REACTIONS OF 1,2-DIHYDROQUINOLINES

III.* ADDITION OF BENZENE AND HALOBENZENES TO THE DOUBLE BOND OF 2,2,4-TRIMETHYL-1,2-DIHYDROQUINOLINES

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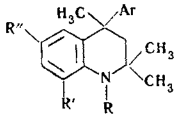
The addition of benzene to 2,2,4-trimethyl-1,2-dihydroquinoline (I) in the presence of $AlCl_3$ requires prior protonation or acylation of the amino group. Electron-donor substituents in the benzene ring of I hinder the reaction. The addition of halobenzenes proceeds under more severe conditions to give only para-substituted 4-aryl-2,2,4-trimethyl-1,2,3,4-tetrahydroquinolines.

We have previously shown that the hydrochloride or N-acetyl derivative of 2,2,4-trimethyl-1,2-dihydroquinoline (I) in the presence of anhydrous aluminum chloride add benzene [1] or alkylbenzenes [2] at the carbon–carbon double bond to form 4-aryl-2,2,4-trimethyl-1,2,3,4-tetrahydroquinolines (II). In this research we have made an additional study of this reaction. It turned out base I itself does not add benzene, even when excess aluminum chloride is used at room temperature, but gives dimerization and polymerization products on heating, while the hydrochloride or N-acetyl derivatives add benzene at room temperature after a few minutes. (Compound I is no longer detected by chromatography, and a spot of II appears.) The reaction barely proceeds at all when $AlCl_3$ is replaced by iron or zinc chlorides or when strong mineral acids are used. Illumination with UV light does not initiate the reaction. Solvents such as diethyl ether, nitromethane, dibutyl ether, or nitrobenzene that are capable of giving stable complexes with $AlCl_3$ inhibit the reaction. The introduction of a benzoyl group rather than on acetyl group into the 1-position or the in-

TABLE 1. 2,2,4-Trimethyl-4-aryl-1,2,3,4-tetrahydroquinolines

				Mp, °C	λ_{max}, nm	lg ε	Reaction time	Empirical formula	Found, %		Calc., %		Yield, %
R	R′	R″	Ar						C	H	C	H	
C_6H_5CO	H	H	C_6H_5	141—142	—	—	0,5	$C_{25}H_{25}ON$	84,64	7,01	84,46	7,08	85
CH_3CO	H	CH_3	C_6H_5	132—133	—	—	0,25	$C_{21}H_{25}ON$	82,29	8,28	82,04	8,20	90
CH_3CO	CH_3	CH_3	C_6H_5	153—154	249	4,53	0,25	$C_{22}H_{27}ON$	82,24	8,43	82,17	8,46	92
H	H	H	C_6H_4Cl	66—67	—	—	1,0	$C_{18}H_{20}ClN$	75,45	7,17	75,64	7,05	60
H	CH_3	CH_3	C_6H_4F	114—115	—	—	5,0	$C_{20}H_{24}FN$	80,81	8,15	80,77	8,13	76
H	H	H	C_6H_4Br	91—92	256 305	4,16 3,56	5,0	$C_{18}H_{20}BrN$	65,15	6,11	65,45	6,10	62
CH_3CO	H	H	C_6H_4Br	179—180	—	—	5,0	$C_{20}H_{22}OBrN$	64,51	6,06	64,51	5,96	63
H	CH_3	H	C_6H_4Br	120—121	—	—	5,0	$C_{19}H_{22}BrN$	66,16	6,40	66,28	6,44	75
H	CH_3	CH_3	C_6H_4Br	95—96	310	3,57	5,0	$C_{20}H_{24}BrN$	67,10	6,74	67,03	6,75	62
CH_3CO	H	CH_3O	C_6H_5	119—120	—	—	48,0	$C_{21}H_{25}O_2N$	78,15	7,95	77,98	7,89	80

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*See [1,2] for communications I and II.

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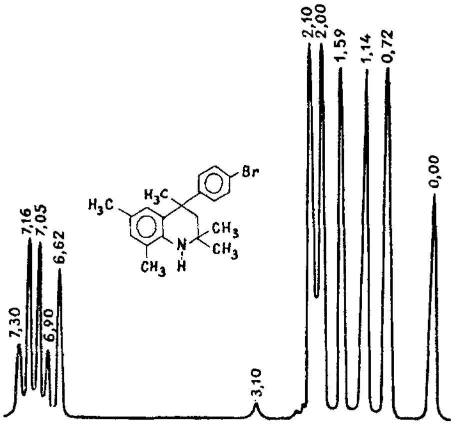
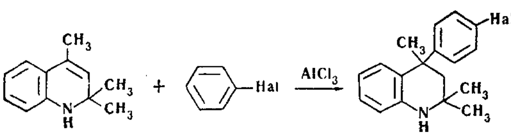


Fig. 1. PMR spectrum of 2,2,4,6,8-pentamethyl-4-(p-bromophenyl)-1,2,3,4-tetrahydroquinoline (III).

troduction of a methyl group into the benzene ring of the dihydroquinoline only slightly inhibits the reaction. However, a methoxyl group in the 6-position substantially inhibits the reaction by weakening the polarization of the double bond. Base I apparently forms a stable complex with $AlCl_3$, in which both the nitrogen atom and the carbon–carbon double bond can serve as donor groups. As is well known [3], the formation of stable complexes blocks many reactions of aromatic amines in the presence of $AlCl_3$. Protonation or acylation intensifies the polarization of the carbon–carbon double bond which, as is usually the case in the alkylation of the aromatic ring by olefins [3], initially adds a proton from $HAlCl_4$ with subsequent electrophilic attack by the resulting cation on the aromatic ring. The electrophilicity of this cation is intensified through the effect of the $AlCl_4^-$ gegenion, but it is still not very high. In particular, dihydroquinoline I does not add aromatic compounds with electron-acceptor substituents but is sufficiently reactive for reaction with halobenzenes. We synthesized a number of compounds of the II type using this route (see Table 1). A CH_3 group in the 4-position of the dihydroquinoline provides a considerable steric effect, and the reaction therefore proceeds with a pronounced para orientation. In fact, we were unable in any case to detect admixture of an isomeric compound.



I

II

The structure of II was established by means of PMR spectra. To exclude the superimposition of the signals of the H atoms of the halophenyl group on the signals of the aromatic group of the phenylene residue, we synthesized 2,2,4,6,8-pentamethyl-4-(p-bromophenyl)-1,2,3,4-tetrahydroquinoline (III) via a similar route. The signals at 0.72 and 1.14 ppm in the PMR spectrum (Fig. 1) of this compound are related to the gem methyl groups, which have different chemical shifts as a result of the effect of the phenyl ring in the 4-position. The signal at 1.59 ppm is related to the methyl group in the 4-position. The absence of splitting of this signal indicates that the phenyl group is attached to the same carbon atom. The peaks at 2.00 and 2.10 ppm are assigned to the methyl groups bonded to the aromatic ring. Unresolved signals of the H_5 and H_7 protons are observed at 6.62 ppm. The two doublets of the interacting protons of the bromophenyl group with chemical shifts of 6.90, 7.05, 7.16, and 7.30 ppm unambiguously indicate the para orientation of the halogen.

EXPERIMENTAL

The PMR spectra in carbon tetrachloride with hexamethyldisiloxane as the internal standard were recorded by V. A. Budylin with an RS-60 spectrometer with an operating frequency of 60 MHz. The purity of the substances was monitored by chromatography in a thin layer of aluminum oxide [benzene–ethanol (9 : 1), development with UV light].

4-Aryl-2,2,4-trimethyl-1,2,3,4-tetrahydroquinolines. Anhydrous aluminum chloride (0.05 mole) was added to a suspension of 0.025 mole of the hydrochloride (or 1-acyl derivative) of 2,2,4-trimethyl-1,2-dihydroquinoline in 50 ml of aromatic hydrocarbon or halobenzene, and the mixture was shaken at room temperature. At the end of the reaction (as monitored by thin-layer chromatography) which, depending on the reagents, takes several minutes to 5 h, ice was added to the mixture. After decomposition of the complex, the organic layer was separated, and the aqueous layer was extracted with ether. The extracts were combined, washed with a weak solution of alkali and water, and dried with sodium carbonate. The solvent was removed by distillation, and the residue was crystallized from ethanol or, in individual cases, from heptane. The constants and yields of the compounds obtained are presented in Table 1.

LITERATURE CITED

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3. G. A. Olah, Friedel-Crafts and Related Reactions, Vol. 2, New York (1964), Chap. 14.