(0.70 mmol) of dibenzothiophene was added. After 48 h at 55 °C the mixture was worked up, first with glacial acetic acid and then with 6 N aqueous HCl. A sample of the biphenyl (95%) was analyzed by MS and IR measurements. The product was a mixture of 14.3% 2,2′-dideuterio- and 25.3% 2-deuteriobiphenyl, together with 60.4% biphenyl.

(e) Workup with *o*-Deuterioacetic Acid. The reaction between $(COD)_2Ni$, 2,2′-bipyridyl, and $LiAlH_4$ in 15 mL of THF was conducted on a 1.5 mM scale as in section d. Workup with CH_3CO_2D gave 94.5% biphenyl and a mixture of 2.3% 2-deuterio- and 3.2% 2,2′-dideuteriobiphenyl.

Hydrodesulfurization of Dibenzothiophene (3) with Nickel Salts and Metal Hydrides. (a) 2,2′-Bipyridyl and $LiAlH_4$. A solution of 200 mg (0.73 mmol) of nickel(II) acetylacetonate and 113 mg (0.73 mmol) of 2,2′-bipyridyl in 15 mL of THF was treated with 26 mg (0.73 mmol) of $LiAlH_4$. After the brown solution was stirred for 30 min at 25 °C, 67 mg (0.36 mmol) of **3** was added. The reaction mixture was heated for 48 h at 55 °C and then given the usual protolytic workup. A GLPC analysis showed a 36% conversion to biphenyl.

A reaction in which 6 molar equiv of $LiAlH_4$ was used with 2 molar equiv each of $Ni(acac)_2$ and 2,2′-bipyridyl to desulfurize 1 molar equiv dibenzothiophene gave 32% biphenyl.

(b) Use of $NaBH_4$. A reaction analogous to that in section a, except that $NaBH_4$ was substituted for $LiAlH_4$, gave a 6% conversion to biphenyl, either in THF (55 °C) or in triglyme (130 °C).

(c) Use of Diisobutylaluminum Hydride. A green solution of 290 mg (1.83 mmol) of $Ni(acac)_2$ and 285 mg (1.83 mmol) of 2,2′-bipyridyl in 15 mL of toluene was stirred while being treated with 260 mg (1.83 mmol) of $(i\text{-}Bu)_2AlH$. Then 160 mg (0.87 mmol) of **3** was added to the brown solution. After 24 h at reflux and the usual protolytic workup, a GLPC analysis showed a 38% conversion to biphenyl.

Hydrodesulfurization of 2,8-Dimethyldibenzothiophene (9). A deep-violet solution of **1**, prepared from 560 mg (2.03 mmol) of $(COD)_2Ni$ and 220 mg (2.03 mmol) of 2,2′-bipyridyl in 15 mL of THF, was treated first with 80 mg (2.03 mmol) of $LiAlH_4$ and after 30 min with 212 mg (1.0 mmol) of **9**. After 48 h at 55 °C hydrolytic workup gave an 82% yield of 3,3′-dimethylbiphenyl.

Hydrodesulfurization of 3,7-Dimethyldibenzothiophene (10). A reaction mixture of 560 mg (2.03 mmol) of $(COD)_2Ni$ and 220 mg (2.03 mmol) of 2,2′-bipyridyl in 15 mL of THF was treated first with 80 mg (2.03 mmol) of $LiAlH_4$ and then with 212 mg (1.07 mmol) of **10**. After 48 h at 55 °C and the usual workup the GLPC analysis showed a 68% conversion to 4,4′-dimethylbiphenyl but none of the 3,3′ isomer.

Ring Contraction of Sulfur Heterocycles with (2,2′-Bipyridyl)(1,5-cyclooctadiene)nickel (1). (a) Phenoxathiin (11). A violet solution of an equimolar mixture of $(COD)_2Ni$ and 2,2′-bipyridyl in THF (10 mL/1.5 mmol of **1**) was treated with phenoxathiin and the resulting mixture heated at 55 °C for 48 h. The cooled reaction mixture was treated with glacial acetic acid, and the organic products were isolated in the usual way. For four reactions having the following ratios of **11**:**1**, namely, 1:1, 1:2, 1:3, and 1:4, the corresponding conversions to dibenzofuran, as determined by GLPC analysis, were 15%, 79%, 81%, and 78%. Thus, a 1:2 ratio of **11**:**1** was most satisfactory. Also, the side production of diphenyl ether increased as the ratio of **11**:**1** changed: 1:1, 1%; 1:2, 3%; and 1:3, 11%.

(b) Phenothiazine (12). Similar to the procedure in section a, the interaction of 3.15 mmol of **1** in 20 mL of THF with 1.5 mmol of **12** yielded a 75% conversion to carbazole and a 5% conversion to diphenylamine.

(c) Thianthrene (13). Similar to the procedure in section a, the reaction between 3.2 mmol of **1** and 1.3 mmol of **13** gave 55% dibenzothiophene, 15% biphenyl, and 30% **13**.

Hydrodesulfurization of Sulfur Heterocycles (Table III). (a) Phenoxathiin (11). To a violet solution of 2.2 mmol each of $(COD)_2Ni$ and 2,2′-bipyridyl in 20 mL of THF was added 2.2 mmol of $LiAlH_4$. After 60 min at 25 °C 1.0 mmol of **11** was added. The reaction was allowed to proceed for 24 h at 25–30 °C. The usual workup and GLPC analysis showed a mixture of 92% diphenyl ether, 3% dibenzofuran, and 5% **11**.

(b) Phenothiazine (12). A violet solution of 3.9 mmol of **1** in 20 mL of THF was treated with 6.0 mmol of $LiAlH_4$. After 60 min of stirring, 1.8 mmol of **12** was added and the mixture heated for 48 h at 55 °C. The usual workup gave 65% diphenylamine, 5% carbazole, and 30% **12**.

(c) Thianthrene (13). A violet solution of 3.0 mmol of **1** in 20 mL of THF was treated with 3.0 mmol of $LiAlH_4$, and then 1.4 mmol of **13** was added. After 48 h at 55 °C and the usual workup, the following products were found: 15% biphenyl, 5% dibenzothiophene, benzene, and **13**.

Acknowledgment. We owe the opportunity to conduct this investigation to the support provided by Grants DE-FG22-81PC40782 and 84PC70786 from the U.S. Department of Energy. We are appreciative of pertinent experimental data provided by the work of Dr. Andrzej M. Piotrowski and Stephen R. Sexsmith.

Registry No. 1, 55425-72-4; **3**, 132-65-0; **3a**, 92-52-4; **9**, 1207-15-4; **9a**, 612-75-9; **10**, 1136-85-2; **10a**, 613-33-2; **11**, 262-20-4; **11a**, 132-64-9; **11b**, 101-84-8; **12**, 92-84-2; **12a**, 86-74-8; **12b**, 122-39-4; **13**, 92-85-3; benzene, 71-43-2; ethylenediamine, 107-15-3; 2,2′-bipyridyl, 366-18-7; hexamethylphosphorus triamide, 680-31-9; *N,N,N,N′*-tetramethylethylenediamine, 110-18-9; pyridine, 110-86-1; *N,N′*-dimethylpiperazine, 106-58-1; 1,8-bis(dimethylamino)naphthalene, 20734-58-1; 1,10-phenanthroline, 66-71-7; 4-(dimethylamino)pyridine, 1122-58-3.

Do Carbenium Ion Additions toward Alkenes Proceed via π Complexes? A Stereochemical Investigation

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Abstract: Lewis-acid-catalyzed addition reactions of diarylmethyl chlorides with (*E*)- and (*Z*)-2-butene yield the addition products **3a** (>84% anti selectivity) and the products **5–7**, which are formed via 1,2-H and 1,2-CH_3 shifts. The Markovnikov addition products **3b** are generated exclusively from the corresponding reactions with the *E,Z*-isomeric β-methylstyrenes **2b**. While the *E* isomer **t-2b** gives the anti adducts **t-3b** predominantly, (*Z*)-β-methylstyrene reacts with low stereoselectivity. In all cases, the yield of anti adducts increases with increasing stability of the attacking diarylcarbenium ion and decreasing solvent polarity. These observations are interpreted in terms of partially bridged intermediates which are attacked by nucleophiles from the backside.

1. Introduction

Electrophilic additions to carbon–carbon double bonds have been studied in great detail.[1] A wide variety of mechanisms has been detected, and the stereochemical course ranges from high anti[2a–c] or syn[2d] stereoselectivity to a complete loss of stereochemical information[2e] (Scheme I). Concerted and stepwise mechanisms have been reported,[1,2] and the latter processes might

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(2) (a) Schmid, G. H.; Csizmadia, V. M.; Nowlan, V. J.; Garratt, D. G. *Can. J. Chem.* **1972**, *50*, 2457. (b) Schmid, G. H.; Nowlan, V. J. *Can. J. Chem.* **1976**, *54*, 695. (c) Rolston, J. H.; Yates, K. *J. Am. Chem. Soc.* **1969**, *91*, 1469. (d) Dewar, M. J. S.; Fahey, R. C. *J. Am. Chem. Soc.* **1963**, *85*, 3645. (e) Rolston, J. H.; Yates, K. *J. Am. Chem. Soc.* **1969**, *91*, 1477.

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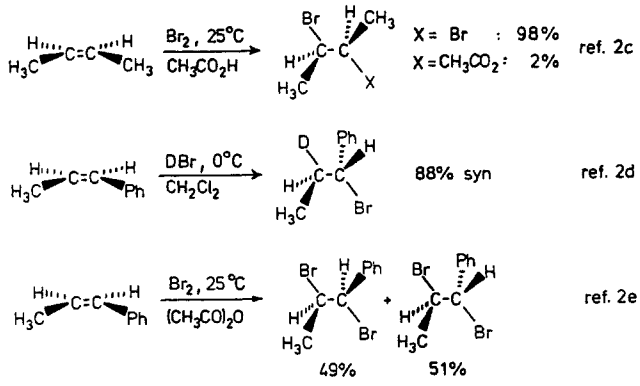
Scheme I



Scheme II

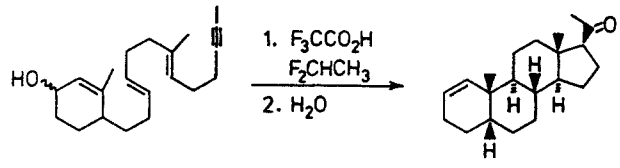


Table I. Relative Alkene/Alkyne Reactivities toward Electrophiles[3]

electrophile	conditions	k(styrene)/ k(phenylacetylene)	k(1-hexene)/ k(1-hexyne)
H^+	48% H_2SO_4, 25 °C	0.65	3.6
Ph_2CH^+	$Ph_2CHCl/ZnCl_2$, CH_2Cl_2, 40 °C	3.8	
Br_2	CH_3CO_2H, 25 °C	2600	65 000
Cl_2	CH_3CO_2H, 25 °C	720	530 000
p-ClC_6H_4SCl	$Cl_2CHCHCl_2$, 25 °C	186	84

proceed via bridged or nonbridged transition states. Modena et al. suggested that electrophiles which react via bridged intermediates may be recognized by high alkene/alkyne reactivity ratios (halogens and sufenyl halides).[3] On the other hand, a low alkene/alkyne reactivity ratio was considered to indicate that bridging is energetically unimportant. Since carbenium ions, like protons, show similar reactivities toward alkenes and alkynes (Table I), these electrophiles were suggested to react via nonbridged intermediates.[3]

This conclusion is in contrast to Dewar's perception of π complexes as intermediates in carbenium ion additions to CC double bonds.[4] Dewar and Reynolds rationalized the high anti stereoselectivity of biomimetic polyene cyclizations[5] by the intermediacy of olefin–carbenium ion π complexes (Scheme II).[4] The stepwise mechanism associated with this proposition is in accord with other recent mechanistic studies.[6]

In spite of the great interest in the mechanism of these intramolecular carbenium ion additions, stereochemical studies of intermolecular carbenium ion additions have not yet been carried out. This situation is surprising since more than 20 years ago Dewar claimed that "there is dire need for data concerning the stereochemistry of additions to olefins where the primary reagent is a carbonium ion."[7]

(3) Melloni, G.; Modena, G.; Tonellato, U. *Acc. Chem. Res.* **1981**, *14*, 227.
(4) Dewar, M. J. S.; Reynolds, C. H. *J. Am. Chem. Soc.* **1984**, *106*, 1744 and references cited therein.
(5) (a) Johnson, W. S. *Angew. Chem.* **1976**, *88*, 33; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 9. (b) Johnson, W. S. *Bioorg. Chem.* **1976**, *5*, 51.
(6) (a) Nishizawa, M.; Takenaka, H.; Hayoshi, Y. *J. Am. Chem. Soc.* **1985**, *107*, 522. (b) Nishizawa, M.; Takenaka, H.; Hayoshi, Y. *J. Org. Chem.* **1986**, *51*, 806. See however: Bartlett, P. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: Orlando, 1984; Vol. III, Chapter 5.
(7) Dewar, M. J. S.; Fahey, R. C. *Angew. Chem.* **1964**, *76*, 320; *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 245.

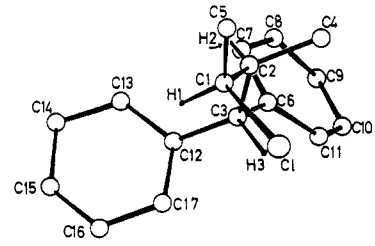
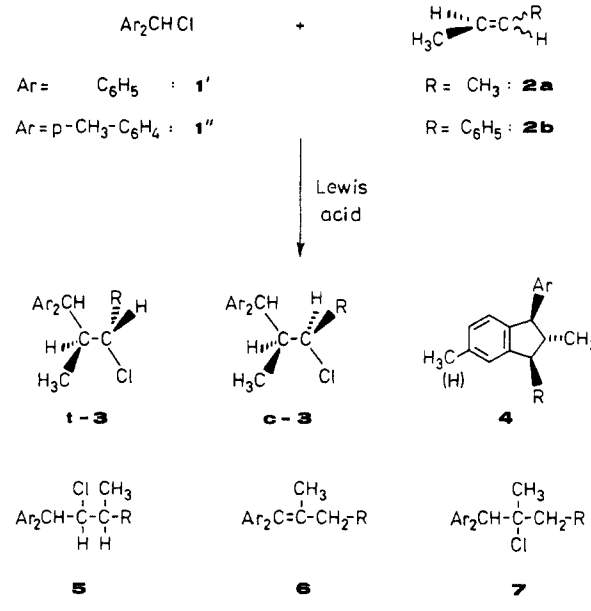


Figure 1. X-ray structure of (*S*,*S*)-3-chloro-2-methyl-1,1-diphenylbutane (**t-3a'**).

Scheme III



Ar \ R	CH_3	C_6H_5
C_6H_5	**3a'-7a'**	**3b'-7b'**
p-CH_3-C_6H_4	**3a''-7a''**	**3b''-7b''**

We have recently developed methods to selectively generate 1:1 addition products via Lewis-acid-catalyzed reactions of alkyl halides with alkenes[8] and report now on the stereochemistry of these reactions.

2. Reaction Products and Structure Determination

The diarylmethyl chlorides **1'** and **1''** react with the *E*,*Z*-isomeric 2-butenes (**2a**) and 1-phenylpropenes (**2b**) in the presence of various Lewis acids to give [1:1] products in high yield (Scheme III).

Table II shows that both isomeric 1-phenylpropenes (**c,t-2b**) react with **1'** and **1''** to give exclusively the regular Markovnikov adducts **c,t-3b** when $ZnCl_2/Et_2O$ is used as the catalyst. When the reactions of **1'** with **c,t-2b** are catalyzed by BCl_3 or $SnCl_4$, the addition products **3b'** are accompanied by approximately 20% of the indane **4b'**. This compound is the sole product of the $TiCl_4$-catalyzed reaction and of the $ZnCl_2$-catalyzed reaction at 40 °C.[9]

The stereoselectivities of these reactions differ considerably. While *trans*-β-methylstyrene (**t-2b**) yields the anti adducts **t-3b**

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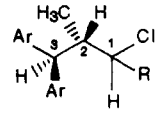
(9) (a) Marcuzzi, F.; Melloni, G.; Modena, G. *J. Org. Chem.* **1979**, *44*, 3022. (b) Marcuzzi, F.; Melloni, G. *J. Chem. Res. Synop.* **1979**, 184; *J. Chem. Res. Miniprint* **1979**, 2287.
(10) Mayr, H.; Striepe, W. *J. Org. Chem.* **1985**, *50*, 2995.

Table II. Products from Lewis-Acid-Catalyzed Reactions of the Diarylmethyl Chlorides **1′** and **1″** with Cis/Trans Isomeric Alkenes in CH_2Cl_2 at −78 °C

Ar	Ar_2CHCl	alkene		Lewis acid	products, %[a] t-3	c-3	4	5	6	7	anti/syn
Ph	**1′**		**t-2a**	$ZnCl_2$[b]	72.6	3.3	–	2.8	6.7	14.6	22
				BCl_3	64.1	9.0	–	5.6	–	21.3	7.1
				$SnCl_4$	69.4	6.4	–	3.2	–	21.0	11
				$TiCl_4$	96.1	–	–	–	–	3.9	>300
			c-2a	$ZnCl_2$[b]	6.8	42.6	–	3.4	4.5	42.3	6.3
				BCl_3	5.9	29.9	–	3.0	–	61.2	5.1
				$SnCl_4$	2.9	30.8	–	0.84	0.45	65.0	11
				$TiCl_4$	2.9	75.6	–	–	1.1	20.4	26
		Ph	**t-2b**	$ZnCl_2$[b]	98.4	1.60	–	–	–	–	62
				BCl_3	69.7	10.3	20	–	–	–	6.8
				$SnCl_4$	75.2	4.8	20	–	–	–	16
				$TiCl_4$	–	–	100	–	–	–	–
		Ph	**c-2b**	$ZnCl_2$[b]	80.5	19.5	–	–	–	–	0.24
				BCl_3	56–62[c]	27–21[c]	17	–	–	–	0.33–0.47
				$SnCl_4$	70.2	12.8	17	–	–	–	0.18
				$TiCl_4$	–	–	100	–	–	–	–
CH_3	**1″**		**t-2a**	$ZnCl_2$[b]	86[d]	–[d]	–[d]	–[d]	4.5[d]	–[d]	>20
			c-2a	$ZnCl_2$[b]	7.6[d]	63[d]	–[d]	–[d]	6.9[d]	10.4[d]	8
		Ph	**t-2b**	$ZnCl_2$[b]	100	–	–	–	–	–	>300
		Ph	**c-2b**	$ZnCl_2$[b]	68.4	31.6	–	–	–	–	0.46

[a] The product distributions described in this table have been determined by HPLC (exception: **1″ + c,t-2a**). A dash indicates ≤0.3% and ≤3% for the reactions monitored by ^1H NMR. [b] $ZnCl_2$ was used as diethyl ether complex;[10] $ZnCl_2$:Et_2O = 0.636. [c] Isomerization **c-2b** → **t-2b** detectable. [d] Determined by ^1H NMR.

Table III. ^1H NMR Spectroscopic Data of the Diasteromeric Addition Products **c,t-3a,b**



	solvent	1-H	2-H	3-H	R	2-CH_3	$J_{1,2}$	$J_{2,3}$
t-3a′	$CDCl_3$	4.00	2.51	3.88	1.47	0.92	1.7	11.4
c-3a′	CCl_4	4.08	2.88	3.62	1.30	0.93	3.4	11.2
t-3a″	$CDCl_3$	4.10	2.45	3.80	1.47	0.91	1.7	11.4
c-3a″	CCl_4	4.07	2.80	3.50	1.27	0.90	3.2	11.1
t-3b′	$CDCl_3$	4.97	2.79	4.02		0.83	2.1	11.2
c-3b′	$CDCl_3$	5.02	3.16	3.65		0.86	4.9	10.0
t-3b″	CCl_4	4.92	2.62	3.92		0.82	2.0	10.7
c-3b″	CCl_4	4.98	3.07	3.58		0.80	4.5	9.5

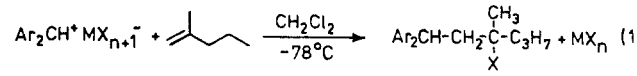
predominantly or exclusively, the reactions of **c-2b** proceed with low stereoselectivity. The major product (**t-3b**) is identical with that obtained in the *trans*-phenylpropene additions. It was demonstrated that the product ratios were identical at low and high degree of conversion and did not alter when the mixture was allowed to stand with the Lewis acids after completion of the reaction.

The corresponding reactions with the 2-butenes **c,t-2a** yield the 1,2-H and 1,2-CH_3 shifted products **5–7** in addition to the regular adducts **c,t-3a**. In contrast to the behavior of the β-methylstyrenes, *both* 2-butene isomers react with high anti stereoselectivity (anti/syn ≥ 84:16).

The stereochemical assignment of the diastereomeric adducts **3a** and **3b** is based on the X-ray analysis of **t-3a′**, the major product obtained from the reaction of diphenylmethyl chloride **1′** with *trans*-butene **t-2a** (Figure 1). The dihedral angles H_1–C_1–C_2–H_2 ≈ 60° and H_2–C_2–C_3–H_3 ≈ 180° derived from Figure 1 are in accord with the corresponding HH coupling constants of 1.7 and 11.4 Hz. The configurational assignments of the analogous products **3a″**, **3b′**, and **3b″** are based on the analogy of their ^1H NMR spectra (Table III). Whereas $J_{2,3}$ is of similar magnitude in all compounds, $J_{1,2}$ is approximately twice as large in the **c** than in the **t** isomers. While 2-H is more shielded in the **t** isomers, 3-H absorbs at higher field in the **c** isomers.

3. Mechanistic Study and Discussion

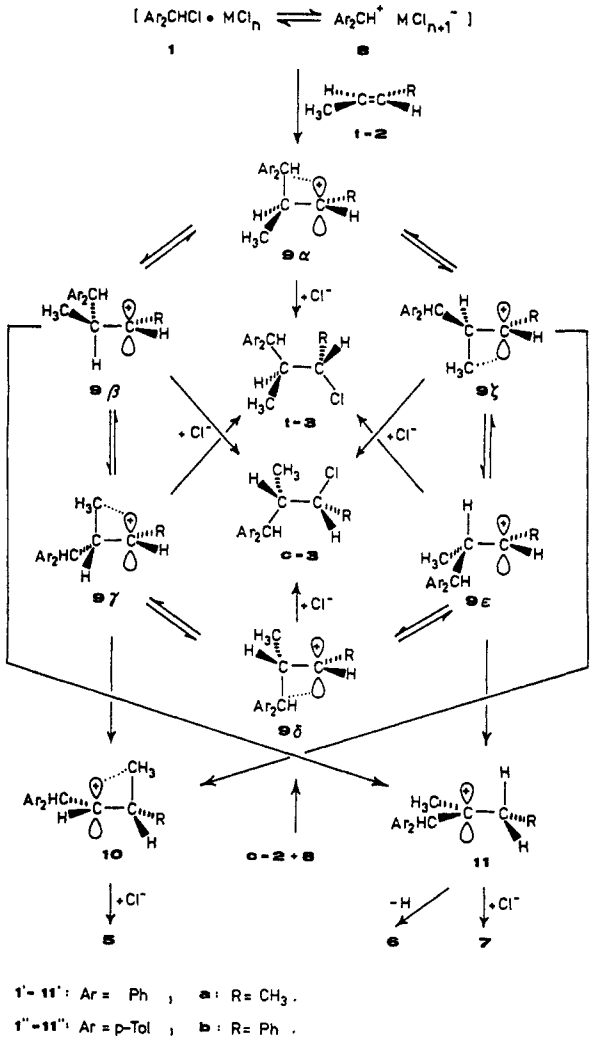
In accord with previous studies,[3,8] it is assumed that the diarylmethyl chlorides **1** ionize to give the diarylcarbenium ions **8**, which attack the alkenes **2** with formation of the cations **9** (Scheme IV). Since different product mixtures are obtained from stereoisomeric alkenes, one must exclude the intermediacy of long-lived freely rotating cations **9**. Ion-pair effects cannot account for the observed stereoselectivities, as their operation would require syn selectivity.[1,7] The observation that the addition rates of diarylcarbenium ions to alkenes (eq 1) are independent of the nature and the concentration of the counterions[11] excludes the operation of an Ad-E3-type mechanism.



To account for the stereoselectivity, we assume that **9** is at least partially bridged, as indicated by the dotted lines in **9α–9ζ** and that the nucleophiles attack **9** from the open side. Conformer **9α**, which is initially formed from **8′** and *trans*-butene (**t-2a**), is trapped faster by Cl^- to give **t-3a′** than it can undergo a 60° rotation to

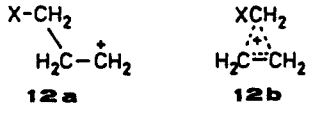
(11) Schneider, R.; Grabis, U.; Mayr, H. *Angew. Chem.* **1986**, *98*, 94; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 89.

Scheme IV



give **9β** or **9ζ**. These conformers may be attacked by Cl^- (→**c-3a′**) or undergo 1,2-H or 1,2-CH_3 shifts to form **11** and **10**, the precursors of **6**, **7**, and **5**. We assume that the low yield of **5** compared with **6** and **7** rather reflects the higher rearrangement tendency of **9β** (→tertiary carbenium ion) compared with **9ζ** (→secondary carbenium ion) than the preferred mode of rotation of **9α**. Cation **9δ** is conformationally more strained than **9α** and is therefore expected to rotate faster. As a consequence, the reaction of **8′** with **c-2a** yields less of the anti adduct (**c-3a′**) and a higher percentage of H-shifted products (Table II).

Comparison of the $ZnCl_2$-catalyzed reactions of **1′** and **1″** with the isomeric 2-butenes shows that the better stabilized ditolylcarbenium ion yields higher amounts of anti adducts and reduced percentages of rearranged products. These data indicate the higher bridging ability of Tol_2CH compared with Ph_2CH. While this interpretation is in accordance with the qualitative VB interpretation of hyperconjugation, it contradicts the conclusion obtained from quantitative MO calculations. Computations with the STO-3G minimal basis set indicated that the energy difference between bridged and nonbridged species **12a** and **12b** is not significantly affected by the nature of X.[12] The cations **9**, which



12a **12b**

are obtained from the addition of **8** to the phenylpropenes **c,t-2b**, are stabilized by benzylic resonance and therefore do not undergo 1,2-shifts to give rearranged products. The bridging tendency of the π delocalized cations **9** (R = Ph) will be lower, and the rotations should be faster. In spite of that, the anti/syn product ratio obtained from the reactions of **1′** and **1″** with *trans*-phenylpropene is rather high, probably because of the low conformational strain in **9α**. On the other hand, the reactions with *cis*-phenylpropene **c-2b** yield only small amounts of anti adducts, because the unfavorable conformers **9δ** rotate faster than they are trapped by the nucleophiles. Both phenylpropene isomers give more anti product with **1″** than with **1′**, analogous to the observations with 2-butenes (see above).

Analysis of the unreacted phenylpropenes during the course of the reaction showed that the high amount of syn adducts obtained from **c-2b** cannot be due to cis–trans isomerization of the alkenes prior to addition. Only in the case of the BCl_3-catalyzed reaction was a certain degree of stereomutation (≈20%; **c-2b** → **t-2b**) detectable. The formation of the indanes **4** has been discussed previously.[9]

If the anti/syn ratio or the anti/rearrangement ratio reflects the relative rates of nucleophilic back-side attack and rotation of **9**, this ratio should increase if the lifetime of the cations **9** is reduced by lowering the solvent polarity. Table IV demonstrates that the anti/syn ratio in the reaction of **1′** with **t-2b** increases from 15.7 to 27.6 when the solvent CH_2Cl_2 is replaced by a 1:1 CH_2Cl_2/petroleum ether mixture. The effect is more pronounced in the reaction with the corresponding cis isomer. Whereas only 15% of the anti adduct is formed in dichloromethane, 58% of anti product is obtained in a 1:1 mixture of petroleum ether and dichloromethane. A further lowering of solvent polarity was not possible because the mixtures became inhomogeneous. Solubility problems also prevented the preparation of solutions containing high concentrations of MX_n^- ions. Table V shows, however, that the presence of benzyltriethylammonium pentachlorostannate increased the yield of anti adduct in the reaction of **1′** with **c-2b**.

The effect of the nature of the Lewis acid on the product composition cannot easily be explained, because very little data on the kinetic stability of complex anions are available. Heublein et al. reported that $TiCl_5^-$ transfers Cl^- to trityl cations faster than $SnCl_5^-$.[13] The higher anti/syn ratio in the $TiCl_4$-catalyzed reactions with the 2-butenes could thus be explained. It is not

Table IV. Influence of the Solvent on the Stereochemistry of Benzhydryl Chloride **1′** Additions to *cis*- and *trans*-Phenylpropene at −78 °C

alkene	Lewis acid	CH_2Cl_2: petroleum ether (v:v)	products, %[a]		
			t-3b′	**c-3b′**	anti/syn
t-2b	$SnCl_4$	∞	94.0	6.0	15.7
		4	95.5	4.5	21.2
		1	96.5	3.5	27.6
c-2b	$SnCl_4$	∞	84.6	15.4	0.182
		4	65.0	35.0	0.538
		1	41.8	58.2	1.39
c-2b	$ZnCl_2$·Et_2O	∞	80.5	19.5	0.242
		4	69.6	30.4	0.437
		1	64.2	35.8	0.558

[a] The $SnCl_4$-catalyzed reactions gave indane **4b′** as side product. The amount of **4b′** decreases with decreasing solvent polarity: ≈20% in CH_2Cl_2, ≈10% in CH_2Cl_2/petroleum ether (4:1, v:v), ≈5% in CH_2Cl_2/petroleum ether (1:1, v:v).

Table V. Influence of Benzyltriethylammonium Chloride (BTEA) on the Stereochemistry of the Benzhydryl Chloride **1′** Addition to *cis*-Phenylpropene **c-2b**

c-2b, mmol/L	68.2	68.6
1′, mmol/L	48.8	48.2
$SnCl_4$, mmol/L	8.6	8.6
BTEA, mmol/L	0.0	3.4
c-3b′/**t-3b′**	0.210	0.327

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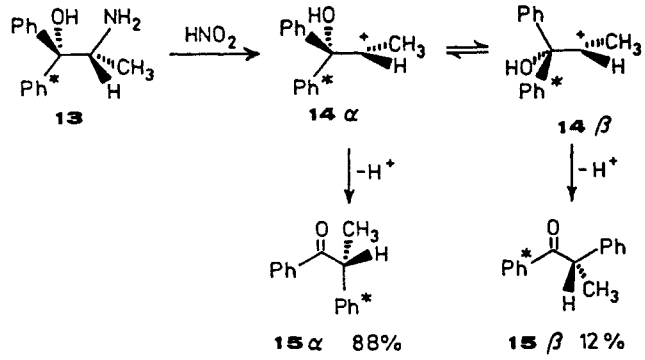
Scheme V



Scheme VI

$k_{rel}(Ph_2CH^+)$[17]	1.0	34	5800
$k_{rel}(Br_2)$[18]	1.0	32	93

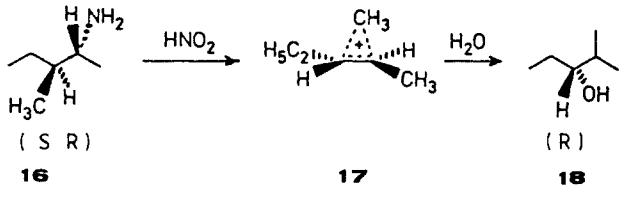
understood, however, why this Lewis acid gives rise to exclusive formation of the indanes **4** in the phenylpropene reactions.

The rationalization of our experimental data by relative rates of rotation and 1,2-migration or nucleophilic back-side attack (conformational control) is precedented in nitrous acid deaminations of acyclic amines.[14]

Collins treated the optically active amine **13** with nitrous acid and isolated the inverted ketone **15α**, in which the labeled phenyl group migrated, and the ketone **15β** with retained configuration, in which the unlabeled phenyl was shifted.[15a] The product ratio indicated that phenyl migration is more rapid than the 60° rotation **14α** ⇌ **14β**, while a 120° rotation was not detectable, (Scheme V).

In a similar experiment, Collins showed that the rates of phenyl migration and 180° rotation are of comparable magnitude, when the carbenium center is stabilized by a phenyl group.[15c]

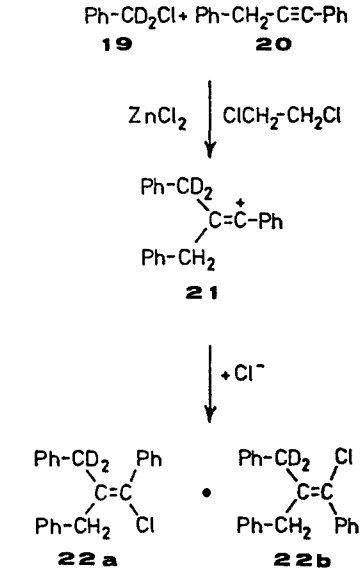
The nucleophilic back-side attack at methyl-bridged carbocations has convincingly been demonstrated by Kirmse and coworkers.[14,15d,e] When **16** was treated with nitrous acid, the tertiary alcohol **18**, which was formed in 15% yield, showed 98.5% inversion at the migration origin.[16] Lewis-acid-catalyzed alkyl halide additions toward alkenes are thus controlled by the same principles as deamination reactions.



4. Conclusions

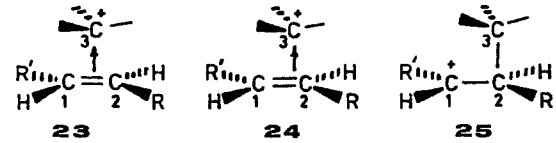
The stereochemical results reported in this work exclude freely rotating classical carbenium ions as intermediates of the electrophilic alkyl halide additions to alkenes. If strongly bridged intermediates were involved, methyl groups at both olefinic termini should increase the reactivity of the alkenes to a similar degree, as reported for brominations[18] (Scheme VI). In previous work we have shown, however, that diarylcarbenium ion additions to alkenes are accelerated by a factor of 6–50 by methyl groups at the attacked vinylic position and of approximately 10^4 at the new carbenium center.[17] These data are best explained by weakly bridged intermediates, the geometry of which is strongly dependent on the nature of the alkene substituents.

The previous suggestion of open transition states in carbenium ion additions has been based on the similarity of reaction rates of comparably substituted alkenes and alkynes.[3] The alkene/alkyne analogy, however, does not hold for the stereochemistry of these additions. In contrast to the behavior of alkenes, reported in this paper, alkyne **20** reacts with labeled benzyl chloride **19** to give the stereoisomeric vinyl chlorides **22a** and **22b** in a 1:1 ratio,[19] in accordance with the intermediacy of the nonbridged



cation **21**. If the bridged cations formed via addition of carbenium ions to alkenes are assumed to be of comparable stability as the corresponding nonbridged species, the comparison of alkene and alkyne reaction rates toward carbenium ions does not allow us to differentiate the alternative intermediates.

Do the bridged intermediates, which are required by the stereochemical studies, correspond to Dewar's π complexes? No, if these π complexes were defined as intermediates separated from the isomeric classical carbenium ions by high barriers,[4] because this assumption would not account for the observation of rearranged products in the 2-butene additions. Yes, if π complexes are considered species on a flat hypersurface which can rapidly interconvert into their slightly less stable nonbridged counterparts. Depending on the substitution pattern, the intermediates will be more or less symmetrical as shown in **23** and **24**, respectively.



Whether a intermediate cationic species with a reduced C_1–C_2–C_3 angle is best described as the unsymmetrical π complex **24** or the classical carbenium ion **25**, which is distorted by nonvertical hyperconjugative stabilization,[20] is a matter of personal taste.

5. Experimental Section

General. NMR spectra were obtained on JEOL JNM-PS-100 and Varian XL-200 spectrometers. Chemical shifts are recorded relative to $(CH_3)_4Si$ as an internal standard. Mass spectra were obtained with CH

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4 B MAT and 311 A MAT instruments (Varian). Preparative MPLC was carried out on a 30 × 2 cm glass column with LiChroprep Si60,15–25 μm as the stationary phase and petroleum ether (bp 40–60 °C) as the eluent. Product analysis by HPLC was carried out with a LDC/Milton Roy HPLC system using 250 × 4.5 mm steel columns. A LDC/Milton Roy spectromonitor D was used for the detection at 254 nm. The Seebach-Prelog *u,l* nomenclature[21] was used to assign the relative stereochemistry of asymmetric centers.

I. Synthesis of 3–7. 1. Diphenylmethyl Chloride (1′) and 2-Butenes c,t-2a. A solution of BCl_3 (6.46 mmol) in 3.8 mL of CH_2Cl_2 was added to a precooled (−78 °C) solution of **1′** (3.05 g, 15.1 mmol) and **t-2a** (8.00 g, 143 mmol) in 50 mL of CH_2Cl_2. After 24 h of standing at −78 °C, the mixture was washed with aqueous ammonia and water and dried over $CaCl_2$. The solvent was evaporated, and the residue was separated by MPLC to give a trace of 1,2-dimethyl-3-phenylindane (≈25 mg, 12.9 min), **5a′** (145 mg, 3.7%, 16.8 min), **7a′** (430 mg, 11%, 17.8 min), and a mixture of t- and **c-3a′** (2540 mg, 65%, 18.6 min).

2-Chloro-3-methyl-1,1-diphenylbutane (**5a′**): mp 87–88 °C (petroleum ether); ^1H NMR ($CDCl_3$) δ 0.73 (d, J = 6.7 Hz, 3 H), 0.95 (d, J = 6.8 Hz, 3 H), 2.00 (m, 1 H), 2.93 (t, $J \approx 7.5$ Hz, 1 H), 5.38 (d, J = 7.8 Hz, 1 H), 7.08–7.30 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 18.65 (q), 21.67 (q), 29.61 (d), 60.52 (d), 65.39 (d), 126.71 (d), 127.44 (d), 127.53 (d), 127.93 (d), 128.22 (d), 129.90 (d), 138.20 (s), 140.77 (s); mass spectrum (70 eV), m/z (relative intensity) 260, 258 (2, 6, M^+), 91 (100).

2-Chloro-2-methyl-1,1-diphenylbutane (**7a′**): mp 39 °C (petroleum ether); ^1H NMR (CCl_4) δ 0.95 (t, $J \approx 7$ Hz, 3 H), 1.47 (s, 3 H), 1.82 (m, 2 H), 3.97 (s, 1 H), 6.97–7.53 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 9.20 (q), 28.62 (q), 36.75 (t), 62.92 (d), 76.59 (s), 126.74 (d), 128.03 (d), 128.06 (d), 130.06 (d), 130.19 (d), 130.22 (d), 140.77 (s), 140.87 (s).

l-3-Chloro-2-methyl-1,1-diphenylbutane (**t-3a**): mp 83–84 °C (pentane); ^1H NMR, see Table III; ^{13}C NMR δ 11.28 (q), 23.69 (q), 43.35 (d), 56.51 (d), 60.97 (d), 126.13 (d), 126.32 (d), 127.89 (d), 128.04 (d), 128.47 (d), 128.59 (d), 143.18 (s), 143.43 (s); mass spectrum (96 eV), m/z (relative intensity) 260, 258 (11, 37, M^+), 168 (44), 167 (100). Anal. Calcd for $C_{17}H_{19}Cl$: C, 78.90; H, 7.40. Found: C, 78.87; H, 7.30.

Crystal and Data Collection Parameters for **t-3a′**: space group, $P2_1/c$; a = 899.6 (4) pm, b = 1470.1 (4) pm, c = 1150.7 (4) pm, β = 108.3°, V = 1444.9 × 10^{-24} cm^3, Z = 4, d_r = 1.19 g/cm^3. A total of 2766 reflections (2384 independent reflections) was measured on a Philips PW 1100 diffractometer using AgKα radiation (range 0° < θ ≤ 19°). The structure was solved and refined with the program system Crystan 22 (R = 0.120; R_w = 0.044).

A solution of $ZnCl_2$ (2.59 g) in diethyl ether (3.1 mL) and CH_2Cl_2 (6.2 mL) was added to a solution of **c-2a** (3.90 g, 69.5 mmol) in 50 mL of CH_2Cl_2 at −78 °C. Compound **1′** (5.00 g, 24.7 mmol) dissolved in 20 mL of CH_2Cl_2 was added and allowed to react for 8 h at −78 °C. Workup as described above yielded a mixture (5.40 g) of **c-** and **t-3a′**, **6a′**, and **7a′** (1:0.6:0.2 by ^1H NMR) which was crystallized from ethanol to give **c-3a′** (2.40 g, 38%) as fine needles.

u-3-Chloro-2-methyl-1,1-diphenylbutane (**c-3a′**): mp 79–81 °C; ^1H NMR see Table III; ^{13}C NMR ($CDCl_3$) δ 12.13 (q), 17.81 (q), 43.71 (d), 56.45 (d), 59.85 (d), 126.32 (d), 126.47 (d), 127.47 (d), 127.77 (d), 128.53 (d), 128.80 (d), 142.70 (s), 143.30 (s); mass spectrum (70 eV), m/z (relative intensity) 260, 258 (1.1, 3.8, M^+), 222 (16), 168 (34), 167 (100). Anal. Calcd for $C_{17}H_{19}Cl$: C, 78.90; H, 7.40. Found: C, 78.90; H, 7.40.

1,1-Diphenyl-2-methyl-1-butene (**6a′**), a component of this reaction mixture, was independently synthesized by treating **t-3a′** (708 mg, 2.74 mmol) with $ZnCl_2$ (2.8 g) and diethyl ether (3.3 mL) in CH_2Cl_2 (6.7 mL) for 4 days at 20 °C. The catalyst was washed out with aqueous ammonia, and the organic layer was dried and distilled to give **6a′** (489 mg, 80%) as a colorless liquid: bp 65–73 °C (bath)/1.3 × 10^{-3} mbar; ^1H NMR (CCl_4) δ 1.03 (t, J = 7.5 Hz, 3 H), 1.77 (s, 3 H), 2.15 (q, J = 7.5 Hz, 2 H), 7.15 (s, 10 H). Anal. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.49; H, 8.07.

2. Diphenylmethyl Chloride (1′) and 1-Phenylpropenes c,t-2b. Compound **t-2b** (0.80 g, 6.8 mmol), $ZnCl_2$ (0.26 g) in 0.3 mL of diethyl ether, and **1′** (1.30 g, 6.41 mmol) were combined in 50 mL of CH_2Cl_2 at −78 °C. After 13.5 h the mixture was worked up as described above to give *u*-1-chloro-2-methyl-1,3,3-triphenylpropane (**t-3b′**) (1.23 g, 60%) as long needles: mp 90–91 °C; ^1H NMR, see Table III; ^{13}C NMR ($CDCl_3$) δ 11.19 (q), 45.38 (d), 56.51 (d), 66.40 (d), 126.23 (d), 126.56 (d), 126.92 (d), 127.32 (d), 127.86 (d), 127.98 (d), 128.47 (d), 128.83 (d), 140.82 (s), 143.03 (s), 143.21 (s); mass spectrum (70 eV), m/z (relative intensity) 322, 320 (6, 18, M^+), 167 (100). Anal. Calcd for $C_{22}H_{21}Cl$: C, 82.35; H, 6.60. Found: C, 82.47; H, 6.64.

The analogous reaction of **1′** with **c-2b** gave a 1:3 mixture of **c-** and **t-3b′** which was fractionally crystallized with ethanol to isolate the minor isomer. *l*-1-Chloro-2-methyl-1,3,3-triphenylpropane (**c-3b′**): mp 117–118 °C; ^1H NMR see Table III; ^{13}C NMR ($CDCl_3$) δ 13.14 (q), 44.53 (d), 54.97 (d), 65.16 (d), 126.35 (d), 127.98 (d), 128.38 (d), 128.86 (d), 137.93 (s), 142.70 (s), 142.91 (s).

Treatment of either **c-** or **t-3b′** with 0.5 equiv of $TiCl_4$ in CH_2Cl_2 at −78 °C (45 min) gave *t*-2-methyl-*r*-1,*c*-3-diphenylindane (**4b′**) in quantitative yield: mp 92–93 °C [lit.[9b] mp 91–92 °C]; ^{13}C NMR ($CDCl_3$) δ 15.41 (q), 56.67 (d), 58.39 (d, double int.), 124.34 (d), 126.53 (d), 126.71 (d), 128.35 (d), 128.71 (d), 143.06 (s), 146.67 (s).

3. Bis(4-methylphenyl)methyl Chloride (1″) and 2-Butenes c,t-2a. A solution of $ZnCl_2$ (834 mg) in 1.0 mL of diethyl ether and 2.0 mL of CH_2Cl_2 was added to a precooled (−78 °C) solution of **1″** (3.40 g, 14.7 mmol) and **t-2a** (2.30 g, 41.0 mmol) in 70 mL of CH_2Cl_2. The reaction mixture was poured onto aqueous ammonia after 22 h and worked up as described above. The crude product (oil) contained **t-3a″** and **6a″** in a 20:1 ratio (^1H NMR). Crystallization from petroleum ether yielded *l*-3-chloro-2-methyl-1,1-bis(4-methylphenyl)butane (**t-3a″**) (3.60 g, 86%): mp 77–78 °C; ^1H NMR, see Table III. Anal. Calcd for $C_{19}H_{23}Cl$: C, 79.56; H, 8.08. Found: C, 79.13; H, 8.06.

The analogous reaction of **1″** with **c-2a** yielded 88% of a 0.12:1.0:0.11:0.16 mixture of **t-3a″**, **c-3a″**, **6a″**, and **7a″** (analyzed by ^1H NMR).

4. Bis(4-methylphenyl)methyl Chloride (1″) and 1-Phenylpropenes t,c-2b. Compounds **t-2b** (1.21 g, 10.2 mmol) and **1″** (2.01 g, 8.71 mmol) reacted in the presence of $ZnCl_2$ (0.28 g) and ether (0.33 mL) in 80 mL of CH_2Cl_2 at −78 °C within 3 h to give *u*-1-chloro-2-methyl-3,3-bis(4-methylphenyl)-1-phenylpropane (**t-3b″**) (2.70 g, 89%) as needles: mp 84–85 °C (ethanol); ^1H NMR, see Table III. Anal. Calcd for $C_{24}H_{25}Cl$: C, 82.62; H, 7.22. Found: C, 82.33; H, 7.20.

The analogous reaction of **1″** with **c-2b** gave a viscous oil (**t-3b″**:**c-3b″** = 2:1) with bp 175–180 °C (bath)/1.3 × 10^{-3} mbar (1.10 g, 73%).

II. Determination of the Stereoselectivity. Diphenylmethyl Chloride (1′) and (*E*),(*Z*)-2-Butenes t,c-2a. Compounds **1′** (0.5 ± 0.05 mmol) and **t-2a** or **c-2a** (3.5–8.5 mmol; purity > 99.6% by GC) were dissolved in 50 mL of absolute CH_2Cl_2 at −78 °C. The Lewis acid (1.0–2.0 mmol) was added and stored at −78 °C for 14–22 h. The solution was poured on aqueous ammonia, washed with water, dried with $CaCl_2$ and analyzed by HPLC. Conditions: silica gel nucleosil 50-5 (Macherey & Nagel), isooctane, 1.40 mL/min; **5a′** (9.60 min), **7a′** (10.70 min), **c-3a′** (11.20 min), **t-3a′** (11.80 min), or nucleosil 5 C_{18}, acetonitrile:H_2O:THF = 38:38:24, 1.40 mL/min; **7a′** (12.59 min), **t-3a′** (12.75 min), **c-3a′** (13.31 min), **5a′** (13.79 min), **6a′** (16.59 min). Since **c-** and **t-3a′** were not basis line separated on silica gel, and **t-3a′** and **7a′** were not basis line separated on the C_{18} material, each run was analyzed with both separation conditions.

Diarylmethyl Chlorides 1′ and 1″ and (*E*),(*Z*)-1-Phenylpropenes t,c-2b. Solutions of **1′** (0.48–0.62 mmol) and **t-2b** (100% by GC, 0.67–0.73 mmol) or **c-2b** (97.6% by GC, 0.66–0.72 mmol) in 50 mL of absolute CH_2Cl_2 were cooled at −78 °C. Lewis acids (0.25–2.0 mmol) were added, and samples, which were drawn at different times (before and after completion of the reaction), were analyzed by GC (Apiezon L, 100 °C; **c-2b**, 2.76 min; **t-2b**, 3.70 min) and HPLC. Conditions: Nucleosil 7 OH (diol) (Macherey & Nagel), isooctane: *tert*-butyl methyl ether = 125:1, 1.40 mL/min; **4b′** (3.25 min), **c-3b′** (4.27 min), **t-3b′** (4.50 min). Analogous experiments (without GC analysis) have been carried out in mixtures of CH_2Cl_2 and petroleum ether (Table IV).

The reaction of **1″** (0.44 mmol) with **t-2b** (0.70 mmol) and **c-2b** (0.73 mmol) in CH_2Cl_2 (50 mL) was catalyzed by $ZnCl_2$ (1.9 mmol). The products were analyzed by HPLC. Conditions: Nucleosil 5 NO_2 (Macherey & Nagel), isooctane:diethyl ether = 99:1, 1.35 mL/min); **c-3b″** (5.3 min), **t-3b″** (5.8 min).

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

Registry No. 1′, 90-99-3; **1″**, 13389-70-3; **t-2a**, 624-64-6; **c-2a**, 590-18-1; **t-2b**, 873-66-5; **c-2b**, 766-90-5; **t-3a′**, 102434-92-4; **c-3a′**, 102434-93-5; **t-3a″**, 102434-94-6; **c-3a″**, 102434-95-7; **t-3b′**, 102436-14-6; **c-3b′**, 102436-13-5; **t-3b″**, 102436-18-0; **c-3b″**, 102436-17-9; $ZnCl_2$, 7646-85-7; BCl_3, 10294-34-5; $SnCl_4$, 7646-78-8; $TiCl_4$, 7550-45-0.

Supplementary Material Available: Atomic coordinates, thermal parameters, interatomic distances and angles (2 pages). Ordering information is given on any current masthead page.

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