DERIVATIVES OF 3,4-DIHYDRO-3-THIOXO-2-QUINOXALINYLACETIC ACID*

Jaromír TOMAN and Jiří KLICNAR

Department of Organic Chemistry,
Institute of Chemical Technology, 532 10 Pardubice

Received April 19th, 1985

Ethyl 3,4-dihydro-4-methyl-3-thioxo-2-quinoxalinylacetate has been prepared by thionation of the 3-oxo derivative. The mechanism is discussed of the reaction of this ester with diethylamine giving the two non-isomerizing ketimine–enamine tautomers and 1,2-dihydro-1,3-dimethyl-2--thioxoquinoxaline. Structure has been studied of the reaction product of both this derivative and its 3-oxo analogue with sodium hydride in dimethyl sulphoxide.

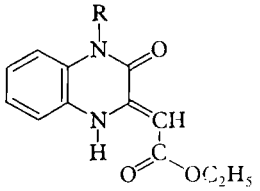
Our earlier reports[1,2] give chemical properties of 2-ethoxycarbonylmethylene-3-oxo--1,2,3,4-tetrahydroquinoxaline (*I*). In context with further studies we were interested in the effect of replacement of oxygen for sulphur in the 3-oxo group on reactivity and stability of the enamino ester form.

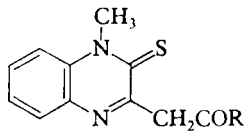
For the preparation we chose direct thionation of the better soluble 4-methyl derivative *II* with tetraphosphorus decasulphide in boiling chlorobenzene; at shorter reaction times formation of the decomposition products (which were observed in thionation of 1,2-dihydro-1-methyl-2-oxoquinoxaline[3]) is suppressed. The experiments at lower temperature were unsuccessful, during longer heating the decomposition could not be prevented even by addition of a base[3]. The wave number value of the band ν(C=O) 1 752 cm^{-1} in the IR spectrum of the solid sample indicates the ketimine tautomeric structure of ethyl 3,4-dihydro-4-methyl-3-thioxo-2-quinoxalinyl acetate (*III*), whereas the oxygen analogue *II* represents an enamine. The ^{1}H NMR spectrum in deuteriochloroform shows 70% of the ketimine form. The methyl ester analogue *IV* was prepared in similar way.

Some cognate derivatives exhibit biological activity[4], so we tried to prepare the corresponding amides. The reaction of ester *III* with ammonia or amines was carried out at 170°C except for aniline where additional catalysis with sodium was applied[5]. The reaction of ester *III* with ammonia gave 3,4-dihydro-4-methyl-3-thioxo-2--quinoxalinylacetamide (*V*), the reactions with amines gave N-cyclohexyl- (*VI*), N-butyl- (*VII*), N-allyl- (*VIII*), N-(3-dimethylamino)propyl- (*IX*), N-phenyl- (*X*),

* Part XVI in the series Studies in Quinoxaline Series; Part XV: This Journal *49*, 976 (1984).

and N-(2-furyl)methyl-3,4-dihydro-4-methyl-3-thioxo-2-quinoxalinylacetamide (*XI*). The band of thioxo group ν(C=S) in the IR spectra of the amides *IV*–*XI* and esters *III* and *IV* was found in the wave number interval from 1 125 to 1 139 cm^{-1}, the wave number values of the band of amidic carbonyl are given in Table I.





I, R = H
II, R = CH_3

III, R = OCH_2H_5
IV, R = OCH_3
V, R = NH_2
VI, R = $NHCH(CH_2)_5$
VII, R = $NH(CH_2)_3—CH_3$
VIII, R = $NHCH_2CH—CH_2$
IX, R = $NH(CH_2)_3N(CH_3)_2$
X, R = NHC_6H_5
XI, R = $NHCH_2C—(CH)_3—O$
XIII, R = $N(C_2H_5)_2$

In contrast to these amonolysis experiments the reaction product of ester *III* and diethylamine was separated chromatographically into 3 individual compounds: the least polar one which showed no carbonyl group in its IR spectrum was identified as 1,2-dihydro-1,3-dimethyl-2-thioxoquinoxaline (*XII*). Presumably it was formed from the corresponding carbanionic leaving group in decomposition of the tetrahedral intermediate. This carbanion is more stable than that of the 3-oxo analogue, its basicity being comparable with that of ethanolate (see below), hence it is also comparable with ethoxide in the role of a leaving group. An alternative explanation – hydrolysis of the ester *III* with the water traces present in the amine and subsequent decarboxylation – could be excluded, because the derivative *XII* was not formed during heating of the ester *III* with triethylamine containing 3% water even at 230°C.

The product from the second chromatographical fraction showed a carbonyl band at 1 630 cm^{-1} corresponding to a tert-amidic group. A singlet of CH_2 group at 4·33 ppm in the ^{1}H NMR spectrum, the absence of ν(N—H) band, and mass spectroscopy indicate the ketimine tautomeric structure of N,N-diethyl-3,4-dihydro-4-methyl-3-thioxo-2-quinoxalinylacetamide (*XIII*). The third compound (with the highest polarity) is isomeric with amide *XIII* (they both have identical M^+ values), and a signal of =C—H group at 6·03 ppm indicates enamine tautomeric form of 2-(N,N-diethylcarbamoyl)methylene-4-methyl-3-thioxo-1,2,3,4-tetrahydroquinoxaline

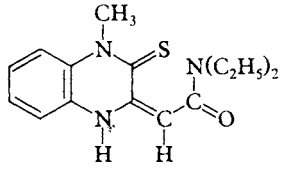
TABLE I

Products of amonolysis of ester *III*

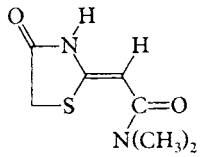
Product	Temperature, °C (time, h)	Yield g (%)	M.p., °C solvent	ν(C=O)[a] cm^{-1}	Formula (mol.wt.)	Calculated/found % C	% H	% N
V	170 (2)	0·5 (36)	218–221 ethanol	1 660 vs, b	$C_{11}H_{11}N_3OS$ (233·3)	56·65 56·27	4·72 4·77	18·02 18·06
VI	160 (3)	1·15 (61)	223–224 1-propanol	1 635 vs	$C_{17}H_{21}N_3OS$ (315·4)	64·76 64·81	6·66 6·38	13·33 13·60
VII	135 (1)	0·7 (41)	175–178 ethyl acetate	1 641 vs	$C_{15}H_{19}N_3OS$ (289·4)	62·28 62·20	6·57 6·70	14·53 14·89
VIII	160 (1·5)	0·8 (49)	201–204 benzene–ethyl acetate 1 : 1	1 650 vs	$C_{14}H_{16}N_3OS$ (273·4)	78·86 78·87	7·03 6·70	19·71 19·63
IX	160 (2)	1 (42)	149–151 ethanol	1 660 vs	$C_{16}H_{22}N_4OS$ (318·4)	60·38 60·53	6·91 7·23	17·61 17·87
X	220 (2)	1·2 (65)	232–235 acetic acid	1 660 vs	$C_{17}H_{15}N_3OS$ (309·4)	66·01 66·09	4·85 4·73	13·59 13·26
XI	160 (2)	0·9 (48)	200–201 ethanol	1 651 vs	$C_{16}H_{15}N_3O_2S$ (313·4)	— —	— —	13·41 13·21
XIII	170 (4)	0·15 (10)	122–125 cyclohexane–ethyl acetate (20 : 1)	1 638 vs	$C_{15}H_{19}N_3OS$ (289·4)	— —	— —	— —
XIV	170 (4)	0·20 (13)	178–183	1 635 vs	$C_{15}H_{19}N_3OS$ (289·4)	— —	— —	— —

[a] The band intensities: vs very strong, s strong, m medium, sh shoulder, b broad band.

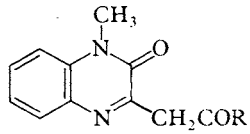
(*XIV*). In contrast to the enamino esters *I* and *II*, the band of ν(N—H) at 3 260 cm^{-1} is intensive, and the structure of the compound studied is supposed to be better expressed (in solid state) by the formula *XIV* without intramolecular hydrogen bond of the enaminoamide group similar to the enaminone *XV* (ref.[6]).



XIV



XV



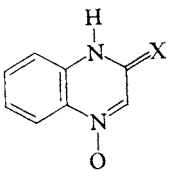
XVI, R = NH_2
XVII, R = $NHCH_3$
XVIII, R = $N(CH_3)_2$
XIX, R = $N(CH_2CH_2)_2O$

Neither of the tautomers *XIII* and *XIV* underwent isomerization in protic and aprotic solvents even in the presence of acidic or basic catalysts. In comparison with the 3-oxo derivative *I*, whose tautomerization was studied in detail[2], the activation energy of the 3-thioxo derivatives *XIII* and *XIV* is probably much too high, hence the isomerization only proceeds at elevated temperatures which are also sufficient for the amidation of the thioxo ester *III* to take place.

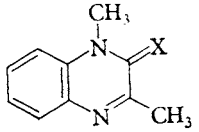
At similar reaction conditions the ester *II* was amonolyzed to 3,4-dihydro-4-methyl--3-oxo-2-quinoxalinylacetamide (*XVI*), and its reaction with amines gave the corresponding N-methyl (*XVII*) and N,N-dimethyl (*XVIII*) derivatives as well as 3,4-dihydro-3-oxo-2-quinoxalinylacetmorpholide (*XIX*). The ^{1}H NMR spectra of *XVI* in hexadeuteriodimethyl sulphoxide indicated the enamine/ketimine ratio to be 2 : 1 and 1 : 1 at 100 and 60°C, respectively, whereas the N,N-dimethyl derivative *XVIII* only contains traces of the ketimine tautomeric form at 60°C (Table II).

For preparation of thioxo ester type *III* we chose the reaction of 3,4-dihydro-3--thioxoquinoxaline-1-oxide (*XX*) with ethyl acetoacetate in the presence of a base. Literature[7] gives the synthesis of the N-oxide *XX via* α-benzoyl-2-nitrothioacetanilide prepared from 2-nitrophenyl isothiocyanate. We chose a simpler approach consisting in direct thionation of 3,4-dihydro-3-oxoquinoxaline-1-oxide (*XXI*) with tetraphosphorus decasulphide in pyridine. The N-oxide *XXI* (which was prepared[8] in low yields from 2-nitroaniline and ethyl acetoacetate and subsequent cyclization of acetoacet-2-nitroanilide) was obtained more advantageously by replacement of ethyl acetoacetate by diketene which is considered non-reactive to less basic amines (even with catalysis by pyridine[9] or at elevated temperature[1]). A distinct increase in reactivity of 2-nitroaniline and in purity of the product was reached by using catalysis with pyridinium perchlorate in pyridine when the reaction was exothermic even

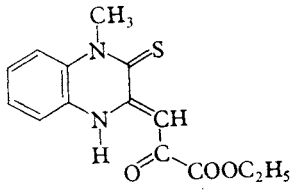
in lower-boiling benzene. In contrast to the oxygen analogue *XXI* (ref.[8]), the N-oxide *XX* did not react with ethyl acetoacetate.



XX, X = S
XXI, X = O



XXII, X = S
XXIII, X = O



XXIV

We also tried to prepare the ester *III* by condensation of 1,2-dihydro-1,3-dimethyl--2-thioxoquinoxaline (*XXII*) (ref.[10]) with dimethyl carbonate. The reaction did not gave the ester *III* even on application of sodium hydride as the base, although the analogous reaction with the oxo derivative *XXIII* is smooth[8]. The more reactive ester – diethyl oxalate – reacted with the thioxo derivative *XXII* to give a product which was identified as 2-ethoxalylmethylene-4-methyl-3-thioxo-1,2,3,4-tetrahydroquinoxaline (*XXIV*). Its enamine structure is supported by the very intensive ν(C=C) band at 1 590 cm^{-1} which is characteristical for enaminones, the wave number values of the two carbonyl groups being at 1 615 and 1 738 cm^{-1}. The NH group

TABLE II
Amides XVI–XIX

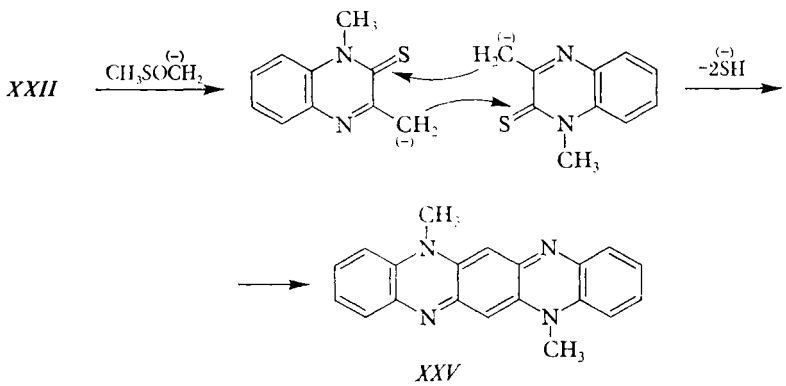
Product	Temperature, °C (time, h)	Yield g (%)	M.p., °C solvent	ν(C=O)[a] cm^{-1}	Formula (mol.wt.)	Calculated/Found % C	% H	% N
XVI	173 (1)	0·3 (23)	208–210 1-propanol	1 670 m[b] 1 650 vs	$C_{11}H_{11}N_3O_2$ (217·2)	60·82 60·83	5·10 5·18	19·35 19·63
XVII	180 (1·5)	0·7 (48)	198–199 ethanol	1 675 s[b] 1 630 vs	$C_{12}H_{13}N_3O_2$ (231·3)	62·32 62·53	5·67 5·21	18·17 18·06
XVIII	180 (1·5)	0·75 (51)	138–139 ethanol[c]	1 660 s[b] 1 628 vs	$C_{13}H_{15}N_3O_4$ (245·3)	63·66 63·93	6·16 6·08	17·13 17·02
XIX	180 (1)	0·9 (38)	184–186 ethanol[c]	1 662 vs[b] 1 626 vs	$C_{15}H_{17}N_3O_3$ (287·3)	62·70 62·60	5·96 6·57	14·63 14·35

[a] See the footnote in Table I; [b] the bands of 3-oxo group; [c] the samples were sublimed before the analysis.

bound to oxygen atom of the ketocarbonyl group by an intramolecular hydrogen bond exhibits a diffuse absorption band with the maximum at 3 100 cm^{-1} (measured in chloroform). As compared with the oxygen analogue[11], the 3-thioxo ester *XXIV* exhibits a bathochromic shift of the bands in electronic spectrum by $\Delta\lambda$ 40 nm.

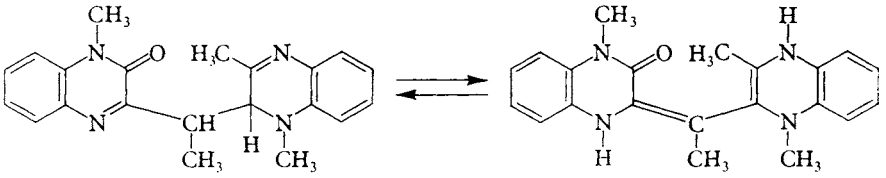
The lower reactivity of derivative *XXII* in the ester condensations is probably connected with more extensive charge delocalization in the carbanion. This explanation is supported by the acidity difference between the oxygen and sulphur analogues *XXIII*, *XXII*: the latter is completely ionized in sodium methoxide solution (2 mol l^{-1}), whereas the former is not ionized even at a concentration of 4 mol l^{-1} sodium methoxide. Values of the ionization constants could not be determined due to relatively rapid decomposition of the two derivatives. A similar example of instability of dihydrooxoquinoxalines to methoxide was given earlier[12].

Another attempt at condensation of the thioxo derivative *XXII* with dimethyl carbonate made use of sodium hydride in dimethyl sulphoxide (dimsyl sodium) at room temperature. We isolated, however, a product without ester group and exhibiting identical mass and IR spectra with those of the known[13] 5,12-dimethyl--5,12-dihydroquinoxalino[2,3-*b*]phenazine (*XXV*). The latter species was obviously formed by nucleophilic addition of the carbanion of the thioxo derivative *XXII* and elimination of hydrogensulphide anion connected with formation of the 1,4--benzoquinoid section in the product *XXV*. This desulphurization ring closure represents the third known procedure for obtaining the derivative *XXV* which was suggested for use in dyeing of polyacrylic fibres[14].



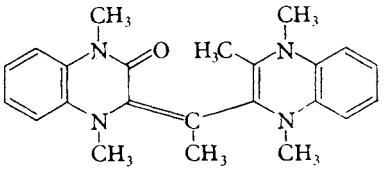
An analogous reaction was also carried out with the oxo derivative *XXIII*, of course without addition of dimethyl carbonate which did not take part in the reaction. No reaction took place when cold, after heating at 60°C we isolated a product whose IR spectrum contained a ν(C=O) band of tert-amidic group at 1 642 cm^{-1}, δ(C—H) bands of methyl groups attached to both nitrogen (1 421 cm^{-1}) and carbon

(1 370 cm^{-1}). From elemental analysis, mass and ^1H NMR spectra we could derive the probable structure of 2-(1-(1,4-dihydro-1,3-dimethyl-2-quinoxalinyl)-ethylidene)-4-methyl-3-oxo-1,2,3,4-tetrahydroquinoxaline (*XXVI*). We suppose that the condensation of methyl group with amidic carbonyl group of the second molecule and partial reduction with hydride were accompanied by methylation with dimsyl sodium at the α-carbon atom of the side chain. The alkylation effects of dimethyl suphoxide at similar conditions were observed with 1,3-butadiene[15] and heterocyclic compounds[16].

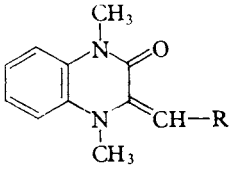


XXVI a *XXVI b*

Solubility of the product *XXVI* in ethoxide indicates formation of an anion or dianion of the dienamine form *XXVIb*. This tautomeric form is also supported by the absence of the proton signal at the tert-carbon atom of the *XXVIa* form from the ^1H NMR spectrum. The alkylation with methyl iodide gave a product from which we could isolate (chromatographically) a compound whose elemental analysis and mass specirum indicate the structure of 2-(1-(1,4-dihydro-1,3,4-trimethyl-2-quinoxalinyl)ethylidene)-1,4-dimethyl-3-oxo-1,2,3,4-tetrahydroquinoxaline (*XXVII*).



XXVII



XXVIII, R = H
XXIX, R = CH_3

Except for the ionization causing a colour change, the oxo derivative *XXIII* does not react with dimsyl sodium at room temperature. Alkylation of the anion formed with methyl iodide gave a product representing (according to the GC-MS analysis) a mixture of two compounds which could not be separated on preparative scale. Analysis of the mass spectrum (based on the study[17] of fragmentation of quinoxaline derivatives) suggests that the two compounds are 3-methylene- (*XXVIII*) and 3--ethylidene-1,4-dimethyl-3-oxo-1,2,3,4-tetrahydroquinoxaline (*XXIX*).

EXPERIMENTAL

The melting points were determined with a Kofler apparatus. The IR spectra were measured with a Spektromom 2000 apparatus, the wave numbers being calibrated with polystyrene. The ^{1}H NMR spectra were measured with a Tesla BS 487 B apparatus at 80 MHz in hexadeuteriodimethyl sulphoxide with tetramethylsilane as the internal standard. The GC-MS and MS analyses were carried out with a Varian Mat 44 S apparatus at 70 eV. The ionization was followed[12] with a UV-VIS apparatus (Zeiss, Jena).

Ethyl 3,4-Dihydro-4-methyl-3-thioxo-2-quinoxalinylacetate (*III*)

Solution of 44·5 g (0·181 mol) ester *II* in 750 ml chlorobenzene was stirred at 125°C, and 60 g tetraphosphorus decasulphide was added thereto during 5 min. After 5 min boiling, the mixture was cooled to 50°C. The solution was separated from a greasy portion which was washed with 200 ml dichloromethane. Combined organic phases were washed with 4 × 250 ml aqueous ammonia and 100 ml water. The solution was dried by heating and filtered through an alumina column (activity II), and the product mixture was eluated with benzene. The first eluates were separated from the product solution, and the tary byproducts remained in the column. The eluate was concentrated in vacuum (water pump), diluted with 50 ml ethanol, left to stand in cold place 1 h, and the raw product was collected by suction (m.p. 93–100°C). Recrystallization from ethanol gave 17·5 g (37%) yellow crystals, m.p. 98–103°C. For elemental analysis the product was purified by column chromatography (alumina activity I; benzene–cyclohexane 3 : 1), m.p. 103–105°C. ^{1}H NMR spectrum (deuteriochloroform): 5·64 ppm (s) =CH, 4·20 ppm (s) CH_2, 4·11 ppm (s) N–CH_3. For $C_{13}H_{14}N_2O_2S$ (262·3) calculated: 59·52% C, 5·38% H, 10·68% N; found: 59·84% C, 5·58% H, 10·70% N. Th emethyl ester *IV* was prepared analogously, yield 41%, m.p. 137–140°C (sublimation above 120°C). For $C_{12}H_{12}N_2O_2S$ (248·3) calculated: 58·04% C, 4·82% H, 11·18% N; found: 58·20% C, 4·84% H, 11·13% N.

Amonolysis of the Esters *III* and *II*

The ester *III* (1·5 g; 6 mmol) was heated in a sealed ampoule with 10 ml respective amine (Table I) or ethanolic ammonia. The mixture was concentrated in vacuum, and the unreacted amine was extracted with cold ether, and the product was recrystallized (Table I). In the case of the reaction with diethylamine the mixture was separated by column chromatography (silica gel, benzene–ethyl acetate 1 : 1). The first fraction gave 0·3 g (26%) compound *XXII*, m.p. 147–148°C, ref.[10] gives m.p. 148°C. IR spectrum: ν(C=S) 1 130 cm^{-1}. Two subsequent chromatographical fractions gave the tautomers *XIII* and *XIV* with identical M^+ value 289. *XXIII*: 289 (55), 218 (91), 217 (63), 216 (100), 190 (84), 189 (59), 188 (86), 187 (10), 145 (11), 144 (8), 143 (12), 129 (12), 103 (11), 102 (12), 100 (18), 72 (47). The reaction conditions of the amonolysis of 3-oxo derivative *II* and analytical data of the amides obtained are given in Table II.

3,4-Dihydro-3-thioxoquinoxalin-1-oxide (*XX*)

A mixture of 2·7 g (20 mmol) 3-oxo derivative *XXI* (ref.[8]) and 7·2 g finely ground tetraphosphorus decasulphide in 100 ml anhydrous pyridine was heated at 70°C with stirring 2 h. The solvent was removed by distillation in vacuum (water pump), and the residue was diluted with 100 ml water. The raw product was collected by suction, washed with methanol, and recrystallized from ethanol. Yield 2·9 g (81%) yellow needles, m.p. 185–186°C, ref.[7] gives the same value.

Acetoacet-2-nitroanilide

A solution of 138 g, (1 mol) 2-nitroaniline and 93 g (1·1 mol) diketene in 400 ml benzene was treated with 1 ml pyridine solution in 0·5 equivalent of 70% perchloric acid. After the exothermic reaction ceased, the reaction mixture was boiled 30 min, cooled, and extracted with 1·2 mol 5% sodium hydroxide solution. The extract was washed with 150 ml benzene and acidified (Congo Red) at the temperature below 10°C. The product was collected by suction and washed with 3 × 250 ml water. After drying the yield was 154 g (75%) product with m.p. 58—62°C; the product was used for cyclization to the N-oxide *XXI*. After recrystallization from ethanol m.p. 66—67°C, ref.[8] gives m.p. 68°C.

2-Ethoxalylmethylene-4-methyl-3-thioxo-1,2,3,4-tetrahydroquinoxaline (*XXIV*)

A mixture of 1·8 g (10 mmol) thioxo derivative *XXII* (ref.[10]), 0·6 g sodium hydride, 6 ml diethyl oxalate, and 30 ml toluene was boiled with exclusion of air humidity 2 h. The product was decomposed with water and acetic acid, the organic phase was separated and concentrated. The precipitated product was recrystallized from 2-ethoxyethanol to give 1·65 g (57%) orange needles, m.p. 194—196°C. For $C_{14}H_{14}N_2O_3S$ (290·3) calculated: 58·91% C, 4·85% H, 9·65% N; found: 58·92% C, 5·00% H, 9·47% N.

5,12-Dimethyl-5,12-dihydroquinoxalino[2,3*b*]phenazine (*XXV*)

With exclusion of air humidity, 2·3 g (13 mmol) thioxo derivative *XXII* (ref.[10]) was added at 20°C to solution of dimsyl sodium obtained from 0·72 g (30 mmol) sodium hydride and 50 ml dimethyl sulphoxide at 50°C. After 1 h stirring the mixture was diluted with water, the precipitated product was collected by suction and extracted with 3 × 100 ml boiling ethanol. The red solution was concentrated to give 0·8 g blue needles, m.p. 294°C (determined only approximately due to dark colour), ref.[13] gives m.p. 297°C. Mass spectrum: 312 (100), 297 (93), 282 (31), 156 (24). IR spectrum (KBr disc): ν(C=N) 1 565 cm^{-1}, ν(C—H) of N-methyl groups 2 870, 3 000 cm^{-1} were identical (as well as the value of molecular ion) with the published data[13].

Condensation of Compound *XXIII* by Action of Dimsyl sodium

a) Solution of 2·2 g (13 mmol) oxo derivative *XXIII* in 15 ml dimethyl sulphoxide was added drop by drop to solution of 0·72 g (30 mmol) sodium hydride in 50 ml dimethyl sulphoxide at 50°C. After 0·5 h stirring on boiling water bath, the green reaction mixture was decomposed with 150 ml water and 10 ml acetic acid. The precipitated product was collected by suction, washed with water and methanol, and the unreacted portions were extracted with boiling dioxane. After recrystallization from acetic acid the yield was 0·6 g orange crystals of compound *XXVI*, m.p. 317—320°C (sublimation above 260°C). ^{1}H NMR spectrum (trifluoroacetic acid): 3·01 ppm singlet of four methyl groups, multiplet of aromatic protons 7—8 ppm. Mass spectrum: M^+ 346 (20), 199 (10), 198 (8), 187 (40), 173 (15), 159 (55), 157 (33), 145 (100), 131 (45). For $C_{21}H_{22}N_4O$ (346·4) calculated: 72·80% C, 6·40% H, 16·17% N; found: 72·72% C, 6·75% H, 16·50% N.

b) The reactants were mixed as ad *a*), and the mixture was stirred 0·5 h, whereupon 3 ml methyl iodide was added. After cooling red crystals were separated with m.p. 258—260°C. Mass spectrum: M^+ 374 (46), 359 (22), 199 (91), 188 (58), 187 (52), 185 (47), 184 (36), 173 (73), 172 (83), 161 (100), 157 (47), 147 (32), 145 (67), 133 (67). For $C_{23}H_{26}N_4O$ (374·5) calculated: 73·77% C, 7·00% H, 14·96% N; found: 73·51% C, 6·89% H, 14·90% N.

c) The reactants were mixed as ad *a*), stirred at room temperature 5 min, and treated with 5 ml methyl iodide. The reaction mixture was extracted with chloroform, the extract was washed

with water, dried, and the solvent was evaporated to give 0·1 g orange needles with m.p. 160°C which did not change on recrystallization from acetic acid. The TLC (Silufol, benzene–ethyl acetate 1 : 1) showed only one spot. Mass spectrum of compound *XXVIII*: M^+ 188 (100), 173 (50), 159 (69), 145 (19); *XXIX*: M^+ 202 (92), 187 (100), 174 (98), 158 (58).

REFERENCES

1. Toman J., Klicnar J., Macháček V.: This Journal *43*, 2179 (1978).
2. Macháček V., Toman J., Klicnar J.: This Journal *43*, 1634 (1978).
3. Spinner E.: J. Chem. Soc. *1962*, 3129.
4. Asano K., Asai S.: Yakugaku Zasshi *78*, 450 (1958); Chem. Abstr. *52*, 18428 (1958).
5. Johnson A., Stene P., Willman N.: Acta Pharm. Suecica *5*, 237 (1968); Chem. Abstr. *69*, 86957 (1968).
6. Taylor P. J.: Spectrochim. Acta 24*A*, 165 (1970).
7. Fusco R., Rossi S.: Gazz. Chim. Ital. *94*, 3 (1964).
8. Tennant G.: J. Chem. Soc. *1964*, 2666.
9. Perekalin V. V., Lerner D. M.: Zh. Obshch. Khim. *32*, 2967 (1962).
10. Badr M. Z. A., El Naggar, El Sherief H. A. H., Mahgroub S. A.: Bull. Fac. Sci. Assiut. Univ. *11*, 97 (1982); Chem. Abstr. *98*, 72055 (1983).
11. Mondelli R., Merlini L.: Tetrahedron *22*, 3253 (1966).
12. Toman J., Štěrba V., Klicnar J.: This Journal *46*, 2104 (1981).
13. Wahl H., Le Bris M. T., Berkovitsch D.: Bull. Soc. Chim. Fr. *1973*, 1289.
14. Brit. 1 168 462 (1969); Chem. Abstr. *72*, 122 927 (1970).
15. Argabright P. A., Hofmann J. E., Schriesheim A.: J. Org. Chem. *30*, 3233 (1963).
16. Russel G. A., Wiener S. A.: J. Org. Chem. *31*, 248 (1966).
17. Toman J., Terentiev P. B., Klicnar J.: Khim. Geterotsikl. Soedin. *1981*, 1118.

Translated by J. Panchartek.