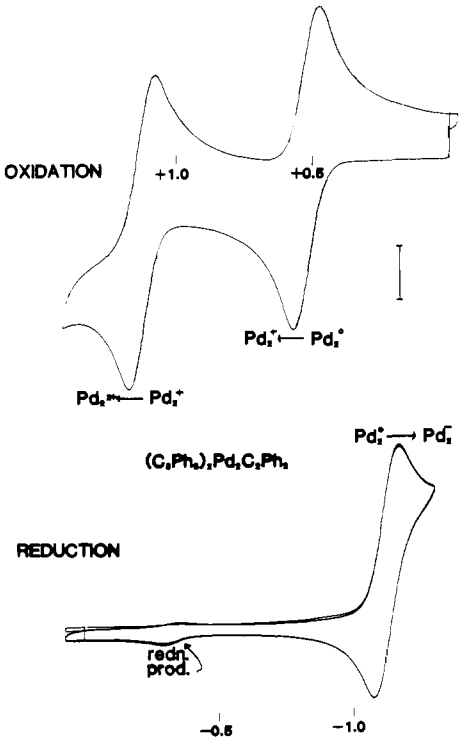

Figure 1. Cyclic voltammograms of **1** in CH_2Cl_2/0.1 M Bu_4NPF_6 at a platinum electrode; scan rate 75 mV s^{-1}. *Y*-axis current marker is 2 μA. Two successive scans are recorded in the reduction curves.

of L, was confirmed by voltammetric experiments at the rpe.

Complex $\mathbf{1}^+$ also reacts with donor solvents such as tetrahydrofuran, acetone, or acetonitrile to give red-to-purple solutions of solvento-complexes, presumably $[(\eta^5\text{-}C_5Ph_5)Pd(solv)_2]^+$, together with a precipitate of **1**. After filtration, addition of L gave a green solution from which **2** could be isolated after column chromatography on silica.

The Pd(II) complexes **2** can be reduced or oxidized by one electron in what are generally reversible processes[5] to give Pd(I) and Pd(III) π complexes, which have apparently been unknown up to this time.[6] Changing the ligand L_2 in **2** results only in minor changes in the potential of the Pd(II)/Pd(I) couple. $E°$ values for the cod, dppe, and bipyridyl complexes of **2** were −0.47, −0.48, and −0.51 V, respectively, in CH_2Cl_2. This strongly suggests that the LUMO orbital in **2** is predominantly metal in composition and that the assigned change of metal oxidation state in the redox process is a reasonable one. This conclusion is qualitatively supported by ESR measurements. Bulk cathodic reduction of $(\eta^5\text{-}C_5Ph_5)Pd(cod)^+$ in CH_2Cl_2 at −0.6 V (−10 °C) consumed one electron as the solution changed from green to red-orange. Monitoring of the electrolyzed solution with an rpe showed that the precursor cation **2** had been quantitatively reduced to the neutral, formal Pd(I) species $(\eta^5\text{-}C_5Ph_5)Pd(cod)$. The reduced solution exhibited a fluid ESR spectrum in which the central line ($\langle g \rangle$ = 2.0706) was flanked by satellites ($\langle a \rangle_{Pd}$ = 25 G) arising from ^{105}Pd ($I = {}^5/_2$, 22.2% natural abundance).

Electrochemical oxidations of **2** have been briefly investigated. Oxidation of the cod and bipy complexes were reversible in CH_2Cl_2 ($E°$ = +1.65 and +1.18 V, respectively), but the dppe complex oxidized irreversibly. Detailed studies are in progress.

Two effects of the pentaphenylcyclopentadienyl ligand,[7] compared to an unsubstituted Cp ligand, are apparent. One is that the electron-withdrawing ability of the phenyl substituent makes low oxidation states more accessible by raising the potential of the redox couple [the Pd(II)/Pd(I) potential for $(\eta^5\text{-}C_5Ph_5)Pd(cod)^+$ is 270 mV more positive than that of $CpPd(cod)^+$].[8] This is the opposite of the effect seen with the pentamethylcyclopentadienyl ligand, which has the effect of lowering the redox potential (making reductions more difficult).[9] The second effect appears to be greater kinetic stability for the π complexes, regardless of the oxidation state. This is supported by our observation that the reduction and oxidation of $CpPd(cod)^+$ are irreversible under the same conditions[8] in which the C_5Ph_5 analogue gives a stable Pd(I) or Pd(III).

The palladium–cyclopentadienyl π bond is notoriously weak and has been an impediment to development of $CpPdL_n$ chemistry.[10] This does not appear to be the case for $(\eta\text{-}C_5Ph_5)Pd$ compounds, and a study of the reactions, redox and otherwise, of these compounds is underway.

Acknowledgment. This research was generously supported by the National Science Foundation, NATO and the SERC. We also gratefully acknowledge a loan of palladium salts from Johnson Matthey.

(5) In THF, the first oxidation of **1** is not completely chemically reversible ($E°$ = +0.71 V), with i_c/i_a = 0.83 at v = 52 mV s^{-1}, due to the slow reaction of $\mathbf{1}^+$ with the solvent.

(6) See, for example: Maitlis, P. M. "The Organic Chemistry of Palladium"; Academic Press: New York, 1971; Vol. I.

(7) See for the preparation of $(C_5Ph_5)^-$: Zhang, R.; Tsutsui, M.; Bergbreiter, D. E. *J. Organomet. Chem.* **1982**, *229*, 109.

(8) The reduction of $(\eta^5\text{-}C_5H_5)Pd(cod)^+$ is irreversible in nonaqueous solvents except at CV scan rates above 5 V/s ($E°$ = −0.74 V). No reversibility was observed for the oxidation of this compound (E_{pk} = +1.85 V).

(9) Koelle, U.; Khouzami, F. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 640.

(10) Maitlis, P. M. *Chem. Soc. Rev.* **1981**, 1.

Stereoselective Synthesis of 1,3-Diol Derivatives and Application to the Ansa Bridge of Rifamycin S

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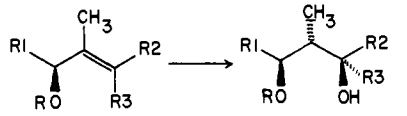
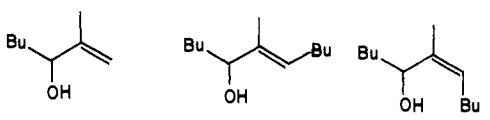
Received December 3, 1982

Olefin hydroboration is particularly useful when it can be directed by preexisting chiral centers. Although examples of such controlled hydroboration with cyclic olefins abound,[1] only a few hydroborations have been reported to give serviceable stereochemical control in acyclic systems.[2] We report here that certain classes of acyclic secondary allylic alcohols undergo hydroboration to yield *threo*-1,3-diols with 8–>15:1 diastereoselection. The general transformation we have examined is shown in eq. 1.



(1)

To find the system giving the highest stereocontrol, several common hydroborating reagents were examined in various solvents by using alcohols **1–3** and their derivatives as substrates. As



1 2 3

outlined in the table, the major product was in nearly all ex-

(1) For example: H. C. Brown, R. Liotta, and L. Brener, *J. Am. Chem. Soc.*, **99**, 3427 (1977); M. H. Gordon, and M. J. T. Robinson, *Tetrahedron Lett.*, 3867 (1968); Y. Senda, S. Kamiayama, and S. Imaizumi, *Tetrahedron*, **33**, 2933 (1977).

(2) G. Schmid, T. Fukuyama, K. Akasaka, and Y. Kishi, *J. Am. Chem. Soc.*, **101**, 259 (1979); W. C. Still and K. P. Darst, *ibid.*, **102**, 7385 (1980); W. C. Still and K. R. Shaw, *Tetrahedron Lett.*, **22**, 3725 (1981); K. C. Nicolaou, M. R. Pavia, and S. P. Seitz, *J. Am. Chem. Soc.*, **104**, 2027 (1982); D. A. Evans, J. Bartroli, and T. Godel, *Tetrahedron Lett.*, **23**, 4577 (1982).

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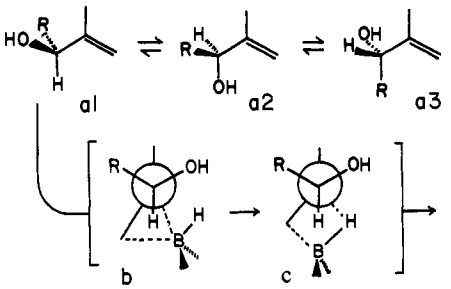
Table I

expt	alcohol	R	reagent	diastereomer ratio[a]	yield,[b] %
1	1	H	BH_3, THF	1:1.4	71
2	1	H	$ThBH_2$, THF	3.5:1	83
3	1	H	Sia_2BH, THF	2.5:1	90
4	1	H	$CHex_2BH$, THF	8.5:1	87
5	1	H	9-BBN, THF	11:1	80
6	1	H	9-BBN, pentane	11:1	88
7	2	H	BH_3, THF	1:1	85
8	2	H	$ThBH_2$, THF	8:1	72
9	2	H	9-BBN, THF	9:1	48[c]
10	3	H	BH_3, THF	6:1	85
11	3	H	$ThBH_2$, THF	>15:1	91
12	3	H	9-BBN, THF	>15:1	31[c]
13	1	$SiMe_3$	9-BBN, THF	10.5:1	57[d]
14	1	$SitBuMe_2$	9-BBN, THF	9:1	94
15	1	$SitBuPh_2$	9-BBN, THF	6:1	74
16	1	CPh_3	9-BBN, THF	5.5:1	79
17	1	CH_2OCH_2Ph	9-BBN, THF	5:1	90
18	1	$COCH_3$	9-BBN, THF	7.5:1	82[d]
19	1	$COCF_3$	9-BBN, THF	14:1	95[d]
20	1	9-BBN-Li^+	9-BBN, THF	4:1	74[d]
21	2	CH_2OCH_2Ph	$ThBH_2$, THF	1:1	80
22	2	$COCF_3$	$ThBH_2$, THF	3.5:1	72[d]
23	3	CH_2OCH_2Ph	$ThBH_2$, THF	>15:1	90

[a] Threo (as defined in eq 1):erythro as measured by ^{13}C NMR of the free alcohol and/or capillary VPC of the silylated alcohol. [b] Yield after isolation by flash chromatography. [c] Yield at 50–60% conversion; thus yields based on unrecovered starting material are considerably higher. [d] Yield of diol after deprotection.

Scheme I

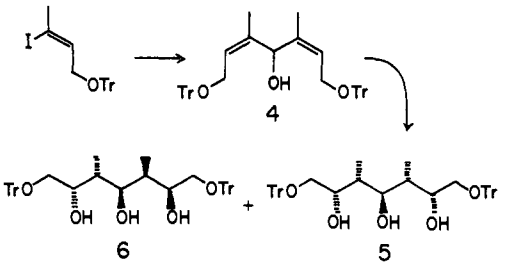


periments the 1,3-diol having the threo stereochemistry diagrammed above.[3]

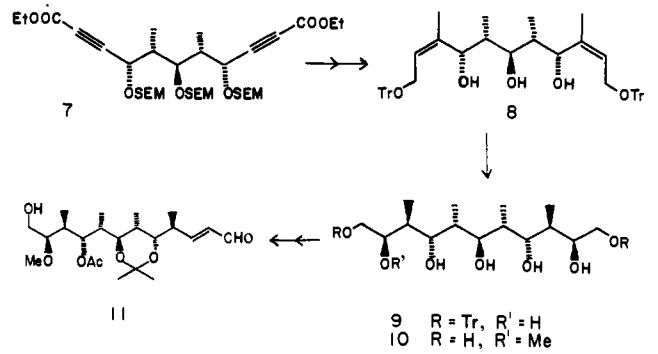
The general procedure used to obtain the results given in Table I consisted of adding the alcohol (1 equiv) to the borane (3 equiv, 0.25–1.0 M) at low temperature. The reaction mixture was then warmed slowly to 25 °C and was allowed to stand until the starting allylic alcohol was consumed.[4] Standard treatment with alkaline peroxide (0 → 25 °C, 18 h) gave the product. As shown in the table, the transformation shows little solvent dependence and is best carried out with the bulkiest borane that gives a convenient reaction rate. Thus 9-BBN is best for hydroboration of terminal olefins like **1** but reacts too sluggishly to be used preparatively with trisubstituted olefins. The more reactive thexylborane is a better choice for such systems.

The overall threo selectivity of the hydroboration may be rationalized by a simple model (Scheme I). Considering the three minimum energy conformations of the starting allylic alcohol, one of the lowest energy conformers (a1) would be expected to be most reactive since it leads to a probable transition state (b or c) having the smallest substituent (H) oriented over the face of the transition-state ring. The approach of borane to the less hindered side of olefinic π system would then lead to the less sterically encumbered transition state and thus to the threo product. The minor *erythro*-diol could arise from borane addition to the more hindered face of a1 or, perhaps more likely, to the less hindered face of a2. Such a picture is supported by the observation that the olefin having a cis substituent (**3**) gives the highest threo stereoselection.

Scheme II



Scheme III



Results with protected alcohols (Table I, experiments 13–23) further demonstrate the reaction's synthetic utility and also reveal some interesting mechanistic points. Both sterically bulky (e.g., trityl) and certain sterically undemanding protecting groups (e.g., benzyloxymethyl) give similarly modest asymmetric induction (5–6:1) with **1**. In contrast, another category of oxygen substituents composed of electrophilic groups like trimethylsilyl, trifluoroacetyl, borane, and hydrogen[5] gives rise to >10:1 stereoselection. While the mechanism behind these differences is not completely clear, a mildly attractive interaction between the latter set of oxygen substituents and the nucleophilic hydride of the borane would be compatible with these results.[6]

The hydroboration of allylic alcohols provides convenient access to the ubiquitous 1,3-diol substructures found in propionate-derived natural products. In the remaining paragraphs, we will demonstrate this point by preparation of the natural stereochemical array found in the ansa bridge of rifamycin.[7] Our strategy is a simple one in which a pair of double allylic alcohol hydroborations parlay one latent chiral center (**4**) first into five (**5**) and then into nine such centers (**9**). Final refunctionalization gives the C17-C28 segment of rifamycin S.

The substrate (**4**, Scheme II) for the first double hydroboration was prepared from 2-butynol by Corey's hydroalumination/iodination[8] (54%), tritylation (93%), and addition to ethyl formate (a, *t*-BuLi/THF–Et_2O; b, HCOOEt, −78 °C; 72%). Hydro-

(3) The 1,3-diol from **1** was identified by comparison with authentic *threo*- and *erythro*-diols prepared as described in the supplementary material. 1,3-Diols from **2** and **3** were identified by the ^{13}C NMR of the meso structures.

(4) Reactions were monitored by TLC after aliquot oxidation (NaOOH).

(5) While hydroboration of **1** is competitive with alcohol deprotonation, alkoxyborane formation with **2** and **3** occurs more rapidly than hydroboration. With **1**, similar stereoselection is found starting with alcohol or alkoxyborane (however, compare the -ate complex, experiment 20).

(6) The attractive interaction either could be dipolar in origin or could result from donation of electron density on hydride into an unoccupied orbital of the oxygen substituent.

(7) Total synthesis: H. Nagaoka, W. Rutsch, G. Schmid, H. Iio, M. R. Johnson, and Y. Kishi, *J. Am. Chem. Soc.*, **102**, 7962 (1980); H. Iio, H. Nagaoka, and Y. Kishi, *ibid.*, **102**, 7965 (1980). Previous ansa-chain syntheses: E. J. Corey and T. Hase, *Tetrahedron Lett.*, 335 (1979); M. Nakata, H. Takao, Y. Ikeyama, T. Sakai, K. Tatsuta, and M. Kinoshita, *Bull. Chem. Soc. Japan.*, **54**, 1749 (1981); H. Nagaoka and Y. Kishi, *Tetrahedron*, **37**, 3873 (1981); S. Masamune, B. Imperiali, and D. S. Garvey, *J. Am. Chem. Soc.*, **104**, 5528 (1982); S. Hanessian, J.-R. Pougny, and I. K. Boessenkool, *ibid.*, **104**, 6164 (1982).

(8) E. J. Corey, J. A. Katzenellenbogen, and G. H. Posner, *J. Am. Chem. Soc.*, **89**, 4245 (1967).

boration first with thexylborane (5 equiv, −78 °C with slow warming to −23 °C) and then with borane itself (4 equiv, −23 °C, 12 h) gave the triols **5** and **6** in 90% yield.[9] NMR analysis of the crude product showed the ratio of the desired *meso* (**5**) to the undesired *dl* (**6**) triols to be 5:1, and pure *meso*-**5** (^{13}C ($CDCl_3$) δ 143.9, 128.6, 127.8, 127.0, 86.8, 79.0, 71.2, 65.3, 36.3, 11.3) was easily isolated by crystallization from ether (mp 186–187 °C).

Conversion to the second diene for the last double hydroboration required nine straightforward steps (average yield per step = 90%). These steps were triol protection ($Me_3SiCH_2CH_2OCH_2Cl$, *i*-Pr_2NEt),[10] catalytic detritylation (H_2, $Pd(OH)_2/C$, EtOH), oxidation ($(COCl)_2$, Me_2SO, Et_3N),[11] 1,1-dibromoalkene formation (CBr_4, Ph_3P), and conversion to the acetylide (BuLi, THF)[12] with trapping by ethyl chloroformate to yield **7** (Scheme III). Addition of methylcuprate (Me_2CuLi, THF, −78 °C),[13] reduction ($LiAlH_4$, Et_2O), tritylation (Ph_3CCl, Et_3N, DMAP), and finally deprotection of the three secondary alcohols (Bu_4NF, HMPA, 85 °C) gave **8**. Hydroboration as described for **4** gave a 76% yield of pentaols which were shown by HPLC and NMR to consist of a 4:1 mixture of *meso*-**9** (^{13}C ($CDCl_3$) δ 143.9, 128.6, 127.8, 127.0, 86.9, 78.8, 72.6, 72.4, 65.3, 37.7, 35.9, 11.4, 10.3) and *dl* products. Although **9** could be isolated by MPLC at this point, it was more convenient to monomethylate one of the less hindered hydroxyls (CH_3I, Ag_2O, 25 °C; 63%) catalytically detritylate (84%), and then isolate pure **10** (mp 192 °C) by simple flash chromatography. The structure of **10** was shown to be correct at this point by conversion to a degradation product of rifamycin SV.[14]

Final transformation of **10** to the rifamycin ansa chain intermediate **11** was effected in ten steps (20% overall yield) by using standard methodology (see supplementary data).[15]

Registry No. **1**, 13019-19-7; **2**, 71581-36-7; **3**, 85067-65-8; **4**, 85067-66-9; **5**, 85067-67-0; **6**, 85114-72-3; **7**, 85067-68-1; **8**, 85067-69-2; **9**, 85067-70-5; **10**, 85067-71-6; **11**, 85067-72-7; **1** (trimethylsilyl derivative), 76966-15-9; **1** (*tert*-butyldimethylsilyl derivative), 85067-73-8; **1** (*tert*-butyldiphenylsilyl derivative), 85067-74-9; **1** (trityl derivative), 85067-75-0; **1** (benzyloxymethyl derivative), 85067-76-1; **1** (acetyl derivative), 26077-07-6; **1** (trifluoroacetyl derivative), 85067-77-2; **1** (9-borabicyclo[3.3.1]nonane derivative), 85082-22-0; **2** (benzyloxymethyl derivative), 85067-78-3; **2** (trifluoroacetyl derivative), 85067-79-4; **3** (benzyloxymethyl derivative), 85067-80-7; *threo*-2-methyl-1,3-heptanediol, 85067-81-8; *erythro*-2-methyl-1,3-heptanediol, 85067-82-9; *meso*-6-methyl-5,7-undecanediol, 85067-83-0; *dl*-6-methyl-5,7-undecanediol, 85114-73-4; *threo*-2-methyl-3-(trimethylsilyloxy)-1-heptanol, 85067-84-1; *threo*-2-methyl-3-(*tert*-butyldimethylsilyloxy)-1-heptanol, 85067-85-2; *threo*-2-methyl-3-(*tert*-butyldiphenylsilyloxy)-1-heptanol, 85067-86-3; *threo*-2-methyl-3-(trityloxy)-1-heptanol, 85067-87-4; *threo*-2-methyl-3-(benzyloxymethoxy)-1-heptanol, 85067-88-5; *threo*-2-methyl-3-(acetyloxy)-1-heptanol, 85067-89-6; *threo*-2-methyl-3-(trifluoroacetyloxy)-1-heptanol, 85067-90-9; *threo*-2-methyl-3-(bicyclo[3.3.1]nonane-9-borato)-1-heptanol lithium salt, 85067-91-0; (5*R**,6*R**,7*S**)-6-methyl-7-(benzyloxymethoxy)-5-undecanol, 85067-92-1; (5*R**,6*R**,7*S**)-6-methyl-7-(trifluoroacetoxy)-5-undecanol, 85067-93-2; (5*S**,6*R**,7*S**)-6-methyl-7-(benzyloxymethoxy)-5-undecanol, 85115-13-5.

Supplementary Material Available: ^1H NMR data for compounds **1–10** and preparations are described for authentic 1,3-diols and for the conversion of **10** to **11** (11 pages). Ordering information is given on any current masthead page.

(9) Reaction of the diene **4** did not go to completion with $ThBH_2$ alone. The *meso*:*dl* ratio was essentially the same as when the product was formed (in reduced yield) with only $ThBH_2$.

(10) B. H. Lipshutz and J. J. Pegram, *Tetrahedron Lett.*, **21**, 3343 (1980).

(11) A. J. Mancuso, S.-L. Huang, and D. Swern, *J. Org. Chem.*, **43**, 2480 (1978).

(12) E. J. Corey and P. L. Fuchs, *Tetrahedron Lett.*, 3769 (1972).

(13) E. J. Corey and J. A. Katzenellenbogen, *J. Am. Chem. Soc.*, **91**, 1851 (1969).

(14) **10** was cleaved ($NaIO_4$, MeOH) and reduced ($LiAlH_4$) to a racemic pentaol (mp 115–117 °C). Rifamycin SV was ozonized (MeOH, −25 °C) and worked up reductively ($NaBH_4$) to give after deacetylation an optically active pentaol (mp 142–145 °C) that was indistinguishable from the synthetic material by IR, ^1H NMR, MS, and ^{13}C NMR ((CD_3COCD_3) δ 83.2, 78.6, 75.8, 71.8, 68.1, 63.2, 59.1, 38.8, 38.4, 36.8, 36.7, 13.6, 10.9, 10.8, 10.2).

(15) This work was supported by grants from the National Institutes of Health and the National Science Foundation.

Chemistry of Carbynes: Reaction of CF, CCl, and CBr with Alkenes

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Carbynes, the monovalent carbon radical family comprising CH and its derivatives, represent the least explored and understood variety of carbon radicals especially when contrasted to their nearest analogues, the carbenes.[1] The primary reason for this lies in the unavailability of a suitable, clean, general source for producing carbynes under conditions applicable to kinetic and mechanistic studies. Consequently, each of the carbyne species—CH, CCl, CBr, CCO_2Et—for which the chemistry has been investigated to date has been generated in an individual way. Each method is complicated by the formation of a number of other reactive radicals, and in fact the carbynes invariably represent only a minor product of the decomposition of the source compound.

CH, CCl, and CBr have been studied in the gas phase by flash and laser photolysis or pulsed radiolysis using C_1 and C_2 hydrocarbons and their halo derivatives as the source material. It was possible by these techniques to measure absolute rate constants for a series of reactions of CH, CCl, and CBr; however, this kinetic approach did not permit the establishment of the mechanistic details of the reactions, which were inferred on the basis of assumed analogies.

On the other hand, the chemistry of CCO_2Et has been investigated in the solution phase.[2] The results of kinetic studies and product analyses suggest that the ground-state doublet carbethoxymethylidyne generated via the in situ photolysis of mercury bis(diazoacetate) ($EtO_2CCN_2HgCN_2CO_2Et$) undergoes concerted, stereospecific cycloaddition to alkenes, regioselective insertion into the C–H bonds of alkanes, alkenes, and alcohols, polar addition to the O–H bonds of alcohols, and cycloaddition to aromatics resulting in ring-expanded products. Hydrogen abstraction did not appear to occur, and absolute rate constants could not be measured.

CH is isoelectronic with the nitrogen atom but in contrast has an electron configuration $1\sigma^2 2\sigma^2 3\sigma^2 1\pi$, giving rise to a $^2\Pi$ ground electronic state. The result is an orbital occupancy that is unique in carbon radical chemistry, in which there is a doubly occupied (lone pair) σ orbital and a singly occupied and an empty π orbital localized on the carbon atom. This electron deficiency endows carbynes with a high reactivity and a distinct electrophilic character. In the case of halocarbynes, overlap between the p_π orbitals of carbon and those of the halogen results in partial multiple-bond formation characterized by the electron configuration...$w\pi^4 x\sigma^2 v\pi^1$ and an accompanying decrease in chemical reactivity.

The purpose of the present communication is to report the first chemical studies of fluoromethylidyne (CF) and the results of a comparative study of CF, CCl, and CBr with a series of alkenes under similar experimental conditions. These halomethylidynes were produced by the flash photolysis of $CHFBr_2$, $CHClBr_2$, and $CHBr_3$, respectively, using the same apparatus and experimental techniques as in previous studies on CCl and CBr.[1] Monitoring of the carbyne concentrations was done by kinetic absorption spectroscopy using the Q_1, P_1 and P_2 bands of the ($\tilde{A}^2\Sigma^+$–$\tilde{X}^2\Pi$(a),

(1) James, F. C.; Choi, H. K. J.; Ruzsicska, B. P.; Strausz, O. P.; Bell, T. N. "Frontiers of Free Radical Chemistry"; Pryor, W. A., Ed.; Academic Press: New York, 1980; pp 139–170.

(2) Strausz, O. P.; Kennepohl, G. J. A.; Garneau, F. X.; DoMinh, T.; Kim, B.; Valenty, S.; Skell, P. S. *J. Am. Chem. Soc.* **1974**, *96*, 5723.

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