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ARYLIDENEHYDROACRIDINES FROM DI(3-ARYLIDENE-2-OXOCYCLOHEXYL)METHANES

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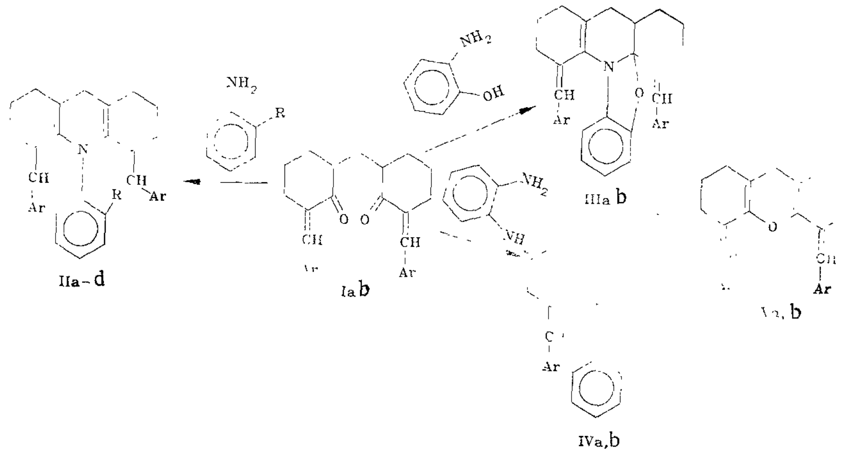
The reaction of di(3-benzylidene-2-oxocyclohexyl)methane and its p-methoxy analog with primary amines results in the formation of derivatives of 4,5-diarylidenehydroacridines, whereas the reaction with o-phenylenediamine is accompanied by the elimination of one arylidene group and gives derivatives of 4-arylidenehydroacridines.

The investigation of α,α'-diarylidene 1,5-diketones [1] is of interest for the synthesis of heterocyclic compounds containing arylidene groups, which have useful, in particular, fluorescence properties [2].

We studied the reaction of di(3-benzylidene-2-oxocyclohexyl)methane (Ia) and its-p-substituted analog Ib with several aromatic amines, which takes place at the carbonyl groups. In all cases, the reaction proceeds with greater difficulty than in the case of diketones without arylidene groups [3, 4] and, as a rule, does not go to completion. Di(3-cyclohexylidene-2-oxocyclohexyl)methane [5], in which the degree of conjugation is smaller and the shielding of the carbonyl group is greater than in diketones Ia and b, according to our data, scarcely reacts with aniline and o-phenylenediamine.



I, III—V a $Ar=C_6H_5$; b $Ar=C_6H_4OCH_3$-p; II a R=H, $Ar=C_6H_5$; b R=H, $Ar=C_6H_4OCH_3$-p; c $R=OCH_3$, $Ar=C_6H_5$; d $R=OCH_3$, $Ar=C_6H_4OCH_3$-p

The products of the reactions of diketones Ia and b with aniline and o-anisidine are

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4,5-diarylidene-1,2,3,4,5,6,7,8,9,10-decahydroacridines (IIa-d), and the products of the reactions with o-aminophenol and o-phenylenediamine are derivatives of benzazolinododecahydroacridines (III and IV). The elimination of the benzylidene group occuring upon the formation of compounds IV was previously noted as a secondary reaction in the condensation of 2-benzylidene-6-(2'-oxocyclohexylmethyl)cyclohexanone with ammonia [6]. Such a result is probably attributable to the priliminary addition of the nitrogenous nucleophile across the C=C bond followed by a reversed Mannich reaction, which often takes place under the conditions employed [7]. The reaction of α,β-unsaturated ketones with o-phenylenediamine is known to take place both at the C=O bond and at the C=C bond and gives 1,5-benzodiazepines [8]. This can also occur in our case, and the decomposition of such a derivative with the elimination of benzaldehyde creates a favorable situation for the closure of an azoline ring, which results in the formation of compounds of type IV.

The IR spectra of compounds II-IV do not contain the absorption bands of carbonyl groups characteristics of the spectra of diketones Ia and b [1]. the absorption bands of the C=C bonds have low intensities and appear in the vicinity of 1630 cm^{-1}, but in the spectra of compounds IIa, c, and d they are scarcely observed. In the spectra of compounds IIb and d and IIIb there are also weak bands in the vicinity of 1670 cm^{-1}, which are probably overtones. The spectra of compounds IIIa and b do not contain absorption bands for the OH group, and the spectra of compounds IVa and b show a single absorption band for a secondary amino group near 3400 cm^{-1}.

In the PMR spectra of the compounds synthesized the signals of the benzylidene protons are found at 6.5-7.6 ppm and are sometimes overlapped by the signals of the aromatic protons. In the spectrum of compound IIIb there are two singlets for the OCH_3 groups at 3.80 and 3.84 ppm, while the spectrum of IVb shows only one singlet (3H) at 3.80 ppm.

According to the mass-spectrometric data, the values for the molecular ions correspond to the calculated molecular weights. Intense peaks for the fragment ions with $m/z = M - 1$ are observed, as is characteristic of the mass-spectrometric fragmentation of 1,4-dihydropyridines [9]. The mass spectra of compounds IIa, IIc, IIIa, and IVa contain peaks of fragment ions with $m/z = M - 91$, and the spectra of compounds IIb, IId, IIIb, and IVb contain peaks of fragmentions with $m/z = M - 121$, which correspond to the elimination of benzyl and p-methoxybenzyl groups, respectively, from the molecular ion.

Compounds II-IV undergo hydrolysis in acidic media. This is characteristic of dihydropyridines [9]. In this case, compounds II and III form octahydroxanthene derivatives Va and b [1], and compounds IV form an unidentified mixture.

EXPERIMENTAL

The IR spectra were recorded on a Specord JR-75 spectrometer in liquid petrolatum and in chloroform, and the PMR spectra were recorded on a Bruker HX-90E spectrometer (90 MHz) in $CDCl_3$ with TMS as an internal reference. The mass spectra were obtained on an LKB-9000 instrument with an ionization energy equal to 90 eV. The occurrence of the reactions and the purity of the products obtained were monitored by TLC on Silufol plates.

Reactions of Diketones Ia and b with Primary Amines. A mixture of 5 mmole of diketone I, 10 mmole of the amine, and 50 mg of p-toluenesulfonic acid in 60 ml of xylene is boiled with a Dean-Stark trap for 12 h until the evolution of water vapor ceases. According to the TLC data, the reaction mixture contains the corresponding hydroacridine, unreacted diketone I, and the amine, as well as octahydroxanthene derivative V.

A. To obtain compounds IIc, IIIa, IIIb, IVa, and IVb, the xylene is distilled off from the reaction mixture at reduced pressure, the residue is treated with 20 ml of ethanol, and the crystallized reaction product is filtered out. In the cases of IIIa, IIIb, IVa, and IVb, the latter is the almost pure hydroacridine, and in the case of IIc, it is a mixture of the unreacted diketone Ia and the hydroacridine. The unreacted diketone I precipitates from the ethanolic filtrate after the separation of the crystals in the cases of IIc and IVd and standing for 24 h. The mixture of compounds IIc and Ia is separated by recrystallization from ethanol: Diketone Ia precipitates first, and then hydroacridine IIc precipitates when the filtrate is allowed to stand.

B. To obtain compounds IIa, b, and d the mixture is cooled, the precipitated unreacted diketone I is filtered out, the xylene is evaporated from the filtrate at reduced pressure,

TABLE 1. Properties of Compounds Synthesized

Compound	mp, *°C	Found, %			Empirical formula	Calculated, %			Yield, %
		C	H	N		C	H	N	
IIa	197—198	89,8	7,0	3,5	$C_{33}H_{31}N$	89,8	7,0	3,2	35 (58)
IIb	207—208	83,5	6,9	2,7	$C_{35}H_{35}NO_2$	83,8	7,0	2,8	26 (50)
IIc	167—169	86,2	7,5	2,7	$C_{34}H_{35}NO$	86,6	7,0	3,0	8 (40)
IId	176—177	81,4	7,1	2,5	$C_{36}H_{37}NO_3$	81,4	7,0	2,6	6 (33)
IIIa	197—199	86,7	6,9	3,0	$C_{33}H_{31}NO$	86,7	6,8	3,1	55
IIIb	184—185	81,3	6,7	2,7	$C_{35}H_{35}NO_3$	81,2	6,8	2,7	52
IVa	176—177	84,8	7,6	7,6	$C_{26}H_{28}N_2$	84,8	7,6	7,6	50
IVb	173—174	81,5	7,5	7,3	$C_{27}H_{30}N_2O$	81,4	7,5	7,0	53 (61)

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*Compounds IIa and b were recrystallized from a 1:1 ethanol—DMFA mixture, IIc, IId, IIIb, and IV are recrystallized from propanol.

Hydrolysis of Derivatives of Arylidenehydroacridines II-IV. A mixture of 50 mg of the hydroacridine, 1 ml of dioxane, and 0.3 ml of conc. HCl is heated in a water bath for 1 h. In the case of compounds II and III, a characteristic brightly colored spot for the corresponding hydroxanthene of type V is identified on the TLC plate, and in the case of compounds IVa and b, these spots are not detected.

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