To this solution was added with stirring tert-butyl hydroperoxide (0.015 mole) over 30 min. To the solution was then added aqueous ammonia to pH 7-9, and the mixture extracted five times with chloroform. Unreacted base was removed by steam distillation.

The reaction products (III) and a mixture of (V) and (VI) were purified by column chromatography (alumina, hexane—chloroform, 3:1). The purity of isomers (V) and (VI) was established by TLC (adsorbent Silpearl, chloroform).

<u>(Quinoxalin-2-yl)-18-crown-6 (III)</u>. PMR spectrum: 3.40-3.70 (22H, m, CH_2O), 5.30-5.40 (1H, m, OCH-Ar), 7.50-8.00 (4H, m, Ar), 8.78 ppm (1H, s, Ar).

<u>(Quinolin-4-yl)-18-crown-6 (V)</u>. PMR spectrum: 3.40-3.71 (22H, m, CH_2O), 5.20-5.38 (1H, m, O—CH—Ar), 7.20-8.11 (5H, m, Ar), 8.82 ppm (1H, d, 2-H, Ar).

<u>(Quinolin-2-yl)-18-crown-6 (VI)</u>. PMR spectrum: 3.42-3.71 (22H, m, CH_2O), 5.32-5.40 (1H, m, O—CH—Ar), 7.20-8.10 ppm (6H, m, Ar).

The elemental analyses of (III), (V), and (VI) were in agreement with the calculated values.

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REDUCTION OF QUINOLINECARBOXYLIC ACIDS BY RANEY ALLOY

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The heterocyclic nucleus in quinolinecarboxylic acids is reduced by Raney alloy (nickel—aluminium) in alkaline media to give 1,2,3,4-tetrahydro-2-,3-,4-,5-,6-, and 8-quinolinecarboxylic acids and 8-methyl-5-quinolinecarboxylic acid and their ethyl esters.

1,2,3,4-Tetrahydroquinolinecarboxylic acids are used in the synthesis of biologically active compounds [1, 2].

The choice of methods for the preparation of 1,2,3,4-tetrahydroquinolinecarboxylic acids is limited, and more often than not reduces to reduction of the heterocyclic ring in quinolinecarboxylic acids with tin in hydrochloric acid [3], zinc in formic acid [4], sodium in butanol [4], a mixture of formic acid and triethylammonium formate (giving the N-formyl derivatives of the acids) [4], or by catalytic hydrogenation in the presence of Adams catalyst [2, 4]. These methods have technical limitations (the use of platinum catalysts, high pressures and temperatures), and do not always give high yields, prompting a search for new modes of reduction of the heterocyclic ring.

We have found that good results are obtained by reducing 2-, 3-, 4-, 5-, 6-, and 8-quinolinecarboxylic acids and 8-methyl-5-quinolinecarboxylic acid (Ia-g) with nickel-aluminum alloy (Raney alloy). This reagent, which is usually used to reduce and hydrogenolyze heteroaromatic substituents [5], has been employed to a limited extent to convert naphthalenes into tetralins, including tetrahydronaphthoic acids [6].

Reduction of quinolines with Raney alloy has not hitherto been reported.

Treatment of the quinolinecarboxylic acids (Ia-g) with Raney alloy in 10% aqueous sodium hydroxide at 20°C proceeds readily to give high yields of the 1,2,3,4-tetrahydroquinoline-

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TABLE 1. Properties of (IIa-f) and (IIIa-c)

Compound	mp, °C, or bp, °C (mm)		IR spectrum, cm^{-1}	Yield, %
	our data	literature data		
IIa	219—220	219—221 [8]	1745 (CO), 3445 (NH)	97
~~IIb~~	~~141—142~~	~~145—146 [8]~~	1747 (CO), 3445 (NH)	78
IIc	96—98	Not isolated in the free state [8]	1736 (CO), 3445 (NH)	87
IId	165—166	146—147 [8]	1748 (CO), 3445 (NH)	75
IIe	168—170	170 [8]	1740 (CO), 3445 (NH)	67
IIf	159—161	161—163 [8]	1736 (CO), 3445 (NH)	70
IIIa	140 (5)	131 (1,5) [4]	1736 (CO), 3438 (NH)	82
IIIb	142 (5)	135—137 (1,5) [4]	1736 (CO), 3448 (NH)	97
IIIc	160 (5)	176 (13) [4]	1736 (CO), 3435 (NH)	70

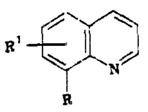
TABLE 2. Properties of (IIg) and (IIId-g)

Compound	mp, °C, or bp, °C (mm)	IR spectrum, cm^{-1}	Found, %			Empirical formula	Calculated, %			Yield. %
			C	H	N		C	H	N	
IIg	130—132 aqueous ethanol	1717 (CO), 3457 (NH)	69,1	6,7	7,1	$C_{11}H_{13}NO_2$	69,0	6,9	7,3	72
IIId	99—100 (5)	1727 (CO); 3438 (NH)	70,3	7,3	6,7	$C_{12}H_{15}NO_2$	70,2	7,4	6,8	50
IIIe	82—83 hexane	1687 (CO); 3437 (NH)	70,5	7,6	6,5	$C_{12}H_{15}NO_2$	70,2	7,4	6,8	97
IIIf	97—99 (5)	1687 (CO); 3418 (NH)	70,1	7,5	6,6	$C_{12}H_{15}NO_2$	70,2	7,4	6,8	74
IIIg	viscous oil	1680 (CO); 3435 (NH)	70,6	6,9	6,8	$C_{13}H_{17}NO_2$	70,7	7,6	6,0	48

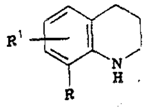
TABLE 3. PMR Spectra of (IIIa-f)

Compound	Chemical shifts, ppm					
	2-H	3-H	4-H	OCH_2	CH_3 (t)	aromatic ring (m)
IIIa	3,85—4,1 m	1,8—2,25 m	2,62—2,85 m	4,18—4,22 m	1,25—1,38	6,45—7,2
IIIb	4,05—4,3 m	3,2—3,6 m	2,9—3,15 q	4,05—4,25 q	1,22—1,31	6,4—7,9
IIIc	3,32—3,64 m	2,96 s	3,2—3,38 m	4,15—4,25 q	1,3—1,35	6,3—7,1
IIId	3,2—3,32 t	1,8—2,1 q	2,91—3,09 q	4,15—4,4 q	1,2—1,42	6,45—7,2
IIIe	3,26—3,38 t	1,82—2,0 q	2,64—2,82 t	4,12—4,38 q	1,22—1,38	6,78—7,62
IIIf	3,32—3,46 t	1,7—1,98 t	2,64—2,78 t	4,14—4,36 q	1,2—1,4	6,34—7,74

carboxylic acids (IIa-g) (Table 1).



Ia-g



II-III.a-g

I—III a—f R=H, g R=CH_3; I, II a R¹=2-COOH, b R¹=3-COOH, c R¹=4-COOH, d, g R¹=5-COOH, e R¹=6-COOH, f R¹=8-COOH; III a R¹=2-$COOC_2H_5$, b R¹==3-$COOC_2H_5$, c R¹=4-$COOC_2H_5$, d, g R¹=5-$COOC_2H_5$, e R¹=6-$COOC_2H_5$, f R¹=$COOC_2H_5$

The ethyl esters of these acids (IIIa-g) are obtained readily by the method described in [7], involving esterification of acids (IIa-g) with ethanol in the presence of sulfuric acid and hydrogen peroxide. The acid (IIg) and the substituted ethoxycarbonyl compounds (IIId-g) have not previously been reported (Tables 1-3). The structures of these compounds are shown unambiguously by their IR and PMR spectra.

EXPERIMENTAL

PMR spectra were obtained on a Varian XL-100 (in $CDCl_3$), internal standard TMS, and IR spectra on a Unicam SP-1000 (in KCl disks). The course of the reactions and the purities of the products were checked by TLC on Silufol plates in the solvent system benzene—ethyl acetate—water, 100:50:1. The quinoline-2 and -4-carboxylic acids used were obtained from

Reanal, and 3-, 5-, 6-, and 8-quinolinecarboxylic acids and 8-methyl-5-quinolinecarboxylic acid were prepared by literature methods. The properties of (IIa-g) and (IIIa-g) are given in Tables 1-3.

1,2,3,4-Tetrahydroquinolinecarboxylic Acids (IIa-g). To a solution of 0.05 mole of the acid (Ia-g) in 50 ml of 10% aqueous sodium hydroxide was added in small portions with stirring over 1 h, 8 g of Raney alloy, and the mixture stirred for 1 h at 20°C. The solid was filtered off and washed with hot water, and 5% hydrogen chloride in ethanol added to the filtrate to pH 2-3 (universal indicator). It was then extracted with chloroform, the organic layer dried over magnesium sulfate, and the solvent removed to give the acids (IIa-g), which were crystallized from aqueous ethanol for analysis. The compounds were homogeneous on TLC. The acids (IIa-g) were used without purification to obtain the esters (IIIa-g).

Ethyl Esters of 1,2,3,4-Tetrahydroquinolinecarboxylic Acids (IIIa-g). A solution of 0.02 mole of the acid (IIa-g) in a mixture of 10 ml of absolute ethanol, 5 ml of conc. sulfuric acid, and 3 ml of 30% hydrogen peroxide was heated at 120°C (in a bath) for 30-40 min. The mixture was then poured into 50 ml of water, 25% ammonia added to pH 6-7, extracted with chloroform, and the organic layer washed with 3% sodium bicarbonate and water, dried over magnesium sulfate, and the solvent removed to give the ethyl esters (IIIa-g).

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DUAL REACTIVITY IN 1,2-DISUBSTITUTED DIHYDRO-N-HETEROAROMATIC SYSTEMS.

12.* AROMATIZATION OF 1-SUBSTITUTED-2-(INDOL-3-YL)-1,2-DIHYDROQUINOLINES WITH 1,3,5-TRINITROBENZENE

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As the electron-acceptor properties of the N-substituents in 1-R-2-(indol-3-yl)-1,2-dihydroquinolines decrease, their ability to undergo heterolysis of the internuclear C—C bond to give ion pairs of 1-R-quinolinium cations and indole anions decreases. Reaction of these ion pairs with 1,3,5-trinitrobenzene gives salts of 1-R-quinolinium cations and the 1-(indol-3-yl)-2,4,6-trinitrocyclohexadiene anion. With undissociated dihydroquinolines, aromatization under similar conditions gives salts of 1-R-2(indol-3-yl)quinolinium cations and the 1,1-dihydro-2,4,6-trinitrocyclohexadiene anion.

In polar solvents, some C-substituted dihydroaromatic compounds dissociate to a heteroaromatic cation and the substituent as an anion [2], displaying dual reactivity on aromatiza-

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*For Communication 11, see [1].

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