tions[12] afforded a product identical in melting point and infrared spectrum with (±)-2, α^{20}D 0.00 ± 0.01° (c 0.684, $l = 2$, 1% aqueous sodium hydroxide),[17] α^{27}_λ 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] $[\alpha]^{25}$D +41.2° (1% aqueous sodium hydroxide); lit.[13] mp 262–264°, $[\alpha]^{20}$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 S$_E$1 Protolysis of Dibenzylmercury

Sir:

Several substitution reactions of organomercurials have been reported to proceed by the S$_E$1 pathway in which ionization of the C–Hg bond to yield a carbanion is the rate-controlling step.[1-5] What at first appeared to be convincing data was presented by Hart and Ingold[6] for the reaction between di-sec-butylmercury and diethylthallic bromide, but recently Jensen and Heyman[7] have shown that the claim was erroneous and that air oxidation of the mercurial was occurring. As a result of our studies with benzylic mercurials, we were interested in the report of Reutov[8] that HCl protolysis of dibenzylmercury (DBM) in a wide variety of solvents proceeded by the S$_E$1 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$_3$CN (5% H$_2$O) > n-C$_4$H$_9$OH > THF > DMF > DMSO, in which order DMSO has a surprisingly feeble ability, when compared with THF or n-C$_4$H$_9$OH, to promote ionization of the C–Hg bond.

The following scheme was considered consistent with these data.

(1) O. A. Reutov, V. I. Sokolov, and I. P. Beletskaya, Dokl. Akad. Nauk SSSR, 136, 631 (1961); Izv. Akad. Nauk SSSR, 1217 (1961).
(2) O. A. Reutov, B. Praisner, I. P. Beletskaya, and V. I. Sokolov, ibid., 970 (1963).
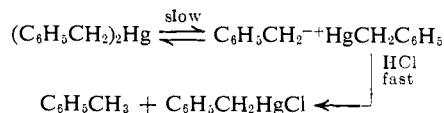(3) E. D. Hughes, C. K. Ingold, and R. M. G. Roberts, J. Chem. Soc., 4372 (1964).
(4) I. P. Beletskaya, V. I. Karpov, V. A. Moskalenko, and O. A. Reutov, Dokl. Akad. Nauk SSSR, 162, 86 (1965).
(5) I. P. Beletskaya, V. I. Karpov, and O. A. Reutov, ibid., 161, 586 (1965).
(6) C. R. Hart and C. K. Ingold, J. Chem. Soc., 4372 (1964).
(7) F. R. Jensen and D. Heyman, J. Am. Chem. Soc., 88, 3438 (1966).
(8) I. P. Beletskaya, L. A. Fedovov, and O. A. Reutov, Dokl. Akad. Nauk SSSR, 163, 1381 (1965).

$$(C_6H_5CH_2)_2Hg \overset{slow}{\rightleftharpoons} C_6H_5CH_2^{-\,+}HgCH_2C_6H_5$$

$$C_6H_5CH_3 + C_6H_5CH_2HgCl \longleftarrow \Big\downarrow {HCl \atop fast}$$

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–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$_6$H$_5$CH$_2$HgCl. 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$_3$CN 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$_3$COOH 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$_6$H$_5$CH$_2$HgCl with HCl established that this

(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.
(10) F. Nerdel and S. Makover, Naturwissenschaften, 45, 490 (1958).
(11) Under comparable conditions CF$_3$COOH was consumed ca. 10^2 times more slowly than HCl.

consecutive reaction was not significant during the reaction time. Also, deliberate addition of $C_6H_5CH_2$-HgCl at the start of a run had essentially no effect on the rate, eliminating product catalysis as a source of the kinetic disturbance. Addition of HCl to CH_3CN was insignificant under these conditions.

We suspected that atmospheric oxygen was to blame for the situation. This was dramatically confirmed by data from runs conducted under a N_2 atmosphere. The consumption of HCl was now very slow, and virtually no disappearance of HCl occurred during the time when the reaction was previously essentially complete. Toward the end of a run medical air was admitted and the consumption of HCl was enormously accelerated. Clearly we are dealing with an oxygen-promoted reaction and protons, halide, and oxygen apparently form a very effective liason for cleavage of the mercurial.[11a] Under oxygen-free conditions, at 40°, the reaction between DBM and HCl correlates well with second-order kinetics for a satisfactory period before consecutive reactions intervene. The period of induction and erratic

(11a) NOTE ADDED IN PROOF. The rate of reaction under aerobic conditions was at least 10^2 greater than that for the reaction under anaerobic conditions. A referee has kindly drawn our attention to a paper by M. M. Kreevoy and R. L. Hansen (*J. Phys. Chem.*, **65**, 1055 (1961)) who noted that the reactions of isopropyl- and *t*-butylmercuric iodides with perchloric acid were profoundly accelerated by oxygen with rate enhancements of *ca.* 10^2–10^3. Although the details of the aerobic reaction are not clear, oxygen insertion into the C–Hg bond may well be a key step in the sequence. Our chief concern was to demonstrate that the reaction was not of the SEl type.

behavior under normal atmospheric conditions are the trademarks of radical-chain processes. Reactions between R_2Hg and O_2 are now well documented.[7,12]

This finding, coupled with that of Jensen,[7] has serious implications for other reported SEl reactions of organomercurials. Thus we are disinclined to accept the report[13] of the "monomolecular protolysis of phenylmercuric bromide in 70% aqueous dioxane," and the reported SEl protolysis of *trans*-ClCH=CHHgCl in DMSO[4] seems unreasonably rapid ($t_{1/2} \sim 9$ min at 20°), considering that such mercurials are prepared and are stable in 6 N HCl.[14] The reactions of ClCH= CHHgCl with both I_2[5] and HCl[4] in DMSO are reported to be of the SEl type, implying identical rates for both reactions. However the iodine cleavage reportedly proceeds more rapidly at *20°* ($k_1 = 3.6 \times 10^{-3}$ sec^{-1}) than does the HCl protolysis at *30°* ($k_1 = 1.3 \times 10^{-3}$ sec^{-1}), suggesting some irregularity.

(12) See, for example, Yu. A. Aleksandrov, O. N. Druzhkov, S. F. Zhil'tsou, and G. A. Razuvaev, *Dokl. Akad. Nauk SSSR*, **157**, 1395 (1964), and subsequent papers.

(13) I. P. Beletskaya, A. E. Myshkin, and O. A. Reutov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **2**, 240 (1965); see also ref 8.

(14) See, for example, A. N. Nesmeyanov and R. Kh. Freidlina, *Bull. Acad. Sci. USSR, Div. Chim. Sci.*, 150 (1945), and subsequent papers.

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Additions and Corrections

New Structural and Stereochemical Aspects of the Cyclization of Olefinic Acetals [*J. Am. Chem. Soc.*, **89**, 170 (1967)]. By WILLIAM S. JOHNSON, ARNE VAN DER GEN, and JOHANN J. SWOBODA, Department of Chemistry, Stanford University, Stanford, California 94305.

The following paragraph should be added at the end of the paper.

Acknowledgment. We thank the U. S. Public Health Service, the National Science Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Mechanisms of Photochemical Reactions in Solution. XLIV. Photodimerization of Cyclohexenone [*J. Am. Chem. Soc.*, **89**, 3482 (1967)]. By ERNEST Y. Y. LAM, DONALD VALENTINE, and GEORGE S. HAMMOND, Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91109.

On page 3483, column 2, the beginning of line 13 should read: enone concentration is 0.05 M.

Mechanisms of Reactions of Thiolsulfinates (Sulfenic Anhydrides). I. The Thiosulfinate–Sulfinic Acid Re-

action [*J. Am. Chem. Soc.*, **89**, 3557 (1967)]. By JOHN L. KICE, CLIFFORD G. VENIER, and LESLIE HEASLEY, Department of Chemistry, Oregon State University, Corvallis, Oregon 97331.

On page 3559, eq 2b should read

$$(ArSO_2H)_{av} = (ArSO_2H)_0 - a(Ib)_0/2 \qquad (2b)$$

The Thiolochromium(III) Ion [*J. Am. Chem. Soc.*, **89**, 3661 (1967)]. By MICHAEL ARDON and HENRY TAUBE, Department of Chemistry, Stanford University, Stanford, California 94305.

On page 3662, column 1, line 13, $Cr(H_2O)_5Cl^{2+}$ should read $Cr(H_2O)_5I^{2+}$.

Steric Hindrance to the Formation of and Protonation of the Nitronate Ion from 2-Aryl-1-nitrocyclohexanes [*J. Am. Chem. Soc.*, **89**, 3906 (1967)]. By F. G. BORDWELL and MARTHA M. VESTLING, Department of Chemistry, Northwestern University, Evanston, Illinois 60201.

On page 3906, column 2, line 18, (axial) should read (equatorial).