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THE THERMAL REACTION OF VINYLOXIRANE

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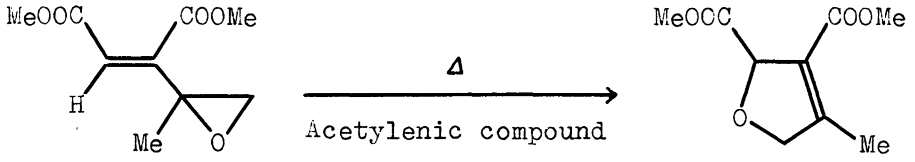
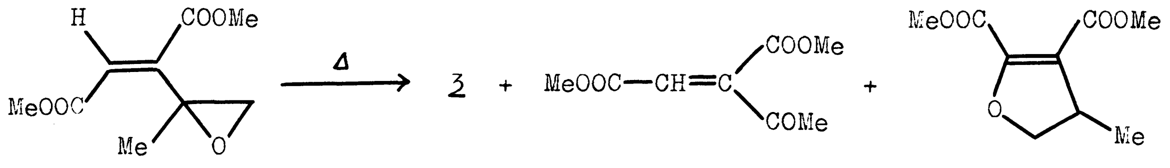
Methyl 4,5-epoxy-3-methoxycarbonyl-4-methyl-trans-2-pentenoate gave dimethyl 4-methyl-2,5-dihydrofuran-2,3-dicarboxylate on being heated with acetylenic compounds, while methyl 4,5-epoxy-3-methoxycarbonyl-4-methyl-cis-2-pentenoate gave methyl 3-methoxycarbonyl-4-oxo-2-pentenoate as a main product.

In the thermal reaction of vinyloxirane, 2,3-dihydrofuran derivatives were produced by cleavage of the C-C bond, and the formation of a carbonyl ylide intermediate was supported as the mechanism of this reaction.[1,2,3] On the contrary, 2,5-dihydrofuran derivatives have not yet been obtained by the thermal reaction of vinyloxirane. However, the formation of 2,5-dihydrofuran intermediate via vinyloxirane was estimated in the reaction of an α,β-unsaturated ketone with dimethylsulfonium methylide.[4,5]

Now, we wish to report outline of the interesting results obtained by the thermal reaction of methyl 4,5-epoxy-3-methoxycarbonyl-4-methyl-trans-2-pentenoate 2a and methyl 4,5-epoxy-3-methoxycarbonyl-4-methyl-cis-2-pentenoate 2b.



2a 3



2b 4 5

These compounds were synthesized in the photoreaction of dimethyl acetylenedicarboxylate 1 and propylene oxide. In a separation of these products with gas chromatography above 200°C, a rearrangement or a decomposition was observed. The thermal reaction of 2a in the presence of 1 led to the formation of dimethyl 4-methyl-2,5-dihydrofuran-2,3-dicarboxylate 3, but in the absence of 1, more than 90% of 2a was recovered. On the other hand, 2b mainly decomposed to methyl 3-methoxycarbonyl-4-oxo-2-pentenoate 4 in the absence of 1, and also gave a small amount of 3 and dimethyl 3-methyl-2,3-dihydrofuran-4,5-dicarboxylate 5.

Then, in order to see the effect of an acetylenic compound on the thermal reaction, the following experiments were carried out. An equal molar amount of an acetylenic compound was added to a chlorobenzene(2 ml) solution of 2a or 2b (5×10^{-2} mmol) in a pyrex tube. The tube was sealed under reduced pressure and heated at 240°C for two hours. The products were analysed by gas chromatography at 160°C, and the results obtained were shown in Table 1.

Table 1. Thermal reaction of 2a and 2b in the presence of acetylenic and olefinic compound

	2a	2b		
Acetylenic and olefinic	Yield(%)[a]			
compound	3	3	4	5
Dimethyl acetylenedicarboxylate	34.7	4.0	1.7	6.2
Methyl propiolate	23.5	7.5	1.4	4.6
Phenylacetylene	34.1	10.1	57.8	4.6
1-Phenylpropyne	28.9	14.1	56.0	1.3
Diphenylacetylene	4.0	10.3	66.2	3.1
Dimethyl maleate	4.7	3.7	74.6	3.5
None	2.8	2.8	50.1	5.9

a) Based on 2a and 2b.

As seen from the table, the formation of 3 from 2a was accelerated by most of the acetylenic compounds used, however the treatment with diphenylacetylene had no effect on the reaction. Further, it was confirmed that 2a hardly gave 3 in the presence of olefinic ester such as dimethyl maleate. In contrast to the results obtained in the case of 2b, 4 and 5 were not detected in the reaction mixture of 2a without regard to the addition of acetylenic compound. On the other hand, an isomerization and a decomposition of 3 or 5 were not observed under the same conditions. From these results thus obtained, it seems likely that the formation of 3 from 2a is responsible for the rearrangement with cleavage of the C-O bond, and the acetylenic compounds play an important role in this reaction.

On heating in the absence of acetylenic or olefinic compound, 2b gave 4 as the main product, and 3 and 5 as minor products. The conversion of 2b to 4 is characteristic of the elimination of methylene group, and a similar behavior is hardly found out in a previous study. This conversion was slightly accelerated by acetylenic hydrocarbons and olefinic ester, while the treatment with acetylenic esters gave a poor yield of 4. By a separate experiment, it was observed that the acetylenic esters reacted with 4 under the same conditions. The formation of 3 from 2b was somewhat increased by the addition of acetylenic hydrocarbons. Thus, it seems that 2b is rearranged into 3 without intermediate formation of 2a, however the mechanism is not sufficiently explained.

In conclusion, it is interesting to note that the rearrangement of 2a is accelerated by the addition of acetylenic compounds, and the conversion of 2b takes place with the elimination of methylene group. Further investigation is awaited to interpret these mechanisms.

The identification of products was accomplished by the following spectroscopic data and elemental analyses.

3: MS, m/e; 200(M^+), 185, 170, 169, 155, 153, 141(base peak), 123, 95, 59.
IR(CCl_4); 1753 and 1726(C=O), 1658 cm^{-1}(C=C).
NMR(CCl_4, 100MHz); δ = 2.18(3H, s, C-CH_3), 3.76(6H, s, $COOCH_3$), 4.66-4.90(2H, m, O-CH_2), 5.16-5.36(1H, m, CH-COO).
Anal; Found: C, 53.50; H, 5.98%. Calcd for $C_9H_{12}O_5$: C, 53.99; H, 6.06%.

4: MS, m/e; 186(M^+), 171, 170, 155(base peak), 139, 123, 113, 59.
IR(CCl_4); 1726(C=O), 1615 cm^{-1}(C=C).
NMR(CCl_4, 100MHz); δ = 2.50(3H, s, CO-CH_3), 3.78(3H, s, $COOCH_3$), 3.85(3H, s, $COOCH_3$), 5.33(1H, s, CH=C).
Anal; Found: C, 51.52; H, 5.38%. Calcd for $C_8H_{10}O_5$: C, 51.61; H, 5.41%.

5: MS, m/e; 200(M^+), 185, 169, 153(base peak), 141, 109, 59.
IR(CCl_4); 1745(C=O), 1638 cm^{-1}(C=C).
NMR(CCl_4, 100MHz); δ = 1.25(3H, d, J=7Hz, C-CH_3), 3.10-3.50(1H, m, CH), 3.64(3H, s, $COOCH_3$), 3.75(3H, s, $COOCH_3$), 4.08(1H, dd, J=6 and 9Hz, CH_2), 4.56(1H, t, J=9Hz, CH_2).
Anal; Found: C, 53.85; H, 6.03%. Calcd for $C_9H_{12}O_5$: C, 53.99; H, 6.06%.

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