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THE UNUSUAL THERMAL ISOMERIZATION IN A SERIES OF SUBSTITUTED BICYCLOBUTANES AND CYCLOBUTENES.

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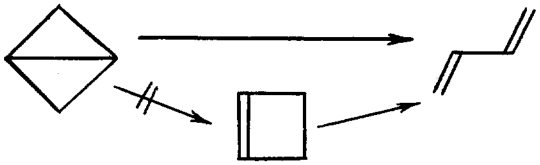
The tendency for bicyclobutane and its derivatives to undergo thermal isomerization forming butadiene-1,3 and its derivatives has of late been reported more than once[1-6]. The recent study of thermal isomerization kinetics of bicyclobutane itself[5,6] has facilitated clearing up the mechanism of this reaction. The investigations performed, permitted to draw a conclusion that the end product of isomerization, that is butadiene-1,3, forms directly from bicyclobutane rather than from the intermediate cyclobutene as one would suppose due to the wellknown property of cyclobutenes to isomerize thermally to yield the corresponding derivatives of butadiene[7].



An analogous conclusion concerning the mechanism of bicyclobutane ring isomerization has been drawn as a result of studying the thermal transformation of 1,3-dimethylbicyclobutane into 2,3-dimethylbutadiene-1,3[4]. As to the possibility of obtaining cyclobutene and its derivatives by the thermal isomerization of bicyclobutane and its derivatives up to now no data are available.

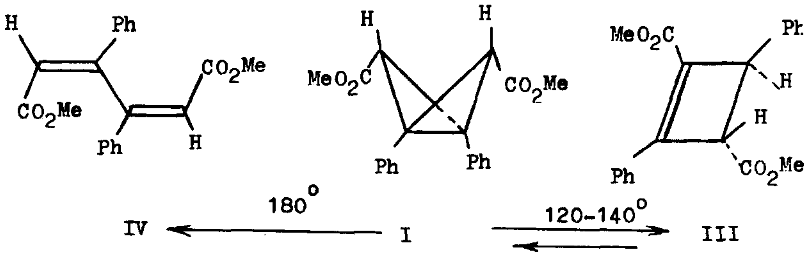
The present paper deals with the description of thermal transformations of dimethyl esters exo-exo (I) and exo-endo (II) isomers of 1,3-diphenylbicyclobutanedicarboxylic-2,4 acid and isomeric to them dimethyl ester of trans-1,3-diphenylcyclobutene-1-dicarboxylic-2,4 acid (III). All the three compounds (I),(II),(III) along with the fourth isomer - dimethyl cis-cis-2,3-diphenylmuconate (IV) - resulted from the reaction between methyl diazoacetate and methyl 1,2-diphenylcyclopropene-1-carboxylate-3 in the presence of Cu-bronze[8]. Not only does study described here amplify the results of earlier experiments in the same sphere, but it also shows the ways of thermal transformations in the series of substituted bicyclobutanes and cyclobutenes to be rather more complex than it has been considered formerly.

This can be best illustrated by the data obtained from the thermal isomerization of the ester (I). If this ester is heated for two hours at 180°, it transforms, as expected into the isomeric ester (IV). But if the same experiment is carried out at a lower temperature, viz. 120-140°, no formation of the ester (IV) is observed at all. Instead, a partial isomerization of the initial (I) into the ester (III) takes place. For example, the ester (I) having been heated for two hours at 130°, 53% of it were found to be transformed into the ester

(III); we succeeded in isolating the unchanged ester (I) in the amount of 30% of the initial weight.

Unlike the isomerization of bicyclobutane into butadiene which is a purely valent isomerization, the transformation of the bicyclobutane (I) into the cyclobutene (III) takes place due to the breaking of the diagonal bond in the ester (I) and the simultaneous migration of one hydrogen atom in a bicyclobutane ring to the neighbouring carbon atom. As mentioned above such an isomerization has never been observed formerly. Bisides, the new reaction turned out to be a reversible one. It has been discovered that heating the ester (III) for two hours at a temperature of 130° results in its, at least 25%, transformation into the ester (I). After the experiment had been over, 60% of the initial unchanged ester (III) was isolate. In case the ester (III) is heated up to 180° it will like the ester (I) isomerize (and now irreversibly) into the diene structure ester (IV). For instance, when heating the ester (III) for 2 hours at 180° it was found that 30% of it isomerized into the ester (IV). Besides, isolated from the products of the reaction were the ester (I) and the unchanged ester (III) in the amounts of 24% and 28.5% of the initial ester (III), respectively.

Due to the fact that the ester (IV) cannot be a product of direct isomerization of the ester (III), the formation of the (IV) from the (III) should be obviously accounted for by the transformation of the latter first into the (I) which in its turn gets isomerized into the (IV) irreversibly.



Because of the difficulties in the quantitative detection of substances formed during the thermal isomerization no exact data on the equilibrium composition in the system (I) $\rightleftarrows$ (III) are now available. Basing on the data so far obtained one can believe the ratio of the isomers (I) and (III) in an equilibrium mixture at a temperature of 130° to be close to 1 : 2. At 130° the equilibrium time is approximately two hours.

The exo-endo isomer (II) is subjected at 180° to the same valent isomerization as the isomer (I), for the only product of the isomerization is the ester (IV). However, when carried out under milder conditions the reaction goes in the direction of forming a dimethyl ester of trans-trans-2,3-diphenylmuconic acid (V)*) representing a less stable geometrical isomer

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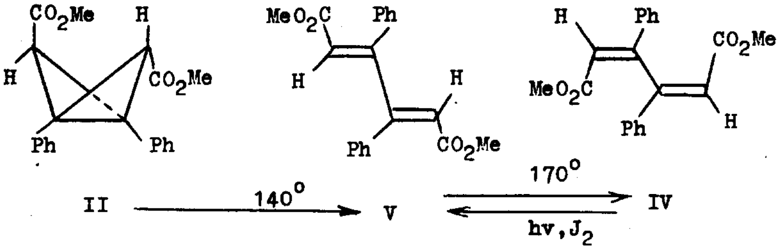
*) We were first to obtain dimethyl trans-trans-2,3-diphenylmuconate (V): m.p. 152°,UV-spectrum (C_6H_{12},mμ): λ_{max}264 (log ε 4.05); IR-spectrum (CCl_4,cm^{-1}) ν_{max}: 1732 (-C=O), 1620, 1605 (conj.C=C);NMR-spectrum (CCl_4,τ): 2.63 M(C_6H_5); 4.20 S(=C-H); 6.55 S(OCH_3). The compound to which this formula was assigned formerly[9,10], did not prove to be an ester of 2,3-diphenylmuconic acid as follows from our investigations.

of the ester (IV). Thus, a one-hour heating of the ester (II) at 140° resulted in the ester (V) with 18% yield of the theoretically possible one. The ester (IV) was never found upon isomerization, and the quantity of the recovered ester (II) was 53% of the initial weight. When raising the temperature up to 170° (the heating time is two hours) 100% of the initial ester (II) gets transformed, but along with the ester (V) there appears a considerable amount of the stable isomer (IV) in the products of the reaction (the yields of the (V) and (IV) being 16 and 68% respectively). Unlike the ester (I) no traces of the cyclobutene (III) could be noticed in any of the experiments. In all cases ester (V) should be considered to be an initial product of the isomerization (II), which ester then transforms under rigid conditions into a stereoisomer (IV). We also observed a reverse transformation of (IV) into (V) when the solution of the (IV) in cyclohexane was exposed to the sunlight in the presence of J_2.



The observed differences in the character of thermal isomerizations of exo-exo and exo-endo isomers, (I) and (II), evidently are caused by the difference of their steric configuration and the ensuing unequal influence of the same groups upon some bonds of bicyclobutane ring.

The results of this work enable us partly to explain the appearance of the esters (III) and (IV) in the products of the reaction between methyl diazoacetate and methyl 1,2-diphenylcyclopropene-1 carboxylate-3 which was reported in the preceding paper[8]. As the reaction itself was carried out at a temperature of 115-120° its initial product - ester (I) - could already under the conditions of the experiment undergo partial transformation into the ester (III).

As stated above a higher temperature namely that of 170-180° is required to achieve the isomerization of the esters (I) or (II) into the ester (IV). Therefore, to account for the ester (IV) formation one should admit either appearance in the reaction medium of a "hot" bicyclobutane, partly isomerizing into the diene (IV) at a temperature lower than 170°, or lowering of the temperature of the isomerization of the (I) and (II) into the (IV) due to the catalytic effect of the reaction medium (Cu - bronze, reaction products, initial compounds).

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