photolysate solution to hydroborate 1-octyne rules out the presence of neutral boron hydrides, such as $(C_6H_5)_2BH$. However, the detection of HD, upon addition of DOAc, and the formation of undeuterated toluene, upon introduction of benzyl chloride and deuterolytic work-up, clearly point to the presence of a borohydride.[8] The detection of varying proportions of monodeuterated biphenyl and terphenyls concludes our justification for the formulation generalized by **4**.

Continuing research strives to employ these rearrangements for the novel preparation and further study of borate(I) salts and for the possible synthesis of interesting boron heterocycles, such as the boracyclopropene nucleus.

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References and Notes

(1) This contribution is part XII of the series, "Rearrangements of Organometallic Compounds" (previous part: *J. Organomet. Chem.*, **71**, C21 (1974)), as well as part III of the series, "Boraaromatic Systems" (previous parts: *ibid.*, **8**, 53 (1967); *J. Am. Chem. Soc.*, **91**, 4575 (1969)).

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(6) *trans*-Stilbene was found in the irradiation of **9**, when less rigorous conditions in the purification of **9** or of the THF were used. Also, prolonged irradiations (>24 hr) led to significant amounts of this isomer. Under the irradiation conditions, the chamber of the Rayonet Reactor, Model RPR 100, had an ambient temperature of *ca.* 45°. Since phenyllithium has been shown to attack THF rather readily above 25° (H. Gilman and B. J. Gaj, *J. Org. Chem.*, **22**, 1165 (1957)), the protolysis of **10** by THF to yield **11** is most likely under the reaction conditions. An alternative route to **10a** from diphenylacetylene and **3** would be a simple addition, without the intervention of **7a.** However, **3** would then be expected to add by nucleophilic attack of $^{-}B(C_6H_5)_2$ on the C≡C bond. Not only are such nucleophilic additions in donor media generally trans additions (J. E. Mulvaney, Z. G. Gardlund, S. L. Gardlund and D. J. Newton, *J. Am. Chem. Soc.*, **88**, 476 (1966)) but any cis stilbenylmetallic derivative that might be formed by such an improbable stereochemical course, would be expected to isomerize rapidly in THF to the trans configuration (D. Y. Curtin and W. J. Koehl, Jr., *J. Am. Chem. Soc.*, **84**, 1967 (1962)).

(7) In formulating sodium diphenylborate(I) as **3**, upon the basis of chemical tests, we leave open the question of its state of association. There is a

$$3 \overset{?}{\rightleftharpoons} [(C_6H_5)_2B{=}B(C_6H_5)_2]^{2-}$$

certain appeal in considering that **3** may exist, wholly or in part, as a dimer of higher aggregate.

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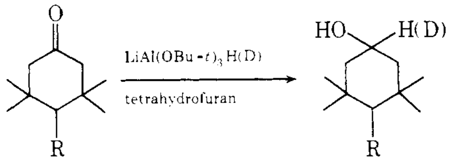
Inverse Kinetic Isotope Effect in the Reduction of Hindered Ketones by $LiAl(OBu\text{-}t)_3H$ and $LiAl(OBu\text{-}t)_3D$[1]

Sir:

The question of whether it might be possible to observe inverse primary isotope effects in borohydride chemistry is an intriguing one which has already attracted attention. In 1960, Davis, Kibby, and Swain reported inverse (0.70) isotope effects in the hydrolysis of sodium borohydride and borodeuteride,[2,3] an effect that was ascribed to a small normal primary isotope effect swamped by three secondary isotope effects of the nonreacting hydrogens. An alternative interpretation for this overall inverse effect was subsequently suggested by Halevi,[4] based on the fact that the reaction involved replacement of a weaker B-H bond by a stronger H-H bond and that therefore the invoking of an inverse *primary* isotope effect was reasonable. The possibility of inverse primary isotope effects was probed in further detail by Bigeleisen who concluded that they would indeed occur under some circumstances, particularly the situation of the product having a very strong force constant compared to that of reactant and the reaction proceeding through a transition state close to product,[5] a conclusion reiterated more recently by Melander.[6] Subsequent experimental work by Davis, however, confirmed the original interpretation of the primary effect being small, but normal, and the overall inverse effect being caused by the secondary effects.[7] Borohydride reduction of ketones also gives rise to overall inverse isotope effects (0.59-0.77), and likely has the same origin.[8,9]

Despite the apparent nonoccurrence of inverse primary isotope effects in borohydride reactions, the idea that such effects can, in principle, occur remains, and in this connection we wish to report some results on the reduction of ketones by $LiAl(OBu\text{-}t)_3H$ and $LiAl(OBu\text{-}t)_3D$, reducing agents devoid of the secondary isotope effect ambiguity. Kinetic isotope effects were measured by competition experiments, the two reducing agents competing for ketone, followed by mass spectral determination of the H/D ratio of alcohol. H/D ratios were obtained from the fragments $(P - H_2O)^+$, because molecular ions were generally of very low intensity. This method was used for all alcohols in this study and was verified by measuring the ratio for those compounds with appreciable molecular ion intensities. In common with substituted borohydride reactions,[7] the primary isotope effect for reduction of most ketones was in fact small and normal, ranging in value from unity to 1.5. However, the reduction of two highly hindered ketones, 3,3,5,5-tetramethylcyclohexanone and 4-acetyl-3,3,5,5-tetramethylcyclohexanone,[10] produced markedly inverse isotope effects of 0.79 ± 0.08 and 0.70 ± 0.08, respectively. The error limits reflect an experimental reproducibility error of ±0.03 and an uncertainty of 0.05 because of possible HDO loss in the fragmentation process in the mass spectrometer. The latter figure was derived from separate experiments with compounds that were fully deuterated at the α carbon position.



R = H $k_H/k_D = 0.79 \pm 0.08$
R = $COCH_3$ $k_H/k_D = 0.70 \pm 0.08$

While our main purpose in this communication at this stage is simply to report the experimental demonstration of the existence of the proposed[4-6] and searched-for[7] inverse isotope effect in this type of reaction, it is clear that these results also have considerable relevance to the unsettled and confused situation regarding the nature of transition states in these reactions. Provided that the mechanism is simply a one-step nucleophilic addition to the carbonyl, the inverse effect is an example of a true primary inverse kinetic isotope effect which, while not unknown, is exceedingly rare.[11] This clearly places severe constraints on the possible structure of the transition state, with linear hydrogen transfer being ruled out unless the transition state is highly unsymmetrical.[12]

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Dependence of ^{31}P Chemical Shifts on Oxygen–Phosphorus–Oxygen Bond Angles in Phosphate Esters

Sir:

We propose an empirical correlation between phosphate ^{31}P chemical shifts and O–P–O bond angles. That some such bond angle relationship probably exists for cyclic phosphate esters has been recognized,[1-3] but a direct bond angle relationship for all classes of phosphate esters has not been established.

Any successful theory must accommodate several apparently conflicting pieces of data. (1) The ^{31}P chemical shift of phosphates is generally insensitive to the chemical identity (R or H) of the group bonded to the phosphate oxygen. (2) The chemical shift is sometimes sensitive to the ionization state of the acid. (3) Association of divalent metal ions[4] and hydrogen bonding donors[5,6] has little effect on the ^{31}P chemical shift other than that explained by a shift in the p*K*. (4) Cyclic five-membered ring phosphate esters are shifted downfield from their acyclic counterparts by 15–20 ppm while cyclic six-membered ring esters are shifted *upfield* by 2–11 ppm from their acyclic analogs.

Several authors have attempted to create a unified theoretical foundation for ^{31}P chemical shifts in all classes of phosphorus compounds.[3,7-9] In one of the more successful theoretical approaches, Van Wazer and Letcher,[3,10] using quantum-mechanical calculations, demonstrate that three factors appear to dominate the ^{31}P chemical shift: electronegativity differences in the P–X bond, changes in the π-electron overlap, and changes in the σ-bond angle.

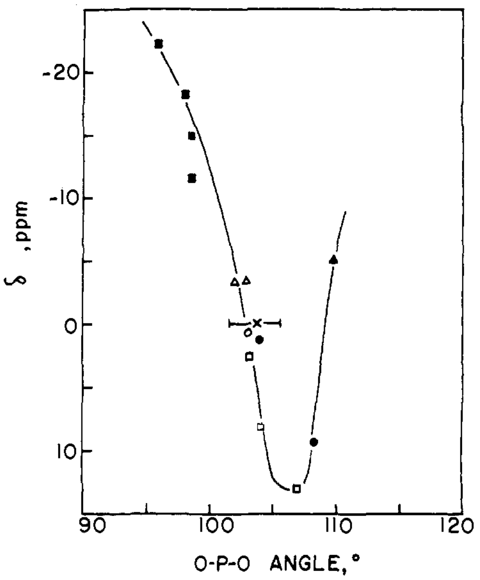

Figure 1. ^{31}P chemical shift of phosphate esters *vs.* O–P–O bond angle (■, five-membered cyclic esters; △, monoester dianions; ×, monoester monoanions; ○, acyclic diester monoanions; ●, acyclic diester free acids; □, six-membered cyclic esters; ▲, Li_3PO_4). Solid line has no theoretical significance.

For phosphoryl compounds Van Wazer concludes that changes in the σ-bond angles make a negligible contribution to the ^{31}P chemical shift,[10] with electronegativity effects apparently predominating.[3] Purdela claims establishing a correlation between X–P–X bond angles and chemical shifts for a wide variety of phosphoryl compounds, however, admitting that the correlation is poor.[9] Westheimer[1] and others[2] have argued that the O–P–O ring angle must play some role in ^{31}P chemical shifts on the basis of cyclic ester shifts, which is inconsistent with Van Wazer's theory. A change in dπ–pπ bonding resulting from bond angle changes was suggested as an explanation for these shifts. Recently Blackburn,[2] compiling all of the known cyclic ester chemical shifts, concluded that these ring shifts must arise from a "complex stereoelectronic effect" not explicable by present theory.

In Table I we have compiled nearly all of the X-ray crystallographic data on phosphates for which a ^{31}P chemical shift is known. The reported O–P–O bond angle shown in Table I is generally that between two phosphate oxygens which are either protonated or esterified. In triesters and monoester dianions they represent the cyclic or(for noncyclic esters) the smallest O–P–O bond angle in the structure.

A plot of ^{31}P chemical shift *vs.* O–P–O bond angle is shown in Figure 1 and demonstrates that a quite simple empirical correlation may be drawn relating the chemical shifts and bond angles of phosphate esters. (We make no claim for applicability of this correlation to other classes of phosphoryl compounds.) Although bond angles in the solid state may significantly differ from those in solution due to crystal packing forces, a simple Gillespie-Nyholm[11] analysis of electron pair repulsions in the phosphates would suggest that these solid-state angles do reflect the expected distortions from tetrahedral symmetry.

Further support for the correlation that we have drawn here is derived from the "anomalous" shifts of the cyclic *vs.* acyclic monoanions and free acids. In the acyclic phosphate