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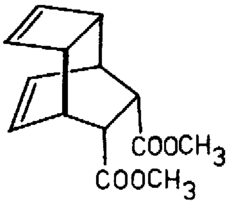
STEREOCHEMISTRY OF ELECTROPHILIC ADDITION TO DIMETHYL TRICYCLO$[4,2,2,0^{2,5}]$DECA-3,7-DIENE-9,10-DICARBOXYLATE. MOLECULAR STRUCTURE OF $Hg(OAc)_2$-ADDITION PRODUCT

Nikolai S.Zefirov*, A.S.Koz'min and V.N.Kirin
Department of Chemistry, Moscow State University, Moscow 117234, USSR
B.B.Sedov and V.G.Rau
Vladimir Pedagogical Institute, Vladimir, USSR

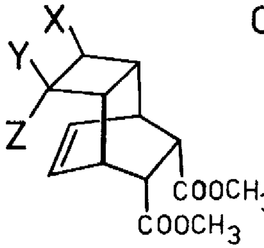
Summary - The molecular structure of the *trans* addition product of $Hg(OAc)_2$ to diester 1 has been determined by X-ray diffraction (represented by formula 3) which leads to a revision of previously claimed *cis*-additions in this series.

Commonly accepted suggestions about the formation of the bridged intermediates (onium ion[1], π-complex[1b], ion-pairs[2] etc.) in Ad_E-reactions[1] are based mainly on the observed *trans*-stereochemistry of these processes.

Hence, rare cases of *cis* addition always attract the attention. Some particular types of olefine structure are believed to be especially liable to undergo unusual *cis* additions, and the diester 1 is one of them. For example, T.Sasaki and co-workers [3] and G.Mehta and P.N.Pandey [4a] have stated that oxymercuration of diester 1 occurs on cyclobutene moiety as *cis* addition to yield the corresponding *cis*-oxymercurials 2 (X=OR, Y=HgCl, Z=H). Similar reaction course has been reported [4b] for the addition of iodine azide to diester 1.



1



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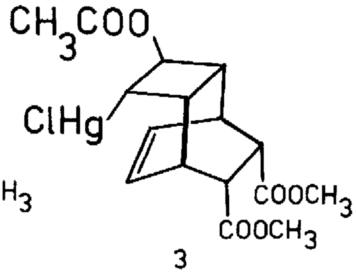

3

Both adducts **2** (X=OR, Y=HgCL, Z=H) and **2** (X=I, $Y=N_3$, Z=H) were shown to have similar stereochemistry by chemical correlation and their *cis*-configuration has been deduced from ^{1}H NMR data.

This alleged exclusive *cis* addition has been interpreted in term of twist strain theory. Additionally, G.Mehta and P.N.Pandey reported "the first non-stereospecific addition" of PhSCl to diester **1** which yields the mixture of *trans* adduct, **2** (X=PhS, Y=H, Z=Cl) and *cis* adduct, 2 (X=PhS, Y=Cl, Z=H)[5] (cf.[6]).

However, the thorough analysis of the experimental data for these "abnormal stereochemical results" reveals some discrepancies, which necessitates the revision of the whole picture.

Firstly, it is well known that stereochemistry of addition of mercuric salts depends on the structure of olefins [7]. However, the cyclobutene undergoes *trans* addition [8] and hence the data of Refs [3,4] cannot be correlated with the wealth of the other data on the structural effects governing the stereochemistry of oxymercuration reactions. Moreover, iodine azide is known to give *trans* adducts [9] exclusively and this fact makes doubtful *cis*-structure ascribed, **2** (X=I, $Y=N_3$, Z=H)[4b].

Secondly, the *cis* addition of $Hg(OAc)_2$ in methanol proceeds usually giving the mixture of acetoxy and methoxy mercurials while the formation of the single methoxy mercurial is typical result for the *trans* addition process[7]. In contrast, the oxymercuration of diester **1** with $Hg(OAc)_2$ in methanol proceeds surprisingly without formation of acetoxy mercuration product [3,4a].

Thirdly, carefull examination of the NMR criteria used for the configurational assignment of the compounds of type **2** revealed some severe inconsistencies in this approach [6,10]. These considerations allowed us to suggest that aforementioned Ad_E-reactions to **1** actually proceed as *trans* addition and the conclusions in Refs. [3-5] are based on the misinterpretation of the ^{1}H NMR spectra.

Previously we attempted to reproduce the results of Ref. [5], but invariably obtained only *trans* adducts **2** (X=ArS, Y=H, Z=Cl, Br) [6] in reactions of ArSZ with diester **1**; their structures have been unambiguously proved by X-ray method [10].

We have repeated the reaction of $Hg(OAc)_2$ with diester 1 in AcOH [3a,4a] and investigated the structure of the adduct (m.p.182° from ethylacetate) [12] by X-ray techniques. Experimental X-ray data were recorded using Syntex $P2_1$ autodiffractometer, Mo Kα. Crystals of the adduct are monoclinic, $P2_1/n$. The cell dimensions are a=10.273(6), b=15.316(8), c=12.226(6) Å, β=112.86°, $D_{calc.}$=2.032. The structure was solved by Patterson method and refined to R_{hkl}=0,078 for 2272 independent reflections. The X-ray molecular structure of the adduct is shown in Fig. 1 and represented by formula 3. There are two points which are clearly evident from our X-ray results: 1) oxymercuration of the diester 1 occurs as trans addition in contrast to the suggestions made in Refs. [3a,4a]. Hence all related cis structures must be revised or reinvestigated; 2) the initial attack of the cyclobutene double bond by electrophilic mercury salt is directed from endo-side. It is noteworthy that addition of other electrophiles such as halogenes [13], sulfenyl halides [6,13] etc. had been shown to proceed as an attack on the exo-side. Such an unusual mode of the initial approach of an attacking electrophile is probably due to the coordination of mercury ion by two double bonds (the discussion of this problem see [7,14]). This type of an attack on diester 1 has been also observed in oxypalladation reaction [3b].

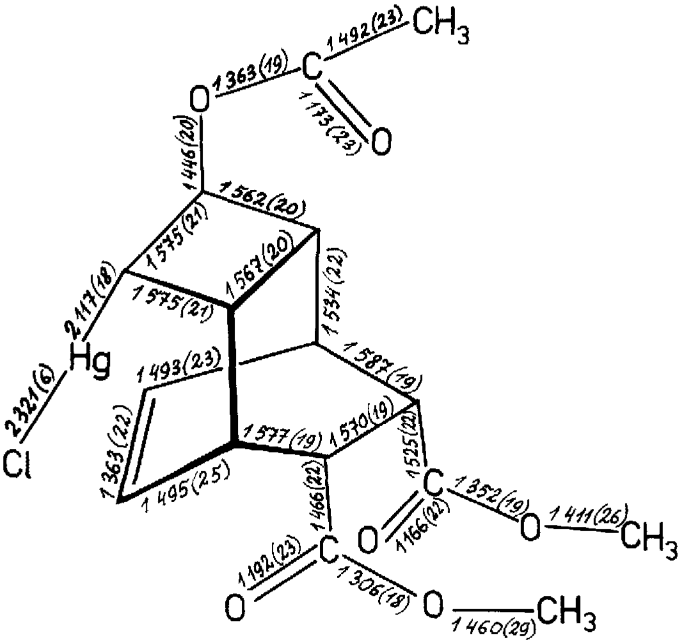

Fig.1. Molecular structure of dimethyl trans-3-endo-chlormercur-4-acetoxy-tricyclo[4,2,2,$0^{2,5}$]dec-7-ene-9,10-cis-endo-dicarboxylate.

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12. The reaction mixture [3,4a,6] was poured (instead of evaporating, cf.[3a,4a]) into excess of brine, the solid was filtered, washed with water, dried in vacuum and recristallised from AcOEt (recrystallisation from methanol[3a,4a] yielded the product with inorganic impurities) to give 89% of **3**.
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