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Electrochemical Reductive Alkylation of Quinolines and Isoquinolines

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The reaction between electrochemically generated anion radicals of quinolines and isoquinolines and *t*-butyl halides gives, *via* an electron transfer reaction and formation of *t*-butyl radicals, *t*-butylated heterocyclic compounds. A large fraction of the alkylation takes place in the carbocyclic ring. The mechanism is discussed in light of the product distribution.

Electrochemical generation of anion radicals in an aprotic medium, such as *N*,*N*-dimethylformamide (DMF), in the presence of an alkyl halide may result in a reductive alkylation of the parent compound.[1–3] The coupling has been proposed to occur between an alkyl radical, formed by cleavage during electron transfer from the anion radical to the alkyl halide, and the parent compound or its anion radical.

In liquid ammonia quinoline [4] has been reductively alkylated cathodically with the formation of approximately equal amounts of 1,2- and 1,4-dialkyldihydroquinoline. The reaction was found to proceed *via* an ECEC-mechanism.

The study of the *t*-butylation of quinoline and isoquinoline derivatives is part of a more general investigation of the preparative aspects of the electrochemical alkylation reaction. A knowledge of the substitution pattern may also be of interest for a discussion of the mechanism of the coupling reaction.

In the investigation are included isoquinoline (*1*), 3-methylisoquinoline (*2*), quinoline (*3*), and 2-methylquinoline (*4*).

RESULTS

Voltammetry. The compounds *1* to *4* were investigated by cyclic voltammetry in DMF/0.1 M TBAI (tetrabutylammonium iodide) with suspended alumina using sweep-rates from 10 to 400 mV/s. All of the compounds gave one reversible wave, even at low sweep rate; the shape of the anodic peak was, however, often distorted at potentials less negative than the anodic peak potential due to adsorption phenomena.

On addition of *t*-butyl chloride to *1* the height of the first wave (at −2.18 V *vs.* aq. SCE) increased somewhat and reached a limit with about 50 % increase; at the same time a new wave at −2.55 V (Fig. 1) grew up to a

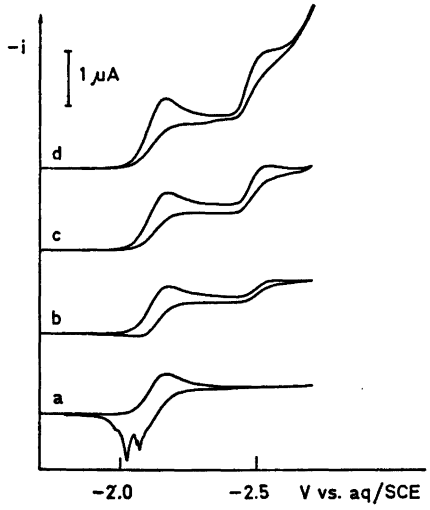


Fig. 1. Cyclic voltammograms of isoquinoline (2.5×10^{-3} M) in DMF/0.1 M TBAI in the presence of *t*-butyl chloride: a, 0; b, 3.2×10^{-3} M; c, 1.3×10^{-2} M; d, 6.5×10^{-2} M. Sweep rate 40 mV/s.

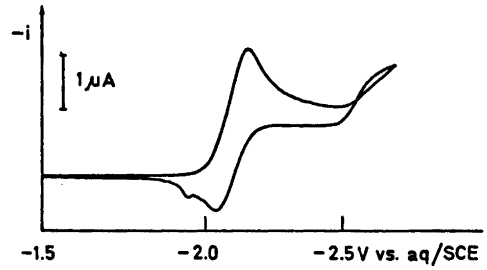


Fig. 2. Cyclic voltammogram of quinoline (2.5×10^{-3} M) in the presence of *t*-butyl chloride (1.3×10^{-2} M). Sweep rate 400 mV/s.

height slightly less than the first one; voltammetry of 6-*t*-butyl-5,6-dihydroisoquinoline showed a peak at −2.55 V. *2*, *3*, and *4* exhibited quite similar behaviour on addition of *t*-butyl chloride.

All the compounds show, at a certain speed rate and in a certain concentration interval of *t*-butyl chloride, a special behaviour illustrated in Fig. 2. At a suitable concentration of *t*-butyl chloride the reverse sweep crosses the forward sweep; a similar phenomenon has been found in cases [5] involving a slow rate-limiting step in the mechanism and has been proposed [6] to be connected with the coupling reaction, in which is formed the electroactive product causing the second wave.

A voltammetric experiment was performed in which naphthalene was added to a solution containing *1* and *t*-butyl chloride in a molar ratio of 1:8. The addition of naphthalene had only a small effect which, if anything, leads to a decrease of the peak height of *1*.

Table 1. Product distribution (isolated yield) in the electrochemical *t*-butylation in DMF containing tetrabutylammonium iodide (TBAI) of *1* (isoquinoline) and *2* (3-methylisoquinoline).

Position of *t*-Bu group	From *1*		From *2*	
	Product	Yield %	Product	Yield %
1	*8*	17	*12*	17
4			*13*	9
5	*7*	19	*10*	3
6	*5*	35	*9*	40
	6	5		
8			*11*	5

Table 2. Product distribution (isolated yield) in the electrochemical *t*-butylation in DMF/TBAI of *3* (quinoline) and *4* (2-methylquinoline).

Position of *t*-Bu group	From *3*		From *4*	
	Product	Yield %	Product	Yield %
2	*14*	16.5		
3/4			*20*	10.5
4	*15*	9.5	*21*	15.5
5	*16*	6	*22*	12
7	*17*	16	*23*	14.5
8			*24*	3.5
Not butylated	*18*	11		
	19	10		

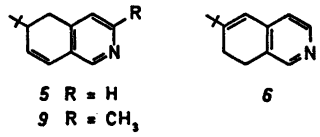
Electrolyses. In Table 1 are given the isolated yields of the products obtained on electrochemical *t*-butylation in DMF of isoquinoline (*1*) and 3-methylisoquinoline (*2*); in Table 2 are given similar data from the reductive alkylation of quinoline (*3*) and 2-methylquinoline (*4*). In Experimental are summarized the main arguments for the proposed structures of the products.

In a competitive alkylation experiment a mixture of 1 g of isoquinoline and 5 g of naphthalene was reduced at −2.2 V (SCE) in the presence of 10 ml of *t*-butyl chloride; extraction of naphthalene and its derivatives from the acidified diluted aqueous DMF with light petroleum separated the neutral fraction from the nitrogen bases. No *t*-butylated naphthalene derivatives were detected by ^{1}H NMR spectroscopy or MS of the neutral fraction.

DISCUSSION

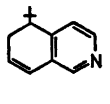
Polarography and cyclic voltammetry of *3* in acetonitrile [7] and liquid ammonia [4] and of *1*, *3*,[8] *2*, and *4*[9] in DMF have been reported. The first reduction leads to the anion radical; $1^{\cdot-}$ in DMF is more stable than $3^{\cdot-}$,[8] which dimerizes faster.

This is in agreement with the preparative results; dimerized products have been isolated (*19*) from the reductive alkylation of *3*, but not from *1*. The dimerization of $3^{\cdot-}$ is, however, not the only reason for its relative instability; on removal of most of proton donor impurities by addition of active alumina a



5 R = H
9 R = CH_3

6



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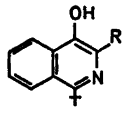
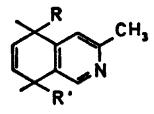
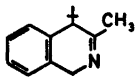


8 R = H
12 R = CH_3



10 R = t-Bu
R' = H
11 R = H
R' = t-Bu



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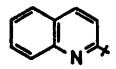

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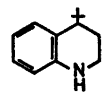

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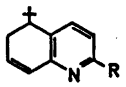
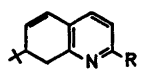
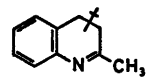


16 R = H
22 R = CH_3



17 R = H
23 R = CH_3



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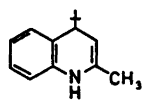

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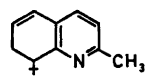

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18 1,2,3,4-Tetrahydroquinoline. 19 Dimer of 18.

reversible wave of *3* is found even at slow sweep rates.

In liquid ammonia the alkylation of quinoline anion radical [4] by primary alkyl bromides has been found to follow an ECEC-mechanism, whereas the reductive alkylation in DMF of aromatic and unsaturated compounds has been discussed in terms of coupling between an alkyl radical and an anion radical and/or the substrate.[1–3]

The two most probable reaction routes may be represented by eqns. (1) to (6), in which A is the heteroaromatic compound and BX is *t*-butyl chloride.

$$A + e^- \rightleftharpoons A^{\cdot -} \quad (1)$$

$$A^{\cdot -} + BX \rightleftharpoons A + [BX]^{\cdot -} \quad (2)$$

$$BX^{\cdot -} \rightarrow B^{\cdot} + X^- \quad (3)$$

$$B^{\cdot} + A^{\cdot -} \rightleftharpoons A + B^- \quad (4)$$

$$B^{\cdot} + A^{\cdot -} \rightarrow AB^- \quad (5)$$

$$B^{\cdot} + A \rightarrow AB^{\cdot} \quad (6)$$

The product distribution in reactions involving radical attack on quinoline and isoquinoline depends on several parameters.[10] In acid solution the protonated hetero ring is pref-

erentially attacked by *t*-butyl and other alkyl radicals,[11] quinoline in the 2 and 4 positions, isoquinoline in position 1. Homolytic methylation of quinoline in excess of quinoline with *t*-butylperoxide or lead tetraacetate showed the following[12] order of positional reactivities $8 > 4 > 5 > 2$ and this agrees with the reactivities in the phenylation of quinoline.[13] Isoquinoline was methylated in low yield under these conditions and only 1-methylated products were isolated.[12]

A slightly different positional reactivity was found in the radical methylation of quinoline using Fenton's reagent in DMSO,[14] here the relative yields in positions 2:4:unknown were 3:2:4. In none of these investigations are the observed positional reactivities in agreement with those predicted by free valence numbers [15] or atom localization energies.[16]

A somewhat better agreement between experiment and theory was found [17] in the phenylation of *3* by benzoyl peroxide in excess of *3*. The positional reactivities were found to be $8 > 5 > 4 > 2 > 3 > 6 \geq 7$, which is qualitatively in agreement with that predicted [17] by the ω^*-method, $8 \geq 5 > 4 > 2 > 3 > 6 \geq 7$.

A comparison of the results described above of radical attack on *1* and *3* with those in Tables 1 and 2 does not give support to the assumption that a radical attack on the heterocyclic compound takes place.

Product distribution in a reaction between alkyl radicals and anion radicals of quinoline or isoquinoline is not known; in the reductive *t*-butylation of pyrene [2] the positional reactivity followed the pattern of the hyperfine coupling constants in the ESR spectrum of pyrene anion radicals, but a comparison of the results in Tables 1 and 2 with the ESR spectra [18,19] of quinoline and isoquinoline anion radical in HMPA reveals no apparent connection.

A competition for methyl radicals showed [12] that isoquinoline is 1.5 times as effective as naphthalene in the methylation reaction. The electrochemical *t*-butylation favours isoquinoline with a much higher factor, > 100. At least two explanations are possible. The *t*-butyl radical could be so much more stable than the methyl radical that a much higher selectivity is obtained. This explanation must be confronted with the fact that the relatively unreactive (compared to methyl radicals) phenyl radicals attack *1* or *3* preferentially to the more easily reducible nitrobenzene, but not by a high selectivity factor.[20] Another explanation is that the coupling reaction occurs between the *t*-butyl radical and an anion radical. The difference in reduction potential between isoquinoline and naphthalene (*25*) is about 0.35 V which is enough to ensure that at the reduction potential of *1* the concentration of $25^{\cdot-}$ is very low; the equilibrium constant for the reaction: $1^{\cdot-} + 25 \rightleftharpoons 1 + 25^{\cdot-}$ is about 10^{-3}.

This is in agreement with the voltammetric competition experiment. If the *t*-butyl radicals attacked *25* a smaller part of *1* would have been attacked and thus removed from the catalytic circle. The fact that no increase in the peak height of *1* is observed on addition of *25* is consistent with the results of the preparative competition experiment.

Although not conclusive, the results from this investigation thus mostly favour the mechanism by which the coupling occurs between the alkyl radical and the aromatic anion radical.

Preparatively, the value of the method is that it opens possibilities for a preparation in a simple way of a number of compounds not easily accessible in other ways.

EXPERIMENTAL

General procedure for electrolysis. The substrate (*1*–*4*, 2 g) was reduced at −2.2 V (aq. SCE) in 160 ml of DMF/0.1 M TBAI at a mercury pool electrode in the presence of 10 ml *t*-butyl chloride. After completion of the reduction the catholyte was acidified to pH 2–3 with 4 N aqueous HCl and the major part of the solvent evaporated *in vacuo*. The residue was made alkaline with an aqueous sodium carbonate solution and extracted several times with ether, which after washing with water and drying over potassium carbonate was evaporated. The residue was separated by column chromatography.

Isoquinoline, $n = 2.5$. Isolated was 2.25 g crude product. The residue was separated on silica using diethyl ether as eluent. The compounds were eluted in the order: *8*, *7*, *5*, *6*.

6-t-Butyl-5,6-dihydroisoquinoline, *5*, liquid. ^{1}H NMR ($CDCl_3$): δ 0.92 (9 H, s); 2.0–2.9 (3 H, m); 6.12 (1 H, dd, 10 Hz, 3 Hz); 6.57 (1 H, dd, 10 Hz, 2 Hz); 7.04 [1 H, d(br) 5 Hz]; 8.2–8.5 (2 H, m). UV (96 % ethanol): λ_{max} 261 nm, log ε 4.02, $\lambda_{shoulder}$ 288 nm, log ε 3.63. The choice between a 5,6- or 7,8-dihydroisoquinoline was made from the UV spectrum; during this investigation it has been observed

that 5,6-dihydroisoquinolines and 7,8-dihydroquinolines have $\lambda_{max} = 265 \pm 4$ nm, 5,6-dihydroquinolines at about 295 nm and 7,8-dihydroisoquinolines about 275 nm.

6-t-Butyl-7,8-dihydroisoquinoline, *6*, liquid. ^{1}H NMR ($CDCl_3$): δ 1.12 (9 H, s); 2.0–2.9 (4 H, m); 6.27 [1 H, s(br)]; 6.92 [1 H, d(br) 5 Hz]; 8.22 [1 H, s(br)]; 8.32 [1 H, d(br), 5 Hz]. UV (96 % ethanol): λ_{max} 273 nm, log ε 4.34; λ_{sh} 295 nm, log ε 3.60.

5-t-Butyl-5,6-dihydroisoquinoline, *7*, liquid. ^{1}H NMR ($CDCl_3$): δ 0.84 (9 H, s); 2.4–3.3 (3 H, m); 5.9–6.5 (2 H, m); 6.8–7.1 (1 H, m); 8.2–8.5 (2 H, m). UV (96 % ethanol): λ_{max} 263 nm, log ε 3.94; λ_{sh} 295 nm, log ε 3.30.

1-t-Butyl-4-hydroxyisoquinoline, *8*, m.p. > 300 °C (from chloroform/light petroleum). ^{1}H NMR [$(CD_3)_2CO$]: δ 1.62 (9 H, s); 7.4–7.8 (2 H, m); 8.08 (1 H, s); 8.25–8.65 (2 H, m). IR (KBr), cm^{-1} (intensity): 3300–2300 (s), 1625 (w), 1590 (s), 1335 (s), 1235 (m), 1075 (m), 990 (m), 872 (m), 770 (s). MS [*m/e* (%)]: 201 (12), 200 (17), 186 (28), 159 (63), 145 (13), 111 (13), 97 (28), 95 (22), 83 (39), 81 (30), 69 (70), 57 (74), 55 (74), 43 (100), 41 (91).

8 is probably formed from the initially obtained product, 1-*t*-butyl-1,4-dihydroisoquinoline; this compound reacts as an enamine with oxygen to a hydroperoxide which under influence of base forms *8*.

3-Methylisoquinoline, $n = 2.1$, 2.2 g of product. The residue was separated on silica using diethyl ether as eluent. The compounds were eluted in the order: *12*, *11*, *9*, *10*, *13*.

6-t-Butyl-5,6-dihydro-3-methylisoquinoline, *9*, liquid. ^{1}H NMR ($CDCl_3$): δ 0.92 (9 H, s); 2.48 (3 H, s); 2.0–2.9 (3 H, m); 6.03 (1 H, dd, 10 Hz, 3 Hz); 6.53 (1 H, dd, 10 Hz, 2 Hz); 6.90 [1 H, s(br)]; 8.13 [1 H, s(br)]. UV (96 % ethanol): λ_{max} 262 nm, log ε 3.95; λ_{sh} 290 nm, log ε 3.48. The choice between a 5,6-dihydro- and a 7,8-dihydroisoquinoline came from the ^{13}C NMR spectrum; the signals from the quaternary carbon atoms (C-4a and C-8a) were identified through selective decoupling of H-4, respectively H-1. Long-range couplings from the methylene protons (H-5) and ethylenic proton (H-8) to the quaternary carbon atoms proved the structure.

5 (or 8)-t-Butyl-5,8-dihydro-3-methylisoquinoline, *10*, liquid. ^{1}H NMR ($CDCl_3$): δ 0.87 (9 H, s); 2.50 (3 H, s); 2.4–2.7 (1 H, m); 3.0–3.3 (2 H, m); 6.05–6.15 (2 H, m); 6.92 [1 H, s(br)]; 8.31 [1 H, s(br)].

8 (or 5)-t-Butyl-5,8-dihydro-3-methylisoquinoline, *11*, liquid. ^{1}H NMR ($CDCl_3$): δ 0.88 (9 H, s); 2.51 (3 H, s); 2.4–2.6 (1 H, m); 3.0–3.3 (2 H, m); 6.0–6.2 (2 H, m); 6.93 [1 H, s(br)]; 8.30 [1 H, s(br)]. UV (96 % ethanol): λ_{max} 265 nm, log ε 3.0. MS [*m/e* (%)]: 201 (1), 145 (47), 144 (100), 143 (17), 115 (17), 57 (23), 41 (20).

10 and *11* move differently on TLC, but their spectra are very similar and there is no evidence available to decide whether it is *10* or *11* that is substituted at C-5.

1-t-Butyl-4-hydroxy-3-methylisoquinoline, *12*, ^{1}H NMR ($CDCl_3$): δ 1.57 (9 H, s); 2.53 (3 H, s); 7.0 [1 H, s(br)]; 7.3–7.5 (2 H, m); 8.1–8.4 (2 H, m). IR (KBr) cm^{-1} (intensity): 3600–2200 (s), 1647 (s), 1620 (s), 1495 (m), 1375 (m), 1355 (m), 1295 (m), 1240 (m), 940 (m), 782 (s). UV (96 % ethanol): λ_{max} 332 nm, log ε 3.48; λ_{max} 285 nm, log ε 3.40. Hydrochloride, m.p. 193–195 °C, contained one mol of water of crystallization according to the elementary analysis. MS [*m/e* (%)]: 215 (19), 214 (23), 200 (39), 173 (100), 159 (20), 130 (20), 115 (23), 77 (26), 69 (19), 57 (33), 55 (37), 43 (53), 41 (53).

12 is probably formed in a similar manner from 1-*t*-butyl-1,4-dihydro-3-methylisoquinoline as *8* from its precursor. *12* is not stable in solution and is in nonpolar solution easily transformed under influence of diffuse daylight by uptake of 1 mol oxygen to the 1-hydroperoxide (*26*), which is stable in the crystalline state. ^{1}H NMR of *26* ($CDCl_3$): δ 0.86 (9 H, s); 2.36 (3 H, s); 7.3–8.2 (4 H, m); 12.2 (1 H, br.s). IR (KBr) cm^{-1} (intensity): 3200–2800 (s), 1680 (s), 1645 (m), 1600 (m), 1455 (m), 1255 (m), 1205 (m), 1187 (m), 1050 (m), 932 (m), 748 (s).

4-t-Butyl-1,4-dihydro-3-methylisoquinoline, *13*, liquid. ^{1}H NMR ($CDCl_3$): δ 0.94 (9 H); 2.2–2.3 (3 H, m); 3.30 (1 H, t, 1.5 Hz); 4.6–4.8 (2 H, m); 7.1–7.3 (4 H, m). MS [*m/e* (%)]: 201 (2), 186 (3), 145 (76), 144 (100), 143 (25), 115 (21), 77 (11), 57 (52), 41 (32).

Quinoline, $n = 2.0$. The residue was separated on silica using diethyl ether as eluent and eluted in the order (*14*+*15*), *18*, *19*, *17*, *16*. *14* and *15* were separated on a column of silica using a mixture of 20 % ether and light petrol.

2-t-Butylquinoline, *14*, liquid. ^{1}H NMR ($CDCl_3$): δ 1.45 (9 H, s), 7.3–8.25 (6 H, m); identical with the published spectrum.[21] Probably obtained from the dihydro compound by oxidation during work-up.

4-t-Butyl-1,2,3,4-tetrahydroquinoline, *15*, liquid. ^{1}H NMR ($CDCl_3$): δ 0.93 (9 H, s); 1.4–2.3 (2 H, m); 2.4–2.6 (1 H, dd, 5 Hz, 2.5 Hz); 3.20–3.45 (2 H, m); 3.65 [1 H, s(br)]; 6.30–6.70 (2 H, m); 6.85–7.15 (2 H, m). The tetrahydroderivative is probably obtained because the primarily formed 1,4-dihydroquinoline derivative rearranges into the more easily reducible 3,4-dihydro derivative, which is a cyclic derivative of an aldehyde; if the *t*-butyl group were in the 2-position, the azomethine compound would be a derivative of a ketone and thus less easily reducible.

5-t-Butyl-5,6-dihydroquinoline, *16*, liquid. ^{1}H NMR ($CDCl_3$): δ 0.83 (9 H, s); 2.1–2.95 (3 H, m); 6.1–6.85 (2 H, m); 6.98 (1 H, dd, 7.5 Hz, 5 Hz); 7.35 (1 H, dd, 7.5 Hz, 2 Hz); 8.48 (1 H, dd, 5 Hz, 2 Hz). UV (96 % ethanol): λ_{max} 250 nm, log ε 4.18; λ_{max} 293 nm, log ε 3.95. The assignment of the structure is not definite;

however, the coupling pattern of the ethylenic protons is best accounted for by assuming a methylene group at C-6, but the signals were not well enough resolved to allow an unambiguous assignment.

7-t-Butyl-7,8-dihydroquinoline, *17*, liquid. ^{1}H NMR ($CDCl_3$): δ 0.90 (9 H, s); 2.0–2.7 (1 H, m); 2.8–3.2 (2 H, m); 6.02 (1 H, dd, 10 Hz, 3 Hz); 6.43 (1 H, dd, 10 Hz, 2 Hz); 6.98 (1 H, dd, 7.5 Hz, 4.5 Hz); 7.22 (1 H, dd, 7.5 Hz, 2 Hz); 8.30 (1 H, dd, 4.5 Hz, 2 Hz). UV (96 % ethanol), broad maximum at λ 265 nm, log ε 4.15.

1,2,3,4-Tetrahydroquinoline, *18*, was identified through its NMR spectrum.[22]

Dimer of 1,2,3,4-Tetrahydroquinoline, *19*. ^{1}H NMR ($CDCl_3$): δ 1.3–2.1 (2 H, m); 2.4–2.9 (3 H, m); 3.5–3.95 (1 H, m); 4.25 [1 H, s(br)]; 6.35–7.20 (4 H, m).

Reduction of *2-methylquinoline*, $n = 2.2$. The residue, 2.3 g, was separated on a silica column using acetone (20 %)–light petroleum (80 %) as eluent. Products were eluted in the order: (*24* + *23* + *22*), *20*, *4*, *21*. *22* + *23* + *24* was separated on a similar column using acetone (8 %)–light petroleum (92 %) as eluent.

3 (or 4)-t-Butyl-3,4-dihydro-2-methylquinoline, *20*, liquid. ^{1}H NMR ($CDCl_3$): δ 0.78 (9 H, s); 3.32 (3 H, s); 2.1–2.5 (1 H, m); 2.85–3.0 (2 H, m); 7.0–7.4 (4 H, m). The pattern in the ^{1}H NMR between δ 2 and 3 looks like that of *5*, *9*, *17*, and *23*, which would suggest the *t*-butyl group in the 3-position, but the argument does not carry sufficient weight to prove the structure.

4-t-Butyl-1,4-dihydro-2-methylquinoline, *21*, m.p. 121–123 °C. ^{1}H NMR ($CDCl_3$): δ 0.83 (9 H, s); 2.29 (3 H, s); 2.62 (1 H, d, 1.5 Hz); 4.11 (1 H, d, 1.5 Hz); 7.1–7.4 (4 H, m). IR (KBr) cm^{-1} (intensity): 3250 (s), 2950 (m), 1640 (m), 1475 (m), 1425 (m), 1045 (m), 1003 (m), 991 (m), 778 (m), 758 (s).

The compound is unstable and the real yield may be somewhat higher than the isolated one given in Table 2.

5-t-Butyl-5,6-dihydro-2-methylquinoline, *22*, liquid. ^{1}H NMR ($CDCl_3$): δ 0.82 (9 H, s); 2.48 (3 H, s); 2.3–3.5 (3 H, m); 6.05–6.30 (1 H, m); 6.52 (1 H, dtr, 9 Hz, 1.2 Hz); 6.83 (1 H, d, 8 Hz); 7.23 (1 H, d, 8 Hz). UV (96 % ethanol): λ_{max} 297 nm, log ε 3.95.

7-t-Butyl-7,8-dihydro-2-methylquinoline, *23*, liquid. ^{1}H NMR ($CDCl_3$): δ 0.92 (9, H, s); 2.50 (3 H, s); 2.1–2.6 (1 H, m); 2.85–3.20 (2 H, m); 5.98 (1 H, dd, 10 Hz, 3 Hz); 6.43 (1 H, dd, 10 Hz, 2 Hz); 6.90 (1 H, d, 7.5 Hz); 7.17 (1 H, d, 7.5 Hz). The position of the *t*-butyl group at C-7 rather than at C-6 was found through selective decoupling in the ^{13}C NMR spectrum in a similar manner as described for *9*.

8-t-Butyl-7,8-dihydro-2-methylquinoline, *24*, liquid. ^{1}H NMR ($CDCl_3$): δ 0.89 (9 H, s); 2.50 (3 H, s): 2.60–2.75 (3 H, m): 5.6–6.05 (1 H, m): 6.30 (1 H, dtr, 10 Hz, 1.5 Hz), 6.92 (1 H, d, 8 Hz); 7.18 (1 H, d, 8 Hz).

Competition experiment. Isoquinoline (1 g) and naphthalene (5 g) were reduced at -2.2 V in the presence of 10 ml *t*-butyl chloride, $n = 2.4$ (calculated for the reduction of isoquinoline). After the reduction was completed the catholyte was diluted with water, acidified and extracted with light petroleum, which was washed with water, dried and evaporated. The residue was investigated by NMR, GLC and mass spectroscopy. The aqueous phase was made alkaline, extracted three times with ether, which was washed with water and evaporated. The NMR of the residue resembled that obtained in reductive alkylations in the absence of naphthalene.

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