

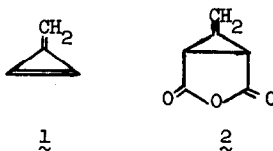
THE PYROLYSIS AND PHOTOLYSIS OF CIS-1-METHYLENECYCLOPROPANE-2,3-DICARBOXYLIC ANHYDRIDE: APPROACHES TO METHYLENECYCLOPROPENE

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Methylenecyclopropene (1) occupies an interesting position in the C_4H_4 class. Evidence for its formation either as a stable compound or a reactive intermediate has not been reported. In contrast, cyclobutadiene has been convincingly detected as a short-lived molecule (1) and more recently tetrahedrane has been suggested (2) as a reactive intermediate. However, substituted methylenecyclopropenes (3) have been prepared and this encouraged us to attempt the isolation of the parent hydrocarbon.



An attractive precursor to 1 is cis-1-methylenecyclopropane-2,3-dicarboxylic anhydride (2) which can be prepared from Feist's acid (4). The former upon thermal activation would be expected to undergo decarbonylation and decarboxylation as does maleic anhydride (5) or phthalic anhydride (6). Alternatively, mercury sensitized photolysis of 2 in the gas phase would also be expected to result in 1 on the basis of recent studies of cyclic anhydrides (7). For example, cis-1,2-cyclobutanedicarboxylic anhydride gave cyclobutene as a primary photo-product (7).

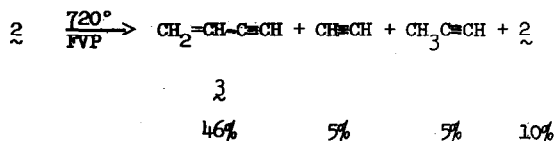
Mass spectral monitoring of the pyrolysate from 2 at low pressures (10^{-4} Torr) and short contact times (ca 1 msec) (flash vacuum pyrolysis (8)) showed that decomposition began to occur at around 500° and that 2 was essentially, completely decomposed at 1000°. The primary

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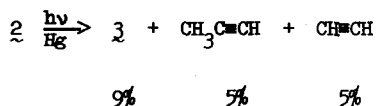
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thermal fragment had m/e 52 (C_4H_4), and its concentration increased regularly as that of the parent molecule decreased. The ionization potential of the former (9.9eV, 1000°) corresponded to that of vinylacetylene (3). Consistently, isolation of the pyrolysate by rapid quenching on a liquid nitrogen cooled dewar revealed that vinylacetylene (3) was the major product in the temperature range 550 - 1000°. The composition of the pyrolysate at 720° is given below (9).



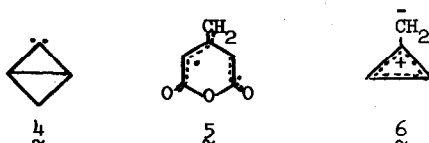
No evidence was obtained for any other C_4H_4 species; no major extraneous absorptions were observed in the nmr spectrum (10) of the pyrolysate nor were there any extraneous peaks observed by glpc.

The Hg sensitized photolysis of $\underset{\sim}{2}$ in a gas flow system at low pressures (7) gave the products listed (9). Considerable polymeric material remained in the liquid nitrogen trap where products were condensed and on the walls of the quartz irradiation tube (11).



The observed products from both pyrolysis and photolysis experiments suggest that $\underset{\sim}{1}$ undergoes isomerization to 3 or fragmentation to acetylene at the reaction conditions. Similar C_4H_4 products were recently obtained from the light induced reaction of carbon suboxide with cyclopropene; the carbene $\underset{\sim}{4}$ and tetrahedrane were proposed intermediates (2).

We recognize that biradical $\underset{\sim}{5}$ may be an important intermediate, especially in the pyrolysis experiments, since it is well known that simple methylenecyclopropanes (12), as well as Feist's acid or ester (13), undergo facile thermal isomerizations through similar intermediates; $\underset{\sim}{5}$ may give $\underset{\sim}{1}$ or isomeric C_4H_4 intermediates which would bypass $\underset{\sim}{1}$. Indeed, the observation of methylacetylene would appear to require some decomposition of $\underset{\sim}{2}$ via a relatively tortuous pathway other than sequential or concerted decarboxylation-decarboxylation.



It is interesting that Baird and Dewar have calculated a heat of formation (79.1 kcal/mol) and strain energy (58.1 kcal/mol) for 1 (14) which are greater than the same quantities calculated for cyclobutadiene (65.0 kcal/mol and 32.8 kcal/mol, respectively) (15). These results are qualitatively consistent with our observations. The difference in stability between the C_4H_4 isomers may be great enough to allow detection of cyclobutadiene as a reactive intermediate but may preclude detection of 1 at comparable conditions. On the other hand, the stability of 1 must be markedly affected by groups which stabilize the dipolar form 6, as evidenced by the substituted methylenecyclopropenes which are isolable (3).

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- Products were determined by glpc and nmr using authentic reference compounds; qualitative analysis was also carried out by ir.
- Two minor nmr absorptions were observed in the vinyl region of vinyl acetylene which were not assigned.

11. The nmr indicated that a small amount of butatriene may have been formed. This, in part, could explain some of the residue.
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