THE SYNTHESIS OF HYDROXY, ACYLOXY, OXO, N-OXIDE OXO, AND MORPHOLINO DERIVATIVES OF HYDROGENATED QUINOLINES AND STUDY OF THEIR RADICAL ANALOGS BY ESR

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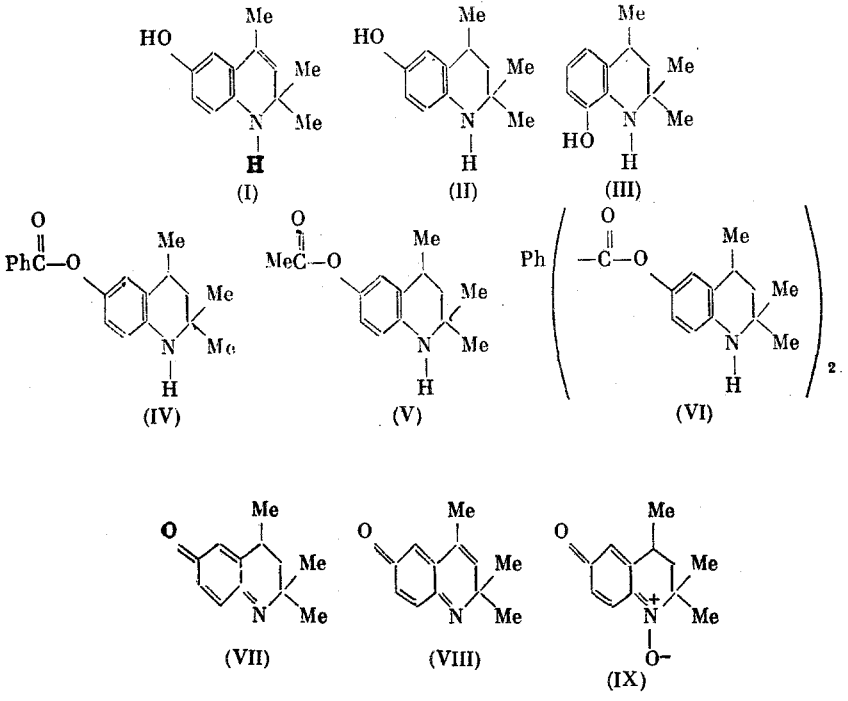
Among active antioxidants the aromatic amines are more effective than sterically hindered phenols [1-6], but because of their coloring propensity and their toxicity, their application is limited. A still greater effectiveness can be expected for bifunctional compounds which combine the properties of amine and phenol, for example the low-toxicity derivatives of hydrogenated quinoline [7]. The aims of the present work have been the synthesis of derivatives of hydrogenated quinoline, a study of their physicochemical properties, as well as the identification of the products of their oxidative conversions.

The hydroxy derivatives of 2,2,4-trimethyl-1,2-di- and of 2,2,4-trimethyl-1,2,3,4-tetrahydroquinolines (I)-(III) were prepared by acid hydrolysis of the corresponding alkoxy-substituted compounds [8]. The acyloxy derivatives of 2,2,4-trimethyl-6-benzoyl-, 2,2,4-trimethyl-6-acetyl-, and 2,2,4-trimethyl-6-terephthaloyl-1,2,3,4-tetrahydroquinoline (IV)-(VI) were synthesized by treating (II) with benzoyl, acetyl, and terephthaloyl chlorides, respectively. The quinonimines of 2,2,4-trimethyl-6-oxo-2,3,4-tri- and 2,2,4-trimethyl-6-oxo-2-monohydroquininoline (VII), (VIII) were obtained by oxidation of (II) and (I) with Ag_2O, and their N-oxides (IX), (X) by catalytic oxidation of (II) and (I) with H_2O_2 (Na_2WO_4 catalyst). The morpholino derivatives of 2,2,4-trimethyl-6-oxo-8-N-morpholino-2,3,4-tri- and 2-monohydroquinolines (XI), (XII) and their N-oxides (XIII), (XIV) were prepared by amination of (VII)-(X) with morpholine.



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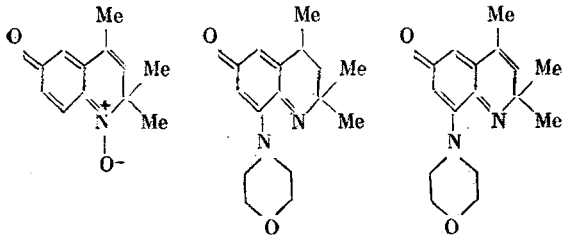
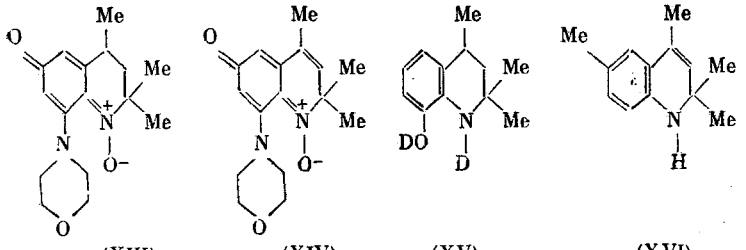
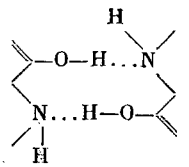


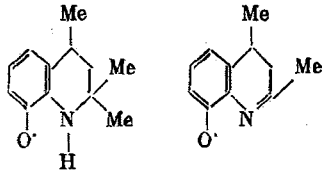
(X) (XI) (XII)



(XIII) (XIV) (XV) (XVI)

The structures of (I)-(XVI) were confirmed by their PMR and IR spectra. By means of PMR the magnetic nonequivalence of the CH_3 groups in position 2 and the methylene protons in position 3 of compounds (II)-(V), (VII), (IX), (XI), (XV) was established. In (I), (X), (XIV), and (XVI) [9] the analogous protons are equivalent. This difference is due to the presence of the asymmetric C atom in position 4 of the first series of tetrahydroquinolines (Table 1).

The PMR and IR spectra of compound (III) indicate that in weak solvating solvents (benzene, toluene, CCl_4) the compound exists in monomeric and polymeric (most probably entirely dimeric) forms in the ratio $\sim$ 1:1. The lifetime of the molecules in each form is quite small ($\sim 10^{-2}$ sec), which produces a strong broadening in the PMR spectrum. From the IR spectra in the $\nu_{>NH}$ and ν_{OH} regions for concentrated and dilute (1000-fold) solutions of (III) it was clear that intramolecular H bonds were not present and that (III) exists in the form of associates of the type  . When dissolved in DMSO, the latter dissociate due to the formation of intermolecular H bonds by the OH and NH groups with the solvent. When a 10^{-2} M toluene solution of (III) is irradiated with UV light (lamp DRSh-1000) [9], relatively stable radicals are formed, which were identified, depending on the experimental conditions, as the aryloxy (A) or the iminoxy (B). In the ESR spectrum of radical (A) (Fig. 1a), which was obtained by photolysis of (III) in the absence of O_2, 15 lines are observed with intensity ratio 1 : 2 : 1 : 3 : 6 : 3 : 4 : 8 : 4 : 3 : 6 : 3 : 1 : 2 : 1. The hfs of the spectrum is due to the interaction of the unpaired electron with the N^{14} nucleus (a_N = 5.3 Oe) and the four coupled equivalent protons with constants of 5.3 and 2.1 Oe. The value of a_N permits the deduction to be made that radical (A) is an aryloxy radical which can correspond to two structures:



(A¹) (A²)

The greatest splitting is observed for the protons in positions 5 and 7 ($a_{H5} = a_{H7}$ = 5.3 Oe). Taking account of the absence of changes in the character of the spectrum of (A) which is obtained for (III) deuterated at the amino and hydroxy groups [compound (XV)] as well as the possibility of splitting CH_4 from a compound of the type (III) [10], structure (A^2) should be reckoned more probable. The lifetime of the radical in an evacuated and in a constantly evacuated medium is similar and is $\sim$ 5 min, which is considerably greater than the lifetime of unshielded and weakly shielded aryloxy radicals (10^{-2}-10^{-6} sec) [11]. Under

TABLE 1. Parameters of the PMR Spectra of Hydrogenated Hydroxyquinolines and Their Derivatives

Compound	Chemical shift δ, ppm													J, Hz						
	solvent	2-CH_3	4-CH_3	H^3[a]	H^4	H^5	H^6	H^7	H^8	NH	OH	OCH_2	NCH_2	$^2J_{(3)-HaHb}$	$^3J_{H^3-H^4}$	$^3J_{C^4H_3-H^4}$	$^4J_{C^4H_3-H^3}$	$^4J_{H^5-H^7}$	$^4J_{H^7-H^8}$	$^4J_{H^6-H^8}$
(I)	Acetone-d	1,12	1,82	5,25	–	6,33	–	6,34	6,24	4,48	8,32	–	–	—	—	—	1,5	2	8	–
(II)	DMSO-d	0,97 1,16	1,11	1,58	2,7	6,51	–	6,29	6,31	4,61	8,23	–	–	13	6	7	–	2,5	8	–
(III)	DMSO-d	1,1 1,22	1,37	1,7	2,8	6,7[b]	6,45[b]	6,75	–	4,3	8,9	–	–	13	5	7	–	2	–	–
(IV)	DMSO-d	1,03 1,11	1,18	1,63[c]	2,63	6,65	–	6,5	6,2	5,26	–	–	–	12	5	7	–	2,5	8	–
(V)	$CDCl_3$	1,1 1,17	1,26 2,2 $\left(\begin{matrix}H_3C\\ \vert\\ C{=}O\end{matrix}\right)$	1,7	2,85	6,85	–	6,65	6,35	3,59	–	–	–	12	6,5	7	–	2,5	8	–
(VII)	CCl_4	1,15 1,32	1,2	1,72	2,6	6,18	–	6,35	6,9	–	–	–	–	13	6	7	–	2	9,5	–
(IX)	$CDCl_3$	1,42	1,25	1,9	2,9[d]	6,05	–	6,3	7,7	–	–	–	–	13	5	7	–	2,5	10	2,5
(X)	CCl_4	1,32	1,85	6,29	—	6,09	–	6,92	7,5	–	–	–	–	—	—	—	1,5	2	10	–
(XI)	CCl_4	1,18 1,33	1,16	1,71	2,58[e]	6,00	–	5,42	–	–	–	3,67	3,20	13	6	7	–	2	–	2,5
(XIV)	CCl_4	1,15	1,75	6,01	–	6,17	–	5,62	–	–	–	3,59	3,04	—	—	—	1,5	2,2	–	–
(XV)	DMSO-d	1,1 1,22	1,37	1,7	2,8	6,7	6,45	6,75	–	–	–	–	–	13	5	7	–	2	–	–
(XVI)[d]	CCl_4	1,15	1,89 2,15 (6-CH_3)	5,10	–	6,77	–	6,61	6,13	3,25	–	–	–	—	—	—	1,5	2	8	–

a) The centers for H_a and H_b overlap the CH_3 group signals. b) $^3J_{H^5-H^6}$ = 8 Hz, $^3J_{H^6-H^7}$ = 8 Hz. c) Protons of the benzoyl fragment: δ $H^{2'}$, $H^{6'}$, = 7.8 ppm, δ $H^{3'}$, $H^{4'}$, $H^{5'}$ = 7.35 ppm. d) $^3J_{H^4-H^5}$ = 3 Hz. e) $^3J_{H^4-H^5}$ = 2.5 Hz. f) Data of [9].

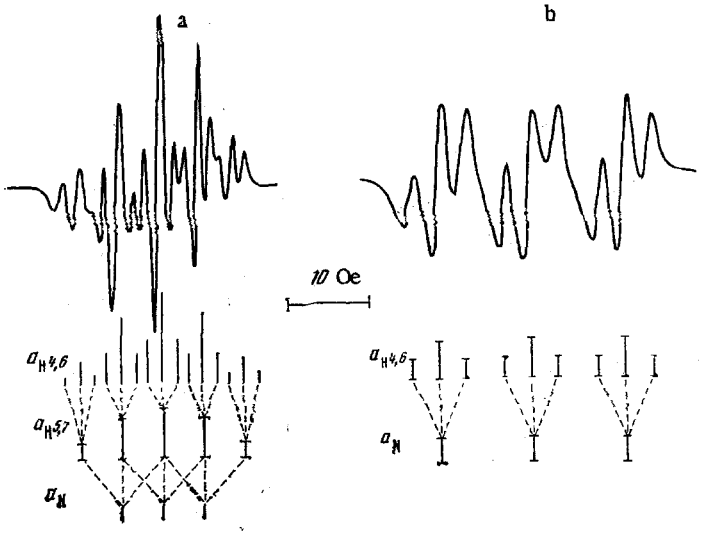


Fig. 1. ESR spectra of radicals (A) and (B) which are formed during UV irradiation (lamp DRSh-1000) of a toluene solution of (III): a) in the absence of O_2 (A); b) with O_2 present, from the accumulated nonparamagnetic product, which on pumping off the O_2 is converted into radical (B).

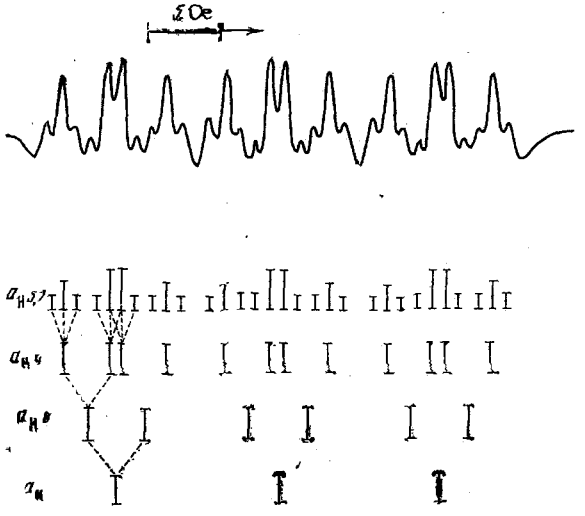


Fig. 2. ESR spectrum of the radicals (C) and (D) obtained by oxidation of toluene solutions of (IV) and (V) with meta-chloroperbenzoic acid.

similar conditions an ESR signal could not be recorded for (I) or (II).

On prolonged photolysis of (III) in the presence of O_2 a nonparamagnetic product accumulates, which on pumping off O_2 is converted into the stable nitroxyl radical (B). The ESR spectrum of (B) consists of 9 lines with a ratio of intensities (1 : 2 : 1) × 3 (Fig. 1b). The hfs of the spectrum is due to the interaction of the unpaired electron with the N^{14} nucleus (a_N = 12 Oe) and the two protons in positions 4 and 6 ($a_{H^4} = a_{H^6}$ = 3.5 Oe). The value of a_N permits the conclusion that the radical (B) is a nitroxyl radical which can correspond to either of two structures:

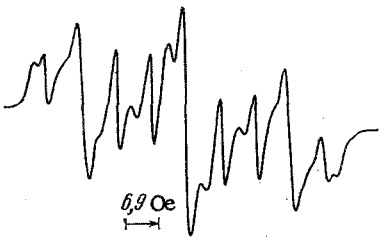
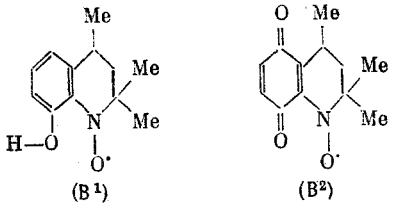
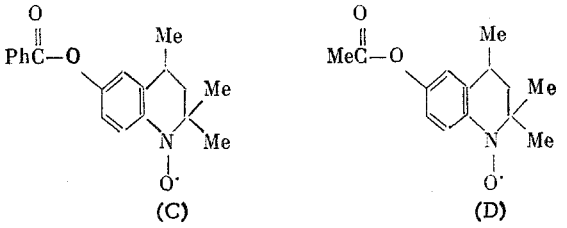


Fig. 3. ESR spectrum of radical (E) obtained by oxidation of a toluene solution of (VI) with meta-chloroperbenzoic acid.



Deuteration of the amino and hydroxy groups of (III) [compound (XV)] did not change the character of the spectrum of (B), which provides a basis for assuming structure (B^2) as the more likely. Under similar conditions for (I) or (II) no ESR signal could be recorded. The radicals (A) and (B) were also obtained by the action of PbO_2 and meta-chloroperbenzoic acid on a toluene solution of (III). They are also formed by heating a solution of (III). By treatment of toluene solutions of (IV) and (V) with meta-chloroperbenzoic acid the nitroxyl radicals (C) and (D) were obtained:



The ESR spectra of radicals (C) and (D) were identical and consisted of 30 lines (Fig. 2). The observed ratio of intensities (1 : 2 : 1 : 1 : 3 : 3 : 1 : 1 : 2 : 1) × 3 is due to splitting by the N^{14} nucleus and the protons at the 8, 7, 5, and 4 positions (a_N = 10.67, a_{H^8} = 3.9, $a_{H^7} = a_{H^5}$ = 1, and a_{H^4} = 2.9 Oe). The ESR spectrum of radical (E) obtained by oxidation of a toluene solution of (VI) with meta-chloroperbenzoic acid is shown in Fig. 3.

EXPERIMENTAL

The PMR spectra were recorded on a Tesla-BS 487-C spectrometer (80 MHz); internal standard HMDS. The IR spectra were recorded on a UR-20 instrument. Characteristic bands were present in the IR spectra for example: for (V) at 3400 (NH), 1730 (C=O), 3030 (C–H aromat.), 2950 (CH_3), 1200 ($C(O)O^-$) and for (VII)-(XIV) at 1650 (C=O) cm^{-1}.

The ESR spectra were recorded at 25°C on the spectrometer (3 cm band) ESR-20 IKhF. Samples were frozen and deoxygenated by repeated evacuation down to 10^{-3} torr. Ultrapure grade toluene was used as the solvent. The concentration of solutions of the radicals (C), (D), and (E) was $\leq 2 \cdot 10^{-4}$ mole/liter.

2,2,4-Trimethyl-6-hydroxy-1,2-dihydroquinoline (I). 2,2,4-Trimethyl-6-ethoxy-1,2-dihydroquinoline (25 g) and 100 ml HBr (sp.g. 1.445) were heated at boiling for 4 h, the ethyl bromide formed being distilled off. The residual liquid was evaporated, dissolved in 100 ml of distilled water, filtered, cooled with ice, and made alkaline with a saturated solution of sodium carbonate to pH 10-11. The precipitate was filtered off, washed on the filter with distilled water, pressed dry, then dissolved in benzene, and the benzene–water azeotrope distilled off, and (I) was further purified by sublimation in vacuum. Obtained 9.75 g (45%) (I), mp 173-175°. Found, %: C 76.07; H 8.14; N 7.29; mol. wt. 189 (mass spectroscopic (MS)). $C_{12}H_{15}NO$. Calculated, %: C 76.20; H 7.94; N 7.40.

2,2,4-Trimethyl-6-hydroxy-1,2,3,4-tetrahydroquinoline (II). In the same way as for (I) from 25 g of 2,2,4-trimethyl-6-ethoxy-1,2,3,4-tetrahydroquinoline, (II) was obtained, yield

55%, mp 184-186°C. Found, %: C 75.44; H 9.04; N 7.48; mol. wt. 191 (MS). $C_{12}H_{17}NO$. Calculated, %: C 75.36; H 8.95; N 7.32.

2,2,4-Trimethyl-8-hydroxy-1,2,3,4-tetrahydroquinoline (III). In the same way as for (I) from 25 g of 2,2,4-trimethyl-8-methoxy-1,2,3,4-tetrahydroquinoline, (III) was obtained. The reaction product, after distilling off the benzene, was washed with hexane, dried, and then sublimed in vacuum at 85°C. Obtained 4.66 g (20%) (III), mp 106-108°C. Found: C 75.41; H 9.02; N 7.50; mol. wt. 191 (MS). $C_{12}H_{17}NO$. Calculated, %: C 75.36; H 8.95; N 7.32.

2,2,4-Trimethyl-6-benzoyloxy-1,2,3,4-tetrahydroquinoline (IV). To 1 g of (II) in 20 ml of absolute benzene and 2 ml triethylamine, with stirring, was added over 1 h a solution of 0.74 g PhCOCl in 5 ml abs. benzene. Then the reaction mixture was stirred 1 h at ∿ 20°C and 1 h at 60°C, cooled, filtered, and the precipitate on the filter ($Et_3N \cdot HCl$) washed with abs. benzene. The benzene was distilled from the filtrate, and the substance recrystallized from hexane. Obtained 1.26 g (60%) (IV), mp 112-114°C. Found, %: C 77.16; H 7.20; N 4.60; mol. wt. 295 (MS). $C_{19}H_{21}NO_2$. Calculated, %: C 77.28; H 7.12; N 4.75. The substance remaining after distilling off the benzene was also purified by chromatography on a column of Al_2O_3, eluent $CHCl_3$; the fraction with R_f 0.28 was recovered.

2,2,4-Trimethyl-6-acetyloxy-1,2,3,4-tetrahydroquinoline (V). In the same way as for (IV) from 1 g (II) and 0.41 g CH_3COCl in the presence of 2 ml Et_3N, (V) was obtained, yield 55%, mp 97-99°C (hexane). Found, %: C 72.28; H 8.29; N 6.25; mol. wt. 233 (MS). $C_{14}H_{19}NO_2$. Calculated, %: C 72.10; H 8.15; N 6.02. Compound (V) was also purified on an Al_2O_3 column (eluent $CHCl_3$); the fraction with R_f = 0.54 was recovered.

2,2,4-Trimethyl-6-terephthaloyloxy-1,2,3,4-tetrahydroquinoline (VI). In the same way as for (IV) from 0.53 g terephthaloyl dichloride and 1.1 g (II) in the presence of 2 ml Et_3N, (VI) was obtained, yield 50% (yellow colored crystals), mp 203-205°C (cyclohexane). Found, %: C 75.22; H 7.14; N 5.60; mol. wt. 512 (MS). $C_{32}H_{36}N_2O_4$. Calculated, %: C 75.00; H 7.04; N 5.46. Compound (VI) was also purified by chromatography on an Al_2O_3 column (eluent $CHCl_3$); the yellow colored fraction with R_f = 0.19 was recovered.

2,2,4-Trimethyl-6-oxo-2,3,4-trihydroquinoline (VII). To a solution of 0.5 g (II) in 20 ml of abs. acetone with stirring was added 3 g of Ag_2O in small portions. The mixture was stirred 2 h, filtered, the acetone distilled off, and the residue chromatographed on an Al_2O_3 column (eluent $CHCl_3$); the yellow colored fraction with R_f = 0.375 was recovered, and the $CHCl_3$ was distilled off. Obtained 0.095 g (19%) of (VII) (yellow crystals), mp 56-58°C. Compound (VII) was readily sublimed in vacuum. Found, %: C 75.38; H 7.88; N 7.11; mol. wt. 189 (MS). $C_{12}H_{15}NO$. Calculated, %: C 76.20; H 7.93; N 7.41.

2,2,4-Trimethyl-6-oxo-2-monohydroquinoline (VIII). In the same way as for (VII) from 0.5 g (I) was obtained (VIII), purified by chromatography on an Al_2O_3 column (eluent $CHCl_3$); the yellow fraction with R_f = 0.34 was recovered, yield 12%, mp 67-69°C. Compound (VIII) was yellow in color and readily sublimes in vacuum. Found, %: C 76.01; H 6.73; N 7.35; mol. wt. 187 (MS). $C_{12}H_{13}NO$. Calculated, %: C 77.00; H 6.95; N 7.50.

N-oxide of 2,2,4-Trimethyl-6-oxo-2,3,4-trihydroquinoline (IX). To a solution of 0.5 g (II) in 30 ml CH_3OH were added 1 ml of 30% H_2O_2, 0.8 g Na_2WO_4, and the mixture kept for 10 days at ∿ 20°C. Then the solution was filtered, the solvent distilled off in vacuum, the residue chromatographed on a column of Al_2O_3 (eluent $CHCl_3$), and the yellow fraction with R_f = 0.32 recovered. After distilling off the $CHCl_3$, 0.12 g (20%) of (IX) was obtained, mp 46-48°C. Compound (IX) was yellow and readily sublimed in vacuum. Found, %: C 69.09; H 7.70; N 6.79; mol. wt. 205 (MS). $C_{12}H_{15}NO_2$. Calculated, %: C 70.21; H 7.32; N 6.86.

N-oxide of 2,2,4-Trimethyl-6-oxo-2-monohydroquinoline (X). Compound (X) was prepared in the same way as (IX) from 0.5 g (I) and purified by chromatography on an Al_2O_3 column (eluent $CHCl_3$); the yellow colored fraction with R_f = 0.32 was recovered. Yield 10%, mp 51-53°C. Compound (X) was yellow and readily sublimed in vacuum. Found, %: C 71.29; H 6.09; N 7.11; mol. wt. 203 (MS). $C_{12}H_{13}NO_2$. Calculated, %: C 71.10; H 6.40; N 6.90.

2,2,4-Trimethyl-6-oxo-8-N-morpholino-2,3,4-trihydroquinoline (XI) [12, 13]. a) A mixture of 0.3 g (VII), 0.15 g morpholine, and 10 ml EtOH was heated at boiling for 2.5 h, evaporated, and the residue chromatographed on an Al_2O_3 column (eluent $CHCl_3$); the red colored fraction with R_f = 0.22 was recovered. After recrystallization from hexane, 0.13 g (30%) of (XI) was obtained as red crystals, mp 135-137°C. Found, %: C 69.85; H 7.76; N 10.45;

mol. wt. 274 (MS). $C_{16}H_{22}N_2O_2$. Calculated, %: C 70.10; H 8.03; N 10.20.

b) A mixture of 1.9 g (II), 20 ml MeOH, 0.5 g $Cu(OAc)_2$, and 1 g morpholine was cooled to 0°C; the free volume above the solvent was filled with O_2, and stirring maintained until absorption was complete. The precipitate which formed was filtered off and washed with benzene. The filtrate was evaporated, and the residue chromatographed on an Al_2O_3 column (eluent $CHCl_3$); the red fraction with R_f = 0.22 was recovered. After recrystallization from hexane, 1 g (37.5%) of (XI) was obtained as red crystals, mp 135-137°C. Found, %: C 69.80; H 7.86; N 10.32; mol. wt. 274 (MS). $C_{16}H_{22}N_2O_2$. Calculated, %: C 70.10; H 8.03; N 10.20. A mixed sample of (XI) with (XI) from experiment (a) gave no depression in melting point. The IR and PMR spectra of (XI) from experiments (a) and (b) were identical.

2,2,4-Trimethyl-6-oxo-8-N-morpholino-2-monohydroquinoline (XII). Compound (XII) was prepared in the same way as (XI) [experiment (a)] from 0.3 g (VIII) and was purified chromatographically on an Al_2O_3 column (eluent $CHCl_3$); the red fraction with R_f = 0.2 was recovered. After recrystallization from hexane, 0.15 g (35%) of (XII) was obtained as red crystals, mp 142-144°C. Found, %: C 70.72; H 7.47; N 10.49; mol. wt. 272 (MS). $C_{16}H_{20}N_2O_2$. Calculated, %: C 70.59; H 7.35; N 10.29.

N-Oxide of 2,2,4-Trimethyl-6-oxo-8-N-morpholino-2,3,4-trihydroquinoline (XIII). The N-oxide (XIII) was prepared in the same way as (XI) [experiment (a)] from 0.3 g (IX), yield 36.4%, red crystals, mp 123-125°C (hexane). Compound (XIII) was also purified by chromatography on an Al_2O_3 column (eluent $CHCl_3$); the red fraction with R_f = 0.185 was recovered. Found, %: C 66.49; H 7.70; N 9.80; mol. wt. 290 (MS). $C_{16}H_{22}N_2O_3$. Calculated, %: C 66.21; H 7.58; N 9.66.

N-Oxide of 2,2,4-Trimethyl-6-oxo-8-N-morpholino-2 -monohydroquinoline (XIV). The N-oxide (XIV) was prepared in the same way as (XI) [experiment (a)] from 0.3 g of (X). Yield 38.2%, red crystals, mp 130-132°C (hexane); (XIV) was purified by chromatography on an Al_2O_3 column (eluent $CHCl_3$); the red fraction with R_f = 0.187 was recovered. Found, %: C 66.85; H 6.74; N 10.07; mol. wt. 288 (MS). $C_{16}H_{20}N_2O_3$. Calculated, %: C 66.60; H 6.95; N 9.75.

CONCLUSIONS

1. The hydroxy, acyloxy, oxo, N-oxide oxo, and morpholino-oxo derivatives of 2,2,4-trimethyl-substituted 1,2,-di- and 1,2,3,4-tetrahydroquinolines have been synthesized. Their structure was confirmed by the IR and PMR spectra.

2. The radicals formed during photolysis of a toluene solution of 2,2,4-trimethyl-8-hydroxy-1,2,3,4-tetrahydroquinoline as well as by oxidation of the acyl derivatives of 2,2,4-trimethyl-6-hydroxy-1,2,3,4-tetrahydroquinoline by meta-chloroperbenzoic acid were recorded and studied by the ESR method.

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THE DEBUTYLATION OF INDAZOLINES UNDER CONDITIONS OF ACID CATALYSIS

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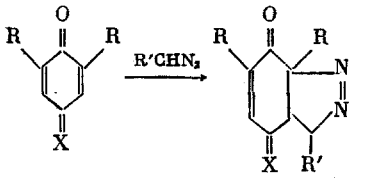
We have established previously [1, 2] that when diazomethane is reacted with N-phenyl-2,6-di-tert-butyl-4-benzoquinonimine, depending on the conditions, formation occurs of either 6,7a-di-tert-butyl-4-phenylimino-7-oxo-3a,7a-dihydro-3H-indazoline (Ib) or 6-tert-butyl-4-phenylimino-7-oxo-1H-indazole. It was also noted that the indazoline (Ib) can, in a number of cases, undergo conversion into the indicated phenyliminoindazole [2]. During this a cleavage of the tert-butyl group from the quaternary C atom (position 7a of the indazoline ring) occurs.

In the present work an attempt is made to ascertain the generality of the given debutylation in a series of indazolines and to establish its mechanism. The required starting indazolines (I) were synthesized by the reaction of 2,6-di-tert-butyl-1,4-quinonoid compounds with diazomethane and diazoethane in ether using 2-10 times excess of the diazoalkane. The structures of the prepared compounds were confirmed by spectroscopic examination (Table 1).



(Ia-e)

R = *t*-Bu. R′ = H, X = O (Ia), NC_6H_5 (Ib), $NOCH_3$ (Ic), $NN(CH_3)_2$ (Id);
R′ = CH_3, X = O (Ie)

Particularly noteworthy are the PMR spectra of the indazolines (Ib) and (Ie), in which a doubling of all the signals is observed. Analysis of the spectra shows that (Ib) and (Ie) exist in two isomeric forms, but the nature of their isomerism differs. In the case of (Ib) a geminal nonequivalence of the methylene protons is observed, induced by the adjacent asymmetric carbon center C^{3a}, whereas in the spectra of (Ie), which contains the asymmetric centers C^3, C^{3a}, C^{7a}, signals for the protons of the diastereoisomers are observed. It is noteworthy that the chemical shifts of the CH_3 group and of H^3 and H^{3a} for the isomers differ considerably in value ($\Delta\delta_{CH_3}$ = 0.67 ppm; $\Delta\delta_{H^3}$ = 1.15; $\Delta\delta_{H^{3a}}$ = 0.56 ppm); for one isomer the CH_3 group signal is shifted towards high field, while for the other isomer it is the H^3 signal.

The observed phenomenon is explained by the difference in the three-dimensional structures of the isomers. Their molecules are nonplanar, the angle between the planes of the ring corresponding to the direction of the covalent bonds with sp^3 hybridization of the C^{3a} and C^{7a} atoms apparently differs very little from 109°; the positions of the t-Bu group and of H^5 and H^{3a} are rather rigidly fixed. This results in the fact that for one of the isomers the CH_3 group is in the trans position to t-Bu at C^{7a} and the H^{3a} proton, and for the other isomer the H^3 proton is in the trans position.

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