SYNTHETIC REACTIONS OF DIMETHYLFORMAMIDE. XXVII.* A SIMPLE SYNTHESIS OF AMINOMALONALDEHYDE DERIVATIVES

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By reaction of glycine, N-methyl-, N-benzyl-, and N-phenylglycine with the formylating agent prepared from dimethylformamide and phosphorus oxychloride, there was obtained a number of aminomalonaldehyde derivatives as the salts *Ib—If*. In connection with investigations on the reactivity of these salts, two methods have been devised for the preparation of aminomalonaldehyde N-acyl derivatives.

In connection with investigations on synthetic reactions of dimethylformamide, a complex reaction has been observed some time ago of the formylating agent obtained from dimethylformamide and phosphorus oxychloride with acids of the R—CH_2—COOH type wherein the substituent R was an aromatic or heterocyclic residue, a halo atom or some derivative of the carboxylic group[1,2]. In this reaction, two formyl residues are introduced under simultaneous decarboxylation; the final product is represented by the trimethinium salts of the type *I*. Aliphatic carboxylic acids

$$[(CH_3)_2N—CH=CR—CH=N(CH_3)_2]\ ClO_4$$

I

a R = aromatic or heterocyclic residue, a halo atom, carboxylic derivatives; *b* R = —HN=CH—$N(CH_3)_2]\ ClO_4$; *c* R = —N=CH—$N(CH_3)_2$; *d* R = —$N(CH_3)$—CH=$N(CH_3)_2]\ ClO_4$; *e* R = —$N(CH_2C_6H_5)$—CH=$N(CH_3)_2]\ ClO_4$; *f* R = —$N(C_6H_5)$—CH=$N(CH_3)_2]\ ClO_4$

do not afford satisfactory results in this reaction. To explain the course of the complex sequence of reactions it has been proposed[1,3] that the determining step consists in the formation of an intermediate with a double bond between the carbon atom of the original carboxylic group and the carbon atom to which the substituent R is attached, namely, of the ketene *II* or of the enol form of the acyl chloride *III*. Addition of the electrophilic formylating agent to the double bond and the subsequent transformations under the formation of the final product *I* may be satisfactorily formulated[3,4]. The important role of the substituent R consists most

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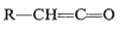
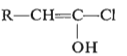
probably in the influence on the formation of the double bond in the assumed intermediate: the above mentioned electronegative groups exert a favourable effect on the course of the reaction in contrast to the electropositive alkyl groups, the effect of which is opposite.



II



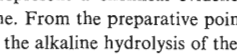
III

As a contribution to the knowledge of the present reaction, glycine and its N-substituted derivatives have been now examined as reactants. It was not *a priori* evident which effect could predominate under the usual reaction conditions, whether the electropositive character (+M) of the free amino group or the electronegative effect (−I) of the ammonium function formed by protonation. The hydrogen atoms of the primary as well as secondary amino groups are known[5,6] to incline to substitution by the action of agents of the Vilsmeier type; such a substitution may exert a considerable effect on the further course of the reaction in view of the changed electronic relations at these amino groups.

As expected, the reaction of glycine with the agent prepared from dimethylformamide and phosphorus oxychloride was rather complex. In addition to decarboxylation and introduction of two formyl residues, a substitution takes place of the amino group hydrogen atoms by the dimethylaminomethylene group. The reaction afforded more than 70% of the diperchlorate *Ib* or the monoperchlorate *Ic*. These salts may be envisaged as derivatives of aminomalonaldehyde, the chemistry of which has been paid very little attention so far. Merely four N-acyl derivatives have been hitherto prepared by a multistep synthesis in connection with investigations on the approach to the synthesis of penicillin[7]. Because of the ready preparation, the salt *Ib* appears as a valuable intermediate for investigations on the chemistry of aminomalonaldehyde and as starting material for other syntheses.

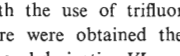
The monosubstituted derivatives of glycine, namely, N-methyl-, N-benzyl-, and N-phenylglycine afforded fair yields of products *Id*–*If*, the structure of which is analogous to that of the salt *Ib*. In these formylations, the reactivity of amino acid hydrochlorides did not differ from that of the free amino acids. Ins contrast to glycine and its monosubstituted derivatives, the attempted formylation of N,N-dimethylglycine did not lead to any derivatives of N,N-dimethylaminomalonaldehyde prepared recently by another route[8]. To our opinion, the success of the formylation depends on the substitution of at least one hydrogen atom of the amino group by the N,N-dimethyliminiomethyl residue $[(CH_3)_2N{=}CH{-}]^{(+)}$. The substituent R is then represented by an amidinium group bearing a positive charge and containing a double bond; such a structural arrangement could effectively stabilize the other double bond in the assumed intermediate of the type *II* or *III*.

We have also examined transformations of the salt *Ib* to the N-acyl derivatives of aminomalonaldehyde (the N-benzoyl derivative has been reported earlier[7]). These transformations also represent a chemical evidence of the structure of the formylation product of glycine. From the preparative point of view, the most useful results have been obtained in the alkaline hydrolysis of the salt *Ib*. Depending on reaction conditions, the alkaline hydrolysis of salts *Ib* and *Ic* may involve several steps. Thus, a brief heating with saturated aqueous potassium carbonate in the presence of ethanol and benzene affords 2-dimethylaminomethyleneamino-3-dimethylaminoacrolein (*IVa*) while a prolonged heating with aqueous triethylamine leads to 2-formamido-3-dimethylaminoacrolein (*IVb*):

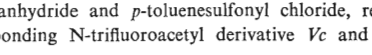


IVa, R = $(CH_3)_2N-CH=N-$; *IVb*, R = O=CH—NH—

When heated with aqueous alkali metal hydroxides, the salts *Ib* and *Ic* are hydrolysed up to the stage of aminomalonaldehyde; this compound is stable in the form of salts but the attempted isolation of the free aldehyde failed. Thus, decomposition occurs even when carbon dioxide is introduced into the alkaline reaction mixture. On the other hand, the reaction mixture resulting after hydrolysis may be directly acylated with anhydrides or acyl halides to afford the corresponding N-acylaminomalonaldehydes. This advantageous procedure may be used in the preparation of the N-acetyl derivative *Va* (yield, 85%) by the action of acetic anhydride and of the earlier reported[7] N-benzoyl derivative *Vb* (by the action of benzoyl chloride). With the use of trifluoroacetic anhydride and *p*-toluenesulfonyl chloride, resp., there were obtained the corresponding N-trifluoroacetyl derivative *Vc* and the N-tosyl derivative *VI*.

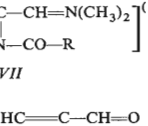


V



VII

VIII



IX

a, R = CH_3; *b*, R = C_6H_5; *c*, R = CF_3

By the action of alkaline reagents, the bis-perchlorate *Ib* loses readily one molecule of perchloric acid to afford the salt *Ic*. When this salt is heated with acetic anhydride, a substitution takes place of the dimethylaminomethylene group at the nitrogen atom by two acetyl groups under the formation of the salt *VIIa*. When the reaction mixture after treatment with acetic anhydride is processed with aqueous potassium carbonate in the presence of 1 : 1 benzene–ethanol, 2-acetamido-3-dimethylaminoacrolein (*VIIIa*) is obtained. By the action of 1M-NaOH, the acrolein derivative *VIIIa* is hydrolysed to the sodium salt of acetamidomalonaldehyde (*Va*). Despite the failure to isolate the N,N-dibenzoyl derivative *VIIb* from the reaction of the salt *Ic* with benzoic anhydride, the alkaline work-up of the reaction mixture afforded two compounds, namely, the earlier reported[7] 2-phenyl-4-formyloxazole (*IXb*) and 2-benzamido-3-dimethylaminoacrolein (*VIIIb*). The acrolein derivative *VIIIb* may also be prepared from the isolated oxazole *IXb* by the action of ethanolic dimethylamine. As reported earlier[7], the alkaline hydrolysis of the oxazole *IXb* affords the known benzamidomalonaldehyde (*Vb*). In contrast to reactions of the salt *Ic* with acetic anhydride or benzoic anhydride, the attempted treatments with trifluoroacetic anhydride or the corresponding acyl halides did not meet with success.

EXPERIMENTAL

Melting points were taken on a heated microscope stage (Kofler block) and are uncorrected. UV spectra were taken on an Optica Milano CF 4 apparatus. IR spectra were measured on a Zeiss, Jena UR-10 apparatus. PMR spectra were recorded on a Varian HA-100 apparatus.

N,N-Dimethyl-N-[2-(dimethylaminomethylene)ammonio-3-dimethylamino]prop-2-enylideneammonium Diperchlorate (*Ib*)

Phosphorus oxychloride (273 ml; 3 mol) was added dropwise under stirring and ice-cooling into dimethylformamide (600 ml), the mixture stirrred for 20 min without cooling, and cooled down again with ice. Glycine hydrochloride (112 g; 1 mol) (prepared by evaporating a mixture of technical glycine and a slight excess of hydrochloric acid, and crystallising the residue twice from 80% aqueous acetic acid) was added portionwise. The whole mixture was heated at 80°C for 4 h and at 125°C for 2 h, cooled down, and decomposed by pouring into water (500 ml), the temperature being maintained at 15—20°C by means of efficient external cooling with dry ice/ethanol. Perchloric acid (70%; 200 ml) was then added at —10°C, the mixture cooled down to —35°C under continuous stirring (to deposit a crystalline precipitate), and kept at this temperature for 2 h. The precipitate was rapidly collected with suction on a sintered glass funnel and washed three times with a small amount of precooled ethanol. Yield, 293·7 g (74%) of the diperchlorate *Ib*, m.p. 218—223°C. The analytical sample, m.p. 226—228°C, was obtained by recrystallisation from methanol. For $C_{10}H_{22}Cl_2N_4O_8$ (397·2) calculated: 30·24% C, 5·58% H, 17·85% Cl, 14·11% N; found: 30·42% C, 5·92% H, 17·63% Cl, 13·99% N. UV spectrum (H_2O): λ_{max} 211 nm (log ε 4·07), 309 nm (log ε 4·58). IR spectrum (KBr): 1698 cm^{-1} (m), 1619 cm^{-1} (s).

N,N-Dimethyl-N-[2-(dimethylaminomethylene)amino-3-dimethylamino]prop-2-enylidene-ammonium Perchlorate (*Ic*)

The diperchlorate *Ib* (39·7 g; 0·1 mol) was dissolved in a refluxing mixture of ethanol (300 ml) and triethylamine (20 ml). The solution was filtered with a small amount of active charcoal while hot and the filtrate allowed to crystallize. Yield, 23·7 g (80%) of the perchlorate *Ic*, m.p. 139—141°C (ethanol). For $C_{10}H_{21}ClN_4O_4$ (296·8) calculated: 40·47% C, 7·13% H, 11·95% Cl, 18·88% N; found: 40·72% C, 7·19% H, 12·09% Cl, 18·90% N. UV spectrum (H_2O): λ_{max} 222 nm (log ε 4·10), 337 nm (log ε 4·40). IR spectrum (KBr): 1 655 cm^{-1} (m), 1 631 cm^{-1} (s), 1 585 cm^{-1} (s).

N,N-Dimethyl-N-[2-(N-methyl-N-dimethylaminomethylene)ammonio-3-dimethylamino]-prop-2-enylideneammonium Diperchlorate (*Id*)

The preparation was performed analogously to that of the salt *Ib*. Sarcosine hydrochloride (2·5 g; 0·02 mol) afforded 4·6 g (56%) of the diperchlorate *Id*, m.p. 230—237°C (decomp.). After two recrystallisations from water, the m.p. was 243—246°C. For $C_{11}H_{24}Cl_2N_4O_8$ (411·3) calculated: 32·13% C, 5·88% H, 17·24% Cl, 13·62% N; found: 32·54% C, 6·04% H, 17·27% Cl, 13·93% N. UV spectrum (H_2O): λ_{max} 216 nm (log ε 4·08), 307 nm (log ε 4·57). IR spectrum (KBr): 1 695 cm^{-1} (s), 1 670 cm^{-1} (m), 1 615 cm^{-1}.

N,N-Dimethyl-N-[2-(N-benzyl-N-dimethylaminomethylene)ammonio-3-dimethylamino]-prop-2-enylideneammonium Diperchlorate (*Ie*)

The preparation was performed analogously to that of the salt *Ib*. N-Benzylglycine (2 g; 0·01 mol) afforded 3 g (61·5%) of the diperchlorate *Ie*, m.p. 233—237°C. After two recrystallisations from water, the m.p. was 257—259°C (decomp.). For $C_{17}H_{28}Cl_2N_4O_8$ (487·5) calculated: 41·90% C, 5·79% H, 14·55% Cl, 11·49% N; found: 41·40% C, 5·75% H, 14·36% Cl, 11·08% N. UV spectrum (H_2O): λ_{max} 206 nm (log ε 4·32), 308 nm (log ε 4·51). IR spectrum (KBr): 1 687 cm^{-1} (s), 1 667 cm^{-1} (m), 1 616 cm^{-1} (vs), 712 cm^{-1} and 683 cm^{-1} (aromatic C—H).

N,N-Dimethyl-N-[2-(N-phenyl-N-dimethylaminomethylene)ammonio-3-dimethylamino]-prop-2-enylideneammonium Diperchlorate (*If*)

The preparation was performed analogously to that of the salt *Ib*. N-Phenylglycine (1·5 g; 0·01 mol) afforded 1·9 g (61·5%) of the diperchlorate *If*, m.p. 297—299°C (water) (decomp.). For $C_{16}H_{26}Cl_2N_4O_8$ (473·2) calculated: 40·59% C, 5·54% H, 14·99% Cl, 11·84% N; found: 40·81% C, 5·62% H, 14·73% Cl, 11·71% N. UV spectrum (H_2O): λ_{max} 252 nm (log ε 3·97), 309 nm (log ε 4·44). IR spectrum (KBr): 1 684 cm^{-1} (m), 1 666 cm^{-1} (m, sh). 1 613 cm^{-1} (s).

2-(Dimethylaminomethylene)-3-dimethylaminoacrolein (*IVa*)

The diperchlorate *Ib* (4 g; 0·01 mol) was added to a mixture of potassium carbonate (15 g), water (60 ml), benzene (30 ml), and ethanol (15 ml) and the whole was rapidly heated to the boiling point under stirring. After 30 min, the mixture was cooled down, and treated with solid potassium carbonate (about 25 g). The inorganic salts were filtered off and discarded. The aqueous phase of the filtrate was separated and the remaining two organic layers were homogenised by the addition of anhydrous potassium carbonate. The aqueous phase was extracted three times with a mixture of benzene–ethanol (2 : 1). The organic solutions were combined, dried over

potassium carbonate, and evaporated under diminished pressure. Repeated distillation of the residue afforded 1·3 g (60%) of the aldehyde *IVa*, b.p. 150°C/0·3 Torr (bath temperature), which solidified on cooling down. The analytical sample was purified by chromatography on 50 g of alumina (benzene and then 98 : 2 benzene–ethanol), crystallisation from methyl ethyl ketone at −40°C, and redestillation; m.p. 34—35°C. For $C_8H_{15}N_3O$ (169·2) calculated: 56·78% C, 8·93% H, 24·83% N; found: 56·92% C, 9·20% H, 25·03% N.

2-Formamido-3-dimethylaminoacrolein (*IVb*)

A mixture of the monoperchlorate *Ic* (1·5 g; 0·005 mol), water (10 ml), and triethylamine (2·5 ml; 0·035 mol) was stirred at 60°C for 7 h and then evaporated to dryness under diminished pressure. The residue was dissolved in ethanol and the solution shaken with saturated aqueous potassium carbonate. The inorganic salts were filtered off and the lower layer of the filtrate was extracted with 1 : 1 benzene–ethanol. The organic layers were combined, dried over potassium carbonate, and evaporated under diminished pressure. The residue was extracted with about 15 ml of boiling acetone, the solution filtered with active charcoal while hot, the filtrate evaporated, and the final residue crystallised from acetone (4 ml) to afford 230 mg of the aldehyde *IVb*; additional 120 mg were obtained from mother liquors. Overall yield, 350 mg (50%). After an additional crystallisation from acetone and sublimation, the aldehyde *IVb* melted at 112—114°C. For $C_6H_{10}N_2O_2$ (142·2) calculated: 50·69% C, 7·09% H, 19·71% N; found: 50·71% C, 7·08% H, 19·94% N.

Acetamidomalonaldehyde (*Va*)

A mixture of the diperchlorate *Ib* (4 g; 0·01 mol) and 2M-NaOH (30 ml) was heated at 60°C for 4 h. The liberated dimethylamine was removed under diminished pressure, the remaining solution diluted with additional 2M-NaOH (20 ml), cooled down, and treated dropwise under efficient stirring with acetic anhydride (3 ml; 0·06 ml). The homogeneous reaction mixture was acidified with dilute sulfuric acid to Congo paper and extracted with seven 30 ml portions of methylene chloride. The extracts were combined, washed with water, dried, and evaporated under diminished pressure. The residue was sublimed at 0·2 Torr to afford 1·14 g (88·5%) of the aldehyde *Va*, m.p. 100—104°C. The analytical sample was purified by crystallisation from tetrachloromethane and sublimation. For $C_5H_7NO_3$ (129·1) calculated: 46·51% C, 5·46% H, 10·85% N; found: 46·65% C, 5·30% H, 10·65% N.

Benzamidomalonaldehyde (*Vb*)

The preparation was performed analogously to that of the aldehyde *Va* using 1·3 ml (0·01 mol) of benzoyl chloride. The insoluble portions were removed by extraction with methylene chloride. After the acidification, the product was extracted with the same solvent. Benzoic acid was removed by fractional sublimation. Yield, 1·05 g (53%) of the aldehyde *Vb*, m.p. 74—76°C (reported[7], m.p. 76—77°C).

Trifluoroacetamidomalonaldehyde (*Vc*)

To a solution of aminomalonaldehyde (see the preparation of compound *Va*) there was added 20 ml of 2M-NaOH and 40 ml of methylene chloride and the resulting mixture was cooled down (−25°C to −30°C). A solution of trifluoroacetic anhydride (5 ml; 0·038 ml) in methylene chloride (40 ml) was then added dropwise under vigorous stirring. The freezing bath was then removed,

the reaction mixture stirred at room temperature for 15 minutes, cooled down again, and acidified with 0·05M-H_2SO_4 to Congo paper. The product was extracted with methylene chloride, purified by sublimation, crystallisation from cyclohexane, and resublimation. Yield, 0·45 g (24·6%) of the trifluoroacetyl derivative *Vc*, m.p. 67—70·5°C. For $C_5H_4F_3NO_3$ (183·1) calculated: 32·80% C, 2·20% H, 31·13% F, 7·65% N; found: 32·77% C, 2·21% H, 31·03% F, 7·74% N.

p-Toluenesulfonamidomalonaldehyde (*VI*)

The preparation was performed analogously to that of compound *Va* using 50 mg of *p*-toluenesulfonic acid and 2·3 g (0·012 mol) of *p*-toluenesulfonyl chloride. The insoluble portions were removed by extraction with ether. Yield, 0·4 g (17%) of the crude aldehyde *VI* which was purified by crystallisation from water and sublimation; m.p. 155—157°C. For $C_{10}H_{11}NO_4S$ (241·2) calculated: 49·80% C, 4·60% H, 5·81% N, 13·27% S; found: 49·80% C, 4·58% H, 5·68% N, 13·31% S.

N,N-Dimethyl-N-(2-diacetylamino-3-dimethylamino)prop-2-enylideneammonium Perchlorate (*VIIa*)

A mixture of the monoperchlorate *Ic* (3·0 g; 0·01 mol) and acetic anhydride (30 ml; 0·41 mol) was heated at 100°C for 2 h, evaporated, the residue diluted with a small amount of ethanol, and kept at −40°C to deposit 0·7 g (21·5%) of the crude perchlorate *VIIa*, m.p. 143—148°C. The analytical sample, m.p. 147—148°C, was obtained by recrystallisation from ethanol. For $C_{11}H_{20}ClN_3O_6$ (325·7) calculated: 40·55% C, 6·18% H, 10·90% Cl, 12·90% N; found: 40·90% C, 6·25% H, 10·92% Cl, 12·90% N. PMR spectrum ($CDCl_3$): δ 7·82 s, 2 H; 3·08 s, 6 H; 3·42 s, 6 H; 2·44 s, 6 H.

2-Acetamido-3-dimethylaminoacrolein (*VIIIa*)

A mixture of the monoperchlorate *Ic* (4·5 g; 0·015 mol) and acetic anhydride (45 ml; 0·62 mol) was heated at 100°C for 2 h and then evaporated under diminished pressure. To the residue there was added a solution of potassium carbonate (16·2 g) in water (80 ml) and a mixture (60 ml) of benzene–ethanol (1 : 1). The whole was heated at 65—70°C for 30 min under stirring, cooled down, and the layers were separated. The aqueous layer was extracted with two portions of benzene–ethanol (1 : 1), the extracts combined with the original organic layer, dried over potassium carbonate, and evaporated under diminished pressure. The residue was dissolved in methylene chloride, the solution filtered, the filtrate evaporated, and the residual solid (2·7 g) crystallised from acetonitrile to afford 1·5 g (64%) of the aldehyde *VIIIa*. The analytical sample, m.p. 198 to 199°C, was obtained by two recrystallisations. For $C_7H_{12}N_2O_2$ (156·2) calculated: 53·83% C, 7·74% H, 17·94% N; found: 54·33% C, 7·95% H, 18·00% N. IR spectrum ($CHCl_3$): 3395 cm^{-1}, 3250 cm^{-1}, 3195 cm^{-1} (inflex), (NH); 1688 cm^{-1} (CO-amide bond); 1609 cm^{-1} (C=C, CH=O); 2740 cm^{-1}, 2835 cm^{-1} (CH-aldehyde bond); 2765 cm^{-1}, 2810 cm^{-1} (CH). PMR spectrum ($CDCl_3$): δ 2·11 singlet, 3 H; 3·12 s, 6 H; 6·72 s, 1 H; 8·72 s, 1 H.

Hydrolysis. A mixture of the acrolein derivative *VIIIa* (0·5 g; 0·0032 mol) and 1M-NaOH (10 ml) was stirred at room temperature for 1 h and then 30 min at 15 Torr to remove dimethylamine. The remaining solution was treated with 1M-HCl (10 ml), extracted with ten 20 ml portions of benzene, the extracts dried, and evaporated. The residue was purified by sublimation to afford 0·3 g (73%) of acetamidomalonaldehyde (*Va*), m.p. 105—106°C, identical with the specimen obtained by acetylation of aminomalonaldehyde (*vide supra*).

2-Benzamido-3-dimethylaminoacrolein (*VIIIb*) and 2-Phenyl-4-formyloxazole (*IXb*)

A finely ground mixture of the monoperchlorate *Ic* (0·6 g; 2 mmol) and benzoic anhydride (1·2 g; 5·3 mmol) was heated at 100°C for 2 h, diluted with a solution of potassium carbonate (3·5 g) in water (18 ml) and with benzene (5 ml), and the whole heated at 70°C for 30 min under stirring. After cooling, the 2-phenyl-4-formyloxazole-containing benzene layer was separated and processed as given below. The aqueous layer was extracted repeatedly with chloroform, the extract evaporated, and the residue (0·2 g) chromatographed on silica gel (20 g) in ethanol to afford 0·1 g of benzoic anhydride and 45 mg of the crude acrolein derivative *VIIIb*, m.p. 175—184°C; after recrystallisation from acetonitrile, m.p. 185—186°C; this product is identical with that obtained from 2-phenyl-4-formyloxazole (*vide infra*). The above benzene layer was evaporated to dryness and the residue (0·7 g) chromatographed on silica gel (30 g) in benzene to afford 170 mg of benzoic anhydride and 170 mg (31%) of 2-phenyl-4-formyloxazole (*IXb*), m.p. 96°C (after two sublimations and crystallisation from cyclohexane); reported[7], m.p. 94°C. For $C_{10}H_7NO_2$ (173·2) calculated: 69·36% C, 4·07% H, 8·09% N; found: 69·23% C, 4·03% H, 8·21% N.

Reaction of the oxazole IXb *with dimethylamine.* A mixture of 2-phenyl-4-formyloxazole (37 mg; 0·21 mmol) and 4·5M ethanolic dimethylamine (4 ml) was heated at 70°C for 1 h and evaporated under diminished pressure to afford 38 mg (85%) of 2-benzamido-3-dimethylaminoacrolein (*VIIIb*), m.p. 188—192°C (after sublimation and crystallisation from acetonitrile). For $C_{12}H_{14}N_2O_2$ (218·3) calculated: 66·04% C, 6·47% H, 12·84% N; found: 66·07% C, 6·48% H, 12·69% N.

Hydrolysis of the oxazole IXb. A mixture of 2-phenyl-4-formyloxazole (50 mg; 29 mmol) and 1M-NaOH (1 ml) was refluxed for 10 min, cooled down, and acidified with 1M-HCl (1 ml) to deposit a precipitate which was collected with suction and dried. Yield, 50 mg (90%) of the dialdehyde *Vb*, m.p. 73—76°C, identical with the reported[7] derivative (m.p. 76—77°C) and with the specimen obtained by benzoylation of the alkaline solution of aminomalonaldehyde (*vide supra*).

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