

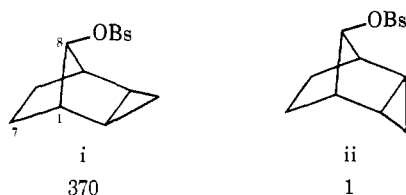
viously<sup>12</sup> in the model system IV. Initially two substituents, one electron donating (CH<sub>3</sub>) and one electron withdrawing (Br), were chosen for study for reasons of synthetic convenience. Tanida has previously determined the relative order of reactivity of esters IX-OBs, IV-OBs, and VIII-OBs to be 5.7:1.0:0.03, respectively, at 77.6°.<sup>12</sup> If a simple steric effect is operative a constant additive factor for the exo cyclopropyl group should obtain and the ratio of relative reactivities for brosylates XI-OBs, VI-OBs, and X-OBs should be essentially identical with that found by Tanida.<sup>12</sup> For an electronic effect such as a, however, one would anticipate substituent modulation of the degree of electron release from the cyclopropane edge bond with a resultant compression of the relative reactivity order XI:VI:X. The acetolysis rate ratios for compounds X-OBs<sup>8</sup> and XI-OBs<sup>8</sup> (Table II) relative to VI-OBs were found to be within experimental error the same as those reported by Tanida for the corresponding substituent effects in the model 7-benznorbornenyl series.

From these initial results we conclude that the evidence is most consistent with a simple steric accelerative effect;<sup>13</sup> however, we cannot at this time rule out steric electronic argument c due to uncertainties regarding the sensitivity of substituent probing to the latter effect.

**Acknowledgment.** Financial support of this research by the National Science Foundation (Grant No. GP-27411 and GP-9412) is gratefully acknowledged.

(12) H. Tanida, T. Tsuji, and H. Ishitobi, *J. Amer. Chem. Soc.*, **86**, 4904 (1964); see also H. Tanida, *Accounts Chem. Res.*, **1**, 239 (1968).

(13) In an attempt to account for the enhanced reactivity of *exo-syn*-8-tricyclo[3.2.1.0<sup>2,4</sup>]octyl brosylate (i) compared to its *endo-syn* isomer ii Haywood-Farmer and Pincock<sup>6c</sup> offered two possible explanations



a favorable stereoelectronic interaction of the exo cyclopropyl group with the incipient carbonium ion center that is formed during concerted Wagner-Meerwein rearrangement of the C-1-C-7 bond or, alternatively, steric acceleration by the proximate methylene group of the exo cyclopropyl ring. Our results suggest that it is the latter effect which accounts for most, if not all, of the rate enhancement of i over ii.

(14) National Science Foundation Cooperative Fellow, 1966-1970.

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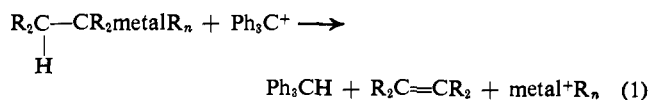
### $\sigma$ - $\pi$ Conjugation of Carbon-Metal Bonds. Dehydrometalation of Alkylmetal Compounds<sup>1</sup>

Sir:

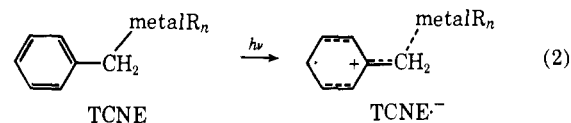
We wish to report an extraordinarily facile hydride abstraction from positions  $\beta$  to carbon-metal bonds.<sup>2</sup>

(1) Supported by the Air Force Office of Scientific Research (Grant No. AFOSR-69-1639A).

(2) (a) Hydride abstraction from ethyl-transition metal compounds has been observed<sup>2b</sup> and attributed to  $\pi$ -complex formation. That the authors chose to offer this reactivity as a property exclusive to transition metals<sup>2c</sup> is testament to the misleading nature of the postulation of d-orbital participation in such cations. Not only is the reactivity not confined to transition metals, but the reactivity is greater in certain

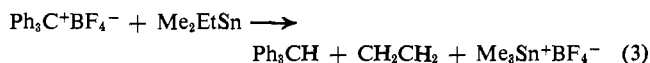


Previous studies revealed a very large effect of the groups  $R_n\text{metal}CH_2^-$  upon the vertical stabilization of positive carbon in such processes as eq 2.<sup>3</sup> These



findings suggested that cations such as  $Me_3SnCH_2CH_2^+$  or  $MeHgCH_2CH_2^+$ , although primary, should be more stable than trityl cation.<sup>3b</sup>

To test this possibility we combined triphenylmethyl tetrafluoroborate with ethyltrimethyltin<sup>4</sup> in methylene chloride. The trityl cation spectrum disappeared almost immediately and triphenylmethane, ethylene, and  $Me_3SnBF_4$  were produced in nearly quantitative yields.<sup>5</sup> Similarly rapid reactions occurred with di-



butylmercury,  $PhCH_2CH_2PbPh_3$ ,<sup>3b</sup>  $(PhCH_2C(-Me)H)_2Hg$ ,<sup>3b</sup> and  $PhC(-Me)HSnMe_3$ . However,  $PhCH_2-SnMe_3$ ,<sup>3b</sup>  $Me_4Sn$ ,  $(PhCMe_2CH_2)Hg$ ,<sup>8</sup> and di-*l*-apocamphylmercury<sup>8</sup> did not react, illustrating the importance of the presence and proper geometry of the  $\beta$  hydrogen. The reaction obeys the rate expression

$$-\frac{d[Ph_3C^+]}{dt} = k_2[Ph_3C^+][R_nMCR_2CHR_2] \quad (4)$$

and shows a very large variation in rate with the nature of the metal in keeping with predictions based on  $\sigma$ - $\pi$  conjugation effects.<sup>3b</sup> Rate data, shown in Table I, illustrate this and other effects.

We have previously demonstrated<sup>3e</sup> the existence of a  $\beta$ -alkylmercuricarbonium ion (mercurinium ion) as an intermediate in reaction 5 and the rearrangement of  $Me_3SiCH_2CD_2^+$ , observed by Cook, Eaborn, and Walton,<sup>9</sup> clearly demonstrates the existence of this  $\beta$

nontransition metal compounds such as  $Et_2Pb$ , etc. See ref 3a,b for further discussions of this matter. (b) M. L. H. Green and P. L. I. Nagy, *J. Organometal. Chem.*, **1**, 58 (1963). (c) C. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Chemistry," Vol. II, Methuen, London, 1968, p 216.

(3) (a) J. C. Ware and T. G. Traylor, *J. Amer. Chem. Soc.*, **89**, 2304 (1967); (b) W. Hanstein, H. J. Berwin, and T. G. Traylor, *ibid.*, **92**, 829 (1970); (c) N. A. Clinton, R. S. Brown, and T. G. Traylor, *ibid.*, **92**, 5228 (1970); (d) W. Hanstein, H. J. Berwin, and T. G. Traylor, *ibid.*, **92**, 7476 (1970); (e) W. Hanstein and T. G. Traylor, *Tetrahedron Lett.*, 4451 (1967).

(4) Prepared by the method of Z. M. Manulkin, *Zh. Obshch. Khim.*, **13**, 46 (1943); *Chem. Abstr.*, **38**, 332 (1944).

(5) Ethylene, identified by mass spectrometry, was evolved in 97% yield. Evaporation of the solvent followed by benzene extraction of the residue, washing, and drying afforded a 73% yield of triphenylmethane. Trimethyltin fluoroborate<sup>6</sup> was identified by nmr. Similar results were obtained with the other organometallic compounds both in methylene chloride and in acetonitrile. In neither solvent have we been able to observe the carbonium ions by nmr or to trap them by subsequent borohydride addition. However, Olah and Clifford<sup>7</sup> have observed the  $RHgCH_2CH_2^+$  ion (which we derive from  $Et_2Hg$ ) in less nucleophilic solvents. Studies of reaction 1 in such solvents are in progress.

(6) H. C. Clark and R. J. O'Brien, *Inorg. Chem.*, **2**, 1020 (1963).

(7) G. A. Olah and P. R. Clifford, *J. Amer. Chem. Soc.*, **93**, 1261 (1971).

(8) S. Winstein and T. G. Traylor, *ibid.*, **78**, 2597 (1956). Other compounds are commercially available or were identified by spectra and analyses.

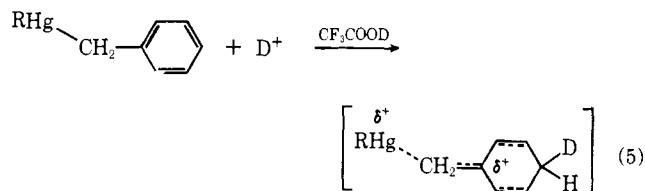
(9) M. A. Cook, C. Eaborn, and D. R. M. Walton, *J. Organometal. Chem.*, **24**, 301 (1970).

**Table I.** Rates of Reaction of Organometallic Compounds with  $\text{Ph}_3\text{C}^+\text{BF}_4^-$  in Acetonitrile at  $29.8^\circ\text{C}$ <sup>a</sup>

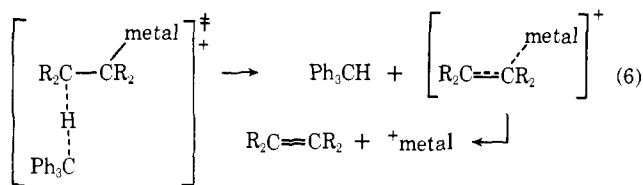
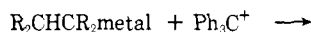
Compound	$k_2, M \text{ sec}^{-1}$	$k_2'$ per hydrogen
Cycloheptatriene	0.413	0.21
$\text{Et}_4\text{Si}$	$6.8 \times 10^{-7}$	$5.7 \times 10^{-8}$
$\text{Et}_4\text{Ge}$	$4.8 \times 10^{-6}$	$4 \times 10^{-6}$
$\text{Et}_4\text{Sn}$	$1.0 \times 10^{-2}$ ( $25^\circ$ )	$8.3 \times 10^{-4}$
$\text{Et}_4\text{Pb}$	5.9	0.49
$\text{Et}_2\text{Hg}$	0.9	0.15
$(\text{Me}_2\text{SnCH}_2)_2\text{CH}_2^b$	0.115	0.058
$\text{Me}_3\text{SnCH}_2\text{CH}_2\text{Ph}$	0.0956	0.048

<sup>a</sup> Rates measured spectrophotometrically as pseudo-first-order disappearance of  $\text{Ph}_3\text{C}^+\text{BF}_4^-$  except for those of  $\text{Et}_4\text{Si}$  and  $\text{Et}_4\text{Ge}$  which were measured as zero-order rates by glc observation of ethylene. <sup>b</sup> The product of this reaction is allyltrimethyltin identified by nmr spectroscopy.

silicon-substituted carbonium ion. We have strong evidence that reaction 5 is accelerated by vertical



stabilization<sup>3b</sup> to produce the geometry indicated. These and the observation (Table I) that a second  $\text{CH}_2\text{SnMe}_3$  accelerates the rate more than does a phenyl group<sup>10</sup> make it very probable that these reactions proceed through the carbonium ion as shown in eq 6.<sup>13-15</sup>



A plot of  $\log k_2'$  against the charge-transfer frequencies of  $\text{Ph}_n\text{MCH}_2\text{Ph}$ -tetracyanoethylene (eq 2) in Figure 1 shows that the vertical stabilization by  $\text{R}_n\text{MCH}_2-$

(10) A second neighboring group can accelerate the rate by only a factor of two<sup>11</sup> whereas there is no limit on the acceleration available from a second vertical stabilizing group.<sup>12</sup> Previous results<sup>3d</sup> show that  $-\text{CH}_2\text{SnMe}_3$  inductive effect is like  $\text{CH}_3$  so that inductive effects are also excluded.

(11) See C. J. Lancelot and P. v. R. Schleyer (*J. Amer. Chem. Soc.*, **91**, 4296 (1969)) for a discussion of the acceleration provided by two bridging groups.

(12) H. Hart and P. A. Law, *ibid.*, **86**, 1957 (1964).

(13) We do not exclude bridging. We only conclude that, in many of the cases we have studied, bridging makes negligible contribution to the stabilization and is therefore of little importance in our discussions of reaction rates or cation stabilizations. Since the energy difference between the symmetrical and unsymmetrical mercurinium ion is thought to be very small, the suggested<sup>14</sup> corner attack in oxymercuration of 7,7-dimethylnorbornene could still partake of the same stabilization of the mercurinium ion as do reactions with the less-hindered norbornene. This interpretation is different from that of Brown and Kawakami<sup>14</sup> who consider the norbornene mercuration intermediate to be like the norbornyl cation obtained by protonation of norbornene.

(14) H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, **92**, 201 (1970).

(15) The existence of  $^+\text{CH}_2\text{CH}_2\text{SiMe}_3$  is clearly demonstrated,<sup>9</sup> and our evidence favors mechanism 6 for other group IV organometallic compounds. However, one-step dehydrometalation is expected for very reactive compounds such as  $\text{Et}_4\text{B}^+$ , etc. Studies of these compounds will be reported later.

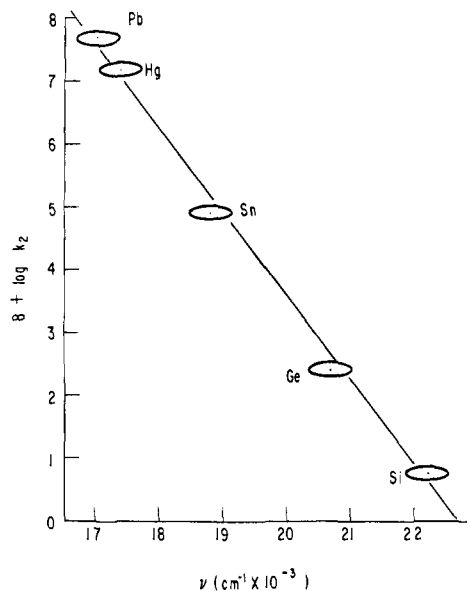


Figure 1. Plot of  $\log k_2'$  for reaction of  $\text{Ph}_3\text{C}^+$  with  $\text{Et}_n\text{M}$  (reaction 1) against charge-transfer frequencies of  $\text{Ph}_n\text{MCH}_2\text{Ph}$  with tetracyanoethylene.<sup>3b,d</sup> See  $k_2'$  per hydrogen in Table I.

is accurately reflected in the rates of hydride abstraction. This is an additional implication that the principal driving force for hydride abstraction from  $\text{Et}_n\text{M}$  is vertical stabilization of an intermediate carbonium ion by  $\text{Et}_n\text{MCH}_2-$ .<sup>16,18</sup>

This reaction offers an attractive alternative to solvolysis as a way of studying stable cations. We are extending this study to other  $\sigma-\pi$  conjugated cations.<sup>3b</sup>

(16) O. A. Reutov, E. V. Uglova, V. C. Makhaev, and V. S. Petrosyan, *Zh. Org. Khim.*, 2153 (1970), proposed a cyclic elimination in the reaction of diisobutylmercury with  $(\text{C}_6\text{H}_5)_3\text{CBr}$  by analogy to the cyclic mechanism generally written for reduction of Grignard reagents. However, such cis elimination is not favored in reaction 1<sup>7</sup> and it might be incorrect for Grignard reductions. The stereochemistries of these reactions are under investigation.

(17) Unpublished work of M. H. Hall.

(18) The nmr results of Olah and Clifford<sup>7</sup> are consistent with and interpreted in terms of a bridged mercurinium ion. However, our previous evidence<sup>3e</sup> for a mercurinium ion as a reaction intermediate indicated it to be  $\sigma-\pi$  conjugated and not bridged.<sup>3e</sup> The structure of bridged ions in nonnucleophilic solvents is, in this case, clearly not an accurate description of the transition state leading to the ion. Recent molecular orbital calculations on both  $\text{CH}_3\text{CH}_2\text{CH}_2^+$ <sup>19</sup> and  $\text{RHgCH}_2\text{CH}^+\text{CH}_2$ <sup>20</sup> seem to confirm our postulate that  $\sigma-\pi$  conjugation is in general much more important than bridging or fragmentation.

(19) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 1813 (1971).

(20) R. S. Bach, private communication.

(21) On leave of absence from Institute Ruder Borskovic, Zagreb, Yugoslavia.

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### Single-Crystal X-Ray Structures of Chemotherapeutic Agents. V. The Structures of 5-Diazo-6-methoxy-6-hydroxyl and 2'-Deoxy-5-diazo-6-hydro-*O*<sup>6</sup>,5'-cyclouridine Hemihydrate

Sir:

The 5-diazo derivatives of uracil and uridine have been shown to possess significant carcinostatic activity.<sup>1</sup>