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SPECTROSCOPIC EVIDENCE FOR THE EXISTENCE OF CYCLIC DIETHYLMALONIC ANHYDRIDE[1]

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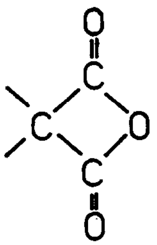
Up to the present, attempts to isolate compounds having a cyclic oxetane-2,4-dione /malonic anhydride 1/ structure or to prove unambiguously their structure have been unsuccessful.

Mironova and Dvorko[2] reported the conversion of succinic, glutaric, phthalic and maleic acids with dicyclohexyl carbodiimide /DCC/ into cyclic anhydrides and dicyclohexyl urea /DCU/. According to our experience[3] the derivatives of malonic acid also react at first in this way but the malonic anhydride formed reacts instantaneously with another DCC molecule or polymerizes. Though Duckworth[4] described the preparation of compounds having a cyclic malonic anhydride structure, the IR bands specified by him /at 1824 and 1760 cm^{-1}/ are inconsistent with the four-membered ring structure, they may be assigned rather to its dimer of structure 2.



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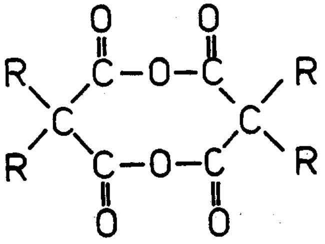

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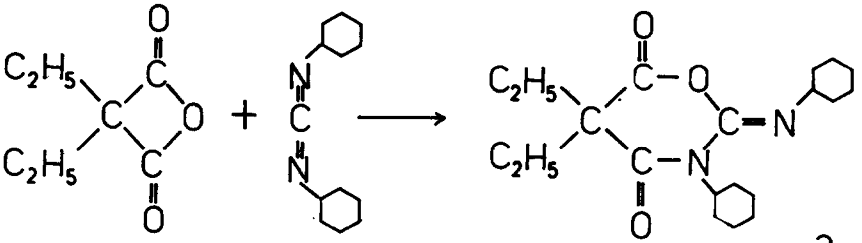

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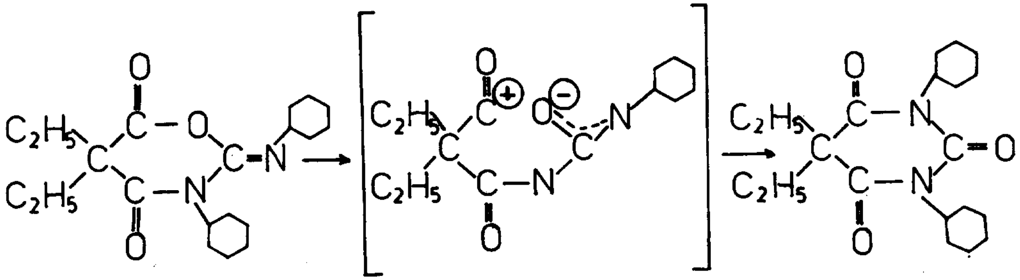
IR bands: 1800 cm^{-1} /carbonyl of O=C-O-O-C=N/; 1720 cm^{-1} /carbonyl of O=C-N-C=N/; 1695 cm^{-1} /C=N bond of O=C-N=C=N-/. NMR bands: /τ= 5.3 1H /-N-CH/; 6.2 1H /=N-CH/; 8.3 24H /CH_2 groups/; 9.1 6H /CH_3 groups/. On the basis of mass spectrum M = 348, molecular formula $C_{20}H_{32}N_2O_3$. Adequate assignment of IR bands is supported by several literature data.[6-8]

Compound 3 is a novel stable example of a compound with an O-acylisourea skeleton. Although according to Khorana[9] these compounds are presumed to be intermediates of acylation carried out with DCC, only few stable derivatives are known.[10]

On allowing the etheral or tetrahydrofuran reaction mixture to stand at room temperature, the formed 3 is partially /about 10 % in 2 days/ rearranged into barbiturate.



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From several reaction mixtures of diethylmalonic acid we also isolated 2 /R= ethyl/, m.p. 202-204^{0}, IR bands at 1820 and 1760 cm^{-1}, showing only CH_2 and CH_3 protons in the NMR spectrum, the elemental analysis of which was consistent with formula 2. The carbonyl bands of succinic anhydride are at

1799 and 1876 cm^{-1}, and the band of β-propiolactone at 1841 cm^{-1}.[5] From the above data, on a qualitative estimation, we may expect in a compound containing a malonic anhydride ring two carbonyl bands between 1900 and 2000 cm^{-1}, of which the band of higher wave number is less intense.

On investigating the reactions between malonic acids and DCC we measured the IR spectrum of the reaction mixture of diethylmalonic acid and DCC /1:1 molar ratio/ in carbon tetrachloride. After 10 minutes reaction time DCU was filtered off. Two bands of medium intensity at 1980 and 1900 cm^{-1} were observed in the IR spectrum, the latter being slightly more intense.

When diethylmalonic acid was reacted with two moles of DCC, and the spectrum taken at the same thickness, the two bands disappeared in the base line, proving that they were not overtones but belonged to a compound which reacted with DCC. When the spectrum was taken from the same mixture at a greater thickness, the two bands appeared again at exactly the same frequencies.

Diethylmalonic anhydride affords with DCC the iminooxazine-dione **3** in a 1,4-dipolar cycloaddition reaction. Though **3** could not be obtained in crystalline form, its structure is unambiguously proved by elemental analysis and the IR and mass spectra. Elemental analysis: found C, 69.13, H, 9.27, N, 8.03; calcd. for $C_{20}H_{32}N_2O_3$ C, 68.92, H, 9.27, N, 8.13. This observation contradicts the statement of Bose and Garratt[11] who claimed to obtain barbiturate in 62.5 % yield from diethylmalonic acid with two moles of DCC in tetrahydrofuran. IR bands of **4** are: 1755 /weak/ and 1690 cm^{-1} /strong/; in the NMR spectrum only one type of N-CH proton appears at $\tau = 5.3$.

The anhydrides of malonic acid and monosubstituted malonic acids are significantly more reactive, and attempts to detect their presence failed. In the reaction with two moles of DCC we obtained the barbiturates described by Bose and Garratt[11], indicating that the oxazine derivatives analogues to **3** are unstable. These reactions and their presumed mechanism will be discussed in detail in a forthcoming paper.[3]

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