

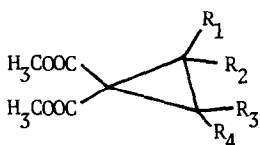
THERMAL REARRANGEMENT OF CYCLOPROPYL AND ALKENYL MALONIC ESTERS

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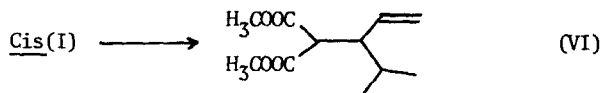
The thermal rearrangement of cyclopropyl ketones to homoallylic ketones is a efficient process which has recently become well documented(1-3). We now wish to report the thermal rearrangement of substituted cyclopropyl esters and to supply a new allylic transformation which occurs at higher temperature.



- (I) $R_1=C_2H_5, R_2=R_4=H, R_3=CH_3$
- (II) $R_1=R_3=CH_3, R_2=R_4=H$
- (III) $R_1=R_2=R_3=CH_3, R_4=H$
- (IV) $R_1=R_2=R_3=R_4=CH_3$
- (V) $R_1=t-Bu, R_2=R_3=R_4=H$

Stereospecific bis-carbomethoxy cyclopropanes were prepared by irradiation of methyl diazomalonnate in olefin(4). The starting material was purified by gas chromatography. All rearrangements were carried out on samples sealed in Pyrex tubes without degassing. After heating, the reaction mixtures were analyzed by vapor phase chromatography, and the structures of the isolated samples determined by n.m.r., infrared and mass spectra.

When cis(I) was heated at 185° for several hours, only five percent rearranged product(VI) was produced and no trans(I) obtained. At temperatures above 245°, rearranged material was found to be the main product that developed.



The reaction profile in Fig. 1 demonstrates that the initial rate of formation of (VI) is much faster than that of the trans(I).

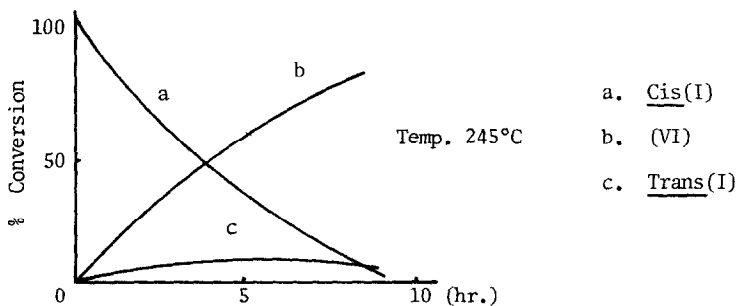
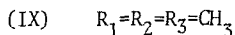
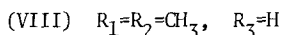
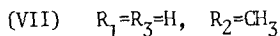
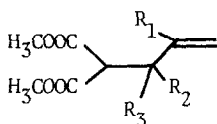
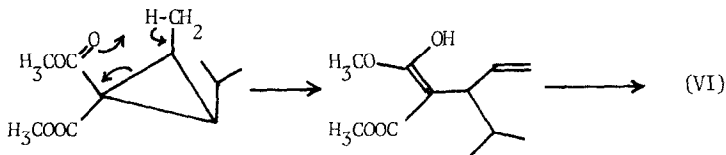


Fig. 1 Pyrolysis of Cis(I)

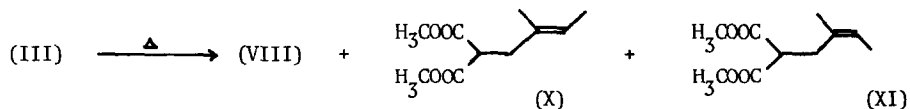
Similar results were obtained in other cyclopropanes. When (II), (III), and (IV) were heated at temperatures above 170° for several hours, nearly quantitatively (VII), (VIII), and (IX) were obtained.



However, (V) was stable under the conditions. Over a period of 24 hours at 300°, it decomposed only slightly. A cis relationship between the carbonyl and methyl group in the cyclopropyl malonate compounds may be necessary for intramolecular mechanism proposed for these rearrangement(5,6). Furthermore, a geometrical restraint on the hydrogen shift of the tertiary isopropyl hydrogen appeared. This is apparently by a steric effect of the two methyl groups.



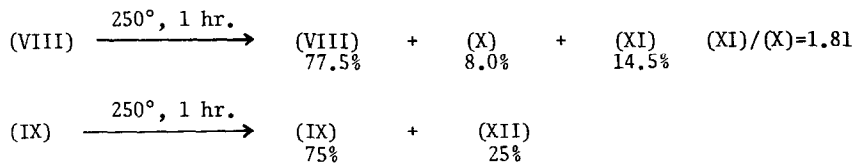
A further interesting thermal rearrangement was observed. When compound(III) was heated at temperatures above 250°, (X) and (XI) were observed with (VIII). The ratio of the products changed slowly with increasing reaction temperature and time. Similar rearrangement was also observed in compound(IV).



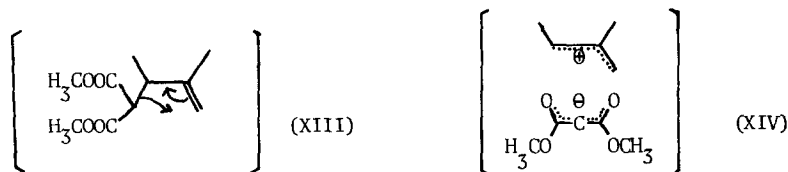
Temp.	Time (hr.)	(VIII)	(X)	(XI)	
170°	12	92%	5.3%	2.7%	
220°	1	78.3	7.5	14.2	
250°	1	46.6	19.6	33.8	(XI)/(X)=1.72



These above experiments suggest that (X) and (XI), and (XII) are formed from the thermal rearrangement of (VIII) and (IX), respectively. In order to test this, (VIII) and (IX) were heated under the above conditions.



These preliminary results show clearly the allylic transformation in which concerted process (XIII) or ion pair intermediate(XIV) may be important.



Further studies to determine the nature of the thermal allylic transformation and the effect of the substitution are in progress.

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