tra of solutions of IX–XVI and XXV–XXXII in $CDCl_3$ and of XVII–XXIV in CD_3OD were recorded with a Jeol JNK-PS-100 spectrometer (100 MHz) relative to tetramethylsilane. The mass spectra were recorded with an LKB-2091 spectrometer equipped with a system for direct introduction of the samples into the ion source at a vaporization temperature of 200°C and an ionizing-electron energy of 70 eV.

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EPOXIDATION OF UNSATURATED ALCOHOLS OF THE DECAHYDROQUINOLINE SERIES

L. I. Ukhova and G. P. Kukso

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The epoxy derivatives of stereoisomeric 1-alkyl-, 1,2-dimethyl-, and 1,2,2-trimethyl-4-vinyl-trans-decahydroquinolols were synthesized by oxidation with performic acid in formic acid solution. The compounds were characterized by their PMR and mass spectra. An analysis of the spectral data made it possible to conclude that the synthesized compounds and the starting vinyl alcohols have the same configurations.

The epoxidation of unsaturated compounds that contain an allylic hydroxy group and a heteroatom in the ring has not been adequately studied. There are only a few communications that deal with the oxidation of olefinic alcohols of the pyran, thiopyran. piperidine [1, 2], and decahydroquinoline [3, 4] series. In addition, owing to their high reactivities, epoxy alcohols are of great interest as intermediates in the synthesis of diverse functionally substituted derivatives that possibly have biological activity. The aim of the present research was to study the oxidation of some 4-vinyldecahydro-4-quinolols and to find the optimum conditions for the preparation of epoxy alcohols of this series.

An analysis of the literature data [5, 6] shows that a convenient method for the preparation of epoxy compounds without involvement of the nitrogen atom, which is sensitive to electrophilic oxidation by peracids, is oxidation with performic acid in formic acid solution, which sharply reduces the nucleophilicity of the nitrogen atom (epoxidation *in situ*). In this method formic acid is both the solvent and the oxygen atom carrier, while performic acid is formed as an intermediate. Although formic acid opens the epoxide ring at a much greater rate than other acids, the high rates of formation and consumption of performic acid prevent its rapid decomposition with the loss of an active oxygen atom. The mechanism of epoxidation by peracids includes a spiran transition state [7].

We investigated the oxidation by performic acid of stereoisomeric 1-alkyl-, 1,2-dimethyl-, and 1,2,2-trimethyl-4-vinyl-trans-decahydro-4-quinolols (I–VIII), the synthesis of which was previously described in [8–10]. As a result of varying the ratio and concentrations of the

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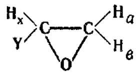
reactants and the reaction temperature and time we found the optimum conditions for its occurrence. We found that when 30% hydrogen peroxide in a fourfold excess with respect to the unsaturated compound is used at 25-30°C, the reaction takes place in 4 days with only slight polymerization, and the yields of epoxy alcohols reach 70%. An increase in the temperature accelerates the oxidation **significantly**; however, the loss of an active oxygen atom due to decomposition of the peracid is intensified simultaneously, and polymerization is accelerated. The oxidation of ethylene alcohols of the decahydroquinoline series in dilute performic acid proceeds more favorably than in concentrated performic acid [4]. This is explained by the fact that water, by solvating the performic acid, lowers its effective concentration and thereby decreases the rate of epoxidation as compared with oxidation by concentrated performic acid. In the case of oxidation with dilute performic acid the reaction takes place with less heat evolution, and this suppresses polymerization and the formation of products of further transformation of the epoxy alcohols. Of no less importance for the yields of the epoxy alcohols are the use of ammonium hydroxide as a neutralizing agent for the reaction mixtures and neutralization at no higher than 0°C. Replacement of ammonia by a stronger alkaline agent such as K_2CO_3 leads to a sharp decrease in the yields of the desired products due to the formation of polymers. One might have expected that vinyl alcohols I-VIII would undergo allylic isomerization under the oxidation conditions and that the reaction products would be mixtures of two epoxides, viz., an epoxide with a normal structure and a spiro epoxy compound. However, vinyl alcohols remained unchanged after standing for 4 days in formic acid solution at 30°C, as evidenced by the identical character of their PMR spectra and the spectra of the starting vinyl alcohols (Table 1) and the absence of melting-point depressions for mixtures of the samples.

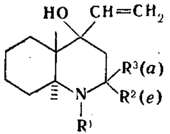
We established that exclusively epoxy derivatives IX-XVI are formed as the oxidation products under the conditions that we found and that they do not undergo hydrolysis. The orientations of the substituents in the C_2 and C_4 positions of starting vinyl alcohols I-VIII were established by spectral methods in [11-13]. The structures of the epoxy alcohols obtained from them were confirmed by the results of elementary analysis and the IR, PMR, and mass spectra. A narrow absorption band at ~3070 cm^{-1} due to the stretching vibrations of the CH group of the epoxide ring [14] and a characteristic (for the epoxide ring) intense band at 880 cm^{-1} are observed in the IR spectra of all epoxy compounds IX-XVI. One absorption band of a hydroxy group linked by means of an intramolecular hydrogen bond with the oxygen atom of the epoxide ring at 3570 cm^{-1} is observed in the spectra of dilute solutions in CCl_4.

In the PMR spectra (at an operating frequency of 10 MHz) of IX, XI, and XIII with an axial epoxide group the signals of the protons of the 

ring (an ABX system) are resolved (Table 2), whereas in the case of equatorial isomers X, XII, XIV, XV, and XVI they form a complex multiplet with an integral intensity of three protons with a width of ~26 Hz and a chemical shift (δ) of 2.76-2.84 ppm. However, the high-resolution spectra (at an operating frequency of 300 MHz) of epoxy alcohols X and XV with an equatorial epoxide function give resolved signals of H_a, H_b, and H_x protons. In the case of the epimeric (with respect to the C_4 atom) epoxy alcohols IX and X the ABX proton system that is normal for epoxy compounds is transformed to a first-order AMX system. The SSCC of the protons of the epoxide ring of these compounds were confirmed by double homonuclear resonance, whereas for XV they were found from an analysis of the ABX spectrum recorded at 100 Hz. The chemical shifts and SSCC of the epoxide protons found are in good agreement with the available literature data [15] and constitute evidence that oxidation products IX-XVI are actually epoxy alcohols. The assignments of the protons of the piperidine ring in XIII-XV, which form an $ABMX_3$ system, were confirmed by double homonuclear resonance.

The presence of intense peaks of $[M - C_2H_3O]^+$ ions, which are formed as a result of detachment of an epoxy group, is characteristic for the mass spectra of epoxy alcohols IX-XVI. A comparison of the mass spectra of the epimeric (with respect to the C_4 atom) of the epoxy compounds shows that the $[M - C_2H_3O]^+$ ion peaks have greater relative intensities in the case of IX, XI, and XIII than in the case of X, XII, and XIV (Table 3). These data are in agreement with the principles established for other 4-alkyl-trans-decahydro-4-quinolols [12] and confirm the axial orientation of the epoxy group in IX, XI, and XIII and the equatorial orientation in X, XII, and XIV. The mass spectra of epoxy alcohols XIII-XV are also distinguished by the relative intensity of the peak of $[M - CH_3]^+$ ions, which are formed as a result of detachment of a methyl group from the C_2 position: The $I_{[M - CH_3]^+}/I_{[M]^+}$ value for

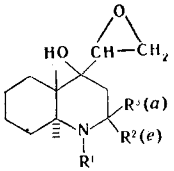
TABLE 1. PMR Spectra of 1-Alkyl-, 1,2-Dimethyl-, and 1,2,2-Trimethyl-4-vinyl-trans-decahydro-4-quinolols (I-VIII)



Compound	R^1	R^2	R^3	R_f	Configuration	δ, ppm (H_a C=C H_c H_b)			J, Hz			δ, ppm ((M)H, (X)H_3C C_2—C_3 H_a(A), H_e(B))					J, Hz			
						A	B	C	J^{cis}_{AB}	J^{trans}_{AC}	J^{gem}_{BC}	R^1*	X	M	A	B	MX	MA	MB	AB
I	CH_3	H	H	0,64	*e*	6,60	5,59	5,45	11,7	18,1	1,9	2,42	—	—	—	—	—	—	—	—
II	CH_3	H	H	0,82	*a*	6,18	5,53	5,41	11,3	18,5	1,9	2,42	—	—	—	—	—	—	—	—
III	C_2H_5	H	H	0,66	*e*	6,57	5,62	5,47	11,7	18,1	1,9	1,04	—	—	—	—	—	—	—	—
IV	C_2H_5	H	H	0,83	*a*	6,15	5,54	5,39	11,3	18,1	1,9	1,07	—	—	—	—	—	—	—	—
V	CH_3	CH_3	H	0,60	*e*	6,57	5,63	5,45	11,7	18,3	1,9	2,40	1,13	2,48	1,71	1,90	6,0	12,3	3	−13
VI	CH_3	CH_3	H	0,82	*a*	6,13	5,51	5,36	11,3	18,1	1,9	2,40	1,11	2,60	1,59	1,69	6,0	12	3	−15
VII	CH_3	H	CH_3	0,53	*a*	6,12	5,48	5,33	11,3	17,8	1,9	2,45	1,27	3,31	2,14	1,57	7,5	6	2,3	−15
VIII	CH_3	CH_3	CH_3	0,78	*a*	6,13	5,48	5,34	11,3	18,1	1,9	2,36	1,24	1,21	$\delta_{AB}=1,66$		—	—	—	−15

*The shift of the protons of only the methyl group of the R^1 substituent is presented.

TABLE 2. 1-Alkyl-, 1,2-Dimethyl-, and 1,2,2-Trimethyl-4-ethyleneoxido-trans-decahydro-4-quinolols



Compound	R^1	R^2	R^3	Configuration of 4-OH	mp, °C	R_f	δ, ppm (H_x, H_y C—C(O) H_a, H_b)			J, Hz			δ, ppm ((M) H, (X) H_3C C_2—C_3 H_a (A), H_e (B))					J, Hz				Found, %			Empirical formula	Calc., %			Yield, %
							A	B	X	AB	AX	BX[a]	R^1	X	M	A	B	MX	MA	MB	AB	C	H	N		C	H	N	
IX[b]	CH_3	H	H	*e*	136—138	0,72	2,78	2,97	3,28	6	4	2	2,31	—	—	—	—	—	—	—	—	68,4	9,8	6,5	$C_{12}H_{21}NO_2$	68,2	10,0	6,6	70
X	CH_3	H	H	*a*	147—149	0,90	2,77	2,80	2,89	4	5	3	2,30	—	—	—	—	—	—	—	—	68,5	10,2	6,6	$C_{12}H_{21}NO_2$	68,2	10,0	6,6	68
XI	C_2H_5	H	H	*e*	113—114	0,75	2,84	2,96	3,30	6	4	2	1,03	—	—	—	—	—	—	—	—	69,6	10,3	6,2	$C_{13}H_{23}NO_2$	69,3	10,3	6,2	67
XII	C_2H_5	H	H	*a*	147—149	0,94	—	—	—	—	—	—	1,05	—	—	—	—	—	—	—	—	69,1	10,5	6,2	$C_{13}H_{23}NO_2$	69,3	10,3	6,2	70
XIII	CH_3	CH_3	H	*e*	121—122	0,76	2,77	2,98	3,28	6	4	2	2,30	1,16	2,42	1,57	1,86	6	13	3	—	69,4	10,3	6,2	$C_{13}H_{23}NO_2$	69,3	10,3	6,2	69
XIV	CH_3	CH_3	H	*a*	112—113	0,88	—	—	—	—	—	—	2,30	1,10	2,43	1,59	1,57	6	10	3	14	69,3	10,2	—	$C_{13}H_{23}NO_2$	69,3	10,3	6,2	62
XV	CH_3	H	CH_3	*a*	118—119	0,66	2,69	2,72	2,81	4	5	3	2,34	1,18	3,20	2,20	1,70	7,5	6	2	14	69,3	10,2	6,2	$C_{13}H_{23}NO_2$	69,3	10,3	6,2	70
XVI	CH_3	CH_3	CH_3	*a*	129—131	0,97	—	—	—	—	—	—	2,24	1,17[c]	1,14	1,80	1,62	—	—	—	14	70,2	10,3	5,7	$C_{14}H_{25}NO_2$	70,2	10,5	5,9	72

[a] Only the shift of the protons of the methyl group of the R^1 substituent is presented. [b] The PMR spectra of IX, X, and XV were recorded with a Varian SC-300 spectrometer. The SSCC of the epoxide protons for epimeric epoxy alcohols IX and X were substantiated by homonuclear double resonance. [c] The shift of the 2-CH_3 group of 1,2,2-trimethyl-4-ethyleneoxido-trans-decahydro-4-quinolol is presented.

TABLE 3. Ratios of the Intensities of the Ion Peaks in the Mass Spectra of Epoxy Alcohols IX-XVI

Compound	$I[M-C_2H_3O]^+/I[M]^{+\cdot}$	Compound	$I[M-C_2H_3O]^+/I[M]^{+\cdot}$	$I[M-CH_2]^+/I[M]^{+\cdot}$
IX	9,0	XIII	5,5	3,0
X	7,1	XIV	5,0	3,6
XI	9,1	XV	4,2	5,0
XII	7,1	XVI	3,6	12,0

XV is greater than for XIII and XIV, which makes it possible to conclude that XV has an axial methyl substituent in the C_2 position and that XIII and XIV have an equatorial methyl substituent in the C_2 position. Thus the data obtained confirm the correspondence between the configurations of the synthesized epoxy compounds IX-XVI and the configurations of starting vinyl alcohols I-VIII.

EXPERIMENTAL

A 42-ml (0.4 mole) sample of 29% hydrogen peroxide (sp. gr. = 1.11 g/ml) was added in four 10-ml portions to a solution of 0.1 mole of the unsaturated alcohol in 70 ml of 99% formic acid (sp. gr. = 1.22 g/ml), and the mixture was maintained at 25-30°C for 4 days. The course of the reaction was followed by means of thin-layer chromatography (TLC), which was carried out on 70 × 25 mm plates with Woelm Al_2O_3 (neutral) in a chloroform—ethanol (10:1) system. The reaction mixture was then diluted with 120 ml of ice water, 120 g of finely crushed ice was added, and the mixture was neutralized with vigorous stirring with saturated ammonium hydroxide at no higher than 0°C. The base was extracted repeatedly with chloroform, and the extract was dried over magnesium sulfate. The solvent was removed *in vacuo*, and the crude product was purified to remove the starting alcohol and polymeric substances by crystallization from hexane—ethyl acetate (5:1). Compounds XI and XIV were purified by crystallization from hexane. The results of elementary analysis, the physicochemical constants, and the yields of the synthesized epoxy alcohols IX-XVI are presented in Table 2.

The IR spectra of solutions of IX-XVI were obtained with a UR-20 spectrometer. The PMR spectra of solutions (~5%) of the compounds in $CDCl_3$ were obtained with a JEOL INK-PS-100 spectrometer with tetramethylsilane as the internal standard. The mass spectra were obtained with an LKB-2091 spectrometer equipped with a system for direct introduction of the samples into the ion source at a vaporization temperature of 200°C and an ionizing-electron energy of 70 eV.

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SYNTHESIS AND AUTOOXIDATIVE TRANSFORMATION OF 2-(2-AMINOPHENYL)-4-HYDROXY-3-PHENYL-1-ISOQUINOLONE

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and S. P. Valter

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2-(2-Aminophenyl)-4-hydroxy-3-phenyl-1-isoquinolone was unexpectedly obtained in the reaction of 3-(α-bromobenzyl)-3-bromophthalide with o-phenylenediamine. The isoquinolone in chloroform undergoes autooxidation by air oxygen to give 2-(2-aminophenyl)-3-hydroperoxy-3-phenyl-1,4-dioxo-1,2,3,4-tetrahydroisoquinoline, which is subsequently converted to N-(2-benzamidophenyl)phthalimide. A mechanism is proposed for the rearrangement of the hydroperoxide.

It is known [1-3] that 3-substituted 3-halophthalides react with aromatic amines to give two series of derivatives, viz., 3-aminophthalides and 3-hydroxyisoindolinones. The aim of the present research was to investigate the reaction of 3-(α-bromobenzyl)-3-bromophthalide (I) with o-phenylenediamine. It has been shown [4] that the reactions of phthalide I with alkylamines and aniline lead to N,N'-disubstituted 2-α-aminophenylacetylbenzamides. However, it was established by a spectroscopic reinvestigation that these compounds have the ring structure of 3-α-aminobenzyl-3-hydroxyisoindolinones [5].

It might be assumed that primary nucleophilic attack on the phthalide I molecule by o-phenylenediamine would take place at the $C{=}O$ group and that subsequent cyclization would lead to ten-membered heteroring II or, which is more likely, to its isomers III and IV. The possible products of this reaction (II-V) can undergo interisomerization due to intramolecular reversible reactions involving nucleophilic addition of the $N{-}H$ group to the $C{=}O$ bond. A number of products with different structures can be formed as a result of the less probable primary nucleophilic attack at the $C{-}Br$ bonds in the I molecule.

It turned out unexpectedly that 2-(2-aminophenyl)-4-hydroxy-3-phenyl-1-isoquinolone (VI) is formed in good yield when the reaction between equimolar amounts of phthalide I and o-phenylenediamine is carried out in refluxing dioxane in the presence of triethylamine.

Isoquinolone VI is soluble in both acids and alkilis. An NH band (3395 cm^{-1}), a broad OH band (3230 cm^{-1}), and bands at 1654, 1621, and 1578 cm^{-1} are observed in the IR spectrum of crystalline VI (Fig. 1); this is in good agreement with the literature data [6-8] for 2-substituted 4-hydroxy-3-phenyl(or alkyl)-1-isoquinolones.

The problem of the assignment of these bands is not clear-cut [8], since the band at 1578 cm^{-1} is the most intense band in the spectrum of the crystalline substance (see Fig. 1). Such a low frequency does not make it possible to assign this band to the absorption of the $C{=}O$ group of the isoquinolone. The presence of a very wide band at 3230 cm^{-1} provides a basis for the assumption that strong $C{=}O...H{-}O{-}$ intermolecular hydrogen bonds exist in the crystalline state and that this in turn may lead to redistribution of the electron density in the

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