1,3-DIPOLAR CYCLOADDITION OF C-BENZOYL-N-PHENYLNITRONE WITH FURAN DERIVATIVES. ANOMALOUS DEHYDROGENATION OF CYCLOADDUCTS WITH 2,3-DICHLORO-5,6-DICYANO-1,4-BENZOQUINONE*

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C-Benzoyl-N-phenylnitrone reacted with 2-R-substituted (R = phenyl, CH_2OH, CH_2OCOCH_3, CH_2SH) furan derivatives at 55°C by a 1,3-dipolar cycloaddition reaction to the unsubstituted furan double bond to give mono- and bisadducts. 2,5-Dimethylfuran afforded monoadduct only. Dehydrogenations of monoadducts of 5-R-2-phenyl-3-benzoyl-3a,6a-dihydrofuro[3,2-c]isoxazolines with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone proceeded anomalously at 60°C: dehydrogenation followed by electrocyclic opening afforded the corresponding ketonitrones. This method of dehydrogenation offers a new preparation of nitrones and further exemplifies the exploitation of products of 1,3-dipolar cycloadditions for synthetic purposes.

Basing upon interpretation of the perturbation interaction diagram for 1,3-dipolar cycloadditions of nitrones with furan it was found[1] that the reaction is controlled by the limit frontier orbital interaction LU (nitrone)—HO (furan) according to Sustman's classification of 1,3-dipolar cycloadditions[2-4]. The monocycloadduct *IIa* and two biscycloadducts *IIIa* (*syn* and *anti*)[1] were obtained by reacting C-benzoyl-N-phenylnitrone *I* with furan at 60°C; with 2-methylfuran and 2-ethyl-furan, products of 1,3-addition *IVb* and *IVc* (ref.[5]) were isolated in addition to monoadducts *IIb*, *IIc* and the bisadduct *IIIb*. This paper deals both with the reaction of *I* with furfuryl alcohol (IP = 8·49 eV), 2-furfuryl acetate (IP = 8·69 eV), 2,5-dimethylfuran (IP = 7·97 eV), 2-furfuryl mercaptan and dehydrogenation of monoadducts *IIb*, *IIa*, *IIe*, and *IIf* with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. Values of ionization potentials given in parentheses for furan derivatives were determined from their charge-transfer complexes with tetracyanoethylene, as presented in the next paper[6]. All values of ionization potentials are lower than the value for furan itself (IP = 8·81 eV, ref.[1]). Since the reaction of *I* with furan derivatives is controlled by the interaction LU (*I*)—HO (furan derivative), one could anticipate their enhanced reactivity when compared with furan[7,8].

1,3-Dipolar cycloaddition of benzoylnitrone I with the respective furan derivatives is regio- and stereospecific, this being in line with the literature[9]; it afforded monoadducts II and bisadducts III in very good yields (Scheme 1, the numbering of formulas for various R is as follows: a H, b CH$_3$, c C$_2$H$_5$, d CH$_2$OH, e CH$_2$OCOCH$_3$, f C$_6$H$_5$, g CH$_2$SH); they were found to be stable under the given reaction conditions. More bisadducts III than monoadducts II were formed (Table I) when using a very little (2-fold) excess of the furan derivative, because II are compounds of dihydrofuran type and consequently, more reactive than the starting furan derivatives. The 1,3-dipolar cycloaddition of furan derivatives requires to overcome their resonance energy, which is higher than that of enolethers of monoadducts II. A great (25-fold) excess of the furan derivative resulted in formation of monoadducts II only. On the other hand, 2-furfuryl alcohol gave, even in such an excess, the bisadduct $IIId$ as a main product. This anomaly can be rationalized by a favourable arrangement for the consecutive cycloaddition of the monoadduct IId with nitrone I through the hydrogen bond between hydrogen of the hydroxymethyl group and nitrone I oxygen. The above-mentioned hydrogen bond can be observed in the mixture of I with 2-furfuryl alcohol in the UV spectrum[13]. As found, the cycloadditions proceed smoothly in a nitrogen atmosphere under exclusion of light and moisture[1] at 55°C and were completed after 16 h (TLC, chloroform–n-heptane 8 : 2). Higher reaction temperature resulted in lowering yields, temperatures above 90°C furnished tarry products. Physical and analytical data of new compounds, which were purified by chromatography on a silica gel column, are given in Table I. Elemental analysis, mass, UV and IR spectra clearly indicated the formation of cycloadducts. Their structure was deduced on the basis of ^{1}H-NMR spectral data using also the INDOR and decoupling techniques. The chemical shifts, coupling constants and the numbering of the heterocyclic system are listed in Table II and in the Scheme 1. The ^{1}H-NMR spectra of cycloadducts II and III are in full accordance with those of monoadducts IIb, IIc and the bisadduct $IIIb$, (ref.[1,5]). Thus e.g. in the monoadduct IIf, where R stands for phenyl, the ^{1}H-NMR (δ, ppm) signals at 5·35 (d), 5·66 (dd), 5·81 (s) and 6·06 (d) were ascribed to protons H$_A$, H$_5$, H$_3$, and H$_4$. The spin-decoupling of the ^{1}H-NMR spectrum at 484 Hz, associated with the H$_4$ resonance, reduced the doublet of doublet at 5·66 to a doublet H$_5$, and was of no effect on the doublet at 5·35 H$_A$. This experiment evidenced the correct attribution of proton signals of the isoxazolidine skeleton H$_3$, H$_4$ and H$_5$ and also that of dihydrofuran proton H$_A$ (Table II). The value of coupling constant of bridgehead protons $J_{4,5} = $ = 7 Hz indicated the cis arrangement thus evidencing both the stereospecificity of the 1,3-dipolar cycloaddition and the concerted reaction of benzoylnitrone I with the listed furan derivatives. Signal of the isoxazolidine proton H$_3$ appeared in the ^{1}H-NMR spectrum as a singlet and therefore, one is entitled on the basis of the zero value of the coupling constant $J_{3,4}$ to ascribe the structure with an anti arrangement of the bridgehead dihydrofuran protons and the isoxazolidine H$_3$

Physical Properties and Elemental Analyses

Compound R	Formula (mol.w.)	M.p., °C (yield, %)	$\nu(CO)$ cm^{-1}	$\lambda_{\max}$ (log ε)	Calculated/Found		
					% C	% H	% N
IId CH$_2$OH	C$_{19}$H$_{17}$NO$_4$ (323·3)	168—170 (21)	1 695 3 568^a 3 681^a	246 (4·54)	70·57 70·69	5·30 5·25	4·33 4·20
IIe CH$_2$OCOCH$_3$	C$_{21}$H$_{19}$NO$_5$ (365·4)	108—110 (71)	1 693 1 744	245 (4·42)	69·03 69·21	5·24 5·14	3·83 4·08
IIf C$_6$H$_5$	C$_{24}$H$_{20}$NO$_3$ (370·4)	121—122 (38)	1 692	246 (4·30)	77·82 78·10	5·44 5·45	3·78 4·06
IIg CH$_2$SH^b	C$_{19}$H$_{17}$NO$_3$S (339·4)	133—135 (64)	1 694	246 (4·68)	67·23 67·11	5·05 5·12	4·12 4·26
IIId CH$_2$OH	C$_{33}$H$_{28}$N$_2$O$_6$ (548·6)	200—202 (54)	1 695 3 567^a 3 679^a	246 (4·45)	72·25 72·29	5·14 5·08	5·11 5·10
IIIe CH$_2$OCOCH$_3$	C$_{35}$H$_{30}$N$_2$O$_7$ (590·6)	142—144 (12)	1 694 1 747	246 (4·72)	71·17 71·34	5·12 5·17	4·74 4·95
IIIf C$_6$H$_5$	C$_{38}$H$_{31}$N$_2$O$_5$ (595·6)	178—180 (40)	1 699	246 (4·66)	76·62 76·90	5·25 5·15	4·70 4·93
V CH$_3$	C$_{20}$H$_{19}$NO$_3$ (321·4)	147—148 (46)	1 682 1 695	244 (4·41)	74·74 74·71	5·96 5·80	4·36 4·38
VIIIa H	C$_{18}$H$_{13}$NO$_3$ (291·3)	163—164 (83)	1 680	314 (4·82) 261 (4·51)	74·21 74·41	4·49 4·52	4·81 4·92
VIIIb CH$_3$	C$_{19}$H$_{15}$NO$_3$ (305·3)	133—134 (90)	1 681	326 (4·87) 256 (4·50)	74·73 74·78	4·95 4·87	4·58 4·79
VIIIe CH$_2$OCOCH$_3$	C$_{21}$H$_{17}$NO$_5$ (363·4)	— (75)	1 680 1 742	321 260	69·41 —	4·72 —	3·85 —
VIIIf C$_6$H$_5$	C$_{24}$H$_{18}$NO$_3$ (368·4)	143—144 (88)	1 679	366 (4·83) 349 (4·50)	78·24 78·21	4·92 5·06	3·80 3·02

^{a} ν(OH); ^{b} % S calculated: 9·58% S; found: 9·81% S.

proton to monoadduct *IIf*. The substituent R at the furan ring is of minimum effect on the value of chemical shift of isoxazolidine moiety protons; a greater effect was exerted on the value of chemical shift H$_A$. The ^{1}H-NMR spectrum of the mono-adduct *IIg* (R = CH$_2$SH) was excluded from the series, since the H$_3$, H$_4$ and H$_A$
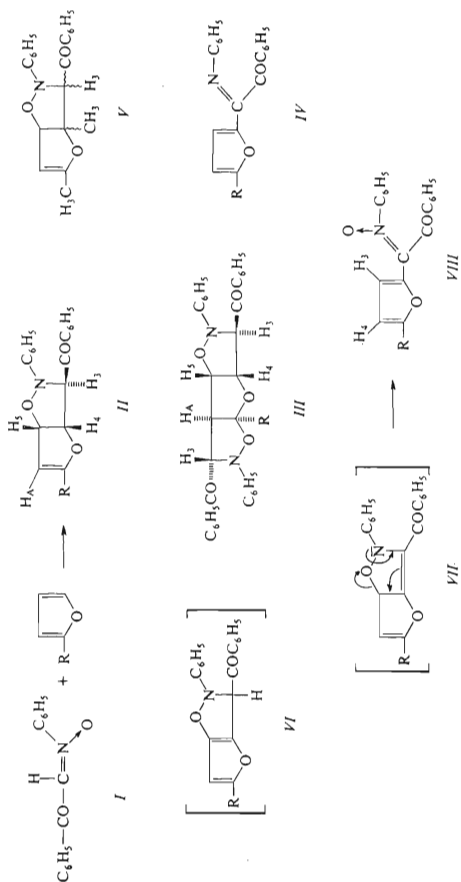
SCHEME 1

proton signals appeared, due to the close values of chemical shifts, as a complex multiplet with 5·97—6·20. Their correct assignment and also the determination of coupling constants were enabled by using the combination of INDOR technique, decoupling experiment and application of a shift reagent. The mutual doublet-doublet interactions at 424 Hz (H_5) with the doublet at 487 Hz (H_4) and partly also with the doublet-doublet at 478·5 Hz (H_A) were determined employing the INDOR technique. Decoupling of the signal at 424 Hz belonging to the H_5 resonance reduced the complex multiplet at 5·97—6·20 to a doublet at 6·16 (H_3), the singlet

TABLE II

Chemical Shifts and Coupling Constants of the Synthesized Substances (δ, ppm; J, Hz)

Compound	H_3	H_4	H_5	H_A	Aromatic m	Other
IId	5·76 s	5·96 d (7·0)	5·53 dd (7·0, 2·0)	5·01 d (2·0)	6·92—8·09	CH$_2$, 3·60 s
IIe	5·76 s	5·98 d (6·5)	5·66 dd (6·5, 2·0)	5·10 d (2·0)	5·87—8·12	CH$_2$, 4·05 s CH$_3$, 1·97 s
IIf	5·81 s	6·05 d (6·5)	5·66 dd (6·5, 2·2)	5·35 d (2·2)	6·62—8·09	—
IIg	6·16 d (3·1)	6·08 d (8·1)	5·31 dd (8·1, 1·7)	5·98 dd (3·1, 1·7)	6·75—8·01	CH$_2$, 3·56 s
IIId	5·68 s 6·12 s	5·06 d (6·0)	4·55 d (6·0)	3·83 s	6·75—7·97	CH$_2$, 3·30 s OH, 4·75 b
IIIe	5·07 s 5·39 s	4·97 d (4·2)	4·48 d (4·2)	4·28 s	6·90—8·05	CH$_2$, 4·18 s CH$_3$, 1·85 s
IIIf	5·44 s 5·21 d	5·06 d (4·0)	4·66 dd (4·0, 1·0)	4·13 dd (1·0, 0·5)	6·83—8·02	—
V	5·25 s	—	5·14 d (2·0)	4·70 m (2·0, 1·0)	6·37—8·19	CH$_3$, 2·90 d CH$_3$, 1·71 s
VIIIa	8·22 d (3·5)	6·62 dd (3·5, 1·7)	7·43 d (1·7)	—	7·10—7·82	—
VIIIb	8·16 d (3·5)	6·28 m (3·5, 0·5)	—	—	7·22—7·82	CH$_3$, 2·20 d (0·5)
VIIIe	8·16 d (3·5)	6·61 d (3·5)	—	—	7·13—7·80	CH$_2$, 4·88 s CH$_3$, 1·88 s
VIIIf	8·21 d (3·2)	6·79 d (3·2)	—	—	7·00—7·85	—

at 6·08 (H_4) and the doublet at 5·98 (H_A). Coupling constants $J_{4,5} = 8·1$ Hz, $J_{5,A} = 1·7$ Hz and $J_{3,4} = 0$ Hz are analogous to preceding monoadducts and proved the like sterical arrangement of hydrogen atoms. The coupling constant $J_{3,A} = 3·1$ Hz was surprisingly high; the mutual interaction of H_3 and H_A protons was evidenced by the INDOR technique, as well. Adducts $IIa-IIf$ did not show this interaction at all.

Pure bisadducts $IIId-IIIf$ were obtained without any chromatographic purification after concentration of the reaction mixture under reduced pressure by trituration with ether, when the reaction on nitrone I was carried out in a 2-fold excess of furan derivative. Their structures were determined from elemental analyses and by spectral means. The UV spectra of monoadducts II and bisadducts III did not display significant differences. The structure of bisadducts III was adduced from ^{1}H-NMR spectral data and theoretical considerations for bisadducts $IIIa$ and $IIIb$ presented in our preceding papers[1,5]. The loss of ring current effect due to an attachment of further molecule of nitrone I was manifested by a considerable shift of chemical shift values for all tetrahydrofuran protons ($\delta = 1·0 - 1·2$ ppm). The H_A proton signal appeared as a singlet (bisadducts $IIId$ and $IIIe$), or a doublet with a very little coupling constant $J_{5,A} = 1·0$ Hz ($IIIf$), this evidencing the *anti* arrangement of H_5 and H_A. Similarly, the zero value of coupling constants also indicated the *anti* arrangement of H_3 isoxazolidine protons with those of tetrahydrofuran ring. Bisadduct $IIIf$ had the coupling constants $J_{A,5} = 1·0$ Hz and $J_{3,A} = 0·5$ Hz. One experiment with 2-furfuryl mercaptane in a great excess led to the formation of a monoadduct.

The 1,3-addition product of general formula IV, as well as the reverse regioisomer were not found in the reaction mixture. The formation of 1,3-addition products IV was explained[5] by a mechanism involving a zwitterionic intermediate for which a high electron density in position 2 of the furan ring was needed, since the nitrone I is a weak electrophile only. The π-electron densities for 2-furan derivatives were calculated by the *ab initio* method[10] in the series $C_2H_5 > CH_3 > H$, CH_2OH. The π-electron densities of furan derivatives employed in this paper were not higher than with furan, where the presence of IV was similarly not found. The absence of 1,3-addition products might well be rationalized through π-electron densities according to the mechanism[5] already mentioned.

The reaction of nitrone I with 2,5-dimethylfuran afforded a cycloadduct $C_{12}H_{19}$. .NO_3 showing in its mass spectrum a peak of molecular radical ion at m/z 321 to which structure of the monoadduct V was ascribed on the basis of analytical and spectral evidences. The UV spectrum indicated the isoxazolidine structure, the ^{1}H-NMR spectrum showed the bridgehead of proton H_5 as a doublet with $J_{5,A} = 2·0$ Hz typical of dihydrofuran derivatives[11]. Signals of protons of methyl groups and that of H_5 were assigned by means of interaction between H_A and methyl group $J_{CH_3,A} = 1·0$ Hz.

Structures of the synthesized compounds were verified also by mass spectra. As found, these compounds are thermally unstable and a cycloreversion took place at temperatures of the ionizing chamber over 100°C. Molecular ions in the spectra are either little pronounced or absent, especially with bisadducts. Table III lists mass spectral data of *IIa*, *IIb*, *IIe* and *IIg*. Fragmentation of the molecular ion of compound *IIb* is seen in Scheme 2. The metastable transitions were verified in the first field free region.
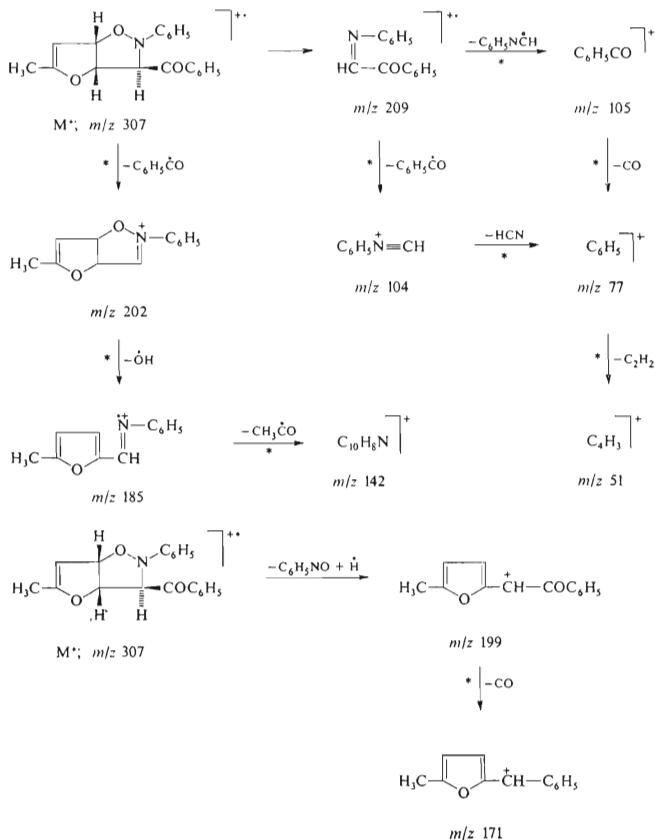
Our preceding papers reported the structure elucidation of cycloadducts *II* by spectral means only. A chemical proof by acid hydrolysis with dilute hydrochloric acid, alkaline hydrolysis or bromination in tetrachloromethane led to decomposition of dihydrofuroisoxazolidine system and thereby to unidentified compounds. In this connection the dehydrogenation of mono adducts *II* was studied in attempting to obtain the heterocyclic furoisoxazolidine system *VI*. The use of dehydrogenating reagents as *e.g.* an active MnO_2, $Pb(OAc)_4$ in dichloromethane or tetrachloromethane at room temperature yielded oligomers of benzoylnitrone *I*. The ^{1}H-NMR spectrum of crude reaction mixtures after removal of volatile components under reduced pressure contained only signals of aromatic protons. With chloranile in benzene

TABLE III

Mass Spectra of the Synthesized Compounds

Compound	m/z (relative intensity[a])
IIa	293, $M^{+\cdot}$ (5), 225 (4), 172 (9), 171 (68), 170 (35), 143 (11), 142 (15), 122 (28), 117 (5), 116 (4), 115 (11), 106 (7), 105 (75), 104 (24), 93 (5), 81 (4), 78 (10), 77 (100), 76 (5), 79 (4), 68 (17), 52 (5), 51 (35), 50 (11), 43 (17), 41 (4), 49 (21).
IIb	307, $M^{+\cdot}$ (4), 209 (8), 203 (11), 202 (72), 200 (13), 199 (15), 186 (6), 185 (36), 184 (22), 171 (13), 170 (7), 157 (4), 143 (6), 142 (11), 122 (12), 106 (6), 105 (53), 104 (55), 82 (29), 81 (15), 77 (100), 76 (4), 54 (5), 53 (17), 52 (6), 51 (33), 50 (10), 43 (14), 41 (4), 39 (17).
IIe	365, $M^{+\cdot}$ (1), 260 (8), 243 (8), 225 (5), 209 (9), 201 (15), 200 (24), 184 (6), 140 (8), 122 (19), 106 (16), 105 (79), 104 (51), 98 (15), 97 (4), 94 (4), 93 (11), 91 (4), 81 (32), 80 (5), 78 (11), 77 (100), 76 (5), 74 (4), 66 (5), 65 (6), 69 (8), 53 (14), 52 (18), 51 (40), 50 (14), 45 (6), 43 (33), 41 (10), 49 (14).
IIg	339, $M^{+\cdot}$ (0), 321 (5), 210 (4), 209 (20), 114 (14), 106 (13), 105 (45), 104 (81), 86 (5), 82 (6), 81 (63), 78 (25), 77 (100), 76 (7), 74 (4), 53 (44), 52 (14), 51 (56), 50 (21), 45 (10), 39 (27).

[a] Table lists peaks of relative intensity $\geqq 4\%$ with the exception of those of molecular radical ions.

at 60°C the cycloadducts *II* remained unaltered, at a higher temperature in toluene products of cycloreversion were formed. Differential thermal analysis of cycloadducts *II* showed the compounds under investigation to be stable up to 90°C after which they underwent cycloreversion.

M⁺˙; *m/z* 307 → *m/z* 209 $\xrightarrow{-C_6H_5N\overset{.}{C}H}$ C₆H₅CO⁺ *m/z* 105

$-C_6H_5\overset{.}{C}O$

m/z 202

$-\overset{.}{O}H$

m/z 185 $\xrightarrow{-CH_3\overset{.}{C}O}$ C₁₀H₈N⁺ *m/z* 142

$-C_6H_5\overset{.}{C}O$

C₆H₅N⁺=CH *m/z* 104 $\xrightarrow{-HCN}$ C₆H₅⁺ *m/z* 77

$-CO$

$-C_2H_2$

C₄H₃⁺ *m/z* 51

M⁺˙; *m/z* 307 $\xrightarrow{-C_6H_5NO + \overset{.}{H}}$ *m/z* 199

$-CO$

m/z 171

SCHEME 2

Compound *IIb* reacted with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in benzene at 60°C for 3 h to give a yellow compound of $M^{+\cdot}$ 305 evidencing the successful dehydrogenation. The spectral data did not fit the presumed structure of furoisoxalidine heterocyclic system. The ^{1}H-NMR spectrum lacked the bridgehead dihydrofuran protons H_4 and H_5, and also the isoxalidine H_3 proton; instead of the anticipated two singlets characteristic of structure *VI*, two mutualy interacting doublets (proved by the INDOR technique) at 6·28 and 8·16 $J_{3,4}$ = 3·5 Hz, indicative of 2,5-disubstituted furan derivatives appeared. The presence of the above-mentioned doublets excluded the alternative structure *VII*, which might be formed by elimination of hydrogens H_3 and H_4. The isolated substance, was assigned the structure of C-benzoyl--C-(5-methyl-2-furyl)-N-phenylnitrone (*VIIIb*), which accorded with the ^{1}H-NMR spectrum. Doublet at 6·28 was ascribed to the proton H_4 (numbering with regard to the 2,5-disubstituted derivative) on the basis of interaction with the methyl group, which was observable even upon high resolution of the spectrum. Doublet H_3 revealed an unexpectable high value of chemical shift (8·16 ppm) as a consequence of deshielding by the nitrone oxygen. *E.g.* in compound *IVb* differing from *VIIIb* by the very absence of oxygen, the chemical shift of H_3 makes 6·67. Signal of the H_3 doublet in *VIIIb* was considerably shifted by the shift reagent, this evidencing the correct assignment. The equally great downfield shifts were observed also with other nitrones[12]. The regeneration of the furan system, associated with the dehydrogenation of *IIb* with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, also followed from the methyl group signal position, which, due to the establishment of the ring current effect changed from 1·31 to 2·20. Another proof provided the UV spectrum showing a noticeable hypsochromic shift of the absorption maximum: *IIb* λ_{max} 246 nm, *VIIIb* 327 nm. Structure of the nitrone moiety of *VIIIb* evidenced the presence of the fragment at m/z 289 originating from $M^{+\cdot}$ by the loss of oxygen, this being a diagnostic feature of nitrones. The remaining part of the mass spectrum was identical with that of *IVb* (ref.[5]). The IR spectrum displayed bands at $1133\ cm^{-1}$ ($N{\rightarrow}O$) characteristic of nitrones ($\sim$$1200\ cm^{-1}$ ref.[13]), at $1677\ cm^{-1}$ $\nu(C{=}O)$ for *VIIIb*, which is lower than that for the starting monoadduct *IIb* ($1691\ cm^{-1}$) this being in accordance with formation of an α,β-unsaturated nitrone system.

Compound *VIIIb* is assumed to be formed according to the following mechanism: derivative *VII* originating from dehydrogenation was electrocyclically opened in agreement with the Woodward–Hoffmann selection rules by an allowed reaction under formation of *VIIIb*. The unilatelar shift of the reaction toward the opened acyclic structure was due to thermodynamic factors, *i.e.* to a regeneration of the furan heterocyclic system in conjugation with the nitrone grouping. Dehydrogenation of monoadducts *IIa*, *IIe*, *IIf* with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone under the same conditions led analogously to so far unknown ketonitrones *VIIIa*, *VIIIe* and *VIIIf* (Table I). The formation of a conjugated furan system was manifested by a great effect of the substituent attached at furan ring on the *K* band in the UV

spectra (for *VIIIa* λ_{max} 314 nm, for *VIIIf* λ_{max} 366 nm). The assignment of proton signals in *VIIIa* was effected by means of INDOR technique, coupling constants $J_{3,4} = 3.5$ Hz and $J_{4,5} = 1.7$ Hz fully agreed with the structure of 2-substituted derivative. Comparison of methylene groups signals attached to the furan of di-hydrofuran ring in *VIIIe* (δ CH$_2$ = 4.88 ppm) and in *IIe* (4.18 ppm) indicated the ring current effect associated with the re-formed furan ring. Compound *VIIIe* is a yellowish oil undergoing decomposition. The respective spectra were measured immediately after isolation of the substance by a preparative thin layer chromatography. Yields of dehydrogenation varied within 75—90%.

The presented method of preparation of ketonitrones *via* dehydrogenation of di-hydrofuroisoxazolidines with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone offered a further possibility to exploit products of 1,3-dipolar cycloaddition reactions for synthetic purposes. Isoxazolidines have hitherto been utilized for preparation of N-substituted γ-amino alcohols[14] and β-amino ketones[15].

EXPERIMENTAL

Yields, uncorrected melting points and analytical data of the synthesized compounds are listed in Table I. IR spectra of saturated chloroform solutions were measured in 0.6 mm-NaCl cells with a UR-20 (Zeiss, Jena) spectrophotometer in the 700—3 800 cm^{-1} range; reading accuracy ± 1 cm^{-1} (Table II). ^{1}H-NMR spectra of deuteriochloroform solutions were recorded with a BS—487 C (Tesla, Brno) apparatus operating at 80 MHz with tetramethylsilane as an internal reference. The position of lines was determined by an in-built frequence reader (Table II). Mass spectra given in Table III were taken with a MS 902 S (AEI Manchester) instrument provided with a direct inlet system at an ionizing electron energy 70 eV, ion current 100 μA and 80°C ionization chamber temperature. UV spectra were measured with a UV VIS spectrophotometer (Zeiss, Jena) in methanolic solution. The reaction course and the purity of compounds were monitored by TLC using Silufol (Kavalier, Votice) plates (detection by the filtered 254 nm UV light, or with iodine vapours). C-Benzoyl-N-phenylnitrone *I* was prepared according to[16] from nitrosobenzene and phenacylpyridinium bromide, 2-furfuryl alcohol and 2-furfuryl mercaptan were commercially available, 2-furfuryl acetate was obtained from furcuryl alcohol according to[17], 2-phenylfuran according to[18] using isopentyl nitrite or n-propyl nitrite. Silica gel and Silica gel LSL (Lachema, Brno) were employed for column and TLC chromatography, respectively, using 45 g of the latter carrier for a 20 × 20 cm plate, 2 mm-coating; solvent system chloroform–n-heptane 8 : 2 for cycloaddition reactions and benzene for reaction products.

Cycloaddition of *I* with Furan Derivatives

The mixture of *I* (2.25 g, 10 mmol), furan derivative (250 mmol), and toluene (40 ml) under nitrogen at 55—60°C for 15 h was concentrated *in vacuo* (rotary pump, 55°C bath temperature) and the oily residue was separated on silica gel packed column. Yield: *IIe* 73%, *IIf* 69% *V* 46%. A solid was obtained when using 2-furfuryl alcohol from which bisadduct *IIId* was obtained in 54% by washing with ether. The concentrated filtrate was separated by TLC chromatography to furnish the monoadduct *IId* in a 21% yield.

Bisadducts *IIId* and *IIIe* were obtained under the same reaction conditions and using a two-fold excess of the furan derivative; *IIIf* was obtained using methanol instead of ether for trituration

the distillation residue. Analogously, monoadducts *II* were obtained from the filtrates, which were purified by column chromatography through silica gel and crystallized from dichloromethane–hexane.

Dehydrogenation of *II* with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone

The mixture of monoadducts *II* (1·5 mmol), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (4·5 mmol) and benzene (40 ml) was heated at 60°C for 3 h, filtered, concentrated under diminished pressure and separated by preparative TLC, benzene being the eluent. Good separation was assured by rechromatography. Yields before crystallization from dichloromethane–hexane are listed in Table I. Work-up in an orthodox way, *i.e.* filtration, washing with 2M-NaOH, water, drying with $MgSO_4$ and concentration under diminished pressure afforded products in substantially lower yields.

REFERENCES

1. Fišera Ľ., Kováč J., Poliačiková J., Leško J.: Monatsh. Chem. *111*, 909 (1980).
2. Sustmann R.: Pure Appl. Chem. *40*, 569 (1974).
3. Houk K. N.: Accounts Chem. Res. *8*, 361 (1975).
4. Huisgen R.: J. Org. Chem. *41*, 403 (1976).
5. Fišera Ľ., Kováč J., Poliačiková J.: Heterocycles *12*, 1005 (1979).
6. Fišera Ľ., Gaplovský A., Timpe H. J., Kováč J.: This Journal, in press.
7. Houk K. N., Sims J., Duke R. E., Strozier R. W., George J. K.: J. Amer. Chem. Soc. *95*, 7287 (1973).
8. Houk K. N., Sims J., Watts C. R., Luskus L. J.: J. Amer. Chem. Soc. *95*, 7301 (1973).
9. Huisgen R., Seidl H., Brüning I.: Chem. Ber. *102*, 1102 (1969).
10. John J. G., Raďom L.: J. Amer. Chem. Soc. *100*, 3981 (1978).
11. Korrer P. K., Van der Haak P. J., Steinberg G., De Boer T. J.: Rec. Trav. Chim. Pays — Bas *84*, 1265 (1965).
12. Mukherjee D., Domelsmith L. N., Houk K. N.: J. Amer. Chem. Soc. *100*, 1954 (1978).
13. Kubota T., Yamakawa M., Mori Y.: Bull. Chem. Soc. Jap. *36*, 1552 (1963).
14. Tufariello J. J., Asrof Ali Sk.: Tetrahedron Lett. *1978*, 4647.
15. Oppolzer W., Petrzilka M.: Helv. Chim. Acta *61*, 2755 (1978).
16. Kroehnke F.: Chem. Ber. *80*, 298 (1947).
17. Gilman H., Blatt A. H.: *Organic Syntheses*, Coll. Vol. I., p. 285.
18. Fišera Ľ., Kováč J., Komanová E., Leško J.: Tetrahedron *30*, 4123 (1974).