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REDUCTION OF ENAMINES OF THE 3,3-DIALKYL-3,4-DIHYDROISOQUINOLINE SERIES

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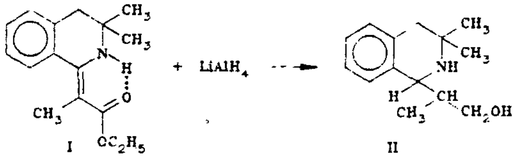
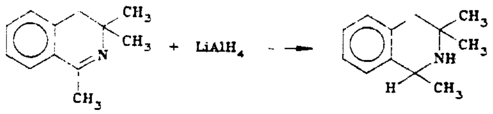
Lithium aluminum hydride reduced enamines of the 3,3-dialkyl-3,4-dihydroisoquinoline series to the corresponding tetrahydroisoquinolines. In the presence of a hydrogen atom at the β-carbon atom of the enamino ester the action of lithium aluminum hydride and alkylmagnesium bromide leads to the products from the condensation of two molecules of the initial compound.

Lithium aluminum hydride effectively reduces enamines, but various reaction products are formed, depending on the presence and the nature of the substituents [1]. This reaction has been studied in the series of α-(1,2,3,4-tetrahydro-1-isoquinolylidene) carboxylic esters [2]. We reproduced it as applied to enamines of the 3,3-dialkyl-3,4-dihydroisoquinoline series. Here it was found that ethyl α-(3,3-dimethyl-1,2,3,4-tetrahydro-1-isoquinolylidene)propionate (I) is reduced by an excess of the reagent to 2-(3,3-dimethyl-1,2,3,4-tetrahydro-1-isoquinolyl)propanol (II):



I II

Similarly, 1,3,3-trimethyl-3,4-dihydroisoquinoline (III), which exhibits the characteristics of an enamine, is converted by the action of lithium aluminum hydride into 1,3,3-trimethyl-1,2,3,4-tetrahydroisoquinoline (IV):



III IV

The structures of compounds (II) and (IV) are confirmed by the data from IR and PMR spectroscopy. The IR spectrum of (II) contains absorption bands due to the stretching vibrations of the O–H and N–H bonds at 3640 and 3340 cm^{-1}, respectively. The stretching vibrations of the N–H bond in the spectrum of (IV) are at 3210 cm^{-1}. In both cases there is no absorption characteristic of the initial compounds [3] in the region of 1800-1600 cm^{-1}. The PMR spectra are given in Table 1.

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TABLE 1. PMR Spectra of Compounds (II, IV, VII)

Compound	δ, ppm (in $CDCL_3$)				
	CH_3	CH_2	CH	NH (s)	ArH (m)
II*	0,85 d, 3H 1,05 s, 3H 1,22 s, 3H	—†	—†	—†	6,82—7,38, 4H
IV‡	1,00 s, 3H 1,17 s, 3H 1,37 d, 3H	2,03 s, 2H	3,70—4,20 m, 1H	2,53, 1H	6,80—7,10, 4H
VII	1,20 s, 12H 1,20 t, 6H	2,68 s, 4H; 4,00 q, 4H	4,98 s, 1H	8,88, 1H	6,90—7,60, 8H

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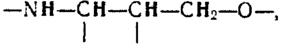
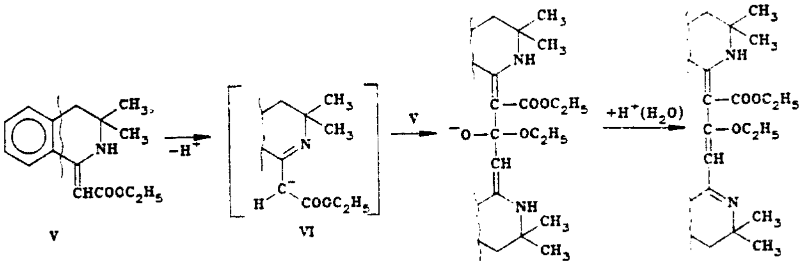
*δ_{OH} 4.28 ppm (s, 1H).

†Part of the spectrum in the range of 2.15-4.08 ppm has a complex form and cannot be interpreted by the usual methods. The overall integral intensity of this group of signals corresponds to 7H. It clearly contains the AB quartet of the 2H at the $C_{(4)}$ atom of the heterocycle and also the signals for the  $-NH-\underset{|}{C}H-\underset{\underset{CH_3}{|}}{C}H-CH_2-O-$, protons, which form a complex multispin system.

‡With the addition of trifluoroacetic acid the signal for the protons of the methylene group is transformed into an AB quartet with chemical shifts of 2.53 and 3.18 ppm, respectively.

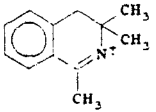
The action of lithium aluminum hydride on ethyl (3,3-dimethyl-1,2,3,4-tetrahydro-1-isoquinolylidene)acetate (V) leads to an unexpected result. Compound (VII), i.e., the product from the condensation of two molecules of the initial ester (V), is formed as the main reaction product. The action of Grignard reagents leads to the same condensation. It is clear that these reactions have an identical scheme. The key stage is the generation, from compound (V), of a nucleophilic mesomerically stabilized anion (VI), which is readily capable of reacting with unreacted molecules of the initial ester. Both lithium aluminum hydride and Grignard reagents, which are capable of combining with a proton irreversibly, are suitable for this purpose.



V VI VII

The reaction is also interesting in that an excess of the Grignard reagent (C_2H_5MgBr) remains throughout the process (with the direct order of addition of the reagents), but the second stage of the reaction, i.e., nucleophilic attack by the anion (VI) on the carbonyl carbon atom of the neutral molecule of the ester (V), is realized successfully even under these conditions. This means, first, that the first stage of the reaction takes place so slowly that a significant part of compound (V) is present in the reaction mixture in unchanged form; second, the affinity of the obtained anion (VI) to the carbonyl carbon atom of the ester group in compound (V) is higher than that of ethylmagnesium bromide. The mesomeric anion (VI) is a softer nucleophile than ethylmagnesium bromide and reacts significantly more quickly with the neutral molecules of the ester (V). This agrees well with previously published data on the reactivity of ethyl (3,3-dimethyl-1,2,3,4-tetrahydro-1-isoquinylidene)acetate toward nucleophilic reagents [4].

In order to determine the structure of (VII) we recorded its IR, PMR, and mass spectra and obtained an elemental analysis. The purity was checked by TLC in a 9:1 mixture of chloroform and acetone followed by development with a benzene solution of chloranil. The IR spectra contain absorption bands at 3280 and 1650 cm^{-1}, due to the stretching vibrations of the N—H and C═O bonds involved in the formation of an intramolecular hydrogen bond. A strong band at 1615 cm^{-1} .corresponds to the stretching vibrations of the conjugated C═C and C═N bonds. The PMR spectrum is given in Table 1. In the mass spectrum there is a molecular ion peak at 473,* but the peak of the $[M + H]^+$ (474) ion has significantly higher relative intensity, as is often observed in the spectra of nitrogen-containing compounds [5]. In addition, the spectrum contains peaks for the $[M - 15]^+$, $[m - 43]^+$, $[M - 44]^+$, and $[M - 115]^+$ ions with relative intensities of 2-3% and peaks for the $[M - 173]^+$ and $[M - 273]^+$ ions with relative intensities of 6-7%. The peaks for the ions 173 (56%) and 158 (81%), present in all the mass spectra of the 1-substituted 3,3-dimethyl-3,4-dihydroisoquinolines, have high relative intensity, and their most likely structures are the following:



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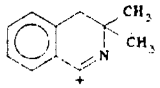

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EXPERIMENTAL

The PMR spectra were recorded on an RS-60 instrument at 60 MHz in deuterochloroform solutions with TMS as internal standard. The IR spectra were recorded on a UR-20 spectrometer (0.01 M) in carbon tetrachloride. The mass spectra were recorded on a Varian MAT-600 instrument at 70 eV at 170 and 200°C.

2-(3,3-Dimethyl-1,2,3,4-tetrahydro-1-isoquinolyl)propanol (II). To a mixture of 10 mmole of the ethyl ester (I) in 10 ml of absolute ether with vigorous stirring we added a solution of 10 mmole of lithium aluminum hydride in ether. The reaction mass was boiled with constant stirring for 4 h and decomposed with water. The precipitate was washed thoroughly with ether (5 × 100 ml), and the combined ether extracts were dried with magnesium sulfate and filtered. The ether was distilled, and the residue was recrystallized from carbon tetrachloride. The yield was 68%, mp 85-86°C. Hydrochloride, mp 185-187°. Found, %: C 76.8, H 9.7, N 6.3. $C_{14}H_{21}NO$. Calculated, %: C 76.7, H 9.6, N 6.4

Compound (IV) was obtained similarly and was isolated in the form of the salicylate. The yield was 71%; mp 204.5-205.5°C (from acetone). Found, %: C 82.2, H 9.8, N 8.0. $C_{12}H_{17}N$. Calculated, %: C 82.2, H 9.9, N 8.0.

Ethyl 4-(3,3-Dimethyl-3,4-dihydro-1-isoquinolyl)-2-(3,3-dimethyl-1,2,3,4-tetrahydro-1-isoquinolylidene)-3-ethoxy-3-butenoate (VII). The compound was obtained similarly. The oil obtained after distillation of the ether was dissolved in 3 ml of acetone and placed in a chromatographic column filled with calcined aluminum oxide. The product was eluted with acetone, and the fraction not containing the initial compound (V) was collected. The process was controlled by TLC in a 9:1 mixture of chloroform and acetone; R_f 0.65. The yield of (VII) was 62%. Found, %: C 76.4, H 7.7, N 5.9. $C_{30}H_{36}N_2O_3$. Calculated, %: C 76.2, H 7.7, N 5.4.

The reaction with the Grignard reagent was carried out by the usual procedure, and the products were separated by chromatography as indicated above.

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LUMINESCENCE SPECTRAL CHARACTERISTICS OF 1-(3-BUTENYL)-3-ARYLBENZO[f]QUINOLINES

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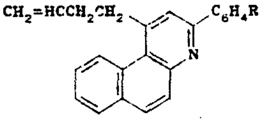
The effect of the nature of the substituents and the solvent on the absorption and fluorescence spectra and on the fluorescence quantum yield was studied in the series of 1-(3-butenyl)-3-arylbenzo[f]quinolines.

Earlier we investigated the spectral characteristics of a whole series of derivatives of benzo[f]quinoline and showed that many of them luminesce strongly in solutions [1, 2]. While continuing a study into the effect of structural factors on the luminescence spectral characteristics in the series of benzo[f]quinoline derivatives, we investigated the absorption and fluorescence spectra and the fluorescence quantum yields of 1-(3-butenyl)-3-arylbenzo[f]quinolines (I-V):



I-V

I R=H; II R=*p*-OCH$_3$; III R=*p*-F; IV R=*p*-Br; V R=*o*-OH

The bases (I-V) were obtained by the condensation of arylidene-2-naphthylamines with allylacetone in the presence of a protic catalyst [3]. The electronic absorption spectra of 1-(3-butenyl)-3-arylbenzo[f]quinolines have the form typical of the spectra of benzo[f]quinoline derivatives [1] and are characterized by three absorption bands: β (279-285 nm), p (294 nm), and α (345-370 nm) bands. The long-wave band has vibrational structure. The introduction of substituents R (Table 1) increases the intensity of all the absorption bands without having an appreciable effect on their positions. The exception is the hydroxyl group, which is at the ortho position of the phenyl ring and gives rise to a bathochromic shift of the α band with a simultaneous increase in its intensity.

The 1-(3-butenyl)-3-arylbenzo[f]quinolines luminesce strongly in solutions. The fluorescence spectra of the compounds show clearly defined vibrational structure (Table 1). They have mirror symmetry in the long-wave absorption band and lie in the UV region (λ_{max} ~370-400 nm). The Stokes shift of the fluorescence band amounts on the average to 30 nm. The substituents at the para position of the phenyl ring lead to a bathochromic shift of the fluorescence band in all the investigated solvents. The quantum yields of fluorescence for compounds (I-V) vary within wide limits (between 15 and 68%), and this is due to the different nature of the solvent. Thus, by changing the probability of singlet—triplet conversion, halogens reduce the quantum yield of fluorescence, and the quenching effect becomes stronger with increase in the atomic number of the halogen [4]. For instance, the quantum yield of luminescence for compound (IV) (R = Br) is half the quantum yield for fluorobenzo[f]quinoline (III). Such a decrease in the intensity can be explained by the increase in the weight of the radical and the associated loss of energy on the intramolecular vibrations. The fluo-

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