yield) of α,α-bis(trimethylsilyl)benzyl phenyl selenide (**11**, mp 100 °C): NMR δ 0.16 (s, 18 H), 7.1–7.5 (m, 8 H), 7.8–8.0 (m, 2 H); IR 2965, 1485, 1258, 873, 850 cm^{-1}.

Anal. Calcd for $C_{19}H_{28}SeSi_2$: C, 58.28; H, 7.21. Found: C, 58.28; H, 7.16.

Phenyl Trimethylsilyl Ketone (12). To a stirred solution of 0.391 g (1 mmol) of **11** in 5 mL of dichloromethane was gradually added 2.1 mmol of H_2O_2 (0.24 mL of 30% H_2O_2 in 0.3 mL of water). The resulting solution was vigorously stirred for 3 h. The reaction mixture was added to 7% $NaHCO_3$ solution and extracted with 3 × 15 mL of ether–pentane. The combined extracts were washed with 10% HCl solution and saturated NaCl solution and dried (Na_2SO_4). After solvent removal preparative TLC gave 0.081 g (46%) of phenyl trimethylsilyl ketone[12] (**12**) [NMR δ 0.39 (s, 9 H), 7.3–7.5 (m, 3 H), 7.7–7.9 (m, 2 H); IR 2970, 2900, 1618, 1595, 1580, 1259, 1217, 840, 784, 694 cm^{-1}; *m/e* (calcd for $C_{10}H_{14}OSi$, 178.08139) 178.08138] along with 9 mg (8%) of benzaldehyde.

Acknowledgment. We thank the National Science Foundation and the Du Pont Co. for financial support and Mr. David Ting for technical assistance.

Registry No.—**1a**, 56253-59-9; **1b**, 61665-38-1; **2a**, 61634-66-0; **2b**, 61634-67-1; **4**, 1923-01-9; **8**, 61634-68-2; **9b**, 61634-69-3; **11**, 61634-70-6; **12**, 5908-41-8; **13**, 61634-71-7; diphenyl diselenide, 1666-13-3; benzyl chloride, 100-44-7; benzyl phenyl selenide, 18255-05-5; Me_3SiCl, 75-77-4; methyl iodide, 74-88-4; bis(3-trifluoromethyl)phenyl diselenide, 53973-75-4; benzyl *m*-trifluoromethylphenyl selenide, 61634-72-8; chlorodimethylsilane, 1066-35-9.

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Reaction of β-Methylselenium Trichloride with Some Simple Alkenes[1]

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The addition reaction of β-methylselenium trichloride to (*E*)- and (*Z*)-2-butene, (*E*)- and (*Z*)-1-phenylpropene, propene, methylpropene, 3-methylbutene-1, and 3,3-dimethylbutene-1 gave β-chloroalkyl methyl selenide dichlorides by anti-stereospecific addition. The regiochemistry depends upon the substituents on the double bond: a phenyl substituent gives exclusively the Markownikoff orientation while anti-Markownikoff orientation predominates in the case of alkyl groups.

It is known from previous work that 2,4-dinitrophenylselenium trichloride adds to carbon–carbon double bonds in a stereospecific manner.[2] In acetic acid, carbon tetrachloride, chloroform, and methylene chloride, these reactions are suitably interpreted as anti electrophilic additions. Little, however, appears to be known about the addition of the aliphatic analogue to alkenes and alkynes.

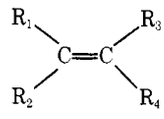
Three alkylselenium trichlorides, $RSeCl_3$, R = CH_3, C_2H_5, and i-C_3H_7, have been reported.[3] Of these only methylselenium trichloride is reasonably stable. Ethylselenium trichloride may be prepared in situ, but has not been isolated. Isopropylselenium trichloride, although apparently formed in situ, immediately decomposes to isopropyl chloride and selenium tetrachloride.

Methylselenium trichloride (MSTC), though first prepared in 1968, has not been the subject of more than very preliminary studies of chemical reactivity.[3] Wynne and George reported[3] the preparation of two distinct forms of MSTC based on their solubility in methylene chloride. The major difference appears to be that the soluble form, hereafter referred to as β-MSTC, is dimeric in solution. The less soluble, α-MSTC, appears to be monomeric.

As part of our continuing investigations into the mechanism(s) of addition of organic selenium halides to alkenes and alkynes we have initiated a study of the reactivity of both forms of MSTC. In this paper we wish to report the stereo- and regiochemistry of the products of addition of β-MSTC to a series of simple alkenes.

Results

As a probe into the stereo- and regiochemistry of this reaction, we have investigated the addition of β-MSTC to two pairs of *E* and *Z* alkenes, the 2-butenes (**1** and **2**) and the 1-phenylpropenes (**3** and **4**), and four unsymmetrical terminal



	R_1	R_2	R_3	R_4
1	CH_3	H	H	CH_3
2	CH_3	H	CH_3	H
3	C_6H_5	H	H	CH_3
4	C_6H_5	H	CH_3	H
5	CH_3	H	H	H
6	CH_3	CH_3	H	H
7	i-C_3H_7	H	H	H
8	t-C_4H_9	H	H	H

Table I. Product Composition of Addition of β-Methylselenium Trichloride to Some Unsymmetric Alkenes in Methylene Chloride Solution at 25 °C

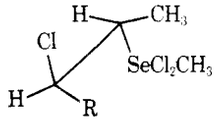
Registry no.	Alkene	Percentage distributions[a] Kinetic product composition M*	aM*	Thermodynamic product composition M*	aM*
24572-14-3	Propene	61	39	16	84
563-45-1	3-Methyl-1-butene	24	76	0	100
558-37-2	3,3-Dimethyl-1-butene	16	84	0	100
115-11-7	Methylpropene	17	83	100	0
766-90-5	(*Z*)-1-Phenylpropene	100	0	100	0
873-66-5	(*E*)-1-Phenylpropene	100	0	100	0

[a] M* = Markownikoff isomer; aM* = anti-Markownikoff isomer.

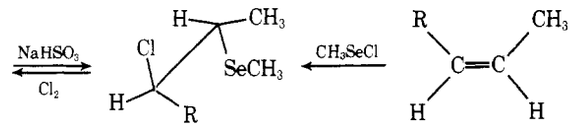
alkenes, propene (**5**), methylpropene (**6**), 3-methylbutene-1 (**7**), and 3,3-dimethylbutene-1 (**8**).

The reaction of β-MSTC with either (*Z*)- or (*E*)-2-butene at 25 °C in methylene chloride occurs instantly and quantitatively to yield compounds **9a** and **10a,** respectively. Under the same conditions β-MSTC reacts with (*Z*)- or (*E*)-1-phenylpropene to yield **9b** and **10b,** respectively. No difference in product composition was observed in the presence or absence of light or added oxygen.

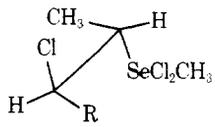
Reduction of the products **9a, 9b, 10a,** and **10b** to the corresponding selenides by the method of Funk and Weiss[4] yields **11a, 11b, 12a,** and **12b.** These selenides are equivalent in all



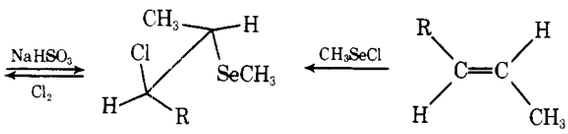
9a, R = CH_3
b, R = C_6H_5



11a, R = CH_3
b, R = C_6H_5



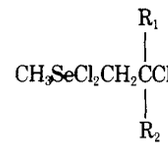
10a, R = CH_3
b, R = C_6H_5



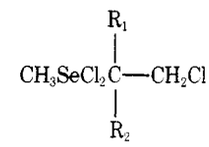
12a, R = CH_3
b, R = C_6H_5

respects to those synthesized independently by the known anti stereospecific addition of methaneselenenyl chloride to (*Z*)- and (*E*)-2-butene and (*Z*)- and (*E*)-1-phenylpropene.[2] Furthermore the selenides **11a, 11b, 12a,** and **12b** were readily converted to their corresponding selenide dichlorides **9a, 9b, 10a,** and **10b** by direct chlorination using an equimolar amount of molecular chlorine or sulfuryl chloride. These data indicate that the additions are anti stereospecific and furthermore regiospecific in the Markownikoff sense in the case of the 1-phenylpropenes.[5]

The reaction of β-MSTC with propene gives two products, **13a** and **14a,** in the ratio 61:39. After standing for 2–3 days,



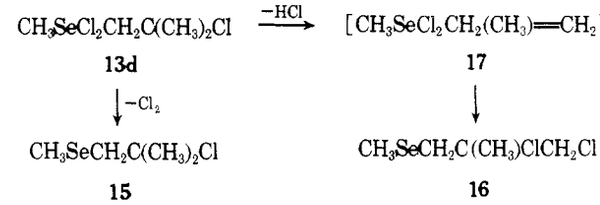
13a, R_1 = H; R_2 = CH_3
b, R_1 = H; R_2 = *i*-Pr
c, R_1 = H; R_2 = *t*-Bu
d, R_1 = CH_3; R_2 = CH_3



14a, R_1 = H; R_2 = CH_3
b, R_1 = H; R_2 = *i*-Pr
c, R_1 = H; R_2 = *t*-Bu
d, R_1 = CH_3; R_2 = CH_3

the ratio changes to 16:84. From their NMR spectra, it is apparent that **13a** and **14a** are the Markownikoff and anti-Markownikoff iomers, respectively. Mixtures of regioisomers were also obtained by the addition of β-MSTC to 3-methyl-1-butene, 3,3-dimethyl-1-butene, and methylpropene. The kinetic and thermodynamic product distributions are summarized in Table I.

The isomerization of the products from the addition of β-MTSC to methylpropene occurs very rapidly in chloroform-*d* ($t_{1/2}$ = 9 min). Furthermore the final product **13d** loses chlorine to form 2-chloro-2-methylpropyl methyl selenide (**15**)



13d **17**

15 **16**

over a period of about 5 h. The identity of this product was established by independent synthesis from methaneselenenyl chloride and methylpropene.

Upon standing compound **13d** also forms a second product, 2,3-dichloro-2-methylpropyl-1 methyl selenide (**16**), identified on the basis of both its NMR and mass spectrum.[6]

The formation of **16** may be attributed to simultaneous dehydrochlorination of **13d** to yield **17** with loss of molecular chlorine from the selenium atom and subsequent chlorination of the newly formed carbon–carbon double bond. Dehydrochlorination of **15** followed by chlorination would also yield **16.** This path seems less likely, however, in view of the apparent stability of **15** under the reaction conditions. The relative ratio of **15** to **16** under conditions of thermodynamic control was found to be approximately 7:5 after 6 days.

The proton magnetic resonance spectra of the adducts given in Table II are in accord with their proposed structures. For example, the methine protons of **9a** appear as a symmetrical multiplet composed of 13 peaks centered at δ 4.61 ppm, when run at 60 MHz. The 100-MHz spectrum resolved this multiplet into 14 lines interpreted as two overlapping doublets of

Table II. The Observed Proton Magnetic Resonance Parameters for the Adducts of β-Methylselenium Trichloride

Alkene	Adduct	Registry no.	Chemical shift assignments,[a] δ, ppm					
			CH_3Se	H_3	H_2	H_1	H_1'	H_2'	H_3'
Propene	M (13a)	61634-30-8	3.48 s		1.79 d		3.9–4.5 m (3 H)		
	aM (14a)	61634-31-9	3.62 s				4.24, 4.19 AB q, 4.87 m, 1.71 d		
3-Methyl-1-butene	M (13b)	61634-32-0	3.66 s	1.07 d			3.9–4.5 m (3 H)		1.12 d
	aM (14b)	61634-33-1	3.63 s	1.04 d	2.13 m		4.27, 4.15 AB q, 4.70 ddd, 2.08 m		1.11 d
3,3-Dimethyl-1-butene	M (13c)	61634-34-2	3.73 s	1.30 s (9 H)			4.2–4.6 (3 H)		
	aM (14c)	61634-35-3	3.67 s				4.28, 4.14, 4.63 ABC spin system		
								1.13 s (9 H)	
Methylpropene	M (13d)	61634-36-4	3.65 s		1.95 s (6 H)		4.45 s (2 H)		
	aM (14d)	61634-37-5	3.35 s			4.15 s (2 H)		1.90 s (6 H)	
(Z)-2-Butene[b]	threo (9a)	61634-38-6	3.47 s		1.77 d	4.58 m	4.75 m	1.68 d	
(E)-2-Butene[c]	erythro (10a)	61634-39-7	3.52 s		1.88 d	4.42 q′	4.85 q′	1.72 d	
(Z)-1-Phenylpropene	threo-M (9b)	61634-40-0	3.43 s			5.48 d	4.87 dq	1.38 d	
(E)-1-Phenylpropene	erythro-M (10b)	61634-41-1	3.33 s			5.50 d	4.82 dq	1.98 d	

[a] All chemical shifts are reported relative to internal Me_4Si in chloroform-*d* solution. [b] Registry no., 590-18-1. [c] Registry no., 624-64-6.

quartets at δ 4.75 and 4.58 ppm. These doublets of quartets were assigned to the methine protons geminal to the *Se,Se*-dichloroselenomethyl group and the chlorine atom, respectively. These assignments are based on the criteria previously established[2] that protons geminal to the tetravalent selenium are deshielded relative to those geminal to a chlorine atom, where other structural characteristics are equivalent. Assignment of the methyl doublets which arise from protons vicinal to the *Se,Se*-dichloroselenomethyl group and the chlorine atom is not quite as clean-cut. The proton–proton coupling interactions show that the high-field doublet at δ 1.68 may be unambiguously assigned to the methyl group geminal to the selenium atom. Thus the remaining methyl doublet at δ 1.77 may be assigned to the methyl group geminal to the chlorine atom.

The ^1H NMR spectrum of the methine region of **10a** derived from (*E*)-2-butene has, in contrast to that of **9a**, two distinct "quintets" located at δ 4.85 and 4.42 ppm, respectively. Assignments were made as above and are reported in Table II.

The observed vicinal methine proton–proton coupling constants for **9a** and **10a** are 4.5 and 7.1 Hz, respectively. These data are in accord with their assignment as the threo and erythro isomers of 3-chlorobutyl-2-methylselenium dichloride, respectively.

The ^1H NMR data for **9b** and **10b** are in accord with anti stereospecific addition to **3** and **4**. It is known[7] that in the ^1H NMR spectra of racemic erythro and threo isomers of 1,2-disubstituted 1-arylpropanes the β-methyl protons of the erythro isomer always appear at lower field than those of the corresponding threo isomer.

Supporting data are available from the ^{13}C NMR spectra. The assignment of carbon resonances is based on criteria similar to that derived from the ^1H NMR results and in addition upon the well-documented structural dependence of carbon-13 chemical shifts. Thus the methine carbons directly bonded to the *Se,Se*-dichloroselenomethyl group are considerably deshielded compared to those bonded to the chlorine atom. The methyl carbon geminal to the *Se,Se*-dichloroselenomethyl group should experience a strong shielding effect from the chlorines bonded to the selenium atom (γ-gauche effect). Thus the high-field methyl carbons at δ 12.21 and 12.98 ppm for compounds **9a** and **10a**, respectively, are readily assigned. Assignments were further confirmed through the use of off-resonance proton decoupling experiments. Spectral parameters are given in Table III.

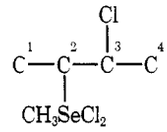
Discussion

The fact that radical initiators or scavengers do not affect the product composition suggests that the reaction does not involve radical intermediates. The facile nature of the reaction with these electron-rich alkenes further supports the view that the reaction is ionic and possibly electrophilic.

The quantitative formation of different products from each of two pairs of (*E*)- and (*Z*)-isomeric alkenes is clear evidence that the addition of β-methylselenium trichloride occurs stereospecifically. The fact that the same product is formed either by addition of β-methylselenium trichloride to (*Z*)-1-phenylpropene or by chlorination of *threo*-1-chloro-1-phenyl-2-propyl methyl selenide establishes that **9b** and **10b** are the isomeric threo and erythro adducts, respectively. Consequently the addition of β-methylselenium trichloride to these acyclic alkenes occurs in an anti-stereospecific manner within the experimental limits of our ^1H NMR analysis.

The nature of the substituents on the alkene significantly influences the regiochemistry of the product. Phenyl substituents lead to regiospecific addition to form products of Markownikoff orientation. This suggests that the polar effect of the phenyl ring is dominant in the product determining

Table III. Carbon-13 Magnetic Resonance Parameters of β-Methylselenium Trichloride Adducts



Alkene	Adduct	Chemical shift assignments, δ, ppm				
		C_1	C_2	C_3	C_4	CH_3Se
Propene	M (13a)		7.0 t	53.5 d	24.5 q	40.8 q
Propene	aM (14a)	14.8 q	70.5 d	51.8 t		44.9 q
(Z)-2-Butene	threo (9a)	12.2 q	78.0 d	57.1 d	22.5 q	41.2 q
(E)-2-Butene	erythro (10a)	13.0 q	75.5 d	57.5 d	23.6 q	41.5 q

Table IV. Kinetic Product Distribution for the Addition of Benzenesulfenyl Chloride, Benzeneselenenyl Chloride, and β-Methylselenium Trichloride to Some Unsymmetrical Alkenes in Methylene Chloride at 25 °C

Alkene	C_6H_5SCl[a]		C_6H_5SeCl[b]		β-CH_3SeCl_3[c]	
	M*	aM*	M*	aM*	M*	aM*
$CH_3CH=CH_2$	32	68	59	41	61	39
i-$PrCH=CH_2$	0	100	12	88	24	76
t-$BuCH=CH_2$	0	100	0	100	16	84
$(CH_3)_2C=CH_2$	14	86	100	0	17	83

[a] Registry no., 931-59-9. [b] Registry no., 5707-04-0. [c] Registry no., 37826-07-6.

Table V. Physical and Analytical Data for the β-Methylselenium Trichloride Adducts

Alkene	Adduct	Mp, °C	Anal., %					
			Carbon		Hydrogen		Chlorine	
			Calcd	Found	Calcd	Found	Calcd	Found
(Z)-2-Butene	**9a**	104	23.41	23.90	4.32	4.22	41.47	41.64
				23.50		4.27		41.30
(E)-2-Butene	**10a**	64	23.41	23.38	4.32	4.00	41.47	41.09
Methylpropene	**13d**	53	23.41	23.63	4.32	4.36	41.47	41.16
(Z)-1-Phenylpropene	**9b**	93	37.71	37.45	4.11	4.04	33.59	33.61
(E)-1-Phenylpropene	**10b**	76	37.71	37.57	4.11	3.89	33.39	33.73

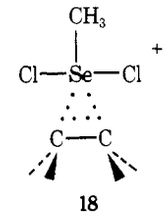
step. Alkyl substituents lead to nonregiospecific addition. Products of both Markownikoff and anti-Markownikoff orientation are formed.

The rapidity of these additions and the lack of a suitable method to determine the rate of disappearance of either reactants precludes a kinetic investigation at this time. In the absence of such data, the stoichiometry and structure of the rate-determining transition state cannot be determined. However, from the product data, it is possible to draw conclusions regarding the product-determining transition state.

The nonregiospecific addition of β-methylselenium trichloride to alkyl-substituted ethylenes is strong evidence against an open ion intermediate immediately prior to the product-determining transition state. While the anti-stereospecific addition to the 1-phenylpropenes is consistent with such a view, a nonrotating open carbonium ion cannot be ruled out.

The kinetically controlled product composition for the addition of benzenesulfenyl chloride, benzeneselenenyl chloride, and β-methylselenium trichloride to simple alkenes show many similarities.[8] The data are given in Table IV. In general the product with anti-Markownikoff orientation is preferred which indicates that the steric effect of the alkyl group is important. Thus as the steric bulk of the alkyl substituent increases so does the percentage of the anti-Markownikoff isomer.

The data for the additions of benzenesulfenyl and benzeneselenenyl chloride to alkenes can best be explained by proposing a mechanism involving a bridged product determining transition state. By analogy a bridged product determining transition state, similar to the ion **18**, can be proposed



18

for the addition of β-methylselenium trichloride to alkenes. Which of the two carbon atoms in the three-member ring of ion **18** will be attacked by the chloride ion depends upon the polar and steric factors of the substituents. For the alkyl groups steric effects dominate while polar effects are more important when a phenyl ring is the substituent.

In view of the known dimeric nature of β-methylselenium trichloride in methylene chloride solution, it is apparent that the above interpretation may be an oversimplication. It is, of course, possible that the adducts prepared in these reactions are really 2:2 adducts. Attempts to resolve this question were inconclusive. In the solid state, Rast molecular weight determinations indicate a monomeric state for **9a, 10a, 11a,** and

12a. Similar results were obtained from electron impact mass spectrometry. Cryoscopic data for related compounds such as dimethyl selenide dichloride indicate a preferred monomeric state in solution.

A monomeric intermediate could be formed by a nucleophilic attack by the alkene on the dimer forming ion **18** and a $CH_3SeCl_4^-$ counterion. Work continues on this problem.

Experimental Section

All melting points are uncorrected. Microanalyses were carried out by A. B. Gygli Microanalysis Laboratory. ^1H NMR spectra were run on a Varian T-60 or HA-100 spectrometer. ^{13}C NMR spectra were run on a Varian CFT-20 spectrometer using a 16K memory. Chloroform-*d* was used as an internal lock and reference. All spectra were referenced to Me_4Si as an internal standard. The olefins were obtained commercially and their purity verified by GLC and ^1H NMR.

β-Methylselenium trichloride was prepared by the method of Wynne and George.[3a]

Methylene chloride was purified as previously described.[2]

The determination of product compositions and the preparation of analytical samples were carried out as previously described.[6] The elemental analyses for the adducts are given in Table V where available.

No evidence of a molecular ion was found in the mass spectra of the adducts. This is in agreement with previous studies on the mass spectral fragmentation of dialkyl selenide dichlorides.[9] Characteristic peak clusters representative of loss of chlorine radical and molecular chlorine from the molecular ion were observed. For adducts **9b** and **10b**, a cleavage of the $M^+ - Cl_2$ fragment with loss of C_6H_5CHCl to give a $CH_3Se{=}CHCH_3^+$ cation radical at *m/e* 123 was observed. Such a result is consistent with the Markownikoff orientation of the adducts **9b** and **10b**.

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Reaction of Crystalline Fluoro Olefins with Bromine Vapor[1]

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Crystalline fluoro olefins of general structure 4-R-$C_6H_4C(CF_3){=}CF_2$ (R = Ph, 4′-ClC_6H_4, 4′-BrC_6H_4, 4′-MeC_6H_4, 4′-$HO_2CC_6H_4$, and HO_2C) and 3-$HO_2CC_6H_4C(CF_3){=}CF_2$ have been reacted with bromine vapor. Addition to the double bond occurs only in light, while aromatic substitution is a predominant side reaction in R = Ph and 4′-MeC_6H_4. Exposure of any of the first four olefins to bromine vapor results in the formation of a solution of bromine and the olefin. The reactions of the carboxylic acid substituted olefins are true gas–solid processes as a liquid phase is not formed during the reaction. The addition products are formed as a polycrystalline phase.

The gas–solid addition reactions of halogens with crystalline olefins have been reported with increasing frequency. Very early research was performed primarily for synthetic goals;[2] but recent work has been directed at understanding the influence of the crystal lattice upon the course of the reaction.[3] The gas–solid addition of bromine to substituted cinnamic acids was reported to occur without the formation of a liquid phase on the crystals. The reactions were fast and gave the trans adducts.[4] The gas–solid addition of chlorine to *trans*-stilbene was accompanied by the formation of a hard coating on the surface of the crystals which prevented complete reaction.[5] Finally, an asymmetric synthesis was reported for the reaction of bromine vapor with a single crystal of 4,4′-dimethylchalcone ($P2_12_12_1$).[6] Continuation of this work has correlated the absolute configuration of the starting material in the solid with the optical rotation of the product.[7]

The double bond in polyfluorinated olefins is electron poor, such that the usual reactions are attack by nucleophiles, so brominations of fluorinated olefins are usually performed under conditions which favor radical additions.[8] It was of interest to determine if fluorinated olefins would exhibit relatively high solid-state reactivity toward bromine—as has been reported for cinnamic acid derivatives[4]—and what some of the physical characteristics of these reactions would be under different conditions.

Results and Discussion

The initial phase of the work examined the reactions of substituted 2-(4-biphenylyl)-*F*-propenes, **1**, with bromine vapor. These olefins were conveniently prepared from trifluoromethyl ketones via a Wittig reaction with triphenylphosphine and dibromodifluoromethane[9] (cf. Experimental Section). Interestingly, crystals of these olefins could not be grown until traces of unknown impurity were removed by column chromatography. The 4′-carboxylic acid derivative, **1e**, was prepared from **1c** via the Grignard. The physical