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SYNTHESIS AND SPECTRAL CHARACTERISTICS OF 1,4-DIARYL-2- ARYLIDENEBENZHYDRAZIDINES

B. I. Buzykin, N. G. Gazetdinova, S. K. Yakupova,
A. P. Stolyarov, Z. S. Titova, and Yu. P. Kitaev

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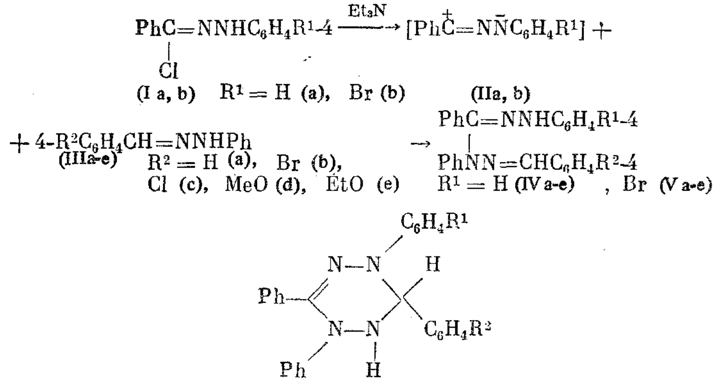
Hydrazidines are used extensively in the synthesis of nitrogen heterocycles, complexones, and analytical reagents [1-5]. Nevertheless, there are many groups of hydrazidines which are represented by only one or two compounds [1]. For instance, 1,4-diphenyl-2-benzylidenebenzhydrazidine (IVa), obtained by the mild oxidation of benzaldehyde phenylhydrazone (IIIa) [6, 7], is the sole representative of its group. It is noteworthy that anisaldehyde and tolualdehyde phenylhydrazones fail to form arylidenebenzhydrazidines under these conditions.

It has recently been shown [2] that the hydrazidine (IVa) is obtained by the reaction between the hydrazone (IIIa) and C,N-diphenylnitrilimine (IIa) by 1,3-addition. In order to evaluate the synthetic possibilities of this route, we have examined the reaction of the hydrazones (IIIa-e) with the nitrilimine (IIa) and C-phenyl-N-(4-bromophenyl)nitrilimine (IIb), generated from benzoyl chloride phenyl- and 4-bromophenylhydrazones (Ia, b) by treatment with triethylamine.

The reactions of the nitrilimines (IIa, b) with phenylhydrazones (IIIa-e) did not proceed cleanly, resulting in low yields of the desired products (Table 1). The compositions of the reaction mixtures were not examined in detail, and only in the synthesis of the hydrazidine (Va) was the 1,3-diphenylbenzo-1,2,4-triazinyl radical (VI) isolated, identical with the compound described in [2].



(VIII)

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1588-1593, July, 1983. Original article submitted September 20, 1983.

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TABLE 1. Properties of Hydrazines (IVa-e) and (Va-e)

Hydrazine	R^1	R^2	Mp, degC	Yield, %	Molecular formula	Found/calculated			ν NH, cm^{-1}		δ NH, cm^{-1}	
						C	H	N	vaseline	CCl_4	dioxane	DMSO
(IVa)	H	H	203–205	29	$C_{26}H_{22}N_4$ [2]	–	–	–	3312[a]	3322[b]	9,07	9,93
(IVb)	H	Br	159–161	16	$C_{26}H_{21}BrN_4$	66,77/66,52	4,63/4,48	11,79/11,94	3234	3324[c]	9,01	10,13
(VIc)	H	Cl	158–160	14	$C_{26}H_{21}ClN_4$	73,27/73,50	4,90/4,94	12,95/13,19	3235	3324[d]	9,98	10,08
(IVd)	H	MeO	148–150	32	$C_{27}H_{24}N_4O$	77,27/77,14	5,72/5,71	13,25/13,33	3245	3324	8,87	10,10
(IVe)	H	EtO	112–114	16	$C_{28}H_{26}N_4O$	77,77/77,42	6,00/5,99	12,74/12,90	3240	3324	9,01	10,05
(Va)	Br	H	147–149	9	$C_{26}H_{21}BrN_4$	66,73/66,52	4,42/4,48	11,81/11,94	3235	3324	9,03	–
(Vb)	Br	Br	170–172	27	$C_{26}H_{20}Br_2N_4$	56,72/56,93	3,67/3,65	10,16/10,22	3243	3324	9,03	10,22
(Vc)	Br	Cl	163–165	33	$C_{26}H_{20}BrClN_4$	61,80/61,96	4,06/3,97	11,23/11,12	3237	3324	9,09	–
(Vd)	Br	MeO	150–152	29	$C_{27}H_{23}BrN_4O$	64,80/64,93	4,50/4,61	11,01/11,22	3240	3324[e]	9,06	10,21
(Ve)	Br	EtO	148–150	29	$C_{28}H_{25}BrN_4O$	65,69/65,49	4,98/4,87	10,88/10,91	3235	3324	9,05	10,24

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[a] Together with a low-intensity band at 3327 cm^{-1}. [b] In dioxane, 3240 cm^{-1}, $CHCl_3$ 3320 cm^{-1}, benzene 3312 cm^{-1}. [c] In $CHCl_3$ 3322 cm^{-1}. [d] In dioxane 3260 cm^{-1}, benzene 3292 cm^{-1}. [e] In dioxane 3262 cm^{-1} with a shoulder at 3232 cm^{-1}.

TABLE 2. Spectral Characteristics of Arylhydrazones (Ia, b) and (IIIa-f) $4\text{-}R^2\text{–}C_6H_4\text{–}C(R^3)\text{=}NNH\text{–}C_6H_4\text{–}R^1\text{-}4$

Hydrazone	R^1	R^2	R^3	Mp, deg C	ν NH, cm^{-1}			δ NH, ppm		λ_{max}, nm (log e), ethanol
					vaseline	CCl_4	dioxane	dioxane	DMSO	
(Ia)	H	H	Cl	130–131	3310	3338	3270	8,67	9,85	333(4,33), 295(4,03), 234(4,22)
(Ib)	Br	H	Cl	121–122	3315	3336	3265	8,76	9,99	338(4,30), 304(4,15), 240(4,13)
(IIIa)	H	H	H	157–158	3315	3335	3280	8,68	10,26	347(4,38), 304(4,08), 237(4,15)
(IIIb)	H	Br	H	116–117	3304	3335	3270	8,84	10,39	357(4,42), 305(4,00), 244(4,20)
(IIIc)	H	Cl	H	127–128	3309	3336	3270	8,83	10,37	356(4,39), 304(4,01), 244(4,18)
(IIId)	H	MeO	H	120–121	3312	3336	3275	8,41	10,04	348(4,40), 305(4,22), 246(4,11)
(IIIe)	H	EtO	H	118–119	3312	3335	3276	8,30	9,99	349(4,39), 304(4,21), 245(4,10)
(IIIf)	Br	H	H	128–129	3313	3338	3272	8,71	10,37	350(4,43), 316(4,24), 240(4,12)

TABLE 3. UV Spectra of Hydrazines (IVa-e) and (Va-e), λ_{max}, nm (log ε)

Hydrazine	Ethanol	Dioxane	Acetonitrile
(IVa)	339(4,55), 297(4,26), 242(4,49)	337(4,57), 296(4,27), 243(4,52)	339(4,55), 297(4,26), 242(4,49)
(IVb)	346(4,35), 255(4,23), 224(4,44)	350(4,32), 258(4,19), 224(4,45)	347(4,33), 257(4,20), 223(4,42)
(IVc)	346(4,42), 253(4,27), 246(4,29)[a], 223(4,46)	351(4,30), 258(4,16), 224(4,39)	346(4,33), 255(4,18), 223(4,40)
(IVd)[b]	341(4,53), 298(4,28), 245(4,40), 232(4,41)	343(4,46), 296(4.17), 247(4,32), 228(4,37)	341(4,41), 295,(4,15), 286(4,14), 245(4,28)[a] 227(4,36)
(IVe)	341(4,41), 294(4,14), 246(4,30), 227(4,36)	349(4,36), 253(4,18), 227(4,36)	351(4,39), 261(4,26), 227(4,44)
(Va)	352(4,41), 226(4,19), 226(4,27)	354(4,40), 266(4,21), 227(4,31)	354(4,38), 267(4,19), 223(4,31)
(Vb)	350(4,39), 263(4,21), 225(4,42)	351(4,38), 255(4,20), 225(4,43)	350(4,38), 267(4,22), 222(4,43)
(Vc)	351(4,34), 263(4,18), 224(4,40)	351(4,39), 265(4,20), 224(4,44)	351(4,37), 265(4,22), 222(4,41)
(Vd)	349(4,42), 263(4,18), 225(4,36)	352(4,40), 268(4,22), 225(4,42)	341(4,51), 295(4,26), 264(4,20)[a], 245(4,32), 226(4,40)
(Ve)	349(4,44), 267(4,21), 225(4,39)	352(4,41), 267(4,24), 225(4,44)	341(4,50), 297(4,26), 245(4,31), 226(4,38)

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[a] Shoulder.

[b] Mixture of acicular and prismatic crystals on attaining equilibrium.

The hydrazidines (IVb-e) and (Va-e) were crystalline solids, usually colorless or pale cream in color.

Attention is drawn to the fact that in the IR spectra (solid phase) in the case of the unsubstituted hydrazidine (IVa), νNH is substantially higher than in the remaining compounds (Table 1). In CCl_4 solution, however, the frequencies of these vibrations were practically the same for all the compounds.

Since the νNH values of solutions of hydrazidines (IV) and (V) in CCl_4 are independent of the nature of the substituent, and are similar to those for the hydrazones (Ia, b) and (IIIa-f) (Table 2), benzil phenylosazone (VII) (3320 cm^{-1} in CCl_4), and the phenylhydrazone group of 1,4-diaryl-2-ethoxycarbonylbenzhydrazidine (3311 cm^{-1} in CCl_4 [8]), it can be taken that hydrazidines (IVa-e) and (Va-e) in these solutions exist in the noncyclic form without intramolecular or intermolecular hydrogen bonds. In dioxane solution, however, as in the cases of phenylhydrazones (I) and (III), associates are formed with the solvent, resulting in a decrease in νNH (Tables 1 and 2). The absence of intramolecular hydrogen bonding in solutions of hydrazidines (IV) and (V) is also indicated by the PMR spectra since the position of the NH signal is dependent on the polarity of the solvent. The νNH values for hydrazidines (IVa-e) and (Va-e) and the corresponding arylhydrazone starting materials (IIIa-e in dioxane and DMSO are comparable (Tables 1 and 2), so that one can regard the electronic and steric interactions as being analogous.

If, in crystals of the hydrazidines (IVb-e) and (Va-e), intermolecular hydrogen bonding occurred involving the substituent (Cl, Br, OAlk) of the NH ... R^2 type, then the value of $\Delta\nu(CCl_4\text{-crystal})$ of ≈80-90 cm^{-1} should be comparable with that for the related phenylhydrazone (III), for which it is less: (IIIa) 20, (IIIb) 31, and (IIId) 24 cm^{-1}. The considerable reduction in νNH in the spectra of hydrazidines (IVb-e) and (Va-e) on passing from solutions in CCl_4 to the crystals may be interpreted as being due to the formation in the crystals of a cyclic tautomer (VIII), or a fairly strong intermolecular NH...N hydrogen bond [cf. $\Delta\nu(CCl_4\text{—dioxane})$], although the anomaly in the case of the unsubstituted hydrazidine (IVa) is difficult to explain in either case, and an unambiguous answer could probably only be provided by x-ray structural analysis.

The postulation of the existence of intramolecular NH...N hydrogen bonds, which would be possible for the $E_{C=N}E_{N-N}\cdot Z_{N-C}\cdot Z_{C=N}E_{N-N}$ geometric isomers in crystals of (IVb-e) and (Va-e), is

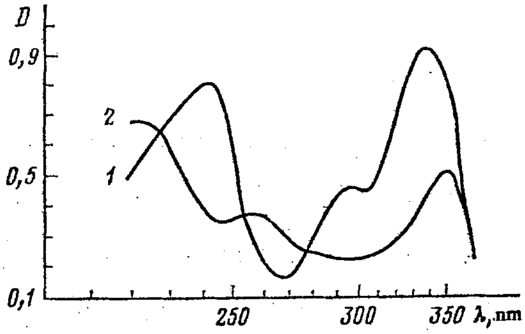

Fig. 1. UV Spectra: 1) hydrazidine (IVa); 2) hydrazidine (IVb) in dioxane, c ≈ $2 \cdot 10^{-5}$ mole/liter.

likewise not confirmed by the UV spectra. If intramolecular hydrogen bonding were present, an extended conjugated system should exist incorporating both arylhydrazone moieties, but the UV spectra of hydrazidines (IVa) (λ_{max} ≈ 350, 295, 255, 245 nm) (IVc) (λ_{max} ≈ 350, 275, 240 nm), and (Vc) (λ_{max} ≈ 350, 270, 240 nm) in vaseline oil, and hydrazidines (IVd) (λ_{max} ≈ 345, 300, 250, 235 nm) and (IVe) (λ_{max} ≈ 350, 285, 260, 230 nm) in crystalline films, differ little in the shapes and positions of the bands from the spectra of hydrazidines (IVa–e) and (Va–e) in solution (Table 3). The UV spectra indicate that the chromophore systems of the two arylhydrazone moieties comprising the hydrazidines (IV) and (V) are discrete, and consequently that they are unfolded around the central C—N bond, so that the spectra of the hydrazidines (IV) and (V) and the phenylhydrazones (IIIa–f) (Table 2) are virtually identical.

Similar unfolding of the phenylhydrazone moieties around the central C—C bond occurs in the β-form of osazone (VII) [9], the UV spectrum of which in ethanol (λ_{max}, nm (log ε): 341 (4.54), 298 (4.25), 240 (4.52) [7]) is also similar to that of phenylhydrazone (IIIa). The more planar γ-isomer of osazone (VII) with intramolecular NH...N bonds absorbs at longer wavelengths: 399 (4.08), 322 (4.28), 242 (4.31) nm [7].

The longer-wavelength band in the spectra of hydrazines (IV) and (V) exhibits a hypsochromic shift as compared with the analogous band for the phenylhydrazones (III), which is readily explicable in terms of the nature of the long-wavelength transition in the spectra of phenylhydrazones [10], together with the fact that in the nonplanar conformation of the hydrazidines (IV) and (V) each moiety will function as a receptor with respect to the other. Just such an effect has been observed in spectra of the β-osazone (VII) [7] and benzoyl chloride phenylhydrazones (Ia, b), in which the Cl atom functions as the acceptor group (Table 2).

The medium- and short-wavelength bands in the spectra of hydrazidines (IVa) and (IVb) in ethanol, dioxane, and acetonitrile differ slightly in their positions (Table 3 and Fig. 1) more probably as a result of conformational differences than the influence of the substituent, since the spectra in CCl_4 are almost identical: (IVa) 338 and 303 nm, (IVb) 343 and 303 nm. On storage, or on heating to 50°C, of solutions of the hydrazidine (IVb) in dioxane or acetonitrile, the spectra show irreversible changes, the intensities of the 255 and 224 nm bands decreasing, bands at 295 and 245 nm appearing and increasing in intensity, and a slight hyposochromic shift occurring in the long-wavelength band (≈340 nm). These results indicate that two conformational forms are present in solutions of the hydrazidines (IV) and (V): a (≈340, 295, 245 nm), and B (≈350, 260, 225 nm), which apparently differ in some small respects in the interaction of the separate moieties.

The spectrum of hydrazidine (IVe) in CCl_4 (340, 305 nm) is similar to that of the hydrazidine (IVa) (form A), and in acetonitrile, to the spectrum of freshly prepared solutions of the hydrazidine (IVb) (form B), but in dioxane in addition to the bands typical of form B, there are also indications of bands typical of form A, the intensities of which after one day reach normal values (B → A transition). Signs of the two forms are also present in the spectrum of an alcoholic solution of the hydrazidine (IVe), but on storage or heating a solution in acetonitrile the spectrum clearly shows a transition from B to A. This transition is also seen on storing or heating dioxane solutions of the hydrazidine (Vd), whereas in acetonitrile both forms are found, and in CCl_4, form A only (341, 305 nm). The changes in dioxane are also reflected in the IR spectra, νNH at 3260 cm^{-1} undergoing a shift to 3240 cm^{-1} after one day.

On crystallization, hydrazidine (IVd) gives a mixture of different forms, viz., small prisms mp 148-152°C and fine needles melting at 98-102°C, followed by resolidification and remelting at 146-150°C, like the unseparated crystal mixture. The prismatic and acicular crystals were separated manually, since it was not possible to find a solvent for fractional crystallization. The IR spectrum of the "needles" in vaseline oil showed, in addition to νNH at 3245 cm^{-1}, an additional band at 3264 cm^{-1}, whereas the "prisms" showed a single band at 3324 cm^{-1}. In CCl_4, the spectra of both forms were identical with νNH at 3324 cm^{-1}. A complex situation, indicative of the presence in solution of two forms, is found with the UV spectra, which differ in the ratios of the intensities of the bands at 295, 260, 245, and 225 nm depending on the solvent and the type of crystals dissolved ("needles", "prisms", or a mixture of the two). After some time had elapsed, equilibrium was established with form A predominating (Table 3).

The substituted hydrazidines (IVb-e) were thermally more stable than the unsubstituted compound (IVa), since they remained unchanged on boiling in benzene for many hours. Attempts were made to rearrange the hydrazidines (IVc, d, e) in boiling anisole to the corresponding benzil phenylosazones, as in the rearrangement of the hydrazidine (IVa) to the β-osazone (VII) [2]. However, in all cases only the benzotriazinyl radical (VI) was obtained, in fairly high yields (60-75%).

EXPERIMENTAL

IR spectra were recorded on a UR-20 spectrometer, UV spectra on a Specord UV-VIS spectrometer, and PMR on a Varian T-60 spectrometer. Melting points were determined on a Böetius hot plate. TLC was carried out on Silufol UV-254 plates.

1-Phenyl-2-(4-R^2-benzylidene)-4-(4-R^1-phenyl)benzhydrazidines (IVb-e) and (Va-e). To a mixture of 0.01 mole of the chlorohydrazone (Ia) or (Ib) and 0.01 mole of the appropriate hydrazone (III) on 50 ml of dry benzene was added 0.015 mole of Et_3N, and the mixture was boiled under reflux for 6 h. After keeping for 12 h at 20-25°C, $Et_3N \cdot HCl$ was filtered off, the benzene removed under reduced pressure, and the residue dissolved in 50 ml of ethanol with gentle warming. On cooling, a solid separated which was filtered off, washed with ethanol (3 × 5 ml), and recrystallized from a mixture of ethanol and acetone (4:1) to give the hydrazidine. The purities of the hydrazidines obtained (IVb-e) and (Va-e) were checked by TLC on Silufol UV-254 plates. Elemental analysis are given in Table 1.

CONCLUSIONS

1. Reaction of C,N-diphenylnitrilimines with benzaldehyde arylhydrazones has given new representatives of the arylidenebenzhydrazidines.

2. In solution, 1,4-diaryl-2-benzylidenehydrazidines have a nonplanar structure, and can exist in two conformational forms.

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