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# UNEXPECTED THERMOLYSIS OF THE N,N-DIETHYLAMIDE OF AN ALLENE-1,3-DICARBOXYLIC ACID : SYNTHESIS OF A 6-AMINO-α-PYRONE.

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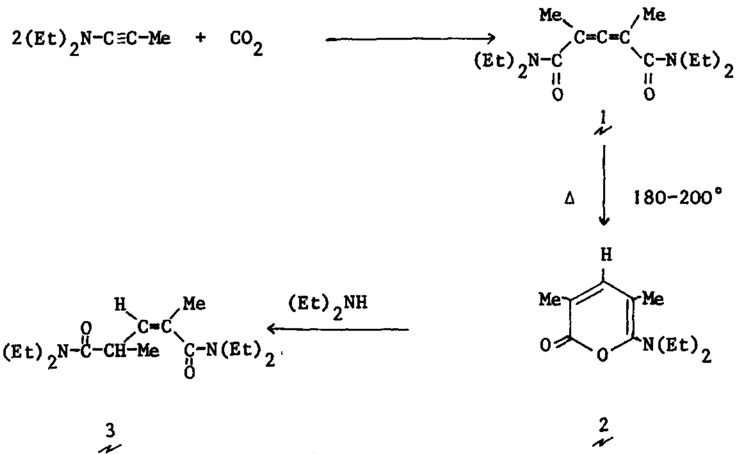
The cycloaddition of diethylaminopropyne (1) with carbon dioxide gives, in almost quantitative yields (2), the bis-N,N-diethylamide of 2,4-dimethyl-2,3-pentadiene dioic acid 1, a member of the class of allenic diacids of which only the simplest member, allene-1,3-dicarboxylic acid (glutinic acid) has yet been described (3) :

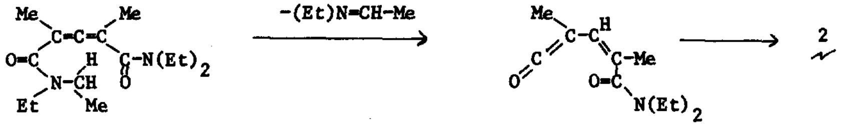

Scheme I

We now show that this allenic diamide 1, while a stable liquid at moderate temperature, undergoes an unexpected thermal transformation, starting at about 180° under vacuum (0.1 mm), leading in 40 % yield, to the as yet unknown 6-amino-α-pyrone 2 :bp (0.05 mm) 72° ; ir ($CCl_4$) 1720 $cm^{-1}$ ; nmr (4) ($C_6D_6$) δ 0.95 ppm (6H), 1.65 ppm (3H), 1.95 ppm (3H), 2.9 ppm (4H), 6.5 ppm (1H), mass spectrum (4), (70 eV) m/e (rel intensity) : 195 ($M^+$, 80), 167 (100) 152 (88), 138 (75), 123 (30), 110 (65), 95 (30), 72 (20), 67 (100).

Diethylamine reacts with 2 (15 h, reflux in ether) to give in quantitative yield (Scheme I) the corresponding bis-N,N-diethylamide of cis-α,γ-dimethyl glutaconic acid 3 : bp (0.005) 105° ; ir (film) 1640 cm$^{-1}$ ; nmr ($C_6D_6$) δ 1.7 ppm (d, vinylic methyl, J=1.6 Hz), 5.65 ppm ($d_1$ x $d_2$, vinylic H, $J_1$=10 Hz, $J_2$=1.6 Hz).

The diamide 3 has the same vpc retention time as that of one of the two isomers from the semi-hydrogenation of the allenic amide 1 and its mass spectrum shows the same fragmentation with that of the bis-N,N-diethylamide of trans α,γ-dimethyl glutaconic acid (2).

We would like to suggest that the thermolysis of the allenic diamide 1 is initiated by a cyclic 1,5-migration of one of the methylenic hydrogens of the ethylamino group (reverse ene-synthesis (5)) with simultaneous rupture of the carbon-nitrogen bond of the amide, thus leading to the intermediary ketene 4. The latter then undergoes heterocyclization to the α-pyrone 2 (Scheme II). The relative facility of this unusual transformation is undoubtly due to the fact that the structural situation is such that strain is not increased in the transformation allene ⟶ ketene, while conjugation is greater in the intermediary ketene.



1 Scheme II 4

The thermolysis of the allenic diamide 1 which can be made in 15 min. in 95 % yield from $CO_2$ and diethylaminopropyne, constitutes a particularly simple and efficient route to 6-amino-α-pyrones of type 2.

We are pursuing these studies with other allenic amides to establish the generality of this thermolysis and are attempting to get conclusive proof of its mechanism.

## References:

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