Vicinal Multifunctional Compounds. Tautomerism and Isomerism in the Condensation Products of 2-Hydroxyimino-3-oxobutanal or 3-Hydroxyiminopentane-2,4-dione with Benzylamines

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The blue products from the condensation of 2-hydroxyimino-3-oxobutanal (1a) with benzylamine and a series of its substituted derivatives have been isolated and identified as (*Z*)-α-nitroso-β-enaminones (3a). In contrast, condensation of 3-hydroxyiminopentane-2,4-dione (1b) with benzylamines gave colourless α-hydroxyimino-β-imino-ketones (2b). In both series there exist in solution equilibria between the nitroso-enaminones (3) and hydroxyimino-ketones (2). The configurational problems and the influence of steric and solvent effects on the distribution of tautomers and isomers at equilibrium are discussed.

DURING our work on the formation of imidazole derivatives from 3-hydroxyiminopentane-2,4-dione (1b) and benzylamines,[1,2] we became interested in the compounds arising as possible intermediates in the cyclization. Such compounds, previously described as Schiff bases of undefined configuration,[3,4] can exist as one or some combination of three potential tautomers and various isomers: hydroxyimino-imino-ketones (2b), four isomers; nitroso-enaminones (3b), two isomers; and nitroso-enols (4b), four isomers.

Tautomeric equilibria and isomerism problems in multifunctional compounds bearing vicinal sp^2 carbon atoms have been previously studied [5,6] (see also below).

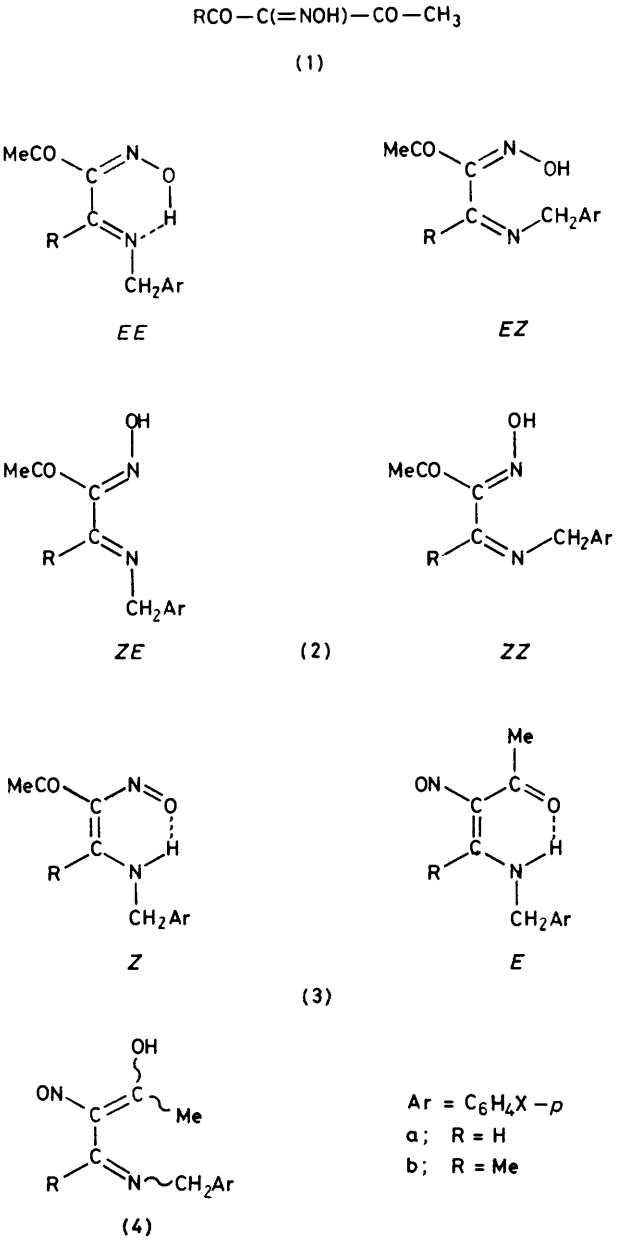
In order to understand the structural parameters which affect isomerism and/or tautomerism in compounds such as (2) we have studied the condensation products of benzylamines with 2-hydroxyimino-3-oxobutanal (1a) and 3-hydroxyiminopentane-2,4-dione (1b).

RESULTS AND DISCUSSION

Condensation Products of Benzylamines with 2-Hydroxyimino-3-oxobutanal (1a).—Nitrosation of 3-oxobutanal gives an unstable 2-hydroxyimino-derivative (1a) which reacts, in turn, with benzylamines to yield condensation products, isolated as blue solids. These give green solutions in methylene chloride, chloroform, ethanol, and dimethyl sulphoxide.

Spectral Data in Chloroform and Methylene Chloride.—Relevant spectral data are as follows: (i) ^1H and ^{13}C n.m.r. spectra show only one species; (ii) u.v. and visible absorptions near 260, 330 and 550 nm point to a conjugated system and a nitroso-group [7]; (iii) absorptions in the i.r. spectra at 1 670—80 cm^{-1} and in the ^{13}C n.m.r. spectra near δ 195 indicate a conjugated, but not intramolecularly hydrogen-bonded, carbonyl group; (iv) a broad i.r. absorption near 3 000 cm^{-1} and a low-field resonance (δ 14—17) in the ^1H n.m.r. spectra indicate an intramolecularly-bonded hydrogen † (see Table). Although the data suggest the (*Z*)-nitroso-enamino-

† For a discussion of the i.r. absorptions of NH in enaminones see, H. F. Holtzclaw, J. P.Collman, and R. M. Alire, *J. Am. Chem. Soc.*, 1958, **80**, 1100.



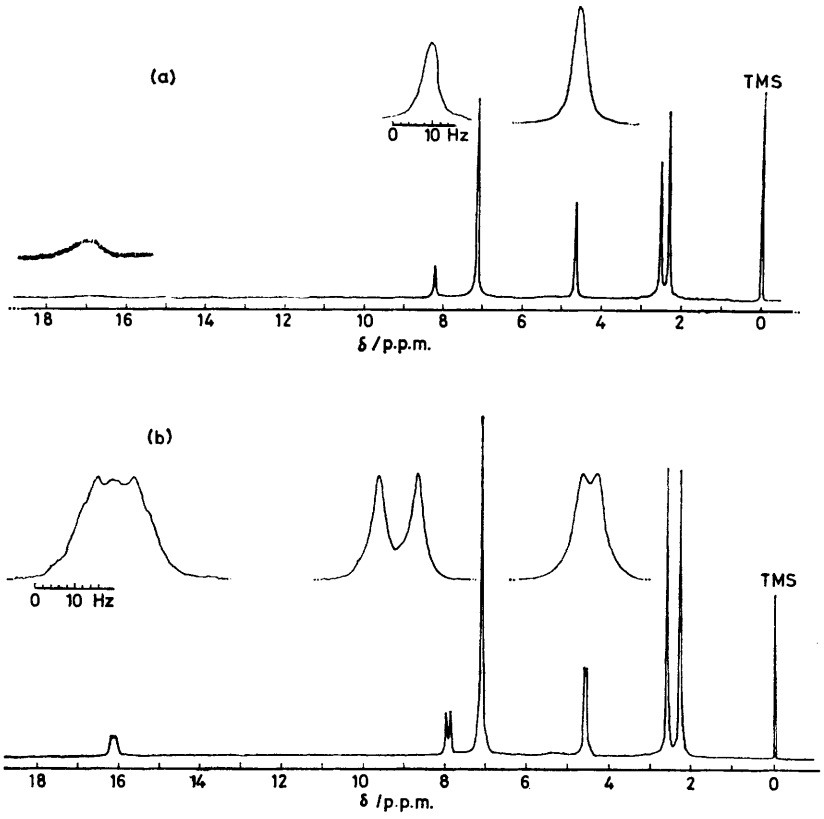


FIGURE ^{1}H N.m.r. spectra of condensation products of compound (1a) with *p*-methylbenzylamine: (*a*) in CD_2Cl_2 at 25 °C; (*b*) in CD_2Cl_2 at −80 °C. The expansion of CH_2, CH and NH signals are reported in offset.

structure (3a), no coupling between CH, NH, and the benzylic CH_2 could be observed at room temperature [Figure (a)]. However the ^{1}H n.m.r. spectrum at −80 °C shows the following coupling constants: $J_{HC\cdot HN}$ 9 Hz, $J_{NH\cdot CH_2}$ 3.2 Hz [Figure (b)]. These values are lower than the ones expected for the structure (*Z*)-(3a). In fact coupling constants of 13—14 Hz have been reported for HC·NH in a *s-trans*-conformation, and coupling constants of 5—7 Hz have been found for the $NH\cdot CH_2$ system.[8,9,10] At −40 °C, collapse of the CH, NH, and CH_2 multiplets is observed, and at room temperature the signals are still broad. This behaviour suggests that, below −40 °C, the nitroso-isomer (*Z*)-(3a) reaches equilibrium, in an interval that is fast on the n.m.r. time scale, with the hydroxyimino-tautomer (*EE*)-(2a).[11] According to the Garbish equation, *ca.* 70% of the compound present is the nitroso-tautomer (*Z*)-(3a).* The lack of coupling at room temperature indicates more complex equilibria and suggests that, together with a fast exchange of proton, a fast rotation around the C(3)–C(4) double bond could occur.[12,13] This is supported by broad i.r. absorption near 1 620 cm^{-1} that points to the tautomer (*E*)-(3a) which has a conjugated, intramolecularly hydrogen-bonded carbonyl group. All the reported spectral data show that both nitroso-isomers (*Z*)-(3a) and (*E*)-(3a), and at least the hydroxyimino-tautomer (*EE*)-(2a), contribute to the rapidly established complex equilibria at room temperature.

Spectral Data in Ethanol and Dimethyl Sulphoxide.—U.v. spectra in ethanol are very similar to those in chloroform, and ^{1}H n.m.r. spectra in dimethyl sulphoxide are similar to those in methylene chloride (Table), allowing us to conclude that the same species are present in the different solvents.

Solid State.—The i.r. spectra of the blue crystals in KBr which show a broad absorption at 3 000 cm^{-1} and a carbonyl absorption at 1 680 cm^{-1} suggest structure (*Z*)-(3a) in the solid state; an *X*-ray analysis of a representative compound is in progress.

Condensation Products of Benzylamines with 3-Hydroxyiminopentane-2,4-dione (1b).—Condensation products of benzylamines with 3-hydroxyiminopentane-2,4-dione (1b) were isolated as colourless crystals. The solids give almost colourless solutions in dimethyl sulphoxide and ethanol, but it is worth noting that they dissolve in methylene chloride, chloroform, benzene, and acetonitrile, yielding violet solutions from which the colourless crystals again separate upon concentration or cooling.

Solid State.—I.r. spectra in KBr show absorptions at 1 680 cm^{-1} (CO) and near 1 000 cm^{-1} (=N–O), supporting

* E. W. Garbisch, *J. Am. Chem. Soc.*, 1963, **85**, 1696. The relative ratio of the two tautomers (*Z*)-(3a) and (*EE*)-(2a) can be evaluated from the equation K_e = N (*Z*)-(3a)/N (*EE*)-(2a) = $J_{obs.}/13 - J_{obs.}$, where K_e is the equilibrium constant and 13 is the expected coupling constant for the HC·NH system in the tautomer (*Z*)-(3a). The allylic coupling for the $HC{=}NCH_2$ system in the tautomer (*EE*)-(2a) has been neglected.

Relevant spectral data for the condensation products of 2-hydroximino-3-oxobutanal (1a) and 3-hydroximino-pentane-2,4-dione (1b) with benzylamine

N.m.r. δ Values	Solvent	Condensation products of (1a) with benzylamine		Condensation products of (1b) with benzylamine			
		$CDCl_3$	$(CD_3)_2SO$	$CDCl_3$		$(CD_3)_2SO$	
	Tautomer or isomer	*a*	*a*	*b*	(*EZ*)-(2b)	(*EZ*)-(2b)	(*ZE*)-(2b)
	Percent of tautomer or isomer	*c*	*c*	85	15	60	40
	^{1}H n.m.r. $C(1)H_3$	2.57	2.56	2.56	2.28	2.38	2.20
	=CH or $C(5)H_3$	8.3br	8.01br	2.43	2.15 (t, 1.2 Hz)	2.0 (t, 1.2 Hz)	2.10 (t, 0.8 Hz)
	CH_2	4.72br	4.72br	4.7br	4.15br	4.13br	4.6br
	NH(OH)	*d*	*d*	14—18		12.2br	12.2br
	^{13}C n.m.r. $C(1)H_3$	24.8	*e*	27.2	24.4 *f*	24.5 *f*	30.5
	$C(5)H_3$			16.9	25.1 *f*	25.1 *f*	13.4
	CO	196.7		198.6	195.1	194.7	200.1
	C–N=O (C=N–O)	149.9		151.9	154.7	155.1	159.1
	C–NH (C=N)	152.4		164.9	164.5	160.5	163.5
	CH_2	60.6		50.2	57.9	57.3	54.6
		g		*h*			
I.r.		$CHCl_3$	KBr (*Z*)-(3a)	$CHCl_3$		KBr (2b) *i*	
$\nu_{max.}$/cm^{-1}	NH(OH)	3 000vbr	3 050vbr	3 000vbr		2 600vbr, 1 850vbr	
	CO	1 685br 1 620br	1 670br	1 680br 1 610br		1 680br	
	=N–O					1 025	
U.v.–vis		$CHCl_3$	EtOH	$CHCl_3$		EtOH (2b) *i*	
$\lambda_{max.}$/nm		257 (14.000)	252 (15.300)	249 (8.700)		230 (11.000)	
(ϵ/l mol^{-1} s^{-1})		337 (6.000)	332 (9.000)	319 (5.500)			
		585 (19.4)	543 (25.3)	540 (41)			

a This set of signals corresponds to a rapidly established equilibrium, relative to the n.m.r. time scale, among tautomers and isomers (*Z*)-(3a), (*E*)-(3a), (*EE*)-(2a). *b* This set of signals corresponds to a rapidly established equilbrium, relative to the n.m.r. time scale, among tautomers and isomers (*Z*)-(3b), (*E*)-(3b), (*EE*)-(2b). *c* Only one set of signals was detected. *d* NH Was not detected; in the compound derived from *p*-methylbenzylamine in $CDCl_3$ it occurs at δ 17vbr and in $(CD_3)_2SO$ at δ 14vbr. *e* In $(CD_3)_2SO$ the compound is unstable and a good ^{13}C n.m.r. spectrum was not obtained. *f* The assignments can be reversed. *g* Other ^{13}C n.m.r. signals: C_6H_5 *j* (junction C of the phenyl) 135.0, *o* 129.0, *m* 127.9, *p* 128.2. *h* Other ^{13}C n.m.r. absorptions: C_6H_5 *j* 135.1, *o* 129.2, *m* 127.5, *p* 128.3. *i* Undefined configuration.

the assignment of the imino-hydroxyimino-structure (2b) (undefined configuration) for the solids; a hydrogen-bond between the hydroxyimino-hydrogen and the imino-nitrogen is indicated by broad absorptions at 2 800 and 1 800 cm^{-1}.*

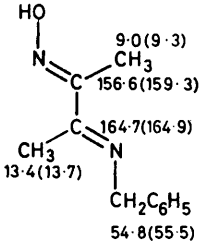
Spectral Data in Chloroform and Methylene Chloride.—Spectral data in these solvents are similar to those of the condensation products of compound (1a) with benzylamines, but there are some differences which become evident particularly in the ^{1}H n.m.r. spectra. While only one species is detected in the methylene chloride solution, two different species are present in chloroform. In methylene chloride the only species present is characterized by broad benzylic CH_2 and NH resonances. At −80 °C no coupling constants between CH_2 and NH are detected, while the signals are still broad. These data suggest that complex equilibria, reached quickly on the n.m.r. time scale, are established among nitroso-isomers (*Z*)-(3b) and (*E*)-(3b) and hydroxyimino-tautomer (*EE*)-(2b) at all the temperatures investigated. In chloroform solution, which gives a set of signals corresponding to such fast-established equilibria, a minor species is also present (ratio *ca.* 4 : 1), to which we assign the hydroxyimino-structure (*EZ*)-(2b) (see Table and discussion below).

Spectral Data in Dimethyl Sulphoxide or Ethanol.—U.v. absorption at 230 nm in ethanol reveals only hydroxyimino-tautomers (2b). N.m.r. spectra in dimethyl sulphoxide show two hydroxyimino-isomers (relative ratio 3 : 2). We assign the structure (*EZ*)-(2b) to the major isomer and the structure (*ZE*)-(2b) to the minor one. Such structures are suggested by the following data: (i) *J* 1.2 Hz (CH_3 and CH_2) in the major isomer (*EZ*)-(2b) points to a homoallylic system $CH_3C{=}NCH_2$ in the *trans*-configuration, whereas 0.8 Hz in the minor isomer (*ZE*)-(2b) stands for a *syn*-configuration.† (ii) The trend of the C(5)-methyl absorptions in the ^{13}C n.m.r. spectra, δ 25 and 13 for (*EZ*)-(2b) and (*ZE*)-(2b) respectively, can be explained by different configurations: the absorption at higher field of the minor isomer (*ZE*)-(2b) confirms a *syn*-configuration at the C=N

* An *X*-ray analysis of the condensation product of (1b) with *p*-methylaniline demonstrated that it had an imino-oximino-structure like (*EZ*)-(2b): V. Bertolasi, G. Gilli, A. C. Veronese, *Acta Crystallogr. Sect. B*, in the press.

† Distinct homo-allylic coupling constants, quite similar to the present ones, were assigned to *anti*- and *syn*-Schiff bases: K. Tori, M. Ohtsuru, and T. Kubota, *Bull. Chem. Soc. Jpn.*, 1966, **39**, 1089. In *N*-benzyliminoacetone, only the methyl *anti*- to the benzyl group was reported to be coupled (*J* 1 Hz): H. A. Staab, F. Vogtle, and A. Mannschreck, *Tetrahedron Lett.*, 1965, 697.

bond,[14] which also fits in with data from model compound (5) (Scheme).[15] (iii) A comparison of pertinent ^{13}C n.m.r. data of the two isomers (Table) with ^{13}C n.m.r. data obtained for related model compounds (Scheme)



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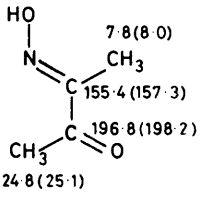

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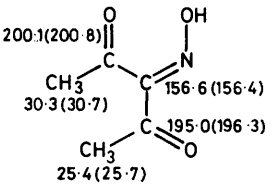


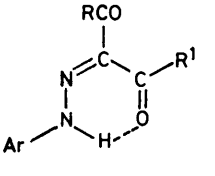
(1b)

SCHEME

^{13}C N.m.r. absorptions of model compounds in $(CD_3)_2SO$; the data in $CDCl_3$ are reported in parentheses

allows us to assign to each isomer the configuration of its hydroxyimino-moiety. From these data we can deduce that the configurations of the keto-oxime moieties are different; furthermore, signals due to the CH_3CO carbons correspond to either of the CH_3CO groups in compound (1b). In the ^{13}C n.m.r. spectra of the major isomer (*EZ*)-(2b), the two carbons are at *ca.* δ 195 and 25, which indicates a configuration such as that present in the *anti*-keto-oxime (6).* In the minor isomer (*ZE*)-(2b), the signals at δ 200 and 30 suggest the alternative *syn*-configuration. (iv) The difference in the ^1H n.m.r. chemical shifts of the benzylic CH_2 in the two isomers, δ 4.1 and 4.6 for (*EZ*)-(2b) and (*ZE*)-(2b) respectively, can be explained by the anisotropy of C=O and hydroxyimino C=N: molecular models in fact indicate shielding of CH_2 in the major isomer (*EZ*)-(2b) in which the benzylic CH_2 lies perpendicularly over the CO·C=NO plane.†

A comparison with analogous multifunctional compounds shows that (i) in 2-arylhydrazones of 1,2,3-triketones equilibria occur almost exclusively between the two diversely chelated isomers (7) and (8), steric factors playing only a minor role;[5] (ii) in 4-arylamino-3-arylhydrazonobutan-2-ones, rapidly established equilibria exist at room temperature between tautomers (9) and (10), polar solvents favouring the enaminone tautomer.[11] Our work shows that in the condensation compounds of 2-hydroxyimino-3-oxobutanal (1a) and 3-hydroxyiminopentane-2,4-dione (1b) with benzylamines the situation is more complex and the importance of steric effects and solvents in the distribution of tautomers and isomers is stressed. The presence of a hydrogen or a methyl group in the chain plays a major role in determining the structures of the compounds both as solids and in solution. The nitroso-enaminone structures (3) are stabilized by the conjugation and by hydrogen



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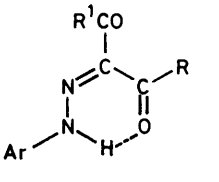

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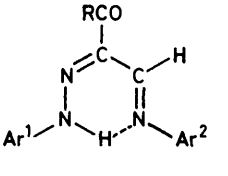

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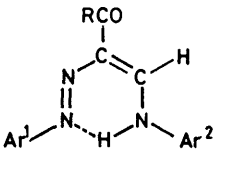

(10)

bonds; the steric repulsion between the C(5)-methyl and the acetyl group in the condensation products derived from compound (1b) and benzylamines hinders the planarity and thus destabilizes the nitroso-structure (3) and favours the hydroxyimino-tautomer (2).

The change in behaviour of compounds derived from the diketone (1b) in solution can be explained by the different abilities of the solvents to form hydrogen bonds with the compounds. Chloroform and methylene chloride stabilize the nitroso-enamino-tautomers allowing the formation of intramolecular hydrogen-bonds; ethanol and dimethyl sulphoxide stabilize in turn the hydroxyimino-imino-structures (2b) through intermolecular hydrogen-bonds with solvent molecules.[16] In both series of compounds, and in the investigated solvents, the contribution of enol tautomers (4) could not be demonstrated.

Finally an isomerization of the type described here for the species (*Z*)-(3) and (*E*)-(3) has been reported for enaminones [8,13] and related compounds [17] and its mechanism has been recently investigated in nitroenaminones.[12]

EXPERIMENTAL

M.p.s are uncorrected and were determined in open capillaries or on a Kofler hot-stage apparatus (indicated

* For the configuration of α-keto-oximes see: (*a*) F. H. Hallen, J. Trotter, and D. Rogers, *J. Chem. Soc. B*, 1971, 166; (*b*) A. F. Ferris, *J. Org. Chem.*, 1960, **25**, 12; (*c*) G. Ribaldone, L. Marangoni, and A. Nenz, *Chim. Ind. (Rome)*, 1964, **46**, 621. The ^{13}C n.m.r. spectrum of compound (6) shows the absorption of the methyl near to the hydroxyimino-group at high field (δ 8.0) thus confirming the *anti*-keto-hydroxyimino-structure; see also: G. E. Hawkes, K. Hervig, and J. D. Roberts, *J. Org. Chem.*, 1974, **39**, 1017.

† As note * on preceding page.

Ko.). U.v. visible absorption maxima (nm) were recorded with a Hitachi Perkin-Elmer model 124 DB spectrometer; absorbances are given in parentheses after the maxima. I.r. spectra were run with a Perkin-Elmer model 157 G spectrometer. ^{1}H N.m.r. spectra were obtained at 90 MHz, with tetramethylsilane as internal standard (δ 0.0 p.p.m.) using a Perkin-Elmer R32 spectrometer. ^{13}C N.m.r. spectra were measured at 80 MHz with a Bruker WP-80 instrument. Concentrations are 10% in the solvents indicated unless otherwise specified. Signals are singlets unless otherwise specified.

Condensation Products of Compound (1a) *with Benzylamines.*—*4-Benzylamino-3-nitrosobut-3-en-2-one* (3a; X = H).—4,4-Dimethoxybutan-2-one (1.32 g, 10 mmol) was dissolved in 1N-hydrochloric acid (10 ml, 10 mmol), stirred for 30 min at room temperature, cooled to 0 °C, and treated for 30 min at 0 °C with a solution of sodium nitrite (0.76 g, 11 mmol) in water (4 ml). The nitrous vapours having been removed under reduced pressure, the reaction mixture was treated with acetic acid (0.57 ml, 10 mmol) and with benzylamine (0.98 ml, 9 mmol) and stirred for 10 min at room temperature: the separated violet crystals were washed with water and dried *in vacuo* [P_2O_5: 1.208 g (59%)]. The crude product was purified in a Sephadex LH 20 column, with chloroform as eluant; the blue-green fraction was concentrated to dryness under reduced pressure: violet crystals, 0.893 g (43%), m.p. 88—89 °C, were obtained (Found: C, 64.6; H, 5.9; N, 13.6. $C_{11}H_{12}N_2O_2$ requires C, 64.69; H, 5.92; N, 13.71%). Spectral data are reported in the Table.

4-p-Methylbenzylamino-3-nitrosobut-3-en-2-one (3a; X = Me).—This compound was obtained as structure (3a; X = H) (crude product 52%) and purified on a Sephadex LH 20 column (39%), m.p. 119—120 °C [chloroform, diethyl ether, and light petroleum (b.p. 40—70 °C), 1 : 1 : 3] (Found: C, 65.6; H, 6.55; N, 12.7. $C_{12}H_{14}N_2O_2$ requires C, 66.03; H, 6.46; N, 12.86%); $\lambda_{max.}$ ($CHCl_3$) 258 (ε 15 600), 339 (7 600), and 595 nm (13.5); $\lambda_{max.}$ (EtOH) 256 (ε 15 500), 335 (10 300), and 565 nm (34); $\nu_{max.}$ ($CHCl_3$) 3 000vbr, 1 685br, 1 625br, 1 360, 1 290, and 1 020 cm^{-1}; $\nu_{max.}$ (KBr) 3 000vbr, 1 670br, 1 635, 1 610, 1 355, 1 310, 1 170, and 750 cm^{-1}; δ($CDCl_3$) 2.35 (CH_3), 2.57 (CH_3CO), 4.69br (CH_2), 7.18 (C_6H_4), 8.25br (CH), and 17vbr (NH; δ[$(CD_3)_2SO$] 2.3 (CH_3), 2.58 (CH_3CO), 4.68br (CH_2), 7.22 (C_6H_4), 7.99br (CH), and 14vbr (NH); in this solution the compound decomposed in *ca.* 30 min.

4-p-Methoxybenzylamino-3-nitrosobut-3-en-2-one (3a; X = OCH_3).—This compound was obtained as (3a; X = H) (crude product 39%; after purification 27%). It was recrystallized as (3a; X = Me), m.p. 100—102 °C (Found: C, 61.35; H, 5.9; N, 11.85. $C_{12}H_{14}N_2O_3$ requires C, 61.52; H, 6.02; N, 11.96%); $\lambda_{max.}$ ($CHCl_3$) 259 (ε 17 900), 338 (8 500), and 586 nm (26); (EtOH) 226 (ε 26 200), 257 (16 900), 333 (10 800), and 556 nm (32); $\nu_{max.}$ ($CHCl_3$) 3 000vbr, 1 680, and 1 610 cm^{-1}; $\nu_{max.}$ (KBr) 3 000vbr, 1 670, 1 635, and 1 615 cm^{-1}; δ($CDCl_3$) 2.59 (CH_3), 3.82 (CH_3O), 4.68 (CH_2), 6.96, 7.22 (C_6H_4, A_2B_2, *J* 9 Hz), and 8.2br (CH); δ[$(CD_3)_2SO$] 2.59 (CH_3), 3.8 (CH_3O), 4.7 (CH_2), 7.0, 7.3 (C_6H_4, A_2B_2, *J* 9 Hz), and 8.0br (CH); in this solution the compound decomposed in *ca.* 20 min.

4-p-Chlorobenzylamino-3-nitrosobut-3-en-2-one (3a; X = Cl).—This compound was obtained as (3a; X = H) (crude product 62%; after purification 48%), and purified as (3a; X = Me), m.p. 119—122 °C (Found: C, 55.25; H, 4.55; Cl, 14.9; N, 11.51. $C_{11}H_{11}ClN_2O_2$ requires C, 55.22; H, 4.64; Cl, 11.85; N, 11.73%); $\lambda_{max.}$ ($CHCl_3$) 258 (ε 13 100), 341 (4 200), and 602 nm (16); $\lambda_{max.}$ (EtOH) 220 (ε 29 300), 255sh, 335 (7 200), and 571 nm (21.8); $\nu_{max.}$ ($CHCl_3$) 3 000vbr, 1 690br, and 1 615 cm^{-1}; $\nu_{max.}$ (KBr) 3 000vbr, 1 670, 1 630, and 1 610 cm^{-1}; δ($CDCl_3$) 2.52 (CH_3), 4.72br (CH_2), 7.21, 7.39 (C_6H_4, A_2B_2, *J* 9 Hz), 8.4br (CH), and 17vbr (NH). In [$(CD_3)_2SO$] the compound decomposed in a few minutes.

Condensation Products of Compound (1b) *with Benzylamines.*—*3-Hydroxyimino-4-p-methoxybenzyliminopentan-2-one* (2b; X = OMe).—*Procedure A. In water.* A solution of compound (1b) (1.03 g, 8 mmol) and *p*-methoxybenzylamine (1.1 g, 8 mmol) in water (15 ml) was stirred for 2 h at room temperature. The solid which separated was filtered off, washed with water, and dried *in vacuo* (P_2O_5). It was obtained as colourless prisms, 1.64 g (83%), m.p. 138—139 °C (chloroform–light petroleum). The crystals gave red-violet solutions in chloroform, ethyl acetate, and acetonitrile, and almost colourless solutions in ethanol and dimethyl sulphoxide.

Procedure B. In acetonitrile. A solution of compound (1b) (0.64 g, 5 mmol) and *p*-methoxybenzylamine (0.68 g, 5 mmol) in acetonitrile (10 ml) was stirred for 2 h at room temperature. The separated solid was filtered off, washed with acetonitrile, and dried: it was obtained as colourless prisms (0.66 g). The red mother-liquor was concentrated to dryness and treated with light petroleum to yield a further 0.48 g of the same compound (total yield 90%) (Found: C, 62.5; H, 6.35; N, 11.1. $C_{13}H_{16}N_2O_3$ requires C, 62.89; H, 6.50; N, 11.28%); $\lambda_{max.}$ (EtOH) 227 (ε 21 600), and 520 nm (2.5); $\lambda_{max.}$ ($CHCl_3$) 250 (ε 8 300), 319 (6 100), and 545 nm (41); $\nu_{max.}$ (KBr) 2 800—2 300vbr, 1 950—1 850vbr, 1 680, 1 610, 1 310, and 1 030 cm^{-1}; $\nu_{max.}$ ($CHCl_3$) 3 000vbr, 1 680br, 1 610br, 1 310, and 1 250 cm^{-1}. The ^{1}H n.m.r. ($CDCl_3$) spectrum shows two species (9 : 1): (i) the major species corresponds to a rapidly established equilibrium between at least (*Z*)-(3b), (*EE*)-(2b), and (*E*)-(3b); 2.45 (CH_3), 2.57 (CH_3CO), 3.81 (OCH_3), 4.61br (CH_2), and 15—17 (NH); (ii) (*EZ*)-(2b); 2.11 (q, *J* 1.2 Hz, CH_3), 2.39 (CH_3CO), 3.72 (OCH_3), and 4.17br (CH_2).

4-Benzylimino-3-hydroxyiminopentan-2-one (2b; X = H).—This compound was obtained by procedure A (85%) or B (80%) as colourless prisms, m.p. 127—128 °C (chloroform–light petroleum) (Found: C, 65.75; H, 6.45; N, 12.95. $C_{12}H_{14}N_2O_2$ requires C, 66.03; H, 6.47; N, 12.84%). Spectral data are reported in the Table.

3-Hydroxyimino-4-p-methylbenzylaminopentan-2-one (2b; X = Me).—This compound was obtained by procedure A (90%) as colourless prisms, m.p. 140—141 °C (ethyl acetate) (Found: C, 67.1; H, 7.05; N, 11.95. $C_{13}H_{16}N_2O_2$ requires C, 67.22; H, 6.94; N, 12.06%). Relevant spectral data are similar to those of (2b; X = H), $\lambda_{max.}$ ($CHCl_3$) 250 (ε 8 500), 318 (5 300), and 541 nm (55); $\lambda_{max.}$ (EtOH) 214 (ε 16 200), and 218 nm (16 800).

4-p-Chlorobenzylamino-3-hydroxyiminopentan-2-one (2b; X = Cl).—This compound was obtained by procedure A (68%) or B (63%) as colourless prisms, m.p. 142—146 °C (chloroform–light petroleum) (Found: C, 56.9; H, 5.2; Cl, 14.15; N, 11.15. $C_{12}H_{13}ClN_2O_2$ requires C, 57.03; H, 5.18; Cl, 14.03; N, 11.09%). Relevant spectral data are similar to those of (2b; X = H), $\lambda_{max.}$ (EtOH) 222 nm (ε 19 900).

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