1,3-Dipolar cycloadditions of heterocycles XV.* Synthesis of 3-(X-phenyl)-4,6-dimethoxy-3a,4,6,6a--tetrahydrofuro[3,4-*d*]isoxazoles

L. ŠTIBRÁNYI, Ľ. FIŠERA, and Y. RYBECKÁ

Department of Organic Chemistry, Slovak Technical University, CS-812 37 Bratislava

Received 11 June 1986

Dedicated to Professor Ing. J. Kováč, DrSc., in honour of his 60th birthday

The title compounds were prepared by 1,3-dipolar cycloaddition of substituted benzonitrile oxides (X = H, 4-CH_3, 4-OCH_3, 4-Cl, 3-Cl, 4-F) at the equimolar mixture of *cis*- and *trans*-2,5-dimethoxy-2,5-dihydrofurans. *Anti* cycloaddition was exclusive with the *cis* and predominant with *trans* derivatives. Irradiation of the prepared derivatives leads to photolabile products.

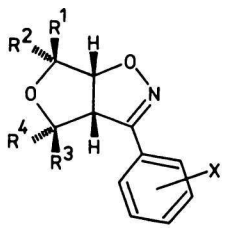
Заглавные соединения были получены путем 1,3-диполярного циклоприсоединения замещенных окисей бензонитрила (X = H, 4-CH_3, 4-OCH_3, 4-Cl, 3-Cl, 4-F) к эквимолярной смеси *цис*- и *транс*-2,5--диметокси-2,5-дигидрофуранов. *Анти*-циклоприсоединение было исключительным при *цис*- и преобладающим при *транс*-производных. Облучение полученных производных ведет к образованию фотолабильных продуктов.

There has been a revival of interest in the photochemistry of isoxazoline derivatives [1—9]; the photoreactions described so far were nonselective. In our previous papers we have shown [10—19] that they can be made selective, giving heterocyclic enamino aldehydes, by introduction of an oxygen atom in the β-position to the isoxazoline oxygen.

According to the results of *Caramella* and coworkers [20] the cycloaddition of unsubstituted benzonitrile oxide on the *cis*-2,5-dimethoxy-2,5-dihydrofuran proceeds to 99 % in an *anti* fashion. The reason for this the authors see in the energetically favourable conformation of the transition state caused by the tendency of the methoxy group to occupy a pseudoaxial position at the bicyclic system (anomeric effect), the energy difference between the *cis* and *trans* addition being 11.2 kJ mol^{-1}.

* For Part *XIV* see *Chem. Papers 40*, 685 (1986).

Now we report on the photochemical activity of bicyclic isoxazolines, having two oxygen atoms in β-position relative to the oxygen of heterocycle. One of these oxygens belongs to the tetrahydrofuran ring, the other is exocyclic. Such derivatives could be prepared by cycloaddition at the dimethoxytetrahydrofuran skeleton, represented by a mixture of *cis*- and *trans*-2,5-dimethoxy-2,5-dihydrofuran. With respect to the methoxy group in the position 6 the reaction can proceed as *anti* cycloaddition to form *II* and *I*, or as *syn* cycloaddition to form derivatives *III*, *IV* (Scheme 1).



				X
I	$R^1 = R^4 = OCH_3$	$R^2 = R^3 = H$	*a*	H
II	$R^1 = R^3 = OCH_3$	$R^2 = R^4 = H$	*b*	4-CH_3
III	$R^2 = R^4 = OCH_3$	$R^1 = R^3 = H$	*c*	4-Cl
IV	$R^2 = R^3 = OCH_3$	$R^1 = R^4 = H$	*d*	3-Cl
			e	4-F
			f	4-OCH_3

Scheme 1

The requisite nitrile oxides were generated by two methods; the first one was a recently described [21] *in situ* procedure, in which substituted benzaldoximes were oxidized by hypochlorite solution, the reaction being catalyzed by triethylamine. The second method used was the more conventional treatment of benzhydroximoyl chlorides with triethylamine in ether [22]. Although simple the hypochlorite procedure gave unacceptably low yields (max. 17 %); from the reaction mixtures only derivatives *II* — products of an *anti* addition at the *cis*-dimethoxydihydrofuran could be isolated. Better, though more complicated, proved to be the method starting from hydroximoyl chlorides. Yields of derivatives *II* were in the range of 18—26 %, *anti* addition products *I* were formed in only 2—5 % yield. The parent benzonitrile oxide gave with the *cis* dimethoxy derivative only product of *anti* addition (*IIa*, yield = 28 %) as well as two products with the *trans* derivative in trace amounts (*IVa*, yield = 1 %, *Ia*,

yield = 3 %). Halogenated benzonitrile oxides reacted only in *anti* fashion to *IIc*—*IIe* with *cis* and *Ic*—*Ie* with the *trans* derivative.

Similarly methoxy- and methyl-substituted nitrile oxides underwent an *anti* addition to *cis* derivatives to form *IIb*, *IIf*. On the whole our results were in accordance with those of [21]. In all cases the *cis* derivative had higher reactivity than the *trans*, so much that the less reactive donor-substituted benzonitrile oxides failed to react with the *trans* isomer. 1,3-Cycloadditions at heterocycles were found [23] to be governed by the dominant frontier interaction LUMO (dipole)—HOMO (heterocycle), where donor substituents at the dipole lowered the reaction rate.

Structures of all prepared compounds were assigned based on elemental analyses, IR, ^{1}H and ^{13}C NMR as well as mass spectral data. ^{13}C NMR spectra revealed that chemical shifts of carbons of methoxy groups are fairly independent of the substitution at the benzene ring. Methoxy groups of *cis* derivatives produced two δ-signals in the region 55.98—55.36 ppm, the difference between them being the greatest in derivatives with donor substituents, *e.g.* for *IIb* $\Delta\delta = 0.4$ ppm. In halogenated derivatives this difference was lower, on average 0.18 ppm. Methoxy groups of *trans* derivatives produced in ^{13}C NMR spectra only one δ-signal in the region 55.28—55.62 ppm with the exception of *Id*, which displayed two δ-signals at 0.3 ppm apart. Similar dependence of chemical shifts was observed for C-4 and C-6 carbons, the signals of which in *cis* derivatives were shifted downfields by about 4 ppm. δ-Signals of C-4 were found at 112.01——111.21 ppm in *cis* derivatives, those of *trans* derivatives at 107.06—107.34 ppm. C-6 carbons of *cis* derivatives displayed δ-signals at 110.45—109.35 ppm, those of *trans* isomers at 105.91—106.04 ppm. Substituents at the benzene ring influenced more C-6 than C-4 carbons, donor substituents causing a downfield shift.

As expected, δ-signals of the bridge carbons C-6a and C-3a reflect their different environment; those of C-6a being deshielded by the contiguous oxygen of the isoxazoline and downfield shifted to 90.31—89.53 ppm in *cis* derivatives and to 90.50—90.31 ppm in *trans* derivatives. Values of $\Delta\delta$ for C-3a and C-6a carbons in *cis* and *trans* derivatives showed, that δ-signals of C-3a are more sensitive to structural changes — for C-6a carbons $\Delta\delta$ did not exceed 0.5——0.7 ppm, while for C-3a the $\Delta\delta$ values climbed over 2.6 ppm. Signals of methoxy groups in *cis*-substituted derivative in ^{1}H NMR spectra were generally well separated, only those of *IIc* and *IIa* showed a barely discernible split ($\Delta\delta = 0.1$—0.2 ppm).

trans Orientation of methoxy groups in the prepared derivatives is borne out by two singlets at $\delta = 3.32$—3.48 ppm, $\Delta\delta = 0.9$—0.13 ppm. Interestingly the multiplicity of signals of methoxy groups in ^{1}H NMR and ^{13}C NMR spectra of *cis* and *trans* derivatives was reversed. While in *cis* derivatives proton NMR

spectra showed mostly one signal and ^{13}C NMR spectra two signals, the reverse was true for the *trans* derivatives.

Chemical shift of H-4 and H-6 protons was practically not influenced by substituents at the benzene ring. H-6 protons in *cis* derivatives gave singlets at $\delta = 5.21$—5.08 ppm, donor substituents causing an upfield shift. Coupling constant $J_{3a,6a}$ was 9 Hz in *cis* and 6—8 Hz in *trans* derivatives. H-6 protons of *cis* derivatives displayed singlets at $\delta = 5.07$—5.27 ppm, in *trans* derivatives H-6 protons were more structure-dependent and their signals were spread over a δ-region 4.37—5.52 ppm. The same was true for H-3a protons, the signals of which were at $\delta = 4.32$—5.58 ppm in *trans* and at $\delta = 4.21$—4.41 ppm in *cis* derivatives.

Characteristic feature of mass spectra of all synthesized compounds was the splitting of the isoxazoline ring *via* cycloreversion. Attempts at photochemical reactions of the prepared derivatives were unsuccessful under all used reaction conditions. This indicates that photochemical processes are more complex when an additional exocyclic β-oxygen is present in the molecule. ^1H NMR spectral analysis of the crude reaction mixture after the photolysis revealed that certain part of *IIa* did indeed change to a heterocyclic enamino aldehyde *VIII*, as indicated by a stable singlet at $\delta = 8.96$ ppm, typical of an aldehydic group. Furthermore the spectra of reaction mixtures contained signals of the CH—NH group and a singlet of methoxy group. At least one part of the reaction mechanism was then consistent with our previous findings [10—19], however, all attempts to isolate the enamino aldehyde failed to produce anything but polymers.

Experimental

Melting points are uncorrected. Mass spectra were recorded on an MS 902 S spectrometer with direct inlet system at ionizing energy 70 eV and an ionizing current of 100 μA. ^1H NMR spectra were recorded with a Tesla BS 487 C spectrometer at 80 MHz in deuteriochloroform unless otherwise stated, with tetramethylsilane as internal standard. ^{13}C NMR spectra were determined in deuteriochloroform on a Jeol spectrometer using tetramethylsilane as internal standard. UV spectra were measured in methanol solutions with a Perkin—Elmer 323 apparatus with temperature control of the measured samples, ε values expressed in $m^2 mol^{-1}$. Low-pressure Toshiba GL-15 (15 W) lamp in quartz sleeve was used for photochemical reactions.

3-Phenyl-4,6-dimethoxy-3a,4,6,6a-tetrahydrofuro[3,4-d]isoxazole

To the mixture of 2,5-dimethoxy-2,5-dihydrofuran (10 g; 76 mmol) and benzhydroximoyl chloride (11.8 g; 76 mmol) in 30 cm^3 of dry ether was during 1 h added

triethylamine (12.2 cm^3; 87 mmol) in 20 cm^3 of ether. During the addition the temperature was kept at 0 °C, the reaction mixture was then stirred and left to stand overnight. The precipitated triethylamine chloride was filtered off, the filtrate concentrated *in vacuo* and chromatographed at silica gel column, eluted with cyclohexane—ethyl acetate (volume ratio = 3 : 1). Besides unreacted dipolarophile and two benzonitrile oxide dimers the chromatography furnished:

a) 3-Phenyl-4,6-dimethoxy-3a,4,6,6a-tetrahydrofuro[3,4-*d*]isoxazole (*IIa*), yield = = 5 g (28 %), m.p. = 89 °C. For $C_{13}H_{15}NO_4$ (M_r = 249.20) w_i(calc.): 62.70 % C, 6.06 % H, 5.62 % N; w_i(found): 63.09 % C, 6.21 % H, 5.78 % N. UV spectrum, λ_{max}/nm (log {ε}): 259 nm (2.83). Mass spectrum, *m/z*: 249 ($M^{+\bullet}$). ^{1}H NMR spectrum, δ/ppm: 7.23—7.71 (m, 5H, H_{ar}), 5.28 (s, 1H, H-6), 5.23 (d, $J_{3a,6a}$ = 9.0 Hz, 1H, H-6a), 5.16 (s, 1H, H-4), 4.38 (d, 1H, H-3a), 3.47 (q, OCH_3), 3.46 (q, OCH_3). ^{13}C NMR spectrum, δ/ppm: 151.16 (s, C=N), 130.47, 129.10, 126.89, 128.32 (C_{ar}), 111.30 (d, C-6), 109.35 (d, C-4), 89.53 (d, C-6a), 59.71 (d, C-3a), 55.94 and 55.75 (q, OCH_3).

b) 3-Phenyl-4,6-dimethoxy-3a,4,6,6a-tetrahydrofuro[3,4-*d*]isoxazole (*IIIa*), yield = = 1 %, m.p. = 83 °C. For $C_{13}H_{15}NO_4$ (M_r = 249.20) w_i(found): 63.03 % C, 6.38 % H, 5.72 % N. UV spectrum, λ_{max}/nm (log {ε}): 259 nm (2.83). Mass spectrum, *m/z*: 249 ($M^{+\bullet}$). ^{1}H NMR spectrum, δ/ppm: 7.24—7.72 (m, 5H, H_{ar}), 5.05 (s, 1H, H-4), 4.73 (d, $J_{6,6a}$ = 6 Hz, 1H, H-6), 4.68 (d, d, 1H, H-6a), 3.85 (d, 1H, H-3a), 3.37 (s, 3H, OCH_3), 3.17 (s, 3H, OCH_3). ^{13}C NMR spectrum, δ/ppm: 157.76 (s, C=N), 131.12, 129.43, 128.65, 127.61, 126.44 (C_{ar}), 108.50 (d, C-6), 106.81 (d, C-4), 87.32 (d, C-6a), 66.53 (d, C-3a), 56.13 (q, OCH_3), 55.35 (q, OCH_3).

c) 3-Phenyl-4,6-dimethoxy-3a,4,6,6a-tetrahydrofuro[3,4-*d*]isoxazole (*Ia*), yield = = 3 %, m.p. = 145 °C. For $C_{13}H_{15}NO_4$ w_i(found): 63.11 % C, 6.21 % H, 5.60 % N. UV spectrum, λ_{max}/nm (log {ε}): 256 nm (3.10). Mass spectrum, *m/z*: 249 ($M^{+\bullet}$). ^{1}H NMR spectrum, δ/ppm: 7.25—7.70 (m, 5H, H_{ar}), 5.40 (d, $J_{3a,6a}$ = 6.0 Hz, 1H, H-6a), 5.27 (s, 1H, H-6), 5.06 (d, $J_{3a,4}$ = 9.0 Hz, 1H, H-4), 4.30 (d, d, 1H, H-3a), 3.46 (s, 3H, OCH_3), 3.35 (s, 3H, OCH_3). ^{13}C NMR spectrum, δ/ppm: 155.68 (s, C=N), 129.69, 128.39, 127.22 (C_{ar}), 107.34 (d, C-6), 106.04 (d, C-4), 90.31 (d, C-6a), 57.05 (d, C-3a), 55.62 (q, OCH_3).

The procedure described for *Ia*—*IIIa* was further utilized for the reaction with the following substituted benzonitrile oxides:

4-Chlorobenzonitrile oxide to give:

a) 3-(4-Chlorophenyl)-4,6-dimethoxy-3a,4,6,6a-tetrahydrofuro[3,4-*d*]isoxazole (*IIc*), yield = 25 %, m.p. = 118—120 °C. For $C_{13}H_{14}ClNO_4$ (M_r = 283.21) w_i(calc.): 55.03 % C, 4.97 % H, 4.94 % N; w_i(found): 55.21 % C, 5.04 % H, 4.89 % N. UV spectrum, λ_{max}/nm (log {ε}): 269 nm (3.19). Mass spectrum, *m/z*: 283 ($M^{+\bullet}$). ^{1}H NMR spectrum, δ/ppm: 7.35—7.66 (m, 4H, H_{ar}), 5.28 (s, 1H, H-6), 5.19 (s, 1H, H-4), 5.15 (d, $J_{3a,6a}$ = 9.0 Hz, 1H, H-6a), 4.26 (d, 1H, H-3a), 3.47 (s, 6H, 2 × OCH_3). ^{13}C NMR spectrum, δ/ppm: 154.33 (s, C=N), 136.49, 129.41, 128.06, 126.77 (C_{ar}), 111.21 (d, C-6), 109.22 (d, C-4), 89.86 (d, C-6a), 59.56 (d, C-3a), 55.98 and 55.81 (q, q, 2 × OCH_3).

b) 3-(4-Chlorophenyl)-4,6-dimethoxy-3a,4,6,6a-tetrahydrofuro[3,4-*d*]isoxazole (*Ic*), yield = 4 %, m.p. = 157 °C. For $C_{13}H_{14}ClNO_4$ w_i(found): 55.42 % C, 5.31 % H, 4.99 % N. UV spectrum, λ_{max}/nm (log {ε}): 265 nm (3.16). Mass spectrum, *m/z*: 283 ($M^{+\bullet}$). ^{1}H NMR spectrum, δ/ppm: 7.44—7.74 (m, 4H, H_{ar}), 5.48 (d, $J_{3a,6a}$ = 6.0 Hz, 1H,

H-6a), 5.21 (s, 1H, H-6), 5.05 (d, $J_{3a,4}$ = 9.0 Hz, 1H, H-4), 4.66 (d, d, 1H, H-3a), 3.43 (s, 3H, OCH_3), 3.31 (s, 3H, OCH_3). ^{13}C NMR spectrum, δ/ppm: 155.71 (s, C=N), 135.01, 129.58, 128.59 (C_{ar}), 107.06 (d, C-6), 105.95 (d, C-4), 90.39 (d, C-6a), 57.22 (d, C-3a), 55.42 (q, OCH_3).

3-Chlorobenzonitrile oxide to give:

a) 3-(3-Chlorophenyl)-4,6-dimethoxy-3a,4,6,6a-tetrahydrofuro[3,4-*d*]isoxazole (*IId*), yield = 27 %, m. p. = 95 °C. For $C_{13}H_{14}ClNO_4$ (M_r = 283.71) w_i(found): 55.11 % C, 5.02 % H, 4.93 % N. UV spectrum, λ_{max}/nm (log{ε}): 265 nm (3.14). Mass spectrum, *m/z*: 283 ($M^{+\bullet}$). ^1H NMR spectrum, δ/ppm: 7.28—7.69 (m, 4H, H_{ar}), 5.28 (s, 1H, H-6), 5.12 (s, 1H, H-4), 5.24 (d, $J_{3a,6a}$ = 9.0 Hz, 1H, H-6a), 4.25 (d, 1H, H-3a), 3.47 (s, 6H, 2 × OCH_3). ^{13}C NMR spectrum, δ/ppm: 154.21 (s, C=N), 135.14, 139.46, 126.77, 124.90, 111.24 (C_{ar}), 109.17 (d, C-6), 91.91 (d, C-4), 89.92 (d, C-6a), 59.41 (d, C-3a), 55.98 (q, OCH_3), 55.81 (q, OCH_3).

b) 3-(3-Chlorophenyl)-4,6-dimethoxy-3a,4,6,6a-tetrahydrofuro[3,4-*d*]isoxazole (*Id*), yield = 3 %, m.p. = 94 °C. For $C_{13}H_{14}ClNO_4$ w_i(found): 55.28 % C, 5.41 % H, 4.99 % N. UV spectrum, λ_{max}/nm (log{ε}): 263 nm (3.08). Mass spectrum, *m/z*: 283 ($M^{+\bullet}$). ^1H NMR spectrum, δ/ppm: 7.27—7.63 (m, 4H, H_{ar}), 5.41 (d, $J_{3a,6a}$ = 7.0 Hz, 1H, H-6a), 5.26 (s, 1H, H-6), 5.09 (d, d, $J_{3a,4}$ = 9.0 Hz, 1H, H-4), 4.30 (d, d, 1H, H-3a), 3.46 (s, 3H, OCH_3), 3.36 (s, 3H, OCH_3). ^{13}C NMR spectrum, δ/ppm: 155.72 (s, C=N), 134.32, 131.40, 129.64, 127.18, 125.31 (C_{ar}), 107.06 (d, C-6), 105.95 (d, C-4), 90.50 (d, C-6a), 57.27 (d, C-3a), 55.58 (q, OCH_3), 55.28 (q, OCH_3).

4-Fluorobenzonitrile oxide to give:

a) 3-(4-Fluorophenyl)-4,6-dimethoxy-3a,4,6,6a-tetrahydrofuro[3,4-*d*]isoxazole (*IIe*), yield = 18 %, m.p. = 68 °C. For $C_{13}H_{14}FNO_4$ (M_r = 267.11) w_i(calc.): 58.42 % C, 5.28 % H, 5.24 % N; w_i(found): 58.41 % C, 5.58 % H, 5.51 % N. UV spectrum, λ_{max}/nm (log{ε}): 257 nm (3.13). Mass spectrum, *m/z*: 267 ($M^{+\bullet}$). ^1H NMR spectrum, δ/ppm: 7.11—7.75 (m, 4H, H_{ar}), 5.27 (s, 1H, H-6), 5.14 (s, 1H, H-4), 5.22 (d, $J_{3a,6a}$ = 9.0 Hz, H-6a), 4.27 (d, 1H, H-3a), 3.47 (s, 3H, OCH_3), 3.49 (s, 3H, OCH_3). ^{13}C NMR spectrum, δ/ppm: 154.21 (s, C=N), 158.89, 128.99, 124.49, 116.71, 115.83 (C_{ar}), 111.21 (d, C-6), 109.23 (d, C-4), 89.68 (d, C-6a), 59.79 (d, C-3a), 55.93 (q, OCH_3), 55.75 (q, OCH_3).

b) 3-(4-Fluorophenyl)-4,6-dimethoxy-3a,4,6,6a-tetrahydrofuro[3,4-*d*]isoxazole (*Ie*), yield = 2 %, m.p. = 132—134 °C. For $C_{13}H_{14}FNO_4$ w_i(found): 58.49 % C, 5.31 % H, 5.18 % N. UV spectrum, λ_{max}/nm (log{ε}): 256 nm (3.10). Mass spectrum, *m/z*: 267 ($M^{+\bullet}$). ^1H NMR spectrum, δ/ppm: 7.01—7.74 (m, 4H, H_{ar}), 5.51 (d, $J_{3a,6a}$ = 6.0 Hz, 1H, H-6a), 5.21 (s, 1H, H-6), 5.04 (d, $J_{3a,4}$ = 9.0 Hz, 1H, H-4), 4.66 (d, 1H, H-3a), 3.43 (s, 3H, OCH_3), 3.31 (s, 3H, OCH_3). ^{13}C NMR spectrum, δ/ppm: 155.16 (s, C=N), 154.64, 129.43, 128.78, 116.17, 114.74 (C_{ar}), 107.81 (d, C-6), 105.91 (d, C-4), 90.31 (d, C-6a), 57.05 (d, C-3a), 55.62 (q, OCH_3).

4-Methoxybenzonitrile oxide to give:

a) 3-(4-Methoxyphenyl)-4,6-dimethoxy-3a,4,6,6a-tetrahydrofuro[3,4-*d*]isoxazole (*IIf*), yield = 9 %, m.p. = 136—138 °C. For $C_{14}H_{17}NO_5$ (M_r = 279.23) w_i(calc.): 60.15 % C, 6.08 % H, 5.01 % N; w_i(found): 60.06 % C, 6.03 % H, 5.01 % N. UV spectrum, λ_{max}/nm (log{ε}): 272 nm (3.29). Mass spectrum, *m/z*: 279 ($M^{+\bullet}$). ^1H NMR spectrum, δ/ppm (deuterated acetone): 6.99—7.68 (m, 4H, H_{ar}), 5.21 (s, 1H, H-6), 5.12 (s, 1H, H-4), 4.45

(d, $J_{3a,6a}$ = 9.0 Hz, 1H, H-6a), 5.12 (d, 1H, H-3a), 3.86 (s, 3H, OCH_3), 3.43 (s, 6H, 2 × OCH_3). ^{13}C NMR spectrum, δ/ppm (deuterated acetone): 155.54 (s, C=N), 129.04, 121.89, 115.26 (C_{ar}), 111.88 (d, C-6), 110.32 (d, C-4), 90.05 (d, C-6a), 60.55 (d, C-3a), 55.36 (q, OCH_3), 55.75 (q, OCH_3).

4-Methylbenzonitrile oxide to give:

a) 3-(4-Methylphenyl)-4,6-dimethoxy-3a,4,6,6a-tetrahydrofuro[3,4-*d*]isoxazole (*IIb*), yield = 14 %, m.p. = 123—125 °C. For $C_{14}H_{17}NO_4$ (M_r = 263.22) w_i(calc.): 63.86 % C, 6.51 % H, 5.32 % N; w_i(found): 63.99 % C, 6.80 % H, 5.45 % N. UV spectrum, λ_{max}/nm (log{ε}): 265 nm (3.14). Mass spectrum, *m*/*z*: 263 ($M^{+\bullet}$). ^{1}H NMR spectrum, δ/ppm (deuterated acetone): 7.24—7.62 (m, 4H, H_{ar}), 5.21 (s, 1H, H-6), 5.11 (s, 1H, H-4), 5.13 (d, $J_{3a,6a}$ = 9.0 Hz, 1H, H-6a), 4.37 (d, 1H, H-3a), 3.41 (s, 6H, OCH_3), 2.37 (s, 3H, OCH_3). ^{13}C NMR spectrum, δ/ppm (deuterated acetone): 155.93 (s, C=N), 141.25, 130.47, 127.48, 126.82 (C_{ar}), 112.01 (d, C-6), 110.32 (d, C-4), 90.31 (d, C-6a), 60.31 (d, C-3a), 55.87 (q, OCH_3), 55.49 (q, OCH_3), 21.31 (q, CH_3).

References

1. Giezendanner, H., Marky, M., Jackson, B., Hansen, H.-J., and Schmid, H., *Helv. Chim. Acta 55,* 745 (1972).
2. Giezendanner, H., Rozenkranz, H. J., and Schmid, H., *Helv. Chim. Acta 56,* 2588 (1973).
3. Claus, P., Iurgen, H., Heingartner, H., Jackson, B., and Schmid, H., *Helv. Chim. Acta 57,* 2173 (1974).
4. Matsuura, T. and Ito, Y., *Tetrahedron Lett. 1973,* 2283.
5. Ito, Y. and Matsuura, T., *Tetrahedron Lett. 31,* 1373 (1975).
6. Mukai, T., Kumagai, T., and Seshimoto, O., *Pure Appl. Chem. 49,* 287 (1977).
7. Seshimoto, O., Kumagai, T., Shimizu, K., and Mukai, T., *Chem. Lett. 1977,* 1195.
8. Kumagai, T., Shimizu, K., Kawamura, Y., and Mukai, T., *Tetrahedron Lett. 37,* 3365 (1981).
9. Kumagai, T., Kawamura, Y., and Mukai, T., *Chem. Lett. 1983,* 1357.
10. Fišera, Ľ., Laudár, S., and Timpe, H.-J., *Chem. Lett. 23,* 148 (1983).
11. Fišera, Ľ., Laudár, S., Timpe, H.-J., Zálupský, P., and Štibrányi, L., *Collect. Czechoslov. Chem. Commun. 49,* 1193 (1984).
12. Fišera, Ľ., Štibrányi, L., Máťušová, A., Oremus, V., and Timpe, H.-J., *Tetrahedron Lett. 1984,* 2731.
13. Fišera, Ľ., Oremus, V., Štibrányi, L., Timpe, H.-J., and Máťušová, A., *Collect. Czechoslov. Chem. Commun. 50,* 1982 (1985).
14. Fišera, Ľ., Konopíková, M., Štibrányi, L., and Timpe, H.-J., *Collect. Czechoslov. Chem. Commun. 50,* 1971 (1985).
15. Fišera, Ľ. and Oravkin, J., *Chem. Papers 39,* 783 (1985).
16. Fišera, Ľ., Oremus, V., Timpe, H.-J., Štibrányi, L., and Zálupský, P., *Collect. Czechoslov. Chem. Commun. 51,* 2158 (1986).
17. Fišera, Ľ., Oravec, P., Štibrányi, L., Kožina, N. D., and Badovskaya, L. A., *Synthesis 1986,* 565.
18. Kožina, N. D., Fišera, Ľ., Oravec, P., Timpe, H.-J., Štibrányi, L., and Badovskaya, L. A., *Collect. Czechoslov. Chem. Commun. 51,* 2167 (1986).
19. Fišera, Ľ., Štibrányi, L., Máťušová, A., and Oravkin, J., *Chem. Papers 40,* 693 (1986).
20. Caramella, P., Marinone, B., Albini, F., Vitali, D., Rondan, N. G., Wu, Y.-D., Schwartz, T. R., and Houk, K. N., *Tetrahedron Lett. 1984,* 1875.

21. Lee, G. A., *Synthesis 1982,* 508.
22. Werner, A. and Buss, H., *Ber. 27,* 2193 (1894).
23. Fišera, Ľ., *Wiss. Z. Karl-Marx-Univ. Leipzig, Math.-Naturwiss. R. 32,* 390 (1983).

Translated by P. Zálupský