.), b. p. 96°/0·5 mm. (Found: C, 83·6; H, 9·7; N, 6·8%); 1-*methyl*-2-iso*propyl*- (20 g.), b. p. 80°/0·5 mm. (Found: C, 83·6; H, 8·9; N, 7·7%); 1-*ethyl*-2-iso*propyl*- (18 g.), b. p. 86—88°/0·6 mm. (Found: C, 83·4; H, 9·5; N, 6·8%).

*Experiments with Cadmium Dialkyls.*—The cadmium dialkyls were prepared by Gilman and Nelson's method (*Rec. Trav. chim.*, 1936, **55**, 518) and shown to be free from the alkylmagnesium halides from which they were derived. Quinoline methiodide or a similar salt (0·1 mole) was stirred for 4 hr. at the room temperature with an ether solution of the dialkylcadmium (0·2 mole). Water was then added, the precipitate of cadmium hydroxide was removed and washed with ether, and the ether solutions were combined, dried with solid potassium hydroxide, filtered, and evaporated, and the residual red oil was distilled. In all the examples studied distillation occurred at a constant temperature, leaving no residue. The distillates gave 1 : 2-dialkylquinolinium iodides when oxidised with alcoholic iodine. The dihydroquinolines obtained by the dialkylcadmium reaction were identical with those prepared by the use of Grignard reagents. The following notes record briefly the evidence of identity of the products obtained by the Grignard and dialkylcadmium reactions. Reference letters are those in Table 3.

*Quinoline series.* (*a*) 1 : 2-Dihydro-1 : 2-dimethylquinoline, b. p. 62°/0·4 mm., 74°/0·8 mm. (Found: C, 83·1; H, 8·5; N, 9·0%), was oxidised by iodine to quinaldine methiodide, m. p. 193°. (*b*) 2-Ethyl-1 : 2-dihydro-1-methylquinoline, b. p. 76°/0·5 mm. (Found: C, 83·2; H, 8·8; N, 7·7%), was oxidised to 2-ethylquinoline methiodide, m. p. 168°. (*c*) 1 : 2-Dihydro-1-methyl-2-propylquinoline, b. p. 96°/0·7 mm. (Found: C, 83·7; H, 9·0; N, 7·9%), was oxidised to 2-propylquinoline methiodide, m. p. 185°. (*d*) 1 : 2-Dihydro-1-methyl-2-*iso*propylquinoline, b. p. 90°/0·7 mm. (Found: C, 83·8; H, 8·7; N, 7·3%), was oxidised to 2-*iso*propylquinoline methiodide, m. p. 190°. (*e*) 1-Ethyl-1 : 2-dihydro-2-methylquinoline, b. p. 88°/1 mm. (Found: C, 83·1; H, 8·4; N, 7·9%), gave on oxidation, quinaldine ethiodide, m. p. 239° (decomp.). (*f*) 1 : 2-Diethyl-1 : 2-dihydroquinoline, b. p. 86°/0·7 mm. (Found: C, 83·1; H, 9·5; N, 7·2%), gave 2-ethylquinoline ethiodide, m. p. 170°, on oxidation. (*g*) 1-Ethyl-1 : 2-dihydro-2-propylquinoline, b. p. 104°/0·7 mm. (Found: C, 83·3; H, 9·7; N, 6·8%), gave 2-propylquinoline ethiodide, m. p. 179—180°, on oxidation. (*h*) 1-Ethyl-1 : 2-dihydro-2-*iso*propylquinoline, b. p. 98°/0·6 mm. (Found: C, 83·5; H, 9·5; N, 7·3%), on oxidation with alcoholic iodine gave a tar from which no solid derivative could be prepared. (*i*) 1 : 2-Dihydro-2-methyl-1-propylquinoline, b. p. 84°/0·5 mm. (Found: C, 83·5; H, 9·1; N, 8·0%), gave on oxidation quinaldine propiodide, m. p. 173°. (*k*) 2-Ethyl-1 : 2-dihydro-1-propylquinoline, b. p. 100°/0·6 mm. (Found: C, 83·8; H, 9·6; N, 6·7%), gave 2-ethylquinoline propiodide, m. p. 208°. (*l*) 1 : 2-Dihydro-1 : 2-dipropylquinoline had b. p. 106°/0·7 mm. (Found: C, 83·7; H, 9·9; N, 6·4%). (*m*) 1 : 2-Dihydro-1-propyl-2-*iso*propylquinoline had b. p. 104°/0·7 mm., 100°/0·5 mm. (Found: C, 84·0; H, 9·6; N, 6·5%). (*n*) 1 : 2-Dihydro-2-methyl-1-*iso*propylquinoline, b. p. 76°/0·5 mm. (Found: C, 83·4; H, 9·0; N, 7·8%), on oxidation gave quinaldine *iso*propiodide, m. p. 224° (decomp.). (*o*) 2-Ethyl-1 : 2-dihydro-1-*iso*propylquinoline, b. p. 90°/0·6 mm. (Found: C, 83·7; H, 9·6; N, 7·1%), gave 2-ethylquinoline *iso*propiodide, m. p. 195°. (*p*) 1 : 2-Dihydro-2-propyl-1-*iso*propylquinoline had b. p. 106°/1 mm. (Found: C, 83·5; H, 9·8; N, 6·4%). (*q*) 1 : 2-Dihydro-1 : 2-di*iso*propylquinoline had b. p. 112°/1·5 mm. (Found: C, 83·8; H, 9·4; N, 6·9%).

iso*Quinoline series.* (*a*) 1 : 2-Dihydro-1 : 2-dimethyl*iso*quinoline had b. p. 68°/1 mm. (Found: C, 83·1; H, 8·1; N, 8·7%). (*b*) 1-Ethyl-1 : 2-dihydro-2-methyl*iso*quinoline had b. p. 76°/0·7 mm. (Found: C, 83·3; H, 8·8; N, 8·2%). (*c*) 1 : 2-Dihydro-2-methyl-1-propyl*iso*quinoline had b. p. 78°/0·4 mm. (Found: C, 83·0; H, 9·4; N, 7·5%). (*d*) 1 : 2-Dihydro-2-methyl-1-*iso*propyl*iso*quinoline had b. p. 86°/0·5 mm. (Found: C, 83·4; H, 9·1; N, 7·6%). (*e*) 2-Ethyl-1 : 2-dihydro-1-methyl*iso*quinoline had b. p. 74°/1 mm. (Found: C, 82·9; H, 8·9; N, 7·9%). (*f*) 1 : 2-Diethyl-1 : 2-dihydro*iso*quinoline had b. p. 84°/0·5 mm. (Found: C, 83·2; H, 9·4; N, 7·4%). (*g*) 2-Ethyl-1 : 2-dihydro-1-propyl*iso*quinoline had b. p. 89°/0·5 mm. (Found: C, 83·6; H, 9·5; N, 6·7%). (*h*) 2-Ethyl-1 : 2-dihydro-1-*iso*propyl*iso*quinoline had b. p. 76°/0·2 mm. (Found: C, 83·3; H, 9·4; N, 7·2%). (*i*) 1 : 2-Dihydro-1-methyl-2-propyl*iso*quinoline had b. p. 104°/2·5 mm. (Found: C, 83·2; H, 9·2; N, 7·4%). (*j*) 1-Ethyl-1 : 2-dihydro-2-propyl*iso*quinoline had b. p. 96°/0·5 mm. (Found: C, 83·6; H, 9·2; N, 7·0%). (*k*) 1 : 2-Dihydro-1-methyl-2-*iso*propyl*iso*quinoline had b. p. 92°/1 mm. (Found: C, 83·6; H, 9·4; N, 7·4%). (*l*) 1-Ethyl-1 : 2-dihydro-2-*iso*propyl*iso*quinoline had b. p. 88°/0·6 mm. (Found: C, 83·6; H, 9·1; N, 7·2%). In other experiments no nuclear substitution was observed when the reagent was sodiofluorene, piperidine, morpholine, or toluene-*p*-sulphinic acid.

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