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Reaction of *N*-(1-Phenylalkylidene)benzylamines with Benzoyl Cyanides[1)]

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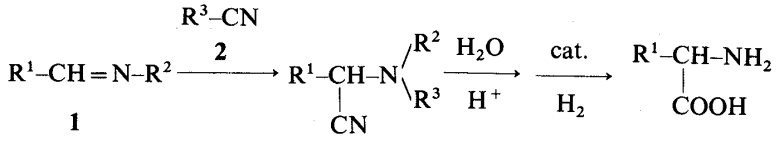
Reactions of various aldimines **4a**—**f** with 4-nitrobenzoyl cyanide (**2b**) gave the Reissert-type compounds **5a**—**f**. However, reaction of *N*-(1-phenylpropylidene)benzylamine (**7a**) with **2b** gave 1-benzyl-4-hydroxy-5-imino-3-methyl-4-(4-nitrophenyl)-2-phenyl-4,5-dihydropyrrole (**8a**). Similar reactions of **7b**, **7c**, and **12** with **2b** gave the pyrrole derivatives **8b**, **11**, and **13**, respectively. Next, the reaction of *N*-cyclohexylidenecyclohexylamine (**14**) with benzoyl cyanide (**2a**) was re-examined. The structure of the adduct **16** was different from that of the Reissert-type compound **15** described by Dornow and Lüpfert.[3)]

Keywords——Reissert reaction; benzoyl cyanide; 4-nitrobenzoyl cyanide; aldimine; ketimine; X-ray analysis; dihydropyrrole; cyclization

Acyl cyanides are readily available and useful reagents for the formation of carbon-carbon bonds.[2)] The reaction of aldimines or ketimines with **2a** generally gives addition products (Reissert-type compounds) to the C=N double bond.[3–5)] In recent years, benzoyl cyanide (**2a**) and trimethylsilyl cyanide (**2c**) have been shown to be excellent reagents for the conversion of Schiff bases (**1**) to *N*-substituted-α-aminonitriles (**3**), which can be hydrolyzed to the corresponding amino acids.[6)]



1 **3**

2a: $R^3 = C_6H_5CO-$
2b: $R^3 = 4\text{-}NO_2\text{-}C_6H_4CO-$
2c: $R^3 = (CH_3)_3Si-$

Chart 1

On the other hand, several examples[7)] are known of the reaction of imines, in which the imino carbons are bound to alkyls possessing at least one hydrogen at C_1 (C–C=N–), with acylating agents to give *N*-acylenamines or *C*-acylenamines. We now report that the reaction of benzoyl cyanide with ketimines[8)] containing enolizable hydrogen gives the cyclic products.

First, the reaction of the aldimine **4a** with 4-nitrobenzoyl cyanide (**2a**) in xylene afforded [*N*-benzyl-*N*-(4-nitrobenzoyl)amino]phenylacetonitrile (**5a**). This product **5a** was identified by comparison with a sample of **5a** prepared from 4-nitrobenzoyl chloride and *N*-(benzylamino)phenylacetonitrile (**6a**).[9)] Similar reactions of the aldimines **4b**—**f** with **2b** gave the addition products **5b**—**f**, respectively. The results are summarized in Table I.

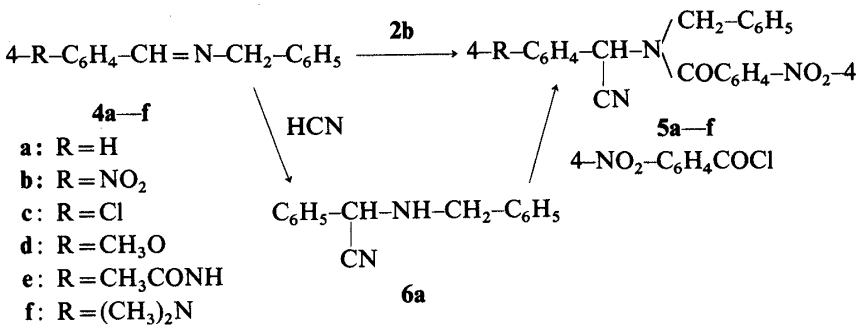


Chart 2

Further reaction of *N*-(1-phenylpropylidene)benzylamine (**7a**) containing enolizable hydrogen[11] with **2b** gave a 41% yield of the adduct **8a**. The compound **8a** has the molecular formula $C_{24}H_{21}N_3O_3$ on the basis of its elemental analysis data and mass spectrum (MS) (M^+, *m/e*: 385), and these data suggest that **8a** is a 1 : 1 adduct. The infrared (IR) spectrum of **8a** shows characteristic stretching bands at 3390 (OH), 3290 (NH), and 1638 cm^{-1} (C=N). Its ^1H-nuclear magnetic resonance (NMR) spectrum exhibits signals due to a methyl group at 1.39 ppm (s), two protons of methylene at 4.38 and 4.63 ppm (AB-type, J=16 Hz), and two protons at 6.12 ppm (br) which disappeared on addition of D_2O. The signals of the ^{13}C-NMR spectrum indicate a methyl group (8.4 ppm, q), a methylene group (45.7 ppm, t), a quaternary carbon (82.2 ppm, s), six quaternary olefinic carbons (117.0, 129.8, 137.4, 141.5, 147.4, and 148.2 ppm, 6s), and an imino carbon (175.6 ppm, s). These spectral data suggest that **8a** contains three aromatic rings and an imino group. As the structure of **8a** could not be satisfactorily elucidated from these spectral data, the structure of **8a** was eventually determined by X-ray crystallographic analysis as 1-benzyl-4-hydroxy-5-imino-3-methyl-4-(4-nitrophenyl)-2-phenyl-4,5-dihydropyrrole. The adduct **8a** was converted to the benzoylate **9** by treatment with benzoyl chloride.

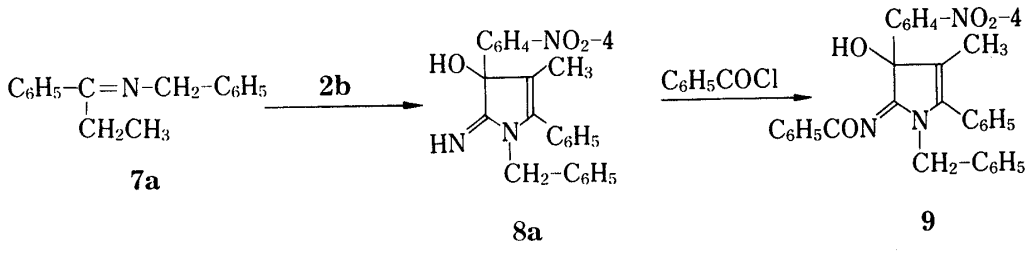


Chart 3

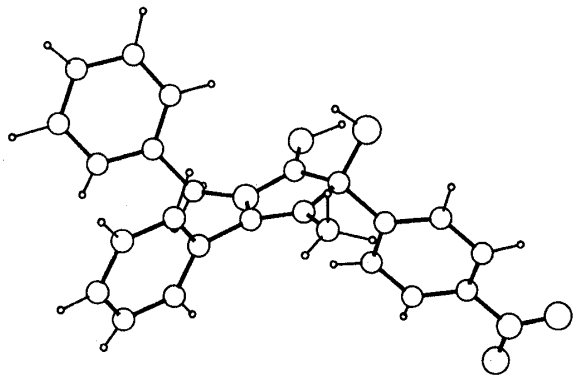


Fig. 1. Conformation of the Molecule of **8a**

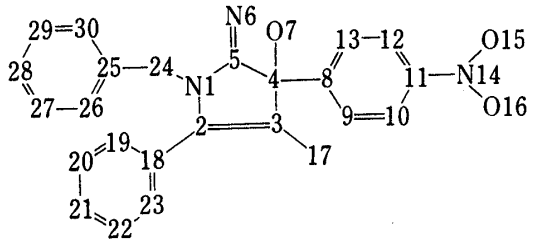


Fig. 2. Numbering of the Atoms in **8a**

TABLE I. Analytical, IR, and ^{1}H-NMR Spectral Data for **5b—f**

Compd. No.	R	React. time (h)	Yield (%)	mp (°C)	Formula		Analysis (%) C	Analysis (%) H	Analysis (%) N	IR[b] ν_{max}^{KBr} cm^{-1} C=O	^{1}H-NMR δ (in $CDCl_3$) –CH–	^{1}H-NMR δ (in $CDCl_3$) –CH_2Ph
5b	NO_2	50[a]	12	164—165	$C_{22}H_{16}N_4O_5$	Calcd	63.46	3.87	13.46	1646	6.55 (s)	4.53, 4.72 (each d)
						Found	63.46	3.99	13.42			
5c	Cl	10	39	161—162	$C_{22}H_{16}N_3O_3Cl$	Calcd	65.11	3.97	10.35	1633	6.65 (s)	4.35, 4.58[c] (each d)
						Found	64.62	4.06	10.64			
5d	CH_3O	8[a]	39	182—183	$C_{23}H_{19}N_3O_4$	Calcd	68.81	4.77	10.47	1630	6.64 (s)	4.33, 4.61 (each d)
						Found	68.52	4.86	10.12			
5e	CH_3CONH	9[a]	53	179—181.5	$C_{24}H_{20}N_4O_4$	Calcd	67.28	4.71	13.08	1645	6.50 (s)	4.36, 4.67[c] (each d)
						Found	66.78	4.59	13.00			
5f	$(CH_3)_2N$	9[a]	9	146—148	$C_{24}H_{22}N_4O_3$	Calcd	69.55	5.35	13.52	1640	6.53 (s)	4.24, 4.56 (each d)
						Found	69.34	5.34	13.38			

a) Benzene was used instead of xylene. *b*) The C=N band of α-*N*-substituted nitriles was absent.[6,10] *c*) DMSO-d_6 was used instead of $CDCl_3$.

TABLE II. Final Positional ($\times 10^4$) and Anisotropic Thermal ($\times 10^4$) Parameters with Estimated Standard Deviations in Parentheses

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N (1)	6486 (2)	4042 (1)	2442 (5)	65 (2)	18 (1)	212 (7)	1 (1)	−3 (4)	0 (2)
C (2)	7460 (3)	4305 (1)	1998 (6)	65 (3)	16 (1)	203 (9)	4 (1)	7 (5)	−3 (2)
C (3)	8294 (3)	4162 (1)	3432 (6)	71 (3)	16 (1)	194 (8)	2 (1)	−3 (5)	−8 (2)
C (4)	7587 (3)	3877 (1)	4813 (5)	73 (3)	17 (1)	173 (8)	2 (1)	−6 (4)	−1 (2)
C (5)	6570 (3)	3816 (1)	4196 (6)	78 (3)	15 (1)	200 (8)	2 (1)	14 (5)	3 (2)
N (6)	7612 (3)	4618 (1)	663 (5)	80 (3)	22 (1)	210 (8)	6 (1)	8 (4)	21 (2)
O (7)	8845 (2)	4680 (1)	3970 (4)	82 (2)	18 (1)	259 (7)	−4 (1)	−6 (4)	−17 (2)
C (8)	9180 (3)	3745 (2)	2764 (6)	61 (3)	17 (1)	204 (8)	3 (1)	1 (4)	−3 (2)
C (9)	8934 (3)	3336 (2)	1498 (6)	70 (3)	17 (1)	251 (10)	0 (1)	−15 (5)	−10 (2)
C (10)	9742 (3)	2966 (2)	851 (6)	88 (3)	19 (1)	215 (9)	4 (1)	2 (5)	−12 (2)
C (11)	10801 (3)	3021 (2)	1512 (6)	73 (3)	21 (1)	222 (9)	9 (1)	12 (5)	−6 (2)
C (12)	11057 (3)	3404 (2)	2807 (7)	57 (3)	29 (1)	294 (12)	5 (1)	−6 (5)	−16 (3)
C (13)	10243 (3)	3775 (2)	3443 (7)	77 (3)	22 (1)	271 (11)	0 (1)	−16 (6)	−20 (3)
N (14)	11659 (3)	2631 (2)	796 (6)	86 (3)	32 (1)	323 (11)	23 (1)	25 (6)	1 (3)
O (15)	12610 (3)	2726 (2)	1275 (7)	82 (3)	48 (1)	507 (13)	25 (1)	3 (6)	−38 (3)
O (16)	11425 (3)	2258 (2)	−234 (6)	135 (4)	46 (1)	515 (14)	29 (2)	1 (7)	−94 (3)
C (17)	8007 (4)	3693 (2)	6546 (6)	93 (4)	28 (1)	186 (9)	−3 (2)	−9 (5)	2 (3)
C (18)	5567 (3)	3572 (2)	5046 (6)	76 (3)	22 (1)	209 (9)	−1 (1)	−10 (5)	13 (3)
C (19)	5139 (4)	3851 (2)	6463 (7)	87 (4)	35 (1)	238 (11)	−1 (2)	24 (6)	4 (3)
C (20)	4182 (4)	3643 (3)	7260 (8)	104 (5)	54 (2)	302 (14)	−1 (3)	29 (8)	6 (5)
C (21)	3677 (4)	3149 (3)	6578 (8)	101 (5)	57 (2)	299 (15)	−17 (3)	−1 (7)	49 (5)
C (22)	4107 (5)	2862 (2)	5177 (9)	126 (5)	36 (1)	414 (18)	−32 (2)	−4 (9)	16 (4)
C (23)	5064 (4)	3070 (2)	4370 (8)	123 (5)	23 (1)	334 (14)	−9 (2)	8 (8)	8 (3)
C (24)	5454 (3)	4125 (2)	1517 (7)	77 (3)	23 (1)	225 (10)	−5 (1)	−25 (5)	2 (3)
C (25)	4690 (3)	4562 (2)	2387 (6)	70 (3)	25 (1)	222 (10)	−1 (1)	−30 (5)	5 (3)
C (26)	3610 (4)	4423 (2)	2701 (12)	61 (3)	43 (2)	702 (28)	−5 (2)	8 (9)	−27 (6)
C (27)	2908 (4)	4834 (3)	3510 (16)	71 (4)	54 (2)	1099 (46)	2 (2)	47 (13)	−70 (9)
C (28)	3302 (5)	5374 (3)	3989 (12)	109 (5)	48 (2)	630 (26)	28 (3)	3 (11)	−48 (6)
C (29)	4393 (4)	5508 (2)	3698 (9)	116 (5)	32 (1)	408 (17)	7 (2)	10 (9)	−20 (4)
C (30)	5065 (4)	5099 (2)	2915 (8)	83 (4)	27 (1)	332 (14)	−1 (2)	0 (7)	−14 (3)

Thermal parameters are in the form $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.

TABLE III. Bond Lengths (Å)

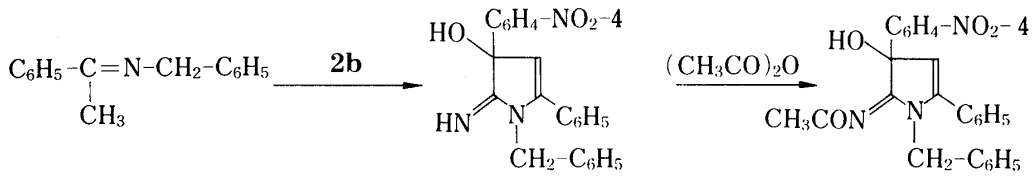
N (1)–C (2)	1.447 (6)	C (12)–C (13)	1.391 (6)
N (1)–C (5)	1.368 (5)	N (14)–O (15)	1.229 (5)
N (1)–C (24)	1.450 (5)	N (14)–O (16)	1.199 (6)
C (2)–C (3)	1.326 (6)	C (18)–C (19)	1.364 (7)
C (2)–C (18)	1.487 (6)	C (18)–C (23)	1.401 (6)
C (3)–C (4)	1.512 (6)	C (19)–C (20)	1.395 (7)
C (3)–C (17)	1.486 (6)	C (20)–C (21)	1.387 (9)
C (4)–C (5)	1.530 (6)	C (21)–C (22)	1.364 (9)
C (4)–O (7)	1.424 (4)	C (22)–C (23)	1.398 (8)
C (4)–C (8)	1.527 (5)	C (24)–C (25)	1.519 (6)
C (5)–N (6)	1.264 (5)	C (25)–C (26)	1.368 (6)
C (8)–C (9)	1.382 (6)	C (25)–C (30)	1.373 (6)
C (8)–C (13)	1.391 (6)	C (26)–C (27)	1.414 (10)
C (9)–C (10)	1.388 (6)	C (27)–C (28)	1.376 (10)
C (10)–C (11)	1.384 (6)	C (28)–C (29)	1.375 (8)
C (11)–C (12)	1.362 (7)	C (29)–C (30)	1.379 (7)
C (11)–N (14)	1.477 (6)		

TABLE IV. Bond Angles (°)

C (2)–N (1)–C (5)	109.2 (3)	C (10)–C (11)–N (14)	117.4 (4)
C (2)–N (1)–C (24)	124.3 (3)	C (12)–C (11)–N (14)	120.1 (4)
C (5)–N (1)–C (24)	124.3 (3)	C (11)–C (12)–C (13)	119.3 (4)
N (1)–C (2)–C (3)	111.1 (3)	C (12)–C (13)–C (8)	119.5 (4)
N (1)–C (2)–C (18)	119.1 (3)	C (11)–N (14)–O (15)	116.1 (4)
C (3)–C (2)–C (18)	129.9 (4)	C (11)–N (14)–O (16)	120.7 (4)
C (2)–C (3)–C (4)	108.8 (4)	O (15)–N (14)–O (16)	123.1 (4)
C (2)–C (3)–C (17)	127.4 (4)	C (2)–C (18)–C (19)	118.9 (4)
C (4)–C (3)–C (17)	123.8 (3)	C (2)–C (18)–C (23)	120.1 (4)
C (3)–C (4)–C (5)	102.9 (3)	C (19)–C (18)–C (23)	121.0 (4)
C (3)–C (4)–C (8)	111.3 (3)	C (18)–C (19)–C (20)	120.4 (5)
C (3)–C (4)–O (7)	115.0 (3)	C (19)–C (20)–C (21)	118.6 (5)
C (5)–C (4)–O (7)	109.8 (3)	C (20)–C (21)–C (22)	121.5 (5)
C (5)–C (4)–C (8)	110.9 (3)	C (21)–C (22)–C (23)	120.1 (5)
O (7)–C (4)–C (8)	106.9 (3)	C (22)–C (23)–C (18)	118.4 (5)
N (1)–C (5)–C (4)	107.2 (3)	N (1)–C (24)–C (25)	113.3 (4)
N (1)–C (5)–N (6)	125.3 (4)	C (24)–C (25)–C (26)	120.4 (4)
C (4)–C (5)–N (6)	127.5 (3)	C (24)–C (25)–C (30)	121.3 (4)
C (4)–C (8)–C (9)	120.6 (3)	C (26)–C (25)–C (30)	118.3 (4)
C (4)–C (8)–C (13)	119.5 (4)	C (25)–C (26)–C (27)	119.8 (5)
C (9)–C (8)–C (13)	119.9 (4)	C (26)–C (27)–C (28)	120.6 (5)
C (8)–C (9)–C (10)	120.9 (4)	C (27)–C (28)–C (29)	119.4 (6)
C (9)–C (10)–C (11)	117.9 (4)	C (28)–C (29)–C (30)	119.1 (5)
C (10)–C (11)–C (12)	122.5 (4)	C (29)–C (30)–C (25)	122.8 (4)

A crystal with dimensions of $0.6 \times 0.6 \times 0.8$ mm was selected for the X-ray examination. This crystal was orthorhombic ($a=12.109$, $b=22.916$, $c=7.678$ Å, and $Dc=1.244$ g/cm^{-3}), and the space group was $P2_12_12_1$ with four molecules per unit cell. A total of 2206 reflections were measured with a Rigaku AFC/3 automatic goniometer using Cu-$K\alpha$ radiation with a graphite monochromator. The structure was solved by direct methods with the MULTAN program,[12] and block-diagonal least-squares refinement of non-hydrogen atoms with anisotropic temperature factors for all atoms gave the final R-value of 0.054 for all observed reflections. The atomic parameters with their estimated standard deviations are listed in Table II. The numbering system and a stereoscopic view of the molecule are shown in Figs. 1 and 2, respectively. The bond lengths and angles are given in Tables III and IV, respectively.

Similar reaction of *N*-(1-phenylethylidene)benzylamine (**7b**) containing enolizable hydrogen[11] with **2b** gave a 1 : 1 adduct, 1-benzyl-4-hydroxy-5-imino-4-(4-nitrophenyl)-2-phenyl-4,5-dihydropyrrole (**8b**), and its IR spectrum (like that of **8a**) indicates the absence of carbonyl and nitrile groups, and the presence of a secondary amino group and tertiary alcohol at 3290 and 1130 cm^{-1}, respectively. The ^{1}H-NMR spectrum of **8b** shows a signal due to the



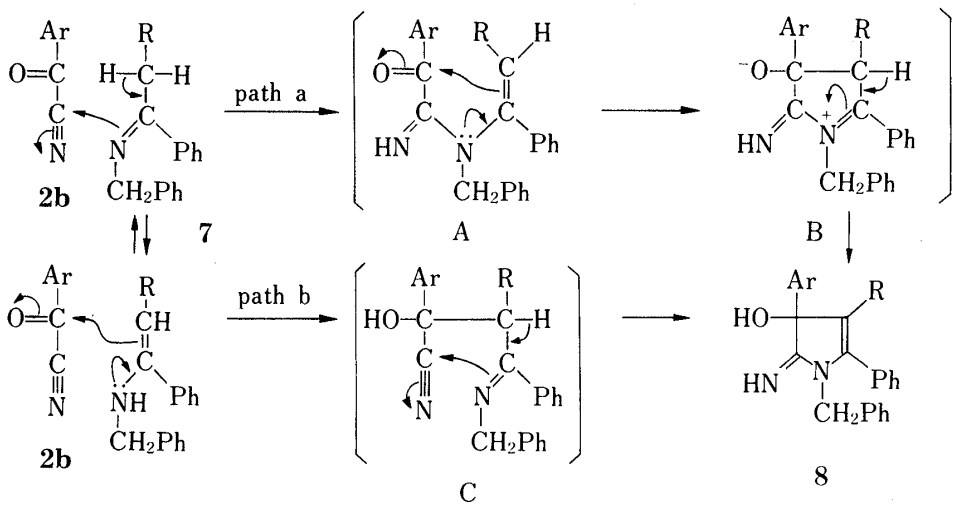
7b **8b** **10**

Chart 4

methylene protons at 4.68 ppm (s) and a signal due to the olefinic proton at 5.31 ppm (s). The structure of **8b** was also supported by the ^{13}C-NMR spectrum as detailed in the experimental

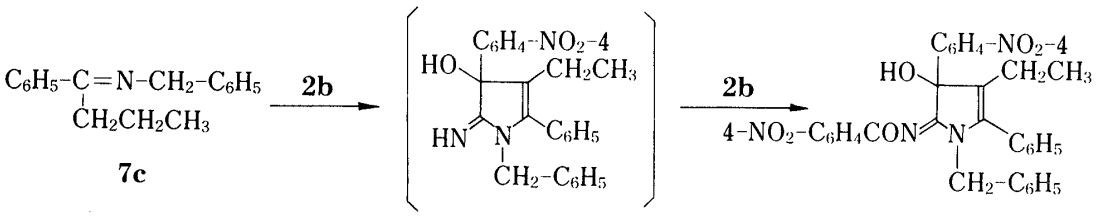
section. Further evidence for the structure was obtained by acetylation of **8b** to afford the *N*-acetylimine **10**.

The formation of the adducts **8a**, **b** can be explained in terms of two possible routes as shown in Chart 5. In path a, addition of the imine nitrogen of the imine **7** to **2b** forms the



$Ar = C_6H_4 - NO_2\text{-}4$

Chart 5



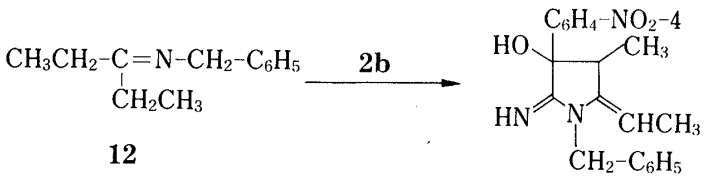


Chart 6

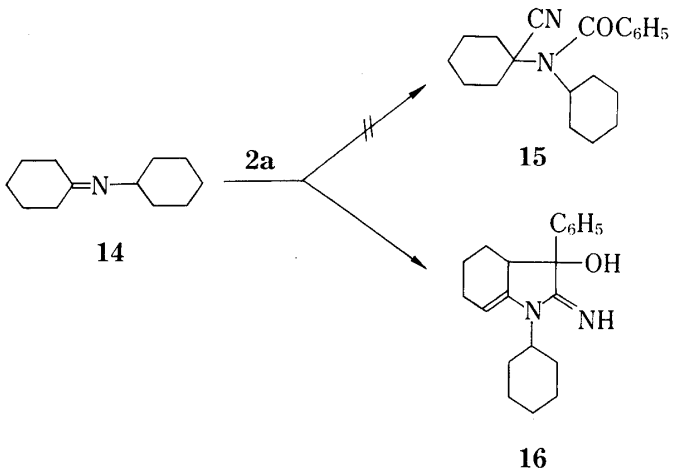


Chart 7

intermediate A which is transformed into the cycloadduct B. Prototropy of B gives rise to the dihydropyrrole **8**. On the other hand, in path b addition of the enamine form of **7** to **2b** gives the cyanohydrine intermediate C, which cyclizes to give the adduct **8**.

Reaction of compound **7c** with **2b** gave rise to **11** *via* the assumed adduct **8c**. Lastly, reaction of an alkylketimine, *N*-(1-ethylpropylidene)benzylamine (**12**), with **2b** was carried out to give 1-benzyl-2-ethylidene-4-hydroxy-5-imino-3-methyl-4-(4-nitrophenyl)pyrrolidine (**13**) in 30% yield.

Dornow and Lüpfert[3] proposed that the addition product of *N*-cyclohexylidene-cyclohexylamine (**14**) to **2a** is the Reissert type compound **15**, but our results suggest that this product is the cycloadduct **16**. We re-examined this reaction and confirmed that the structure of this adduct, mp 181—182 °C (lit.[3] mp 189 °C), is 1-cyclohexyl-3-hydroxy-2-imino-3-phenyl-3a,4,5,6-tetrahydroindoline (**16**) from the spectral data detailed in the experimental section.

Further work on the reactions of ketimines containing enolizable hydrogen with **2b** is in progress.

Experimental

All melting points were measured in a Yanaco MP-3 apparatus and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded on JEOL PS-100 and JEOL FX-60 spectrometers, respectively. Chemical shifts are given in δ-values referred to internal tetramethylsilane. Mass and IR spectra were taken on JEOL D-300 and JASCO DS-701G instruments, respectively.

Reaction of *N*-(Benzylidene)benzylamine (4a) with 4-Nitrobenzoyl Cyanide (2b)——General Procedure: A mixture of 1.10 g (5.64 mmol) of **4a** and 1.00 g (5.68 mmol) of **2b** in 30 ml of dry xylene was refluxed for 8 h, then concentrated *in vacuo*, and the residue was washed with Et_2O to give a crystalline substance. Recrystallization from EtOH gave 0.68 g (32%) of *N*-benzyl-*N*-(4-nitrobenzoyl)aminophenylacetonitrile (**5a**) as yellow prisms, mp 152—153 °C. *Anal.* Calcd for $C_{22}H_{17}N_3O_3$: C, 71.15; H, 4.61; N, 11.32. Found: C, 70.99; H, 4.77; N, 11.31. IR ν_{max}^{KBr} cm^{-1}: 1643 (C=O), 1517 (NO_2). ^{1}H-NMR (in $CDCl_3$): 4.27 and 4.55 (2H, each d, J=16 Hz, C$\underline{H}_2$Ph), 6.67 (1H, s, Ph–C$\underline{H}$). ^{13}C-NMR (in $CDCl_3$): 50.4 (t, $\underline{C}H_2$Ph), 50.4 (d, $\underline{C}$H–CN), 115.8 (s, CN), 170.0 (s, NCO). MS *m/e*: 371 (M^+), 280 ($M^+ - CH_2Ph$), 150 (NO_2–C_6H_4–CO^+).

The other compounds **5b**—**f** were obtained by a procedure similar to that described for **5a**, and the data are summarized in Table I.

Another Synthesis of 5a from *N*-(Benzylamino)phenylacetonitrile (6a)[9]——A solution of 0.5 g (2.25 mmol) of **6a** in 5 ml of Et_2O was poured into 20 ml of saturated sodium bicarbonate solution, then a solution of 0.39 g (2.10 mmol) of 4-nitrobenzoyl chloride in 5 ml of Et_2O was added. The mixture was shaken thoroughly for several minutes, and the resulting precipitates were collected by filtration. Recrystallization from EtOH afforded 0.67 g (86%) of **5a**. This sample was identified by mixed melting point determination with the compound obtained from **4a** and **2b**.

Reaction of *N*-(1-Phenylpropylidene)benzylamine (7a) with 2b——A mixture of 2.54 g (11.4 mmol) of **7a** and 2.00 g (11.4 mmol) of **2b** was allowed to stand for 24 h at room temperature. Then the reaction mixture was concentrated *in vacuo*, and the residue was washed with Et_2O to give a crystalline substance. Recrystallization from EtOH afforded 1.84 g (41%) of 1-benzyl-4-hydroxy-5-imino-3-methyl-4-(4-nitrophenyl)-2-phenyl-4,5-dihydropyrrole (**8a**) as yellow prisms, mp 168—170 °C. *Anal.* Calcd for $C_{24}H_{21}N_3O_3$: C, 72.16; H, 5.30; N, 10.52. Found: C, 71.89; H, 5.25; N, 10.46. IR ν_{max}^{KBr} cm^{-1}: 3390 (br, O–H), 3290 (N–H), 1638 (C=N), 1130 (C–O). ^{1}H-NMR (in $CDCl_3$): 1.39 (3H, s, CH_3), 4.38 and 4.63 (2H, each d, J=16 Hz, C$\underline{H}_2$Ph), 6.12 (2H, br, =NH and OH, D_2O-erasable). ^{13}C-NMR (in $CDCl_3$): 8.4 (q, CH_3), 45.7 (t, $\underline{C}H_2$Ph), 82.2 (s, C(4)), 117.0 (s, C(3)), 129.8, 137.4, 141.5, 147.4, and 148.2 (5s, C(2) and 4C in aromatic rings), 175.6 (s, C(5)). MS *m/e*: 399 (M^+), 381 ($M^+ - H_2O$), 308 ($M^+ - CH_2Ph$), 91 ($PhCH_2^+$). The sample utilized for X-ray crystallographic analysis was obtained by recrystallization from EtOH.

Benzoylation of 8a——A solution of 1.00 g (2.50 mmol) of **8a** in 50 ml of Et_2O was poured into 40 ml of 10% sodium bicarbonate solution, then a solution of 0.35 g (2.50 mmol) of benzoyl chloride in 20 ml of Et_2O was added. The reaction mixture was shaken thoroughly for several minutes, and the resulting precipitates were collected by filtration. Recrystallization from MeOH afforded 1.11 g (88%) of 1-benzyl-5-benzoylimino-4-hydroxy-3-methyl-4-(4-nitrophenyl)-2-phenyl-4,5-dihydropyrrole (**9**) as colorless needles, mp 190—192 °C. *Anal.* Calcd for $C_{31}H_{25}N_3O_4$: C, 73.94; H, 5.00; N, 8.35. Found: C, 74.08; H, 4.96; N, 8.33. IR ν_{max}^{KBr} cm^{-1}: 3400 (O–H), 1587 (C=O), 1150 (C–O). ^{1}H-NMR (in DMSO-d_6): 1.34 (3H, s, CH_3), 3.06 (1H, br, OH, D_2O-erasable), 4.67 and 4.97 (2H, each d, J=16 Hz, C$\underline{H}_2$Ph). MS *m/e*: 503 (M^+).

Reaction of *N*-(1-Phenylethylidene)benzylamine (7b) with 2b——A mixture of 1.19 g (5.68 mmol) of **7b** and 1.00 g

(5.68 mmol) of **2b** in 50 ml of dry benzene was stirred for 1 h at room temperature. The resulting precipitates were collected by filtration. Recrystallization from MeOH gave 1.05 g (48%) of 1-benzyl-4-hydroxy-5-imino-4-(4-nitrophenyl)-2-phenyl-4,5-dihydropyrrole (**8b**) as colorless plates, mp 152—154 °C. *Anal.* Calcd for $C_{23}H_{19}N_3O_3$: C, 71.67; H, 4.97; N, 10.90. Found: C, 71.74; H, 5.06; N, 10.95. IR ν_{max}^{KBr} cm^{-1}: 3300 (N–H), 1644 (C=C and C=N). ^{1}H-NMR (in DMSO-d_6): 4.68 (2H, s, C$\underline{H}_2$Ph), 5.31 (1H, s, H–C(3)), 6.63 (1H, s, OH, D_2O-erasable), 7.56—7.92 (1H, br, =NH, D_2O-erasable). ^{13}C-NMR (in DMSO-d_6): 44.8 (t, $\underline{C}H_2$Ph), 79.1 (s, C(4)), 108.8 (d, C(3)), 130.8, 138.2, 146.6, 148.3, and 150.3 (5s, C(2) and 4C in aromatic rings), 174.3 (s, C(5)). MS *m/e*: 385 (M^+), 278 ($M^+ - NH_2CH_2Ph$), 91 ($PhCH_2^+$).

Acetylation of 8b——A solution of 1.0 g (2.60 mmol) of **8b** in 10 ml of acetic anhydride was warmed for 2 h at 100 °C then poured into 30 ml of water. The reaction mixture was allowed to stand at room temperature for about 0.5 h, then neutralized with saturated sodium bicarbonate, and the resulting precipitates were collected by filtration. Recrystallization from EtOH gave 0.98 g (88%) of 5-acetylimino-1-benzyl-4-hydroxy-4-(4-nitrophenyl)-2-phenyl-4,5-dihydropyrrole (**10**) as colorless crystals, mp 168—170 °C. *Anal.* Calcd for $C_{25}H_{21}N_3O_4$: C, 70.24; H, 4.95; N, 9.83. Found: C, 70.02; H, 5.04; N, 10.02. IR ν_{max}^{KBr} cm^{-1}: 3400 (br, O–H), 1729 (C=O), 1684 (N–C=O). ^{1}H-NMR (in $CDCl_3$): 2.67 (3H, s, $COCH_3$), 3.67 (1H, br, OH, D_2O-erasable), 3.68 and 3.84 (2H, each d, J=14 Hz, C$\underline{H}_2$Ph), 7.15 (1H, s, H–C(3)). MS *m/e*: 427 (M^+), 106 ($PhCH_2NH^+$), 91 ($PhCH_2^+$).

Reaction of *N*-(1-Phenylbutylidene)benzylamine (7c) with 2b——A mixture of 0.67 g (2.82 mmol) of **7c** and 0.50 g (2.84 mmol) of **2b** in 30 ml of dry benzene was stirred for 6 h at room temperature, then concentrated *in vacuo*, and the residue was purified by preparative TLC using benzene as a developing solvent to provide 0.28 g (18%) of 1-benzyl-3-ethyl-4-hydroxy-5-(4-nitrobenzoylimino)-4-(4-nitrophenyl)-2-phenyl-4,5-dihydropyrrole (**11**) as yellow crystals, mp 168—171 °C. *Anal.* Calcd for $C_{32}H_{26}N_4O_6$: C, 68.32; H, 4.66; N, 9.96. Found: C, 68.07; H, 4.67; N, 10.00. IR ν_{max}^{KBr} cm^{-1}: 3400 (O–H), 1587 (C=O), 1525 (NO_2), 1153 (C–O). ^{1}H-NMR (in C_5D_5N): 0.86 (3H, t, J=8 Hz, $CH_2C\underline{H}_3$), 1.75—2.47 (2H, m, C$\underline{H}_2CH_3$), 4.97 (1H, s, OH, D_2O-erasable), 5.02 and 5.25 (2H, each d, J=16 Hz, C$\underline{H}_2$Ph). ^{13}C-NMR (in C_5D_5N): 14.3 (q, $CH_2\underline{C}H_3$), 17.9 (t, $\underline{C}H_2CH_3$), 46.8 (t, $\underline{C}H_2$Ph), 84.7 (s, C(4)), 174.0 and 175.3 (2s, C(5) and C=O). MS *m/e*: 562 (M^+), 150 (NO_2–C_6H_4–CO^+), 91 ($PHCH_2^+$).

Reaction of *N*-(1-Ethylpropylidene)benzylamine (12) with 2b——A mixture of 1.00 g (5.71 mmol) of **12** and 1.00 g (5.68 mmol) of **2b** in 30 ml of dry benzene was stirred for 24 h at room temperature. The resulting precipitates were collected by filtration, and subjected to silica gel column chromatography with AcOEt as an eluent to give a crystalline substance. Recrystallization from AcOEt gave 0.6 g (30%) of 1-benzyl-2-ethylidene-4-hydroxy-5-imino-3-methyl-4-(4-nitrophenyl)-pyrrolidine (**13**) as yellow needles, mp 160—165 °C. *Anal.* Calcd for $C_{20}H_{21}N_3O_3$: C, 68.36; H, 6.02; N, 11.96. Found: C, 68.18; H, 6.15; N, 11.73. IR ν_{max}^{KBr} cm^{-1}: 3400 (br, O–H), 3310 (N–H), 1627 (C=N), 1515 and 1347 (NO_2), 1197 (C–O). ^{1}H-NMR (in $CDCl_3$): 1.19 (3H, d, J=7 Hz, CH_3), 1.60 (3H, d, J=7 Hz, CH_3), 3.07 (1H, q, J=7 Hz, H–C(3)), 4.74 (1H, q, J=7 Hz, =C$\underline{H}CH_3$), 4.77 (2H, s, C$\underline{H}_2$Ph), 6.05 (2H, s, =NH and OH, D_2O-erasable). MS *m/e*: 351 (M^+).

Reaction of *N*-Cyclohexylidenecyclohexylamine (14) with Benzoyl Cyanide (2a)——A solution of 1.31 g (10.0 mmol) of **2a** in 30 ml of dry Et_2O was added to a solution of 1.79 g (10.0 mmol) of **14** in 10 ml of dry Et_2O, and the mixture was allowed to stand for 24 h. The resulting precipitates were collected by filtration. Recrystallization from MeOH afforded 2.15 g (70%) of 1-cyclohexyl-3-hydroxy-2-imino-3-phenyl-3a,4,5,6-tetrahydroindoline (**16**) as colorless crystals, mp 182—183 °C (lit.,[3] mp 189 °C). *Anal.* Calcd for $C_{20}H_{26}N_2O$: C, 77.38; H, 8.44; N, 9.03. Found: C, 77.19; H, 8.45; N, 8.79. IR ν_{max}^{KBr} cm^{-1}: 3380 (br, O–H), 3290 (N–H), 1617 (C=N), 1132 (C–O). ^{1}H-NMR (in DMSO-d_6): 4.05 (1H, tt, J_1=12 Hz, J_2=4 Hz, N–CH), 5.02 (1H, dd, J_1=7 Hz, J_2=5 Hz, H–C(7)), 5.56 (1H, br, =NH). ^{13}C-NMR (in DMSO-d_6): 48.8 (d, C(3a)), 52.2 (d, N–CH), 79.1 (s, C(3)), 94.8 (d, C(7)), 140.3 and 142.6 (2s, C(7a) and $\underline{C}$–C(3)), 170.9 (s, C(2)). MS *m/e*: 310 (M^+), 292 ($M^+ - H_2O$), 228 ($M^+ - C_6H_{11}$).

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