served out-of-plane hydrogen wagging modes correspond to bands at 711 and 816 cm^{-1}, both substantially weaker than the 732-cm^{-1} band in benzaldehyde itself. This observation requires the nonbonding orbital to have substantial density in the para region of the ring, if not at the para hydrogen atom itself.

(3) The lifetime ratio for the two-spin in-plane magnetic sublevels of the T(nπ*) state is 0.4.[12] Equation 3 would predict this ratio to be $\ll 1$ for a localized orbital.

If photophysical processes in benzaldehyde are well described by a strongly delocalized n orbital as required by observations 1-3, then consideration of the vibronic spin–orbit coupling process described by eq 4 suggests an unusual process. Normally a weak T$_2$-($\pi\pi$*) $\leftarrow$ S$_0$ is not found coupled to the strong T$_1$(nπ*) $\leftarrow$ S$_0$ because of the intrinsic weakness of T$_2$ $\leftarrow$ S$_0$ (lifetimes for $\pi\pi$* states $\sim 10^{-1}$ sec, for nπ* states $\sim 10^{-2}$–10^{-3} sec in carbonyl compounds). In benzaldehyde S$_1$ and T$_1$ are both generated by π* $\leftarrow$ n and T$_2$ is described by ^{3}L$_a$($\pi\pi$*).[13] Since S$_1$ is the principal perturbing singlet,[13] eq 4 gives $f^a{}_{S_0 \rightarrow T_1} \propto \langle n|H_{s0}{}^{0\sigma}|\pi\rangle^2 \cdot \langle \pi|H_{ve}(Q_a)|n\rangle^2$, taking into account that oxygen is the atom with the highest nuclear charge. A strongly delocalized n orbital allows the vibronic factor to be sufficiently large for T$_2$($\pi\pi$*) $\leftarrow$ S$_0$ to have an important vibronic interaction with the strong T$_1$(nπ*) $\leftarrow$ S$_0$ in benzaldehyde. We have recently observed, in the T$_1$(nπ*) $\rightarrow$ S$_0$ phosphorescence of benzaldehyde at 4.2°K (where sufficient resolution to sort out vibrations is obtained), active nontotally symmetric vibrations coupling T$_1$ to T$_2$.[13]

Our conclusions then are that substantially delocalized orbitals are more appropriate in describing photophysical processes in benzaldehyde than localized ones. Other areas where a delocalized model may also be fruitful are photochemistry and radiationless processes.

Acknowledgment. The authors thank Dr. Eugene A. Scarzafava for valuable discussions.

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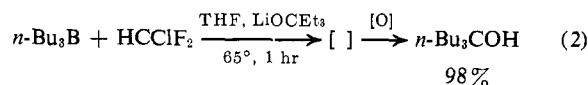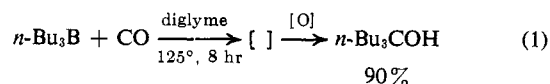(13) (a) R. Zwarich and L. Goodman, *ibid.*, 7, 609 (1970); (b) M. Koyangi and L. Goodman, *J. Chem. Phys.*, in press.

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Alkoxide-Induced Reactions of Tri-*n*-butylborane with Chlorodifluoromethane and Related Trisubstituted Methanes. A New, Facile Route from Organoboranes to the Corresponding Trialkylcarbinols

Sir:

Tri-*n*-butylcarbinol is obtained in essentially quantitative yield, 98%, from the rapid reaction of chlorodifluoromethane with tri-*n*-butylborane under the influence of lithium triethylcarboxide. Other trisubstituted methanes, such as chloroform, dichlorofluoromethane, and dichloromethoxymethane (1,1-dichlorodimethyl ether), also react readily, although in these cases the yields are somewhat lower, in the range of 80–85%. Consequently, this development provides an alternative to the carbon monoxide reaction as a route to the trialkycarbinols,[1–3] with the advantage of proceeding considerably more rapidly at lower temperatures.

$$n\text{-Bu}_3\text{B} + \text{CO} \xrightarrow[125°, \ 8 \ hr]{\text{diglyme}} [\ ] \xrightarrow{[O]} n\text{-Bu}_3\text{COH} \qquad (1)$$
$$90\%$$

$$n\text{-Bu}_3\text{B} + \text{HCClF}_2 \xrightarrow[65°, \ 1 \ hr]{\text{THF, LiOCEt}_3} [\ ] \xrightarrow{[O]} n\text{-Bu}_3\text{COH} \qquad (2)$$
$$98\%$$

The reaction of organoboranes with carbon monoxide provides a highly promising new route *via* hydroboration from olefins to tertiary alcohols.[3,4] However, for certain readily isomerized organoboranes it would be desirable to have an alternative reaction which would proceed readily at temperatures of 25–75°, a temperature range in which the isomerization of organoboranes is not significant.[5]

One approach that we considered was the preparation of trichloromethyllithium at low temperatures and its reaction with the organoborane. Indeed, the reaction of dichloromethyllithium with triarylboranes does provide a satisfactory route to the diarylcarbinols[6] (eq 3).

$$\text{Ar}_3\text{B} + \text{LiCHCl}_2 \xrightarrow{-74°} [\ ] \xrightarrow{[O]} \text{Ar}_2\text{CHOH} \qquad (3)$$
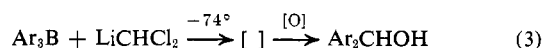
Accordingly, we prepared trichloromethyllithium from *n*-butyllithium and chloroform at $-110°$[7,8] and added tri-*n*-butylborane. The reaction mixture was allowed to come to room temperature. Oxidation of the intermediate with alkaline hydrogen peroxide provided a 37% yield of tri-*n*-butylcarbinol.

The instability of trichloromethyllithium[7] and the difficulties in preparing and utilizing it at very low temperatures on a preparative scale led us to search for a more convenient solution. We have recently realized considerable success in inducing the reaction of organoboranes with α-halo esters, ketones, and nitriles with alkoxide bases.[9] Accordingly, we decided to explore the possibility of inducing a reaction of chloroform and related trisubstituted methanes with a representative organoborane such as tri-*n*-butylborane with typical alkoxide bases.

Various alkoxides were examined. The results indicated that the more hindered alkoxides offered advantages, presumably because coordination with the organoborane was less complete. Thus in the reaction of chloroform with tri-*n*-butylborane potassium *tert*-butoxide provided a yield of 30% at both 0 and 65°. The yield improved with potassium triethylcarboxide, 50% at 0° and 59% at 65°. The reactions induced by the corresponding lithium bases were much slower, so that the higher temperature, 65° (refluxing THF), was adopted. Under these conditions lithium *tert*-butoxide gave a 55% yield in 1 hr, whereas lithium

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triethylcarboxide gave an 85% yield. The yields quoted were realized with reaction mixtures containing 1 molar equiv each of tri-n-butylborane and chloroform, and 2 molar equiv of the alkoxide. Use of 1 molar equiv of base resulted in lower yields.

The 85% yield realized with lithium triethylcarboxide appeared promising. Accordingly, the latter conditions were adopted for a study of the relative effectiveness of related trisubstituted methanes. The results are summarized in Table I.

Table I. Reaction of Tri-n-butylborane with Representative Trisubstituted Methanes under the Influence of Lithium Triethylcarboxide[a]

Reagent	Oxidation products, %[b]	
	n-Bu$_3$COH	n-Bu$_2$CO
Chloroform	85	5
Dichlorofluoromethane	79	20
Chlorodifluoromethane	98	Trace
Fluoroform	0	0
1,1-Dichlorodimethyl ether[c]	80	0.5
Trimethyl orthoformate	0	0

[a] The reaction mixture containing 10 mmol each of the organoborane and the reagent, and 20 mmol of the base heated under reflux in THF-n-hexane for 1 hr. [b] Glpc analysis. [c] Only 1 molar equiv of base was required and used.

The remarkably high yield realized with chlorodifluoromethane was especially interesting and led to a more detailed study of this reagent. The results are summarized in Table II.

Table II. Reaction of Tri-n-butylborane with Chlorodifluoromethane under Various Conditions

Base	Equiv of base	Temp, °C	Time, hr	Oxidation products, %		
				n-Bu$_3$-COH	n-Bu$_2$-CO	n-BuOH
tert-BuOK	1	25	20	53	0	25
tert-BuOK	2	25	20	75	0	14
Et$_3$COK	2	0	1	57	0	23
Et$_3$COLi	1	25	20	43	0	37
Et$_3$COLi	2	25	1	88	0	
Et$_3$COLi	2	25	3	93	0	
Et$_3$COLi	2	25	20	97	0	1.5
Et$_3$COLi	2	65	1	98	0	1.5

Consequently, it appears that the reaction of chlorodifluoromethane with tri-n-butylborane under the influence of lithium triethylcarboxide proceeds satisfactorily even at 25°, so that this reaction provides the desired convenient room-temperature route from organoboranes to the corresponding trialkylcarbinols.

The following procedure is representative of those followed in this study. Into the usual dry reaction flask maintained under nitrogen was placed 20 ml of THF and 1.82 g of tri-n-butylborane (10.0 mmol). The flask was cooled to 0° and 11.5 ml of a 1.75 M solution of lithium triethylcarboxide (20.0 mmol) in hexane (prepared from n-butyllithium and triethylcarbinol) was added, followed by addition of the chlorodifluoromethane introduced as a gas. The reaction mixture was brought to reflux temperature and maintained there for 1 hr. The mixture was cooled, 5 ml each of 3 M sodium acetate and 30% hydrogen peroxide were added, and oxidation was completed

by refluxing for 1 hr. Solid potassium carbonate was added, the organic phase was separated, undecane was added to serve as an internal standard, and the product was determined by glpc analysis on a 6-ft column (10% Carbowax). There was found 98% tri-n-butylcarbinol, trace amounts of di-n-butyl ketone, and 1.5% 1-butanol.

The procedure utilizing chloroform is somewhat more convenient. In cases where the slightly lower yield, 85%, is not serious, the reaction with chloroform may be preferred.

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Heavy-Atom Solvent Effect on the Photoaddition of Acenaphthylene and Cyclopentadiene

Sir:

Considerable interest has been evinced in the photochemical heavy-atom solvent effect. The photochemical dimerization of acenaphthylene (1) was shown to involve a legitimate heavy-atom solvent effect on interstate crossing efficiency.[1] There is a heavy-atom effect on the cross cycloaddition of 1 with acrylonitrile,[2] and recently the heavy-atom effect was utilized to cross-cycloadd 1 to maleic anhydride to form a product which ultimately led to the synthesis of pleiadiene.[3] All of these reactions are [2 + 2] cycloadditions. We report here the first known example of the heavy-atom solvent effect on a [4 + 2] photochemical cycloaddition.

The ground-state Diels–Alder reaction between 1 and cyclopentadiene (2) occurs in a sealed tube at 175° to produce the endo and exo isomers of 7,10-methano[6b,7,10,10a]tetrahydrofluoranthene in a ratio of about 3:1, respectively.[4] We have found that endo-3
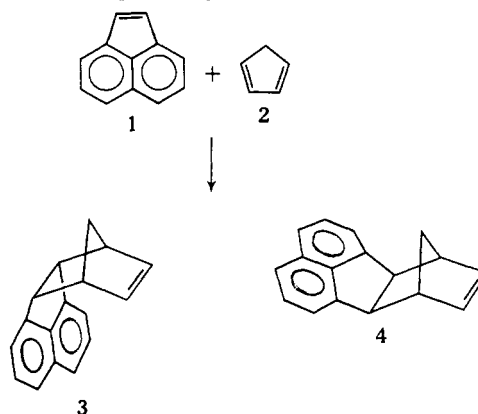
and exo-4 are produced in good yields at 25° by irradiating dilute mixtures of 1 in an excess of 2 in a heavy-atom solvent with 3660-Å light. Using a benzophenone-sensitized isomerization of *trans*-stilbene as

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