does not depend on the overlap factor between the vibrational wave functions of the T_1 state and the isoenergetic, C–H vibrationally excited S_0 level. It is the latter which is strongly affected by deuteration. The magnitude of the energy gap $T_1 \rightarrow S_0$, which otherwise determines the overlap factor,[13] may therefore be expected to be without any effect on the high rate of the radiationless $T_1 \rightarrow S_0$ process.

We conclude that positive evidence in favor of triplet intermediates is available, whereas evidence against them is either disputable or not relevant.

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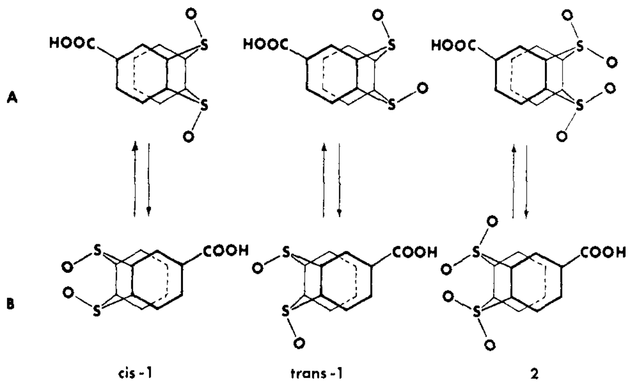
Conformational Flexibility of Thianthrene and Its Oxides[1]

Sir:

Thianthrene, the *cis*- and *trans*-5,10-dioxides, and the 5,5,10,10-tetroxide have folded structures in the crystal state,[2] with dihedral angles in the neighborhood of 130°. While dipole moment evidence[3,4] indicates that folding about the line joining the sulfur atoms is maintained in solution, it is recognized that the molecule of thianthrene and its derivatives oscillates rapidly through a planar position, as deduced from theoretical estimates[5–7] (3–7 kcal/mole) of the activation energy barrier which separates the folded molecule of thianthrene from its inverted form, from failure to separate the stereoisomers which result from folding,[5,8] and from dipole moment[4] and nmr[9] studies. Similar conclusions have been arrived at from studies of analogous heterocyclic systems.[6,8,10,11]

In light of the overwhelming evidence attesting to conformational flexibility in thianthrene and its derivatives, a recent report by Janczewski and Charmas[12] assumes particular importance. The finding by these authors that oxidation of the optically active forms[13] of *cis*- and *trans*-2-thianthrenecarboxylic acid 5,10-dioxide (**1**) affords optically active 2-thianthrenecarboxylic acid 5,5,10,10-tetroxide (**2**) is of far-reaching significance, for the following reasons. Isolation of optically active disulfone **2** demonstrates unequivocally that the tricyclic structure is *rigidly* folded; the resistance of **2** to racemization under the drastic conditions of preparation (oxidation of **1** with 30% hydrogen peroxide in glacial acetic acid at 105–115° for 5 hr) and purification (recrystallization from boiling glacial acetic acid) shows that a surprisingly high energy barrier (*i.e.*, of the order of 25 kcal/mole or greater[14]) separates the enantiomeric conformers of **2**; and the observation[12] that (+)-*cis*-**1** and (+)-*trans*-**1** both give (+)-**2** with $[\alpha]^{20}$D +18.18° while (−)-*cis*-**1** and (−)-*trans*-**1** both give (−)-**2** with $[\alpha]^{20}$D −18.18° can only mean that both *cis*- and *trans*-sulfoxides **1** contain the two possible diastereomeric conformers in *identical* ratios. The last point is illustrated in Chart I, with arbitrarily chosen configurations and conformations: only the same ratio of *cis*-**1A**:*cis*-**1B** and of *trans*-**1A**:*trans*-**1B** can result in the same ratio of (+)-**2**:(−)-**2**, *i.e.*, in the same optical rotation of **2**. Alternatively, the conformers of *cis*- and *trans*-**1** must exist predominantly in one of the two possible forms (*e.g.*, **A**), exhibiting a thermodynamic preference which is particularly unexpected for *trans*-**1**.

Chart I



We now report that the claims[12] of Janczewski and Charmas cannot be substantiated. The preparation and resolution of *cis*- and *trans*-**1** were repeated, giving results in essential agreement with those reported.[13] When racemic *cis*-**1** was heated for 5 hr with 30% hydrogen peroxide in glacial acetic acid at 105–115°, the product (±)-**2** had mp 306–308° (lit.[12] 312–314°, lit.[13] 300–301°, lit.[15] 302–303°) and an infrared spectrum identical with that reported.[12] *Anal.* Calcd for $C_{13}H_8O_6S_2$: C, 48.14; H, 2.49; S, 19.77. Found: C, 48.32, H, 2.44; S, 19.86; M^+, *m/e* 324. Oxidation of (−)-*cis*-**1** (mp 278–280° with resolidification and remelting at 296–298°[16], $[\alpha]^{25}$D −134° (1% aqueous sodium hydroxide); lit.[13] mp 285–287°, $[\alpha]^{20}$D −126.57° (1% aqueous sodium hydroxide)) under the same condi-

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(11) The conformational rigidity ascribed to conformers of 9-[(N-methyl-3-piperidyl)methyl]thioxanthene (W. Michaelis, O. Schindler, and R. Signer, *Helv. Chim. Acta*, **49**, 42 (1966)) is more properly described by the statement that one of the two forms (*i.e.*, the a′,a′ form in the *cis* isomer and the a′,e′ form in the *trans* isomer) exists as by far the most populous component in a *mobile* conformational equilibrium.[6]

(12) M. Janczewski and W. Charmas, *Roczniki Chem.*, **40**, 1243 (1966); for a preliminary report, see ref 13.

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(14) For example, taking the half-life of racemization as 10 min at 105°, if $\Delta S^{\ddagger}$ = 0 eu, $\Delta H^{\ddagger}$ = 27.3 kcal/mole.

(15) H. Gilman and D. R. Swayampati, *J. Am. Chem. Soc.*, **79**, 208 (1957).

(16) At the melting point the optically active forms of *cis*- and *trans*-**1** suffer racemization by pyramidal inversion at sulfur (*cf.* D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordon, and K. Mislow, *ibid.*, **88**, 3138 (1966)); furthermore, the *trans* form isomerizes to the *cis* form (K. Mislow, P. Schneider, and A. L. Ternay, Jr., *ibid.*, **86**, 2957 (1964)), mp 296–298°.

tions[12] afforded a product identical in melting point and infrared spectrum with (±)-**2**, $\alpha^{20}\text{D}$ 0.00 ± 0.01° (*c* 0.684, *l* = 2, 1% aqueous sodium hydroxide),[17] $\alpha^{27}{}_{\lambda}$ 0.000 ± 0.001° in the region 600–310 nm (*c* 0.317, *l* = 0.1, 1% aqueous sodium hydroxide).[18] Identical results were obtained starting from (+)-*trans*-**1** (mp 252–253° with resolidification and remelting at 296–298°,[16] $[\alpha]^{25}\text{D}$ +41.2° (1% aqueous sodium hydroxide); lit.[13] mp 262–264°, $[\alpha]^{20}\text{D}$ +40.17° (1% aqueous sodium hydroxide)).

The expected conformational flexibility of the thianthrene tetroxide system has thus been demonstrated, and the contrary conclusions[12] are invalidated.

[17] Schmidt and Haensch visual polarimeter.

[18] Cary Model 60 automatic recording spectropolarimeter.

[19] Public Health Service Postdoctoral Fellow, 1967.

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On the Purported SE1 Protolysis of Dibenzylmercury

Sir:

Several substitution reactions of organomercurials have been reported to proceed by the SE1 pathway in which ionization of the C–Hg bond to yield a carbanion is the rate-controlling step.[1–5] What at first appeared to be convincing data was presented by Hart and Ingold[6] for the reaction between di-*sec*-butylmercury and diethylthallic bromide, but recently Jensen and Heyman[7] have shown that the claim was erroneous and that air oxidation of the mercurial was occurring. As a result of our studies with benzylic mercurials, we were interested in the report of Reutov[8] that HCl protolysis of dibenzylmercury (DBM) in a wide variety of solvents proceeded by the SE1 mechanism. This reaction has been reinvestigated and we now wish to communicate that carbanions are not involved.

The following is a summary of the observations reported by the Russian workers:[8] (1) the reaction was first order with respect to DBM and zero order with respect to acid in solvents DMSO, DMF, acetonitrile with water contents ranging from 0 to 25 mole%, tetrahydrofuran, and 1-butanol; (2) an increase in the water content of the solvent acetonitrile decreased the reaction rate, although the reaction was still first order over-all; (3) the rate sequence as a function of solvent was CH_3CN (5% H_2O) > $n\text{-}C_4H_9OH$ > THF > DMF > DMSO, in which order DMSO has a surprisingly feeble ability, when compared with THF or $n\text{-}C_4H_9OH$, to promote ionization of the C–Hg bond.

The following scheme was considered consistent with these data.

$$\begin{tikzcd}
(C_6H_5CH_2)_2Hg \arrow[r, shift left, "\text{slow}"] & C_6H_5CH_2^{-}\,{}^{+}HgCH_2C_6H_5 \arrow[l, shift left] \arrow[dl, "\text{HCl fast}"] \\
C_6H_5CH_3 + C_6H_5CH_2HgCl &
\end{tikzcd}$$

A number of aspects of the investigation and interpretation seemed questionable for the following reasons.[9] (1) It seemed strange to us that DBM was apparently stable in aqueous acetonitrile in the absence of acid. Protic capture of the carbanions would be expected to be rapid, and a hydrolytic demercuration should ensue. (2) No products were identified, nor was the function of the atmosphere apparently probed. (3) The kinetics were obtained on reaction mixtures containing equimolar amounts of HCl and DBM. Never were these concentrations varied independently, thus prohibiting full kinetic analysis. No acid, other than HCl, was employed as a proton source. (4) The reaction seemed unreasonably fast when compared with the HCl cleavage in dioxane, reported[10] to proceed by second-order kinetics. That THF and dioxane differed so markedly in their abilities to promote C–Hg bond ionization seemed strange. (5) The effects of solvents on the rates seemed inexplicable on any reasonable grounds, considering the postulated heterolytic pathway. The explanation advanced by the Russian workers is absolutely untenable, since it proposes slight changes in the "effectiveness" of the acid as a result of solvent–acid interactions. It should be clear that the role of acid is postulated to be post rate determining, and hence information on such a step does not follow from the kinetics. (6) As judged by the illustrations of kinetic plots, rarely was the reaction followed for the duration of 1 half-life.

Our studies have shown that the reactions of DBM with HCl yield some toluene (vpc) and benzylmercuric chloride (proton spectrum with the characteristic $^{199}Hg\text{–}CH_2$ spin coupling). We could detect no significant amounts of dibenzyl in the nmr spectrum. However, studies (*via* nmr) did indicate a significant departure from the anticipated 1:1 stoichiometry of DBM to $C_6H_5CH_2HgCl$. We established that DBM experienced no reaction in aqueous acetonitrile during 6 hr at 40°, under which conditions the reported half-life for carbanion production was *ca.* 40 min. This strongly suggests that carbanions are not being generated in this medium.

The kinetics of the reaction between DBM and HCl in aqueous CH_3CN were followed by titration of residual acid. Plotted as first order in DBM, the line showed a very serious drift to faster rates. The data were only poorly reproduced by second-order plots, with a serious rate acceleration after an initial slower period. Other kinetic schemes, designed to allow for possible halide ion participation, did not correlate the data any better. However, the initial slopes of the first-order plots were clearly a function of HCl concentration, although some erratic behavior was encountered. Use of CF_3COOH as a proton source led to a much depressed rate,[11] confirming that carbanion generation was not rate determining. Independent measurements on the rate of cleavage of $C_6H_5CH_2HgCl$ with HCl established that this

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[9] The reaction was followed by estimating ionic chloride by a mercurimetric technique ($Hg(NO_3)_2$ in acid solution). We could envisage several problems with this procedure.

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[11] Under comparable conditions CF_3COOH was consumed *ca.* 10^2 times more slowly than HCl.