

atom, C(63), being 0.78 Å out of the best plane through the other five atoms. C(63) has a large isotropic thermal parameter and this may indicate a freedom to "pass" through the plane of the ring in the isolated molecule. Such behavior would be consistent with the observed broadening of the signal from the two protons on this carbon atom in the nmr spectrum of streptovarone.<sup>10</sup>

The methylene chloride molecules occupy well-defined positions surrounded by several antibiotic molecules. The solvent molecule is so oriented that there is a C...O distance of 3.09 Å and Cl—C...O angles of 115 and 122°, indicating a C—H...O (amide) hydrogen bond. Such C—H...O hydrogen bonds have been noted to occur with chloroform and dichlorobromomethane.<sup>11</sup>

Since coupling constants and chemical shifts of the other streptovaricins are nearly identical<sup>1</sup> with that of streptovaricin C, we assume their stereochemistry is like that in derivative 5.

Of particular interest is the observation that the relative configuration at every comparable chiral center of 5 is identical with that in rifamycins B<sup>12a</sup> and Y<sup>12b</sup> and tolypomycin,<sup>13</sup> although the geometry of the dienamide unit is reversed (trans, cis for 1–5 vs. cis, trans for rifamycins B and Y). This identity of relative configurations and the strong positive rotations of streptovaricin C (+602°)<sup>14</sup> and rifamycin S (+476°)<sup>15</sup> argue for identical absolute configurations<sup>16</sup> as well (*i.e.*, that shown for 5: 6*S*, 7*S*, 8*R*, 9*R*, 10*S*, 11*S*, 12*R*, 13*S*, 14*R*). The helicity of the *ansa* (bridged) system is P.<sup>17</sup>

**Acknowledgment.** This investigation was supported in part by Public Health Service Research Grant No. AI 01278 from the National Institute of Allergy and Infectious Diseases.

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(18) Alfred P. Sloan Research Fellow, 1968–1970.

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Andrew H.-J. Wang, Iain C. Paul\*<sup>18</sup>  
Kenneth L. Rinehart, Jr.\* Frederick J. Antosz<sup>19</sup>  
Department of Chemistry, University of Illinois  
Urbana, Illinois 61801

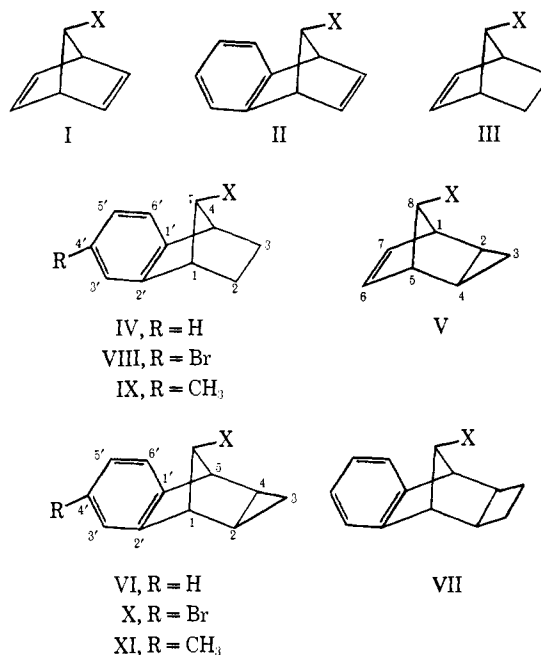
Received August 13, 1971

### Enhanced Solvolytic Reactivity in the *exo-syn*-Tricyclo[3.2.1.0<sup>2,4</sup>]oct-6-en-8-yl Series. Evidence for Extensive Steric Acceleration

Sir:

The additional solvolytic rate enhancement provided by the *syn* double bond in 7-norbornadienyl and anti

7-benznorbornadienyl derivatives I<sup>1</sup> and II<sup>2</sup> compared to the corresponding anti dihydro systems III<sup>3</sup> and IV<sup>2</sup> may be ascribed to either a ground-transition state effect<sup>4</sup> or to extra charge delocalization into the adjacent nonconjugated  $\pi$  center in the transition state, *i.e.*, a homoconjugative reinforcing effect.<sup>1,4</sup> In view of the magnitude of direct edge participation by cyclopropane in the *endo*-tricyclo[3.2.1.0<sup>2,4</sup>]octan-8-yl system<sup>5</sup> it appeared instructive to examine the reactivities of appropriate *exo* cyclopropanated analogs of I and II for possible homoconjugative reinforcing effects by cyclopropane.<sup>6</sup> Accordingly we have examined the solvolytic reactivity of *exo-syn*-tricyclo[3.2.1.0<sup>2,4</sup>]oct-6-en-8-yl *p*-nitrobenzoate (V-OPNB) and *exo-anti*-5,6-benztricyclo[3.2.1.0<sup>2,4</sup>]octen-8-yl brosylate (VI-OBs) in addition to related systems. We now wish to report that these cyclopropanated esters represent an extreme of solvolytic reactivity in their respective series, although evidence presented below suggests that these rate enhancements should not be ascribed to homoconjugative electron release by cyclopropane.



As reported earlier by several groups of workers,<sup>7</sup> alcohol V-OH is available as the major component of

(1) S. Winstein and C. Ordonneau, *J. Amer. Chem. Soc.*, **82**, 2084 (1960).

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(5) (a) M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. S. Haywood-Farmer, *ibid.*, **89**, 1954 (1967); (b) H. Tanida, T. Tsuji, and T. Irie, *ibid.*, **89**, 1953 (1967); (c) J. S. Haywood-Farmer and R. E. Pincock, *ibid.*, **91**, 3020 (1969).

(6) Recent photoelectron spectroscopic examination of *exo*- and *endo*-tricyclo[3.2.1.0<sup>2,4</sup>]oct-6-ene by P. Bischof, E. Heilbronner, H. Prinzbach, and H. D. Martin [*Helv. Chim. Acta*, **54**, 1072 (1971)] has revealed significant homoconjugative interaction between the  $\pi$  orbital of the double bond and the symmetric Walsh orbital  $e_s$  of the cyclopropane ring in the *exo* isomer. The extent of interaction approaches that found between the  $\pi$  orbitals of the two double bonds in norbornadiene. On the other hand only negligible interaction was detected between the double bond and the cyclopropane ring in the *endo* isomer.

(7) J. Haywood-Farmer, R. E. Pincock, and J. I. Wells, *Tetrahedron*, **22**, 2007 (1966); B. Halton, M. A. Battiste, R. Rehberg, C. L. Deyrup, and M. E. Brennan, *J. Amer. Chem. Soc.*, **89**, 5964 (1967); S. C. Clarke, K. J. Frayne, and B. L. Johnson, *Tetrahedron*, **25**, 1265 (1969).

**Table I.** Solvolytic Rate Constants and Activation Parameters in 70% Aqueous Acetone

ROPNB <sup>a</sup>	Temp, °C	10 <sup>5</sup> k <sub>1</sub> , sec <sup>-1</sup>	Rel k <sub>1</sub> (126.2°)	Rel k <sub>1</sub> (25°)	ΔH <sup>‡</sup> , kcal/mol	ΔS <sup>‡</sup> , eu
I-OPNB	90.2	1.74 <sup>b</sup>			24.8 <sup>b</sup>	-15.1 <sup>b</sup>
	124.7	37.2 <sup>b</sup>				
	126.2	42.0 <sup>c</sup>	156			
III-OPNB	25	7.76 × 10 <sup>-4</sup> <sup>c</sup>		955		
	126.2	0.270 <sup>b</sup>	1.0		25.6 <sup>d</sup>	-21.2 <sup>d</sup>
	100	1.9 × 10 <sup>-2</sup> <sup>d</sup>				
25	8.1 × 10 <sup>-7</sup> <sup>e</sup>		1.0			
V-OPNB	75	1.66			25.2	-10.5
	90	7.46				
	126.2	170 <sup>c</sup>	630			
	25	4.07 × 10 <sup>-3</sup> <sup>c</sup>		5000		

<sup>a</sup> 0.01 M. <sup>b</sup> C. L. Deyrup, Ph.D. Dissertation, Boston University, 1970. <sup>c</sup> Extrapolated value from data at other temperatures. <sup>d</sup> Value cited for 70% aqueous dioxane in ref 5c. <sup>e</sup> Estimated value assuming the slope of the Arrhenius plot is identical with that for I-OPNB.

**Table II.** Acetolyses Rates and Activation Parameters

ROBs <sup>a</sup>	Temp, °C	10 <sup>5</sup> k <sub>1</sub> , sec <sup>-1</sup>	Rel k <sub>1</sub> (25°)	Rel k <sub>1</sub> (60°)	ΔH <sup>‡</sup> , kcal/mol	ΔS <sup>‡</sup> , eu
II-OBs	25	0.12 <sup>b</sup>	120		26.8 <sup>b</sup>	4.45 <sup>b</sup>
	60	16.1 <sup>b</sup>		92		
IV-OBs	25	1.0 × 10 <sup>-3</sup> <sup>c</sup>	1.0		27.6 <sup>b</sup>	-2.3 <sup>b</sup>
	60	0.176 <sup>c</sup>		1.0		
VI-OBs <sup>d</sup>	25	5.35	5350		23.5	-1.2
	35	20.1				
	45	68.9				
	60	414 <sup>e</sup>				
VII-OBs <sup>f</sup>	60	14.1	(5.9)	2360		
VIII-OBs	60	4.1 × 10 <sup>-3</sup> <sup>g</sup>	5.6	80	(0.05)	
	25	5.6 × 10 <sup>-3</sup> <sup>h</sup>		0.02		
X-OBs <sup>f</sup>	60	21.4		122		
XI-OBs <sup>d,f</sup>	25	31.3	31,300			

<sup>a</sup> 0.1 M in 0.1 M NaOAc in HOAc unless noted. <sup>b</sup> Reference 2. <sup>c</sup> Extrapolated value from data at other temperatures in ref 2. <sup>d</sup> 0.02 M in 0.1 M NaOAc in HOAc. <sup>e</sup> Extrapolated value from data at other temperatures. <sup>f</sup> 0.01 M in 0.05 M NaOAc in HOAc. <sup>g</sup> Estimated from data in ref 12 assuming a similar Arrhenius plot slope to that of 4'-chloro derivative (IV-OBs, R = Cl). <sup>h</sup> Extrapolated value calculated from data at other temperatures in ref 12.

a 4-5 component mixture. Fractional distillation of this mixture followed by preparative glpc gave homogeneous V-OH which was converted to its para nitrobenzoate derivative V-OPNB,<sup>8</sup> mp 114-115°, in good yield. Alcohol VI-OH and its brosylate derivative VI-OBs, mp 139-140°, have been previously described.<sup>9</sup>

The solvolyses of V-OPNB and VI-OBs were followed titrimetrically in 70% aqueous acetone and anhydrous acetic acid, respectively. Satisfactory first-order rate plots were obtained for each ester and the resultant rate constants (k<sub>1</sub>) and activation parameters are compared with the corresponding values for related systems in Tables I and II. These data clearly reveal that ionization of the cyclopropanated esters V and VI is accelerated over that for their anti 7-norbornenyl counterparts III and IV by a factor of between 10<sup>3</sup> and 10<sup>4</sup>. It is perhaps more surprising that the cyclopropyl esters are more reactive than the corresponding 7-norbornadienyl derivatives I and II by factors of 5 and 45, respectively. Product analysis (glpc) revealed that the retained alcohol V-OH and retained acetate VI-OAc,<sup>8</sup> mp 51-53°, were the sole products in nearly quantitative yield from solvolysis of the respective esters V-OPNB and VI-OBs.

The extra rate enhancement provided by the exo-fused cyclopropyl ring may be accounted for by one

(or more) of the following: (a) a homoconjugative reinforcing effect by the cyclopropane C-2-C-4 edge bond; (b) a ground-transition state effect (relief of nonbonded interactions in the transition state, *i.e.*, steric acceleration); (c) a bending of the bridge carbon further over toward the anti double bond or benzene ring as a result of nonbonded repulsions between the bridge substituent and the cyclopropyl endo methylene hydrogen. In an effort to gain more insight into the steric factors operating in these systems the acetolysis of *exo-anti*-benztricyclo[4.2.1.0<sup>2,5</sup>]non-9-yl brosylate (VII-OBs),<sup>8,10</sup> mp 159-160°, was examined and found to be intermediate in reactivity (Table II) between IV and VI. This result is in accord with either factor b or c since nonbonded repulsions between the bridge and the exo-fused ring would appear to be less severe in the ground state for VII than for VI. On the other hand the possibility that the rate factor k<sub>VII</sub>/k<sub>IV</sub> of 10<sup>2</sup> could be accounted for by a cyclobutyl homoconjugative reinforcing effect seems quite remote.<sup>11</sup>

To further probe the nature of this cyclopropyl acceleration the effect of substituents in the 4' position of VI was examined and compared to that found pre-

(10) Our appreciation is extended to Dr. John Nebzydoski for the preparation of this brosylate from its corresponding alcohol VII-OH obtained from another study: M. A. Battiste and J. W. Nebzydoski, *J. Amer. Chem. Soc.*, **91**, 6887 (1969).

(11) The magnitude of the rate difference for direct edge participation by cyclopropane compared to cyclobutane (*ca.* 10<sup>9</sup>-10<sup>10</sup>) supports this conclusion. See M. A. Battiste and J. W. Nebzydoski, *ibid.*, **92**, 4450 (1970), or M. Sakai, A. Diaz, and S. Winstein, *ibid.*, **92**, 4452 (1970), and references cited therein.

(8) All new compounds gave correct elemental analyses and mass spectral assurances of sample purity and molecular weight. Other spectral data (nmr, ir) were in accord with assigned structures.

(9) M. A. Battiste and M. E. Brennan, *Tetrahedron Lett.*, 5857 (1966).

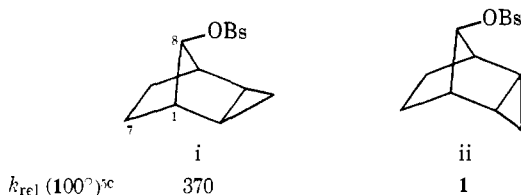
viously<sup>12</sup> in the model system IV. Initially two substituents, one electron donating (CH<sub>3</sub>) and one electron withdrawing (Br), were chosen for study for reasons of synthetic convenience. Tanida has previously determined the relative order of reactivity of esters IX-OBs, IV-OBs, and 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>8c</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.

Merle A. Battiste,\* Paul F. Ranken,<sup>14</sup> Robert Edelman

Department of Chemistry, University of Florida  
Gainesville, Florida 32601

Received September 3, 1971

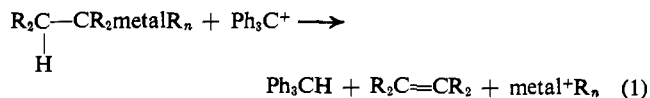
### $\sigma$ - $\pi$ Conjugation of Carbon-Metal Bonds. Dehydrometalation of Alkylmetal Compounds<sup>1</sup>

Sir:

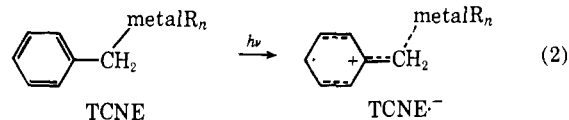
We wish to report an extraordinarily facile hydride abstraction from positions  $\beta$  to carbon-metal bonds.<sup>2</sup>

(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

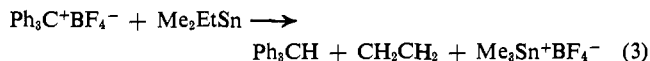


Previous studies revealed a very large effect of the groups  $\text{R}_n\text{metalCH}_2^-$  upon the vertical stabilization of positive carbon in such processes as eq 2.<sup>3</sup> These



findings suggested that cations such as  $\text{Me}_3\text{SnCH}_2\text{CH}_2^+$  or  $\text{MeHgCH}_2\text{CH}_2^+$ , 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  $\text{Me}_3\text{SnBF}_4$  were produced in nearly quantitative yields.<sup>5</sup> Similarly rapid reactions occurred with di-



butylmercury,  $\text{PhCH}_2\text{CH}_2\text{PbPh}_3$ ,<sup>3b</sup>  $(\text{PhCH}_2\text{C}(\text{Me})\text{H})_2\text{Hg}$ ,<sup>3b</sup> and  $\text{PhC}(\text{Me})\text{HSnMe}_3$ . However,  $\text{PhCH}_2\text{SnMe}_3$ ,<sup>3b</sup>  $\text{Me}_4\text{Sn}$ ,  $(\text{PhCMe}_2\text{CH}_2)\text{Hg}$ ,<sup>8</sup> and di-1-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

$$-\frac{d[\text{Ph}_3\text{C}^+]}{dt} = k_2[\text{Ph}_3\text{C}^+][\text{R}_n\text{MCR}_2\text{CHR}_2] \quad (4)$$

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  $\text{Me}_3\text{SiCH}_2\text{CD}_2^+$ , observed by Cook, Eaborn, and Walton,<sup>9</sup> clearly demonstrates the existence of this  $\beta$

nontransition metal compounds such as  $\text{Et}_2\text{Pb}$ , 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  $\text{RHgCH}_2\text{CH}_2^+$  ion (which we derive from  $\text{Et}_2\text{Hg}$ ) 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).