

SYNTHETIC REACTIONS OF DIMETHYLFORMAMIDE. XXVIII.* DIAZOMALONALDEHYDE

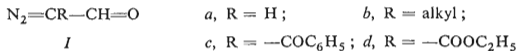
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Diazomalonaldehyde (*II*) was prepared on reaction of nitrous acid with aminomalonaldehyde. The main product of its thermic decomposition under various conditions is polymeric formylketene (*VIII*). The formation of phenylmalonaldehyde (*V*) during the decomposition of diazomalonaldehyde in benzene, and the formation of compound *XI* — a by-product of diazomalonaldehyde decomposition — may be explained by an intermediary formation of diformylcarbene (*VI*).

Some time ago two types of substances with a diazo group vicinal to an aldehyde group have been prepared in our laboratory: aliphatic diazoaldehydes *Ia, b*, prepared on reaction of *N*-substituted β -aminoacroleins with *p*-toluenesulfonylazide¹, and two acyldiazoaldehydes *Ic* and *Id*, obtained on formylation of diazoacetophenone and ethyl diazoacetate with dimethylchloromethyleneammonium chloride². In connection with this finding we already tried earlier to obtain the simplest dicarbonyl diazo compound, diazomalonaldehyde (*II*), but neither of the mentioned methods brought us to our goal.



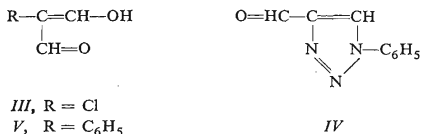
In this paper a simple synthesis of diazomalonaldehyde is described which was realized in connection with the study of the reactivity of aminomalonaldehyde the convenient synthesis of which was described recently³. Aminomalonaldehyde is stable only in alkaline solution and decomposition occurs even when carbon dioxide is introduced into the alkaline reaction mixture. However, if its alkaline solution is acidified in the presence of sodium nitrite, a reaction takes place resulting in the formation of a dark red solution which gradually becomes lighter; from the reaction mixture the required diazomalonaldehyde may be isolated in good yield.

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Diazomalonaldehyde is a weakly yellow liquid miscible with water. It can be distilled *in vacuo*; however, on overheating, or when brought in contact with some catalysts decomposing diazo compounds, a violent explosion takes place. The structure of diazomalonaldehyde follows both from analytical and spectral data. The symmetry of the molecule of this compound is best evident from its PMR spectrum formed by a single singlet of the aldehyde groups. On the basis of its IR spectrum all characteristic features of dialdehyde *II* may be identified, especially the strong interaction of the diazo group with the aldehyde groups, which causes an electron shift in the direction represented by one of the dipolar structures *IIb*. The UV spectrum contains one maximum (227 nm) the position of which does not shift with the change of solvent; in this feature it differs distinctly from diazoacetaldehyde¹ and diazoketones⁴; the analogous band in their UV spectra is very sensitive to the change of solvent.



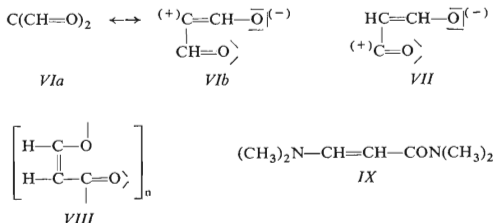
Diazomalonaldehyde is characterized, similar to other diacyldiazo compounds⁵, by a relatively high stability in acid medium. The half-time of its decomposition in 0.1N sulfuric acid at room temperature is about 24 hours. The reaction with hydrogen chloride in dioxan, affording chloromalonaldehyde (*III*) also takes place slowly. The aldehydic nature of both formyl groups of diazomalonaldehyde is affected by the interaction with the diazo group to such an extent that this substance does not display the usual reactions of the carbonyl group. Only when diazomalonaldehyde is reacted with aniline hydrochloride reaction of one of the aldehyde groups with the amino group evidently takes place, but the formation of the Schiff base is accompanied by cyclisation, affording thus triazine *IV*. Similar reactions are known⁶. In contrast to other diazo compounds of various types diazomalonaldehyde is surprisingly sensitive towards alkalis. In dilute aqueous alkali hydroxides or in aqueous triethylamine it decomposes rapidly; diazoacetaldehyde (*Ia*) is formed after the loss of one aldehyde group. Under the effect of triethylamine in benzene the decomposition of diazomalonaldehyde takes place in a quite different manner. A mere trace of amine causes the liberation of nitrogen and precipitation of an insoluble polymer the structure of which we shall discuss below.



A characteristic feature of the chemistry of diazo compounds is their decomposition to carbenes. However, in this respect diazomalonaldehyde was found to be

rather unreactive. While the structurally very close diazomalonaldehyde reacts with benzene, for example, smoothly to a derivative of norcaradiene⁷, diazomalonaldehyde does not react under conventional conditions. Only in the presence of an allylic complex with palladium(II) chloride, which is known as one of the most active catalysts for diazo compounds decomposition⁸, a reaction takes place the product of which is, in addition to an appreciable amount of a polymeric substance, phenylmalonaldehyde (V). The formation of the polymeric substance was also observed in experiments aiming at other reactions known from diazo compounds chemistry, as for example in the attempt at decomposition in cyclohexene, reaction with iodine, decomposition in higher boiling solvents, pyrolysis in gas phase, etc.

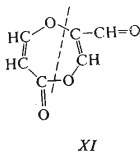
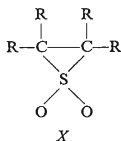
The analysis of the polymer formed by decomposition of diazomalonaldehyde under various conditions corresponds to the composition $C_3H_2O_2$, i.e. to the composition of diformylcarbene or any other particle formed by its isomerisation. Its IR spectrum contains bands corresponding to a carbonyl group conjugated with a double bond (1758 cm^{-1} and 1633 cm^{-1} , both bands of approximately the same intensity) and C—H bond (3090 cm^{-1} , 1316 cm^{-1}). In the PMR spectrum a doublet of unequal protons on a disubstituted double bond in *cis*-configuration is visible. In aqueous alkali the polymer is dissolved irreversibly and on reaction with ethanolic dimethylamine solution it affords dimethylamide of 3-dimethylaminoacrylic acid (IX).



These facts agree best with the structure represented by formula VIII corresponding to one of the possible forms of the polymeric formyl ketene. The configuration of the polymeric chain, represented schematically by formula VIII, is supported, in addition to the PMR spectrum, also by the ratio of intensities of the bands of C=C and C=O groups, from which *s-cis*-configuration of these structural elements may be deduced with great probability⁹. The formation of structure VIII may be explained easily by polymerization of the dipolar form of formyl ketene VII which is formed by rearrangement of the temporarily formed diformylcarbene VI.

In addition to the identification of the products of addition of diformylcarbene to other components we also tried to obtain its dimerisation product; this product

should be identical with the so far undescribed tetraformylethylene in which the properties of an extremely strong electron acceptor (close to those of tetracyanoethylene) could be expected. The attempts at thermic dimerisation did not succeed. From diazo compounds chemistry it is known that in some instances dimerization may be carried out indirectly: by reaction with sulfur dioxide episulfone *X* is first formed which is then transformed pyrolytically to the required dimer¹⁰. However, diazomalonaldehyde does not react with sulfur dioxide even in the presence of a catalyst. Only when heated in a sealed ampoule at 90–100°C does decomposition take place; the main product (>95%) in this case too is the polymeric formylketene *VIII*. However a crystalline easily sublimating substance was isolated in approximately 2% yield the elemental analysis of which (found by high resolution mass spectrometry) corresponds to the expected diformylcarbene dimer (C₆H₄O₄). The PMR spectrum, however, displayed four different protons of this character: two unequal protons on a *cis*-substituted double bond (analogous as in the polymeric formylketene *VIII*), another isolated olefinic proton and a typical aldehydic proton. The cyclic structure *XI* corresponds best to the PMR data and the mass spectrum. The formation of this compound may be explained by cycloaddition of the dipolar form of diformylcarbene *VI* and the dipolar form of formylketene *VII*, formed by rearrangement. Compound *XI* was also isolated in poor yield after several additional attempts at the decomposition of diazomalonaldehyde, for example after long boiling in benzene under catalysis with a complex of trimethyl phosphite with copper(I) iodide.



The results obtained in experiments with the decomposition of diazomalonaldehyde may be summarised into a single scheme: When compared with other diazocarbonyl compounds the reactivity of diazomalonaldehyde is appreciably decreased in consequence of a strong interaction of the diazo group with two aldehydic groups. If its decomposition is forced by more drastic conditions or the addition of a catalyst, a labile, strongly electronegative diformylcarbene (*VI*) is formed which may react with another component (for example benzene in the formation of phenylmalonaldehyde), but which rearranges exceptionally easily to formylketene (*VII*). This undergoes predominantly a rapid polymerisation, but a side-reaction with the unrearranged carbene may also take place affording the cyclic compound *XI*.

EXPERIMENTAL

The melting points were determined on a Kofler block and are uncorrected. The mass spectra were measured on a double focussing AEI MS-902 apparatus. The IR spectra were recorded with a Zeiss Jena UR-10 spectrophotometer, the UV spectra on an Optica Milano CF 4 apparatus, and the PMR spectra on Varian HA-100.

Diazomalonaldehyde (II)

A mixture of N,N-dimethyl-N-[2-(dimethylaminomethylene)amino-3-dimethylamino]prop-2-enylideneammonium perchlorate³ (15 g; 0.05 mmol) and 125 ml of 2M-NaOH was heated at 40°C under stirring for 10 hours. The solution was filtered with a small amount of charcoal and concentrated on a rotary evaporator. The volume was made up to 100 ml and 4 g (0.065 mol) of sodium nitrite were added. The mixture was cooled at -10 to -15°C and acetic acid (15 ml; 0.25 mol) was added dropwise to it under stirring (internal temperature not exceeding -5°C). The cooling bath was taken off and the mixture stirred at room temperature for another 2 hours during which the dark red turbid solution cleared up. The reaction mixture was extracted six times with 200 ml of dichloromethane and each extract was washed 2 times with 25 ml of a 10% potassium hydrogen carbonate solution and 20 ml of water. The combined extracts were dried over magnesium sulfate and the solvent distilled off through a column under reduced pressure (distillation temperature about 20°C, maximum bath temperature 45°C). The residue was distilled under magnetic stirring in a vacuum (oil pump, 0.3 Torr, bath temperature 40–50°C). Pressure restoration was carried out with nitrogen, Yield 2.85 g (58%) of diazomalonaldehyde. A sample for analysis was redistilled. For C₃H₂N₂O₂ (98.1) calculated: 36.75% C, 2.06% H, 28.57% N; found: 36.56% C, 2.26% H, 28.39% N. PMR spectrum (CDCl₃); δ 9.67 s. IR spectrum (CCl₄): ν (N=N) 2161, 2131; ν (C=O) 1691, 1675, 1658; ν (C—C) 1266, 1227, 1207; δ (C—H) 1405, 1375; ν (C—H) 2835, 2740 cm⁻¹. UV spectrum (ethanol): λ_{max} 227 nm (log ϵ 4.15), inflexion 241 nm (log ϵ 4.04) and 256 nm (log ϵ 3.94).

Phenylmalonaldehyde (V)

To 10 ml of benzene 35 mg of an allylic complex with palladium(II)chloride⁸ was added and the mixture refluxed for one hour under stirring and simultaneous dropwise addition of 690 mg (7 mmol) of diazomalonaldehyde in 10 ml of benzene. The mixture was refluxed for 5.5 hours and the benzene solution filtered from the catalyst and the insoluble polymer (total 0.29 g). The polymer was washed with benzene, the benzene fractions were combined and extracted 6 times with 10 ml 5% potassium hydrogen carbonate; each extract was reextracted three times with benzene. The bicarbonate solutions were combined and phenylmalonaldehyde set free by acidification with 1M-H₂SO₄ and extracted with chloroform. Yield 200 mg (25%) of a product melting at 85–90°C, which was further purified by sublimation and crystallisation from methylcyclohexane. M.p. 91–94°C (lit.¹² gives m.p. 92–93°C). The IR spectrum was identical with that of authentic phenylmalonaldehyde^{11,12}.

Chloromalonaldehyde (III)

To a solution of 46 mg (0.5 mmol) of diazomalonaldehyde in 2 ml of dioxan 1.1 ml of a 4.5M hydrogen chloride solution in dioxan was added and the mixture stirred at room temperature. After 6 hours the starting material was no longer present (the reaction was followed by thin-layer chromatography in benzene-ethanol 3 : 1). Dioxan was distilled off and the residue sublimated.

Yield 13 mg (25%) of a product melting at 140–143°C the mass spectrum of which was identical with that of authentic chloromalonaldehyde. (Lit.¹³: m.p. 145–146°C).

1-Phenyltriazole-4-carbaldehyde (IV)

To a solution of 98 mg (1 mmol) of diazomalonaldehyde in 2 ml of water 390 mg (3 mmol) of aniline hydrochloride in 3 ml of water were added upon which a yellow precipitate separated out which was filtered off under suction after 30 minutes standing. Yield 167 mg (95.5%) of product, m.p. 98–100°C. Sample for analysis was crystallised from tetrachloromethane. For $C_9H_7N_3O$ (173.2) calculated: 62.42% C, 4.07% H, 24.26% N; found: 62.14% C, 3.98% H, 24.35% N. Mass spectrum: $M^+ = 173$. IR spectrum ($CHCl_3$): $\nu(C=O)$ 1700, $\nu(\text{triazole})$ 1536, $\nu(CHO)$ 2770, 2850, $\nu(C-H \text{ of triazole})$ 3150 cm^{-1} .

Diazoacetaldehyde (Ia)

To one ml of a 10% solution of triethylamine in water 93 mg (1 mmol) of diazomalonaldehyde were added under cooling with ice. After 5 minutes the reaction was over (according to thin-layer chromatography a single product was formed — development with methanol). The product was extracted with dichloromethane and the extract washed gradually with 0.5M- H_2SO_4 , twice with water and then dried. Distillation gave 10 mg of a product which was identified by IR and PMR as diazoacetaldehyde¹.

Polymeric Formylketene (VIII) and 2,6-Dioxo-5-oxocyclohepta-3,7-dienecarbaldehyde XI

A) Into a glass ampoule containing 0.3 g (3 mmol) of diazomalonaldehyde 6 ml of sulfur dioxide were condensed and the ampoule sealed and heated at 90°C for 7.5 hours. After cooling it was opened, sulfur dioxide evaporated and the solid residue triturated with dichloromethane. The insoluble polymer (200 mg, i.e. 98%) was filtered off under suction. For $(C_3H_2O_2)_x$ calculated: 51.44% C, 2.88% H; found: 50.90% C, 2.88% H. IR spectrum (KBr): $\nu(C=O)$ 1758; $\nu(C=C)$ 1633; $\delta(C-H)$ 3090; $\nu(C-H)$ 1316 cm^{-1} . PMR ($DMSO-d_6$): 7.40 d, $J = 6-7$ Hz; 5.80 d, $J = 6-7$ Hz.

The dichloromethane solution was evaporated and the dry residue sublimated twice. The obtained compound XI (5 mg; 2%) had m.p. 114–116°C. PMR ($CDCl_3$): δ 7.51 d (1 H), $J = 5.8$ Hz; 6.01 d (1 H), $J = 5.8$ Hz; 9.80 s (1 H), 7.18 s (1 H). Mass spectrum: $M^+ 140$; m/e 112, 84, 71, 69, 29; high resolution: For $C_6H_4O_4$ calculated: 140, 0110; found: 140, 0119. IR spectrum (CCl_4): $\nu(C=O)$ 1777, 1747, 1649, 1618 (sh.) cm^{-1} ; $\nu(C=C)$ 1573 cm^{-1} . UV spectrum (ethanol) λ_{max} 229 nm (log ϵ 4.10); 308 nm (log ϵ 3.89).

B) To a solution of 300 mg of diazomalonaldehyde in 3 ml of benzene 7 mg of triethylamine were added under cooling with ice and water. The solution became turbid. Cooling was stopped but stirring continued. The next day 200 mg (95%) of product were filtered off with suction, identical according to its IR spectrum and analysis with compound VIII.

N,N-Dimethylamide of 3-Dimethylaminoacrylic Acid (IX)

To 2 ml of a 2N dimethylamine solution in ethanol 20 mg of polymeric formylketene (VIII) were added. After dissolution the solvent was evaporated and the residue sublimated. Yield 20 mg (50%) of compound IX which after a double sublimation melted at 60–64°C. (Literature¹⁴, m.p. 62–64°C). For $C_7H_{14}N_2O$ (142.2) calculated: 59.13% C, 9.92% H, 19.70% N; found:

59.17% C, 9.99% H, 19.70% N. PMR (CDCl₃) δ 7.43 d (1 H), $J = 12.2$ Hz; 4.77 d (1 H), $J = 12.2$ Hz; 2.95 s (6 H); 2.86 s (6 H).

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