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Abstract

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DETERMINATION OF THE STEREOCHEMISTRY OF THE ADDITION OF MERCURY SALTS TO OLEFINS BY MEANS OF THE MERCURY SALT OF TRINITROMETHANE

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The addition of mercury salts to olefins may be—depending on their structure—both a cis- and a trans-addition. Thus, oxymercuration of olefins of the cyclohexene type proceeds as a trans-addition ([1,2]), whereas oxymercuration of norbornene ([1]) or of the dimethyl ester of 3,6-endoxotetrahydrophthalic acid ([2]) is a cis-addition.

In the works of S. S. Novikov and V. A. Tartakovskii with co-workers ([3–6]), it was shown for a number of examples that the mercury salt of trinitromethane (I) is capable of adding to a double bond according to scheme (A), with formation of derivatives of α-trinitromethylmercuri-γ-trinitropropane (III):

$$
\begin{array}{lll}
>C{=}C< + XHgX \rightleftharpoons >C{-}C< & & \\
\qquad\qquad\qquad\qquad\quad HgX & \qquad X = C(NO_2)_3 & (I) \\
\qquad\qquad\qquad\qquad\quad (II) & &
\end{array}
$$

$$
\begin{array}{llll}
(A) & X^- & \longrightarrow & X - \dot{C} - \dot{C} - HgX \\
 & & & (III) \\
(B) & H_2O & \longrightarrow & HO - \dot{C} - \dot{C} - HgX + HX \\
 & & & (IV)
\end{array}
$$

When the reaction is carried out in water, one may also expect the reaction to proceed according to scheme (B), with formation of derivatives of β-hydroxy-α-trinitromethylmercuriethane (IV). Under such conditions, however, formation of compounds of type IV is possible only if they are stable in an acidic medium, since the trinitromethane that is liberated is itself a relatively strong acid ($k = 6.8 \cdot 10^{-1}$ ([7])). Stereochemically, the course of the oxymercuration reaction according to scheme (B) should be identical for any mercury salts, especially if one takes into account the possibility of intermediate formation of a dicationic mercuronium ion.

As for the deoxymercuration reaction, according to the data of (8) it is initiated by reversible addition of a proton to the hydroxy or alkoxy group, with subsequent formation of an ion of type II. A kinetic study of the deoxymercuration reaction in an acidic medium showed that the activation enthalpy in the case of cis compounds is greater by 5-8 kcal/mole than for trans compounds, i.e., cis-IV (with $X = Cl$) are much more stable in an acidic medium than trans-IV (with $X = Cl$). The derivatives of type III ($X = C(NO_2)_3$), obtained according to scheme (A), are extremely stable in an acidic medium (5), since their demercuration must be accompanied by cleavage of a C—C bond.

Thus, the features of the addition of the mercury salt of trinitromethane (I) to a double bond are due, on the one hand, to the formation of a new C—C bond, which makes III stable in an acidic medium, and, on the other, to the relatively strong acidity of trinitromethane, which accounts for the instability of products of type IV under the reaction conditions.

On this basis, we believe that addition of the mercury salt of trinitromethane to a double bond can be used for determining

stereochemistry of the addition to it of other mercury salts. For this purpose one should carry out the reaction of some olefin with an aqueous solution of the mercury salt of trinitromethane; formation of an addition product of type III ($X = C(NO_2)_3$) will indicate that the oxymercuration of this olefin proceeds as a trans-addition, whereas formation of a product of type IV will indicate cis-addition.

Indeed, if the addition of a mercury salt to an olefin proceeds as trans-addition, then upon treatment of the olefin with an aqueous solution of the mercury salt of trinitromethane (I), only III will be formed. Formation of trans-IV will not occur, since, as noted above, compounds of this type, irrespective of the anion X, are extremely readily deoxymercurated under the action of acids, including the trinitromethane that is liberated: thus, for example, the addition of I to cyclohexene, irrespective of the solvent, always proceeds according to scheme (A) (4).

If the addition of a mercury salt to an olefin is cis-addition, then the reaction of this olefin with the mercury salt of trinitromethane (I) will proceed according to scheme (B), since the cis-IV formed, in contrast to trans-IV, is stable in acid medium and should not undergo deoxymercuration under the action of the trinitromethane liberated.

In the present work we have established that, for norbornene (V) and dimethyl 3,6-endoxotetrahydrophthalate (IX), addition of the mercury salt of trinitromethane (I) in water proceeds as cis-addition, i.e., with formation of products of type cis-IV according to the schemes:

The cis-configuration of VI was confirmed by a reverse synthesis of this compound from acetoxymercuri derivative VII (9). The exchange reaction of VII with sodium chloride led to cis-chloromercuri derivative VIII, identical with that reaction scheme: norbornene (V) reacts with I/H2O to give (VI), interconverting with acetoxymercuri alcohol (VII), which with NaCl gives chloromercuri alcohol (VIII); dimethyl 3,6-endoxotetrahydrophthalate (IX) reacts with I/H2O to give (X), which with NaCl gives (XI).

Figure 1: reaction scheme: norbornene (V) reacts with I/H2O to give (VI), interconverting with acetoxymercuri alcohol (VII), which with NaCl gives chloromercuri alcohol (VIII); dimethyl 3,6-endoxotetrahydrophthalate (IX) reacts with I/H2O to give (X), which with NaCl gives (XI).

described in the literature ([9]), while the exchange reaction with the mercury salt of trinitromethane gave VI. The cis-configuration of X was confirmed by converting it into chloromercuri derivative XI, the configuration of which had been established by us earlier ([2,10]).

It is probable that, for determining the stereochemistry of the addition of mercury salts to olefins, an alcoholic solution of the mercury salt of trinitromethane (I) can also be used; in that case, in the event of cis-addition, the reaction will lead to an alkoxy derivative.

Experimental Part

exo-cis-2-Trinitromethylmercuri-3-oxy-1,4-endomethylenecyclohexane (VI). a) A mixture of 0.3 g of norbornene (m.p. 44–44.5° in a sealed capillary) and 1.6 g of the mercury salt of trinitromethane (I) in 6.4 ml of water is stirred for 12 h and left overnight. The yellow precipitate that separates is filtered off, giving, in different experiments, from 0.8 g to 1.4 g of VI with m.p. 117-118° (after washing with petroleum ether).

Found, %: C 20.21, 20.18; H 2.50, 2.59, Hg 43.31, 43.25

$C_8H_{11}O_7N_3Hg$. Calculated, %: C 20.79; H 2.39; Hg 43.45

In some experiments, along with VI, an oil was obtained which, by analogy with ([4]), was probably a symmetrization product. b) A mixture of 0.6 g of norbornene and 2 g of mercuric acetate in 20 ml of water in the presence of 4 drops of nitric acid is stirred for 12 h and left overnight. The solution is separated into two equal parts, and to one of them an aqueous solution of sodium chloride is added. This gives 0.9 g of VIII with m.p. 124° (from aqueous alcohol). Literature data: m.p. 124–128° ([9]).

Found, %: C 24.13, 24.08; H 3.20, 3.15; Cl 10.33, 10.46; Hg 56.52, 56.59

$C_7H_{11}OHgCl$. Calculated, %: C 24.20; H 2.88; Cl 10.22; Hg 57.79

The second half is treated with an aqueous solution of I; a precipitate of VI with m.p. 117–118° separates at once. A mixed-melting-point test with the sample described above showed no depression of the melting point.

Dimethyl ester of exo-cis-4-oxy-5-trinitromethylmercury-3,6-endoxohexahydrophthalic acid (X). A mixture of 5 g of IX (m.p. 120°) with a solution of 11.5 g of the mercury salt of trinitromethane in 40 ml of water is stirred for 12 hr and left overnight. The precipitate is separated, giving 9 g (70%) of X as a light-yellow powder. After reprecipitation from ethyl acetate with petroleum ether, X is obtained as a white powder with m.p. 175–176°.

Found, %: C 22.87, 22.68; H 2.72, 2.68; Hg 34.40, 34.40
$C_{11}H_{13}O_{12}N_3Hg$. Calculated, %: C 22.77; H 2.24; Hg 34.61

Dimethyl ester of exo-cis-4-oxy-5-chloromercury-3,6-endoxohexahydrophthalic acid (XI). A mixture of 6 g of X and 0.7 g of sodium chloride in 180 ml of water is heated for 3 hr on a boiling water bath with stirring and left overnight. The precipitate is separated, giving 4 g (83%) of X; m.p. 246° (with decomp.; from methanol).

Found, %: C 25.95, 26.13; H 2.92, 2.98
$C_{10}H_{13}O_6HgCl$. Calculated, %: C 25.80; H 2.79

A mixed-melting-point test with authentic XI ([10]) showed no depression of the melting point.

Thus, for determining the stereochemistry of the addition of mercury salts across a double bond, an aqueous solution of the mercury salt of trinitromethane can be successfully used.

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Note: Figure translations are in progress. See original paper for figures.