Studies on Synthetic Pyrethroids. (VI)

Synthesis of Chrysanthemum-dicarboxylic Acid. (Supplement). Mechanism of Addition of Ethyl Diazoacetate to Ethyl $\alpha\delta$-Dimethylsorbate

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The mechanism of the addition of ethyl diazoacetate to sorbic acid esters is discussed. The possible intermediate pyrazoline and the stepwise decomposition thereof would be more reasonable for the elucidation of the formation of cyclopropane and acyclic compounds, as well as of cyclopropane products resulted from inversion of $\gamma\delta$-ethylenic bond of asymmetrical sorbic esters during the addition of diazoacetate.

As was reported in the previous paper,[1] ethyl diazoacetate (**II**) added predominantly to the $\gamma\delta$-ethylenic bond of ethyl $\alpha\delta$-dimethylsorbate (**I**) to give the geometrical isomers of naturally derived chrysanthemum-dicarboxylic acid, as well as an acyclic structural isomer (**III**) thereof under the conditions employed.

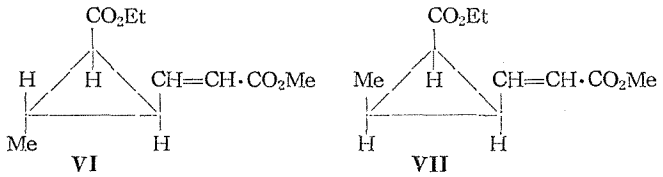
The mechanism of the addition of aliphatic diazo-compounds to olefins remains uncertain, but the participation of free radicals is rather favoured at present. However, the formation of the acyclic structural isomer (**III**) of synthetic chrysanthemum-dicarboxylic acid in our experiment (i) and the isolation of a pyrazoline intermediate[2] during the addition in one of the present reaction conditions favour the pyrazoline intermediate mechanism rather than free radical mechanism.

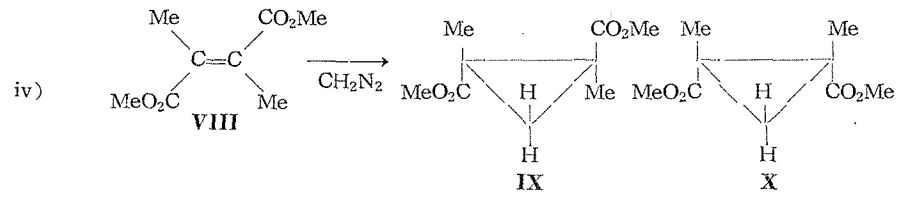
Furthermore, Harper and Reed have recently isolated[3] the cyclopropane derivative resulted from the addition of diazoacetate to methyl sorbate in which inversion of the ethylenic bond took place during the addition (iii), and two other similar cases in which inversion was confirmed, have been reported: that of the addition of dimethyl *trans*-but-2-ene-2,3-dicarboxylate[4] (iv), and of dimethyldiazomethane to ethyl maleate[5] (v).

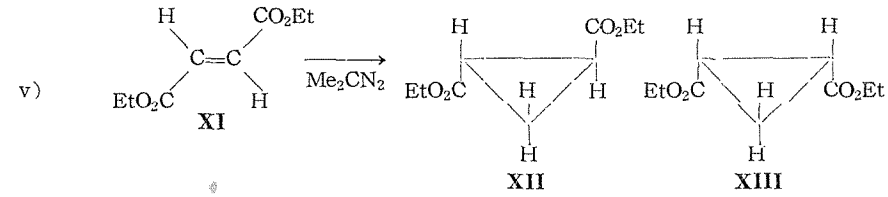
i) $\underset{\mathbf{I}}{Me_2C{=}CH{\cdot}CH{=}C(Me)CO_2Et} \xrightarrow[\mathbf{II}]{N_2CHCO_2Et} \underset{\mathbf{III}}{Me_2C{=}C(CH_2{\cdot}CO_2Et){-}CH{=}C(Me)CO_2Et}$

ii) $\mathbf{I} \xrightarrow[\mathbf{II}]{} \underset{\mathbf{IV}}{Me_2C{-}CH(CH{\cdot}CO_2Et){-}CH{=}C(Me)CO_2Et}$

iii) $\underset{\mathbf{V}}{MeCH{\overset{t}{=}}CH{-}CH{\overset{t}{=}}CH{\cdot}CO_2Me} \xrightarrow{} \mathbf{II}$







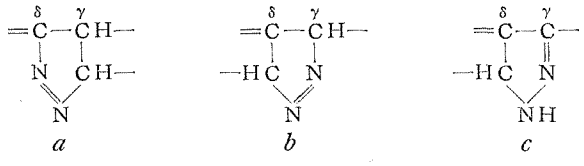
From these evidences it seems probable that the addition of diazoacetate would not proceed by a simultaneous addition of the alkoxycarbonylmethylene radical at both ends of the ethylenic bond, but proceed by stepwise process.

In order to explain the formation of these products by the free radical mechanism, either cyclopropane intermediate or diradical should be postulated. Cyclopropane derivatives i.e. chrysanthemum-dicarboxylate in this case, are too rigid, as is well known, to be regarded as an intermediate which decomposes to give the acyclic compound (**III**) by ring fission, and to give rise to the inversion by intramolecular rearrangement.

The assumption of successive occurrence of diradicals are thermodinamically not reasonable.

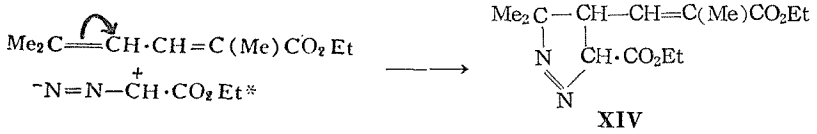
The authors prefer the pyrazoline intermediate mechanism which could explain satisfactorily the formation of all these addition products mentioned above, one of the important evidences for which being the isolation of pyrazoline compound during the addition under one of the present reaction conditions.

Although the structure of the pyrazoline intermediate isolated in our reaction (i) was not established, three following structures are theoretically possible:



Among these, Δ^2-structure *c* and Δ^1-structure *b* are excluded because these structures can not give rise to the acyclic isomer (**III**), in which the diazoacetate residue attaches to the γ-carbon atom of the sorbate. By exclusion, Δ^1-structure *a* is con-

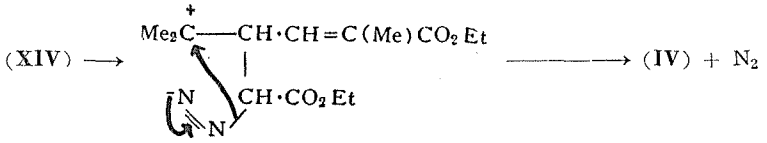
sidered to be that of the existing pyrazoline intermediate and this is also supported by the following scheme of formation:



This structure agrees with the fact that the pyrazoline gave no acetyl derivative.

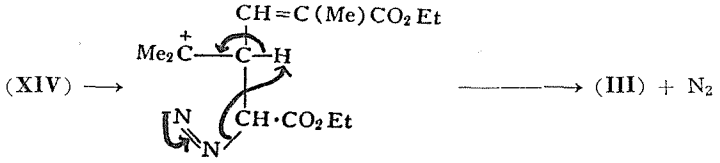
The intermediate pyrazoline dicarboxylic ester so formed (**XIV**) is postulated to decompose with expulsion of nitrogen to give the cyclopropane derivative (**IV**) in (ii), and similarly (**VI**) in (iii), (**IX**) in (iv), (**XII**) in (v) respectively:

Scheme A.



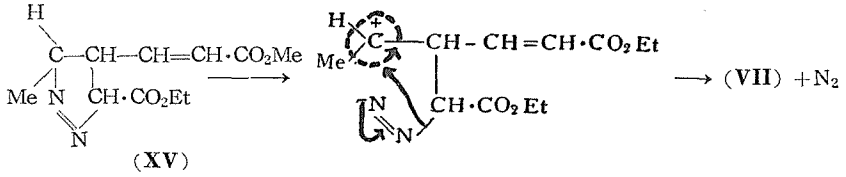
For the formation of acyclic isomer (**III**), the pyrazoline is postulated to decompose with migration of a hydrogen originally attached to γ-carbon atom and expulsion of nitrogen as shown below:

Scheme B.



For the formation of the cyclopropane derivatives, in which inversion of the ethylenic bond occurs during the addition, the intermediate pyrazoline (**XV**), possibly formed by the same process as in the case of (**XIV**), is postulated to decompose with expulsion of nitrogen and inversion at δ-carbon atom as shown below:

Scheme C.



The scheme of decomposition of the pyrazoline intermediate in each reaction would depend upon the reaction conditions employed.

The discussion is based on the experimental evidences described in the preceding part V[1].

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(1) Inouye, *ibid.* in press.
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(5) Guha, *Ber.* **70**, 1688 (1937).