STUDIES IN THE QUINOXALINE SERIES. VII.*
CYCLIZATION REACTIONS OF SOME 2-METHOXYLCARBONYLQUINOXALINE DERIVATIVES

J. KLICNAR, M. HÁJEK, J. HOFFMANN and M. VEČEŘA

Department of Organic Chemistry,
Institute of Chemical Technology, Pardubice

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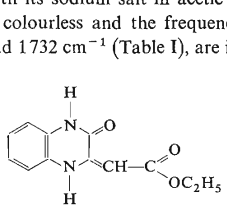
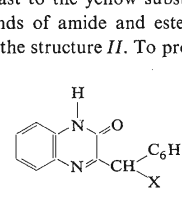
Ethyl 3,4-dihydro-3-oxo-2-quinoxalinylphenylacetate has been prepared and its structure proved by spectral data, cyclization to the respective lactone and its hydrazinolysis. Derivatives of pyridazo[3,4-*b*]- and pyrrolo[2,3-*b*]-quinoxaline have been obtained by condensation of ethyl 3-chloro-2-quinoxalinylphenylacetate with hydrazine and aniline respectively; their enamine structure is discussed.

In the part III of this Series[1], we described syntheses and reactions of derivatives of ethyl 3,4-dihydro-3-oxo-2-quinoxalinylacetate (*I*), the tautomeric structure of which was proved later by Chapman[2]. The present report deals with the chemical properties of phenyl derivative of the ester *I*.

We have prepared ethyl 3,4-dihydro-3-oxo-2-quinoxalinylphenylacetate (*II*) by reaction of 1,2-diaminobenzene with ethyl phenyloxalacetate in ethanol, or better, with its sodium salt in acetic acid. In contrast to the yellow substance *I*, this ester is colourless and the frequencies of the bands of amide and ester carbonyl, 1670 and 1732 cm^{-1} (Table I), are in accord with the structure *II*. To prove this structure,



I



II, X = $CO_2C_2H_5$ *VI*, X = CONHN=$CHCH_3$
IV, X = H *VII*, X = CONHN=$C(CH_3)_2$
V, X = $CONHNH_2$ *VIII*, X = CONHN=CHC_6H_5

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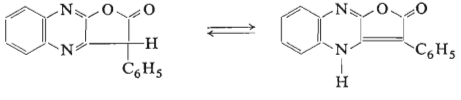
we prepared 2,3-dihydro-2-oxo-3-phenylfuro[2,3-*b*]quinoxaline (*III*) by heating the ester *II* in diphenyl ether. IR spectrum of this substance in solid state shows two intensive bands in carbonyl region at 1725 and 1620 cm^{-1} (Table I). The frequency value 1725 cm^{-1} is too low to be ascribed to γ-lactone carbonyl, and therefore we suppose a tautomeric structure *IIIb* with conjugated C=O group. This structure is supported also by the band of associated imino group, ν(NH) 3338 cm^{-1} and two intensive bands at 1344 and 1317 cm^{-1} due to the vibration ν(C—N) which are characteristic for aromatic secondary amines. The absorption band at 1620 cm^{-1} is apparently due to valency vibration of the conjugated C=N group of quinoxaline nucleus, and it is overlapped by a band of deformation vibration δ(NH). The broad band mentioned contains also the frequency ν(C=C) which is lowered to 1611 cm^{-1} in the case of cyclopentene (see ref.[3]). IR spectrum of the lactone *III* in chloroform contains bands at 1620, 1637, 1722, and 1770 cm^{-1}. The first two frequencies apparently belong to valency vibration of C=N and C=C groups and deformation vibration δ(NH). The more intensive of the both carbonyl bands at 1722 cm^{-1} corresponds to the conjugated C=O group and hence to the tautomeric structure *IIIb*, the band with higher frequence ν(C=O) 1770 cm^{-1} belongs to the tautomer *IIIa*. NH group of enamine form *IIIb* absorbs by two bands at 3410 cm^{-1} (free) and 3330 cm^{-1} (associated). Polar character of the lactone and the shift of long-wave maximum in UV spectrum as compared with the spectrum of ester *II* (Table I) are also in accord with enamine structure *IIIb*.



IIIa *IIIb*

Lactonisation of the phenyl derivative *II* and similarly of the analogous methyl derivative[4] and failure of this reaction in the case of ester *I* confirm also the structure of the ester *II* and *ortho*-quinoid structure of ester *I*. Lactonisation of ester *II* is favourably influenced by steric effect of the phenyl group too. Alcaline hydrolysis of ester *II* gives the corresponding acid which decarboxylates easily to 3,4-dihydro-3-oxo-2-benzylquinoxaline (*IV*).

Through hydrazinolysis of lactone *III*, we have obtained the expected 3,4-dihydro-3-oxo-2-quinoxalinylphenylacethydrazide (*V*) which we have further characterized by condensation with carbonyl compounds. We have prepared N'-ethylidene-(*VI*), N'-isopropylidene-(*VII*), and N'-benzylidene-3,4-dihydro-3-oxo-2-quinoxalinylphenyl acethydrazide (*VIII*). From the reaction times and yields it follows that the reactivity of carbonyl compounds decreases in the series: benzaldehyde > acetaldehyde > acetone. Hydrazinolysis of ester *II* under the same conditions gave,

TABLE I

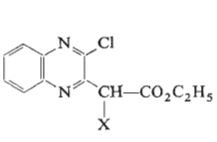
Ultraviolet (in methanol) and Infrared (KBr discs) Spectra of Quinoxalines

Compound	UV λ_{max}, nm	UV (log ε)	IR vibration, cm^{-1} [b] ν(C=O)	IR vibration, cm^{-1} [b] ν(NH)
I	219·5 (4·52) 224·0 (4·53) 259·6 (3·95)	357·0 (4·24) 373·5 (4·28) 393·0 (4·09)	1 690 vs, 1 654 vs	3 310 b
II	204·6 (4·54) 228·5 (4·34) 281·0 (3·84)	338·0 (3·85)	1 732 vs, 1 670 vs	3 165 m
III	204·5 (4·40) 221·0 (4·51)	398·0 (4·26) 275·0 (4·27)	1 725 vs, 1 722 vs[c] 1 770 m[c]	3 338 m 3 410 m[c] 3 330 m[c]
[a]	204·8 (4·41) 226·5 (4·35)	343·5 (3·84) 279·0 (3·81)	1 680 vs, 1 650 s	3 300 m, 3 410 m
V	216·0 (4·72) 235·0 (4·26)	327·5 (4·38) 342·0 (4·50) 358·0 (4·35)	1 665 vs, 1 640 s	3 305 b, 3 180 b
VII	214·0 (4·33) 230·0 (4·43)	340·0 (3·82) 280·0 (3·83)	1 672 s	3 215 m
IX	204·6 (4·43) 250·0 (4·50)	320·0 (3·86) 330·2 (3·82)	1 750 vs[d]	—
X	211·5 (4·23) 240·1 (4·48)	321·2 (3·89) 331·0 (3·83)	1 739 vs[d], 1 757 vs[d]	—
XI	203·4 (4·35) 281·0 (4·37) 414·0 (4·03)	234·0 (4·44) 334·0 (3·97)	1 674 s	3 320 m, 3 197 b
XII	204·5 (4·55) 283·4 (4·37)	240·5 (4·47) 335·0 (3·96) 415·2 (4·07)	1 651 vs 1 691 s[c]	3 350 m

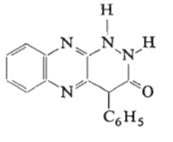
[a] 3,4-Dihydro-3-oxo-2-quinoxalinylacethydrazide[1]; [b] vs very strong, s strong, m medium, b broad band; [c] in chloroform; [d] in tetrachloromethane.

however, only a small amount of hydrazide *V* along with a more polar yellow substance with a higher nitrogen content. Amount of this substance in reaction mixture increased with increasing reaction time and dilution of the hydrazine used. The substance contains two hydrazido or hydrazino groups, as it condenses with two mol of a carbonyl compound (acetone, crotonaldehyde, cinnamaldehyde). We could not determine its structure.

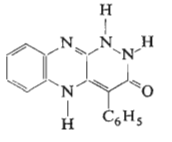
In contrast to the hydrazide prepared from the ester *I* (see ref.[1]), the Curtius degradation of the hydrazide *V* gave a product of different type. An azide was probably formed on nitrosation; the azide was stabilized by splitting off of azoimide and, on simultaneous cyclization, gave the lactone *III*. The formation of lactones during the Curtius degradation was observed in the case of degradation of azides of γ- and δ-hydroxycarboxylic acids[5]. In the present case, the course of the reaction is determined by the structure of product, because the lactone *IIIb* is stabilized by conjugation of the both benzene nuclei through anil group and the enamine double bond. Whereas 3,4-dihydro-3-oxo-2-quinoxaline aldoxime is formed in nitroso-



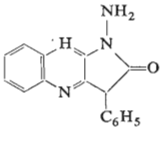
IX, X = H
X, X = C_6H_5



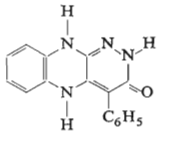
XIa



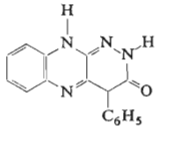
XIb



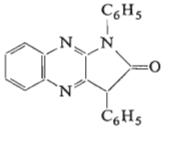
XIe



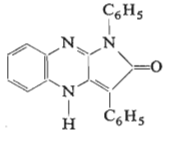
XId



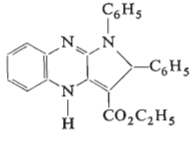
XIc



XIIa



XIIb



XIII

decarboxylation of ester *I*[1], no nitrosation of the methine group of the side chain at 2 position takes place with ester *II* under the same conditions, so that we obtained the benzoyl derivative *IV* instead of the expected isonitroso derivative. Nitrosation does not occur probably because of impossibility of stabilization of primary nitroso compound in the form of isonitroso derivative.

We have prepared 3-chloroderivatives from esters *I* and *II* by the reaction with phosphorus oxychloride. α-Hydrogens of methoxycarbonylmethylene groups in 2 position of the both compounds are not enolized, as the frequencies ν(C=O) in spectra of ethyl 3-chloro-2-quinoxalinylacetate (*IX*) (1750 cm^{-1}) and ethyl 3-chloro-2-quinoxalinylphenyl acetate (*X*) (1739, 1757 cm^{-1}) correspond to wave numbers of ester carbonyls of saturated carboxylic acids. Doublet in the spectrum of the derivative *X* can be ascribed to two conformation isomers of the ethoxycarbonyl group with respect to chlorine in 3 position, or to Fermi resonance. We have found the absorption band characteristic for C—Cl bond at 1050 cm^{-1} (vs) with the both esters. Substitution of hydrogen of the lactam group by chlorine results in a hypsochromic shift of the long wave band in UV spectra of the derivatives *IX* and *X*.

By a reaction of the chloroderivative *X* with hydrazine we have obtained a condensation product which, according to elemental analysis, is 4-phenyl-3-oxo-1,2,3,4-tetrahydropyridazo[3,4-*b*]quinoxaline (*XI*). On the basis of a negative test with Ehrlich reagent we could exclude a less probable structure *XIe* with pyrrol nucleus. Our structure is, after all, supported by other acylation reactions of hydrazine which occur with the participation of the both nitrogens, and by the fact that the compounds with six-membered rings are more stable than those with five-membered ones. We presume that the compound exists in solid state as the tautomer *XIb* with the both benzene nuclei conjugated, as the frequency of lactam carbonyl 1674 cm^{-1}, band ν(N—H) 3320 cm^{-1} correspond to the given structure (Table I). A further diffusion band at 3197 cm^{-1} is probably due to valence vibration of the lactam NH group which is strongly associated. The band 1628 cm^{-1} can be interpreted similarly as the frequency 1620 cm^{-1} in the spectrum of the lactone *IIIb*. We consider the structures *XIa*, *XIc*, and *XId* to be less stable because of a smaller extent of conjugation, and we excluded the lactim structures with respect to the presence of carbonyl. We have proved the possibility of cyclization to pyrrol derivative by the reaction of the chloroderivative *X* with aniline whereupon 1,3-diphenyl-2,3-dihydro-2-oxopyrrolo[2,3-*b*]quinoxaline (*XII*) has been obtained. With respect to the presence of the bands ν(N—H) 3350 cm^{-1}, ν(C=O) 1651 cm^{-1}, ν(C=N) 1615 cm^{-1}, and ν(C—N) 1301 and 1332 cm^{-1} in the spectrum of this derivative, we suppose that the compound exists as a tautomer *XIIb*. The frequency ν(N—H) stands in a good agreement with the value 3360 cm^{-1} found by Vaughan and Tripp[6] with 1,2-diphenyl-2,3-dihydro-3-ethoxycarbonylpyrrolo[2,3-*b*]quinoxaline which exists as the enamine *XIII* too. The spectrum of the compound *XII* in chloroform shows a further band ν(C=O) at 1691 cm^{-1} which we have ascribed to the carbonyl of the tautomer

XIIa. UV spectra of the derivatives *XI* and *XII* show a considerable similarity (Fig. 1), spectrum of the lactone *III* differs by a hypsochromic shift of the long-wave maximum which can be connected with different donor properties of nitrogen and oxygen in position 1.

Our attempts at cyclocondensation of chloro derivative *IX* with hydrazine resp. aniline resulted in obtaining the starting ester along with traces of the products not further identified. The easy cyclization of the phenyl derivative *X* and, on the other hand, the low reactivity of the substance *IX* can be explained by steric influence of the phenyl group, because the ring closure releases steric strain during this reaction as well as during the lactonisation of the ester *II*. The reactions are facilitated also by stabilization of the products, resulting from the mentioned conjugation of the both benzene nuclei.

EXPERIMENTAL

Melting points were determined by means of a Kofler apparatus. Samples for elemental analyses and spectral measurements were dried 24 hours over phosphorus pentoxide in vacuum of oil pump. Samples were chromatographed on alumina thin layer (activity III according to Brockmann) using following eluents: chlorobenzene–ethyl acetate 9 : 1 (S_1), benzene–ethyl acetate 1 : 1 (S_2), and cyclohexane–acetone 3 : 1 (S_3). Electron spectra were measured on spectrophotometer Unicam SP 800 using about 1.10^{-4}M solutions in methanol, IR spectra were measured in the range 670—3700 cm^{-1} in KBr discs (2 mg/1 g KBr) using a spectrophotometer UR 20 (Zeiss, Jena) with NaCl and LiF prisms. Soluble derivatives *IX* and *X* were measured in carbon disulphide and tetrachloride, lacton *III* in chloroform too. The values of wave numbers were corrected by calibration with polystyrene.

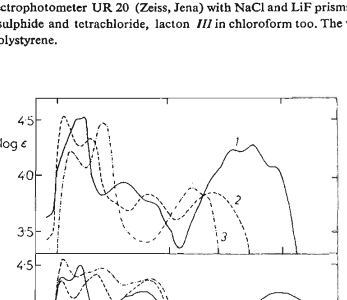


FIG. 1

Electron Spectra of Quinoxalines

1 Ethyl 3,4-dihydro-3-oxo-2-quinoxalinylacetate (*I*), *2* ethyl 3,4-dihydro-3-oxo-2-quinoxalinylphenylacetate (*II*), *3* ethyl 3-chloro-2-quinoxalinylphenylacetate (*X*), *4* 2,3-dihydro-2-oxo-3-phenylfuro[2,3-*b*]quinoxaline (*III*), *5* 4-phenyl-3-oxo-1,2,3,4-tetrahydropyridazo[3,4-*b*]quinoxaline (*XI*), *6* 1,3-diphenyl-2,3-dihydro-2-oxopyrrolo[2,3-*b*]quinoxaline (*XII*).

Ethyl 3,4-Dihydro-3-oxo-2-quinoxalinylphenylacetate (*II*)

a) A mixture of 5·4 g (0·05 mol) 1,2-diaminobenzene in 150 ml 50% ethanol and 13·2 g (0·05 mol) ethyl phenyloxalacetate was heated to boiling 45 minutes. After cooling and standing 2 hours the precipitated product was collected by suction, washed with ethanol and dried at 60°C. After recrystallization from ethanol, 5·15 g (34%) needles were obtained, m.p. 196—198°C, subl. p. 180°C.

b) A solution of 10·8 g (0·1 mol) 1,2-diaminobenzene in 250 ml ethanol and 28·8 g (0·1 mol) sodium salt of ethyl phenyloxalacetate in diluted acetic acid (7 ml/250 ml water) was heated to boiling 45 minutes. After isolation as above, 23 g (75%) needles were obtained having the same melting point. For $C_{18}H_{16}N_2O_3$ (308·3) calculated: 70·11% C, 5·23% H, 9·09% N; found: 70·02% C, 5·32% H, 9·09% N.

2,3-Dihydro-2-oxo-3-phenylfuro[2,3-*b*]quinoxaline (*III*)

a) 3 g (0·01 mol) of ester *II* was heated to boiling in 100 ml diphenyl ether 90 minutes. In the course of heating, the mixture gradually turned yellow and a green fluorescence appeared. After distilling the ethanol formed and 2 hours standing cold, the mixture was poured in 100 ml petrol, the precipitated substance was collected by suction, washed with ether and dried at 60°C. After two crystallizations from ethanol, 2·15 g (84%) of yellow substance with green fluorescence was obtained, m.p. 269—270·5°C. For $C_{16}H_{10}N_2O_2$ (262·1) calculated: 73·27% C, 3·84% H, 10·68% N; found: 73·16% C, 3·83%, 10·68% N.

b) 1 g (0·015 mol) sodium nitrite was dissolved in a solution of 0·9 g (0·003 mol) hydrazide *IV* in 10 ml 2M-NaOH. The solution was diluted with water to 200 ml and 2M-HCl was added with stirring and cooling (ice) until an evident acid reaction. The precipitated product was collected by suction, washed with water until neutral reaction and dried. After recrystallization from ethanol, 0·77 g (85%) of yellow crystals were obtained, m.p. 269—270°C. Mixture melting point with a sample of lactone *III* did not show any depression.

An attempt at lactonization of ester *I* was carried out analogously to *a*). On chromatography with S_1 system, the product gave a spot of starting substance (R_F 0·90) and two yellow very weak spots (R_F 0·27 and 0·00) which were not identified.

3,4-Dihydro-3-oxo-2-benzylquinoxaline (*IV*)

a) A solution of 2 g (0·065 mol) of ester *II* in 10 ml 50% KOH was heated to boiling 30 minutes, whereupon crystals of potassium salt separated. After cooling the reaction mixture was acidified with 2M-HCl until acid reaction (the salt dissolved and carbon dioxide was evolved). The precipitate formed was filtered, washed with water and dried at 60°C. Yield 1·44 g (94%) of yellow crystals, m.p. 197—199°C (ethanol). Ref. [7] gives m.p. 196°C.

b) A solution of 1 g ester *II* (0·032 mol) in 5 ml 50% KOH was heated to boiling 30 minutes and diluted with 50 ml water. After addition of 2·8 g (0·032 mol) potassium nitrite, 1M-H_2SO_4 was added with stirring and cooling until evident acid reaction. Carbon dioxide was evolved from the reaction mixture and a yellow precipitate separated. This was filtered and washed with water until neutral. After recrystallization from acetone (charcoal), 0·7 g (90%) yellow needles were obtained, m.p. 195—196°C. Mixture melting point with the substance *IV* did not show any depression.

c) A solution of 0·4 g (0·0015 mol) hydrazide *V* in 20 ml conc. hydrochloric acid with 0·5 g (0·008 mol) sodium nitrite was heated at 60°C. 0·3 g (84%) needles, m.p. 196—198°C were isolated after cooling.

3,4-Dihydro-3-oxo-2-quinoxalinylphenylacethydrazide (*V*)

A solution of 2·6 g (0·01 mol) lactone *III* in 100 ml ethanol was heated with 3 ml hydrazine hydrate (61% N_2H_4) 1 hour to boiling whereupon a product separated which, after cooling, was collected by suction and washed with water until neutral. After crystallization from ethanol, 2·65 g (90%) needles were obtained which begin to sublime at 210°C and decompose at 260°C. For $C_{16}H_{14}N_4O_2$ (294·3) calculated: 65·29% C, 4·80% H, 19·04% N; found: 65·09% C, 5·03% H, 18·92% N.

Product of the hydrazinolysis of ester *II* began to decompose at 240°C and the decomposition products melted at 310°C. It was crystallized from ethanol and water until constant elemental analysis: 54·67% C, 4·84% H, 30·79% N.

Hydrazones *VI*— *VIII*

The hydrazones were prepared by two hours boiling of 0·005 mol hydrazide *V* with an equivalent amount of carbonyl compound in 15 ml 50% ethanol. The products were isolated after concentration of reaction mixture and recrystallized from ethanol. Results are given in Table II.

Ethyl 3-Chloro-2-quinoxalinylacetate (*IX*)

12 ml phosphorus oxychloride was added to a mixture of 7·75 g (0·03 mol) of ester *I* and 2 ml pyridine with stirring. The reaction mixture was heated to boiling 10 minutes, poured on 250 g ice and neutralized with a saturated soda solution to litmus. The separated redbrown precipitate was filtered. A further amount of the product was obtained by extraction of the mother liquor with ether. Combined products were recrystallized from 50% ethanol (charcoal) and gave 5·4 g of redbrown product. Chromatography using S_2 system gave three spots (hue and R_F are given): yellow, 0·95; pink, 0·80; red, 0·00. The product corresponding to the yellow spot was isolated by column chromatography (20 cm; S_2 system) and recrystallized twice from ethanol to give 2·4 g (32·8%) yellow needles, m.p. 79—79·5°C. For $C_{12}H_{11}ClN_2O_2$ (250·7) calculated: 57·49% C, 4·43% H, 11·17% N; found: 57·33% C, 4·56% H, 10·90% N.

TABLE II
Hydrazones *VI*— *VIII*

Oxo compound (reaction time, h)	Product (yield, %)	M.p. °C	Formula (mol. weight)	Calculated/Found		
				% C	% H	% N
Acetaldehyde (4·5)	*VI* (50)	239—241	$C_{18}H_{16}N_4O_2$ (320·3)	—	—	17·49 17·35
Acetone (8)	*VII* (35)	237—239	$C_{19}H_{18}N_4O_2$ (334·4)	68·24 68·43	5·42 5·34	16·76 16·53
Benzaldehyde (2)	*VIII* (87)	264—265	$C_{23}H_{18}N_4O_2$ (382·4)	72·23 72·12	4·74 4·72	14·65 14·63

Ethyl 3-Chloro-2-quinoxalinylphenylacetate (*X*)

The derivative was prepared similarly as the substance *IX* and after isolation was homogeneous. 5·05 g (24%) needles, m.p. 87·5—88·5°C was obtained. For $C_{18}H_{15}ClN_2O_2$ (326·8) calculated: 66·16% C, 4·63% H, 11·18% Cl, 8·56% N; found: 66·08% C, 4·81% H, 10·97% Cl, 8·82% N.

4-Phenyl-3-oxo-1,2,3,4-tetrahydropyridazo[3,4-*b*]quinoxaline (*XI*)

1·64 g (0·02 mol) of ester *X* was heated to boiling with 20 ml 80% hydrazine hydrate 1 hour. The reaction mixture was poured in 100 ml hot water, ethanol was added to dissolution, and the solution was filtered with charcoal. After cooling, the precipitated orange substance was collected by suction and chromatographed using S_2 system (hue and R_F of spots are given): yellow, 0·00; yellow, 0·35; and S_3 system: yellow, 0·10; yellow, 0·40. The pure substance (S_2, R_F 0·35) was separated on an alumina column (20 cm, S_2 system) and recrystallized from 50% ethanol. Yield 0·41 g (32%), m.p. 251—253°C (decomp.). For $C_{16}H_{12}N_4O$ (276·3) calculated: 69·55% C, 4·38% H, 20·20% N; found: 69·55% C, 4·67% H, 20·17% N.

1,3-Diphenyl-2,3-dihydro-2-oxopyrrolo[2,3-*b*]quinoxaline (*XII*)

0·325 g ester *X* (0·001 mol) and 5 ml aniline was heated to boiling 2 hours. After concentrating to half volume the mixture was cooled at 0°C, diluted with the same volume of methanol and the precipitated product was filtered. After two crystallizations from diluted ethanol (1 : 1), 0·15 g (44·5%) yellow needles were obtained, m.p. 287—289°C. Yellow spot in S_2 system R_F 0·31. For $C_{22}H_{15}N_3O$ (337·4) calculated: 78·32% C, 4·48% H, 12·46% N; found: 78·54% C, 4·58% H, 12·42% N.

Elemental analyses were carried out in the Department of Analytical Chemistry, Institute of Chemical Technology, Pardubice.

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STUDIES IN THE QUINOXALINE SERIES. VII.

CYCLIZATION REACTIONS OF SOME 2-METHOXYCARBONYLQUINOXALINE DERIVATIVES

J.Klicnar, M.Hájek, J.Hofman and M.Večeřa

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AMINO ACIDS AND PEPTIDES. CIII.

INFRARED SPECTRA AND CONFORMATIONS OF METHYLAMIDES OF N-ACYLATED AMINO ACIDS WITH A HYDROXYL GROUP IN THE SIDE CHAIN

J.Smolíková, A.Vítek and K. Bláha

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