Hydroboration Kinetics. 5. Kinetics of the Reaction of 9-Borabicyclo[3.3.1]nonane with Representative Haloalkynes in Carbon Tetrachloride. The Effect of Halogen Substitution upon the Stoichiometry and Rate of Hydroboration[1]

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Abstract: The stoichiometry and rate of the hydroboration of a number of representative 1-halo-1-alkynes have been investigated. The kinetics of these compounds complement those observed for the unsubstituted terminal alkynes. While the unsubstituted terminal alkynes show kinetics which are first order in $(9\text{-BBN})_2$, several of the 1-halo-1-alkynes display kinetics which are three-halves order—first order in haloalkyne and one-half order in $(9\text{-BBN})_2$. Because many of the substituted compounds display kinetics which are intermediate between first and three-halves order, the relative reactivities were established by competitive studies. These reactions reveal the rate-retarding effect of the halogen substituent: 1-hexyne, 100; 1-iodo-1-hexyne, 12.3; 1-bromo-1-hexyne, 1.01; 1-chloro-1-hexyne, 0.422. Therefore, the effect of the chlorine substituent is to reduce the rate of hydroboration by a factor of 237. The reactions give monohydroboration products in high yields with reasonable reaction times which increase upon increasing the number or the potency of the electron-withdrawing groups attached to the triple bond. No dihydroboration products were observed.

Introduction

The hydroboration of 1-halo-1-alkynes is a key step in the syntheses of *trans*-alkenes,[2] *trans,trans*-dienes,[3] and *cis*-1-halo-1-alkenes.[4] These types of compounds have gained importance due to the recent interest in insect pheromones, which often contain one or more cis or trans double bonds. Because of the utility of this important reaction, it seemed of interest to investigate its mechanism and rate of reaction. One method of carrying this out would be to study the kinetics of the reaction. Recently, it has been determined that 9-borabicyclo[3.3.1]nonane, 9-BBN, is an excellent hydroborating agent for studying the hydroboration kinetics of alkenes,[5] haloalkenes,[6] and alkynes[7] as well as many other classes of compounds.[8]

In all cases in which the kinetics of the hydroboration with 9-BBN of unsaturates have been studied, the explanation accounting for the kinetics includes the following equations. The hydroboration reaction proceeds via dissociation of the dimer (eq 1) and subsequent reaction of the monomer with the unsaturated

$$(9\text{-BBN})_2 \rightleftharpoons 2\,9\text{-BBN} \qquad (1)$$

compound (eq 2). Therefore, the observed kinetic order is de-

$$9\text{-BBN} + \begin{pmatrix}\text{alkene}\\ \text{haloalkene}\\ \text{alkyne}\end{pmatrix} \longrightarrow B\text{-}\begin{pmatrix}\text{alkyl}\\ \text{haloalkyl}\\ \text{alkenyl}\end{pmatrix}\text{-9-BBN} \qquad (2)$$

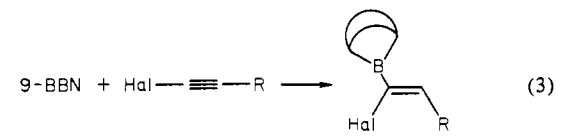
pendent upon the reactivity of the unsaturate. If the unsaturated compound is reactive enough, the rate-determining step is the first step, and kinetics which are first order in $(9\text{-BBN})_2$ are observed. For less reactive unsaturates, the second step is rate determining, and the kinetics displayed are three-halves order—first order in unsaturate and one-half order in $(9\text{-BBN})_2$.

It should be pointed out that under the same reaction conditions as used in this investigation, the reaction of 9-BBN with an unsubstituted alkyne involves a third reaction step in addition to the two (eq 1 and 2) shown above. This step is the hydroboration of the *B*-alkenyl-9-BBN product of eq 2, and the overall result is gem-dihydroboration of the alkyne.[7] However, this third step is relatively slow and does not interfere with the measurements of the kinetics so long as only the first half of the reaction is considered.[7]

For the reasons stated above, we have chosen to examine the hydroboration via $(9\text{-BBN})_2$ of haloalkynes in order to establish the stoichiometry, kinetics, and rate of reaction.

Results

It has been found that under the same reaction conditions as employed in this study, the hydroboration via 9-BBN of unsubstituted 1-alkynes gives considerable dihydroboration at the 1-position.[8] Fortunately, for the 1-halo-1-alkynes, dihydroboration is not a complicating factor, and the reaction stops after 1 equiv of 9-BBN is consumed, with monohydroboration occurring at the 1-position (eq 3). In determining the effect of the halogen substituent upon the hydroboration reaction, the reaction rate of the sustituted compound is compared to the rate of the first hydroboration of the parent compound.



(3)

The kinetic results for the hydroboration of the haloalkynes and their unsubstituted parent compounds are shown in Table I. The kinetics of hydroboration of the haloalkynes are of the same type as the unsaturated compounds studied previously, in which the order of the reaction is dependent upon the reactivity of the substrate (eq 1 and 3). Of the alkynes listed, only 1-hexyne reacts fast enough to display first-order kinetics. One or more electron-withdrawing groups seem to retard the rate of the hydro-

(1) Presented in part at the 181st National Meeting of the American Chemical Society, Atlanta, GA, Mar 1981; American Chemical Society: Washington, DC; 1981; ORGN 66.
(2) Negishi, E.; Katz, J.-J.; Brown, H. C. *Synthesis* **1972**, 555–556.
(3) Negishi, E.; Yoshida, T. *J. Chem. Soc., Chem. Commun.* **1973**, 606.
(4) Zweifel, G.; Arzoumanian, H. *J. Am. Chem. Soc.* **1967**, *89*, 5086–5088.
(5) (a) Brown, H. C.; Scouten, C. G.; Wang, K. K. *J. Org. Chem.* **1979**, *44*, 2589–2591. (b) Wang, K. K.; Brown, H. C. *Ibid.* **1980**, *45*, 5303–5306.
(6) Nelson, D. J.; Brown, H. C., preceding paper in this issue.
(7) Wang, K. K.; Scouten, C. G.; Brown, H. C. *J. Am. Chem. Soc.* **1982**, *104*, 531.
(8) Wang, K. K. Ph.D. Dissertation, Chemistry Department, Purdue University, 1979.

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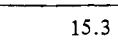
Table I. Relative Reactivities and Rate Constants for the Hydroboration with $(9\text{-BBN})_2$ of Haloalkynes and Their Parent Compounds in CCl_4 at 25 °C

compd no.	haloalkyne	rel reactivities:  = 100	rel reactivities: = 100	rate constants: 10^4k_1, s^{-1}, or $10^4k_{3/2}$, $M^{-1/2}$ s^{-1}	type of kinetics
1	H–≡ 	15.3	100	1.52	first order
2	I–≡ 	1.88	12.3	intermediate	
3	H–≡–Ph[a]	1.41	9.22	intermediate	
4	I–≡ 	1.31	8.56		
5	I–≡–Ph	0.515	3.36	intermediate	intermediate
6	Br–≡ 	0.304	1.99		
7	Br–≡ 	0.303	1.98		
8	Br–≡ 	0.250	1.63		
9	Br–≡ 	0.196	1.28		
10	Br–≡ 	0.155	1.01	intermediate	
11	Cl–≡ 	0.110	0.721	0.651	
12	Cl–≡ 	0.0645	0.422	0.372	three-halves order
13	Br–≡–Ph	0.0189	0.124	0.149	
14	Cl–≡–Ph	0.00838	0.0548	0.0570	

[a] Data from ref 7.

Table II. The Effect of Halogen Substitution on the Reactivity of Various Alkynes toward 9-BBN

haloalkyne	parent[a]	factor by which reactivity is lowered: Cl	Br	I
Hal–≡ 	H–≡ 	164	59.6	13.7
Hal–≡–Ph	H–≡–Ph	168	74.4	2.74
Hal–≡ 	H–≡ 	237	99.0	8.13
Hal–≡ 	H–≡ 		194	
Hal–≡ 	H–≡ 		439	

[a] Data from ref 7.

boration step, making the reaction follow kinetics of three-halves order—first order in haloalkyne and one-half order in $(9\text{-BBN})_2$. However, many of them do not fit into either category but display intermediate kinetic behavior.

Because the reactions of many of the compounds displayed first-order or intermediate kinetics, no information about their relative reactivities could be obtained from the kinetic studies. Therefore, competitive reactions were designed in order to determine the relative reactivities of the haloalkynes (Table I). It has been observed that, for two unsaturates displaying three-halves-order kinetics, the ratio of their relative reactivities is very close to the ratio of their three-halves-order rate constants. Therefore, it seems that the relative reactivities of the haloalkynes give us information regarding the rate, k_2, of the second step (eq 3) in the hydroboration reaction. This last idea becomes especially useful for the compounds displaying first-order or intermediate kinetics, since we have no other method for obtaining information about the relative rates of their hydroboration steps.

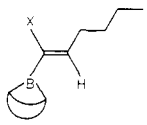
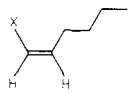
Four separate groups of 1-halo-1-alkynes were studied in order to determine the relative effects of 1-chloro, 1-bromo, and 1-iodo substituents upon various alkyne systems. The first two systems (Table II), the 1-hexynes and the 1-octynes, were chosen to allow us to observe the electron-withdrawing effects of the halogen substituents upon a triple bond having an electron-releasing

Table III. ^{13}C NMR Data for the 1-Haloalkynes, $X\text{–}C_1{\equiv}C_2\text{–}R$, and Their Parent Compounds[a]

X	R	^{13}C shifts (±0.05 ppm): C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
H	*n*-Bu	67.31	83.06	17.35	30.14	21.19	12.53		
Cl	*n*-Bu	56.71	69.22	21.66	30.35	18.15	13.01		
Br	*n*-Bu	37.36	79.88	21.88	30.51	19.24	13.19		
I	*n*-Bu	−5.86	94.89	22.33	31.05	20.99	13.99		
H	*n*-Hex	67.48	83.16	17.82	28.12[f]	27.98[f]	30.93	22.05	13.20
Cl	*n*-Hex	56.75	69.33	22.34	28.29	28.29	31.16	18.53	13.58
Br	*n*-Hex	37.36	79.85	22.51	28.46[f]	28.39[f]	31.31	19.57	13.70
I	*n*-Hex	−6.22	94.73	22.84	28.84[f]	28.74[f]	31.57	21.18	14.33
H	Ph	77.14	83.24	121.71[b]	131.47[c]	127.67[d]	128.04[e]		
Cl	Ph	67.83	69.40	122.04[b]	131.73[c]	128.06[d]	128.28[e]		
Br	Ph	50.18	80.39	122.47[b]	131.77[c]	128.10[d]	128.42[e]		
I	Ph	8.96	94.85	123.37[b]	132.52[c]	128.54[d]	129.07[e]		
H	Et	67.3[g]	85.0[g]	...	...				
H	*i*-Pr	66.83	89.68	20.01	22.51				
H	*t*-Bu	66.14	92.38	26.83	30.52				
Br	Et	37.04	81.15	13.18	13.32				
Br	*i*-Pr	37.38	85.08	21.68	22.34				
Br	*t*-Bu	37.11	87.64	28.45	30.47				

[a] Shifts are relative to external $CDCl_3$. [b] Ipso position. [c] Ortho position. [d] Meta position. [e] Para position. [f] Interchangeable. [g] Data from ref 15.

Table IV. Representative H NMR Chemical Shifts (ppm) for the Vinylic Protons of (α-Halo-1 hexenyl)-9-BBN Compounds and *cis*-1-Halo-1-hexenes in CCl_4

X		
Cl	6.82	5.5–6.1 (m)
Br	7.01	5.8–6.2 (m)
I	6.87	5.8–6.4 (m)

substituent. The phenylacetylenes (Table II) allow investigation of the halogen effects on a conjugated triple bond. The last group (Table III), consisting of the 1-bromo derivatives of 1-butyne, 3-methyl-1-butyne, and 3,3-dimethyl-1-butyne, permitted an examination of the effect of substituting methyl groups α to the triple bond.

Our results of these studies show that, in general, replacing a hydrogen or alkyl group which is attached to the triple bond with a group which reduces electron availability such as halogen or phenyl decreases the rate of the reaction. In considering the effect of increasing the bulkiness of the alkyl group attached to the triple bond, in the halogenated compounds, the rate-retarding steric and mesomeric effects seem to play a more important role than the rate-increasing effects. This was not found in the case of the nonhalogenated alkynes.[7]

Times needed for these reactions (0.4 M) to proceed to 95% completion are as follows: 1-chloro-1-hexyne, 2.5 days; 1-bromo-1-hexyne, 11 h; 1-iodo-1-hexyne, 8, h. Others will be given in a later paper describing the synthetic aspects of these reactions in detail.[13] These values indicate that the reactions could be quite useful in synthesis, and reaction times could be reduced still further if a slight excess of 9-BBN were used.

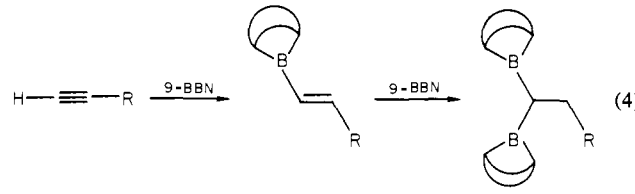
Discussion

A. Stoichiometry. The 1-haloalkynes undergo 9-BBN hydroboration at the 1-position, while unsubstituted alkynes undergo dihydroboration at the 1-position. The failure of the substituted alkynes to experience dihydroboration could be due to the deactivation of the π bond and the increased steric hindrance, which are caused by the halogen substituent. However, the fact that 3-hexyne undergoes dihydroboration leads us to believe that electronic rather than steric effects are more important in limiting the reaction of 9-BBN with 1-halo-1-alkynes to monohydroboration products only.

B. Regioselectivity. As stated abbove, the haloalkynes investigated were found to undergo hydroboration at the 1-position. The relative importance of electronic and steric effects in these compounds is demonstrated by the result that none of the haloalkynes investigated, including the iodoalkynes, gave enough hydroboration at the 2-position to be detected by GC or NMR.

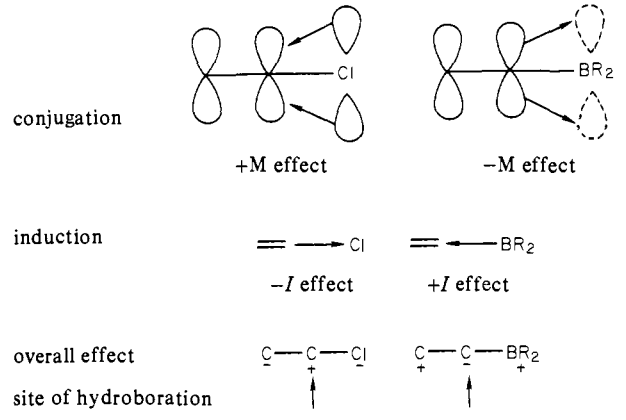
The idea of electronic effects being important in the regioselectivity of the hydroboration of halogenated or nonhalogenated alkynes is in agreement with ^{13}C NMR data for the alkynes. In Table IV one sees that for 1-hexyne the difference in the ^{13}C NMR shifts for C_1 and C_2 is 15.75, with C_1 at higher field. Since ^{13}C shifts often show a sensitivity to the amount of electron density at particular carbon atoms,[9] we could use these data to predict a higher electron density at C_1 than at C_2. One can also see that a similar situation exists for the haloalkynes as well as for all of the other alkynes and haloalkynes examined in this paper. It is true that some shift differences may be traceable to effects other than electron density changes, such as anisotropic effects.[9a] However, if we do use the ^{13}C data to reflect electron densities, in each case, the site predicted to have a higher electron density is the one at which hydroboration occurs.

In the case of unsubstituted alkynes, electronic and steric effects probably act together to make the first hydroboration of the alkyne occur at the terminal position. However, the second hydroboration step places boron at the same carbon atom, yielding the gem-dibora derivative (eq 4). Since the gem derivative is also obtained in



(4)

the hydroboration of 3-hexyne, it must be electronic rather than steric effects causing the gem product to be preferred. This is easily explained in terms of a charge alternation effect which would be the result of the combined inductive and mesomeric effects. The effect of a boron substituent on the direction of hydroboration of an alkene is the opposite of that of the halogens. A vinyl halide favors placement of boron at the 2-position, while a vinylborane favors it at the 1-position. This is because the inductive and conjugative effects of Hal and B act in opposite manners as shown below. Therefore, hydroboration seems to occur in these alkenes at the site of greatest electron availability which seems to be determined primarily by the mesomeric effect.



Chlorine sustitution in 1-hexyne reduces the C_1–C_2 ^{13}C NMR shift difference from 15.75 in the parent to 12.51 ppm (Table III). This indicates that the effect of chlorine on 1-hexyne is to make C_1 more positive and C_2 more negative. This effect of chlorine on the alkynes agrees with the above analysis of its +M effect on alkenes. The same situation is also observed in 1-chloro-1-octyne and in chlorophenylacetylene.

This raises the question as to why contrasting regiochemistry of hydroboration is observed for the 1-chloroalkynes and the 1-chloroalkenes. It should be remembered that the +M effect in the chloroalkynes is a small one relative to the stronger charge pattern of the alkyne moiety, which places more electron density at the 1-position. It should also be pointed out that chlorine, bromine, and iodine are capable of exerting a −M effect as well as a +M effect in these compounds,[10a] and this seems to be more apparent in the NMR data of the bromo- and iodoalkynes than in that of the alkynes containing chlorine. However, the possibility of heavy halogen effects[10b] by bromine or iodine makes analysis of NMR data on the compounds containing these groups difficult. Thus, it appears that at least in the chloroalkynes, hydroboration at C_1 may be linked to a strong charge pattern set up by the alkyne moiety which places a higher electron density at C_1 than at C_2.

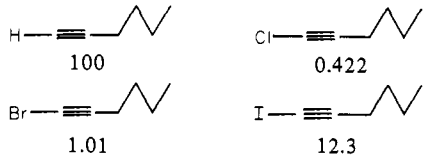
The reason for the apparent higher electron density at C_1 than at C_2 in unsubstituted alkynes is not well understood. However, hyperconjugation by CH must not be an important effect, for as one progresses from 1-butyne to 3-methyl-1-butyne to 3,3-dimethyl-1-butyne, one finds a decrease in the C_1 shift and an

(9) (a) Nelson, G. L.; Williams, E. A. "Progress in Physical Organic Chemistry", Wiley: New York, 1976; Vol. 12, pp 229–342. (b) Sardella, D. J. *J. Am. Chem. Soc.* **1973**, *95*, 3809.

(10) (a) Delavarenne, S. U.; Viehe, H. G. "Chemistry of Acetylenes"; Marcel Dekker: New York, 1969; Chapter 10. (b) Maciel, G. E. "Topics in Carbon-13 NMR Spectroscopy"; Wiley: New York, 1974; Chapter 2.

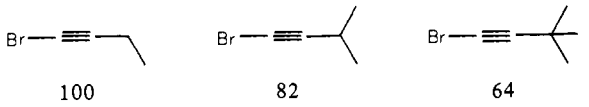
increase in the C_2 shift (see Table IV). This corresponds to an increase in the electron density at C_1 and a decrease in that at C_2. This result is not what one would expect from stepwise replacement of H by methyl if hyperconjugation were important.

C. Rate of Hydroboration. The steric and electronic effects of the halogen substituents bring about dramatic rate reductions in the hydroboration with 9-BBN of the 1-haloalkynes compared to their parent compounds. From Table I, it is obvious that a group such as halogen, which reduces the electron availability in the π bond, reduces the rate of hydroboration. We find (Table II) that the amount by which the halogen decreases the reaction rate decreases in the order Cl > Br > I, which is the trend one would expect if induction by the halogens were important.

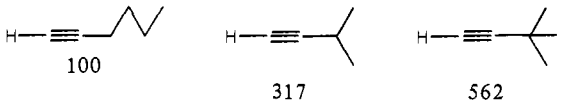


This rate reduction is presumably due to steric effects as well as electronic effects, but since the largest halogen substituent, iodine, has the smallest effect, the electronic effects must outweigh the steric effects in the cases of the bromine and chlorine substituents.

The magnitude of rate reduction upon halogen substitution does not seem to vary greatly in the hexyne, octyne, or phenylacetylene systems.

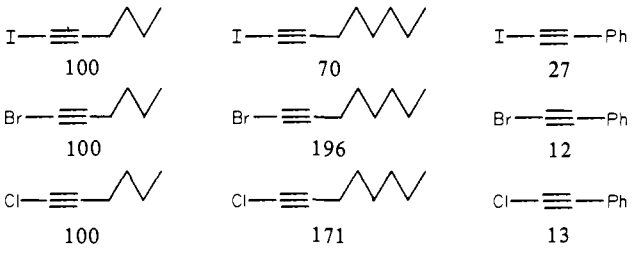


However, branching of the alkyl group in the bromoalkynes has a significant rate-retarding effect in contrast to the nonhalogenated alkynes[6] (Table III).

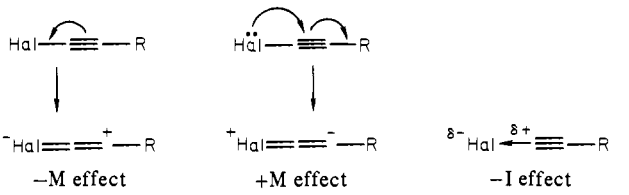


An explanation for this observation could be that the bromobutynes, in comparison to the nonhalogenated butynes, have greater steric requirements for hydroboration with 9-BBN. This could lead to the rate-retarding steric effects of the methyl groups outweighing their rate-increasing inductive effects[9a] in the methyl-substituted bromobutynes.

While the rate of reaction of most of the alkynes seems fairly sensitive to a change in alkyl group, the iodoalkynes show much less sensitivity to this.



In observing the change in charge polarization across the triple bond reflected in the ^{13}C NMR data for the haloalkynes (Table III), one notices that the polarization decreases in the order I > Br > Cl. This could correspond to an increase in the amount of negative charge or electron density at C_2 and a decrease in that at C_1, as one proceeds from the iodo- to the bromo- to the chloro-substituted compounds. These observations correlate with the rate of hydroboration (which occurs at C_1) in the order I > Br > Cl. The reason for *nucleophilic* attack occurring at the 2-position in 1-chloro-1-alkynes has been cited[14] as the decrease in electron density at that position caused by the −M effect of chlorine. Because the regioselectivity and the rate of hydroboration depend on the electron availability at specific sites in the molecule, this same reasoning should be applicable to the question of why hydroboration does *not* occur at the 2-position.



As stated earlier, the differences in the ^{13}C NMR data for 1-hexyne and the 1-halo-1-hexynes seem to indicate that the importance of the −M effect in the haloalkynes decreases in the order I > Br > Cl. In view of these results, it would have been very interesting to have studied the fluoroalkynes. This is because in these compounds, no −M effect is possible since no d orbitals are available to allow conjugation in that direction. Only a +M interaction would be possible in the 1-fluoro-1-alkynes. Because of this, one might predict that in the fluoroalkynes, hydroboration at the 1-position would (1) proceed at a rate slower than the corresponding chloro analogues or (2) switch to the 2-position if electron density at the 1-position decreased enough. Indeed, it has been observed that while *nucleophilic* attack occurs at the 2-position in 1-chloro-1-alkynes, it occurs at the 1-position in 1-fluoro-1-alkynes.[10] Unfortunately, the fluoro alkynes are difficult to prepare and handle, and often they are very unstable.[10] Therefore, we were not able to include them in this study.

Conclusion

The hydroboration with 9-BBN of haloalkynes gives only monohydroboration at the 1-position. It proceeds through two steps: (1) dissociation of $(9\text{-BBN})_2$ and (2) hydroboration of the alkyne with 9-BBN monomer. These reaction steps account for the results that faster reacting alkynes show first-order kinetics, while slower reacting ones display kinetics which are three-halves order—first order in haloalkyne and one-half order in $(9\text{-BBN})_2$. The halogen substituents have a rate-retarding effect upon hydroboration in the order Cl > Br > I. These reactions have high yields and reasonable reaction times which are longer with more electron-withdrawing groups attached to the triple bond. Our results show that these reactions should be very useful synthetically.

Experimental Section

General Data. The general procedures for manipulation of boron reagents,[11] preparation of $(9\text{-BBN})_2$,[12] and distillation of CCl_4[11] have been discussed elsewhere.

Preparation of 1-Halo-1-alkynes. The haloalkynes were prepared by using procedures similar to those given in sections 8.18 and 8.20 of ref 11. Modifications to the procedures were as follows. (1) In the preparation of the 1-bromo-1-alkynes, methylene chloride instead of ether was used for extraction. Yields were 50–75%. (2) The 1-iodo-1-alkynes were prepared by using the procedure given in section 8.20 except I_2 (−78 °C) and methylene chloride were substituted for TsCl (−50 °C) and pentane, respectively. Yields were ~95%. In all cases, removal of THF (17 mmHg) before aqueous workup was beneficial.

Identification of Hydroboration Products. Formation of α-halovinyl-9-BBN compounds was indicated by the appearance of a triplet in the vinyl region of the ^1H NMR spectra (J = 7 Hz). Addition of acetic acid then gave the ^1H NMR spectrum expected for *cis*-1-halo-1-alkenes (Table IV). No evidence for dihydroboration was found with 1:1 mixtures of 9-BBN and 1-halo-1-alkynes

Instruments. A Wilks Scientific Corp. Model Miran-1A variable-filter infrared spectrometer was used to monitor the disappearance of the boron–hydrogen bridges of $(9\text{-BBN})_2$ by recording the absorption at 1570 cm^{-1}. The reaction mixture was pumped through a 0.10 mm Wilks NaCl precision sealed flow-through cell at a rate of 4 mL/min. In those cases in which the reaction product absorbed in the region of 1570 cm^{-1}, only the first portion of the reaction was monitored in order to minimize error.[13]

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^{11}B and ^{13}C NMR spectra were obtained on a Varian FT-80A instrument. ^1H NMR spectra were recorded on a Varian T-60 (60 MHz) instrument. GC analyses were carried out on a Hewlett-Packard 5750 equipped with a thermal conductivity detector and connected to a Hewlett-Parkard integrator for determining peak areas. GC columns used were as follows: $^1/_4$ in. × 6 ft 10% SE-30 on 60/80 mesh Chromosorb W and $^1/_4$ in. × 6 ft 15% Carbowax 1540 on 60/80 mesh Chromosorb W.

Procedures. The determination of the kinetics of haloalkyne hydroboration was carried out by the quantitative IR method.[5b] The alkene/haloalkyne pairs studied by competitive hydroboration include cyclohexene/1-chloro-1-hexyne, *cis*-4,4-dimethyl-2-pentene/1-bromo-1-hexyne, 2-methyl-2-butene/1-iodo-1-hexyne, cyclohexene/1-chloro-1-octyne, *cis*-3-hexene/1-bromo-1-octyne, 2-methyl-2-butene/1-iodo-1-octyne, methylcyclohexene/chlorophenylacetylene, cyclohexene/bromophenylacetylene, cyclohexene/iodophenylacetylene, *cis*-3-hexene/1-bromo-1-butyne, 2-methyl-2-butene/1-bromo-3-methyl-1-butyne, and 2-methyl-2-butene/1-bromo-3,3-dimethyl-1-butyne. The relative reactivities of the alkenes used have been determined previously.[5] The results are summarized in Table II.

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Registry No. 9-BBN, 280-64-8; $(9\text{-BBN})_2$, 70658-61-6; $H_2C{=}CH(CH_2)_3CH_3$, 592-41-6; $HC{\equiv}C(CH_2)_3CH_3$, 693-02-7; $IC{\equiv}C(CH_2)_3CH_3$, 1119-67-1; $IC{\equiv}C(CH_2)_5CH_3$, 81438-46-2; $IC{\equiv}CPh$, 932-88-7; $BrC{\equiv}CCH_2CH_3$, 50405-39-5; $BrC{\equiv}C(CH_2)_5CH_3$, 38761-67-0; $BrC{\equiv}CCH(Me)CH_3$, 54105-74-7; $BrC{\equiv}CC(Me)_2CH_3$, 13601-86-0; $BrC{\equiv}C(CH_2)_3CH_3$, 1119-64-8; $ClC{\equiv}C(CH_2)_5CH_3$, 64531-26-6; $ClC{\equiv}C(CH_2)_3CH_3$, 1119-66-0; $BrC{\equiv}CPh$, 932-87-6; $ClC{\equiv}CPh$, 1483-82-5; $HC{\equiv}C(CH_2)_7CH_3$, 764-93-2; $HC{\equiv}CPh$, 536-74-3; $HC{\equiv}CCH(Me)CH_3$, 598-23-2; $HC{\equiv}CC(Me)_2CH_3$, 917-92-0; $HC{\equiv}C(CH_2)_5CH_3$, 629-05-0; $HC{\equiv}CCH_2CH_3$, 107-00-6; (*E*)BrC(9-BBN)=CHBu, 82415-27-8; (*E*)ClC(9-BBN)=CHBu, 82415-28-9; (*E*)IC(9-BBN)=CHBu, 82415-29-0; (*Z*)BrCH=CHBu, 13154-12-6; (*Z*)ClCH=CHBu, 50586-18-0; (*Z*)ICH=CHBu, 16538-47-9.

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Cobalt-Mediated 1,4-Acylation/Alkylation of 1,3-Dienes

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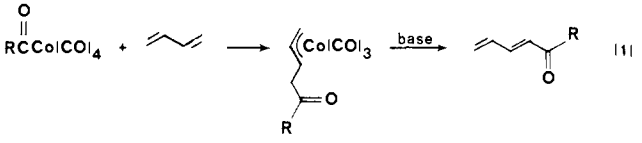
Abstract: Acylcobalt complexes prepared from $NaCo(CO)_4$ and organic halides reacted with butadiene, isoprene, and allene to form (acyl-π-allyl)cobalt complexes. Reaction of these with stabilized carbanions resulted in alkylation at the unsubstituted π-allyl terminus. The procedure provides an overall 1,4-acylation/alkylation of 1,3-dienes in which three carbon–carbon bonds are formed in a one-pot, four-step reaction sequence.

The cobalt carbonyl anion, $[Co(CO)_4]^-$, is a weak base ($pK_a \sim 1$) but a modest nucleophile. It reacts with active organic halides (primary and secondary alkyl, allyl, benzyl) and tosylates by an S_N2 process to generate alkylcobalt carbonyl complexes, $RCo(CO)_4$, which readily insert carbon monoxide under mild conditions to produce acylcobalt carbonyl complexes, $RCOCo(CO)_4$. When treated with an alcohol, these cleave to produce esters, resulting in the overall conversion of an organic halide to an ester.[1] Acylcobalt complexes react with 1,3-dienes to produce π-allylcobalt complexes by insertion of the diene into the cobalt–acyl carbon bond. These acylated π-allylcobalt complexes react with base to regenerate the diene, resulting in an acyldiene synthesis (eq 1).[2]



(1)

A number of π-allylmetal complexes react with nucleophiles at the π-allyl ligand, resulting in transfer of the allyl group from the metal to the nucleophile. This process is particularly well-developed for π-allylpalladium complexes. Both carbon[3] and nitrogen[4] nucleophiles react cleanly, and the process has been used extensively in the synthesis of a variety of natural products.[5] Other π-allylmetal complexes have been much less studied in their re-

Table I. Acylation/Alkylation of 1,3-Butadiene (Eq 3)

RX	W	Y	Z	procedure	products (% yield)[a]
CH_3I	CO_2Me	CO_2Me	H	A	1 (20), 2 (10)
CH_3I	CO_2Me	CO_2Me	H	B	1 (39), 2 (23)
CH_3I	CO_2Et	CO_2Et	Me	A	1 (17)[b]
CH_3I	CO_2Et	CO_2Et	Me	B	1 (49)
CH_3I	COMe	CO_2Et	H	A	1 (35)
CH_3I	COMe	CO_2Et	H	B	1 (43)
CH_3I	CN	CO_2Et	H	A	1 (3), 2 (14)[c]
CH_3I	CN	CO_2Et	H	B	1 (5),[d] 2 (44)[d]
$PhCH_2Br$	CO_2Et	CO_2Et	Me	A	1 (7)
$PhCH_2Br$	CO_2Et	CO_2Et	Me	B	1 (18)
$PhCH_2COCl$	COMe	CO_2Et	H	A	1 (39)
$BrCH_2CO_2Et$	CO_2Me	CO_2Me	H	A	1 (47)
$BrCH_2CO_2Et$	CO_2Me	CO_2Me	H	B	1 (35)

[a] Yields are for isolated purified material. [b] With 1 equiv of added H_2O, the yield was 40%. [c] A third product, 1 bearing a methyl group at the enol position, was isolated in 17% yield. [d] These materials were not separated from each other. The reported isomer distribution is calculated from NMR data. Upon separation, 2% of 1 and 26% of 2 was obtained. The $NaCo(CO)_4$ was prepared by the reaction of $Co_2(CO)_8$ with NaOH in THF. This gives $NaCo(CO)_4$ with 0.80 equiv of H_2O/Co. For procedure A, the water was removed by treatment with NaH. For procedure B, the water was not removed.

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