J = 8.5 Hz); IR (neat) 1750 cm^{-1} (C=O); mass spectrum, m/e 170 (M^+). Anal. Calcd for $C_6H_9F_3O_2$: C, 42.36; H, 5.33. Found: C, 42.44; H, 5.34.

Methyl 2-methyl-3,3,3-trifluoropropionate [2a-(b)]:[20] ^1H NMR (C_6D_6) δ 1.05 (d, J = 7.0 Hz, 3 H), 2.76 (m, 1 H), 3.26 (s, 3 H); ^{19}F NMR (C_6D_6) δ -69.8 (d, J = 8.0 Hz).

Isopropyl 2-methyl-3,3,3-trifluoropropionate [2a-(c)]: ^1H NMR ($CDCl_3$) δ 1.27 (d, J = 7.0 Hz, 6 H), 1.38 (d, J = 7.0 Hz, 3 H), 3.12 (septet, J = 7.0 Hz, 1 H), 5.05 (septet, J = 7.0 Hz, 1 H); ^{19}F NMR ($CDCl_3$) δ -70.3 (d, J = 7.0 Hz); IR (neat) 1745 cm^{-1} (C=O); mass spectrum, m/e 184 (M^+). Anal. Calcd for $C_7H_{11}F_3O_2$: C, 45.65; H, 6.02. Found: C, 45.68; H, 5.92.

Ethyl 4,4,4-trifluorobutyrate [3a-(a)]:[22] ^1H NMR ($CDCl_3$) δ 1.27 (t, J = 6.6 Hz, 3 H), 2.1-2.7 (m, 4 H), 4.15 (q, J = 6.6 Hz, 2 H); ^{19}F NMR ($CDCl_3$) δ -67.7 (t, J = 10.5 Hz); IR (neat) 1740 cm^{-1} (C=O); mass spectrum, m/e 170 (M^+).

Methyl 4,4,4-trifluorobutyrate [3a-(b)]:[21] ^1H NMR (C_6D_6) δ 1.7-2.3 (m, 4 H), 3.26 (s, 3 H); ^{19}F NMR (C_6D_6) δ -66.8 (t, J = 10.0 Hz).

Isopropyl 4,4,4-trifluorobutyrate [3a-(c)]: ^1H NMR ($CDCl_3$) δ 1.25 (d, J = 7.0 Hz, 6 H), 2.3-2.7 (m, 4 H), 5.0 (septet, J = 7.0 Hz, 1 H); ^{19}F NMR ($CDCl_3$) δ -67.3 (t, J = 10.0 Hz); IR (neat) 1740 cm^{-1} (C=O); mass spectrum, m/e 184 (M^+). Anal. Calcd for $C_7H_{11}F_3O_2$: C, 45.65; H, 6.02. Found: C, 45.40; H, 5.79.

2-Methyl-3,3,3-trifluoropropionic acid (4a):[20] ^1H NMR ($CDCl_3$) δ 1.48 (d, J = 7.2 Hz, 3 H), 3.28 (m, 1 H), 10.18 (br s, 1 H); ^{19}F NMR ($CDCl_3$) δ -70.6 (d, J = 8.1 Hz); IR (neat) 1725 cm^{-1} (C=O); mass spectrum, m/e 142 (M^+).

4,4,4-Trifluorobutyric acid (5a):[22,23] ^1H NMR ($CDCl_3$) δ 2.1-2.8 (m, 4 H), 9.10 (br s, 1 H); ^{19}F NMR ($CDCl_3$) δ -67.7 (t, J = 10.2 Hz); IR (neat) 1725 cm^{-1} (C=O); mass spectrum, m/e 142 (M^+).

Hydroesterification and Hydrocarboxylation of Pentafluorostyrene (PFS). The following procedure is typical. A 50-mL stainless steel autoclave fitted with a magnetic stirring bar was charged with a palladium catalyst (3×10^{-2} mmol), PFS (582 mg, 3 mmol), and either alcohol (1 mL) in acetone (4 mL) or water (0.3 mL) in acetic acid (4 mL), sealed up, and then purged by filling (20 atm) and releasing twice with carbon monoxide. The autoclave was pressurized with carbon monoxide up to the desired pressure, and then heating and stirring were started. After the reaction was run for the necessary period of time, the autoclave was cooled to room temperature and carefully depressurized. The reaction mixture was submitted to quantitative GLC analysis by using decane as the internal standard, and the products were isolated by preparative GLC. The structures of the products were determined on the basis of their spectral data and elemental analyses. Results are summarized in Tables II and IV.

Methyl 2-(pentafluorophenyl)propionate (2b): ^1H NMR ($CDCl_3$) δ 1.55 (d, J = 7.0 Hz, 3 H), 3.71 (s, 3 H), 4.05 (q, J = 7.0 Hz, 1 H); ^{19}F NMR ($CDCl_3$) δ -143.4 (m, 2 F), -156.4 (t, J = 20.0 Hz, 1 F), -162.6 (m, 2 F); IR (neat) 1750 cm^{-1} (C=O); mass spectrum, m/e 254 (M^+). Anal. Calcd for $C_{10}H_7F_5O_2$: C, 47.27; H, 2.76. Found: C, 47.17; H, 2.78.

Methyl 3-(pentafluorophenyl)propionate (3b): ^1H NMR ($CDCl_3$) δ 2.60 (t, J = 7.0 Hz, 2 H), 3.03 (t, J = 7.0 Hz, 2 H), 3.68 (s, 3 H); ^{19}F NMR ($CDCl_3$) δ -144.0 (m, 2 F), -157.3 (t, J = 20.0 Hz, 1 F), -163.0 (m, 2 F); IR (neat) 1750 cm^{-1} (C=O); mass spectrum, m/e 254 (M^+). Anal. Calcd for $C_{10}H_7F_5O_2$: C, 47.27; H, 2.76. Found: C, 47.24; H, 2.81.

2-(Pentafluorophenyl)propionic acid (4b): mp 91-92 °C; ^1H NMR ($CDCl_3$) δ 1.55 (d, J = 7.0 Hz, 3 H), 4.11 (q, J = 7.0 Hz, 1 H), 11.45 (br s, 1 H); ^{19}F NMR ($CDCl_3$) δ -142.9 (m, 2 F), -155.9 (t, J = 21.0 Hz, 1 F), -162.5 (m, 2 F); IR (KBr) 1720 cm^{-1} (C=O); mass spectrum, m/e 240 (M^+). Anal. Calcd for $C_9H_5F_5O_2$: C, 45.02; H, 2.10. Found: C, 45.00; H, 2.23.

3-(Pentafluorophenyl)propionic acid (5b): mp 95-96 °C; ^1H NMR ($CDCl_3$) δ 2.6-2.9 (m, 2 H), 2.9-3.3 (m, 2 H), 10.86 (br s, 1 H); ^{19}F NMR ($CDCl_3$) δ -144.1 (m, 2 F), -157.1 (t, J = 20.0 Hz, 1 F), -162.9 (m, 2 F); IR (KBr) 1715 cm^{-1} (C=O); mass spectrum, m/e 240 (M^+). Anal. Calcd for $C_9H_5F_5O_2$: C, 45.02; H, 2.10. Found: C, 45.11; H, 2.14.

Registry No. **1a**, 677-21-4; **2a**, 653-34-9; **2a**-(a), 56354-75-7; **2a**-(b), 339-17-3; **2a**-(c), 86994-26-5; **2b**, 86994-28-7; **3a**-(a), 371-26-6; **3a**-(b), 2365-82-4; **3a**-(c), 86994-27-6; **3b**, 86994-29-8; **4a**, 381-97-5; **4b**, 719-30-2; **5a**, 406-93-9; **5b**, 2002-92-8; $PdCl_2$, 7647-10-1; PPh_3, 603-35-0; $PdCl_2(PPh_3)_2$, 13965-03-2; $PdCl_2$(dppb), 29964-62-3; $PdCl_2$(dppf), 72287-26-4; $SnCl_2$, 7772-99-8.

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Notes

Regioselectivity of 1,3-Dipolar Cycloadditions of (Phenylsulfinyl)- and (Phenylsulfonyl)alkenes

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In a previous paper[2] two of us have reported the cycloaddition of nitrilimines to unsymmetrical disubstituted electron-deficient alkenes, with $PhSO_2$ as a substituent group. Here we examine the chemical behavior of nitrilimine **1** and nitrile oxide **2** toward both sulfinyl- and sulfonylalkenes **3** and **4**, respectively. The aim of our work is to get a better understanding of the influence of PhSO and $PhSO_2$ groups on the regioselectivity of the cycloaddition reactions of alkene dipolarophiles. Up to now the use of α,β-unsaturated sulfoxides and sulfones as dipolarophiles in 1,3-dipolar cycloaddition reactions is quite limited.[3]

A perturbation molecular orbital treatment has been performed in order to rationalize the experimental results.

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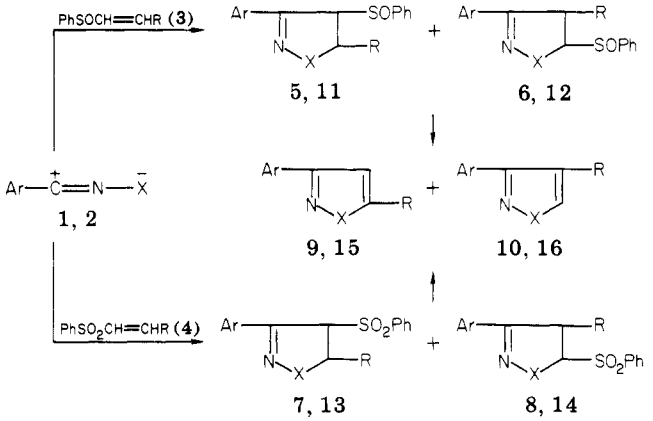
Table I. Reaction of 1 with 3 and 4

dipolarophile	reaction time, h	products[a] (yield, %)	R_5/R_4 ratio[b]
3a	20	9a[c] (56)	
3b	20	9b[d] (16) + 10b[d] (15)	52:48
3c	20	9c[e] (34) + 10c[f] (14)	71:29
3d	24	9d[g] (63) + 10d[d] (24)	73:27
4a	48	9a (75)	
4b	72	9b (20) + 10b (15)	65:35
4c	48	7c (50) + 10c (5)	90:10
4d	24	7d[g] (82) + 10d (5)	95:5

[a] Compounds 9 and 10 are coincident for R = H. [b] The labels 5 and 4 indicate the position of the R substituent in the products; the ratio was determinated by NMR analysis of the crude product mixture. [c] Reference 4. [d] Reference 5. [e] Reference 6. [f] Reference 7. [g] Reference 2.

Scheme I[a]



[a] 1, 5, 6, 7, 8, 9, 10: Ar = Ph; X = NPh. 2, 11, 12, 13, 14, 15, 16: Ar = 3,5-Cl_2-2,4,6-Me_3C_6; X = O. For a, R = H; b, R = Me; c, R = Ph; d, R = COPh.

Results

Reaction of Diphenylnitrilimine (1) with Compounds 3 and 4. All the reactions have been carried out by refluxing under nitrogen a benzene solution of 1-(α-chlorobenzal)-2-phenylhydrazine with an equimolar amount of the appropriate *trans*-disubstituted-alkenes in the presence of $N(Et)_3$. Reaction times, yields, and regioisomer ratios are reported in Table I.

In the case of sulfinylalkenes, the pyrazoline adducts **5** and **6** have never been isolated, while the analogous 4-$PhSO_2$-substituted adducts were isolated for R = Ph (**7c**) and R = COPh (**7d**) (Scheme I). Such compounds have the expected trans configuration, suggested by the coupling constant of pyrazoline protons.[6]

No 5-$PhSO_2$-substituted pyrazoline could be isolated, in agreement with the known facile elimination of the leaving group in position **5** of pyrazolines[8] and isoxazolines.[9]

Reaction of 3,5-Dichloromesitylnitrile Oxide (2) with Compounds 3 and 4. All reactions were carried out in benzene solution with an equimolar amount of nitrile oxide **2** and *trans*-(phenylsulfinyl) and -(phenylsulfonyl)alkenes **3** and **4**. Reaction times, yields, and regioisomer ratios are reported in Table II.

Table II. Reaction of 2 with 3 and 4

dipolarophile	reaction time, h	products[a] (yield, %)	R_5/R_4 ratio[b]
3a	6	15a (58)[b]	
3b	24	[15b + 16b] (45)[c]	55:45
3c	19	15c[d] (20) + 16c (41)	33:67
3d	4	15d (21) + 16d (54)	27:73
4a	4	13a (7) + 14a (73)	9:91
4b	24	13b (54) + 14b (6)	90:10
4c	24	[13c + 14c] (75)[c]	60:40
4d	2	[13d + 14d] (88)[c]	75:25

[a] Compounds 15 and 16 are coincident for R = H. [b] See footnote *b* in Table I. [c] Overall yield because one of the two regioisomers could not be isolated in the pure state. [d] Reference 10.

The isoxazoline adduct of (phenylsulfinyl)alkenes has never been isolated, while (phenylsulfonyl)alkenes give stable and isolable isoxazoline derivatives (Scheme I). $PhSO_2H$ elimination from 5-(phenylsulfonyl)-substituted isoxazolines can be achieved by reaction with DABCO. With R = COPh, both regioisomers undergo $PhSO_2H$ elimination, even on silica gel. The structures of isoxazoles **15** and **16** have been assigned on the basis of the chemical shift of the proton of the isoxazole ring, while isoxazolines have been identified both by transformation in the corresponding isoxazoles **15** and **16** and by NMR analysis (see Table III).

Coupling constants of isoxazoline protons (J = 4.5–8.5 Hz) are in agreement with the expected trans configuration.[11] Among the couples of regioisomers, the 5-(phenylsulfonyl)-substituted compounds have the lowest coupling constant, as shown for isomeric couples of isoxazolines bearing an electron-withdrawing substituent.[11c,d]

In the case of (phenylsulfinyl)alkenes, some side products have been isolated, together with cycloadducts, namely, diphenyl disulfide, *N,N'*-bis(3,5-dichloro-2,4,6-trimethylphenyl)urea and, in the case of **3a**, the 1,2-bis(phenylsulfinyl)ethane.[12]

Discussion

The observed regioselectivities have been considered in light of the perturbation theory. The PMO treatment was performed as previously described,[13] by partitioning the interaction energy between the reacting systems into three components: E_{mixing} (attractive), $E_{repulsive}$, and E_{polar}.

Table IV gives the difference (ΔE) between the interaction energies for the formation of regioisomers R_5 and

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Table III. Physical and Spectral Data of the New Compounds[a]

compd	mp, °C (recrystn solvent)	NMR ($CDCl_3$),[b] δ
7c	160 (ethanol)	4.95 (1 H, d, J = 3.5), 6.05 (1 H, d, J = 3.5)
13a	192 (benzene-hexane)	1.96 (3 H, s), 2.46 (3 H, s), 2.52 (3 H, s), 4.7-5.3 (3 H, m), 7.15-7.65 (5 H, m)
13b	134 (benzene-hexane)	1.60 (3 H, d, J = 6), 1.88 (3 H, s), 2.42 (3 H, s), 2.50 (3 H, s), 4.63 (1 H, d, J = 8.5), 5.45 (1 H, m), 7.1-7.6 (5 H, m)
13c	185 (benzene-hexane)	1.74 (3 H, s), 2.42 (3 H, s), 2.58 (3 H, s), 4.86 (1 H, d, J = 6.7), 6.32 (1 H, d, J = 6.7), 7.1-7.8 (10 H, m)
13d	161 (diisopropyl ether-hexane)	1.95 (3 H, s), 2.45 (3 H, s), 2.60 (3 H, s), 6.00 (1 H, d, J = 6.5), 6.54 (1 H, d, J = 6.5), 7.1-7.8 (8 H, m), 8.0-8.3 (2 H, m)
14a	148 (benzene-hexane)	2.25 (6 H, s), 2.52 (3 H, s), 3.60, 3.84 (2 H, AB part of ABX, J_{AB} = 19.0, J_{AX} = 10.8, J_{BX} = 6.0), 5.57 (1 H, dd, J = 10.8 and 6.0), 7.4-7.8 (3 H, m), 7.9-8.1 (2 H, m)
14b	150 (benzene-hexane)	1.32 (3 H, d, J = 6), 2.27 (6 H, s), 2.52 (3 H, s), 4.25 (1 H, m), 5.15 (1 H, d, J = 5.8), 7.4-7.8 (3 H, m), 7.9-8.2 (2 H, m)
14c	*c*	2.14 (6 H, s), 2.46 (3 H, s), 5.27 (1 H, d, J = 4.5), 5.68 (1 H, d, J = 4.5)[d]
14d	*c*	2.20 (6 H, s), 2.40 (3 H, s), 5.93 (1 H, d, J = 4.8), 6.18 (1 H, d, J = 4.8)[d]
15a	80 (hexane)	2.15 (6 H, s), 2.58 (3 H, s), 6.35 (1 H, s), 8.61 (1 H, s)
15b	*c*	2.55 (3 H, s), 5.90 (1 H, s)[d]
15d	149 (hexane)	2.21 (6 H, s), 2.59 (3 H, s), 7.00 (1 H, s), 7.4-7.8 (3 H, m), 8.1-8.3 (2 H, m)
16b	*c*	1.80 (3 H, s), 8.33 (1 H, s)[d]
16c	199 (hexane)	2.10 (3 H, s), 2.26 (3 H, s), 2.60 (3 H, s), 7.0-7.4 (5 H, m), 8.77 (1 H, s)
16d	124 (benzene-hexane)	2.13 (6 H, s), 2.55 (3 H, s), 7.3-7.9 (5 H, m), 8.95 (1 H, s)

[a] All the isolated products gave satisfactory elemental analyses (±0.3% for C, H, and N). [b] J in hertz. [c] Not isolated in the pure state. [d] These signals were inferred from the NMR spectrum of the regioisomeric mixture.

Table IV. Interaction Energy Differences

distance: r, Å	interaction term	$\Delta E = E_{R_5} - E_{R_4}$ (meV) 1 + 3 Me	H	Ph	PhCO	1 + 4 Me	H	Ph	PhCO
	mixing	−108	−59	−94	−24	−99	−60	−98	−36
1.85	repulsive	46	21	38	2.7	47	27	46	13
	polar	−506	−416	−495	−520	−348	−271	−353	−390
	mixing	−1.7	4.8	−3.3	1.4	−3.1	2.4	−4.3	−0.7
2.65	repulsive	16	7.1	13	1.0	17	10	16	4.4
	polar	−322	−271	−317	−331	−228	−185	−231	−253
		2 + 3				2 + 4			
		Me	H	Ph	PhCO	Me	H	Ph	PhCO
	mixing	−141	−74	−124	−30	−132	−80	−131	−46
1.85	repulsive	90	41	75	5.3	93	53	90	25
	polar	−754	−626	−739	−729	−563	−453	−568	−580
	mixing	−0.4	6.2	−2.3	2.0	−1.8	3.7	−3.3	−0.2
2.65	repulsive	23	10	19	1.3	24	14	24	6.5
	polar	−463	−391	−456	−451	−358	−295	−361	−369

R_4 calculated for symmetric approaches at two different distances.[14] A negative value of ΔE means that R_5 is the preferred regioisomer.

The most significant indications that can be drawn from Table IV are the sequences of the propensities of the various dipolarophiles to give the R_5 isomer. The repulsive term shows the sequence PhCO > H > Ph > Me at both distances, and the mixing term gives Me > Ph > PhCO at 1.85 Å and Ph > Me > PhCO > H at 2.65 Å, irrespectively of whichever dipole and dipolarophile are considered. Therefore, these two terms do not accomodate the experimental results. By contrast, the polar term gives sequences that depend on the dipole and dipolarophile and are insensitive to the distance. This term does succeed in matching most of the observed trends: PhCO > Ph > H (reactions of **2** with sulfones), Me > Ph > PhCO (reaction of **2** with sulfoxides), PhCO > Ph > Me (reaction of **1** with sulfones), and PhCO > Ph (reaction of **1** with sulfoxides). Only the experimental results of the reactions between **2** and **4b** and between **1** and **3b** are not fully matched.

Interestingly, from Table IV the unsubstituted vinylphenyl sulfone and sulfoxide are expected to have the lowest propensities to give R_5 isomers. However, the ob-

(14) The distance r = 1.85 Å is close to the one suggested by Houk, K. N.; Sims, J.; Watts, C. R.; Luskus, L. J. *J. Am. Chem. Soc.* **1973**, *95*, 7301. The second was considered by Bastide, J.; El Ghandour, N.; Henri-Rousseau, O. *Bull. Soc. Chim. Fr.* **1973**, 2290.

served preferred formation of the isomer **14a** shows that in this case steric factors must play the most important role.

An alternative way to rationalize the observed regioselectivities is given by a simple qualitative frontier approach. CNDO/2 computations indicate a lowering of LUMO energy and, to a greater extent, of HOMO energy in going from **1** to **2**. CNDO/2 and EH computations suggest that sulfones are less nucleophilic than sulfoxides. In fact, the values of the energies, $-E_{HOMO}$ (eV), of sulfones are in the range 12.1–12.9 (CNDO/2) and 11.2–11.5 (EH) and those of sulfoxides are in the ranges 11.6–12.1 (CNDO/2) and 10.68–10.72 (EH).

Thus, one can reasonably argue that the reactions of **1** are essentially dipole HOMO controlled, while those of **2** involve also the interaction dipole LUMO–dipolarophile HOMO, whose importance increases in going from sulfones to sulfoxides. As a consequence, the observed preferences of **1** to give the R_5 isomer can be well rationalized. In fact, in the interaction nitrilimine HOMO–dipolarophile LUMO, the larger coefficients lead in every case to the R_5 isomers, and this tendency increases according to the sequence Me < Ph < PhCO in correspondence of the lowering of the dipolarophile LUMO energy.

The increase of the propensity to give R_5 isomers in going from sulfoxides to sulfones is attributable to the greater polarization of LUMO's that occurs in the latter case. For the reactions involving **2**, the experimental results could be rationalized taking into account the interaction dipole LUMO–dipolarophile HOMO. Unfortunately, the values of the coefficients in the dipolarophile HOMO's are poorly meaningful, since these frontier orbitals are scarcely localized on the vinylic double bond. Thus, it is impossible to determine the consequences of such an interaction. In conclusion, both approaches help to understand the origin of the observed regioselectivity, showing the important role of both polar and frontier charge-transfer interactions.

Experimental Section

All melting points were determined on a Büchi apparatus and are uncorrected. NMR spectra were recorded on Varian A-60 and EM-390 spectrometers with $CDCl_3$ as a solvent and tetramethylsilane as an internal standard; chemical shifts are given in δ units: s = singlet; d = doublet; m = multiplet; dd = double doublet.

Dipolarophiles. Sulfinyl- and sulfonylalkenes were prepared according to standard procedures.[3a,15]

Dipoles. 1-(α-Chlorobenzal)-2-phenylhydrazine (**1**)[6] and 3,5-dichloromesitylnitrile oxide (**2**)[10] were already known and were prepared according to the reported methods.

Reaction of Compound 1 with Compound 3: General Method. Triethylamine (0.04 mol) was added to a solution of (phenylsulfinyl)alkenes (0.01 mol) and α-chlorobenzaldehyde phenylhydrazone (0.01 mol) in benzene (100 mL), and the mixture was refluxed for 20 h (see Table I). The solvent was evaporated off, and the residue was chromatographed on silica gel. Elution with benzene gave the products listed in Table I.

Reaction of Compound 1 with Compound 4: General Method. Triethylamine (0.01 mol) was added to a solution of (phenylsulfonyl)alkenes (0.01 mol) and α-chlorobenzaldehyde phenylhydrazone (0.01 mol) in benzene (50 mL), and the mixture was allowed to stand at room temperature for several hours (see Table I). The benzene solution was washed with water and dried (Na_2SO_4). The solvent was evaporated off, and the residue was chromatographed on silica gel. Elution with toluene gave the products listed in Table I. The reaction of **1** with **4a** gave also as side product 1,2-bis(phenylsulfonyl)ethane.[16]

Reaction of Compound 2 with Compound 3: General Method. 3,5-Dichloromesitylnitrile oxide (0.01 mol) and (phenylsulfinyl)alkenes (0.01 mol) were dissolved in benzene (80 mL) and refluxed, under nitrogen, for variable times (see Table II). After the mixture was cooled, the *N,N'*-bis(3,5-dichloro-2,4,6-trimethylphenyl)urea[13b] was filtered off, the solvent was evaporated, and the residue was chromatographed on silica gel. Elution with benzene gave the product listed in Table II. The reaction of **2** with **3a** gave also as a side product the 1,2-bis(phenylsulfinyl)ethane.

Reaction of Compound 2 with Compound 4: General Method. A solution of **2** (6 mmol) and **4** (6 mmol) in benzene (60 mL) was refluxed for the time indicated in Table II. The solvent was removed under reduced pressure and the residue was worked up as follows. In the case of **4a**, recrystallization of the crude product from benzene–hexane gave **14a** in 60% yield; the residue from the mother liquor was chromatographed on a silica gel column, with diisopropyl ether as eluant, to afford a further amount of **14a** (13%), followed by **13a** (7%). When starting from **4b**, the product mixture was chromatographed on a silica gel column, with 95:5 benzene–ethyl acetate as an eluant, to give some uncharacterized material, followed by **13b** (54%); further elution gave **14b** (6%). In the case of **4c**, fractional recrystallization of the crude product from benzene–hexane afforded pure **13c**; attempted isolation of **14c** by chromatographic methods was unsuccessful. In the case of **4d**, the crude product was recrystallized from diisopropyl ether–pentane to give a 1:1 mixture of **13d** and **14d**. The residue from the mother liquor was submitted to repeated recrystallizations from diisopropyl ether–ethanol to give **13d**; column chromatography on silica gel of the 1:1 mixture of **13d** and **14d** resulted in a 1:1 mixture of **15d** and **16d**.

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Registry No. **1**, 15409-32-2; **2**, 13456-86-5; **3a**, 20451-53-0; **3b**, 67652-99-7; **3c**, 40110-66-5; **3d**, 66287-01-2; **4a**, 5535-48-8; **4b**, 28691-72-7; **4c**, 16212-06-9; **4d**, 960-41-8; **7c**, 86729-03-5; **13a**, 86747-53-7; **13b**, 86729-04-6; **13c**, 86729-05-7; **13d**, 86729-06-8; **14a**, 86729-07-9; **14b**, 86729-08-0; **14c**, 86729-09-1; **14d**, 86729-10-4; **15a**, 86729-11-5; **15b**, 86729-12-6; **15d**, 86729-13-7; **16b**, 86729-14-8; **16c**, 86747-54-8; **16d**, 86729-15-9.

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Allylstannanes. Synthesis, Structure, and Reactions of 2-Methylene-1,3-propanediylbis[trimethylstannane] and -[triphenylstannane]

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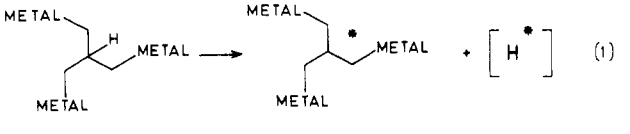
Compounds in which a carbon–hydrogen bond is adjacent to several carbon–metal bonds promise to be good reducing agents, since transfer of hydrogen may produce a carbocation or a radical highly stabilized by hyperconjugation (eq 1).[1,2] This promise is fulfilled by stannane



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