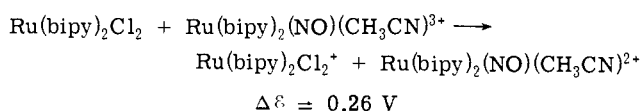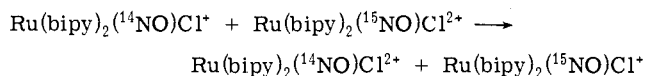in marked contrast to $[Fe(CN)_4NO]^{2-}$ where a large ^{57}Fe hyperfine interaction has been observed ($A_{ISO} = -7.21$ G) and the unpaired electron appears to be localized largely on the metal.[18]

The similarities between nitroprusside ion and the ruthenium nitrosyl complexes indicate that the molecular orbital scheme developed by Manoharan and Gray for the nitroprusside ion[20] is also appropriate for the ruthenium nitrosyl complexes. In that scheme the lowest unoccupied molecular orbital is largely $\pi^*(NO)$ in character with some metal d character.

The ruthenium nitrosyl complexes provide an unusual example where simple electron transfer occurs to and from a coordinated ligand. The nitrosyl complexes are moderately strong oxidants whose reduction potentials fall in a range which overlaps the potentials for closely related Ru(III)/Ru(II) couples (e.g., $Ru(bipy)_2Cl_2^{+/0}$ at 0.32 V). The nitrosyl complexes undergo facile electron transfer. From stopped flow measurements at 25° in acetonitrile, the reaction

$$Ru(bipy)_2Cl_2 + Ru(bipy)_2(NO)(CH_3CN)^{3+} \longrightarrow$$
$$Ru(bipy)_2Cl_2^+ + Ru(bipy)_2(NO)(CH_3CN)^{2+}$$
$$\Delta \varepsilon = 0.26 \text{ V}$$

occurs with $k > 10^6 \ M^{-1} \ sec^{-1}$ (assuming that the reaction is second order). By observing the appearance of $\nu(^{14}NO)$ (1940 cm^{-1}) and the disappearance of $\nu(^{15}NO)$ (1900 cm^{-1}) in the region 1860–1970 cm^{-1} in acetonitrile, we estimate that for the self-exchange reaction

$$Ru(bipy)_2(^{14}NO)Cl^+ + Ru(bipy)_2(^{15}NO)Cl^{2+} \longrightarrow$$
$$Ru(bipy)_2(^{14}NO)Cl^{2+} + Ru(bipy)_2(^{15}NO)Cl^+$$

$k > 10^2 \ M^{-1} \ sec^{-1}$, at room temperature.

We recently reported that efficient, light-catalyzed, net intramolecular electron transfer occurs between Ru(III) and coordinated azide ion[21]

$$Ru(bipy)_2(N_3)_2^+ + CH_3CN \xrightarrow{h\nu}$$
$$Ru(bipy)_2(CH_3CN)(N_3)^+ + \tfrac{3}{2}N_2$$
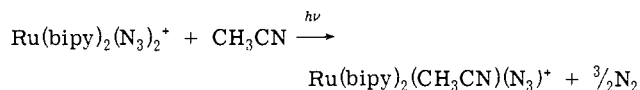
It is interesting to note that in the nitrosyl complexes the roles of ligand and metal can apparently be reversed. Upon uv irradiation a seemingly efficient, light-induced reaction occurs (eq 1) which is quantitative as shown by gas evolution and spectral studies. At least in the formal sense, reac-

$$Ru^{II}(bipy)_2(\overset{+}{NO})Cl^{2+} + CH_3CN \xrightarrow{312 \text{ nm}}$$
$$Ru^{III}(bipy)_2(CH_3CN)Cl^{2+} + NO \quad (1)$$
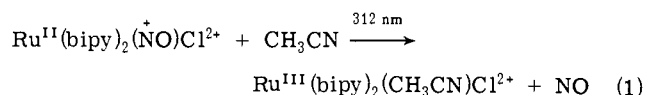
tion 1 involves net electron transfer from ruthenium to the nitrosyl group.

The redox properties of the nitrosyl complexes reinforce the idea that, in an appropriate coordination environment, the nitrosyl group can be adequately described as a chemically modified form of the nitrosonium ion. The nitrosyl complexes reported here are potentially versatile electron transfer reagents with synthetically controllable reduction potentials and have low kinetic barriers to electron transfer.

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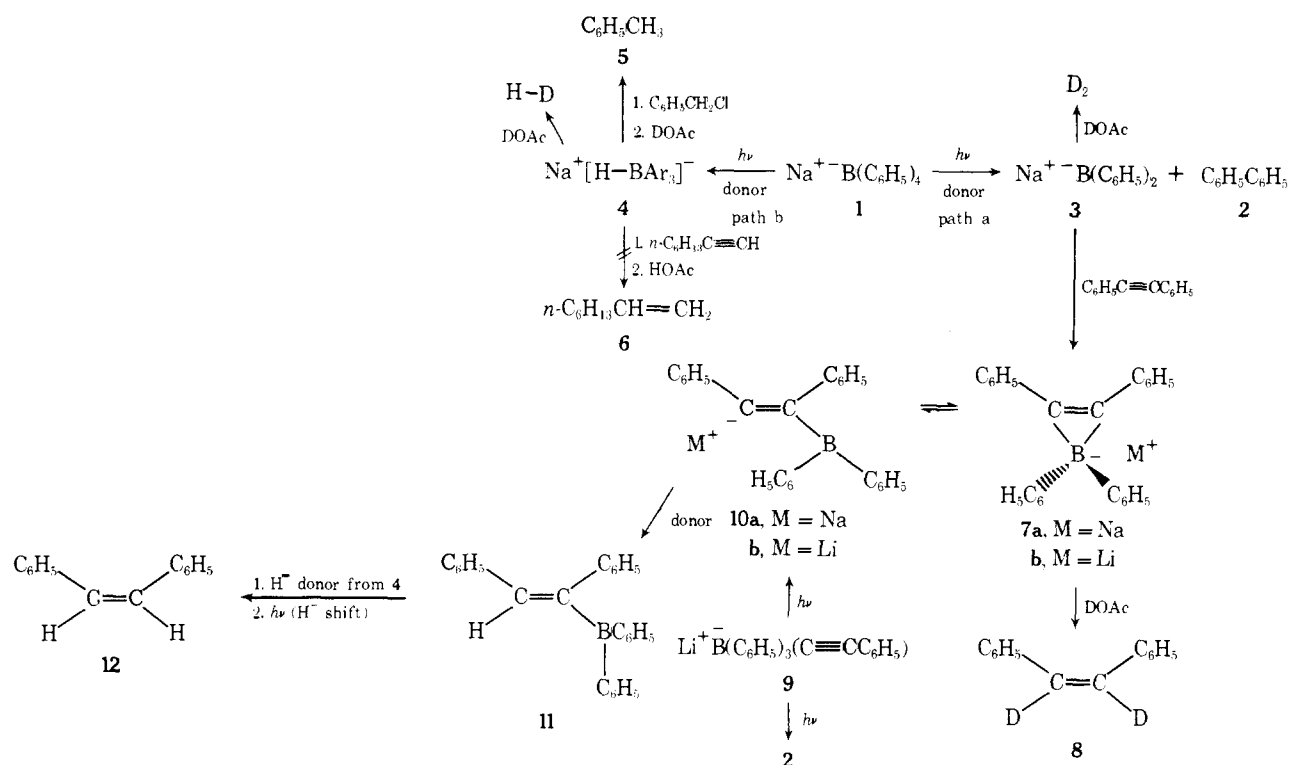*Chapel Hill, North Carolina 27514*

Generation of Boracarbenoid and Boracyclopropene Intermediates from the Photolysis of Tetraorganoborate Salts in Aprotic Media[1]

Sir:

The photolysis of tetraarylborate salts in protic media, under anaerobic[2,3] or aerobic[3] conditions, has led to novel dihydrobiaryl or biaryl coupling products, respectively. As an extension of our interest in chemically induced 1,2-aryl shifts from boron to carbon,[4] we have been led to examine such rearrangements initiated photochemically under aprotic conditions and under nitrogen. By avoidance of hydroxylic solvents we hoped to generate and detect the potentially interesting boron fragments and rings thought to be involved in these photochemical processes.

We now wish to report that the irradiation at 254 nm of sodium tetraphenylborate(III) (**1**) in anhydrous tetrahydrofuran or 1,2-dimethoxyethane causes two principal photoreactions: (a) the direct formation of biphenyl (**2**) and a solution reagent having the properties of sodium diphenylborate(I) (**3**) and (b) the generation of a mixture of sodium arylborohydrides(III) (**4**), where the aryl group can be phenyl, biphenylyl, and *m*- or *p*-terphenylyl groups (Scheme I). Furthermore, in the course of characterizing these reaction pathways, we have uncovered evidence that sodium diphenylborate(I) (**3**), whose anion is isoelectronic with a carbene, does behave in a carbenoid fashion toward diphenylacetylene. Generation of **3** by irradiation of **1** in DME and in the presence of diphenylacetylene and subsequent treatment

Scheme I

$C_6H_5CH_3$

5

$$H\text{-}D$$
$$DOAc$$

1. $C_6H_5CH_2Cl$
2. DOAc

D_2

DOAc

$$Na^+[H\text{-}BAr_3]^- \xleftarrow[\text{donor}]{h\nu} Na^{+-}B(C_6H_5)_4 \xrightarrow[\text{donor}]{h\nu} Na^{+-}B(C_6H_5)_2 + C_6H_5C_6H_5$$

4 path b **1** path a **3** **2**

1. L n-$C_6H_{13}C\equiv CH$
2. HOAc

$C_6H_5C\equiv CC_6H_5$

$n\text{-}C_6H_{13}CH\text{=}CH_2$

6

(boracyclopropene structures)

10a, M = Na
b, M = Li

7a, M = Na
b, M = Li

DOAc

donor

$Li^+\,^-B(C_6H_5)_3(C\equiv CC_6H_5)$

9

$h\nu$

(stilbene structures 11, 12, 2, 8)

1. H^- donor from **4**
2. $h\nu$ (H^- shift)

12

11

2

8

with DOAc gave a 1:7 ratio of *trans*- and *cis*-stilbenes in total yield of 45%, based upon the acetylene consumed. By a combination of nmr and mass spectral analysis, the *cis*-stilbene was shown to be composed of 20% of α,α'-dideuterio-, 40% of α-deuterio-, and 40% of undeuterated- stilbenes. These results are consonant with the formation of **7a** and **10a**, with the eventual destruction of **10a** and its successor **11a** by attack on the solvent. As substantiation for the existence of such a boracyclopropene nucleus as a diphenyl(diphenylvinylene)borate(III) salt (**7**), we were then able to observe a highly selective 1,2-phenyl shift in the irradiation of lithium triphenyl(phenylethynyl)borate(III)[5] (**9**) in THF, where acetolysis of the reaction products gave a 1:5.6 ratio of biphenyl to stilbene. The formation of the latter was stereospecific, however, as only the cis isomer was detected. Furthermore, acetolysis of such a photolysate with DOAc and spectroscopic analysis showed the *cis*-stilbene to be 45% α,α'-dideuterated, 44% α-deuterated and 11% undeuterated. In this case, the lower polarity of the carbon–lithium bond thus seems to give the most reasonable intermediates, **7b** and **10b**, a greater resistance to proton abstraction from the solvent and of cis–trans isomerization.[6]

The biphenyl obtained in 40–70% overall yield by the irradiation in THF solution of either sodium tetraphenylborate(III) (**1**) or in 15% yield from lithium triphenyl(phenylethynyl)borate(III) (**9**), followed by treatment with DOAc, was *ca.* 65% undeuterated and 35% monodeuterated. Photolysis of **1** in DME tended to give a higher proportion (85%) of undeuterated biphenyl. Also, the composition of the hydrogen gas obtained from the irradiation of **1** and treatment with DOAc was solvent dependent, even though the total gas yield, based upon the moles of **1**, remained between 65 and 80% after 24 hr of irradiation: a THF medium led to 20% D_2, 75% DH, and 5% H_2, while a DME medium gave 75% D_2 and 25% HD. The yield of terphenyls, both deuterated and undeuterated, was lower in DME (3%) than in THF (12%). These results support the interpretation that path a is at least two to six times more important than path b in the photodecomposition of **1** in THF or in

DME, respectively (ratio of $C_6H_5\text{-}C_6H_5:C_6H_5\text{-}C_6H_4D$), and that sodium diphenylborate(I) (**3**, the source of D_2) is more stable in DME than in THF.

Although treatment with DOAc or with diphenylacetylene has helped to delineate the chemical nature of **3**,[7] analogous irradiations of sodium phenyl(tri-*m*-tolyl)borate (**13**), sodium phenyl(tri-*p*-tolyl)borate (**14**), and sodium bis(*o,o'*-biphenylene)borate (**15**)[4] were necessary to arrive at a description of how the undeuterated biphenyl was formed. Irradiation of **13** or **14** in THF and acetolytic work-up yield a 1.1:1.0 mixture of *m*-methylbiphenyl:m,m'-bitolyl from **13** and a 1.0:2.7 mixture of *p*-methylbiphenyl:p,p'-bitolyl from **14**. The absence of any isomeric biaryls and *especially biphenyl itself* rules out any type of biaryl coupling except at carbon–boron bonds and any *interionic reaction*. Finally, prolonged irradiation of spiro salt **15** failed to lead to any biaryl coupling, which should have yielded, in this case, *o,o'*-quaterphenyl upon acetolysis. No photoreaction occurred after 24 hr and acetolysis provided a quantitative yield of biphenyl. From the behavior of **13** and **14** and the inertness of **15**, we conclude that path a, leading to **2** and **3**, involves bridging of the aryl group in consummating the 1,2-shift (**16**). Since the spiro structure in **15**, where the biphenylene rings are perpendicular, cannot attain such bridging without excessive strain (**17**), the photoreaction cannot occur (cf. ref 4).

(structures 16, 17, 15)

$h\nu$

16 **17** **15**
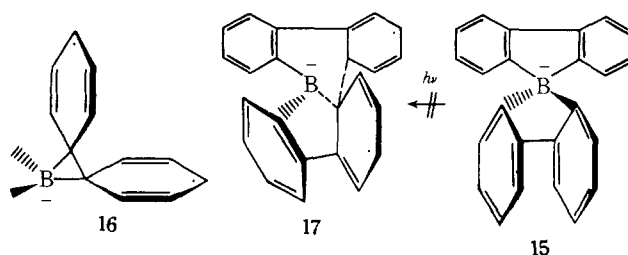
Finally, mention should be made of the chemical chacterization of **4**, the product of minor path b. The failure of the

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.

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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(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

$$3 \overset{?}{\rightleftharpoons} [(C_6H_5)_2B{=\!=}B(C_6H_5)_2]^{2-}$$
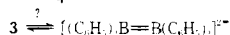
certain appeal in considering that **3** may exist, wholly or in part, as a dimer of higher aggregate.

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Inverse Kinetic Isotope Effect in the Reduction of Hindered Ketones by LiAl(OBu-t)₃H and LiAl(OBu-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-t)₃H and LiAl(OBu-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 – H₂O)⁺, 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 = COCH₃ $k_H/k_D = 0.70 \pm 0.08$
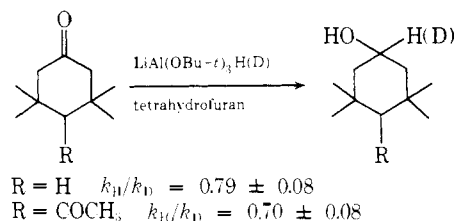
While our main purpose in this communication at this stage is simply to report the experimental demonstration of the existence of the proposed[4-6] and searched-for[7] inverse isotope effect in this type of reaction, it is clear that these results also have considerable relevance to the unsettled and 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]