Synthesis and structures of 1-[1-(4-R-benzoyl)-2-ethoxyvinyl]-2-dicyanomethylene-1,2-dihydropyridines

I. A. Aitov,[a] *V. N. Nesterov,*[b]* *Yu. A. Sharanin,*[a] *and Yu. T. Struchkov*[b]†

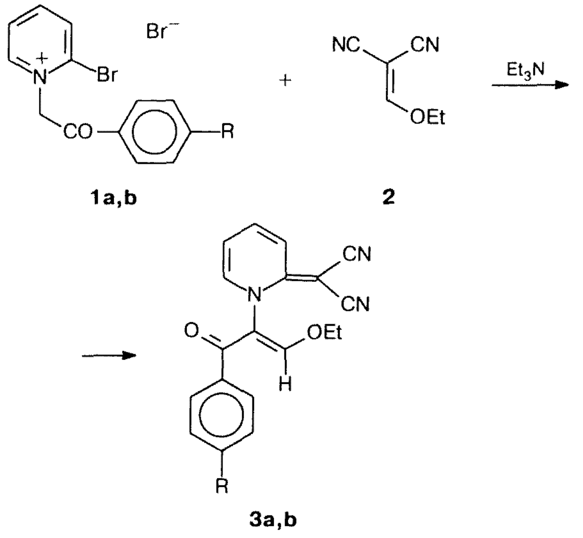
[a]*East-Ukraine University, 2 ul. Oboronnaya, 348011 Lugansk, Ukraine.*
Fax: +7 (064 2) 53 3127
[b]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

The reaction of (4-R-benzoyl)(2-bromopyridinium) methylides with ethoxymethylenemalononitrile is stereoselective and affords *Z*-1-[1-(4-R-benzoyl)-2-ethoxyvinyl]-2-dicyanomethylene-1,2-dihydropyridines. The structure of 1-[1-(4-chlorobenzoyl)-2-ethoxyvinyl]-2-dicyanomethylene-1,2-dihydropyridine has been established by X-ray structural study.

Key words: pyridinium ylides, stereoselectivity; 2-dicyanomethylene-1,2-dihydro-1-vinylpyridines, X-ray structural study.

It is known that the reactions of pyridinium ylides with alkoxymethylene derivatives of methylene-active compounds result in the replacement of the alkoxyl group and afford the corresponding zwitterions.[1] As part of continuing studies,[2] in this work we studied the reactions of 2-bromopyridinium ylides (**1**) (obtained *in situ* from 1-aroylmethyl-2-bromopyridinium bromides and triethylamine) with ethoxymethylenemalononitrile (**2**).

The reaction of 1-benzoylmethyl-2-bromopyridinium bromide (**1a**)[3] with **2** in the presence of an equimolar amount of triethylamine affords 1-(1-benzoyl-2-ethoxyvinyl)-2-dicyanomethylene-1,2-dihydropyridine (**3a**) in low yield (in a mixture with the starting compound **1a**). When a two-fold excess of the base was used, we succeeded in increasing the yield of compound **3a** to 72 %. 1-[1-(4-Chlorobenzoyl)-2-ethoxyvinyl]-2-dicyanomethylene-1,2-dihydropyridine (**3b**) was synthesized in a similar manner.



1a,b **2** **3a,b**

R = H(**a**), Cl(**b**)

The data of ^{1}H NMR spectra of compounds **3a,b** are indicative of the presence of only one isomer (with respect to the C=C bond in the *N*-vinyl fragment).

In order to unambiguously establish the structures of the products of the reaction of **1** with **2**, we have performed an X-ray structural study of compound **3b**. The overall view of molecule **3b** is shown in Fig. 1; the bond angles are given in Table 1.

The value of the N(1)—C(7)—C(15)—O(2) torsion angle (−2.0°) indicates that this compound has the structure of a *Z* isomer. The conformation of 1,2-dihydropyridine ring of the molecule (deviations of the atoms from the mean plane of the cycle are no more than ±0.019 Å) can be described as a highly flattened half-chair: the N(1) and C(2) atoms deviate from the plane through the remaining four atoms in opposite directions by 0.027 and −0.016 Å, respectively (the fragment is planar within ±0.007 Å). This slight distortion of the the heterocycle geometry does not preclude the π,π conjugation of the planar dicyanomethylene fragment with the C(3)=C(4) double bond as well as with the lone electron

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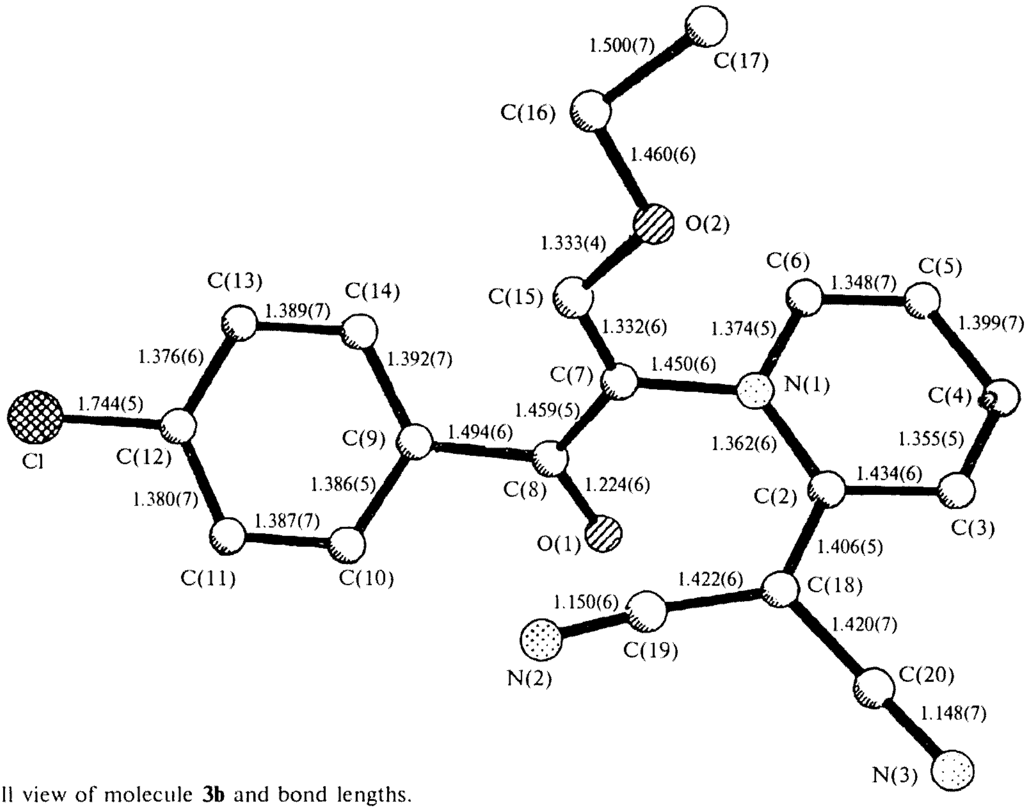

Fig. 1. Overall view of molecule **3b** and bond lengths.

pair of the trigonal N(1) atom (the sum of the van der Waals radii is 360(1)°). This is confirmed, on the one hand, by a substantial shortening of the N(1)—C(2) bond to 1.362(6) Å (compared to the N(1)—C(7) bond (1.450(6) Å)) and the C(2)—C(3) bond to 1.434(6) Å (the standard length of the conjugated C(sp^2)—C(sp^2) single bond is 1.455 Å)[4] and, on the other hand, by an appreciable elongation of the C(3)=C(4) double bond to 1.355(5) Å (the standard length of the C(sp^2)=C(sp^2) double bond is 1.331 Å)[4] and OF the exocyclic C(2)=C(18) double bond to 1.406(5) Å. Conjugation between the cyano groups and the C(2)=C(18) double bond is less pronounced.

A similar redistribution of interatomic distances in an analogous conjugated fragment has been previously found in the molecule of 5-amino-4,6-dicyano-3-dicyanomethylene-1,8,8-trimethyl-2-azabicyclo[2.2.2]oct-2-ene[5] as well as in the molecule of 6-methyl-4,6-diphenyl-2-dicyanomethylene-1,2,5,6-tetrahydronicotinonitrile; the structure of the latter is described by resonance structures with the charge redistribution.[6]

Intramolecular steric nonvalent contacts in molecule **3b** are responsible for the twist of the dihydropyridine and the benzene cycle relative to the planar conjugated fragment C(15)=C(7)—C(8)=O(1) by 103.7 and 137.0°, respectively, as well as for a slight increase (compared to the ideal value of 120°) in the values of the N(1)—C(2)—C(18) (124.1°), C(2)—C(18)—C(19) (128.0°), and C(8)—C(7)—C(15) (127.2°) bond angles.

Table 1. Bond angles (ω) in molecule **3b**

Angle	ω/deg	Angle	ω/deg
C(15)—O(2)—C(16)	115.9(4)	C(8)—C(9)—C(10)	116.9(4)
C(2)—N(1)—C(6)	122.8(4)	C(8)—C(9)—C(14)	123.1(3)
C(2)—N(1)—C(7)	122.6(3)	C(10)—C(9)—C(14)	119.7(4)
C(6)—N(1)—C(7)	114.6(4)	C(9)—C(10)—C(11)	120.0(5)
N(1)—C(2)—C(3)	115.4(3)	C(10)—C(11)—C(12)	119.2(4)
N(1)—C(2)—C(18)	124.1(4)	C(1)—C(12)—C(11)	118.7(3)
C(3)—C(2)—C(18)	120.5(4)	C(1)—C(12)—C(13)	119.2(4)
C(2)—C(3)—C(4)	121.8(4)	C(11)—C(12)—C(13)	122.1(4)
C(3)—C(4)—C(5)	119.9(4)	C(12)—C(13)—C(14)	118.3(5)
C(4)—C(5)—C(6)	118.9(4)	C(9)—C(14)—C(13)	120.7(4)
N(1)—C(6)—C(5)	121.1(4)	O(2)—C(15)—C(7)	120.9(4)
N(1)—C(7)—C(8)	114.4(4)	O(2)—C(16)—C(17)	106.7(4)
N(1)—C(7)—C(15)	118.3(3)	C(2)—C(18)—C(19)	128.0(4)
C(8)—C(7)—C(15)	127.2(4)	C(2)—C(18)—C(20)	117.9(4)
O(1)—C(8)—C(7)	119.4(4)	C(19)—C(18)—C(20)	114.1(3)
O(1)—C(8)—C(9)	119.3(3)	N(2)—C(19)—C(18)	174.2(5)
C(7)—C(8)—C(9)	121.3(4)	N(3)—C(20)—C(18)	179.4(4)

Table 2. Atomic coordinates ($\times 10^4$ for Cl, O, N, and C; $\times 10^3$ for H) in molecule **3b**

Atom	*x*	*y*	*z*
Cl	446(2)	9704(1)	2029(1)
O(1)	3617(4)	9187(3)	6510(2)
O(2)	3300(3)	3921(3)	7817(2)
N(1)	3669(4)	6655(4)	8225(3)
N(2)	7008(5)	6079(5)	5410(3)
N(3)	9326(5)	6101(5)	8078(4)
C(2)	5168(5)	6641(4)	8369(3)
C(3)	5223(5)	6905(5)	9475(3)
C(4)	3879(5)	7104(5)	10325(3)
C(5)	2389(5)	7038(5)	10137(3)
C(6)	2314(5)	6817(5)	9095(3)
C(7)	3359(5)	6578(4)	7126(3)
C(8)	3219(5)	8085(4)	6308(3)
C(9)	2574(5)	8320(4)	5236(3)
C(10)	3279(5)	9221(5)	4260(3)
C(11)	2647(5)	9607(5)	3262(4)
C(12)	1292(5)	9117(5)	3266(3)
C(13)	559(5)	8231(5)	4225(4)
C(14)	1222(5)	7821(5)	5213(4)
C(15)	3165(5)	5207(4)	6984(3)
C(16)	2783(6)	2589(5)	7645(4)
C(17)	2916(8)	1345(6)	8715(5)
C(18)	6599(5)	6366(5)	7522(3)
C(19)	6750(5)	6211(5)	6361(4)
C(20)	8103(5)	6227(5)	7831(4)
H(3)	635(5)	689(5)	963(3)
H(4)	388(6)	726(6)	1112(4)
H(5)	144(6)	720(5)	1068(4)
H(6)	132(5)	683(5)	883(3)
H(10)	425(5)	951(5)	427(4)
H(11)	291(7)	1030(7)	264(5)
H(13)	−46(6)	811(6)	419(4)
H(14)	88(6)	713(6)	584(4)
H(15)	293(5)	511(5)	630(4)
H(161)	361(7)	222(6)	689(5)
H(162)	156(5)	299(5)	751(3)
H(171)	204(9)	193(9)	940(7)
H(172)	409(6)	88(6)	884(4)
H(173)	289(7)	24(7)	859(5)

Experimental

The IR spectra were obtained using a Specord M40 spectrometer using KBr pellets. The ^{1}H NMR spectra were recorded on a Bruker WP-100 SY instrument (100 MHz) in DMSO-d_6. Compounds were monitored by TLC on Silufol UV-254 plates using the acetone—benzene system (1 : 3).

1-[*Z*-(1-Benzoyl-2-ethoxyvinyl)-2-dicyanomethylene-1,2-dihydropyridine (3a). Triethylamine (0.84 mL, 6 mmol) was added to a mixture of salt **1** (1.07 g, 3 mmol) and nitrile **2** (0.37 g, 3 mmol) in 3 mL of ethanol at 20 °C. The reaction mass was stirred for 4—6 h. The residue precipitated was filtered off and washed with ethanol and hexane. The yield of compound **3a** was 0.69 g (72 %), m.p. 182—183 °C (from ethanol). Found (%): C, 71.82; H, 4.81; N, 13.36. $C_{19}H_{15}N_3O_2$. Calculated (%): C, 71.91; H, 4.76; N, 13.24. IR, ν/cm^{-1}: 2198, 2204 (C≡N), 1630 (C=O). ^{1}H NMR, δ: 1.24 (t, 3 H, Me); 4.40 (q, 2 H, CH_2); 6.88 (t, 1 H, C(5)H); 7.30 (d, 1 H, C(3)H); 7.44—7.92 (m, 7 H, C(4)H, C(6)H, Ph); 7.96 (s, 1 H, =CH).

1-{*Z*-[1-(4-Chlorobenzoyl)-2-ethoxyvinyl]}-2-dicyanomethylene-1,2-dihydropyridine (3b). Compound **3b** was prepared in the same manner as described for **3a**. The yield of **3b** was 0.69 g (65 %), m.p. 184—186 °C (from benzene). Found (%): C, 64.98; H, 3.94; Cl, 10.07; N, 12.08. $C_{19}H_{14}ClN_3O_2$. Calculated (%): C, 64.87; H, 4.01; Cl, 10.08; N, 11.94. IR, ν/cm^{-1}: 2185, 2201 (C≡N), 1632 (C=O). ^{1}H NMR, δ: 1.25 (t, 3 H, Me); 4.40 (q, 2 H, CH_2); 6.89 (t, 1 H, C(5)H); 7.30 (d, 1 H, C(3)H); 7.56—7.88 (m, 2 H, C(4)H, C(6)H); 7.62 (d, 2 H, Ph); 7.82 (d, 2 H, Ph); 8.01 (s, 1 H, =CH).

X-ray structural study of compound 3b. Crystals of **3b** are triclinic, $a = 8.751(80)$ Å, $b = 8.862(70)$ Å, $c = 12.171(12)$ Å, $\alpha = 76.46(1)$, $\beta = 75.51(2)$, $\gamma = 72.27(1)°$, $V = 857.6(15.3)$ Å^3, $d_{calc} = 1.362$ g cm^{-3}, $Z = 2$, space group $P\bar{1}$. The unit cell parameters and intensities of 3374 independent reflections were measured on a four-circle automated Siemens P3/PC diffractometer (23 °C, Mo-Kα radiation, graphite monochromator, θ/2θ scanning technique to $2\theta_{max} = 56°$). The structure was solved by the direct method using the SHELXTL program package, which makes it possible to reveal all nonhydrogen atoms, and refined by the full-matrix least-squares method with anisotropic temperature factors for nonhydrogen atoms using 2634 reflections with $I \geq 2\sigma(I)$. Hydrogen atoms were located from difference syntheses and were included in the refinement with isotropic temperature factors. The final values of *R* factors were as follows: $R = 0.067$, $R_w = 0.067$. All calculations were carried out using the SHELXTL PLUS program[7] (the PC version). Atomic coordinates are given in Table 2 (the thermal parameters of atoms can be obtained from the authors).

References

1. W. Sliwa, *Wiad. Chem.*, 1982, **36**, 231.
2. A. M. Shestopalov, V. P. Litvinov, Yu. A. Sharanin, I. A. Aitov, and L. A. Rodinovskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 939 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 835 (Engl. Transl.)].
3. C. Djerassi and G. R. Petit, *J. Am. Chem. Soc.*, 1954, **76**, 4470.
4. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, *J. Chem. Soc. Perkin Trans. 2*, 1987, 1.
5. V. N. Nesterov, V. D. Dyachenko, Yu. A. Sharanin, and Yu. T. Struchkov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 169 [*Russ. Chem. Bull.*, 1996, **43**, 160 (Engl. Transl.)].
6. V. A. Tafeenko, Yu. T. Abramenko, A. V. Ivashchenko, K. A. Nogaeva, and S. V. Medvedev, *Khim. Geterotsikl. Soedin.*, 1988, 77 [*Chem. Heterocycl. Compd.*, 1988 (Engl. Transl.)].
7. W. Robinson and G. M. Sheldrick, in *Crystallographic Computing — Techniques and New Technologies*, Oxford Univ. Press, Oxford, 1988, 366.

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