Tetrahedron Vol 47, No 2, pp 219-228, 1991
Printed in Great Britain

0040-4020/91 $3 00+00
Pergamon Press plc

ADDITIONS OF CARBENIUM IONS TO NONCONJUGATED DIENES. THE RETARDING (-I)-EFFECT OF THE SECOND DOUBLE BOND

Bernhard Irrgang and Herbert Mayr*

Institut für Chemie der Medizinischen Universität zu Lubeck,

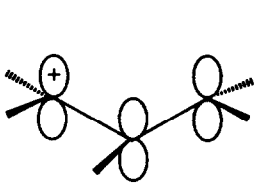
Ratzeburger Allee 160, D-2400 Lübeck

(*Received in Germany* 13 *September* 1990)

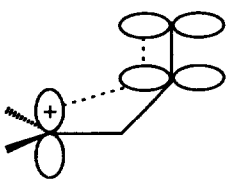
Abstract - Kinetics for the addition of the p-methoxybenzhydryl cation (AnPhCH$^+$, **10**) towards nonconjugated dienes **11** [H_2C=C(CH_3)-(CH_2)$_n$-C(CH_3)=CH_2] have been determined in CH_2Cl_2 at -30° to -70°C Reactivity increases with increasing number of methylene groups separating the two double bonds For n = 4, reactivity reaches the value for saturated alkyl substituents, and nucleophilic assistance of the second double bond is never observed

The stabilization of carbenium ions by π-conjugation is one of the tenets of electronic theory in organic chemistry [1] Stabilizing effects can also be observed, when the conjugated π-system is interrupted by one or more methylene groups (Scheme I) [2] Comparison of the solvolysis rates of compounds **1/2** and **3/4** shows that rate enhancements by several orders of magnitude may be due to these so-called homoconjugative interactions [3]

Scheme I



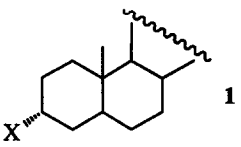
Allyl cation



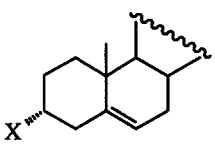
Homoallyl cation

In view of the enormous magnitude of these accelerating effects, it is understandable that much less attention has been paid to the fact that carbenium ions may also be destabilized by the inductive effect of CC double bonds Martin and Schleyer reported that methyleneadamantane **6** solvolyses 10^4 times more slowly than **5**, since **6** yields a carbenium ion with the empty p-orbital perpendicular to the π-orbitals [4] The relative reactivities of **7** and **8** indicate that the double bond between positions 3 and 4 causes an inductive destabilization of the cyclopentyl cation and not a bishomoaromatic stabilization [5] Further examples for the retardation of solvolyses by remote CC double bonds[6] and aromatic rings[7] are known

Scheme II

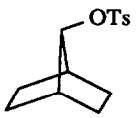


1

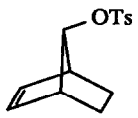


2

k_{rel} 1 $\sim 10^2$ (ref 2b)

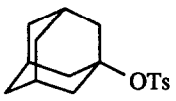


3

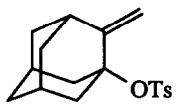


4

k_{rel} 1 10^{11} (ref 3)

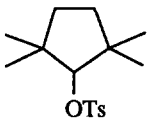


5

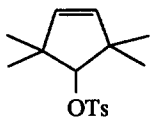


6

k_{rel} 1 10^{-4} (ref 4)



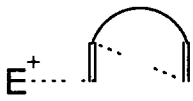
7



8

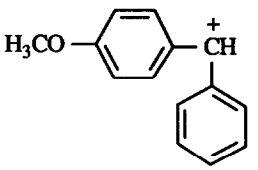
k_{rel} 1 10^{-3} (ref 5)

The addition of electrophiles to alkenes represents an alternative method for the generation of carbenium ions,[8] and it is conceivable that the electrophilic attack at one double bond of a nonconjugated diene is anchimerically assisted by the second double bond as indicated by formula **9** Nucleophilic assistance of this kind has previously been discussed for biomimetic cyclizations [9]



9

Recently, we have described a method to determine the rate of attack of diarylcarbenium ions at alkenes [10] This method has now been used to investigate the influence of additional π-systems on the nucleophilicity of a CC double bond In order to facilitate comparison with related systems,[11] we have again selected the p methoxy substituted benzhydryl cation **10** as the reference electrophile

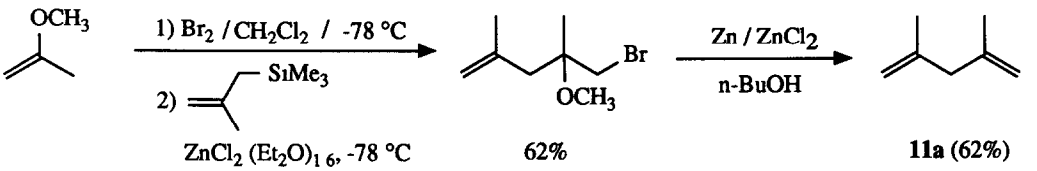


10

Results

Synthesis of the Dienes Several syntheses for 2,4-dimethyl-1,4-pentadiene (**11a**) have previously been reported,[12] among which the addition of 2-methallylzinc bromide to 1-propynylmagnesium bromide[12d] appears to be the most practical one on a laboratory scale Based on investigations by Bäuml in this laboratory, we have developed the synthesis described in Scheme III,[13] which may be considered as an acidic variant of the Boord reaction [14]

Scheme III



Compound **11b** is conveniently accessible by magnesium promoted coupling of 2-methallyl chloride,[15] and compounds **11c** and **11d** were prepared by methylenation of heptane-2,6-dione and octane-2,7-dione, respectively As shown in Scheme IV, normal Wittig-conditions are suited for the synthesis of **11d** The corresponding reaction of heptane-2,6-dione with methylenetriphenylphosphorane gave only very poor yields of **11c**, however, and this conversion was more efficiently performed with CH_2Br_2, Zn, and $TiCl_4$

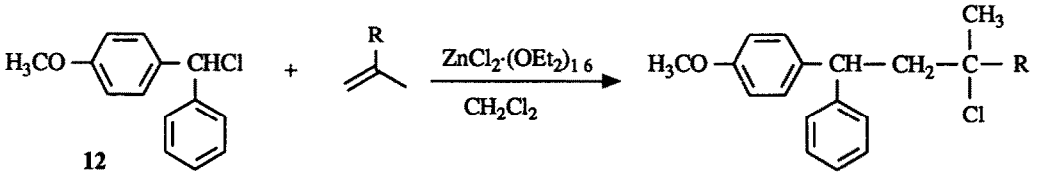
Scheme IV

n = 3 CH_2Br_2, Zn, $TiCl_4$ **11c** (27%)

n = 4 Ph_3PCH_2 **11d** (54%)

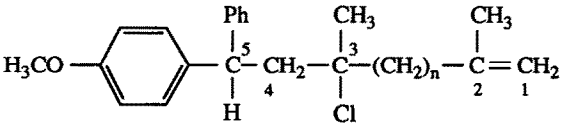
Reaction Products Good yields of the [1 1]-adducts **13a-e** are obtained when **12**, compounds **11a-e** (1.5 - 10 equivalents) and $ZnCl_2$ $(Et_2O)_{1\,6}$ are quickly combined in CH_2Cl_2 at -78°C (Scheme V)

Scheme V



R = $-CH_2-C(CH_3)=CH_2$	**11a**	**13a**	(88%)
$-(CH_2)_2-C(CH_3)=CH_2$	**11b**	**13b**	(80%)
$-(CH_2)_3-C(CH_3)=CH_2$	**11c**	**13c**	(72%)
$-(CH_2)_4-C(CH_3)=CH_2$	**11d**	**13d**	(86%)
$-CH_2-Ph$	**11e**	**13e**	(92%)

Table 1. ^{13}C NMR Chemical Shifts of the Addition Products **13a-e** [a,b]



13

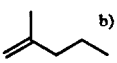
	C-1	C-2	$(CH_2)_n$	C-3	C-4	C-5	2-CH_3	3-CH_3
13a	116 46	141 39	*52 80* *52 97*	*74 00* *74 05*	*50 29* *50 36*	*47 24* *47.27*	24 80	*30.51* *30.56*
13b	109 82	145 05	32 74 *42 72* *42 87*	75 18	49 89	47 38	22.63	*30.49* *30.54*
13c	110 26	145 30	22 65 37 54 *44 05* *44 22*	75 56	49 67	47 38	22.22	*30 59* *30 68*
13d	109.78	145 81	24 40 27 59 37 53 *44 44* *44 60*	*75 42* *75 65*	49 56	47 38	22.32	*30 62* *30 69*
13e	——	——	*51 08* *51 26*	*74 39* *74 42*	*50 06* *50 14*	47 20	——	*29 85* *29 93*

[a] 1 1-Mixtures of diastereomers, signals which are different in the two stereoisomers are identified by italic print [b] Additional signals: OCH_3: δ 55 05 - 55 18, aryl-doublets δ 113 - 131, aryl-singlets: δ 136 - 158

Considerable amounts of [2:1]-products are formed, however, when the dienes **11a-d** are slowly added to a mixture of **12** and Lewis acid. Because of the sensitivity of **11c** towards protons, the reaction of this diene with **12** has been carried out in presence of 2,6-lutidine. In analogy with previous results,[11a] the adducts **13** are mixtures of diastereoisomers (~1:1) as recognized by the twinning of some of the ^{13}C NMR resonances (Table 1). A complete characterization of compunds **13** (^1H NMR, mass spectra, elemental analysis) is given in ref.[15].

Kinetics. The reactions of diarylcarbenium tetrachloroborates with 1,1-dialkylethylenes have been reported to follow second order kinetics, and the attack of Ar_2CH^+ at the alkene is usually rate determining.[10,11a] Analogous results were obtained for the reactions of **10** with the nucleophiles **11a-e**. Since the dienes **11a-d** represent bifunctional nucleophiles, these compounds must be employed in sufficient excess over **10** to avoid reaction of the second double bond.

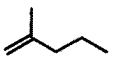
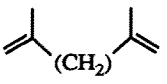
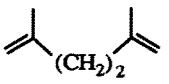
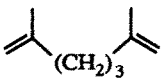
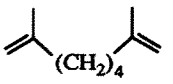
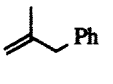
Table 2. Second Order Rate Constants (-70°C) and Activation Parameters for the Reactions of p-Methoxybenzhydryl Tetrachloroborate with the Alkenes **11a-e** in CH_2Cl_2.

Nucleophile	k_2/ L mol^{-1} s^{-1}	$\Delta H^{\neq}$/ kJ mol^{-1}	$\Delta S^{\neq}$/ J mol^{-1} K^{-1}
11a	3.42	24.8 ± 0.5	-110 ± 2
11b	15.1		
11c[a)]	39.2	26.0 ± 0.1	-83 ± 1
11d	53.5	22.8 ± 0.5	-97 ± 2
11e	1.13	27.2 ± 1.0	-107 ± 5
 b)	25.8	19.5 ± 1.5	-119 ± 6

[a)] **10**-$CF_3SO_3^-$ was used instead of **10**-BCl_4^-; [b)] From ref. 10b.

Table 2 shows that the activation entropies for the reactions of **11a-e** are somewhat less negative than those determined for 1,1-dialkylethylenes (-112 to -122 J mol^{-1} K^{-1}). Part of this difference is due to the statistical term (R ln2 = 5.8 J mol^{-1}K^{-1}) leaving a deviation in $\Delta S^{\neq}$, which is only slightly greater than the experimental uncertainty. The further discussion shall, therefore, concentrate on the more precise rate constants.

Scheme VI Relative Reactivities per Double Bond

						
		11a	**11b**	**11c**	**11d**	**11e**
k_{rel}	1.0	0 066	0 29	0 76	1 04	0 044

Scheme VI, which corrects the observed rate constants of **11a-d** for the statistical factor 2, demonstrates that in none of these cases anchimeric assistance by the second double bond takes place. When the two double bonds are separated by just one methylene group (**11a**) the second unsaturation causes a reactivity decrease by a factor of 15 Increasing separation of the two double bonds causes a steady increase of reactivity, and the partial rate constant for **11d** closely resembles that of 2-methyl-1-pentene, indicating that four methylene groups are sufficient to completely insulate the two double bonds from each other

Scheme VI, furthermore, shows similar values for compounds **11a** and **11e**, in accord with the fact that the inductive effects of a phenyl and a 2-propenyl group are comparable [7]

Conclusion. Anchimeric assistance for electrophilic attack does not occur in any of these reactions. As shown in Figure 4 of ref.[10b], the addition of carbenium ion **10** to a 1,1-dialkyl-substituted ethylene is an exergonic step Therefore, nucleophilic assistance of the second double is not needed This observation does not exclude, however, the occurence of concerted processes in biomimetic cyclizations [9] Especially when the initially attacked double bond possesses relatively low nucleophilicity[16] the operation of a multicenter process should become attractive [17]

The low reactivity of compounds **11a** and **11e** compared with the saturated counterpart (Scheme VI) represents a new illustration for the negative inductive effect of CC double bonds, which had been considered an important factor for the interpretation of homoaromatic stabilization and homoantiaromatic destabilization of carbocations and carbanions [18]

Experimental Section

General Techniques. NMR spectra were taken on a Varian XL200 spectrometer using tetramethylsilane as internal standard and $CDCl_3$ as the solvent. Mass spectra were recorded on a 70-250 E VG spectrometer, and for the kinetic experiments, the instrumentation specified in ref.[10] was used

Substrates. *p-Methoxyphenyl-phenyl-methyl chloride* (**12**) was obtained from the corresponding benzhydrol and HCl.[19] *2,5-dimethyl-1,5-hexadiene* (**11b**) was prepared by coupling of 2-methallyl chloride with magnesium,[20] and *2-methyl-3-phenyl-1-propene* (**11e**) was synthesized from 2-methallyl chloride and phenylmagnesium bromide [21]

2,4-Dimethyl-1,4-pentadiene (11a). *2-Methyl-3-trimethylsilyl-1-propene* [22a] In a nitrogen atmosphere, dry THF (100 mL) and chlorotrimethylsilane (8 64 g, 79 5 mmol) are added to magnesium turnings (4 08 g, 168 mmol) at 0 °C. The reaction flask is placed in an ultrasound bath and 1-chloro-2-methyl-propene (11.8 g, 131

mmol) is added dropwise within 3 h, while the temperature is kept at 0 °C The mixture is then stirred for 12 h at 10 °C, and hydrolyzed with a NH_3/NH_4Cl solution (100 mL) The mixture is extracted with three 30 mL portions of pentane, and the combined organic layers are dried over Na_2SO_4 Fractional distillation yields 4 00 g (39%) of 2-methyl-3-trimethylsilyl-1-propene (bp 40-50 °C (bath)/45 mbar, lit [22b,c] 109 °C/1013 mbar)

5-Bromo-4-methoxy-2-methyl-1-pentene [14] A solution of 2-methoxypropene (4 76 g, 66 0 mmol) in CH_2Cl_2 (15 mL) is added dropwise to a cooled (-78 °C) 3 M solution of bromine in CH_2Cl_2 (20 mL) in a N_2-atmosphere The solution becomes almost colorless (15 min) and is transferred into a precooled (-78 °C) dropping funnel In another flask, a 2 M solution of $ZnCl_2$-Et_2O (molar ratio 1 1 6) in CH_2Cl_2 (23 mL) is added to a cold (-78 °C) solution of 2-methyl-3-trimethylsilyl-1-propene (8 47 g, 66 0 mmol) in CH_2Cl_2 (30 mL), before the dropwise addition of the bromoether is accomplished within 30 min. The reaction mixture adopts a dark-red color while kept at -78 °C for 10 h and is then washed with 25% aqueous NH_4Cl solution The organic layer is dried over Na_2SO_4, the solvent is evaporated, and the residue is distilled to give 8 50 g (62%) of the bromoether (30-40 °C (bath)/0 02 mbar), which decomposes when stored at -30 °C for several weeks
^1H NMR (90 MHz, $CDCl_3$) δ 1 27 (s, 3 H), 1 80 br s, 3 H), 2 33 (br s, 2 H), 3 23 (s, 3 H), 3.40 (s, 2 H), 4 80 (mc, 1 H), 4 90 (mc, 1 H)

2,4-Dimethyl-1,4-pentadiene (**11a**) A mixture of 5-bromo-4-methoxy-2-methyl-1-pentene (6 90 g, 33 3 mmol), zinc powder (19 6 g, 300 mmol), $ZnCl_2$ (50 mg), and 1-butanol (15 mL) is stirred and heated at 90-95 °C A mixture of **11a** and of CH_3OH, which distils off within 12 h, is collected in a cooling trap Addition of a few drops of H_2O yields two layers, the upper of which is removed with a syringe and dried over K_2CO_3 to give 2 00 g (62%) of pure **11a** ^1H NMR ($CDCl_3$) δ 1 68 (br.s, 6 H), 2 72 (s, 2 H) 4 74 (br s, 2 H), 4 80 (br s, 2 H) ^{13}C NMR ($CDCl_3$) δ 21 74 (q), 47 13 (t), 111 98 (t), 143 58 (s)

2,6-Dimethyl-1,6-heptadiene (**11c**) Zinc powder (22 9 g, 0 350 mol) is placed into a 1-L flask and heated in vacuo with an open flame After cooling, dibromomethane (20 5 g, 0 118 mol) and dry THF (200 mL) are added This mixture is cooled at 0 °C, and a solution of $TiCl_4$ (17 1 g, 0 090 mol) is added at a rate that the temperature does not exceed 10 °C (ca 3 h) Storage of this suspension in a refrigerator (4-5 °C) for 3 days, as recommended in the literature[24] appears to be important for the success of the reaction After this period, a solution of heptane-2,6-dione (5 00 g, 0 039 mol), prepared from 2,6-lutidine via the corresponding dioxime[25], in dry THF (100 mL) is added at 0 °C within 1 h The mixture is stirred for 10 h at room temperature and cautiously hydrolyzed with 10% aqueous ammonia (150 mL) to give a viscous mash which is filtered over celite The solid residue is vigorously stirred with four 75-mL portions of pentane, and saturated aqueous NaCl solution is added to the combined liquid layers until a separation of the layers takes place The organic layer is then washed with aqueous $NaHCO_3$ solution and water, and is dried over Na_2CO_3/Na_2SO_4 After cautious evaporation of the solvent, the residue is distilled at 5 mbar to give 1 3 g (27%) of slightly contaminated **11c**[23], which is purified by preparative GC ^1H NMR ($CDCl_3$)[23a] δ 1 53-1 69 (m, 2 H), 1 72 (br s, 6 H), 2 01 (br t, J = 7 7 Hz, 4 H), 4 68, 4 70 (2 br s, 4 H) ^{13}C NMR ($CDCl_3$) δ 22 42 (q), 25 56 (t), 37 38 (t), 109 84 (t), 145 93 (s)

2,7-Dimethyl-octa-1,7-diene (**11d**) *Oxidation according to ref* [26] $PdCl_2$ (2 12 g, 0 0120 mol) and CuCl (11 9 g, 0 120 mol) are suspended in a mixture of DMF (60 mL) and H_2O (7 mL) With a gas-tight syringe, 500 mL of O_2 are injected into the vigorously stirred mixture (exothermic!) Octa-1,7-diene (6 61 g, 0 060 mmol) is then added, and O_2 is bubbled through the solution until the absorption of gas ceases and the green colour of Cu(II) reappears The mixture is then filtered, and the filtrate is extracted with three 30-mL portions of diethyl ether The ether fractions are dried over Na_2SO_4, and the ether is evaporated to give crude *octane-2,7-dione* [5 03 g, 59%, ^{13}C NMR ($CDCl_3$) δ 23 15 (t), 29 91 (q), 43 39 (t), 208 65 (s)] which solidifies at <10 °C and is used for the next step without further purification A mixture of methylphosphonium bromide and $NaNH_2$ ("Instant Wittig" by FLUKA, 29 0 g, 69 7 mmol) is stirred in dry THF (400 mL) for 15 min in a N_2-atmosphere at 0 °C A solution of octane-2,7-dione (4 50 g, 31 7 mmol) in THF (50 mL) is added dropwise and stirred for 20 h After hydrolysis with saturated $NaHCO_3$-solution, the aqueous layer is extracted with pentane The organic layers are dried over Na_2CO_3, and the solvents are evaporated Distillation (over Na_2CO_3) at 30 °C/1 mbar (Ref [27] 164 °C/1010 mbar) yields slightly contaminated **11d** (2 31 g, 53%) which is purified by preparative GC ^1H NMR ($CDCl_3$)[23a,27] δ 1 40-1 50 (m, 4 H), 1 71 (br s, 6 H), 2 02 (mc, 4 H), 4 64-4 72 (m, 4 H) ^{13}C NMR ($CDCl_3$)[27] δ 22 39 (q), 27 23 (t), 37 69 (t), 109 68 (t), 146 11 (s)

Preparation of the Adducts 13a-e; Typical Procedure. A solution of **12** (1 40 g, 6 04 mmol) in CH_2Cl_2 (69 mL) is cooled at -78 °C A 2 M solution of $ZnCl_2(Et_2O)_1{}_6$[28] in CH_2Cl_2 (0 64 mL) and **11c** (6 62 g, 60 1 mmol) are successively added in one portion After 20 min, the Lewis acid is desactivated by washing with 25% aqueous ammonia (40 mL), and the organic layer is dried over Na_2SO_4 Solvent and excessive diene are evaporated to give a residue which is purified by filtration over silica gel (eluent: pentane)

Table 3 Products **13a-e** *via* Lewis acid Catalyzed Reaction of **11a-e** with **12**

	11 / mmol	**12** / mmol	$ZnCl_2$ $(Et_2O)_{1.6}$ / mmol	CH_2Cl_2 / mL	Yield / %
a	1.64	0.799	1.6	40	88
b	60.1	6.01	1.3	60	80
c[a]	1.00	0.500	0.76	30	72
d[b]	2.00	1.00	2.0	40	86
e	3.00	2.00	2.0[c]	40	92

[a] Reaction carried out in presence of 0.500 mmol $BzNEt_3Cl$ and 4 drops of 2,6-lutidine, [b] Reaction was carried out in presence of 1.00 mmol $BzNEt_3Cl$, [c] BCl_3 was used instead of $ZnCl_2$ $(OEt_2)_{1.6}$

Kinetic Experiments were carried out following the procedure described previously [10] For experimental details see Table 4

Table 4 Kinetics for the Reaction of p-Methoxy-benzhydryl Tetrachloroborate (**10**-BCl_4^-) with the Nucleophiles **11a-e**

No	T/°C	$[\mathbf{10}]_0$/ mol L^{-1}	$[\mathbf{11}]_0$/ mol L^{-1}	$[BCl_3]_0$/ mol L^{-1}	Conversion/ %	k_2/ L mol^{-1} s^{-1}
*2,4-Dimethyl-1,4-pentadiene (**11a**)*						
263	-39.9	$1.13\ 10^{-4}$	$9.87\ 10^{-4}$	$5.1\ 10^{-2}$	93[a]	26.0
262	-60.0	$1.13\ 10^{-4}$	$1.02\ 10^{-3}$	$4.3\ 10^{-2}$	93[a]	7.36
260	-70.0	$1.17\ 10^{-4}$	$1.03\ 10^{-3}$	$3.5\ 10^{-2}$	90[a]	3.28
261	-80.1	$1.20\ 10^{-4}$	$1.31\ 10^{-3}$	$3.6\ 10^{-2}$	89[a]	1.54
[a] Carried out in the presence of $BzNEt_3Cl$ ($1\ 10^{-2}$ mol L^{-1})						
*2,5-Dimethyl-1,5-hexadiene (**11b**)*						
1	-70.0	$2.20\ 10^{-4}$	$1.14\ 10^{-3}$	$1.3\ 10^{-2}$	79	15.2
2	-70.0	$2.10\ 10^{-4}$	$4.57\ 10^{-3}$	$1.8\ 10^{-2}$	92	15.0

2,6-Dimethyl-1,6-heptadiene (11c)[a]

290	-40 1	1 06·10^{-4}	3 44 10^{-4}	6 9 10^{-4}	76	317
289a	-49 9	1 08 10^{-4}	3 49 10^{-4}	5 4 10^{-4}	63	178
287	-70 0	1 11 10^{-4}	3 59 10^{-4}	4 4 10^{-4}	69	39.2
288	-80 0	1 13·10^{-4}	3 65 10^{-4}	6 3 10^{-4}	51	16 8

[a] **10**-$CF_3SO_3^-$ was used instead of **10**-BCl_4^-

2,7-Dimethyl-1,7-octadiene (11d)

256	-40 0	1 21 10^{-4}	2 70 10^{-4}	2 1 10^{-2}	83	355
257	-60 2	1 07 10^{-4}	4 09 10^{-4}	1 7 10^{-2}	88	99 6
253	-70 0	1 18 10^{-4}	2 82 10^{-4}	1 8 10^{-2}	82	55 9
254	-70 0	1 02 10^{-4}	5 52 10^{-4}	1 5 10^{-2}	83	53 0
258	-79 6	1 17 10^{-4}	5 73 10^{-4}	1 3 10^{-2}	83	26 2

2-Methyl-3-phenyl-prop-1-ene (11e)

266	-39 5	1 13 10^{-4}	1 79 10^{-3}	2 9 10^{-2}	93	10 3
265	-50 9	1 14 10^{-4}	1 82 10^{-3}	2 3 10^{-2}	94	5 18
187	-70 0	8 75 10^{-5}	2 48 10^{-3}	1 7 10^{-2}	80	1 14
188	-70 0	8 76 10^{-5}	1 24 10^{-3}	1 7 10^{-2}	83	1 12
189	-70 0	8 74 10^{-5}	3 10 10^{-3}	1 7 10^{-2}	84	1 12

Acknowledgement We thank A Riemann for experimental assistance and the Deutsche Forschungsgemeinschaft for financial support

References and Notes

(1) See e g March, J *Advanced Organic Chemistry*, 3rd Ed , Wiley New York, 1985, p 144
(2) (a) Winstein, S. in *Carbonium Ions*, Olah, G A., Schleyer, P v R, Eds., Wiley New York, 1972, Vol 3, Chapter 22
(b) Story, P R , Clark, Jr B C. *ibid* , Chapter 23.
(3) (a) Winstein, S , Shatavski, M , Norton, C , Woodward, R B *J Am Chem Soc* **1955**, *77*, 4183
(b) Winstein, S , Shatavski, M *J Am Chem Soc* **1956**, *78*, 592
(c) Winstein, S , Stafford, E T *J Am Chem Soc* **1957**, *79*, 505
(4) (a) Ree, B R , Martin, J. C *J Am Chem Soc* **1970**, *92*, 1660
(b) Buss, V , Gleiter, R , Schleyer, P v R *J Am Chem Soc* **1971**, *93*, 3927
(5) Bentley, T W , Irrgang, B , Mayr, H , Schleyer, P v R *J Org Chem* **1988**, *53*, 3492

(6) (a) Ladika, M; Sunko, D E *J Org Chem* **1985**, *50*, 4544
(b) Jursic, B , Ladika, M , Bosner, B , Kobetic, R , Sunko, D. E *Tetrahedron* **1988**, *44*, 2311
(c) Gream, G E , Serelis, A K *Aust J Chem.* **1978**, *31*, 863
(d) Gream, G E , Serelis, A K.; Stoneman, T I *Aust J Chem* **1974**, *27*, 1711
(e) Ferber, P H ; Gream, G E , Wagner, R. D *Aust J Chem.* **1980**, *33*, 1569
(f) Ferber, P H , Gream, G E *Aust J Chem.* **1981**, *34*, 1051
(g) Bartlett, P. D, Closson, W D , Cogdell, T J. *J Am Chem Soc* **1965**, *87*, 1308
(h) Bartlett, P D , Trahanovsky, W S , Bolon, D A., Schmid, G H *J Am Chem Soc* **1965**, *87*, 1314
(i) Orlovic, M , Polla, E , Borcic, S. *J Org Chem* **1983**, *48*, 2278
(7) (a) Landis, A , VanderWerf, C A *J Am Chem Soc* **1958**, *80*, 5277
(b) Tessler, M M , VanderWerf, C A. *J Org Chem* **1965**, *30*, 405
(8) Olah, G A *Angew Chem.* **1973**, *85*, 183, *Angew Chem Int Ed Engl* **1973**, *12*, 173
(9) Reviews (a) Johnson, W S *Angew Chem* **1976**, *88*, 33, *Angew Chem Int Ed Engl* **1976**, *15*, 9
(b) Bartlett, P A in *Asymmetric Synthesis*, Morrison, J D , Ed , Academic Press· Orlando, 1984, Vol 3, pp 393
(10) (a) Schneider, R , Grabis, U , Mayr, H *Angew Chem* **1986**, *98*, 94, *Angew Chem Int Ed Engl* **1986**, *25*, 89
(b) Mayr, H , Schneider, R , Schade, C , Bartl, J , Bederke, R *J Am Chem Soc* **1990**, *112*, 4446
(11) (a) Mayr, H , Schneider, R , Irrgang, B., Schade, C *J Am Chem Soc* **1990**, *112*, 4454
(b) Mayr, H , Hagen, G *J Chem Soc Chem Commun* **1989**, 91
(12) (a) Hagemeyer, Jr , H J *Ind Eng Chem* **1949**, *41*, 765
(b) Buchta, E , Krönıger, A *Chimia* **1969**, *23*, 225
(c) Dubois, J E , Moulineau, C *Bull Chim Soc Fr* **1965**, 2198
(d) Frangin, Y , Gaudemar, M *Bull Chim Soc Fr* **1976**, 1173
(13) The sequence outlined in Scheme III represents a novel general approach to 1,4-dienes, which will be reported elsewhere
(14) Schlosser, M in *Houben-Weyl, Methoden der Organischen Chemie*, 4th ed , Georg Thieme Stuttgart, 1972, Vol V/1b, p 215
(15) Irrgang, B , *Dissertation*, Medizinische Universität zu Lubeck, 1990.
(16) For a nucleophilicity scale of alkenes towards carbenium ions see ref 11a
(17) An analogous change of mechanism has been observed in solvolytic studies ref 6c-h
(18) (a) Kaufmann, E , Mayr, H , Chandrasekhar, J , Schleyer, P v R *J Am Chem Soc* **1981**, *103*, 1375
(b) Schleyer, P v R , Kaufmann, E , Kos, A J , Mayr, H , Chandrasekhar, J *J Chem Soc Chem Commun* **1986**, 1583 and references cited therein
(19) Bartlett, P D , Nebel, R W *J Am Chem Soc* **1940**, *62*, 1345
(20) (a) Henne, A L , Chanan, H , Turk, A *J Am Chem Soc* **1941**, *63*, 3475.
(b) Tamele, M W , Ott, C J , Marple, K E , Hearne, G *Ind Eng Chem* **1941**, *33*, 115
(c) Campbell, I G M , Harper, S *J Chem Soc* **1945**, 284
(21) Klein, J, Medlik-Balan, A , Meyer, A Y , Chorev, M *Tetrahedron* **1976**, *32*, 1839.
(22) (a) General procedure described by Seyferth, D , Weiner, M A *J Org Chem* **1961**, *26*, 4797
(b) Mironov, V F , Pogonkina, N A *Izvest Akad Nauk SSSR, Otdel Khim Nauk* **1957**, 1199, CA **52**, 6161h
(c) Petrov, A D , Nikishin, G I , Smetankina, N P *Zhur Obscheĭ Khim* **1958**, *28*, 2085, CA **53**, 3038g
(23) (a) Uijttewaal, A P , Jonkers, F L ; Gen, A van der *J Org Chem* **1979**, *44*, 3157
(b) Ansell, M F , Thomas, D A *J Chem Soc* **1961**, 539
(24) (a) Reetz, M T *Organotitanium Reagents in Organic Synthesis*, Springer· Heidelberg, 1980, pp. 223
(b) Lombardo, L *Tetrahedron Lett* **1982**, *23*, 4293
(25) (a) Overberger, C G , Gibb, T B , Chibnik, S , Huang, P , Monagle, J *J Am Chem Soc* **1952**, *74*, 3290
(b) Bailey, W J , Cesare, F *J Org Chem* **1978**, *43*, 1421
(26) Tsuji, W *Synthesis* **1984**, 369
(27) Dauzonne, D , Platzer, N , Demerseman, P , Lang, C , Royer, R *Bull Soc Chim Fr* **1979**, 506
(28) Mayr, H , Striepe, W *J Org Chem* **1985**, *50*, 2995