

PREPARATION, PROPERTIES, AND SYNTHETIC REACTIONS
OF TRIMETHYLAMMONIODIFORMYLMETHYLIDE*

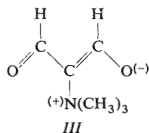
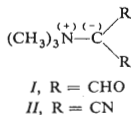
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The reaction of aminomalonaldehyde with methylating agents affords as the final product trimethylammoniodiformylmethylide (*I*), a highly stabilised aliphatic ylide. Compound *I* forms equimolar addition compounds with numerous inorganic salts. Cyclisation reactions of compound *I* afford five-, six-, and seven-membered heterocycles substituted by a quaternary ammonium function.

In connection with investigations on the synthetic utilisation of the readily accessible aminomalonaldehyde¹, the reaction of this compound with alkylating agents has been recently reported². This reaction affords almost exclusively N,N-disubstituted aminomalonaldehydes except for N,N-dimethylaminomalonaldehyde which is obtained under various conditions in low yields only. A more detailed examination of this reaction indicates that the dimethylamino derivative as the primary reaction product of the methylation readily undergoes a further reaction with the methylating agent with the formation of a quaternary nitrogen compound, namely, trimethylammoniodiformylmethylide (*I*). Under suitable reaction conditions, compound *I* may be obtained by methylation of aminomalonaldehyde as an almost exclusive reaction product in about 90% yield. Provided that aminomalonaldehyde is regarded as an amino acid analogue, the present reaction is analogous to the known conversion of glycine to betaine by the action of various methylating agents.



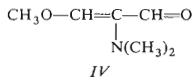
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Compound *I* may be classified as a stable ylide. The most thoroughly investigated group of compounds of this type are stable ylides bearing a positive charge on the quadrivalent phosphorus or trivalent sulfur. On the other hand, only a few stable ylides with a quaternary nitrogen atom has been reported, the trimethylammoniodicyanomethylide³ (*II*) being most closely related to compound *I*. The stability of aliphatic compounds *I* and *II* is obviously due to delocalisation of the negative charge which is transferred to extremely electronegative groups. In the case of compound *I*, this stabilisation may be expressed by a set of mesomeric formulae from which the formula of type *III* with an anionic charge on the oxygen atom asserts itself to a significant extent; the structure *III* can be regarded as a betaine. As it will be seen below, this structure is in accordance with the properties and reactions of the compound in question.

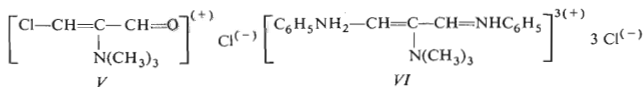
Trimethylammoniodiformylmethylide (*I*) is a crystalline substance which may be sublimed under diminished pressure without decomposition. It is well soluble in polar solvents and its aqueous solution is neutral. The ¹H-NMR spectrum of compound *I* exhibits a singlet of N-methyl protons (9H) and a triplet due to protons of the two formyl groups. As established by means of heteronuclear decoupling, the splitting of the signal of equivalent formyl protons to a triplet is due to the interaction with the nitrogen atom⁴, the coupling constant $J_{(^{14}\text{N}-\text{C}-\text{C}-\text{H})}$ being equal to 3.5 Hz. The IR spectrum displays a very intensive 1586 cm⁻¹ band and a weaker band at about 1644 cm⁻¹; these bands are due to coupled vibrations of both C=O bonds (*cf.*⁴). The UV spectrum shows a strong band at 258 nm, the position and intensity of which is independent of the pH value of the solution contrary to N,N-disubstituted aminomalonaldehydes.

The dipolar character of compound *I* manifests itself in the formation of addition compounds with some inorganic salts. This behaviour may be regarded as analogous to that of some ylides, betaines, carbenes and the like. As observed by Wittig and coworkers^{5,6} in the preparation of trimethylammoniomethylide, the stability and reactivity of this ylide is markedly affected by the formation of a complex with lithium bromide which is present as a coproduct in the reaction mixture. The presence of inorganic salts can also affect the reactivity of some phosphonium ylides⁷, carbenes and the like. The ylide *I* has been now characterised by addition compounds with sodium perchlorate, sodium iodide, zinc iodide, and silver nitrate. The formation of these adducts appears to depend on a proper size of one of the components of the inorganic salt, *i.e.*, the cation or the anion. All the addition compounds in question were obtained in the medium of organic solvents. They are soluble in water and appear to be fully dissociated in this medium. The IR and UV spectra of the addition compounds of the ylide *I* with sodium perchlorate do not differ from those of the free ylide. Compound *I* also forms a stable addition compound with hydrogen chloride; this adduct can be crystallised from ethanol and sublimed under diminished pressure without decomposition.

The stability of compound *I* can be inferred from reactivity assays. The attempted nucleophilic substitution of the quaternary ammonium group was not successful. Thus for example, thin-layer chromatography indicated an unchanged starting material when compound *I* was refluxed with methanolic sodium methoxide for 3 h or heated at 90°C with sodium thiophenoxide in hexamethylphosphoric triamide. The preparation of characteristic aldehyde derivatives also failed. In the attempted cleavage to trimethylamine and diformylcarbene, compound *I* was pyrolysed at about 300°C. Aside from the starting material, only a small amount of a product was detected and identified by means of ¹H-NMR spectrum and reaction with water as the O-methyl derivative of N,N-dimethylaminomalonaldehyde (*IV*). The same compound *IV* was obtained by pyrolysis of the ylide *I* in the presence of cupric oxide. The observed rearrangement of the methyl group in the ylide *I* from the nitrogen atom to the oxygen atom is obviously analogous to the thermal rearrangement of betaine to N,N-dimethylglycine methyl ester⁸.

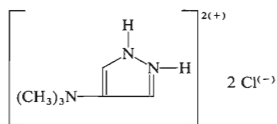


Some types of 1,3-dicarbonyl compounds and their derivatives are known to react with acyl chlorides and particularly with phosgene to afford derivatives, the reactivity of which is markedly higher than that of the starting compounds^{9,10}. The reaction of the present ylide *I* with phosgene gives at room temperature the salt *V*, i.e., a compound of the 3-chloroacetaldehyde type with a reactive chloro atom (*vide infra*). The salt *VI* is obtained as the final product by reaction of the ylide *I* and phenylcarbamoyl chloride. The course of this reaction exhibits some common features with reactions between dimethylcarbamoyl chloride and triformylmethane¹¹, dimethylformamide¹², 3-dimethylaminovinylcarbonyl compounds¹² or carboxylic acids¹³.

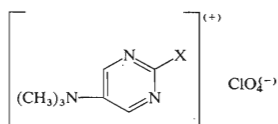


Owing to the ready accessibility, the ylide *I* represents an attractive material for the synthesis of heterocyclic systems substituted by a quaternary ammonium function. In view of the low reactivity, the ylide *I* cannot be used directly; on the other hand, the salt *V* obtained by reaction of the ylide *I* with phosgene, affords with appropriate reactants five-, six-, and seven-membered heterocyclic compounds. In addition to phosgene, the activation can be achieved with the use of acetyl chloride which may be preferably generated in the course of the condensation from acetic anhydride and hydrogen chloride. Under such conditions which are advantageous also from the

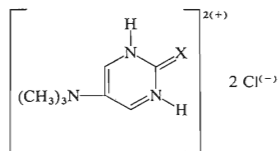
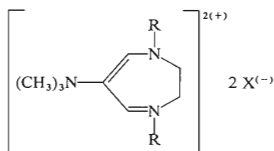
standpoint of the quaternary ammonium group present, the products are deposited in the form of sparingly soluble dihydrochlorides. Provided that the condensation requires a basic medium, milder conditions (room temperature) are used.



VII

VIII, X = H
IX, X = NH₂

The five-membered ring compound, 4-trimethylammoniopyrazolium dichloride (VII) was obtained by heating the salt V with hydrazine hydrate in ethanol and the subsequent saturation of the reaction mixture with hydrogen chloride. In the preparation of pyrimidine derivatives, the usual components were used such as formamide, guanidine, urea, and thiourea. In the former two cases, the products VIII and IX were obtained in 55% and 86% yields, resp., from the quaternary salt V in alkaline medium at room temperature. In the latter two cases, the condensation was performed by introduction of hydrogen chloride into a solution containing in addition to the ylide I and the appropriate component (urea or thiourea) the acetic anhydride which as the generator of acetyl chloride cares for the activation of the ylide. The products X and XI were isolated in 89% and 71% yields, resp. As indicated by the IR spectra of the present pyrimidine derivatives, the condensation products of formamide and guanidine may be expressed by formulae VIII and IX while the oxo and thioxo structures X and XI belong to condensation products of urea and thiourea.

X, X' = O
XI, X = SXII, R = H, X = Cl
XIII, R = CH₃, X = ClO₄

The synthesis of the seven-membered heterocyclic compounds XII and XIII was performed by heating the salt V in ethanol with the corresponding diamines. The

products were isolated as diperchlorates. The above syntheses of heterocyclic compounds may serve as an illustration of the prospective use of the present ylide *I* in this field.

EXPERIMENTAL

Melting points were taken on a heated microscope stage (Kofler block). The $^1\text{H-NMR}$ spectra were measured on a Varian HA-100 apparatus. The IR spectra were recorded on a Zeiss UR-10 apparatus. The UV spectra were taken on a Unicam SP 8000 apparatus. The mass spectrometry was performed on an AEIMS-902 apparatus.

Trimethylammoniodiformylmethylide (*I*)

At 60°C , $\text{N,N-dimethyl-N-[2-(dimethylaminomethylene)amino-3-dimethylamino]prop-2-enylideneammonium perchlorate}^1$ (150 g; 0.5 mol) was added to a solution of sodium hydroxide (100 g; 2.5 mol) in water (1200 ml). The mixture was stirred at 60°C for 4 h and taken down on a rotatory evaporator to the volume of about 500 ml. Sodium hydroxide (80 g; 2 mol) in water (80 ml) was then introduced, followed by a dropwise addition of dimethyl sulfate (232.5 ml; 2.5 mol) with stirring at $15\text{--}20^\circ\text{C}$ over ca 45 min. The stirring was continued for 1 h and the mixture kept in a refrigerator overnight. After the addition of saturated aqueous potassium carbonate (750 ml), the product was extracted with six 500 ml portions of 1 : 1 benzene-ethanol, the solid portions being always filtered off and washed with ethanol; the ethanolic washings were added to the next extraction. The particular extracts were separated, shaken with saturated aqueous potassium carbonate (about 50 ml) and then solid potassium carbonate, combined, dried over solid potassium carbonate overnight, filtered, and evaporated under diminished pressure. The residue was dried and then extracted with six 500 ml portions of boiling benzene. The work-up of the extracts yielded 55 g (85%) of the pure ylide *I*, m.p. $116\text{--}118^\circ\text{C}$, and 2.3 g (3.5%) of the less pure substance *I*, m.p. $114\text{--}118^\circ\text{C}$. The analytical sample was recrystallised from benzene and sublimed; m.p. $117\text{--}118^\circ\text{C}$. For $\text{C}_6\text{H}_{11}\text{NO}_2$ (129.2) calculated: 55.80% C, 8.58% H, 10.84% N; found: 55.80%, 8.49% H, 10.96% N. The $^1\text{H-NMR}$ spectrum (CDCl_3): δ 3.59 s (9 H); 8.51 t (2 H), $J_{(14\text{N}-\text{C}-\text{C}-\text{H})} = 3.5$ Hz. IR spectrum (KBr): $\nu_{\text{as}}(\text{CH}_3)$ 3020; $\nu_{\text{s}}(\text{CH}_3)$ 2955; $\nu(\text{C}-\text{H})$ 2800, 2755; $\nu(\text{C}=\text{O})$ 1590, 1645 sh; $\delta_{\text{as}}(\text{CH}_3)$ 1491, 1464, 1450; $\nu(\text{skeletal})$ 1395; 1268; 1224; $\nu(\text{skeletal})$ 958; 943; 868; 750; 424. IR spectrum (CHCl_3): $\nu(\text{CH}_3)$ 2955; $\nu(\text{C}-\text{H})$ 2805 sh; 2765; $\nu(\text{C}=\text{O})$ 1644, 1586; $\delta_{\text{as}}(\text{CH}_3)$ 1489, 1454; $\nu(\text{skeletal})$ 1400; 1270; 1116; 961; 946; 866. UV spectrum (H_2O): λ_{max} 257 (ϵ 28800).

Addition Compounds of the Ylide *I* with Inorganic Salts

A. $\text{NaClO}_4 + \text{I}$. Saturated solutions of equimolar amounts of the ylide *I* and sodium perchlorate in boiling ethanol were combined, the precipitate collected with suction at 20°C , and recrystallised twice from boiling ethanol. After drying, m.p. $233\text{--}234^\circ\text{C}$. For $\text{C}_6\text{H}_{11}\text{ClNNaO}_6$ (251.6) calculated: 28.64% C, 4.41% H, 14.09% Cl, 5.57% N; found: 28.78% C, 4.47% H, 14.24% Cl, 5.70% N. IR spectrum (KBr): $\nu_{\text{as}}(\text{CH}_3)$ 3030; $\nu_{\text{s}}(\text{CH}_3)$ 2970; $\nu(\text{C}-\text{H})$ 2815, 2795, 2785; $\nu(\text{C}=\text{O})$ 1648 sh, 1586; $\delta_{\text{as}}(\text{CH}_3)$ 1492, 1463; $\nu(\text{skeletal})$ 1398; 1272; 1223; 961; 941; 747; 567; 429; 409 cm^{-1} (ClO_4^- bands omitted).

B. $\text{NaI} + \text{I}$. The preparation was analogous to that given in paragraph *A*. M.p. $286\text{--}291^\circ\text{C}$ (ethanol). For $\text{C}_6\text{H}_{11}\text{INNaO}_2$ (279.1) calculated: 25.82% C, 3.97% H, 45.48% I, 5.02% N; found: 26.07% C, 4.11% H, 45.88% I, 5.32% N.

C. $\text{AgNO}_3 + \text{I}$. The preparation was analogous to that given in paragraph A. M.p. 101–104°C (ethanol). For $\text{C}_6\text{H}_{11}\text{AgN}_2\text{O}_5$ (299.0) calculated: 24.10% C, 3.71% H, 9.37% N; found: 23.53% C, 3.41% H, 8.99% N.

D. $\text{ZnI}_2 + \text{I}$. Filtered saturated solutions of equimolar amounts of the ylide *I* and zinc iodide in ethyl ethyl acetate were combined while hot and the precipitate collected with suction. M.p. 269–272°C. For $\text{C}_6\text{H}_{11}\text{I}_2\text{NO}_2\text{Zn}$ (448.4) calculated: 16.07% C, 2.47% H, 56.61% I, 3.13% N; found: 16.26% C, 2.53% H, 56.45% I, 3.35% N.

Hydrochloride of the ylide I. A solution of the ylide *I* in dichloromethane was saturated with gaseous hydrogen chloride and evaporated under diminished pressure. The residue was crystallised from nitromethane and sublimed. M.p. 192–195°C (decomp.). For $\text{C}_6\text{H}_{12}\text{ClNO}_2$ (165.6) calculated: 43.51% C, 7.30% H, 21.41% Cl, 8.46% N; found: 43.73% C, 7.41% H, 21.12% Cl, 8.33% N.

2-Dimethylamino-3-methoxy-2-propenal (IV)

The ylide *I* (0.5 g) was placed into a 10 ml flask directly attached to a glass tube packed with a mixture of glass wool and cupric oxide, and heated by means of a jacket; the receiver was cooled by a mixture of Dry Ice and ethanol. The apparatus was evacuated (about 11 Torr) and the heating jacket adjusted to about 265°C. The content of the flask was gradually (over about 30 min) volatilised by heating and subjected to pyrolysis in the tube. As indicated by thin-layer chromatography, the material in the receiver contained aside from the starting material a single less polar and more volatile product. Repeated distillation yielded about 20 mg of a substance boiling at 0.35 Torr and about 30°C (bath temperature). Mass spectrum: M^+ (HR) 129,080 (for $\text{C}_6\text{H}_{11}\cdot\text{NO}_2$ calculated: 129.079). $^1\text{H-NMR}$ spectrum (CDCl_3): 2.70 s (6 H), 3.89 s (3 H), 6.38 s (1 H), 8.91 s (1 H). UV spectrum (ethanol): λ_{max} 285 nm (ϵ 5350) and 231 nm (ϵ 8740). A similar result was obtained when the pyrolysis was performed on glass wool alone in the absence of cupric oxide but at a higher temperature (about 300°C).

Reaction of compound IV with water. A solution of compound *IV* (5 mg) in a minimum amount of water was kept at room temperature for about 2 days and evaporated. Repeated sublimation of the residue afforded a substance (m.p. 147–149°C), the mass and IR spectra of which were identical with those of dimethylaminomalonaldehyde¹⁴.

Trimethyl-(2-chloro-1-formyl)vinylammonium Salts

A. *The chloride*. V. Phosgene in chloroform (20 ml of a 20% solution) was added dropwise with ice-cooling into a solution of compound *I* (1.29 g; 0.01 mol) in chloroform (20 ml). Carbon dioxide was evolved and the product deposited in the form of a white precipitate. Evaporator of phosgene and the solvent under diminished pressure afforded an almost quantitative yield of the crude salt *V* which was directly used in further reactions.

B. *Perchlorate*. The chloride *V* in acetonitrile was treated with perchloric acid and the salt isolated by precipitation with ether. The precipitate was recrystallised twice from acetonitrile; m.p. 176–179°C. For $\text{C}_6\text{H}_{11}\text{Cl}_2\text{NO}_5$ (248.1) calculated: 29.05% C, 4.47% H, 28.58% Cl, 5.63% N; found: 28.86% C, 4.66% H, 28.45% Cl, 5.78% N.

N-Phenyl-*N*-(3-phenylammonio-2-trimethylammonio)prop-2-enylideneammonium Trichloride (*VI*)

A cooled (ice) mixture of the ylide *I* (0.129 g; 1 mmol), chloroform (15 ml), and acetic anhydride (0.4 g) was saturated with hydrogen chloride for 15 min, treated with phenyl isothiocyanate (0.180 g; 1.5 mmol) saturated at room temperature with hydrogen chloride for 20 min, and finally refluxed for 2 h. The solid was collected with suction and washed to afford 0.28 g (72%) of compound *VI*, m.p. 210–213 °C. For $C_{18}H_{24}Cl_3N_3$ (388.8) calculated: 55.61% C, 6.22% H, 27.36% Cl 10.81% N; found: 55.80% C, 6.34% H, 26.57% Cl, 10.87% N.

4-Trimethylammoniopyrazolium Dichloride (*VII*)

A solution of compound *V* (0.338 g; 1.83 mmol) in ethanol (10 ml) was added dropwise with cooling and stirring into a solution of 98% hydrazine hydrate (0.101 g; 2 mmol) in ethanol (15 ml). The mixture was refluxed for 30 min, saturated at 0°C with hydrogen chloride for 10 min, and refluxed for 1 h. Yield, 0.64 g (88%) of compound *VII*, m.p. 152–153°C. For $C_6H_{13}Cl_2N_3$ (198.1) calculated: 36.38% C, 6.61% H, 35.71% Cl, 21.21% N; found: 36.80% C, 6.92% H, 35.22% Cl, 21.14% N.

5-Trimethylammoniopyrimidine Perchlorate (*VIII*)

Methanolic sodium methoxide (2 ml of 2*N* solution) was added dropwise with cooling (ice) to a mixture of crystalline formamidine hydrochloride (0.2 g; 2.4 mmol) and ethanol (10 ml). To the suspension, a solution of compound *V* (0.338 g; 1.83 mmol) in ethanol was added and the whole stirred at room temperature for 12 h. The sodium chloride was removed by centrifugation and the supernatant precipitated under cooling with 2 equivalents of perchloric acid. The precipitate was washed and crystallised from 95% ethanol. Yield, 0.24 g (55%) of the perchlorate *VIII*, m.p. 180°C. For $C_7H_{12}ClN_3O_4$ (237.6) calculated: 35.37% C, 5.10% H, 14.93% Cl, 17.68% N; found: 35.36% C, 5.23% H, 15.16% Cl, 17.48% N.

2-Amino-5-trimethylammoniopyrimidine Perchlorate (*IX*)

Methanolic sodium methoxide (3 ml of 2*N* solution) was added with cooling to guanidine hydrochloride (0.19 g; 2 mmol) in 15 ml of ethanol. To this suspension, compound *V* (0.338 g; 1.83 mmol) in ethanol was added and the whole stirred at room temperature for 8 h. The sodium chloride was removed by centrifugation, the supernatant precipitated with 3 equivalents of perchloric acid, and the precipitate crystallised from ethanol. Yield, 0.4 g (86%) of the perchlorate *IX*, m.p. 227–229°C. For $C_7H_{13}ClN_4O_4$ (252.7) calculated: 33.27% C, 5.18% H, 14.03% Cl, 22.18% N; found: 33.70% C, 5.38% H, 14.21% Cl, 21.86% N.

5-Trimethylammonio-2(1*H*)-oxopyrimidinium Dichloride (*X*)

A mixture of the ylide *I* (1.29 g; 10 mmol), glacial acetic acid (20 ml), and acetic anhydride (4.08 g) was saturated under ice-cooling with dry hydrogen chloride for 10 min. Urea (0.72 g; 12 mmol) was then added and the HCl introduced for 10 min. The reaction mixture was then heated at 90°C with stirring for 2 h and cooled down. The solid was collected with suction and washed with a little acetic acid and methanol. Yield, 2.02 g (89%) of compounds *X*, m.p. 191–193°C.

For $C_7H_{13}Cl_2N_3O$ (226.1) calculated: 37.18% C, 5.79% H, 31.36% Cl, 18.58% N; found: 37.11% C, 5.82% H, 31.07% Cl, 18.55% N.

5-Trimethylammonio-2(1*H*)-thioxopyrimidinium Dichloride (XI)

Acetic anhydride (4.08 g) was added to a solution of the ylide *I* (1.29 g; 10 mmol) in acetic acid (10 ml) and the ice-cold mixture saturated with hydrogen chloride. Thiourea (0.85 g; 11.2 mmol) was then added and the introduction of hydrogen chloride continued until the material completely dissolved. The mixture was then stirred at 80°C for 1 h and cooled down. The solid was collected with suction and washed with acetic acid and ethanol. Yield, 1.71 g (71%) of compound *XI*, m.p. 178–179°C. For $C_7H_{13}Cl_2N_3S$ (242.1) calculated: 34.71% C, 5.41% H, 29.28% Cl, 17.35% N, 13.24% S; found: 35.17% C, 5.59% H, 30.06% Cl, 17.12% N, 13.37% S.

6-Trimethylammonion-1*H*-2,3-dihydro-1,4-diazepinium Dichloride (XII)

Ethylene diamine (0.12 g; 2 mmol) and pyridine (0.6 ml) were successively added with cooling to a solution of compound *V* (0.338 g; 1.83 mmol) in ethanol (10 ml), the mixture stirred at room temperature for 30 min, refluxed for 3 h, and kept at room temperature overnight to afford 0.29 g (70%) of the dichloride *XII*, m.p. 250–255°C (90% aqueous ethanol). For $C_8H_{17}Cl_2N_3$ (226.2) calculated: 42.48% C, 7.58% H, 31.36% Cl; 18.58% N; found: 42.79% C, 7.49% H, 30.97% Cl, 18.29% N. Diperchlorate, m.p. 270–276°C (decomp.; 80% aqueous ethanol). For $C_8H_{17}Cl_2.N_3O_8$ (354.1) calculated: 27.13% C, 4.84% H, 20.02% Cl, 11.87% N; found: 27.44% C, 5.04% H, 20.23% Cl, 12.27% N.

1,4-Dimethyl-6-trimethylammonio-1*H*-2,3-dihydro-1,4-diazepinium Diperchlorate (XIII)

To a solution of compound *V* (0.338 g; 1.83 mmol) in ethanol, 1,2-bis(methylamino)ethane (0.18 g; 2 mmol) was added, the mixture refluxed with stirring for 1 h, and cooled down. The solid dichloride was collected with suction and its suspension in ethanol treated with 3 equivalents of perchloric acid. Yield, 0.60 g (85%) of the diperchlorate *XIII*, m.p. 226–228°C (90% aqueous ethanol). For $C_{10}H_{21}Cl_2N_3O_8$ (382.2) calculated: 31.42% C, 5.54% H, 18.55% Cl, 11.00% N; found: 31.57% C, 5.67% H, 18.67% Cl, 11.14% N.

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