PREPARATION AND SYNTHETIC UTILIZATION OF DIARYLMETHYLENEMALONALDEHYDES

Vladimír KRÁL, Ladislav JELÍNEK and David ŠAMAN

Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, 166 10 Prague 6

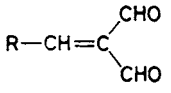
Received November 14, 1988
Accepted March 7, 1989

A general synthetic approach to disubstituted methylenemalonaldehydes consisting in reaction of geminal dihalogeno derivatives with 1,3-bis(dimethylamino)trimethinium perchlorate is described. Solution conformation of the prepared compounds has been determinated by NMR spectroscopy. The prepared compounds were utilized as suitable synthons of pyrazole (*XII*), 4*H*-1,2,6-oxadiazine (*XIV*) and diazepine (*XV*) derivatives.

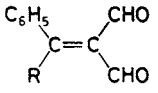
Until recently, the chemistry of methylenemalonaldehyde (*I*) was only very little investigated. Only several derivatives of this type have been prepared because the starting β-dicarbonyl compound (malonaldehyde) is unstable in acid-catalyzed reactions[1]. This drawback can be overcome by using a suitable malonaldehyde derivative. Previous attempts to synthesize such compounds via protected acetals[2] were not satisfactory because of difficult hydrolysis. Many derivatives of alkylidenemalonaldehyde were generated in situ in a basic medium and used immediately in further reactions[3].

We have found that 1,3-bis(dimethylamino)trimethinium perchlorate, a malonaldehyde synthon, reacts with aldehydes to give monosubstituted methylenemalonaldehydes[4], whereas ketones do not react under the same conditions.

In the present communication we describe the synthesis, reactivity and synthetic utilization of disubstituted methylenemalonaldehydes *IIa*–*IIf*. Compounds *IIa* to



I



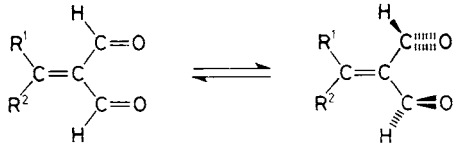
IIa, R = phenyl
IIb, R = 2-thienyl
IIc, R = 4-methoxyphenyl
IId, R = 4-chlorophenyl
IIe, R = 2-pyridyl
IIf, R = 3-pyridyl

IIc have already been described[5], compounds *IId–IIf* were prepared starting from diaryl (heteroaryl) ketones. The ketones were converted into geminal dihalogeno derivatives which reacted with 1,3-bis(dimethylamino)trimethinium perchlorate in the presence of a strong Lewis acid ($AgClO_4$). Products of this electrophilic reaction were hydrolyzed to give the desired dialdehydes *IId–IIf*.

This synthetic method can also be used for the preparation of monosubstituted methylenemalonaldehydes; however, these compounds are generally better accessible from the starting aldehydes[4].

The prepared dialdehydes *IIa–IIf* were isolated in high yields as yellow to red crystalline compounds that were more stable than the monosubstituted methylenemalonaldehydes.

The spatial structure of disubstituted methylenemalonaldehydes *IIa–IIc* was studied by NMR spectroscopy[6] and X-ray diffraction[7]. According to the NMR data the compounds of the type *II* exist in solution in two conformations: the almost planar conformation *IIA* (in polar solvents or in the presence of compounds with which they form complexes, such as $LiClO_4$, CD_3CN, $Mg(ClO_4)_2$) or in the non-planar form *IIB* (in non-polar solvents). The conformation found in the solid state by X-ray diffraction corresponds to *IIB*.



IIA *IIB*

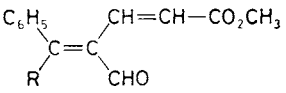
Reactivity of Disubstituted Methylenemalonaldehydes

Whereas 1,4-addition to the α,β-unsaturated dialdehyde system[8–10] and cycloaddition reaction of the —CH=C—CHO fragment[11] are typical for monosubstituted methylenemalonaldehydes *I*, the reactivity of disubstituted methylenemalonaldehydes of the type *II* is markedly different. Their tetrasubstituted double bond is sterically highly hindered and it can be attacked only by very reactive nucleophiles such as hydrazine or trimethyl phosphite. Typical for derivatives *II* are condensation reactions of the formyl group or cyclocondensations of the β-dicarbonyl $=C(CHO)_2$ fragment.

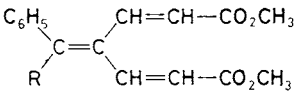
Three reactions involving the formyl groups were investigated: the Wittig reaction, formation of Schiff bases and the Knoevenagel reaction.

As concerns the Wittig reaction, suitable choice of reaction conditions, particularly the molar ratio of compounds *IIa–IIc* to the phosphorane and the reaction tempera-

ture[12], afforded either the monoesters *IVa–IVc* or the diesters *Va–Vb*. As shown by the NMR spectra, the reaction gave products of *trans*-configuration at the double bond as practically the sole products.

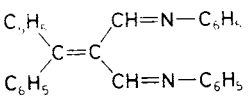


IV a, R = phenyl
IV b, R = 2-thienyl
IV c, R = 4-methoxyphenyl

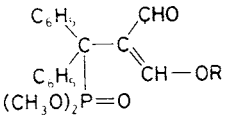


V a, R = phenyl
V b, R = 2-thienyl

Whereas monosubstituted methylenemalonaldehydes *I* react with secondary and tertiary amines to give products of 1,4-addition to the –C=C–CHO system[10], disubstituted methylenemalonaldehydes *II* do not react in this way. With primary amines, methylenemalonaldehydes *I* afford a complex mixture of products. On the other hand, no attack of the C=C double bond in disubstituted aldehydes *II* by primary amines has been observed and, instead, the formyl groups reacted under formation of a Schiff base: thus, e.g. reaction of the dialdehyde *IIa* with aniline afforded the compound *VI* in high yield.



VI



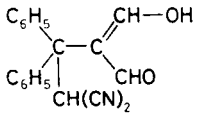
VII a, R = CH_3
VII b, R = H

The reaction with trimethyl phosphite was studied in detail[13] for the monosubstituted derivatives *I*. Compound *IIa* reacted with trimethyl phosphite under formation of the substituted methoxyacrolein *VIIa* which was readily hydrolyzed to give the substituted malonaldehyde *VIIb*. The reaction thus proceeds analogously to that of the monosubstituted derivatives, with the Arbuzov rearrangement and subsequent hydrolysis[13].

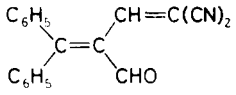
Michael reaction of monosubstituted methylenemalonaldehydes *I* with a series of C-acids (β-dicarbonyl compounds, malononitrile) furnished 1,4-addition products which were further cyclized to pyran derivatives[14]. Treatment of disubstituted methylenemalonaldehydes *II* with C-acids gave a mixture of compounds, limiting thus considerably the synthetic utilization of this reaction. For example, the potassium fluoride- or triethylamine-catalyzed reaction of *IIa* with malononitrile gave rise to a product mixture in which we identified by mass and NMR spectroscopy the product of 1,4-addition to the –C=C–CHO grouping (compound *VIII*), together

with products of condensation of one or both aldehyde groups (compounds *IX* and *X*, respectively), depending on the molar ratio of the reactants.

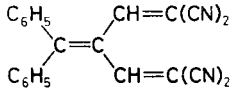
The Knoevenagel reaction of disubstituted dialdehydes *II* took place with one or both formyl groups. In the reaction of compound *IIa* with acetylacetone the subsequent cyclization led to the derivative *XI*.



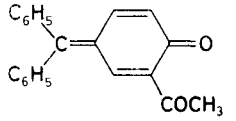
VIII



IX

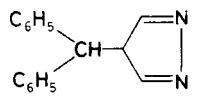


X

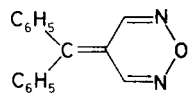


XI

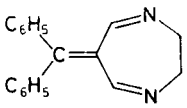
The mono- as well as disubstituted methylenemalonaldehydes represent very advantageous building blocks[15] for the preparation of 5-, 6- and 7-membered heterocyclic systems, in some cases with an exocyclic double bond. Reaction of compound *IIa* with hydrazine hydrate or hydrazine hydrochloride afforded the pyrazole derivative *XII* or its hydrochloride. Interestingly, the reaction did not afford the expected product with the exocyclic C=C double bond, but compound *XII* in which this bond was reduced. Also the reaction of *II* with hydroxylamine hydrochloride was of interest. Instead of the expected bis-oxime, we obtained the 4*H*-1,2,6-oxodiazine derivative *XIII*, formed by dehydration of the primarily arising bis-oxime and cyclization. Compound *IIa* reacted very readily with 1,2-diamines. We isolated in high yields the diazepine derivatives *XIV* and *XV* in the reaction with 1,2-diaminoethane and *ortho*-diaminobenzene, respectively.



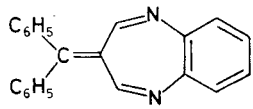
XII



XIII



XIV



XV

TABLE I

Monoesters *IVa*—*IVc* and diesters *Va* and *Vb*

Compound (yield, %)	Reaction time, h	M.p. °C	Formula (M.w.)	Calculated/Found	
				% C	% H
IVa	60	103—105	$C_{19}H_{16}O_3$	78·06	5·52
(96)			(292·3)	78·01	5·46
IVb	60	56—58	$C_{17}H_{14}O_3S$	68·44	4·73
(95)			(298·3)	68·36	4·68
IVc	30	40—41	$C_{20}H_{18}O_4$	74·52	5·63
(78)			(322·3)	74·46	5·59
Va	10	117—118	$C_{22}H_{20}O_4$	75·84	5·79
(89)			(348·4)	75·76	5·82
Vb	6	92—93	$C_{20}H_{18}O_4S$	67·77	5·12
(90)			(354·4)	67·70	5·06

TABLE II

IR, ^{1}H NMR and mass spectra of monoesters *IVa*—*IVc* and diesters *Va* and *Vb*

Compound	Data
IVa	IR: 1 711, 1 680 (C=O). ^{1}H NMR: 9·58 d, 1 H (CHO, J = 2·0); 7·62—7·05 m, 10 H (arom. H); 7·38 dd, 1 H (—CH=, J = 16·5, J' = 2·0); 6·28 d, 1 H (—CH=, J = 16·5); 3·70 s, 3 H ($COOCH_3$). MS: 292 (M^+)
IVb	IR: 1 710, 1 675 (C=O). ^{1}H NMR: 9·80 d, 1 H (CHO, J = 2·0); 7·60—7·00 m, 8 H (arom. H); 7·61 dd, 1 H (—CH=, J = 16·5, J' = 2·0); 6·75 d, 1 H (—CH=, J = 16·5); 3·69 s, 3 H ($COOCH_3$). MS: 298 (M^+)
IVc	IR: 1 710, 1 676 (C=O). ^{1}H NMR: 9·53 d, 1 H (CHO, J = 2·0); 6·88—7·58 m, 9 H (arom. H); 7·42 dd, 1 H (—CH=, J = 16·5, J' = 2·0); 6·15 d, 1 H (—CH=, J = 16·5); 3·84 s, 3 H (OCH_3); 3·72 s, 3 H ($COOCH_3$). MS: 322 (M^+).
Va	IR: 1 710 (C=O). ^{1}H NMR: 7·02—6·95 m, 10 H (arom. H); 7·45 d, 2 H (2 × —CH=, J = 16·3); 6·25 d, 2 H (2 × —CH=, J = 16·3); 3·72 s, 6 H (2 × $COOCH_3$). MS: 348 (M^+).
Vb	IR: 1 711 (C=O). ^{1}H NMR: 7·90 d, 1 H (—CH=, J = 16·5); 7·58—6·90 m, 8 H (arom. H); 7·38 d, 2 H (—CH=, J = 16·5); 6·23 d, 2 H (2 × —CH=, J = 16·5); 3·80 s and 3·68 s, 6 H (2 × $COOCH_3$). MS: 354 (M^+).

The obtained compounds were characterized by their ^{1}H NMR, IR and mass spectra and elemental analysis. The pertinent data are summarized in Tables I–IV.

TABLE III

^{1}H NMR and mass spectra of condensation products *VI*–*XI*

Compound	Data
VI	^{1}H NMR: 8·36 s, 2 H (2 × —CH=N—); 7·40–6·64 m, 20 H (arom. H). MS: 386 (M^+)
VIIb	^{1}H NMR: 7·72–7·12 m, 13 H (arom. H, —CH=, CHO); 3·61 d, 6 H (2 × OCH_3, J(H, P) = 11). MS: 346 (M^+).
IX	^{1}H NMR: 9·47 s, 1 H (CHO); 7·75–7·15 m, 11 H (arom. H, —CH=). MS: 284 (M^+).
X	^{1}H NMR: 7·26–7·60 m, 10 H (arom. H); 5·28 s, 2 H (2 × —CH=). MS: 332 (M^+).
XI	^{1}H NMR: 7·79 dd, 1 H (—CH=CH—CO, J = 10·0, J' = 2·0); 7·50–7·12 m, 12 H (arom. H, —CH=CH—CO, —CH=C—); 2·04 s, 3 H (CH_3CO). MS: 300 (M^+).

TABLE IV

Spectral data of nitrogen heterocycles *XII*–*XV*

Compound	Data
XII	IR: 3 090, 3 066 (C—H); 1 600, 1 496, 1 449, 1 003 (arom.). ^{1}H NMR: 7·50–6·80 m, 12 H (10 × arom. H and 2 × —CH=N); 2·89 bs, 2 H (2 × >CH—). MS: 234 (M^+).
XIII	IR: 1 711, 1 692, 1 690 (C=N); 1 602, 1 585, 1 491, 1 445, 1 003 (arom.); 1 567 (C=C); 1 368 (N—O). ^{1}H NMR 7·62–7·20 m, 10 H (10 × arom. H) 5·72 bs, 2 H (2 × —CH=N—). MS: 248 (M^+)
XIV	IR: 1 647, 1 620 (C=N); 1 601, 1 576, 1 494, 1 445, 1 002 (arom.). ^{1}H NMR: 7·40–6·60 m, 12 H (arom. H, —CH=N—); 3·70–3·50 m, 4 H (N—CH_2—). MS: 260 (M^+)
XV	IR: 1 633, 1 620 (C=N); 1 599, 1 584, 1 506, 1 452, 1 005 (arom.). ^{1}H NMR: 8·76 s, 2 H (—CH=N—); 7·50–6·50 m, 14 H (arom. H). MS: 308 (M^+)

EXPERIMENTAL

Melting points were determined on a Kofler block. Analytical samples were dried over phosphorus pentoxide at 25°C/27 Pa for 24 h. Proton NMR spectra were taken on a Varian XL-200 (FT mode, 200 MHz) and a Tesla BS 467 (CW mode, 60 MHz) instruments in $CDCl_3$ with tetramethylsilane as internal standard. All values were obtained by first order analysis. Chemical shifts are given in ppm and coupling constants (J) in Hz. Infrared spectra were recorded on a Zeiss UR-20 spectrometer in chloroform, wavenumbers are given in cm^{-1}. Mass spectral measurements were performed with a ZAB-EQ, VG analytical instrument, the values are in m/z.

Diarylmethylenemalonaldehydes *IIa*–*IIc* were prepared as described in ref.[5].

Phenyl-4-chlorophenylmethylenemalonaldehyde (*IId*)

1,3-Bis(dimethylamino)trimethinium perchlorate (994 mg, 4·4 mmol) was dissolved in anhydrous nitromethane (25 ml) and the solution was mixed with silver perchlorate (1·658 g, 8 mmol). After cooling to −35°C, phenyl-4-chlorophenyldichloromethane (1·09 g, 4 mmol) was added, the reaction mixture was stirred at room temperature for 10 h in the dark, filtered through Celite and the nitromethane was evaporated in vacuo. The residue was washed three times with dry ether and hydrolyzed with a solution of perchloric acid (3 ml) and sodium chloride (3 g) in water (150 ml). The product was taken up in benzene, the combined benzene extracts were dried over magnesium sulfate, evaporated and chromatographed on a column of silica gel in chloroform; yield 0·56 g (52%) of the product *IId*, m.p. 36–38°C. For $C_{16}H_{11}ClO_2$ (270·7) calculated: 70·99% C, 4·10% H, 13·10% Cl; found: 70·72% C, 4·02% H, 12·98% Cl. ^{1}H NMR spectrum: 9·64 d, 1 H (CHO, J = 1·8); 9·55 d, 1 H (CHO, J = 1·8); 7·20–7·67 m, 9 H (aromatic H). IR spectrum: 2 750, 2 860 (CHO); 1 732 shoulder, 1 710, 1 668 (C=O); 1 591, 1 492, 1 445, 1001 (ring).

Phenyl-2-pyridylmethylenemalonaldehyde (*IIe*) and Phenyl-3-pyridylmethylenemalonaldehyde (*IIf*)

A mixture of 1,3-bis(dimethylamino)trimethinium perchlorate (994 mg, 4·4 mmol), silver perchlorate (1·658 g, 8 mmol), anhydrous nitromethane (30 ml) and calcium carbonate (1 g) was cooled to −35°C and the appropriate phenyl-pyridyldichloromethane (952 mg, 4 mmol) was added. The reaction mixture was stirred at room temperature for 28 h, filtered through Celite and the nitromethane was evaporated in vacuo. The residue was three times triturated with ether and then hydrolyzed with 5% aqueous solution of sodium hydrogen carbonate (100 ml), containing sodium chloride (1 g). The product was extracted (5×) with benzene–dichloromethane (5 : 1), the combined extracts were dried over magnesium sulfate, the solvents were removed in vacuo and the residue was chromatographed on silica gel in dichloromethane. Phenyl-2-pyridylmethylenemalonaldehyde (*IIe*): yield 0·48 g (51%), m.p. 70–72°C. For $C_{15}H_{11}NO_2$ (237·3) calculated: 75·94% C, 4·67% H, 5·90% N; found: 75·76% C, 4·62% H, 5·91% N. ^{1}H NMR spectrum: 9·67 s, 1 H (CHO); 9·53 s, 1 H (CHO); 8·88 ddd, 1 H (aromatic H, J = 5·0; 1·0; 1·0); 7·05–7·82 m, 8 H (aromatic H). IR spectrum: 2 735, 2 763, 2 858 (CHO); 1 717 shoulder, 1 670 (C=O); 1 605 shoulder, 1 597, 1 583, 1 572 shoulder, 1 447, 1 077, 1 030 (ring). Mass spectrum, m/z: 237 (M^+).

Phenyl-3-pyridylmethylenemalonaldehyde (*IIf*): b.p. 110°C/25 Pa; obtained in 59% yield (0·55 g). For $C_{28}H_{22}N_2$ (386·5) calculated: 75·94% C, 4·67% H, 5·90% N; found: 75·81% C, 4·59% H, 5·79% N. ^{1}H NMR spectrum: 9·78 d, 1 H (CHO, J = 1·3); 9·64 d, 1 H (CHO, J = 1·3); 8·78 dd, 1 H (pyridyl, J = 4·5; 2·0); 8·50 bs, 1 H (pyridyl), 7·08–7·72 m, 7 H (aromatic H). IR spec-

trum: 2 748, 2 862 (CHO); 1 729, 1 705, 1 670 (C=O); 1 615, 1 584, 1 557, 1 478, 1 445, 1 078, 1 026, 1 001 (ring).

Mono- and Diesters *IVa*—*IVc* and *Va*—*Vb*

A mixture of dialdehyde *IIa*—*IIc* (10 mmol), methoxycarbonylmethylenetriphenylphosphorane (3·34 g, 10 mmol, 1 equivalent, in the preparation of monoesters *IVa*—*IVc*, or 6·69 g, 20 mmol, 2 equivalents, in the preparation of diesters *Va* and *Vb*), and benzene (30 ml) was stirred at room temperature (for monoesters) or refluxed (for diesters) for the time specified in Table I. The reaction was monitored by TLC. After the end of the reaction, the benzene was evapporated, the product was taken up in ether and the residue was chromatographed on alumina (to remove triphenylphosphine oxide). The ether was evaporated and the product crystallized from hexane. The yields and characteristics of the products are given in Table I.

Schiff Base *VI*

A mixture of dialdehyde *IIa* (236 mg, 1 mmol), benzene (20 ml) and aniline (205 mg, 2·2 mmol) was refluxed for 2 h, The reaction mixture was evaporated on a rotatory evaporator and the product *VI* (378 mg, 98%) was obtained by chromatography on silica gel in chloroform; m.p. 48—50°C. For $C_{28}H_{22}N_2$ (386·5) calculated: 87·01% C, 5·74% H, 7·25% N; found: 86·79% C, 5·70% H, 7·19% N.

2-(Dimethoxyphosphoryl-diphenylmethyl)malonaldehyde (*VIIb*)

A mixture of dialdehyde *IIa* (236 mg, 1 mmol), benzene (20 ml) and trimethyl phosphite (1 ml, 8·5 mmol) was stirred at room temperature for 30 min and then refluxed for 8 h. After evaporation of the solvent in vacuo, the title compound was obtained by chromatography on silica gel in dichloromethane–acetone (10 : 1); yield 155·8 mg (45%), m.p. 66–70°C. For $C_{18}H_{19}O_5P$ (346·5) calculated: 62·43% C, 5·53% H; found: 62·41% C, 5·49% H.

Reaction of Compound *IIa* with Malononitrile

With 1 equivalent. Dialdehyde *IIa* (236 mg, 1 mmol) and malononitrile (66 mg, 1 mmol) were dissolved in dichloromethane (10 ml). Triethylamine (10 mg) was added, the mixture was stirred at room temperature for 30 min, the solvent was evaporated in vacuo and the product *IX* was isolated by chromatography on silica gel in dichloromethane. Yield 162 mg (57%), m.p. 107 to 113°C. For $C_{19}H_{12}N_2O$ (284·3) calculated: 80·27% C, 4·25% H, 9·85% N; found: 80·14% C, 4·23% H, 9·79% N.

With 2 equivalents. The reaction was performed as described in the preceding paragraph, except that 2 equivalents of malononitrile (132 mg, 2 mmol) were employed. The isolated product *X* weighed 173 mg (52%) and melted at 153–155°C. For $C_{22}H_{12}N_4$ (332·4) calculated: 79·50% C, 3·64% H, 16·86% N; found: 79·39% C, 3·60% H, 16·79% N.

In both reactions a minor portion (10%) of the Michael addition product *VIII* was obtained. Mass spectrum, *m/z*: 302.

Reaction of Dialdehyde *IIa* with Acetylacetone

Acetylacetone (100 mg, 1 mmol) and triethylamine (10 mg) were added to a solution of compound *IIa* (236 mg, 1 mmol) in acetonitrile (20 ml). After stirring at room temperature for 12 h,

the reaction mixture was evaporated in vacuo and the product *XI* was isolated by column chromatography on silica gel in chloroform; yield 165 mg (55%), m.p. 134–135°C. For $C_{21}H_{16}O_2$ (300·3) calculated: 83·98% C, 5·37% H; found: 83·91% C, 5·37% H.

Pyrazole Derivative *XII*

Free base. Hydrazine hydrate (75 mg, 1·5 mmol) was added to a solution of compound *IIa* (236 mg, 1 mmol) in benzene (30 ml). The mixture was stirred at room temperature for 5 h, the solvent was evaporated and the residue was purified by chromatography on silica gel in chloroform. Yield 131 mg (56%) of *XII*, m.p. 70°C. For $C_{16}H_{14}N_2$ (234·3) calculated:82 02% C, 6·02% H, 11·96% N; found: 82·17% C, 6·02% H, 11·91% N.

Dihydrochloride. A mixture of compound *IIa* (236 mg, 1 mmol), hydrazine dihydrochloride (115 mg, 1·1 mmol) and acetonitrile (30 ml) was refluxed for 12 h. The separated white product was collected, washed with acetonitrile and dried; yield 245 mg (79%), m.p. >250°C. For $C_{16}H_{16}Cl_2N_2$ (307·3) calculated: 62·53% C, 5·26% H, 23·10% Cl, 9·11% N; found: 62·42% C, 5·27% H, 23·22% Cl, 9·07% N.

4*H*-1,2,6-Oxadiazine Derivative *XIII*

Hydroxylamine hydrochloride (138 mg, 2·5 mmol) was added to a solution of compound *IIa* (236 mg, 1 mmol) in acetonitrile (30 ml). After reflux for 10 h, the unreacted hydroxylamine hydrochloride was filtered off, the solvent was evaporated in vacuo and the product *XIII* was dried; yield 211 mg (74%), m.p. 235–236°C. For $C_{16}H_{12}N_3O$ (248·3) calculated: 77·40% C, 4·87% H, 11·28% N; found: 76·70% C, 4·77% H, 10·95% N.

Diazepine *XIV*

1,2-Diaminoethane (90 mg, 1·5 mmol) and 4M solution of hydrogen chloride in ether (5 ml) were added to a solution of compound *IIa* (236 mg, 1 mmol) in acetonitrile (30 ml). The mixture was refluxed for 2 h, the solid was collected, washed with acetonitrile and dried to give 234 mg(90%) of *XIV*, m.p. 205–208°C. For $C_{18}H_{16}N_2$ (260·3) calculated: 83·04% C, 6·20% H, 10·76% N; found: 83·13% C, 6·19% H, 10·82% N.

Diazepine *XV*

A mixture of compound *IIa* (236 mg, 1 mmol), acetonitrile (30 ml) and *o*-diaminobenzene (162 mg, 1·5 mmol) was refluxed for 18 h, the solvent was evaporated in vacuo and the product was crystallized from benzene–light petroleum; yield 240 mg (78%), m.p. 146–148°C. For $C_{22}H_{16}N_2$ (308·4) calculated: 85·68% C, 5·23% H, 9·09% N; found: 85·55% C, 5·22% H, 9·11% N.

REFERENCES

1. Woodward R. B., Heusler K., Gosteli J., Naegeli P., Oppolzer W., Ramage R., Ranganathan S., Vorbrüggen H.: J. Am. Chem. Soc. *88*, 852 (1966).
2. Reichardt C., Pressler W., Würthwein E. U.: Angew. Chem. *88*, 88 (1976).
3. Tietze L. F.: Angew. Chem. *95*, 840 (1983).
4. Arnold Z., Král V., Dvořák D.: Tetrahedron Lett. *23*, 1725 (1982).
5. Král V., Arnold Z.: Synthesis *1982*, 823.
6. Laatikainen R., Král V.: J. Chem. Soc., Perkin Trans. 2, *1985*, 1091.

7. Pakkanen T. A., Nevelainen V., Král V., Laatikainen R., Arnold Z.: Collect. Czech. Chem. Commun. *52*, 714 (1987).
8. Schönberg A., Singer E., Stephan W., Sheldrick W. S.: Tetrahedron *39*, 2429 (1983).
9. Krebs A., Nickel W. U., Tikwe L., Kopf J.: Tetrahedron Lett. *25*, 1639 (1985).
10. Dvořák D., Arnold Z.: Collect. Czech. Chem. Commun. *52*, 2699 (1987).
11. Dvořák D., Arnold Z.: Tetrahedron Lett. *23*, 4401 (1982).
12. Arnold Z., Král V., Kryshtal G. V., Yanovskaya L. A.: Izv. Akad. Nauk SSSR, Ser. Khim. *1984*, 457.
13. Dvořák D., Šaman D., Buděšínský M., Arnold Z.: Collect. Czech. Chem. Commun. *52*, 2926 (1987).
14. Dvořák D., Šaman D., Hodačová J., Král V., Arnold Z.: Collect. Czech. Chem. Commun. *52*, 2687 (1987).
15. Dvořák D., Arnold Z., Král V. in: *Chemistry of Heterocyclic Compounds, Proceedings of the IXth Symposium on Chemistry of Heterocyclic Compounds, Bratislava, Czechoslovakia,* 23—28 *August 1987* (J. Kováč and P. Zálupský, Eds). Elsevier, Amsterdam 1988.

Translated by M. Tichý.