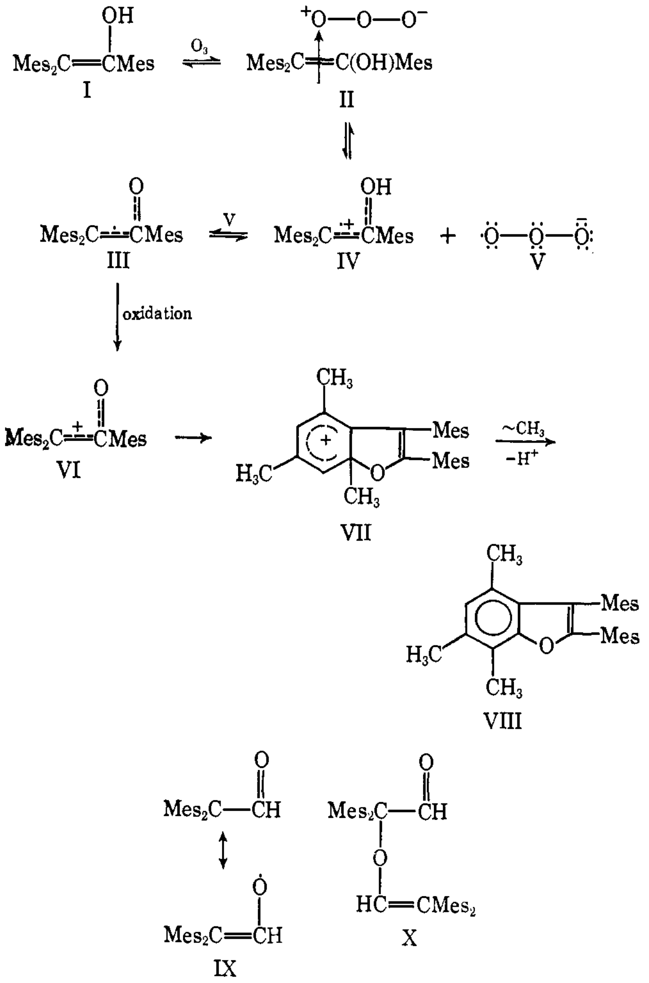
Scheme I



The unresolved singlet epr signal for III could result from a rapid electron transfer between species III and VI. Such was also found for the cation radical from oxidation of tetraanisylethylene.[6]

These results, coupled with previous theory,[7,8] suggest that ozonation of olefins proceeds *via* an initial π complex (*e.g.*, II). This usually either enters into 1,3-dipolar cycloaddition (ozonolysis) or is converted to a σ complex. The latter route increases in importance as steric hindrance to 1,3-dipolar cycloaddition increases and normally results in the formation of epoxides and other "partial cleavage" products.[8] When steric hindrance in the olefin becomes very great and radical stabilizing groups are attached to the doubly bonded carbon atoms, homolytic dissociation of the π complex (*e.g.*, to IV and V) may occur. Loss of a proton from IV (perhaps to V) gives III.

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[8] P. S. Bailey and A. G. Lane *ibid.*, **89**, 4473 (1967).

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Tetrakis(acetoxymercuri)methane

Sir:

Tetrametallomethanes in which the metal atom is silicon,[1] lead,[2] or boron[3] have been made by modified crossed Wurtz reactions, and we have recently reported that one or two boron atoms of $C[B(OMe)_2]_4$ can be replaced by tin, or two by lead.[4] We have now found that mercuric acetate replaces all four boron atoms of $C[B(OMe)_2]_4$ to yield tetrakis(acetoxymercuri)methane, $C(HgOAc)_4$, which is crystalline, water soluble, and stable.

A solution of 3.03 g of tetrakis(dimethoxyboryl)methane, $C[B(OMe)_2]_4$, in 300 ml of absolute ethanol was stirred and heated with 25 g of mercuric acetate, which nearly all dissolved as reflux approached and the product began to precipitate. After 4.5-hr refluxing the mixture was cooled to 25° and filtered to yield 10.8 g (102%) of $C(HgOAc)_4$ contaminated with mercurous acetate (less soluble) and mercuric acetate (more soluble). This was dissolved in 100 ml of boiling water and 2 ml of acetic acid, filtered to remove mercurous acetate, treated with 5 g of sodium hydroxide in 10 ml of water, and boiled to coagulate the hydroxide precipitate. The precipitate was redissolved in 100 ml of boiling water and 15 ml of acetic acid and boiled down to a volume of 35 ml. Addition of 100 ml of ethanol and cooling yielded 7.4 g of crystalline $C(HgOAc)_4$, which was further purified by repetition of the cycle. Pure $C(HgOAc)_4$, mp 265–285° dec, gives a *white* precipitate with aqueous sodium hydroxide, not gray (mercurous) or yellow (mercuric). It also gives a white precipitate (probably $C(HgCl)_4$) with stannous chloride, which is not reduced to mercury, in contrast to mercuric and mercurous salts. The nmr spectrum (in D_2O or DMSO-d_6) shows only the acetate protons. *Anal.* Calcd: C, 10.29; H, 1.15; Hg, 76.37. Found: C, 10.45; H, 1.09; Hg, 76.09.

There is no difficulty in packing four mercury atoms around a central carbon. The usual carbon–mercury distance, 2.07 Å,[5] with tetrahedral bond angles leaves 3.4 Å between mercury atoms, which is 0.1–0.3 Å greater than the van der Waals distance.[5] However, the central carbon atom is well shielded from any kind of direct attack, which may explain the rather inert character of the C–Hg bond in $C(HgOAc)_4$.

In fact, it is somewhat surprising that the fourth mercury atom is able to get into the structure at the same time the last boron is departing, as required by the concerted electrophilic displacement mechanism.[6] Although $C[B(OMe)_2]_4$ serves as a carbanion source in basic media and degrades to $CH_2[B(OMe)_2]_2$ in basic methanol,[3] this does not occur in the weakly acidic medium used for this displacement. Refluxing 0.42 g of $C[B(OMe)_2]_4$ with 0.2 ml of acetic acid in 40 ml of anhydrous methanol for 1 hr followed by evaporation of the solvent yielded 85% of unchanged $C[B(OMe)_2]_4$, purity checked by infrared spectroscopy. These are

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conditions under which mercuric acetate reacts with the $C[B(OMe)_2]_4$, and any sort of first-order process at any stage seems most unlikely. However, the hypothesis of three-center B–C–Hg bonding in the transition state[7] is consistent with a very narrow B–C–Hg angle and small steric requirement, especially if vacant p orbitals on the neighboring mercury atoms enter into weak bonding and further delocalize the electron pair.[6b]

Our survey of the chemistry of $C(HgOAc)_4$ has so far been limited to replacement of outer ligands.[7a] Sodium nitrate precipitates a white solid after a few minutes delay, and the material is insoluble in concentrated nitric acid. A polymeric material containing linkages of the $(RHg)_3O^+$ type[8] seems the most likely structure. The BF_4^- and PF_6^- salts are similarly insoluble. The fluoride is slightly soluble in aqueous hydrofluoric acid. The yellow iodide, $C(HgI)_4$, mp >300°, is slightly soluble in concentrated sodium iodide solutions in water or diglyme, which makes it a candidate for running further reactions. Its carbon content (*Anal.* Calcd: 0.91. Found: 0.98) sets a new low for organic chemistry.

(7) S. Winstein, T. G. Traylor, and C. S. Garner, *J. Amer. Chem. Soc.*, **77**, 3741 (1955).

(7a) NOTE ADDED IN PROOF. The precipitated bromide, presumably $C(HgBr)_4$, reacts with bromine vapor in an evacuated sealed tube at 25° to yield ~75% of carbon tetrabromide, identical with an authentic sample by infrared spectroscopy and mixture melting point.

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(9) (a) Supported by National Science Foundation Grants GP-6069 and GP-9320; (b) Alfred P. Sloan Foundation Fellow, 1966–1968; (c) National Institutes of Health Postdoctoral Fellow, 1968–1969.

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α-Deuterium Effects in SN2 Reactions with Solvent[1]

Sir:

We wish to report α-deuterium rate effects for some well-established SN2 type solvolyses of compounds *closely related structurally* to those for which α-*d* effects have previously been established for *limiting* solvolyses.[2] These results confirm that the major determinant of the α-*d* effect in solvolysis is the nucleophilic (SN2) or limiting (SN1) character of the mechanism and that at the extremes of mechanism the variation in α-*d* effects with alkyl group structural changes are much smaller than those that can be caused by a shift in mechanism.[3] The results also allow some additional analysis of the problem of the mechanism(s) in the "borderline" region of solvolysis.

Solvolysis rates have been measured, using conductometric techniques described earlier,[2,4] for benzyl *p*-bromobenzenesulfonate (brosylate), *p*-trifluoromethylbenzyl brosylate, *p*-nitrobenzyl brosylate, and their α-d_2 analogs in a series of ethanol–water and trifluoroethanol (TFE)–water solvents.[5] The isotope effects for *p*-methylbenzyl chloride,[4] given in Table I as $k_H/k_{\alpha D}$ per D, are not strongly dependent on the water concentration in TFE solutions and are near the value for the limiting reactions of α-phenylethyl chloride (1.15, 25°).[2] We conclude that in these TFE solutions the *p*-methylbenzyl chloride solvolysis is very nearly limiting and that the limiting isotope effects for the 1-phenylethyl and benzyl compounds are very similar. In 50% ethanol, the effect for *p*-methylbenzyl chloride is much lower indicating a significant nucleophilic component.

Table I. α-Deuterium Effects (per D[a]) on Rates of Solvolysis of Some Benzyl Derivatives, 25°

	Leaving group			
	Cl	OBs[b]	OBs[b]	OBs[b]
	Substituent			
Solvents[c]	*p*-CH_3	None	*p*-CF_3	*p*-NO_2
97 *T*	1.142	1.173		1.026[d]
80 *T*		1.159	1.044[d]	
70 *T*	1.140		1.041	1.011[d]
50 *E*	1.086[d]			
70 *E*			1.019	1.006
80 *E*		1.074	1.016	1.005
90 *E*		1.060	1.014	1.002
95 *E*		1.053	1.014	
m-E[e]		0.415	0.304	0.279

[a] $(k_H/k_{\alpha d_2})^{1/2}$; the ratios were reproducible to within ±0.001 in most cases and ±0.002 in a few.[2,4] [b] *p*-Bromobenzenesulfonate. [c] 97 *T* indicates 97 per cent 2,2,2-trifluoroethanol–3 per cent water; 70 *E* indicates 70 vol % ethanol–30 vol % water, etc. [d] Estimated from the observed values at 45° assuming that there is no isotope effect on the Anhenius preexponential term.[4] [e] Winstein–Grunwald *m* value based on reactions in ethanol–water solvents.

As the solvent polarity is increased or as solvent nucleophilicity is decreased, the effects increase markedly for benzyl brosylate, ranging from 1.053 to 1.173. Other work indicates that the α-deuterium effect for a limiting solvolysis[3,6,7] for an arenesulfonate is approximately 1.23 while the nucleophilic extreme appears to be unity or even inverse.[8–10] Thus none of the (unsubstituted) benzyl brosylate solvolyses included in Table I appear to be following a simple nucleophilic or limiting mechanism. The isotope effects and the solvent influences on the effects are much smaller for the *p*-CF_3 derivative and still smaller for the *p*-NO_2 derivative (1.002–1.026). The solvolyses for these last two compounds must be predominately of one mechanistic type since the substituent and solvent influences on the effects are quite small. Because this reaction class is favored by lower solvent polarity and higher solvent nucleophilicity and since low isotope effects correspond to tight transition-state binding, we conclude that the reaction type is SN2. Low α-deuterium rate effects have previously been attributed to SN2 reactions.[8–10] Particularly interesting are the values of about 0.99 and 1.02 per D for the aqueous hydrolyses of CD_3OTS[9] and CH_3–CD_2–OTS[10] (OTS = toluenesulfonate). Although in principle one

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(1) Taken in part from the thesis submitted by M. W. Rapp to the Graduate School of Indiana University in partial fulfillment of the requirements for the Ph.D. degree, 1968.

(2) V. J. Shiner, Jr., W. E. Buddenbaum, B. L. Murr, and G. Lamaty, *J. Amer. Chem. Soc.*, **90**, 418 (1968).

(3) The effects of leaving group variations on α-D effects in limiting reactions have already been analyzed: V. J. Shiner, Jr., M. W. Rapp, M. Wolfsberg, and E. A. Halevi, *ibid.*, **90**, 7171 (1968).

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(5) We believe that the most important solvent change effected as the amount of water in a trifluoroethanol-water solvent is increased is an increase in nucleophilicity.[4] On the other hand, an increasing concentration of water in an ethanol-water solvent mixture affects these solvolyses mainly through the increase in polarity.

(6) W. Dowd, personal communication.

(7) A. Streitwieser, Jr., and G. A. Dafforn, *Tetrahedron Lett.*, 1263 (1969).

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