FURAN-RELATED N-ONIUM SALTS AS SYNTHONS FOR PREPARATION OF 3-FURYLBENZOINDOLIZINES*

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Received June 13th, 1985

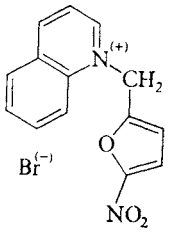
Substituted 3-furylbenzoindolizines *V*—*X* were prepared *via* 1,3-dipolar cycloaddition of ylides generated from the furan-related N-onium salts *I*—*IV* to dimethyl butinedioate, ethyl 3-(5-nitro-2-furyl)-2-propenoate, 1-phenyl-3-(5-nitro-2-furyl)-2-propenone, and 1-phenyl-2-nitroethylene. Structure of the compounds synthesized was confirmed by spectral data.

Our preceding papers concerned the utilization of N-(5-nitro-2-furfuryl)pyridinium bromide and N-(5-nitro-2-furfuryl)isoquinolinium bromide in the synthesis of indolizines, especially benzo[*g*]indolizines[1-4]. This paper presents the preparation of 3-furylbenzoindolizines from another N-onium salts of furan derivatives *I*—*IV* and their properties.

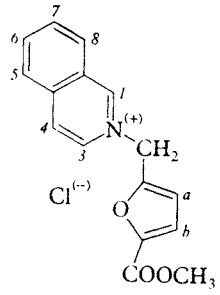
N-(5-Nitro-2-furfuryl)quinolinium bromide (*I*) and N-(5-methoxycarbonyl-2-furfuryl)isoquinolinium chloride (*II*), have a reactive methylene group in the α-position of the furan ring; their azomethine ylides react *in situ* with 1,3-dipolarophiles as dimethyl butinedioate, ethyl 3-(5-nitro-2-furyl)-2-propenoate and 1-phenyl-3-(5-nitro-2-furyl)-2-propenone to yield the substituted 3-(2-furyl)benzo[*e*]indolizines *V*—*VII* and 3-(2-furyl)benzo[*g*]indolizine (*VIII*). Sodium hydride was used to generate ylides of *I* and *II* in dioxane by a several-day agitation mostly at room temperature. The reaction mixture was worked up and the products were purified on an alumina-packed column; their purity was checked by thin-layer chromatography. As shown in optimization experiments, selection of the base is of great importance. Thus, *e.g.* the yield of 1,2-dimethoxycarbonyl-3-(5-nitro-2-furyl)benzo[*e*]indolizine (*V*) rose from 11% with anhydrous potassium carbonate up to 27% with sodium hydride. Temperature increase positively influenced only preparation of *VI*, whilst it was unfavourable to compounds *V*, *VII*, and *VIII*. The relatively low yields (10—29%) are due both sensitivity of 5-nitro-2-furan derivatives towards basic reagents, and a low stability of the dipole originating *in situ*. The reaction

* Part CLXXXVI in the series Furan Derivatives; Part CLXXXV This Journal *50*, 2077 (1985).

was accompanied by a great number of so far unidentified polymers. As evidenced by experiments, reactivity of 5-nitro-2-furylquinolinium methylide formed from *I* is comparable with that of 5-nitro-2-furylisoquinolinium methylide generated from an analogous isoquinolinium salt[3]. Thus, reaction of both these ylides with ethyl 3-(5-nitro-2-furyl)-2-propenoate proceeded in 29 and 31% yields, respectively, and with 1-phenyl-3-(5-nitro-2-furyl)-2-propenone the respective yields were 10 and 16%.



I



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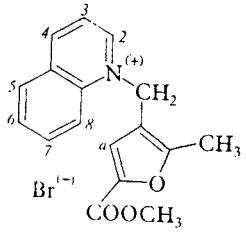
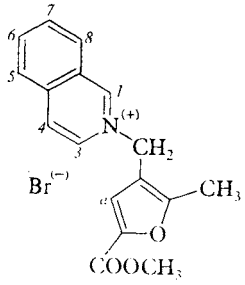


III

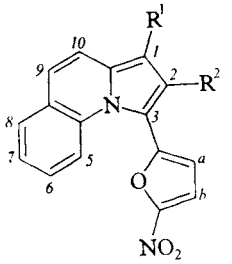


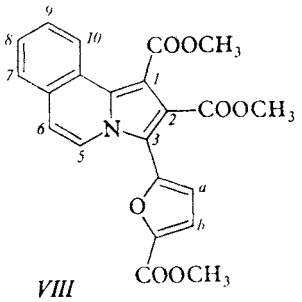
IV

Replacement of the nitro group in position 5 of the furan ring for a methoxycarbonyl grouping was, as anticipated, associated with a decrease of hydrogen acidity of the methylene group of the corresponding N-onium salt resulting in lower yields from *VIII* (12%) when compared with the analogous 3-(5-nitro-2-furyl) derivative (51%), ref.[3].

As reported in ours[1–4] and other papers[5–9], the 1,3-dipolar cycloadditions of *I* and *II* with compounds having an activated multiple bond are also accompanied with a spontaneous aromatization of the 5-membered ring. No primary cycloaddition products, *i.e.* dihydroindolizines or tetrahydroindolizines were isolated from any of these experiments.

The synthesis of 3-furylbenzoindolizines, having the furan ring bound through its β-position to indolizine skeleton started from N-(5-methoxycarbonyl-2-methyl-



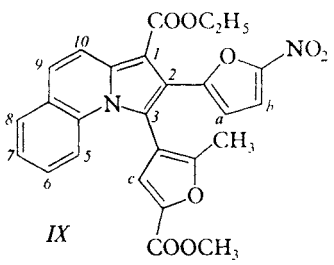


VIII

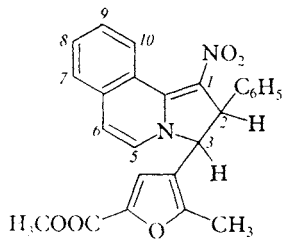
R^1	R^2
V, $COOCH_3$	$COOCH_3$
VI, $COOC_2H_5$	5-NO_2-2-furyl
VII, COC_6H_5	5-NO_2-2-furyl

-3-furfuryl)quinolinium bromide (*III*) or N-(5-methoxycarbonyl-2-methyl-3-furfuryl)isoquinolinium bromide (*IV*). Reaction of ylides, generated from *III* or *IV* with sodium hydride led with dimethyl butinedioate, ethyl 3-(5-nitro-2-furyl)-2-propenoate and 1-phenyl-2-nitroethylene either at an ambient temperature or at elevated temperature to unidentified oily products. Therefore, sodium methoxide was employed for further experiments. Salt *III* reacted with ethyl 3-(5-nitro-2-furyl)-2-propenoate in the presence of this base at an elevated temperature (80–90°C) to give 1-ethoxycarbonyl-2-(5-nitro-2-furyl)-3-(5-methoxycarbonyl-2-methyl-3-furyl)benzo[*e*]indolizine (*IX*), what means that spontaneous aromatization took place. Salt *IV* furnished under the same conditions 1-nitro-2-phenyl-3-(5-methoxycarbonyl-2-methyl-3-furyl)-2,3-dihydrobenzo[*g*]indolizine (*X*) only with 1-phenyl-2-nitroethylene as the dipole. Although the product is the only derivative of dihydroindolizine, which we were able to isolate, it is known that many reactions of this type gave stable 2,3-dihydroindolizines[10,11] tetrahydroindolizines[11–13], or their mixture[14].

Structure of 3-furylbenzoindolizines *V*–*X* was corroborated by elemental analysis and spectral data. Spectral parameters of the synthesized compounds are quite



IX



X

close in many respects. Absorption maximum at 480 nm ($\log \varepsilon = 2{\cdot}98$) of the substituted dihydroindolizine *X* indicates the presence of an extended conjugated system in which also the nitro group in position 1 is embodied; therefore, structure *X* could be ascribed to this derivative. This is also backed by the presence of a shoulder in the electronic spectrum at 263 nm ($\log \varepsilon = 2{\cdot}90$), corresponding to absorption of methyl 5-methyl-2-furancarboxylate measured as a reference substance.

The ^{1}H NMR data verified the correctness of the proposed structure. Protons H_7, H_8, and H_9 of the fused benzene ring of compound *VIII* were seen as a multiplet at $\delta = 7{\cdot}27-7{\cdot}62$ ppm. The H_{10} proton signal of this ring was downfield shifted ($\delta = 8{\cdot}68$) due to the anisotropic effect of the methoxycarbonyl group in position 1. Signals of H_5 and H_6 protons were formed by two doublets at $\delta = 8{\cdot}06$ and 6·89 ppm, respectively. Presence of the furan ring was manifested by two doublets with coupling constant $J_{a,b} = 3{\cdot}7$ Hz. Derivatives *V* ($R^1 = R^2 = COOCH_3$) and *VII* ($R^1 = C_6H_5CO$, R^2 = 5-nitro-2-furyl) revealed in the region of undissolved multiplet of aromatic protons also signals H_b and $H_{b'}$ of 5-nitro-2-furyl groupings in position 3 (compound *V*), or in position 2,3 (compound *VII*). Protons H_2 and H_3 of 2,3-dihydroindolizine *X* resonated as two doublets at $\delta = 6{\cdot}25$ and 4·98 ppm, respectively, with coupling constant $J_{2,3} = 10{\cdot}0$ Hz, this being diagnostic of a *cis*-arrangement.

Mass spectrometric fragmentation of compounds with an ester group commenced with the cleavage of it, followed by a characteristic fragmentation pattern of the furan ring. The five-membered nitrogen-containing heteroring underwent cleavage at last. Typical of the benzoindolizine grouping is the appearance of the fragment ion at *m/z* 128 $[C_9H_6N]^+$ of a relatively low intensity.

These facts allow us to conclude that azomethine ylides generated from N-onium salts *I* and *II*, *i.e.* from salts having the methylene group attached to the α-position of furan are, as expected, more reactive than ylides of salts *III* and *IV* with the methylene group in β-position.

EXPERIMENTAL

Melting points were measured with a Boëtius micro hot-stage, the microanalyses were carried out with a Carlo Erba (Italy) analyser. The purity of products was checked by thin-layer analysis on Silufol sheets (Kavalier, Czechoslovakia). The IR spectra were recorded with a UR-20 (Zeiss, Jena) spectrophotometer, the absorption spectra with a UV VIS (Zeiss, Jena) apparatus. The ^{1}H NMR spectra were run with a Tesla BS 487 C (Czechoslovakia) instrument operating at 80 MHz at 25–80°C tetramethylsilane or hexamethyldisiloxane being the internal standards. The signals were ascribed by an INDOR technique and decoupling. The mass spectra were recorded with an MS 902 S (AEI, Manchester) spectrometer at a 70 eV ionizing energy, 100 μA trap current and 150°C ion source temperature. Ten most intense ions of the spectrum are presented.

Ethyl 3-(5-nitro-2-furyl)-2-propenoate[17] was obtained from 3-(2-furyl)-2-propenoic acid[15] *via* 3-(5-nitro-2-furyl)-2-propenoic acid[16]. 1-Phenyl-3-(5-nitro-2-furyl)-2-propenone was synthesized according to[5] and 1-phenyl-2-nitroethylene according to[18]. N-(5-Nitro-2-furfuryl)-

quinolinium bromide (*I*) was obtained from furfuryl alcohol *via* 5-nitro-2-furfuryl nitrate and 5-nitro-2-furfuryl bromide[19]. Intermediates in the synthesis of N-onium salts *II*—*IV* were methyl 2-furancarboxylate[20], methyl 5-chloromethyl-2-furancarboxylate[21], methyl 5-methyl-2-furancarboxylate[22], and methyl 4-bromomethyl-5-methyl-2-furancarboxylate[23].

N-(5-Methoxycarbonyl-2-furfuryl)isoquinolinium Chloride (*II*)

Isoquinoline (7·2 g, 55 mmol) in benzene (5 ml) was successively added to a stirred solution of methyl 5-chloromethyl-2-furancarboxylate (11·2 g, 50 mml) in benzene (20 ml). The mixture was heated to 60°C for 10 h, cooled, the solid portion was filtered off and crystallized. Yield 13·2 g (78%), m.p. 79—80°C (ethanol–ether 1 : 1). For $C_{16}H_{13}ClNO_3$ (303·7) calculated: 4·61% N; found: 4·32% N. IR spectrum (KBr) $\tilde{\nu}$, cm^{-1}: 1 722 (C=O). UV spectrum (CH_3OH) λ_{max}, nm (log ε, m^2 mol^{-1}): 232 (3·45), 340 (2·53). ^1H NMR spectrum (hexadeuteriodimethyl sulfoxide) δ, ppm: 3·87 (3 H, s, CH_3), 6·4 (2 H, s, CH_2), 7·22 (1 H, d, H_a), 7·43 (1 H, d, H_b), 8·00—9·19 (6 H, m, H_3—H_8), 10·51 (1 H, s, H_1), $J_{a,b}$ = 3·8 Hz.

N-(5-Methoxycarbonyl-2-methyl-3-furfuryl)quinolinium Bromide (*III*)

Ethyl acetate (20 ml) solution of quinoline (5 g, 38 mmol) was stepwise added to a stirred boiling solution of methyl 4-bromomethyl-5-methyl-2-furancarboxylate (9 g, 38 mmol) in ethyl acetate (100 ml). The mixture was refluxed for 16 h, cooled and the precipitate was filtered off and crystallized. Yield 13·4 g (96%), m.p. 187—188°C (ethanol). For $C_{16}H_{15}BrNO_3$ (349·2) calculated: 3·86% N; found: 3·85% N. IR spectrum (KBr) $\tilde{\nu}$, cm^{-1}: 1 722 (C=O). UV spectrum (CH_3OH) λ_{max}, nm (log ε, m^2 mol^{-1}): 239 (3·60), 259 (3·16), 316 (2·90). ^1H NMR spectrum (hexadeuteriodimethyl sulfoxide) δ, ppm: 2·59 (3 H, s, CH_3), 3·75 (3 H, s, OCH_3), 6·30 (2 H, s, CH_2), 7·30 (1 H, s, H_a), 8·05—8·75 (5 H, m, H_3, H_5—H_8), 9·41 (1 H, d, H_4), 9·75 (1 H, d, H_2), $J_{2,3}$ = 6·0 Hz, $J_{3,4}$ = 8·0 Hz.

N-(5-Methoxycarbonyl-2-methyl-3-furfuryl)isoquinolinium Bromide (*IV*)

The title compound was prepared by applying the same procedure starting from methyl 4-bromomethyl-5-methyl-2-furancarboxylate and isoquinoline. Yield 13·8 g (98%), m.p. 220—221°C, (ethanol). For $C_{16}H_{15}BrNO_3$ (349·2) calculated: 3·86% N; found: 3·92% N. IR spectrum (KBr) $\tilde{\nu}$, cm^{-1}: 1 719 (C=O). UV spectrum (CH_3OH) λ_{max}, nm (log ε, m^2 mol^{-1}): 233 (3·67), 262 (3·28), 338 (2·64). ^1H NMR spectrum (hexadeuteriodimethyl sulfoxide) δ, ppm: 2·57 (3 H, s, CH_3), 3·77 (3 H, s, OCH_3), 5·87 (2 H, s, CH_2), 7·52 (1 H, s, H_a), 8·16—8·85 (6 H, m, H_3—H_8), 10·2 (1 H, s, H_1).

1,2-Dimethoxycarbonyl-3-(5-nitro-2-furyl)benzo[*e*]indolizine (*V*)

Sodium hydride (0·24 g, 10 mml) was added to a stirred and cooled suspension of *I* (2·0 g, 6 mmol) and dimethyl butinedioate (0·85 g, 6 mmol) in dioxane (80 ml). The inorganic portion was removed after a three-day stirring at room temperature, washed with chloroform (30 ml) and the solvent was distilled off under diminished pressure. The residue was separated on an alumina-packed column using benzene–acetone (40 : 1) as eluent. Yield 0·63 g (27%), m.p. 234—235°C (acetone). For $C_{20}H_{14}N_2O_7$ (394·3) calculated: 60·91% C, 3·58% H, 7·11% N; found: 60·40% C, 3·22% H, 7·10% N. IR spectrum (KBr) $\tilde{\nu}$, cm^{-1}: 1 897, 1 717 (C=O). UV spectrum (CH_3OH) λ_{max}, nm (log ε, m^2 mol^{-1}): 232 (3·52), 269 (3·33) sh, 337 (3·23), 390 (2·73) sh. ^1H NMR spectrum (hexadeuteriodimethyl sulfoxide) δ, ppm: 3·85 (3 H, s, CH_3), 3·77 (3 H, s, CH_3), 7·14 (1 H, d, H_a), 7·05—8·12 (7 H, m, H_{arom}, H_b), $J_{a,b}$ = 4 Hz. Mass spectrum *m/z*, (relat. intens., %): 394 (100), 364 (15), 363 (31), 362 (35), 359 (35), 348 (31), 320 (69), 316 (62), 203 (19), 202 (23).

1-Ethoxycarbonyl-2,3-bis(5-nitro-2-furyl)benzo[*e*]indolizine (*VI*)

Sodium hydride (0·24 g, 10 mmol) was added to a stirred and cooled suspension of *I* (2·0 g, 6 mmol) and ethyl 3-(5-nitro-2-furyl)-2-propenoate (0·42 g, 2 mmol) in dioxane (80 ml). The mixture was stirred up at 80—90°C for 20 h and one day at room temperature. The inorganic portion was filtered off, washed with chloroform (30 ml) and the solvent was removed under reduced pressure. The residue was separated on an alumina-packed column with chloroform as eluent. Yield 0·27 g (29%), m.p. 207—208°C (acetone). For $C_{23}H_{15}N_3O_8$ (461·4) calculated: 59·87% C, 3·28% H, 9·11% N; found: 60·11% C, 3·48% H, 8·84% N. IR spectrum (KBr) $\tilde{\nu}$, cm^{-1}: 1 705 (C=O). UV spectrum (CH_3OH) λ_{max}, nm (log ε, $m^2\ mol^{-1}$): 228 (3·42), 270 (3·51) sh, 421 (2·58). Mass spectrum, *m/z* (relat. intens., %): 461 (100), 429 (23), 415 (13), 387 (30), 355 (15), 284 (17), 256 (13), 239 (14), 228 (15), 203 (13).

1-Benzoyl-2,3-bis(5-nitro-2-furyl)benzo[*e*]indolizine (*VII*)

Compound *I* and 1-phenyl-3-(5-nitro-2-furyl)-2-propenone were worked up with sodium hydride as with derivative *V*. Separation as in the preceding procedure gave *VII* in a 10% yield, m.p. 292—294°C (acetone). For $C_{27}H_{15}N_3O_7$ (493·4) calculated: 65·72% C, 3·06% H, 8·51% N; found: 64·65% C, 2·73% H, 8·24% N. IR spectrum (KBr) $\tilde{\nu}$, cm^{-1}: 1 645 (C=O). UV spectrum (CH_3OH) λ_{max}, nm (log ε, $m^2\ mol^{-1}$): 221 (3·41), 274 (3·72), 412 (3·36). ^1H NMR spectrum (hexadeuteriodimethyl sulfoxide), δ, ppm: 6·77 (1 H, d, H_a), 6·95 (1 H, d, $H_{a'}$), 7·02—8·37 (13 H, m, H_{arom}, H_b, $H_{b'}$), $J_{a,b}$ = 4·0 Hz, $J_{a',b'}(R^2)$ = 4·0 Hz. Mass spectrum, *m/z* (relat. intens., %): 493 (100), 461 (40), 447 (62), 419 (48), 415 (30), 372 (18), 344 (36), 315 (28), 157 (26), 128 (14).

1,2-Dimethoxycarbonyl-3-(5-methoxycarbonyl-2-furyl)benzo[*g*]indolizine (*VIII*)

Treatment of *II* with dimethyl butinedioate and sodium hydride followed by chromatographic separation on alumina using benzene–acetone (40 : 1) afforded *VIII* in a 12% yield, m.p. 142 to 143°C (acetone). For $C_{22}H_{17}NO_7$ (407·4) calculated: 64·86% C, 4·21% H, 3·44% N; found: 65·01% C, 4·10% H, 3·26% N. IR spectrum (KBr) $\tilde{\nu}$, cm^{-1}: 1 732, 1 707, 1 685 (C=O). UV spectrum (CH_3OH) λ_{max}, nm (log ε, $m^2\ mol^{-1}$): 213 (3·48), 274 (3·36), 320 (3·30). ^1H NMR spectrum (C^2HCl_3) δ, ppm: 3·86 (3 H, s, CH_3), 3·91 (3 H, s, CH_3), 3·98 (3 H, s, CH_3), 6·89 (1 H, d, H_a), 6·89 (1 H, d, H_6), 7·29 (1 H, d, H_b), 7·27—7·62 (3 H, m, H_7—H_9), 8·06 (1 H, d, H_5), 8·68 (1 H, m, H_{10}), $J_{a,b}$ = 3·7 Hz, $J_{5,6}$ = 7·5 Hz. Mass spectrum, *m/z* (relat. intens., %): 407 (100), 376 (47), 320 (15), 318 (12), 304 (15), 230 (15), 202 (13), 187 (18), 183 (13), 144 (16).

1-Ethoxycarbonyl-2-(5-nitro-2-furyl)-3-(5-methoxycarbonyl-2-methyl-3-furyl)benzo[*e*]indolizine (*IX*)

Sodium methoxide (0·54 g, 10 mmol) was added to a stirred and cooled suspension of *III* (2·1 g, 6 mmol) and ethyl 3-(5-nitro-2-furyl)-2-propenoate (1·3 g, 6 mmol) in dioxane (80 ml) and 2-methoxyethanol (10 ml). The inorganic portion was filtered off after a two-day reflux, washed with chloroform and the solvent was distilled off *in vacuo*. The residue was separated by chromatography on alumina with benzene. Yield 0·38 g (13%), m.p. 204—205°C (acetone). For $C_{26}H_{20}N_2O_8$ (488·4) calculated: 63·93% C, 4·13% H, 5·73% N; found: 63·24% C, 4·16% H, 5·43% N. IR spectrum (KBr) $\tilde{\nu}$, cm^{-1}: 1 759, 1 726 (C=O). UV spectrum (CH_3OH) λ_{max}, nm (log ε, $m^2 . mol^{-1}$): 220 (2·20), 256 (2·21), 315 (1·68), 433 (1·84). ^1H NMR spectrum (C^2HCl_3) δ, ppm: 1·10 (3 H, t, CH_3), 2·21 (3 H, s, CH_3), 3·92 (3 H, s, OCH_3), 4·17 (2 H, q, CH_2), 6·90 (1 H, d, H_a), 7·65 (1 H, d, H_b), 7·17—8·15 (7 H, m, H_5—H_{10}, H_c), $J_{a,b}$ = 4 Hz. Mass spectrum, *m/z* (relat. intens., %): 488 (100), 456 (45), 414 (96), 410 (40), 386 (25), 382 (30), 358 (15), 326 (17), 298 (13), 128 (15).

1-Nitro-2-phenyl-3-(5-methoxycarbonyl-2-methyl-3-furyl)-2,3-dihydrobenzo[*g*]indolizine (*X*)

The same procedure was applied when reacting *IV* with 1-phenyl-2-nitroethylene with sodium methoxide. The products were purified by chromatography on alumina, benzene–acetone (5 : 1) being the eluent. Yield 14%, *X*, m.p. 209–210°C (acetone). For $C_{25}H_{20}N_2O_5$ (428·4) calculated: 70·41% C, 4·25% H, 6·56% N; found: 69·93% C, 4·85% H, 5·99% N. IR spectrum (KBr) $\tilde{\nu}$, cm^{-1}: 1 722 (C=O). UV spectrum (CH_3OH) λ_{max}, nm (log ε, $m^2\ mol^{-1}$): 215 (3·15), 242 (3·27), 263 (2·90) sh, 347 (2·20), 480 (2·98). ^{1}H NMR spectrum (hexadeuteriodimethyl sulfoxide) δ, ppm: 2·29 (3 H, s, CH_3), 3·41 (3 H, s, OCH_3), 4·98 (1 H, d, H_2), 6·25 (1 H, d, H_3), 7·85 (1 H, d, H_a), 6·85–8·05 (5 H, m, H_6–H_{10}), 9·56 (1 H, d, H_5), $J_{2,3}$ = 10 Hz, $J_{5,6}$ = 7·5 Hz. Mass spectrum, *m/z* (relat. intens., %): 428 (10), 355 (15), 255 (6), 183 (10), 145 (100), 129 (20), 118 (42), 97 (30), 90 (32), 83 (53).

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Translated by Z. Votický.