# Thermal Ring Opening of *exo,exo*- and *exo,endo*-1,3-Diethyl-2,4-dimethoxycarbonylbicyclobutane

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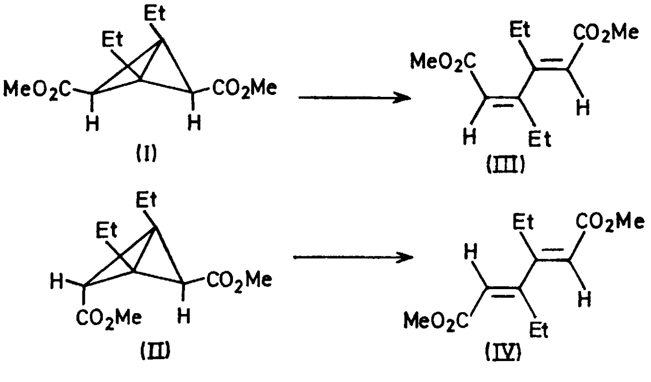
*Summary* Ring opening of *exo,exo*- and *exo,endo*-1,3-diethyl-2,4-dimethoxycarbonylbicyclobutane at 300—400 °C and 1—3 s reaction time follows the Woodward–Hoffman rules.

BICYCLOBUTANES isomerize thermally to butadiene derivatives by a $[_{\sigma}2_s + _{\sigma}2_a]$ process.[1,2] The steric course of the reaction may, however, be masked by isomerization of the products. Thus, the *exo,exo*-1,3-diphenyl-2,4-dimethoxycarbonylbicyclobutane was thought[3] to yield the unexpected *cis,cis*-3,4-diphenylmuconate, and only subsequently it was realized[4] that the latter resulted from primary, unstable *cis,trans*-muconate.

The presence of all possible dienic isomers in the product could also be due to a non-concerted mechanism or to two consecutive concerted reactions involving a cyclobutene intermediate. The above *exo,exo*-compound can also isomerize[4,5] thermally to the corresponding *endo,endo*-isomer;† this, however, would not alter the stereochemical consequences of ring opening.



We have studied the pyrolysis of the *exo,exo*-(I) and the *exo,endo*-(II)—1,3-diethyl-2,4-dimethoxycarbonylbicyclobutane, prepared from $CHN_2CO_2Me$ and 1,2-diethyl-3-methoxycarbonylcyclopropene.[8,9] The isomers have *m/e* 226 and except for some differences in ion intensities, identical fragmentation patterns. The *exo,exo*-structure was assigned to (I) by n.m.r. (in $CDCl_3$), which showed one signal each for the two ring protons, δ 1·25 (s, 2H) and OMe groups 3·68 (s, 6H). The spectrum for (II) fits the *exo,endo*-isomer, δ 2·37 (s, 1 ring-H), 2·72 (s, 1 ring-H) 3·64 (s, 3 $OCH_3$) 3·69 (s, 3 $OCH_3$).

Ring opening of (I) and (II) started at *ca.* 250 °C. At relatively long reaction times, particularly at higher temperatures, (III), (IV) as well as the *cis,cis*-isomer (V), are formed in substantial amounts. However, similarly to the 3,4-diphenyl-diene esters, (III)—(V) interconvert thermally. Hence, for the study of the ring opening step secondary isomerization must be avoided. The required short reaction times can be produced by pyrolysing in a flow of He (see Table). For structural assignment, pure muco-

*Thermal ring opening of* (I) *and* (II) *to dienic esters*

| Temp. (°C) | Time (s) | Muconates (%)[a] (III) | (IV) | (V) |
|---|---|---|---|---|
| | | Pyrolysis of the *exo,exo*-isomer (I) | | |
| 350 | 1·4[b] | 1·0 | 0·0 | 0·06 |
| 350 | 2·8[c] | 1·6 | 0·0 | 0·1 |
| 400 | 1·3[b] | 9·9 | 0·8 | 3·1 |
| 400 | 2·6[c] | 11·6 | 2·5 | 5·6 |
| 420 | 60—90[d,e] | 34·4 | 30·8 | 34·8 |
| | | Pyrolysis of the *exo,endo*-isomer (II) | | |
| 300 | 1·5[b] | 0·0 | 2·1 | 0·05 |
| 300 | 3·1[c] | 0·0 | 2·4 | 0·1 |
| 320 | 15·0[d] | 2·0 | 34·0 | 6·0 |
| 350 | 1·4[b] | 0·0 | 31·0 | 1·8 |
| 350 | 2·8[c] | 1·0 | 55·4 | 7·7 |

[a] Calc. on initial bicyclobutane; impurities present in the samples were not affected by the pyrolysis. [b] In a copper tube 20 in × ¼ in. mounted in an F & M model 500 chromatograph; the He (200 ml/min) was preheated to 200 °C. Samples of 10 μl of (I) or (II) (5% in n-decane) were injected repeatedly. Control of the instrument parameters was not accurate enough to permit rate measurements. The product, collected at the outlet, was analysed on a 50 ft × 0·02 in. SCOT column containing Carbowax 1540, at 150 °C and 20 lb/in² He; retention times (min): (III) 32·0, (IV) 28·0, and (V) 25·5. [c] Conditions as under (a), but He flow 100 ml/min. [d] Carried out in an ordinary laboratory pyrolysis furnace. [e] In addition to the muconates, taken as 100%, the product contained some residual (I) as well as an unidentified by-product, formed only at relatively long times.

† The *endo,endo*-configuration has been established,[4,5] after disproving the cyclobutene structure first assigned to the compound.[3] A claim by some of us[6] to have isolated *endo,endo*-1,3-di-n-propyl-2,4-dimethoxycarbonylbicyclobutane has recently been shown to be in error. On re-examination of the compound we found a weak absorption at 1908 cm⁻¹, characteristic of cyclopropenic double bonds. The i.r. and n.m.r. data[6] support the structure 1-methoxycarbonyl-2,3-di-n-propylcycloprop-2-ene-1-acetic acid methyl ester, in agreement with that reported for the ethyl ester.[7]

nates were isolated from the pyrolysate of (I) at 420 °C by thick l.c. on silica gel, followed by preparative g.l.c.[6] Unambiguous spectral evidence for the configuration of the esters has been reported.[10] The solvent shift ($\Delta$) of the allylic methylene groups in $C_6D_6$, as compared with $CDCl_3$, further confirmed[11] the structure assigned to (I) ($\Delta$ +0·10 p.p.m.) and to (II) ($\Delta$ +0·010 p.p.m.).

The results at the shortest reaction times permit the conclusion that ring opening proceeds in accordance with the rules of Woodward and Hoffmann,[2] since (I) is transformed essentially into the *cis,trans*-muconate (III), and (II) into the *trans,trans*-ester (IV). The small amount of (V) found even at 1·5 s is probably due to some secondary isomerization rather than to a steric "leak" in the first step. However, kinetic data are required to prove this point rigorously. The cyclobutene pathway, which could lead from (I) to (V), seems to be excluded. This mechanism would be expected in the case of (II) to form 1,2-diethyl-*cis*-3,4-dimethoxycarbonylcyclobutene,[2] which should then give (III) and not (V).

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