

ON THE REACTION OF METHYL DIAZOACETATE WITH METHYL
1,2-DIPHENYLCYCLOPROPENE-1-CARBOXYLATE-3 AND THE
FIRST EXAMPLE OF EXO-ENDO ISOMERISM IN A SERIES
OF SUBSTITUTED BICYCLOBUTANES.

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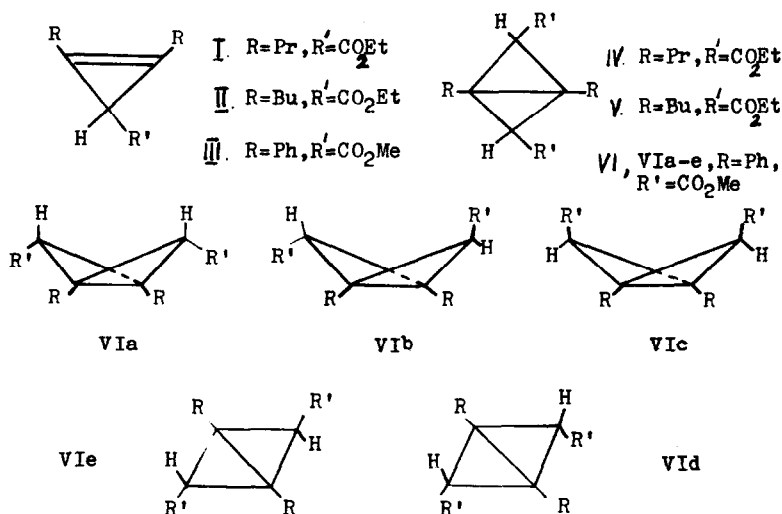
The addition of carbenes to an olefinic bond has often been used for creating the simplest bicyclic ring system i.e. bicyclo (0.1.1.) butane¹⁻¹⁰. Bicyclobutane itself was first obtained by intramolecular cyclization of allylcarbene³. In 1963 we stated that carboethoxycarbene (from ethyl diazoacetate) associates with an intracyclic carbon-carbon double bond of ethyl 1,2-dialkylcyclopropene-1-carboxylates-3 (I) and (II) to form diethyl 1,3-dialkylbicyclobutane dicarboxylates-2,4 (IV) and (V) respectively.*)

The paper deals with the investigation of the reaction between carbomethoxycarbene (from methyl diazoacetate) and methyl 1,2-diphenyl-cyclopropene-1-carboxylate-3 (III) as well as with the solution of the problem of the geometrical isomerism of the type (VI) derivatives i.e. methyl 1,3-diphenyl-bicyclobutanedicarboxylate-2,4 being a product of the

*) In a short time a more detailed information on this point will be published.

reaction involved.

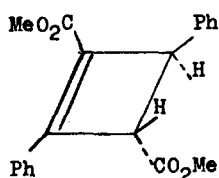
Predicted for ester (VI) may be three geometrical forms - exo-exo (VIa), exo-endo (VIb) and endo-endo (VIc) - in the case of non-planar configuration of bicyclobutane ring¹¹ and two forms - cis - (VIe) and trans- (VIe)- in the case of planar configuration. Thus, the investigation of the three-dimensional isomerism problem may give information on the configuration of the bicyclobutane ring in the type (VI) compounds as well.



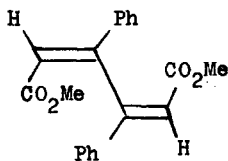
As a result of the reaction being investigated the formation of four isomeric to each other esters has been observed i.e. products of interaction between 1 mole of ester (III) and 1 mole of methyl diazoacetate: 1) exo-exo form (VIa), 2) exo-endo form (VIb), 3) dimethyl trans-1,3-diphenylcyclobutene-1-

*) Satisfactory analyses on C and H have been obtained for all the compounds.

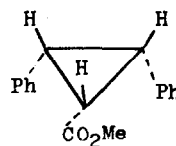
dicarboxylate-2,4 (VII) and 4) dimethyl cis-cis-2,3-diphenylmuconate (VIII). Besides, dimethyl maleate, dimethyl fumarate and some recovered ester (III) were found in the reaction products. The endo-endo form (VIc) failed to be isolated. It may be incapable for existence at all due to its instability. As to obtaining the other two stereoisomer forms (VIa and VIb) they are to be regarded as the first experimental support of the existence of exo-endo (rather than cis-trans) isomerism in a series of bicyclobutane derivatives. Hence, a conclusion can be drawn of a bent configuration of bicyclobutane ring. Obtaining compounds of cyclobutene (VII) and butadiene-1,3 (VIII) structures as by-products is considered to be a new feature of the reaction studied. The paper to be published in the nearest future will deal with the problem of forming these compounds.



VII



VIII



IX

The reaction under investigation was carried out at the temperature of 115-120° (the temperature of the bath) in the nitrogen atmosphere and in the presence of Cu-bronze as a catalyst by slow adding a solution of methyl diazoacetate in n-octane to a solution of ester (III) in the same solvent. Methyl diazoacetate was introduced into the reaction in an amount thrice as great as that precalculated. To separate the reaction

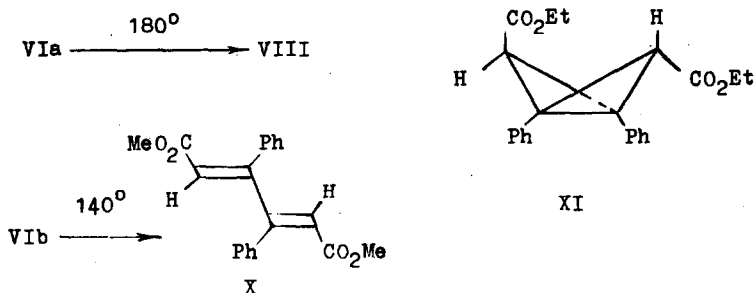
products a column-type chromatography on alumina with hexane-ether as the eluting solvent was used as well as fractional crystallization from organic solvents, while to isolate the ester (III) from the esters (VIa) and (VIb) catalytic hydrogenation over Pd-CaCO₃ followed by chromatography of the mixture (IX), (VIa), (VIb) was applied. The succession of melting points, the values of R_f and per cent yields of the esters (VIa), (VIb), (VII), (VIII) based on the unrecovered ester (III) are presented below: (VIa) 108-109°, 0.43, 7.0%; (VIb) 105-106°, 0.47, 4.4%; (VII) 118-119°, 0.19, 8.8%; (VIII) 114°, 0.31, 8.4%. The amount of the recovered ester (III) is 24% of the initial weight.

The structure of esters (VIa), (VIb) and (VII) not described before has been confirmed with the help of spectral as well as chemical methods. In the case of a known ester (VIII), its independent synthesis has been brought about¹². The identification has been carried out according to the mixture probe and IR, UV and NMR spectra. The spectral characteristics first obtained for this compound are as follows: IR (CCl₄, cm⁻¹): λ_{\max} 1730 (C=O); 1635, 1610 (C=C-C=C). UV (C₆H₁₂, m μ): λ_{\max} 272 (log ϵ 4.44). NMR (40mc, CCl₄, τ): 2.65 b. singlet (C₆H₅); 3.40 singlet (=CH); 6.40 singlet (OCH₃).

The ultraviolet spectra of esters (VIa) and (VIb) show absorption at λ_{\max} 223 m μ (log ϵ 4.12) and at λ_{\max} 220 m μ (log ϵ 4.11) with infl. λ 233 m μ (log ϵ 4.00) respectively, which makes it impossible to take into account any other structure formulae for these compounds containing chromophores: C₆H₅ > < , C₆H₅ > < C₆H₅ (cis), C₆H₅ > < COOR (cis-) /see 13/. In infrared spectra of the esters (VIa) and (VIb) no double bond absorption has been observed. An absorption has been found for

the C=O bond in ester groups at 1745 cm^{-1} and 1742 cm^{-1} respectively.

Giving up the formulae with double bond for the esters (VIa) and (VIb) leads to a conclusion of their belonging to a bicyclobutane series. An additional confirmation of this conclusion has been obtained when carrying out thermal isomerization of (VIa) and (VIb). As is known, bicyclobutane derivatives are subjected to thermal isomerization giving the derivatives of butadiene-1,3^{1,10,14}. At high temperature the esters (VIa) and (VIb) have been found by us to isomerize with the opening of the bicyclobutane ring into the cis-cis and trans-trans 2,3-diphenylmuconates (VIII) and (X), respectively. A more detailed information on this rearrangement will be reported in the next publication.



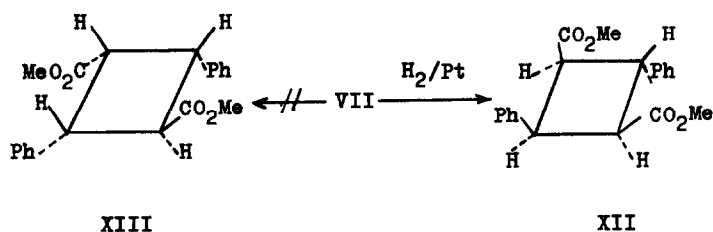
In order to establish the space configuration of the esters (VIa) and (VIb) their NMR-spectra have been analyzed. Here is a NMR-spectrum of the ester (VIa) (40 mc, CCl_4 , τ): 2.65 multiplet (C_6H_5); 6.60 singlet (OCH_3); 8.05 singlet (>C-H). The ratio of the squares of corresponding peaks is near 10 : 6 : 2. The NMR-spectrum of the ester (VIb) is (40 mc, CCl_4 , τ) 2.70 broad singlet (C_6H_5); 6.49 singlet (OCH_3); 6.59 singlet (OCH_3); 6.71 singlet (>C-H). The relative intensities of

corresponding signals are approximately 10,4,3,1. The fact that the protons of two methoxy groups of the ester (VIb) are nonequivalent may serve as an indisputable proof of its exo-endo configuration. All the other stereoisomers - (VIa), (VIc) as well as (VId) and (VIe) - have each pair of methoxyl groups located in the same space position. However, in the isomer (VIb) the protons of bicyclobutane ring are not in equal positions as in methoxy groups. The fact that only one signal (at 6.71τ) of a ring proton has been discovered in the NMR-spectrum of the ester (VIb) should be explained by the superimposing of a signal of another ring proton on that of the OCH_3 group. Such an explanation was confirmed after a NMR-spectrum of the diethyl ester (XI) had been taken: here, signals of both the ring protons (singlets at 6.51τ and 6.73τ) were obtained.

The ester (VIa) has quite a symmetrical structure. Therefore the protons of its methoxy groups as well as the protons of bicyclobutane ring are equivalent and each has one singlet signal in its spectrum. This ester may have both the (VIa) and the (VIc) configurations, the former being favoured due to its greater stability.

The features of the ultraviolet spectrum of the ester (VI) are in close accordance with its assumed structure: the maximum absorption at $270m\mu$ ($\log \epsilon 4.10$) indicates the presence of chromophore $\text{C}_6\text{H}_5\text{C}=\text{C}(\text{COOCH}_3)$ (cis-) responsible for absorption in this region /see 13,15,16/. In the NMR-spectrum (40mc, CHCl_3 , τ) only three signals have been found: 2.9 singlet (C_6H_5); 5.74 singlet (>C-H); 6.33 singlet (OCH_3). The ratio of intensities of the two last signals is 1 : 3 which complies

with the formula (VII). Yet, the character of the NMR-spectrum of the ester (VII) is not clear enough: for two non-equivalent ring protons AB type splitting of their signals would be expected. The final confirmation of the formula (VII) has been obtained as a result of hydrogenation of the ester (VII) over Pt up to dimethyl ester of the γ -truxillic acid (XII). The latter has been identified with the authentic sample of the ester (XII)¹⁷. If cis-addition of hydrogen to the double bond is assumed, the parent ester (VII) must evidently have trans-configuration. Another possible product of ester (VII) hydrogenation - dimethyl ester of epi-truxillic acid (XIII) - has not been obtained.



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