

preparing substituted *cis*-cyclopenta[b]pyrrolidines. Moreover, the facile rearrangement observed in these *trans*-"divinyl"-cyclobutane systems provides, perhaps, the best illustration to date of the powerful accelerating effect on [3,3]-sigmatropic rearrangements provided by the positively charged iminium ion grouping.

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Registry No. 4a, 96617-23-1; 4b, 96617-24-2; 4c, 96617-25-3; 4d, 96617-26-4; 4e, 96617-27-5; 4f, 96617-28-6; 5a, 96617-29-7; 5a¹/₂C₄H₄O₄, 96617-36-6; 5b, 96617-30-0; 5c, 96617-31-1; 5d, 96617-32-2; 5e, 96617-33-3; 5f, 96617-34-4; 6, 17082-61-0; 7, 96617-35-5; PhCH₂NHCH₂CN, 3010-05-7; MeNHCH₂CN, 5616-32-0; PhCH₂NHCH(CH₃)CN, 3010-09-1; MeNHCH(CH₃)CN, 16752-54-8; PhClLi=CH₂, 45680-22-6; CH₃CLi=CH₂, 6386-71-6; CHLi=CH₂, 917-57-7.

Supplementary Material Available: Tables I-VII of atomic positional and thermal parameters, bond distances, and bond angles (7 pages). Ordering information is given on any current masthead page.

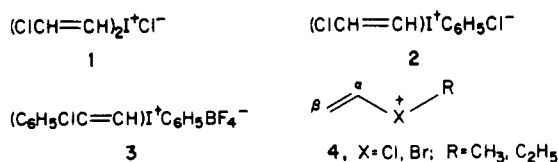
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Methyl- and Ethylvinylhalonium Ions¹

Summary: The first hitherto unknown alkylvinylhalonium ions, the methyl- and ethylvinylbromonium and -chloronium ions, have been prepared by the alkylation of the corresponding vinyl halides with CH₃F(C₂H₅F)-SbF₅ in SO₂ or SO₂ClF solution and characterized by ¹³C NMR spectroscopy.

Sir: The only known divinylhalonium ion is the bis-(*trans*-2-chlorovinyl)iodonium chloride (1) prepared by Nesmeyanov² in 6% yield by reacting (*trans*-2-chlorovinyl)mercuric chloride with iodine trichloride. Several



vinylaryliodonium ions such as the chlorovinylphenyl-

iodonium chloride (2) and (α -chlorostyrylphenyl)iodonium tetrafluoroborate (3) have been prepared.^{3,4} To date, however, no alkylvinylhalonium ions 4 have been reported.

We are now able to prepare alkylvinylhalonium ions 4-R (X = Br, Cl) by alkylating vinyl halides with methyl and ethyl fluoride-antimony pentafluoride complexes in either SO₂ or SO₂ClF solvent. A solution of vinyl bromide in SO₂ClF at -78 °C was slowly added with stirring to a fourfold excess of freshly prepared CH₃F:SbF₅ complex in SO₂ClF at -78 °C to obtain a light yellow colored solution whose ¹³C NMR spectrum at -90 °C showed three absorptions at $\delta^{13}\text{C}$ 132.9 (triplet, $J_{\text{C-H}} = 170.0$ Hz), 120.9 (doublet, $J_{\text{CH}} = 227.0$ Hz) and 44.1 (quartet, $J_{\text{CH}} = 163.0$ Hz). The observed chemical shifts and multiplicities are consistent with the ion being the methylvinylbromonium ion 4-CH₃ (X = Br). Similarly, the ethylvinylbromonium ion 4-C₂H₅ (X = Br) was prepared by using the CH₃CH₂F \rightarrow SbF₅ complex in SO₂ solution. The ion 4-C₂H₅ (X = Br) exhibited four ¹³C NMR absorptions at $\delta^{13}\text{C}$ 136.0 (triplet, $J_{\text{C-H}} = 169.4$ Hz), 116.9 (doublet, $J_{\text{CH}} = 225.0$ Hz), 72.3 (triplet, $J_{\text{C-H}} = 164.0$ Hz), and 15.1 (quartet). It is interesting to compare the ¹³C NMR chemical shifts of 4-CH₃ (X = Br) and 4-C₂H₅ (X = Br) with those of progenitor vinyl bromide [observed at $\delta^{13}\text{C}$ 122.4 (triplet, $J_{\text{C-H}} = 161.9$ Hz) and 114.3 (doublet, $J_{\text{C-H}} = 198.0$ Hz)]. Apparently in the bromonium ions the β -methylene carbons are much more deshielded [10.5 ppm for 4-CH₃ (X = Br) and 13.6 ppm for 4-C₂H₅ (X = Br)] than the α -methine carbons [6.6 ppm for 4-CH₃ (X = Br) and 2.6 ppm for 4-CH₂CH₃ (X = Br)]. Relatively less deshielding of the α -methine carbon in 4-C₂H₅ (X = Br) compared to that in 4-CH₃ (X = Br) can be rationalized by a γ -CH₃ substituent effect in the former.⁵ The best evidence for the formation of the alkylvinylbromonium ion comes from the change in the carbon-hydrogen coupling constant in the α -methine carbons compared to that in the progenitor vinyl bromide [the difference is 29.0 Hz in 4-CH₃ (X = Br) and 27.0 Hz in 4-C₂H₅ (X = Br)]. Such large increase in coupling constant can only occur by the placement of positive charge on the bromine (effect of a strongly electron-withdrawing group). It is, however, not clear why the β -methylene carbons in these alkylvinylbromonium ions get much more deshielded than α -methine carbons similar to those observed in regular allyl cations,⁶ although in the latter such phenomenon can be readily rationalized by allyl delocalization. The methyl- and ethylvinylhalonium ions were stable at -78 °C for only several hours (~4 h) after which polymerization sets in.

Compared to the alkylvinylbromonium ions, the corresponding alkylvinylchloronium ions were found to be less stable. In fact, we were able to prepare only the methylvinylchloronium ion by methylating vinyl chloride using CH₃F \rightarrow SbF₅ in SO₂ClF solution at -90 °C. The ion 4-CH₃ (X = Cl) was stable at -78 °C for less than an hour. In the ¹³C NMR spectrum at -90 °C it showed three resonances at $\delta^{13}\text{C}$ 131.7 (triplet, $J_{\text{C-H}} = 168.9$ Hz), 127.2 (doublet, $J_{\text{C-H}} = 220.0$ Hz), and 50.4 (quartet, $J_{\text{C-H}} = 161.0$ Hz). Compared to the ¹³C NMR chemical shifts of vinyl chloride (Table I) the β -methylene carbon in 4-CH₃ (X = Cl) is much more deshielded (14.5 ppm) than the α -methine

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
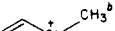

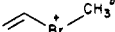
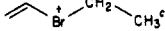
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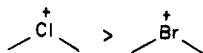
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Table I. ^{13}C NMR Chemical Shifts^a of Alkylvinylhalonium Ions and Their Precursors

ion or precursor	$\delta^{13}\text{C}_\alpha$	$\delta^{13}\text{C}_\beta$	$\delta^{13}\text{C}$ other
	126.1 ($J_{\text{CH}} = 197$ Hz)	117.2 ($J_{\text{CH}} = 161.7$ Hz)	
 4- CH_3 (X=Cl)	127.2 ($J_{\text{CH}} = 220$ Hz)	131.7 ($J_{\text{CH}} = 168.9$ Hz)	50.4, CH_3 ($J_{\text{CH}} = 161$ Hz)
	114.3 ($J_{\text{CH}} = 198$ Hz)	122.4 ($J_{\text{CH}} = 161.9$ Hz)	
 4- CH_3 (X=Br)	120.9 ($J_{\text{CH}} = 227$ Hz)	132.9 ($J_{\text{CH}} = 170$ Hz)	44.1, CH_3 ($J_{\text{CH}} = 163$ Hz)
 4- C_2H_5 (X=Br)	116.9 ($J_{\text{CH}} = 225$ Hz)	136.0 ($J_{\text{CH}} = 169.4$ Hz)	72.3, CH_2 (164.0) 15.1, CH_3

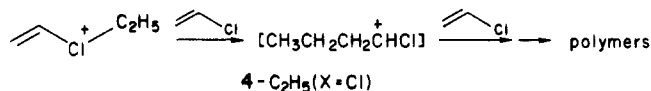
^a In ppm from external capillary Me₄Si. ^b In SO_2ClF , -90°C . ^c In SO_2 , -78°C .

carbon (1.1 ppm). The placement of positive charge on the chlorine atom in 4- CH_3 (X = Cl) is again evident from the increase in the magnitude of α carbon-hydrogen coupling constant relative to that in the progenitor vinyl chloride ($\Delta J = 23.0$ Hz). It is also useful to compare the methyl carbon chemical shifts of 4- CH_3 (X = Cl) with that of 4- CH_3 (X = Br). The larger deshielding observed in the chloronium ion ($\delta \text{CH}_3 = 50.4$) compared to the bromonium ion ($\delta \text{CH}_3 = 44.1$) is indicative of the well-known⁷ deshielding order of halogens



Attempts to prepare the corresponding ethylvinylchloronium ion in $\text{CH}_3\text{CH}_2\text{F} \rightarrow \text{SbF}_5/\text{SO}_2\text{ClF}$ even at -130°C was unsuccessful. Even at these low temperatures rapid

polymerization occurs. It is possible that ethylation of vinyl chloride probably occurs on the chloride first, but since chloronium ions are very reactive and ethyl cation is a reactive primary cation, it is readily transferred from the chlorine atom to the π -bond, via either an intra- or intermolecular process to give a carbocation. This carbocation acts as an initiator to polymerize the excess vinyl chloride. In fact, even in the preparation of 4- CH_3 (X = Br, Cl) and 4- C_2H_5 (X = Br) substantial polymeric side products were obtained and hence no satisfactory ^1H NMR spectra could be obtained. However, these polymeric side products did not hamper the ^{13}C NMR study.



We also attempted to prepare the corresponding alkylvinylidonium ions and all our efforts failed under the reaction conditions. Vinyl iodide seems to be preferentially oxidized under the alkylation conditions. The reported preparation of alkylvinylhalonium ions represents an example of a kinetically controlled selective alkylation of the halogen atoms of the vinyl halides, instead of the carbon-carbon double bond, which subsequently react to give polymeric side products.

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Registry No. 4- CH_3 (X = Br), 96555-15-6; 4- C_2H_5 (X = Br), 96555-16-7; 4- CH_3 (X = Cl), 96555-17-8; $\text{CH}_3\text{F}:\text{SbF}_5$, 35873-33-7; $\text{CH}_3\text{CH}_2\text{F}:\text{Sb}$, 35873-34-8; vinyl bromide, 593-60-2; vinyl chloride, 75-01-4.

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