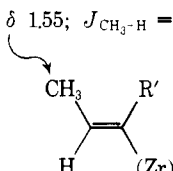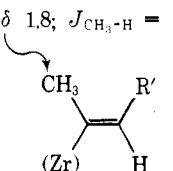for the direct functionalization of acetylenes. We believe it will prove to be the procedure of choice when disubstituted acetylenes are available and functionalized trisubstituted olefins are desired.. For example, when used in tandem with copper(I) reagents,[14] hydrozirconation makes possible the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

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References and Notes

(1) D. W. Hart and J. Schwartz, *J. Am. Chem. Soc.*, **96**, 8115 (1974).
(2) C. A. Bertelo and J. Schwartz, *J. Am. Chem. Soc.*, in press.
(3) P. C. Wailes, H. Weigold, and A. P. Bell, *J. Organomet. Chem.*, **27**, 373 (1971).
(4) In general, **1** reacts 70–100 times faster with acetylenes than with structurally analogous olefins (e.g., terminal acetylenes vs. terminal acyclic olefins).
(5) J. Schwartz, D. W. Hart, and B. S. McGiffert, *J. Am. Chem. Soc.*, **96**, 5613 (1974).
(6) For example, see G. Zweifel, G. M. Clark, and N. L. Polston, *J. Am. Chem. Soc.*, **93**, 3395 (1971).
(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.

$$\delta \ 1.55; \ J_{CH_3-H} = 6.5 \ Hz \qquad \delta \ 1.8; \ J_{CH_3-H} = 1.7 \ Hz$$

(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.
(10) No (C=C) trans products from functionalization of disubstituted acetylenes were detectable by NMR or VPC.
(11) G. Zweifel and C. C. Whitney, *J. Am. Chem. Soc.*, **89**, 2753 (1967); L. I. Zakharkin and V. V. Gavrilenko. *Izv. Akad. NauK SSSR, Engl. Ed.*, 151 (1959).
(12) Determined by NMR analysis as discussed in ref 7.
(13) Yields were determined by VPC and are based on the vinylzirconium(IV) complex.
(14) E. J. Corey and G. H. Posner, *J. Am. Chem. Soc.*, **90**, 5615 (1968); E. J. Corey, J. A. Katzenellenbogen, and G. H. Posner. *ibid.*, **89**, 4245 (1967).

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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
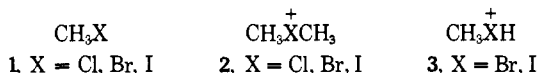
Compound	^{13}C NMR data[a]
1-I[b]	$CH_3, -21.5, {}^1J_{CH} = 150.3$
2-I[c]	$CH_3, 8.7, {}^1J_{CH} = 158.1$
3-I[c]	$CH_3, 2.7, {}^1J_{CH} = 155.2$
1-Br[b]	$CH_3, 10.8$
2-Br[c]	$CH_3, 37.5$
3-Br[c]	$CH_3, 32.6$
4-I[b]	$C_{ipso}, 95.1; C_{ortho}, 137.9; C_{meta}, 130.8; C_{para}, 128.0$
6-H[c]	$C_{ipso}, 100.0; C_{ortho}, 138.6; C_{meta}, 132.8; C_{para}, 132.8$
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.

$$CH_3X \underset{\text{X—CH}_3}{\overset{H^+}{\rightleftharpoons}} CH_3\overset{+}{X}H \longrightarrow CH_3\overset{+}{X}CH_3 + HI$$

$$X = Cl, Br, I$$
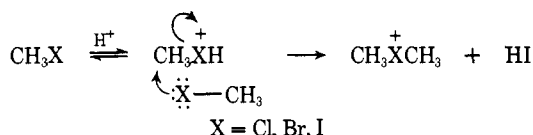
When a solution of iodomethane (**1-I**) in SO_2ClF is added to a solution of HSO_3F–SbF_5 in SO_2ClF at $-78°$, the ^{1}H NMR and ^{13}C NMR spectra both exhibit two resonances, substantially deshielded from **1-I**, in the ratio 2:1. No unreacted **1-I** can be detected. The major species (^{13}C NMR δ 8.7, ^{1}H NMR δ 3.56) is readily assigned to the dimethyliodonium ion (**2-I**)[4] while the minor species (^{13}C NMR δ 2.7, ^{1}H 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).

$$\begin{array}{ccc} CH_3X & CH_3\overset{+}{X}CH_3 & CH_3\overset{+}{X}H \\ \textbf{1,} \ X = Cl, Br, I & \textbf{2,} \ X = Cl, Br, I & \textbf{3,} \ X = Br, I \end{array}$$

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 ^{1}H NMR and ^{13}C NMR resonances deshielded from **4-I**, and similar to those of the methyl phenyliodonium ion

(6-CH₃, Table I). The I-protonated structure **6-H** is therefore assigned to this ion; the shielding of C_{ipso} and the deshielding of C_{ortho} in **6-H** compared to **6-CH₃** is consistent with the removal of a β- and γ-CH₃ group, respectively.[5] As in the case of **3-I**, the proton in **6-H** is evidently exchanging rapidly (on the NMR scale) with the excess acid. **6-H** does not, however, rearrange to **5-I** even when the temperature is raised to −20°.

4, X = Cl, Br, I   **5**, X = Cl, Br, I   **6**, R = H, CH₃
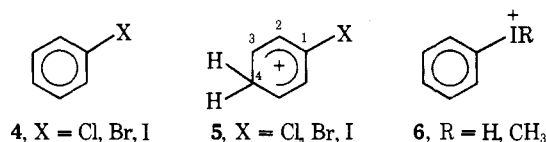
When the dimethylhalonium ions·**2-I**, **2-Br**, are added (as the stable hexafluorantimonate salt) to sulfuric acid (H₂SO₄), no reaction occurs below 0°, but at 30° dimethyl sulfate (**7**)[8] is slowly formed. **1-I** also reacts with H₂SO₄, and, after 2 hr, spectra of the H₂SO₄ solution indicate the presence of **7**[8] and a second species resonating at δ 4.00 (¹H NMR) and δ 1.2 (¹³C NMR) (cf. **3-I**, Table I) and proves the intermediacy of **3-I** in the second methylation step from **2-I** as shown in the reaction scheme. However, when **2-Br** and **2-I** are dissolved in D₂SO₄ at 30°, the ¹H NMR spectrum shows that H–D exchange occurs during the course of the reaction.[9] The H–D exchange is considered to have occurred *via* the intermediacy of methylenemethyliodonium (bromium) ylide (**8-I**, **8-Br**). Aryliodonium ylides have previously been studied and even isolated in a number of cases.[10] Attempts to trap **8-I** formed under basic conditions have, however, so far proved unsuccessful.[11]

further exchange
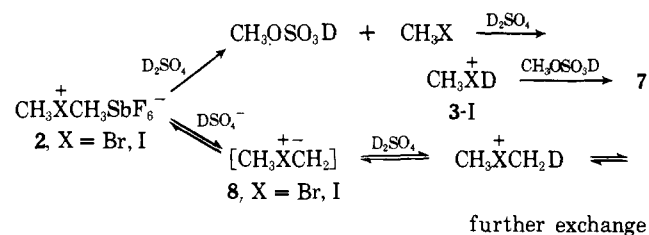
Our results show that alkyl bromides and iodides, indeed can be protonated on the *n*-donor halogen atom to form stable hydridohalonium ions. This observation has direct bearing on the mechanism of Bronsted acid-catalyzed electrophilic alkylation with alkyl halides. The exclusive formation of **6-H** from **4-I** indicates that iodine is also at least as basic toward protonation as the π-donor benzene ring.

References and Notes

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(2) G. A. Olah, "Organic Halonium Ions," Wiley-Interscience, New York, N.Y., in press.
(3) G. A. Olah, J. R. DeMember, Y. K. Mo, J. J. Svoboda, P. Schilling, and J. A. Olah, *J. Am. Chem. Soc*, **96**, 884 (1974); G. A. Olah and J. J. Svoboda, *Synthesis*, 203 (1973).
(4) Spectra as reported previously: G. A. Olah, P. W. Westerman, E. G. Melby, and Y. K. Mo, *J. Am. Chem. Soc.*, **96**, 3565 (1974), and ref 3.
(5) J. B. Stothers, "Carbon-13 Nmr Spectroscopy," Academic Press, New York, N.Y., 1972, Chapter 3.
(6) The inability to observe ³J_{HH} and ²J_{CH} splittings in **3-I** is probably due to rapid proton exchange with the HSO₃F–SbF₅, which resonates as an unusually broad ($W_{1/2}$ = 0.25 ppm) absorption at δ 11–11.5. This exchange is not slowed even at −105°.
(7) Fluorobenzene has previously been reported to yield the *p*-fluorobenzenium ion (**5-F**) under similar conditions: G. A. Olah and T. E. Kiovsky, *J. Am. Chem. Soc.*, **89**, 5692 (1967).
(8) ¹H NMR δ 4.67; ¹³C NMR δ 62.0: confirmed by comparison with an authentic sample of **7** in H₂SO₄.
(9) Indicated by the appearance and continued increase of the HDSO₄ resonance, δ 11.0, during the reaction. Attempts to detect H–D exchange in **2-Br** by quenching the reactions have not been successful.
(10) D. Prikale and O. Neilands, *Zh. Org. Khim*, **6**, 2509 (1970), cf. *Chem. Abstr.* **76** 58766 (1971), and earlier references cited therein; Y. Hayashi, T. Okada, and M. Kawanisi, *Bull Soc. Chem. Jpn.*, **43**, 2506 (1970); W. A. Sheppard and O. W. Webster, *J. Am. Chem. Soc.*, **95**, 2695 (1973); see also ref 2.
(11) 4-*tert*-Butylcyclohexanone gave no products corresponding to oxirane formation and was recovered unchanged under a variety of conditons. cf. E. J. Corey, and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1355 (1965).
(12) Postdoctoral Research Associates.

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1,2- and 1,3-Addition of 1,8-Dehydronaphthalene to Conjugated Acyclic Dienes
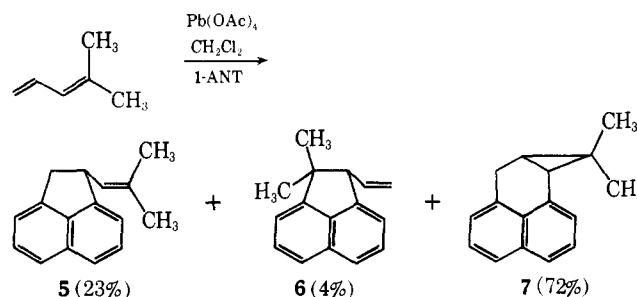
Sir:

Recently we reported that the addition of "1,8-dehydronaphthalene" (**2**)[1] to cyclopentadiene gave a bridged 1,3-adduct as well as 1,2- and 1,4-adducts.[2] This unanticipated result led us to examine the addition of **2** to some acyclic, conjugated dienes, which would not be restricted to an s-cis conformation. In an exploratory experiment, lead tetraacetate oxidation of 1-aminonaphtho[1,8-*de*]triazene (1-ANT, **1**)[1] in a methylene chloride solution of butadiene afforded two 1:1 adducts (ca. 10% yield), identified as vinylacenaphthene (**3**, 43%) and naphtho[1′,8′]bicyclo[4.1.0]hept-2-ene (**4**, 52%).[3] The structure of **4** was confirmed by independent synthesis from phenalene[4,5] using the Harrison version of the Simmons–Smith reaction.[6,7]

1   **2**   **3**   **4**
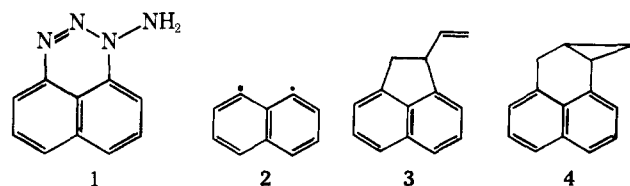
The possibility of 1,3-addition to an acyclic diene is thus established. In the remainder of this paper we would like to present the results of our studies of reactions with alkyl substituted dienes, which serve to delineate the regioselectivity of these reactions and which suggest that these two modes of addition utilize substantially different mechanisms.

With 4-methyl-1,3-pentadiene (eq 1), 1,2-addition occurred preferentially but not exclusively at the less substituted double bond, while 1,3-addition seemed to produce only the adduct corresponding to attack by **2** (or its equivalent) at the less substituted end of the diene. (The analogous reaction of 2,5-dimethyl-2,4-hexadiene, carried out chiefly to obtain PMR chemical shift values for the methyl groups, gave **8** and **9** in the relative amounts indicated below.)

5 (23%)   **6** (4%)   **7** (72%)

(1)