discussed here and leaves little doubt as to the appropriateness of the uncatalyzed reaction as a model.

(4) Omission from these calculations of the data for the *p*-CF$_3$ compound results in $\rho = 5.08 \pm 0.13$, $r = 0.998$ for the correlation with σ and $\rho = 3.25 \pm 0.31$, $r = 0.986$ for the correlation with σ^-.

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(13) A detailed investigation of isotope effects on the reactions reported here is in progress.

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Received November 14, 1974

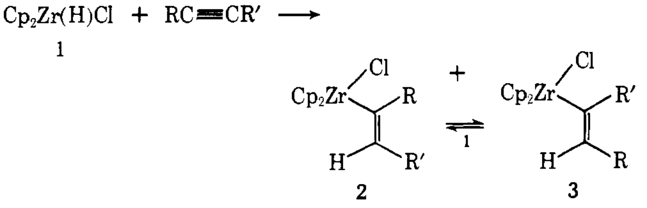
Hydrozirconation. III. Stereospecific and Regioselective Functionalization of Alkylacetylenes via Vinylzirconium(IV) Intermediates

Sir:

Di(η^5-cyclopentadienyl)(chloro)alkylzirconium(IV) complexes have been shown to be useful intermediates in the transformation of olefins into a variety of organic derivatives.[1,2] We have now observed that hydrozirconation of disubstituted acetylenes proceeds stereospecifically with high regioselectivity to yield vinylic Zr(IV) complexes which are, as well, valuable as precursors of trisubstituted olefins.

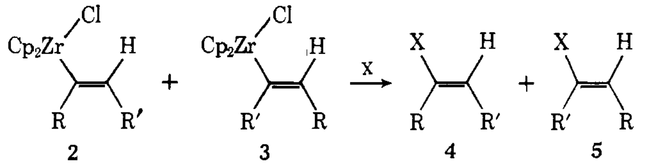
The reaction of (η^5-C$_5$H$_5$)ZrH(Cl) (**1**) with 1-butyne gives trans vinylic derivative **2** which establishes that Z–H addition to the acetylene occurs cis.[3] We have found that addition of **1** to various unsymmetrically *disubstituted* acetylenes occurs readily[4] to give mixtures of vinylic derivatives in which the steric bulk of the alkyl substituents dictates the direction of Zr–H cis β-addition to the triple bond. Thus, for each unsymmetrical acetylene, two vinylzirconium(IV) compounds can be formed which differ only in the point of attachment of the metal to the double bond. We have also observed that, over a period of several hours, this initial mixture of vinylic species can be converted to one with higher regioselectivity, at room temperature, through catalysis with **1** (see Table I). In no case were products derived from allylic rearrangements observed.[5] The regioselectivity found was generally higher than that observed for hydroboration with hindered boranes.[6] The chemical reactivity of these vinylzirconium(IV) compounds renders them useful as intermediates in the facile and selective conversion of dialkylacetylenes to trisubstituted olefins.

Table I



Acetylene	Product ratio (2:3)[7] Initially observed	After treatment with 1
a, R = H; R′ = *n*-C$_4$H$_9$–	>98 : 2	
b, R = CH$_3$; R′ = CH$_3$CH$_2$–	55 : 45	89 : 11
c, R = CH$_3$; R′ = CH$_3$CH$_2$CH$_2$–	69 : 31	91 : 9
d, R = CH$_3$; R′ = (CH$_3$)$_2$CHCH$_2$–	55 : 45	>95 : <5
e, R = CH$_3$; R′ = (CH$_3$)$_2$CH–	84 : 16	>98 : <2
f, R = CH$_3$; R′ = (CH$_3$)$_3$–	>98 : 2	

Table II

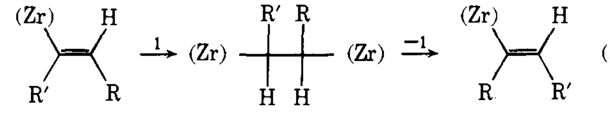


Vinylic complex (ratio 2:3)		X	Product composition[12] (4:5)	Yield[13] (%)
2a + 3a	>98:<2	NBS	>98:<2	75
		NCS	>98:<2	∿100
2b + 3b	72:28[a]	NBS	72:28	97
		NCS	71:29	53
2d + 3d	>95:<5[b]	NBS	>95:<5	75
		NCS	>95:<5	71
2e + 3e	84:16[c]	NBS	83:17	95

[a] Reaction with X performed on aliquot taken during treatment of the complexes with 1. [b] Reaction performed on aliquot taken after treatment of 2d and 3d with 1. [c] Reaction performed on aliquot taken before treatment of 2e and 3e with 1.

The two-step conversion of an acetylene to a functionalized olefin is illustrated as follows. 5-Methyl-2-hexyne (670 mg, 6.67 mmol) was stirred with 1.58 g (6.13 mmol) of **1** in benzene[8] for 2 hr. Removal of the solvent in vacuo gave the vinylic complex (**2d** and **3d**, 55:45)[7] as a pale red oil. The mixture of **2d** and **3d** was redissolved in benzene. Reanalysis of this mixture by NMR[7] after several hours at room temperature revealed that its composition had not changed. However, addition of several milligrams of **1** to this solution resulted in its conversion, slowly to a new mixture of isomers containing >95% **2d** and <5% **3d**.[9] Treatment of a solution of the vinylic complexes with *N*-bromosuccinimide gave, rapidly, the corresponding vinylic bromides in good yield, with retention of (C=C) stereochemistry[10] and with the same composition of positional isomers as that observed for the organometallic precursor (see Tables I and II). In this way, vinylic chlorides were prepared from **2, 3** and NCS, and iodides from **2, 3,** and I$_2$. The yield of vinylic halides so produced was at least as high as that reported for the hydrohalogenation of acetylenes via vinylalanes.[11]

It is interesting to note that, whereas alkylzirconium(IV) complexes positionally rearrange rapidly,[1] no such process occurs for their purified vinylic analogs. We believe that this rearrangement, observed to be catalyzed by **1**, occurs through a dimetalated alkyl intermediate as shown in reaction 1.



(1)

Because of the mildness of reaction conditions and high yields of products formed stereospecifically and with high regioselectivity, hydrozirconation is an attractive method for the direct functionalization of acetylenes. We believe it will prove to be the procedure of choice when disubstituted acetylenes are available and functionalized trisubstituted olefins are desired.. For example, when used in tandem with copper(I) reagents,[14] hydrozirconation makes possible the quick and selective synthesis of trialkyolefins from dialkylacetylene. To this end the direct alkylation of vinylzirconium(IV) complexes is now under study.

Acknowledgments. The authors wish to acknowledge generous support for this work provided by the National Science Foundation (GP-43026X). They also thank C. A. Bertelo and J. A. Labinger for helpful suggestions and comments.

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(4) In general, **1** reacts 70–100 times faster with acetylenes than with structurally analogous olefins (e.g., terminal acetylenes vs. terminal acyclic olefins).
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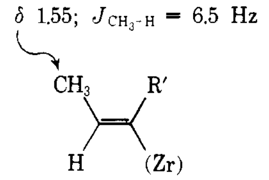
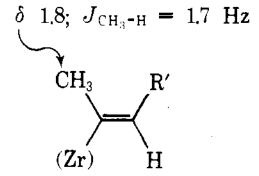
(7) This ratio can be determined by NMR analysis (in C_6D_6) of the mixture; the two types of vinylic methyl protons are clearly distinguishable and comparative integration of their signal is straightforward.





(8) All reactions were performed under purified argon. Solvents were distilled from sodium benzophenone ketyl under argon. This was made possible by admixing 5% tetraglyme with the benzene.
(9) Integration of the vinylic methyl protons from both isomers vs. an internal standard indicated that an isomerization, and not a selective decomposition of one of the isomers, was occurring.
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(13) Yields were determined by VPC and are based on the vinylzirconium(IV) complex.
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Received October 8, 1974

Onium Ions. XV.[1] Alkyl(aryl)hydridohalonium Ions and Methylmethylenehalonium Ylides

Sir:

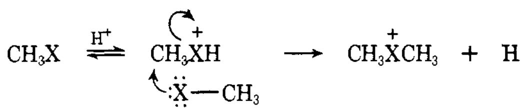
Dialkyl-, arylalkyl-, and diarylhalonium ions have been prepared and studied in detail.[2] Acidic alkyl- or arylhydridohalonium ions (RX^+H) have, however, not been reported and remain a major class of halonium ions yet unobserved. Their importance is significant, as they probably can be involved as intermediates in the Bronsted acid catalyzed transformation reactions of alkyl halides and in protolytic processes of halobenzenes. We would like now to report the first direct observation and NMR spectroscopic study of alkyl(aryl)hydridohalonium ions.

Table I. Carbon-13 Magnetic Resonance Data[a] for Alkyl(aryl)-hydridohalonium Ions, Methylenemethylhalonium Ylides, Related Halobenzenium Ions, and Their Precursors

Compound	^{13}C NMR data[a]
1-I[b]	CH_3, − 21.5, $^1J_{CH}$ = 150.3
2-I[c]	CH_3, 8.7, $^1J_{CH}$ = 158.1
3-I[c]	CH_3, 2.7, $^1J_{CH}$ = 155.2
1-Br[b]	CH_3, 10.8
2-Br[c]	CH_3, 37.5
3-Br[c]	CH_3, 32.6
4-I[b]	C_{ipso}, 95.1; C_{ortho}, 137.9; C_{meta}, 130.8; C_{para}, 128.0
6-H[c]	C_{ipso}, 100.0; C_{ortho}, 138.6; C_{meta}, 132.8; C_{para}, 132.8
6-CH_3[d]	C_{ipso}, 105.2; C_{ortho}, 137.6; C_{meta}, 133.7; C_{para}, 133.7
5-Cl[c]	C_1, 48.2; C_2, 181.1; C_3, 137.5; C_4, 192.0
5-Br[c]	C_1, 48.6; C_2, 179.1; C_3, 141.2; C_4, 188.5

[a] Chemical shifts are in ppm external (capillary) TMS. Coupling constants are in Hz. [b] In SO_2ClF at −70°. [c] In $FSO_3H-SbF_5-SO_2ClF$ at −70°. [d] Data from ref 4.

The self-condensation of alkyl halides in superacid solutions represents a convenient synthetic route to symmetrical dialkylhalonium ions $R-X^+-R$ (X = Cl, Br, I).[3] This reaction formally corresponds to the acid catalyzed condensation of alcohols to ethers and, by analogy, involves the intermediacy of hydridohalonium ions ($R-X^+H$) which subsequently undergo nucleophilic attack by excess alkyl halide.



X = Cl, Br, I

When a solution of iodomethane (**1**-I) in SO_2ClF is added to a solution of HSO_3F-SbF_5 in SO_2ClF at −78°, the ^1H NMR and ^{13}C NMR spectra both exhibit two resonances, substantially deshielded from **1**-I, in the ratio 2:1. No unreacted **1**-I can be detected. The major species (^{13}C NMR δ 8.7, ^1H NMR δ 3.56) is readily assigned to the dimethyliodonium ion (**2**-I)[4] while the minor species (^{13}C NMR δ 2.7, ^1H NMR δ 4.10) is assigned, by analogy, to the methylhydridoiodonium ion (**3**-I); the carbon shielding of **3**-I compared to **2**-I is consistent with the removal of a β-CH_3 group,[5] and both **2**-I and **3**-I become quartets in the proton-coupled ^{13}C NMR spectra with $^1J_{CH}$ values substantially larger than that of **1**-I (Table I).[6] Bromomethane (**1**-Br), under the same conditions, yields two carbon resonances in the ratio 8:1. The major species (δ 37.5) is the dimethylbromonium ion (**2**-Br)[4] while the minor species (δ 32.6) is assigned as the methylhydridobromonium ion (**3**-Br); no unreacted **1**-Br can be detected. Chloromethane (**1**-Cl) reacts under the same conditions to yield only the dimethylchloronium ion (**2**-Cl, ^{13}C NMR δ 49.9)[4] and unreacted **1**-Cl (^{13}C NMR δ 26.0).

CH_3X	$CH_3\overset{+}{X}CH_3$	$CH_3\overset{+}{X}H$
1, X = Cl, Br, I	2, X = Cl, Br, I	3, X = Br, I

Halobenzenes (**4**) do not form diphenylhalonium ions under superacidic conditions but show that the obvious competing reaction to halogen protonation is ring-protonation to benzenium ions (**5**).[7] Indeed, chlorobenzene (**4**-Cl) and bromobenzene (**4**-Br) quantitatively yield the corresponding 4-halobenzenium ions **5** -Cl and **5**-Br (Table I) upon protonation with $FSO_3H-SbF_5-SO_2ClF$ at −78°. Iodobenzene **4**-I, under the same conditions yields a single ion with ^1H NMR and ^{13}C NMR resonances deshielded from **4**-I, and similar to those of the methyl phenyliodonium ion