

Malonic Ester Derivatives of *s*-Triazine

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Reaction of cyanuric chloride with solutions of sodium diethyl malonate led to three products, 2,4,6-tris(dicarbethoxymethylene)hexahydro-*s*-triazine, 2,4-bis(dicarbethoxymethylene)-6-oxohexahydro-*s*-triazine, and 2-dicarbethoxymethylene-4,6-dioxohexahydro-*s*-triazine. The preferred structures (IV,V,VI) are stabilized by chelated N-H \cdots O protons in six membered rings. The assignment of structures was made on the basis of ir, nmr, uv and mass spectral data.

The malonic ester derivatives of *s*-triazine are of interest because of the possibility of tautomerism of the type

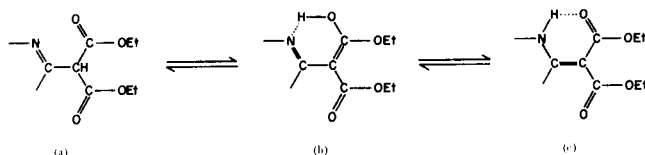


Figure 1

The preparation of compound III was reported in an 1894 paper by W. Kolb (2), who also described attempts to prepare a pure trimalonate derivative of *s*-triazine. We have prepared three malonic ester derivatives of *s*-triazine in a similar manner by replacing all or part of the chlorine atoms of cyanuric chloride in a reaction with the appropriate stoichiometric proportion of sodium diethyl malonate. The remaining chlorine atoms, if any, were readily hydrolyzed by moisture. Thus, one might expect the tri, di and monomalonate derivatives to possess structures I, II and III, respectively.

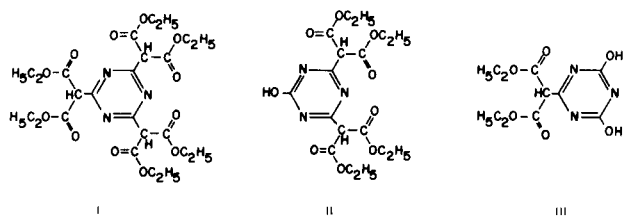


Figure 2

However, by a proton shift of the type (a) \rightarrow (c) shown above, the tri, di and monomalonate derivatives of *s*-triazine might equally well be assigned the structures

IV, V and VI, respectively, in which intramolecular hydrogen bonding would be favored.

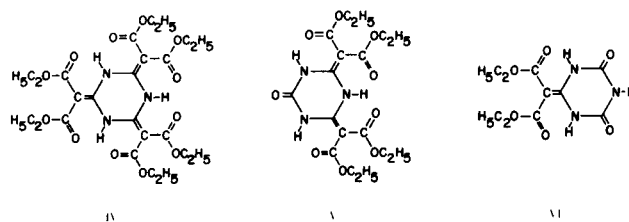


Figure 3

Indeed, our spectroscopic data were best interpreted on the basis of the three derivatives existing almost entirely as these latter structures.

Mass spectroscopy was used to identify each of the three esters which were isolated and purified. The respective parent peaks were at m/e 555, 413 and 271 for the tri, di and monomalonate derivatives. None of the mass spectra showed a significant positive ion fragment corresponding to cleavage of a diethyl malonate group as might have been expected for structures I, II and III.

The nmr spectral shifts of the three derivatives are listed in Table I.

The marked downfield shifts for the NH protons are indicative of strong hydrogen bonding, such as would occur in the structures IV, V and VI involving NH \cdots O chelation in six membered rings. Thus, the absorptions at 13.9 ppm in compound IV and 14.1 ppm in compound V are associated with chelation involving two carboxy groups, while the absorptions at 12.3 ppm in compound V and 12.4 ppm in compound VI are associated with chelation involving only one carboxy group. The NH resonance at 8.9 ppm in compound VI is not involved in an intramolecular hydrogen bond as shown by the fact

TABLE I
Nmr Chemical Shifts (δ) and Integrated Areas

Compound	CH ₃ ppm	CH ₂ ppm	NH ppm
IV	1.32 (18H, triplet)	4.31 (12H, quartet)	13.9 (3H, singlet)
V	1.32 (12H, triplet)	4.28 (8H, two superimposed quartets)	14.1 (2H, singlet) 12.3 (1H, singlet)
VI	1.25 (6H, triplet)	4.23 (4H, quartet)	12.4 (1H, singlet) 8.9 (2H, singlet)

TABLE II
Infrared Stretching Frequencies (in cm⁻¹)

Compound	Amide C=O	Ester C=O	C=C
IV	----	1675	1600
V	1750	1675	1620, 1640
VI	1760	1720	1635

that only this absorption moves upfield upon dilution, indicative of intermolecular hydrogen bonding in this case (3). In no instance was any resonance detected which could be attributed to the methyne protons of structures I, II and III. The two superimposed quartets for the methylene protons of the dimalonate derivative are due to the asymmetry associated with structure V.

The important difference in the ir spectra of the three derivatives lies in the region from 1500 to 1800 cm⁻¹ as shown in Table II for the stretching modes indicated.

The effect of strong chelation as well as conjugation of the ester carbonyl is seen in the marked shifts to lower frequencies for the ester C=O stretching bands of compounds IV and V. This effect is similar to that noted for the carbonyl band of the methyl ester of anthranilic acid which absorbs at 1685 cm⁻¹ due to N-H··O chelation (4). The effect of conjugation is also apparent in the broad C=C stretching bands which are of equal intensity to the C=O stretching bands, and are shifted to lower frequency in compounds IV and V. The broad bands expected for the chelated protons were not readily apparent, perhaps because they are hidden by the CH stretching bands near 3000 cm⁻¹ as is the case in β -amino- α,β -unsaturated ketones (5).

The ultraviolet spectra of the three derivatives in neutral, or slightly acid, 95% ethanol solutions show the following λ max (nm) values: compound IV, 313; compound V, 313; and compound VI, 277. This is again evidence for increased conjugation in the tri and dimalonate derivatives. Upon adding base to alcoholic solutions of compounds IV and V, they became yellow in appearance and showed an absorbance at 360 nm. This behavior is attributed to ionization of an NH proton, and support

for this comes from a titration of compound IV with strong base. A single equivalence point was observed at about pH 11, yielding an equivalent weight approximately equal to the molecular weight of 555. The white crystals that were isolated from the basic solutions of compound IV appeared to be light sensitive, turning bright orange in color. Their nmr spectrum in deuteriochloroform indicated the ester protons were no longer equivalent. The nature of these crystals will be the subject of a future investigation.

EXPERIMENTAL

The ir spectra were taken on a Perkin-Elmer model 621 spectrophotometer by means of potassium bromide discs. The nmr spectra were recorded on a Varian HA-100 spectrometer using deuteriochloroform solutions with TMS as the internal reference. The probe temperature was 28°. Mass spectra were recorded on a Varian M-66 mass spectrometer previously calibrated with perfluorokerosene. The uv spectra were obtained in 95% ethanol solutions using a Cary model 14 recording spectrophotometer. Melting points were determined on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

2,4,6-Tris(dicarbethoxymethylene)hexahydro-*s*-triazine (IV).

Sodium diethyl malonate was prepared by adding 6.44 g. (0.28 g-atm) of sodium to 45 g. (0.28 mole) of diethyl malonate in 200 ml. of dioxane and heating until all the sodium was reacted. To the hot solution was added 18 g. (0.097 mole) of cyanuric chloride, and the solution maintained at reflux for several hours. The solution was filtered and evaporated, and the solid residues were extracted with chloroform. The chloroform was evaporated and the solid crystallized from 95% ethanol and rinsed with acetone to yield slightly yellow crystals. These crystals were further purified by column chromatography using a silicic acid column and a 90% chloroform, 10% methylene chloride solution as the eluting solvent. Recrystallization from 95% ethanol gave about 5 g. of fluffy, white needles, m.p. 182-183°.

Anal. Calcd. for C₂₄H₃₃N₃O₁₂: C, 51.89; H, 5.99; N, 7.56. Found: C, 51.98; H, 5.98; N, 7.45.

2,4-Bis(dicarbethoxymethylene)-6-oxohexahydro-*s*-triazine (V).

The same procedure was followed as for the preparation of compound IV except that 0.28 mole of sodium diethyl malonate was reacted with 0.14 mole of cyanuric chloride. A final crystallization from 95% ethanol gave about 5 g. of fluffy, white needles, m.p. 173-174°.

Anal. Calcd. for C₁₇H₂₃N₃O₉: C, 43.39; H, 5.61; N, 10.16. Found: C, 49.34; H, 5.58; N, 10.08.

2-Dicarbethoxymethylene-4,6-dioxohexahydro-*s*-triazine (VI).

A dioxane solution of sodium diethyl malonate, prepared from sodium (0.92 g., 0.04 g-atom) and diethyl malonate (6.4 g., 0.04 mole) was added dropwise to cyanuric chloride (7.4 g., 0.04 mole) in dioxane and the mixture heated to just below the boiling point for ½ hour. After extraction of the dried product with chloroform, several recrystallizations from hot water gave 2.3 g. of white crystals, m.p. 180-181° (lit. (2), m.p. 181°).

Anal. Calcd. for C₁₀H₁₃N₃O₆: C, 44.28; H, 4.83; N, 15.49. Found: C, 44.43; H, 4.95; N, 15.46.

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