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CHEMISTRY OF DINITROACETONITRILE-III

DINITROACETAMIDE AND ITS DERIVATIVES

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Abstract—Dinitroacetamide was prepared by acid hydrolysis of dinitrocyanomethide salts. Manipulation of preparative quantities of dinitroacetamide or its salts was troublesome due to unfavorable solubility properties and relatively facile decomposition to give dinitromethane derivatives. Dinitroacetamide underwent normal Michael addition reactions and condensed with formaldehyde to give 2,2-dinitro-2-carbamylethanol of which acetate ester and N-acylamido-derivatives were prepared.

THE chemistry of dinitroacetamide has been briefly surveyed. Factors affecting the yield of product and occurrence of by-products were investigated at some length but from an empirical approach since the mechanics of the preparative reaction were never well understood. The chemical properties of dinitroacetamide have been shown to be typical of a geminal dinitrocompound, modified by the general tendency of dinitroacetamide, its salts and derivatives to undergo rather facile hydrolysis of the carbamyl group giving derivatives of dinitromethane. Except for this tendency dinitroacetamide formed salts and gave derivatives having the expected properties in reactions with formaldehyde and with carbonyl-conjugated unsaturated compounds. The Michael adduct of dinitroacetamide with acrylic acid was shown to be identical with the product isolated from the analogous reaction with dinitroacetonitrile tetrahydrate.[1]

Dinitroacetamide was prepared by treatment of solutions of dried sodium, ammonium or potassium dinitrocyanomethide salts in methanol-ethyl acetate solution with gaseous hydrogen chloride. Product was isolated from such reaction mixtures simply by evaporation of all volatile material, i.e. without recourse to any intentional hydrolysis treatment. Some conversion to dinitroacetamide could be effected using methanol or ethanol alone or mixed with ether instead of ethyl acetate; even from concentrated aqueous hydrochloric acid an impure dinitroacetamide could be obtained.

The optimum conditions for the preparative reaction comprised use of approximately the minimum amount of methanol-ethyl acetate solution required for dissolution of the dinitrocyanomethide salt. Greater amounts of alcohol gave increasing quantities of side reaction products, mainly the dinitroacetate ester but also dinitromethane. Separation of dinitroacetamide from crude mixtures containing these compounds as impurities by recrystallization of the dinitroacetamide or its potassium salt was found to be inefficient and wasteful. The dinitroacetamide salt was the most soluble of the three.

The effect of concentrated acids on the hydrolysis of sodium dinitrocyanomethide has been investigated by spectrophotometric means. Concentrated sulfuric, 85 per cent phosphoric, and concentrated hydrochloric acids have been used. Only in the

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[1] Part II C. O. Parker, W. D. Emmons, A. S. Pagano, H. A. Rolewicz and K. S. McCallum, *Tetrahedron* 17, 89 (1962)

case of concentrated hydrochloric acid, however, have the results been sufficiently clear-cut to enable definite conclusions to be reached from the spectrophotometric curves obtained.

Dinitroacetamide and dinitroacetonitrile were found to possess distinctly different ultraviolet absorption curves, i.e. dinitroacetonitrile showed weak absorption peaks at 232, 255 mμ and a strong absorbance at 345 mμ; dinitroacetamide, on the other hand, exhibited strong absorbance at 361 mμ and a broad, low maximum at 280–300 mμ. Two and one half hours after sodium dinitrocyanomethide was dissolved in concentrated hydrochloric acid, the maxima at 232, 255 and 345 disappeared completely. Instead the low, broad maxima at 280–300 mμ and the fairly sharp maximum at 361 mμ appeared. The solutions of sodium dinitrocyanomethide in concentrated hydrochloric acid were examined spectrophotometrically after 2½, 4½, 24 and 48 hr, and absorbancies at 295 and 361 mμ were compared with those from a sample of dinitroacetamide in a solution of similar pH. More than 80 per cent formation of dinitroacetamide was noted after 2½ hr. This was found to decrease to 40–50 per cent after 48 hr. Good duplication of results was obtained in successive experiments. A concentrated hydrochloric acid solution of dinitroacetamide formed *in situ* from sodium dinitrocyanomethide was further concentrated *in vacuo* at a temperature slightly above 26°C. There was no decomposition.

As mentioned previously, the identifiable contaminants accompanying dinitroacetamide were found to be dinitroacetate ester and dinitromethane. There was no difficulty in obtaining pure samples of salts of each of these, the dinitroacetates by alcoholysis of the corresponding alkyl dinitrocyanoacetates[2] and the dinitromethane salts[3] by alkaline hydrolysis of either dinitrocyanomethide or dinitroacetamide salts. Comparison of infrared spectra of dinitroacetamide, methyl dinitroacetate and dinitromethane salts indicated that detectable quantities of dinitromethane salts may have been present in most dinitroacetamide salt samples. On the other hand 3μ N–H bands and 6 μ amide carbonyl bands adequately characterized dinitroacetamide salts as parent species.

EXPERIMENTAL

Dinitroacetamide (dry hydrogen chloride). Two hundred milliliters of anhydrous ether was stirred in a closed flask which was cooled in a freezing mixture (crushed ice-isopropyl alcohol) and protected from moisture with a drying tube while dry hydrogen chloride was bubbled in until the solution was saturated at 5. A solution of 15·3 g (0·1 mole) of dried sodium dinitrocyanomethide in a mixture of 12 ml of anhydrous methanol and 12 ml of ethyl acetate was added rapidly to the stirred, cooled ethereal hydrogen chloride solution causing the temperature to rise to 4–5°. During the next 30 min of stirring, the temperature dropped to 10, and the reaction mixture was allowed to stand overnight immersed in the freezing mixture contained in a Dewar flask. Rapid removal of the sodium chloride formed in the reaction was best accomplished by filtration through Celite. Solvent was removed from the filtrate under reduced pressure. It was found advantageous to redissolve the concentrate in ether when it was essentially free of hydrogen chloride and to dry it with anhydrous magnesium sulfate. When solvent was then completely removed *in vacuo*, the residue crystallized and could be washed onto a filter with methylene chloride and dried. Product thus obtained has amounted to as much as 11·4 g (76·5% yield), m.p. 86–87°.

Dinitroacetamide (aqueous hydrochloric acid). Eighty-three milliliters of concentrated hydrochloric acid was cooled to 10 and stirred while 15·3 g (0·1 mole) of sodium dinitrocyanomethide was added to it in portions. The mixture was stirred for an additional hour at this temperature and was allowed to come to room temperature gradually as the freezing mixture melted. After 16 hr the temperature of

[2] Part IV: C. O. Parker, *Tetrahedron* 17, 109 (1962).

[3] P. Duden, *Ber. Dtsch. Chem. Ges.* 26, 3003 (1893).

the mixture was 20°. It was filtered through Celite and the filtrate was placed in a continuous liquid-liquid extractor with 800 ml of methylene chloride; extraction with boiling methylene chloride was carried out for 8 hr. Solvent was evaporated from the methylene chloride layer leaving a solid residue, which was washed onto a filter with fresh methylene chloride. The crude product weighed 2·2 g (14·7% yield) and melted at 76–77°.

Another preparation was carried out in the same manner. After filtration, the hydrochloric acid reaction mixture was diluted with an equal volume of water. This solution was extracted with 85 ml portions of isopropyl ether. The combined organic extracts were dried with anhydrous sodium sulfate and then with anhydrous magnesium sulfate. Solvent was evaporated leaving a residue which crystallized when covered with methylene chloride and seeded with dinitroacetamide crystals. There was obtained 2·1 g (14·1% yield) of crude dinitroacetamide, m.p. 48–67°.

2,2-*Dinitro-2-carbamylethanol*. Dinitroacetamide (24·2 g, 0·16 mole) was suspended in 20 ml of water and stirred while 13·5 ml of 37% formalin solution was slowly added dropwise. The suspended dinitroacetamide gradually dissolved but the color of the solution was never discharged. After standing overnight at room temperature, the solution was saturated with sodium chloride and extracted with ether. The ether extracts were dried with magnesium sulfate and evaporated, leaving 22 g of vacuum dried waxy yellow solid. After recrystallization from ethylene dichloride there was obtained 11·3 g (39·4% yield) of 2,2-dinitro-2-carbamylethanol, m.p. 104–107°. The infrared spectrum of this material contained bands expected for hydroxyl, amide-carbonyl (1710 cm^{-1}) and *gem*-dinitro groups (1575 cm^{-1}).

When the reaction was carried out by adding the dinitroacetamide (5·0 g, 0·033 mole) to 10 ml of formalin, the solid dissolved very rapidly with slight evolution of heat, giving a nearly colorless solution. Water was evaporated under reduced pressure and the residual, colorless oil was dissolved in ether and dried with magnesium sulfate. Evaporation of solvent and evacuation of the residue at 0·5 mm left 6·8 g (theor. yield 5·9 g). The viscous, oily product was dissolved in isopropyl ether, filtered, evaporated and evacuated again. It was not possible to induce crystallization by extensive manipulation with various solvents at low temperatures. The infrared spectrum of this material was, however, similar in most respects to that described above.

2,2-*Dinitro-2-carbamylethyl acetate*. A mixture of 14 g (0·02 mole) of trifluoracetic anhydride and 3·4 g (0·056 mole) of acetic acid was stirred and warmed to 50–60° under reflux for 15 min. After cooling, a solution of 10·1 g (0·056 mole) of 2,2-dinitro-2-carbamylethanol in 50 ml of ethyl ether was added with continued stirring, and the solution was heated under reflux for 1½ hr. Solvent was evaporated under reduced pressure; the residue was dissolved in methylene chloride and extracted twice with water, twice with 5% sodium bicarbonate solution and again with water. The organic portion was dried with magnesium sulfate. The dried methylene chloride solution was concentrated, cooled in a freezing mixture and diluted with petroleum ether, causing precipitation of 1·5 g (12·1% yield) of crude product, m.p. 55–58°. After three recrystallizations from a methylene chloride-petroleum ether mixture, the melting point remained constant at 60–62°.

(Found: C, 27·00; H, 2·85; N, 19·68. Calc. for $C_5H_7O_7N_3$: C, 27·15; H, 3·17; N, 19·00.)

N-(2,2-*Dinitro-2-carbamylethyl*) *methacrylamide*. Freshly recrystallized methacrylamide (1·7 g, 0·02 mole) and 0·6 g (0·02 mole) of paraformaldehyde were ground together in a mortar. Two drops of saturated aqueous potassium carbonate solution were added to the mixture which was ground further. When the powder was warmed in a bath at 60° for a few minutes, it melted. The nearly clear melt was cooled, dissolved in 10 ml of water and filtered. To the clear filtrate was added 3 g (0·02 mole) of dinitroacetamide. The solution was warmed at 60° for 10 min, cooled, and when crystallization was complete, filtered. The dried product weighed 0·9 g (18·3% yield), m.p. 116–117°. Two recrystallizations from ethylene chloride gave a constant melting point of 120°.

(Found: C, 34·71; H, 4·32; N, 22·72. Calc. for $C_7H_{10}O_6N_4$: C, 34·15; H, 4·07; N, 22·76.)

4,4-*Dinitro-4-carbamylbutyric acid*. A solution of 3·0 g (0·02 mole) of dinitroacetamide in 7 ml of water was mixed with 1·4 g (0·02 mole) of glacial acrylic acid and was allowed to stand overnight at room temperature. When all volatile material was evaporated from the reaction mixture under reduced pressure, the residue crystallized. It was washed onto a filter with methylene chloride, giving 2·8 g (63·4% yield) of product, m.p. 80–95°. After two recrystallizations from ethylene dichloride, the melting point was 115–117°.

(Neut. equiv., Found: 75·0. Calc.: 73·7.)

The infrared spectrum of this material was indistinguishable from a sample of the same compound prepared in a different way.[1]

4,4-Dinitro-4-carbamylbutyramide. A solution of 1·4 g (0·02 mole) of freshly recrystallized acrylamide in 5 ml of methanol was mixed with a solution of 3·0 g (0·02 mole) of dinitroacetamide in 10 ml of methanol. The resulting solution was warmed at 40° for 16 hr, cooled, and a small amount of polymeric material removed by filtration. After solvent had been evaporated from the filtrate, cold water was added to the residue, causing it to crystallize. The product was filtered, washed with cold water, and when dried, weighed 2·7 g (61·3% yield); m.p. 105–106°. After two recrystallizations from ethylene dichloride, the melting point was 110–111°.

(Found: C, 27·67; H, 3·95; N, 24·42. Calc. for $C_5H_8O_6N_4$: C, 27·27; H, 3·64; N, 25·45.)

Sodium dinitroacetamide. Dinitroacetamide (5 g) was dissolved in 10 ml of methanol, the solution was stirred and methanolic sodium hydroxide solution added dropwise while cooling in an ice bath until the solution was faintly alkaline to pH paper. Crystallized salt was filtered, and dried: wt. 5·2 g, m.p. 167° dec. Recrystallization was effected by dissolving the salt suspended in boiling ethanol by addition of a little water, filtering the hot solution, cooling the filtrate and adding ether; m.p. 170° with explosion.

(Found: Na, 14·62. Calc. for $C_2H_2O_5N_3Na$: Na, 13·45.)

Potassium dinitroacetamide was prepared in analogous fashion. It was appreciably less soluble in water than the sodium salt and could be recrystallized from concentrated aqueous solution, m.p. 159° with deflagration.

Silver dinitroacetamide. A solution of 5 g of dinitroacetamide in aqueous methanol was neutralized with a solution of potassium hydroxide in methanol. The solution was warmed to dissolve any crystallized solid. A solution of 5 g of silver nitrate in 10 ml of water was added to the potassium dinitroacetamide solution causing crystallization of silver dinitroacetamide, which was filtered and dried, yield 7·6 g. Recrystallization from water gave 5·2 g, m.p. 130° with deflagration.

(Found: Ag, 44·65. Calc. for $C_2H_2O_5N_3Ag$: Ag, 42·19.)

MELTING-DECOMPOSITION POINTS OF SALTS

	Dinitroacetamide	Methyl dinitroacetate	Dinitromethane
Na	167	212	211–213°
K	159°	213–214	205
Ag	130	168–170	135