METHOXYMERCURATION OF TRANS- AND CIS-1,3-DIPHENYLPROPENONE

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It is generally agreed that oxymercuration of simple unstrained olefins
is stereospecific[1] and that each geometric isomer reacts to give its
characteristic diastereomer uncontaminated with the other. Furthermore,
it has been pointed out[2] that in these cases diastereoisomers are normally
not interconvertible. Thus 1,3-diphenylpropenone (I) has been reported to
react with mercuric acetate in methanol to form 2-acetoxymercuri-3-methoxy-
1,3-diphenylpropanone (II) as a pure diastereomeric product[3] although its
configuration does not seem to have been studied. Recently Bloodworth and
Bunce[4] described the α-methoxymercuration of (I) but did not give any
configurational information.

In this note we report the results obtained from a relatively more
exhaustive study of the said reaction[3]. We now find that the reaction of
both the cis isomer (Ia) and trans isomer (Ib) of 1,3-diphenylpropenone
with mercuric acetate in methanol gives a mixture of diastereoisomers. It
was further observed that the composition of the mixture is independent
of the geoisomeric nature of the starting compound (I) being in both cases
ca. 7:3 with respect to S,R- (IIa) and R,R-2-acetoxymercuri-3-methoxy-
1,3-diphenylpropanone (IIb)[+].

The configurations of compounds (IIa) and (IIb) were assigned on the
basis of the NMR spectral data. In view of the relatively small
conformational preference of Hg, for example in cyclohexane systems[5], and
taking into account the fact that steric repulsion should normally demand

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[+] For simplicity only one of each pair of enantiomers will be mentioned.
The product proportions were determined from the areas under the methoxy-
proton resonance peaks. Spectra were recorded on a Varian A-60 instrument.

that the phenyl and carbonyl group be located as far away from each other
as possible, it seems reasonable to expect that each diastereomer would
show preference for that conformation in which these substituents have a
trans orientation ("a" for S,R and "b" for R,R). Further, since the
validity of the Karplus equation[6] has been shown to hold good for
cyclohexene methoxymercurials[1,7] having maximum values of coupling
constants of approximately 10 Hz for the two vicinal axial protons, it
seems reasonable to assign the higher value of the coupling constant $J_{2,3}$
to the diastereomer R,R.

The corresponding coupling constants and chemical shifts for (IIa) and
(IIb) are given below. A fairly good agreement of these chemical shifts
with those observed for 2-bromomercuri-3-methoxy-1,3-diphenylpropanone
may be noted.

Chemical shifts and coupling constants[+] ($J_{2,3}$) in S,R- (IIa) and
R,R-2-acetoxymercuri-3-methoxy-1,3-diphenylpropanone (IIb)

Diastereoisomer	Protons	Chemical shifts (τ)	$J_{2,3}$ (Hz)
(IIa)	$H_{(2)}$	5.42	6.8
	$H_{(3)}$	4.84	
	OCH_3	6.72	
(IIb)	$H_{(2)}$	5.25	9.8
	$H_{(3)}$	4.76	
	OCH_3	6.78	

[+] These values refer to solutions in $CDCl_3$. TMS was used as internal
reference.

It has been further observed that the corresponding product of
oxymercuration of (Ia) and (Ib) in methanol with or without perchloric,
nitric, hydrochloric and acetic acid, or their respective lithium salts
is always a mixture of the diastereomers (IIa) and (IIb) formed in the

same proportion (ca. 7:3) in each case The NMR spectral examination of interrupted reaction mixtures indicated absence of a possible isomerisation of the starting geometric isomers (Ia and Ib).

Attempts to separate the diastereomeric mixture by fractional crystallization from methanol showed that after the separation of the S,R isomer, the residue has the same composition as that of the original mixture. This seems to indicate that there takes place a gradual transformation of the R,R isomer into an equilibrium diastereomeric mixture from which the separation of the R,R isomer does not seem to be possible. Additional observation of interest in this connection consists in the fact that methanolic solutions containing only the S,R isomer with or without added acetic acid (in the same concentration as results from the oxymercuration reaction), when allowed to stand for intervals shorter than the reaction period were finally shown to contain a mixture of the corresponding diastereoisomers of the same composition as the original reaction product.

Thus, the observed interconversion of the diastereomeric oxymercurials which points to the fact that they cannot be considered as independent adducts, makes it desirable to interpret our results in the light of an apparently contradictory stereochemical nature of the reaction[1]. It seems possible to assume that the mercury of these compounds is ionisable because of its location adjacent to the carbonyl group as has been previously suggested[8], and that the mixture of products is the result of an equilibrium established after the oxymercuration reaction. It seems reasonable to postulate the formation of an intermediate of type " a' " which suffers transformation by conformational isomerisation and migration of mercury from one side of the enolate ion to the other (" b' ").

If the conversion of each enolate ion intermediate into the corresponding diastereomer is rapid, then the ratio S,R:R,R will depend on the energy difference between the two equilibrium intermediates. The higher stability of " a' " which would be responsible for the greater proportion

of the S,R isomer in the mixture is consistent with the postulation of
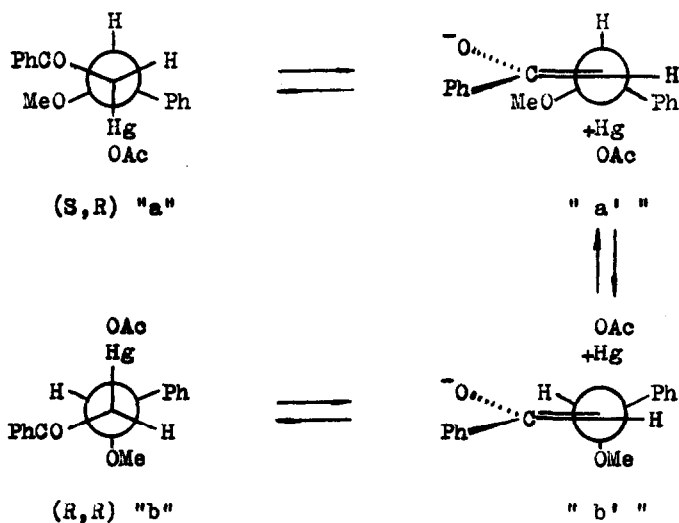
preferred orientation for mercury and oxygen on adjacent carbon atoms
as being gauche[9].

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