boronate ester **7** could be formed reversibly and in high yield under quite mild conditions, and this transformation introduced no change in the symmetry properties of the original array (**4**).

As a carboxylic acid, **7** gave a crystalline salt with quinine which, after four recrystallizations from ethyl acetate, showed $[\alpha]^{25}$ −37.4° (*c* 3.30, methanol).[10] Liberation of **7** by treatment of the salt with aqueous hydrochloric acid gave optically active material, $[\alpha]^{25}$ +39.8° (*c* 4.42, ethyl acetate),[10] which was hydrolyzed in hot aqueous dioxane to **4**, $[\alpha]^{25}$ +57.5° (*c* 2.76, acetone).[10]

Experiments with racemic **4** indicated that it was cleaved to nitro diketone **2** in high yield by lead tetraacetate in benzene.[11] This reaction was now applied to dextrorotatory **4** and the racemization of the isolated product, dextrorotatory **2**, was followed in chloroform solution.[10] First-order rate constants for this process were determined graphically and are recorded in Table I; from these data the following activation parameters were calculated for 25.5° in conventional fashion: $\Delta F^{\ddagger} = 22.9$ kcal/mole; $E_a = 26.1$ kcal/mole; $\Delta H^{\ddagger} = 25.5$ kcal/mole; $\Delta S^{\ddagger} = +9$ eu.

Table I. First-Order Rate Constants

Temp (±0.5°), °C	$k \times 10^5$, sec^{-1}
15.5	2.96
	2.95
25.5	11.4
	11.5
	11.0
30.5	27.2
	27.2

[10] All rotations were measured in a 1-dm cell at 5461 A (mercury green line).

[11] Unsubstituted glycol **2** is oxidized to **1** under these conditions; *cf.* ref 4.

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Neighboring Group Dipolar Effects upon Solvolytic Reactivity

Sir:

Inherent in the hypothesis of neighboring group participation is the difficulty of estimating the rate-retarding effect of the group in the absence of participation.[1] As an approach toward separating the opposing factors of inductive and field destabilization *vs.* the stabilizing effect derived from anchimeric assistance, we have studied the solvolytic behavior of several model compounds which possess a neighboring group locked in a position unfavorable for anchimeric interaction. Rate data for the typical compounds I–IV are given in Table I.

The essential findings of this study are (a) large (factors of 10^4–10^7) rate decelerations relative to the parent compounds, (b) abnormally high infrared carbonyl stretching frequencies for the ketonic carbonyl group derived from the related secondary alcohol, and (c) extensive rearrangement in the product-forming step. We interpret the observed rate retardations in terms of an electrostatic destabilization arising from the interaction of the conformationally fixed dipole of the neighboring group and the developing dipole associated with the departing toxyloxy anion. The related carbonyl compound serves as a model for this transition-state interaction and the high carbonyl stretching frequency is attributable to similar dipolar destabilization in the ground state.[2]

The origin of the very large rate retardations observed for I–IV could be in steric, inductive, or field effects. From a steric standpoint, it is clear that the 2,6-bridging group in compounds I–IV effectively blocks the rear side of the potential cationic center at C_5 and could hinder seriously solvation. However, the corresponding 2,6-ethano-bridged derivative, *exo*-2-brendyl brosylate, solvolyzed at about the same rate as *exo*-2-norbornyl brosylate.[6] As far as the inductive effect of bridged lactone and oxido groups within the norbornyl system is concerned, very little data exist for the rate-retarding influence due to these substituents. Assuming that the lactone function in I might retard the solvolysis to about the same extent as a β-acetoxyl group, one would expect a rate-retardation factor of 10^3 relative to norbornyl tosylate.[7] Neither steric nor simple

[1] For a discussion see E. Grunwald, *J. Am. Chem. Soc.*, **73**, 5458 (1951); S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, **70**, 821 (1948).

[2] These effects are, of course, well recognized; however, attention has not been drawn explicitly to the possible relationship between the carbonyl stretching frequency and the rate of solvolysis in systems possessing neighboring dipolar functions. For example, the carbonyl stretching frequency for an α-bromo ketone possessing an almost coplanar arrangement of the carbonyl group and bromine atom is shifted by 20 cm^{-1} relative to the *trans* orientation. The shift is due to a destabilizing dipolar interaction which is minimized in the *trans* case.[3] Applying the Schleyer-Foote equation[4,5] to this system in which the displacement in the carbonyl stretching frequency is not due to internal angular strain but rather a dipolar effect, one would anticipate a rate retardation of log rel rate = 0.125(20 cm^{-1}) = 2.5. Approximate models exist to test this prediction.[1] At 75°, the relative rates of solvolysis of cyclohexyl brosylate, *trans*-2-bromocyclohexyl brosylate, and *cis*-2-bromocyclohexyl brosylate are 1.00:0.101:1.24 × 10^{-4}. If one assumes that the transition states for solvolysis of the two bromo tosylates have the tosyloxy group in an axial conformation, one can understand the relative rates of solvolysis of the *cis* a,e and *trans* a,a without recourse to anchimeric assistance by bromine in the rate-limiting ionization step.

[3] R. N. Jones, D. A. Ramsay, F. Herling, and K. Dobriner, *J. Am. Chem. Soc.*, **74**, 2828 (1952); E. J. Corey, *ibid.*, **75**, 2301 (1953); N. L. Allinger, J. Allinger, L. A. Freiberg, R. F. Czaja, and N. A. LeBel, *ibid.*, **82**, 5876 (1960).

[4] P. von R. Schleyer, *ibid.*, **86**, 1854, 1856 (1964).

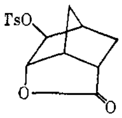
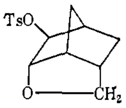
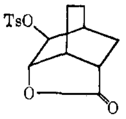
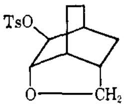
[5] C. S. Foote, *ibid.*, **86**, 1853 (1964); Ph.D. Dissertation, Harvard University, 1961.

[6] Private communication, A. Nickon.

[7] Using the Taft equation with $\alpha^* = 0.85$, $\rho^* = -3.49$, and k_H for norbornyl tosylate at 25° of 2.33×10^{-5} sec^{-1}, one may calculate the rate of solvolysis for the β-acetoxyl derivative to be 2.6×10^{-8} sec^{-1}. This of course does not take into account the position of the acetoxyl group in space relative to the tosyloxy group.

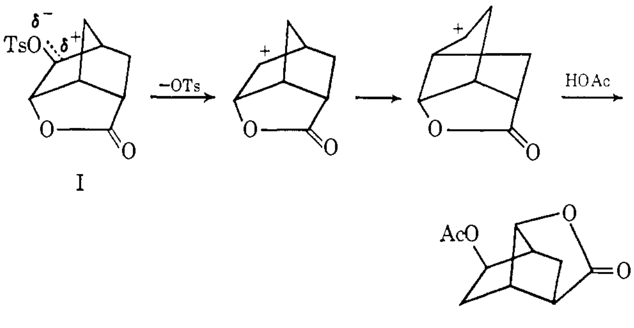
[8] Thus far, no large solvolytic rate variations have been reported for norbornyl derivatives bearing polar substituents. P. G. Gassman and J. L. Marshall, *J. Am. Chem. Soc.*, **87**, 4648 (1965), essentially discount dipole–dipole interactions as being important in the solvolysis of 7-ketonorbornyl tosylates. H. Kwart and T. Takeshita, *ibid.*, **86**, 1161 (1964), find rate variations of less than a factor of 10 for orientated polar substituents. The work of Roberts and co-workers on the *syn*- and *anti*-7-chloro-2-*exo*-norbornyl tosylates has not disclosed any analogous dipolar interactions. The ratio of rates of the *anti* to *syn* isomers is 1.25. Absence of such an effect is due to the lower dipole moment of the carbon–chlorine bond and also the greater distance between the chlorine atom in the *syn* case and the departing tosyloxy group. This may account for the differences between our work and theirs: W. G. Woods, R. A. Carboni, and J. D. Roberts, *ibid.*, **78**, 5653 (1956).

Table I. Acetolysis Rates of 2,6-Bridged Bicyclo[2.2.1]heptyl and Bicyclo[2.2.2]octyl Tosylates Relative to *exo*-2-Bicyclo[2.2.1]heptyl and 2-Bicyclo[2.2.2]octyl Tosylate

Compound[a]	Temp, °C	Rate, sec^{-1}	k_{rel}^{25}	k_{rel}^{100}	$\nu_{C=O}$, cm^{-1}
 I	100.50 160.00 185.00 (25)[d]	5.8×10^{-8} 2.17×10^{-5} 1.43×10^{-4} 1.5×10^{-12}	6.5×10^{-8} [b]	1.4×10^{-6} [b]	1800[e] ($\Delta = 49$)[g]
 II	76.00 100.50 (25)[d]	9.50×10^{-7} 15.8×10^{-6} 3.4×10^{-9}	1.46×10^{-4} [b]	3.9×10^{-4} [b]	1763[f] ($\Delta = 12$)
 III	100.50 160.00 (25°)[d]	8.96×10^{-8} 7.83×10^{-6} 8.1×10^{-11}	2.2×10^{-7} [c]	5.3×10^{-6} [c]	1775[e] ($\Delta = 44$)[h]
 IV	76.00 100.50 (25°)[d]	5.90×10^{-7} 7.5×10^{-6} 1.7×10^{-9}	4.7×10^{-4} [c]	4.5×10^{-4} [c]	

[a] Correct analyses were obtained for I–IV. Melting points are: I, 94–95°; II, 86–87°; III, 90–92°; IV, 143–144°. [b] Rates relative to *exo*-2-norbornyl tosylate: $k^{25} = 2.33 \times 10^{-5}$ sec^{-1} (P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Am. Chem. Soc.*, **87**, 375 (1965)); $k^{100} = 4.08 \times 10^{-2}$ sec^{-1} (calculated from data in Schleyer, *et al.*). [c] Rates relative to 2-bicyclo[2.2.2]octyl tosylate: $k^{25} = 3.61 \times 10^{-6}$ sec^{-1} (H. L. Goering and M. F. Sloan, *ibid.*, **83**, 1992 (1961)); $k^{100} = 1.68 \times 10^{-2}$ sec^{-1} (rates calculated from Goering and Sloan). [d] Calculated rates. [e] For keto group of derived keto lactone. [f] For keto group of derived keto oxide. [g] For 2-norbornanone, $\nu_{C=O}$ 1751 cm^{-1} (CCl_4).[4] [h] For bicyclo[2.2.2]octanone, $\nu_{C=O}$ 1731 cm^{-1} (CCl_4).[4]

inductive effects appear to account for the factor of 10^7 rate retardation observed for lactone I relative to norbornyl tosylate. We propose that the slow rate is due to a strong dipolar repulsion between the lactone dipole and the developing dipole of the C–OTs bond as the carbon–oxygen bond begins to elongate in the ionization process.



I

V

Furthermore, these molecules have a hemispheric shape. Due to the absence of solvent in the cavity of these solutes, the effective dielectric constant of the interior portion would expectedly differ considerably from that of the bulk external solvent. The lines of force of the transannular dipolar interaction traverse the cavity of low dielectric constant with no intervening bulk solvent (acetic acid) available for dipole–dipole charge dispersion. Similar considerations may be applied to II–IV.

This dipolar destabilization is also manifested in a ground-state property, namely, the infrared carbonyl stretching frequency of the keto lactone[9] related to I occurs at 1800 cm^{-1}, while the carbonyl stretching frequency[11] of the closely related 2-brendanone occurs at 1747 cm^{-1}. If the Schleyer–Foote relationship is applied to the system in which the shift in carbonyl stretching frequency is due to dipolar destabilization, one can account for the remarkably slow rate of solvolysis, *i.e.*, log rel rate = 0.125(85 cm^{-1}) = 10.6.

Further support for the interpretation comes from the fact that only rearranged acetoxy lactone V is formed in the solvolysis of I. Thus, the dipolar destabilization is relieved by movement of the positive center to a position more remote with respect to the positive end of the lactone dipole.

Analogous behavior was observed for lactone III. The corresponding keto lactone has $\nu_{C=O}$ 1775 cm^{-1}, log rel rate = 7.5. Furthermore, solvolysis proceeds with complete rearrangement to yield products tentatively identified as 4-*exo*-acetoxy-8-hydroxybicyclo[3.2.1]octane-7-*exo*-carboxylic acid γ-lactone and 8-hydroxybicyclo[3.2.1]octene-2,7-*exo*-carboxylic acid γ-lactone.

As shown in Table I, the bridged oxides II and IV also solvolyze slowly. The carbonyl stretching frequency for the keto oxide related to II occurs at 1763 cm^{-1}; the shift from norbornanone of 12 cm^{-1} is not as large as one might anticipate on the basis of the four orders of magnitude rate difference between II and norbornyl tosylate. The keto oxide related to IV has not been synthesized. As far as products of solvolysis

[9] The keto lactone is very reactive, and considerable difficulty was encountered in its preparation: K. C. Ramey, D. C. Lini, R. M. Moriarty, H. Gopal, and H. G. Walsh, *J. Am. Chem. Soc.*, **89**, 2401 (1967). In fact, Crundwell and Templeton[10] have reported upon their unsuccessful attempts to synthesize this compound.

(10) E. Crundwell and W. Templeton, *J. Chem. Soc.*, 1400 (1964).

(11) A. Nickon, H. Kwasnik, T. Swartz, R. O. Williams, and J. B. DiGiorgio, *J. Am. Chem. Soc.*, **87**, 1616 (1965).

in these cases are concerned, the tendency for rearrangement is not as pronounced as with the related lactones I and III. In both cases unrearranged acetoxy oxide is the major product along with products derived from rearrangement and solvolysis of the oxido group. Complete details of structures will be given in the full manuscript.

Finally, we wish to call attention to the potential application of the type of considerations put forth by Schleyer and Foote concerning systems where dipolar destabilization offers a common origin for both slowed rates of solvolysis and abnormally high carbonyl of the derived ketone.

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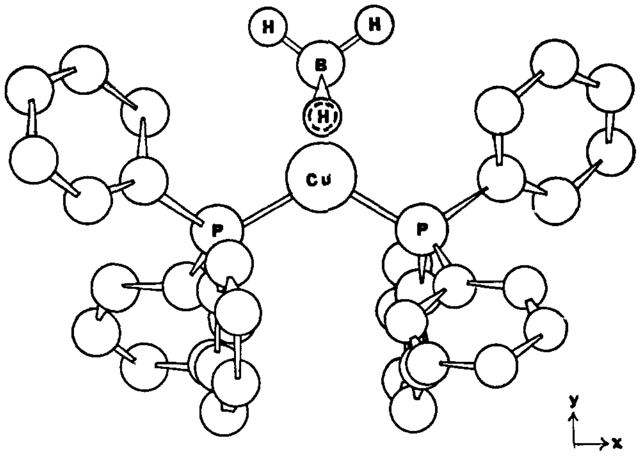


Figure 1. Geometry of borohydridobis(triphenylphosphine)copper(I): Cu–B, 2.18 ± 0.01 A, Cu–P, 2.276 ± 0.003 A, Cu–H, 2.02 ± 0.05 A, B–H, 1.31 ± 0.05 A, P–Cu–P, 123.3 ± 0.2°, P–Cu–B, 118.4 ± 0.1°. Carbon atoms are not labeled. Protons on the phenyl rings are not shown.

Transition Metal Borohydride Complexes. I. The Structure of Borohydridobis(triphenylphosphine)copper(I)

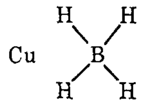
Sir:

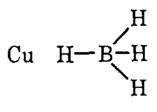
At present, little is known about the mechanistic details of the reduction of transition metal ions by the borohydride ion, BH_4^-. Occasionally, it has been possible to isolate a stable transition metal borohydride complex, cogent examples being $[(\pi\text{-}C_5H_5)_2Ti(BH_4)]$,[1] $[NiA(BH_4)_2]$,[2] and $\{[(C_6H_5)_3P]_2Cu(BH_4)\}$.[3,4] Recently we have begun to study the structures and reactivities of certain of these complexes as a first step toward understanding the detailed manner in which BH_4^- acts as a reducing agent. Here we report the first X-ray structural characterization[5] of a transition metal borohydride complex, borohydridobis(triphenylphosphine)copper(I).

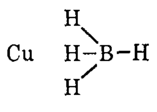
Crystals suitable for X-ray studies, obtained by the method of Cariati and Naldini,[4] were found to have Laue symmetry 2/m with unit cell dimensions $a = 24.64 \pm 0.02$, $b = 9.058 \pm 0.008$, $c = 15.43 \pm 0.01$ A, and $\beta = 116.2 \pm 0.1°$. From the measured density, $\rho = 1.3$ g/cc, and observed systematic absences, hkl, $h + k \neq 2n$, $h0l$, $l \neq 2n$, the space group was ascertained to be C2/c or Cc, with $Z = 4$.

Three-dimensional intensity data were collected on a Picker automated diffractometer using Cu Kα radiation. After applying the usual Lorentz, polarization, and absorption corrections, the data were placed on an approximately absolute scale by Wilson's method. A three-dimensional Patterson map revealed the copper and phosphorus atomic positions, and, from the first difference Fourier map, the 19 remaining nonhydrogen atoms in the asymmetric unit were located.[6] Isotropic refinement of the 1750 independent observable reflections converged to values of 0.094 and 0.077 for the conventional unweighted and weighted factors, R_1 and R_2, respectively. Anisotopic refinement of all atoms further reduced these R factors to 0.077 and 0.066. Examination of a difference Fourier map, prepared by subtracting out the contributions of all nonhydrogen atoms, showed residual peaks in the regions expected for all hydrogen atoms attached to the benzene rings. In addition, the hydrogen atoms of the borohydride group were unambiguously located. No attempt was made to refine the hydrogen atom positional or thermal parameters.[6a]

The molecular structure of borohydridobis(triphenylphosphine)copper(I) is shown in Figure 1. From space group symmetry alone, the complex is required to have over-all twofold symmetry. This result is consistent with previous infrared spectral studies[3,4] of the molecule which suggest that, of the three possible orientations of the BH_4^- group shown below, I is correct. This conclusion is further supported by the


I


II


III

location of both the bridging and terminal hydrogen atoms at an average distance of 1.31 ± 0.05 A from the boron atom.

Both the boron and copper atoms may be considered as having quasi-tetrahedral configurations, in which two sp^3 orbitals from the copper atom participate in two three-center, two-electron bonds with the borohydride group. With this bonding scheme, however,

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(1) R. Nöth and R. Hartwimmer, *Chem. Ber.*, **93**, 2238 (1960).

(2) N. F. Curtis, *J. Chem. Soc.*, 924 (1965), where A is a cyclic tetramine or a noncyclic Schiff base amine.

(3) J. M. Davidson, *Chem. Ind.* (London), 2021 (1964).

(4) F. Cariati and L. Naldini, *Gazz. Chim. Ital.* **95**, 3 (1965).

(5) Since the submission of this communication, a report describing the crystal structure of $Zr(BH_4)_4$ has appeared: P. H. Bird and M. R. Churchill, *Chem. Commun.*, 403 (1967).

(6) The centrosymmetric space group, C2/c, was chosen after careful examination of the Patterson map and appears to be justified by the successful refinement of the structure.

(6a) Note Added in Proof: Subsequent refinement of all hydrogen atom positional and isotropic thermal parameters reduced R_1 to 0.059 and R_2 to 0.044. Slight changes in the molecular geometry of the copper–borohydride attachment resulted from the refinement, the details of which will be reported shortly (S. J. Lippard and K. Melmed, submitted for publication).