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Abstract

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STEREOCHEMISTRY OF σ, π-CONJUGATION

α-CHLOROMERCURYCAMPHENILONE

At the beginning of 1950 one of us (1) compared a number of factors responsible for the reduced (or absent) ability to undergo substitution reactions at atoms (or groups) bonded to the carbon atom at the bridgehead of a bicyclic system. In October 1950 Fawcett' s review (2) on the same subject appeared. Inertness is interpreted there from the standpoint of Bredt' s rule (3) concerning the impossibility of formation of a double bond at the bridgehead of a bicycle. Indeed, a number of phenomena involving inertness of bridgehead atoms in bicyclic systems are naturally explained by Bredt' s rule–these include, for example, the inability of α-bicyclic ketones to enolize, and the impossibility of dehydration and dehydrohalogenation involving H, Hal, and OH atoms at the bridgehead. A number of other phenomena, such as the impossibility of decarboxylation of β-keto acids with a carboxyl group at the bridgehead (camphenilonecarboxylic acid, for example, distils without decomposition at 312°, whereas 1,3,3-trimethylcyclohexanone-2-carboxylic acid decomposes already at room temperature), and the inability of the hydrogens of camphenilone to exchange for deuterium even in the presence of bases (4) (in contrast to monocyclic ketones of analogous structure, 2,6,6-trimethylcyclohexanone and 2-methyl-6-spirodecanone), already requires special proof that the reactions of decarboxylation of β-keto acids and deuterium exchange in ketones proceed through the stage of enolization. The mechanism of decarboxylation is given in the works of Pedersen (5). The widely studied inability of a bridgehead halide to undergo substitution obviously has no relation to Bredt' s rule, but is explained by the necessity of Walden inversion in nucleophilic substitution. Meanwhile, Walden inversion in the rigid system of a bicycle at the bridgehead is impossible. Facts concerning the nonexchangeability of atoms at the bridgehead, which clearly cannot be explained in either of these ways, led one of us in 1950 to suggest that the axes of the σ- and π-electron clouds must be parallel for the full manifestation of σ, π-conjugation, and that conjugation is excluded when these axes are perpendicular (1). This requirement is an analogue of the requirement of planarity in a $\pi\pi$-conjugated system. The present work serves as an example of testing this hypothesis. In 1956, apparently without knowing our 1950 article, Corey and Sneen (5a) published an analogous assumption as applied to the enolization of cyclic ketones with different conformations of the α-C—H bond (axial and equatorial).

The α-chloromercurycamphenilone synthesized by us has a mercury atom bonded to the bridgehead carbon, which is at the same time the α-atom relative to the carbonyl. A mercury atom bonded to the α-carbon of ketones, both open-chain and cyclic, and of aldehydes possesses an exceptional exchangeability, far exceeding that of mercury in its alkyl compounds. α-Chloromercury oxo compounds are hydrolyzed by water in the presence of KI with replacement of mercury by hydrogen. The same replacement is effected by the action of dilute mineral acids in the cold. They are triphenylmethylated by triphenylchloromethane and are readily symmetrized by ammonia into α-mercuri-bis-oxo compounds. Their mercury atom readily undergoes isotopic exchange both with metallic mercury and with sublimate labeled by radioactive Hg^{203}, as was shown in the works of O. A. Reutov and U Yang-ni (^{6}). Symmetrical mercuri-bis-α-oxo compounds are even more reactive.

According to Winstein' s data (^{7}), mercury at the bridgehead in the absence of a carbonyl group (in 4-mercuri-bis-camphane), although less mobile than in dialkyl-

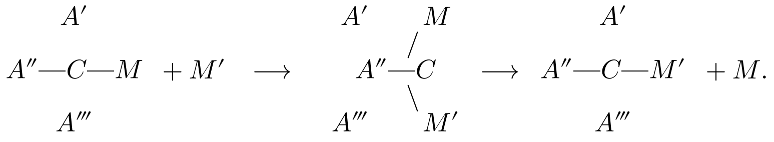
mercury is insignificant. Thus, it is replaced by halide under the action of aqueous solutions of strong mineral acids, or, on heating with concentrated acetic acid, by hydrogen.

4-Chloromercuricamphane is symmetrized under the action of sodium stannite to 4-mercuribiscamphane, and the latter with sublimate readily gives the initial chloromercuricamphane. The sum of these facts indicates that exchanges of this kind proceed without Walden inversion, which is impossible at the bridgehead. Indeed, direct experiments by one of us, O. A. Reutov, and Knoll (^{8}), and by Reutov with coworkers (^{9}), showed that exchange of $R'R''R'''HgCl$, both with Hg^{203} and with $Hg^{203}Br_2$, occurs without change of configuration. Consequently, the mere fact that the mercury is located at the bridgehead cannot be the reason for its inability to undergo exchange. Earlier, in work by one of us and I. F. Lutsenko (^{10}), it was shown that the cause of the mobility of mercury in α-mercurated oxo compounds is not enolization, but conjugation of the $Hg—C$ and $C = O$ bonds. Meanwhile, the mercury atom of α-chloromercuricamphenilone possesses exceptional inertness, unexpectedly exceeding even that of Winstein' s compounds. The influence of the α-carbonyl is completely excluded. At our request, O. A. Reutov and U Yan-tsei (^{6}) compared the exchangeability of mercury in α-chloromercuricamphenilone and in α-bromomercuricyclohexanone. In the first, exchange with Hg^{203} and with $Hg^{203}Br_2$ did not occur at all under any conditions (40 h, 75-100°), whereas in the second, exchange with the metal proceeded to 100% in 2 h at 23°, and with mercuric bromide in 2 h at 50° (acetone). Chloromercuricamphenilone does not react upon many hours' boiling with concentrated hydrochloric acid; the mercury-carbon bond is not affected by ordinary symmetrizing agents, including KJ; reaction with $(C_6H_5)_3CCl$ is absent. Symmetrization to di-α-

camphenilonylmercury was achieved only with difficulty, by heating to 215–220° the corresponding sulfide. The reaction $R_2Hg + HgCl_2 \rightarrow 2RHgCl$ (proceeding without Walden inversion) does proceed in our example, although slowly. Reaction with concentrated acetic acid is completely absent (80°, 13 h). Much more slowly than in Winstein' s compounds proceed both the reduction of chloromercuricamphenilone by $LiAlH_4$ and the reaction with iodine in dioxane. This exceptional inertness of the $Hg—C—C = O$ system, therefore, does not depend on the effect of Walden inversion and is not reducible to Bredt' s rule. The only remaining explanation is the exclusion of conjugation of the $Hg—C—$ and $C = O$-bonds as a result of the perpendicular arrangement of the axes of the electron clouds and the exclusion of the possibility of overlap of the latter.

The regularity formulated by us in 1950 and receiving further evidence in the present work is broader than Bredt' s rule. But it evidently includes Bredt' s rule as a special case. Indeed, overlap of the electron clouds of two σ and π electrons along one of the two pairs of σ- and π-bonds of neighboring carbon atoms is possible to the greatest extent when the axis of the σ-bond and the axis of the π-cloud are parallel. In this case the electron of the σ-bond to some extent begins to play the role of a π-electron, establishing (permanently or in the transition state) an incipient π-bond with the π-electron of the neighboring carbon. If, by the nature of the reaction, as a result of it such an incipient π-bond would have to pass into a real π-bond, Bredt' s prohibition comes into force.

The unexpectedly still greater inertness of mercury in α-chlorocamphenilone compared with Winstein' s compounds also requires explanation. It may be thought that the transition complex in substitution reactions (homolytic and electrophilic), proceeding without Walden inversion, has configuration (II).



$$\begin{matrix} & A' & & & & A' \quad M & & & A' & \\ A''—&C&—M + M' & \longrightarrow & A''—&C & \longrightarrow & A''—&C&—M' + M. \\ & A''' & & & & A''' \quad M' & & & A''' & \end{matrix}$$

(*I*) (*II*) (*III*)

and electrophilic), proceeding without Walden inversion, has configuration (II). The valence angles ACA must be compressed in (II) as compared with (I) or (III), and this should lead to an increase in the activation energy in substitution of an atom at the bridgehead of a bicycle with its rigid structure, diminishing-

to 109° of the C–C″–C valence angles and by the small possibility of further compression of the angles. Such an increase in the activation energy will be still greater if the bicyclic system, instead of a tetrahedral carbon atom with a natural valence angle of 109°, includes a carbonyl carbon with a natural valence angle of 120°, already compressed to a value smaller than 109°. Further compression in this case, as a deviation not from 109° but from 120°, should sharply increase the energy of the transition state. If this reasoning is correct, then replacement of the carbonyl oxygen in α-mercurated camphenilone by hydrogen should increase the mobility of mercury to the degree characteristic of Winstein' s substances. Conversely, replacement of O by CH_2 with formation of the grouping $C{=}CH_2$ should not change the immobility of mercury.

Experimental Part

Since direct mercuration of camphenilone does not proceed under any conditions, and the corresponding halogen derivative is unreactive, we used for our purposes the reaction, developed by Razuvaev and co-workers,[11] of decomposition of organic peroxides in the presence of mercury or mercury salts of carboxylic acids.

Camphenonoyl peroxide was obtained by prolonged shaking of an ethereal solution of camphenonic acid chloroanhydride (m.p. 31°)[12] with an alkaline solution of 10% hydrogen peroxide. The ether layer was extracted repeatedly with a 5% sodium bicarbonate solution. Yield of peroxide 22%, decomposition temperature 110-112°. Iodometric titration gave 91% active oxygen.

$C_{20}H_{26}O_6$.	Found, %:	C 66.46; 66.45; H 7.29; 7.39
	Calculated, %:	C 66.28; H 7.23.

Decomposition of camphenonoyl peroxide in the presence of finely divided metallic mercury in boiling benzene gives only α-phenylcamphenilone—a crystalline substance distilling with steam, m.p. 56-57° (from alcohol).

$C_{15}H_{18}O$.	Found, %:	C 83.93; 83.72; H 8.52; 8.56
	Calculated, %:	C 84.05; H 8.46.

Success was achieved by the reaction of camphenonoyl peroxide with the mercury salt of camphenonic acid, carried out without solvent, in the melt. Two grams of the mercury salt and 1.5 g of the peroxide were thoroughly mixed and cautiously heated, with rapid stirring, to 70-80°. The gradually developing reaction assumes an explosive character, with the liberation of a considerable amount of metallic mercury. After the explosion, the blackened reaction mass was heated for another 30 min.; then, after cooling, an aqueous acetone solution of an excess of potassium chloride was added to it. The mixture was stirred for 3-4 hours, left overnight, and distilled with steam. In the distillate was found α-bicamphenonoyl—a white crystalline substance with a characteristic terpene odor. Plates, m.p. 85-86° from alcohol.

$C_{18}H_{26}O_2$.	Found, %:	C 78.40; 78.52; H 9.33; 9.47
	Calculated, %:	C 78.79; H 9.55.

In addition, an unknown substance with m.p. 122–123° distills with the steam. A large amount of resin remains in the distillation flask, and from the aqueous portion extraction with ether gives 1.4 g of a mixture of camphenonic acid (1.2 g) and α-chloromercuricamphenilone (from 0.2 to 0.4 g). These substances are recrystallized from alcohol. α-Chloromercuricamphenilone is a well-crystallizing white substance, slightly soluble in water and readily soluble in most organic solvents; it does not dissolve in petroleum ether; m.p. 134–136°.

$C_9H_{13}HgClO$. Found, %: C 29.01; 29.01; H 3.46; 3.61; Hg 53.35; 53.34; Cl 9.23; 9.27
Calculated, %: C 28.96; H 3.51; Hg 53.74; Cl 9.49

Acidolysis of chloromercurcamphenilone with boiling conc. hydrochloric acid for 3 hours, or at room temperature for several days, did not take place at all. The starting product was recovered; reaction with H_2S gave only a white needle-like precipitate of the sulfide, m.p. 212–214° (from alcohol).

$C_{18}H_{26}Hg_2SO_2$. Found %: C 30.65; 30.77; H 3.74, 3.85
Calculated %: C 30.56; H 3.70.

In contrast to α-chloromercuracetone and its homologs, α-chloromercurcamphenilone does not react in aqueous solution with potassium iodide with formation of alkali, but gives iodomercurcamphenilone; from alcohol, needles with m.p. 134–135°. It decomposes on standing in the light.

$C_9H_{13}HgJO$. Found %: C 23.54, 23.60; H 2.88, 2.86
Calculated %: C 23.26; H 2.82.

In an attempt at symmetrization with sodium stannite at room temperature, we isolated a low-melting product possessing acidic properties: evidently the ring had opened under the action of alkali.

If chloromercurcamphenilone is treated with an aqueous solution of sodium thiosulfate on heating, the sulfide described above, m.p. 212–214°, is obtained. As a result of heating it to 215–220° for 15 min, extracting the black mass formed with acetone, and boiling the extract with activated charcoal, needles of di-2-camphenilonyldimercury were isolated, m.p. (from aqueous alcohol) 112–114°, in 80% of theory.

$C_{18}H_{26}O_2Hg$. Found %: C 45.77; 45.60; H 5.35; 5.33; Hg 42.39; 41.80
Calculated %: C 45.52; H 5.52; Hg 42.23.

The reverse symmetrization reaction with $HgCl_2$ in absolute ether, after 16 hours, gave chloromercurcamphenilone in 50% yield.

On heating di-α-camphenilonyldimercury to boiling with conc. HCl for 30 min, α-chloromercurcamphenilone was obtained in 88% yield; m.p. 131°.

Reduction of α-chloromercurcamphenilone with excess $LiAlH_4$ in ethereal solution at room temperature over 65 hours gave 72% α-bromomercurcamphenilone (LiBr was present in the reaction medium), m.p. 158°, and about 10% camphenilone, m.p. 84–86° (13).

$C_9H_{13}OHgBr$.	Found %:	C 25.67; 25.99; H 3.40, 3.38; Br 18.69; 18.97; Hg 47.72; 47.82
	Calculated %:	C 25.89; H 3.13; Br 19.14; Hg 48.0.

The reaction of iodomercurcamphenilone with iodine in absolute, peroxide-free dioxane was carried out in a stream of pure nitrogen. The system was evacuated to 0.5 mm and then filled with nitrogen. After eight such cycles the solutions of iodine and iodomercurcamphenilone were mixed at room temperature. No appreciable decolorization occurred. After 45 hours the amount of iodine in the reaction mixture was determined by titration. It was found that only 30% of the iodine taken had entered into reaction.

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