

spectrum, m/e 210 (3, M^+), 177 (12), 121 (16), 99 (45), 97 (40), 96 (100), 81 (34), 55 (13), 43 (27), 41 (12). Anal. Calcd for $C_{14}H_{26}O$: C, 79.94; H, 12.46. Found: C, 79.87; H, 12.48.

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Registry No. 2, 68930-33-6; 3, 78310-15-3; 4a, 84602-70-0; 4b, 83379-15-1; 5, 83379-14-0; 6, 81517-77-3; *cis*-1,3,3,5,5-pentamethyl-4-(1-methylethenyl)cyclohexan-1-ol formate, 84602-71-1; sodium formate, 141-53-7; zinc formate, 557-41-5; zinc chloride, 7646-85-7; formic acid, 64-18-6.

Scope and Limitations of Aliphatic Friedel-Crafts Alkylations. Lewis Acid Catalyzed Addition Reactions of Alkyl Chlorides to Carbon-Carbon Double Bonds

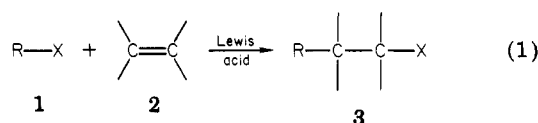
Herbert Mayr* and Wilhelm Striepe

Institut für Organische Chemie der Friedrich-Alexander-Universität Erlangen-Nürnberg, D-8520 Erlangen,
Federal Republic of Germany

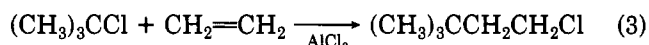
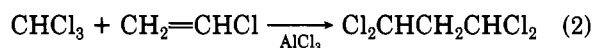
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Lewis acid catalyzed addition reactions of alkyl halides 1 with unsaturated hydrocarbons 2 have been studied. 1:1 addition products 3 are formed if the addends 1 dissociate faster than the corresponding products 3; otherwise, polymerization of 2 takes place. For reaction conditions under which 1 and 3 exist mainly undissociated, solvolysis constants of model compounds can be used to predict the outcome of any such addition reactions if systems with considerable steric hindrance are excluded.

Friedel-Crafts-type reactions are of great importance in the chemistry of aromatic compounds.¹ Their synthetic value in aliphatic chemistry appears to be rather limited,^{1,2} since alkyl halides with Lewis acids are well-known initiating systems in carbocationic polymerizations of alkenes.³ Examples have been reported, however, where reactions of type 1 gave 1:1 addition products in high yields.²



Prins⁴ found that polychloroalkanes alkylate chlorinated alkenes readily in the presence of aluminum chloride (eq 2). Schmerling showed that monohaloalkanes, particularly



tert-alkyl halides, also undergo Lewis acid catalyzed addition reactions with halogenated as well as non-halogenated alkenes (eq 3).⁵ However, "only relatively few Friedel-Crafts alkylations of alkenes by means of alkyl halides are as free from complications as the examples cited above".⁶ The problem arises of how to predict those cases for which Friedel-Crafts alkylations of type 1 work properly.

Table I. Solvolysis Rates of Alkyl Chlorides 1a-m in 80% Aqueous Ethanol at 25 °C

RX	k_1, s^{-1}	ref
$(\text{CH}_3)_3\text{CHCl}$ (1a)	2×10^{-9}	8a
$\text{CH}_2=\text{CHCH}(\text{CH}_3)\text{Cl}$ (1b)	5×10^{-7}	8b
$\text{CH}_2\text{CH}=\text{CHCH}_2\text{Cl}$ (1c)	$\sim 1 \times 10^{-6}$	a
$(\text{CH}_3)_3\text{CCl}$ (1d)	9×10^{-6}	8b,d
$\text{PhCH}(\text{CH}_3)\text{Cl}$ (1e)	1×10^{-5}	8e
$(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{Cl}$ (1f)	$\sim 4 \times 10^{-4}$	a
$\text{PhC}\equiv\text{CC}(\text{CH}_3)_2\text{Cl}$ (1g)	2×10^{-3}	8f
$\text{PhC}(\text{CH}_3)_2\text{Cl}$ (1h)	$\sim 2 \times 10^{-3}$	b
Ph_2CHCl (1i)	2×10^{-3}	8b
$\text{CH}_3\text{OCH}_2\text{Cl}$ (1j)	15	8h
Ph_2CCl (1k)	$\sim 2 \times 10^2$	8i
$\text{CH}_3\text{OCH}(\text{CH}_3)\text{Cl}$ (1l)	>15	
$\text{CH}_3\text{OCH}(\text{Ph})\text{Cl}$ (1m)	>15	

^a Calculated from relative rates of 1b,c,f in 80% ethanol at 44.6 °C.^{8c} ^b Solvolysis rates of 1h and 1i are similar in ethanol.^{8g}

Predominant formation of 1:1 products 3 can be expected if 1 reacts faster with 2 than 3. If the 1:1 product 3 is more reactive than 1, higher addition products will be formed. Recently, one of us suggested that solvolysis rates of model compounds of 1 and 3 (Table I) may be used to differentiate between these two cases.⁷ It was stated that "Lewis acid catalyzed additions of alkyl halides to carbon-carbon multiple bonds can only lead to 1:1 products if the educts dissociate more rapidly than the products". This conclusion is based on the assumption that the relative addition rates of any alkyl halides AX and BX to a common alkene $(\Delta G^\ddagger)_R$ are reflected by the relative dis-

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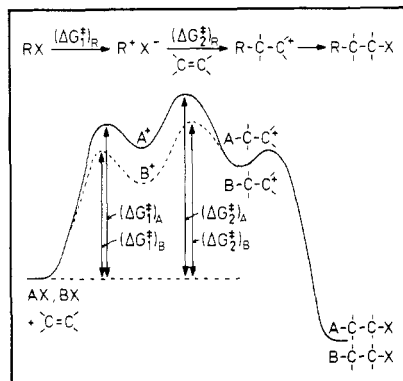
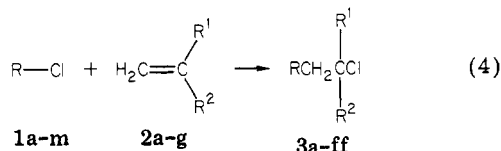


Figure 1. Energy profiles for the Lewis acid catalyzed reactions of alkyl halides AX and BX with a common alkene.

sociation rates of AX and BX (ΔG^\ddagger_{1R}). Noncrossing of the reaction profiles in Figure 1 (i.e., applicability of the Leffler-Hammond postulate⁹) is thus taken for granted. Furthermore, it is assumed that the selected solvolysis rates in 80% ethanol (Table I) are proportional to the rates of the Lewis acid induced dissociation reactions. In this work we studied a variety of Lewis acid catalyzed addition reactions in order to examine the range for which these approximations and the above predictions hold.

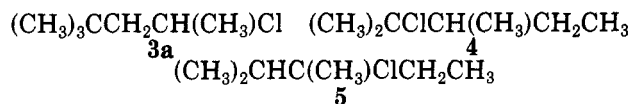
Results

The 1:1 products, obtained from reactions of 1a–m with 2a–g, usually correspond to the Markovnikov addition



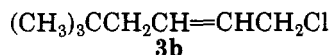
products 3a–ff. Isopropyl chloride (1a), however, the least reactive alkyl chloride in this series, has been reported not to give 1:1 addition products via Lewis acid catalyzed reactions with butadiene (2b) and isoprene (2e).¹⁰ We found that propene (2a) and isobutene (2c) also do not give 1:1 products with 1a (Table II).

In contrast, *tert*-butyl chloride (1d) yields 1:1 products with propene (2a) and butadiene (2b). With different Lewis acids, 1d and 2a give mixtures of 3a, 4, and 5 in



variable yields.^{11,12} When we used $\text{ZnCl}_2\text{-Et}_2\text{O}$ in dichloromethane to catalyze this reaction, 4 and 5 were not detectable in the ¹H NMR spectrum, indicating predominant formation of 3a.

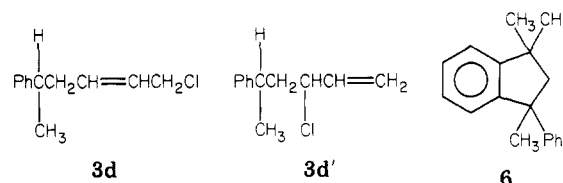
In accord with previous reports,^{10,13} we obtained a moderate yield of 1,4-addition product 3b from *tert*-butyl



chloride (1d) and butadiene (2b), while 1d and isoprene

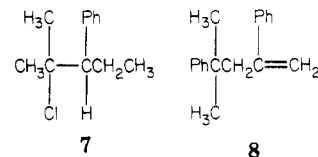
(2e) give oligomers of the general formula $[\text{C}_4\text{H}_9\text{-(C}_5\text{-H}_8\text{)}_{2,3}\text{-Cl}]_{1,9}$ under the same conditions.¹⁰ An attempt to add *tert*-butyl chloride (1d) to isobutene (2c) and styrene (2d) resulted in formation of isobutene oligomers and polystyrene, respectively.

The data on (α -chloroethyl)benzene (1e) additions in Table II are contradictory. Previous workers reported the formation of 1:1 products by ZnCl_2 -catalyzed reactions of 1e with 2a–f.¹⁴ The products were identified by their boiling points or the boiling points of their HCl elimination products. We reproduced the results with 2a–d and identified the products spectroscopically. While the reaction of *tert*-butyl chloride (1d) with butadiene (2b) yielded the 1,4-addition product selectively, 1e and 2b gave a mixture of 1,2- and 1,4-addition products 3d and 3d'. Probably because of the milder reaction conditions employed for the addition of 1e, isomerization of 3d' to the thermodynamically more stable 3d was not complete.



Under a variety of conditions we did not obtain the reported 1:1 products from reaction of (α -chloroethyl)benzene (1e) with isoprene (2e) and α -methylstyrene (2f). When exactly following the literature procedure^{14a} for the reaction of 1e with 2f, we isolated indan 6, a dimer of 2f, with a boiling point similar to that reported for the alleged 2,4-diphenyl-2-pentene.

Cumyl chloride (1h) does not react with the weak nucleophiles propene (2a) and butadiene (2b) when $\text{ZnCl}_2\text{-Et}_2\text{O}$ is used as the catalyst. In both cases condensation products of 1h are formed, since 1h eliminates HCl to give α -methylstyrene which reacts with further 1h. With the less basic catalyst system BCl_3 in dichloromethane, however, good yields of 3i and the 1,4-addition product 3j can be obtained. The "normal" addition product 3i from 1h and 2a is accompanied by a small amount of 7 arising from



successive 1,2 hydride and phenyl shifts in the intermediate carbenium ions. $\text{ZnCl}_2\text{-Et}_2\text{O}$ effectively catalyzes the reactions of 1h with the more nucleophilic alkenes 2c–f. The addition product 3 from 1h and α -methylstyrene (2f) is not observable, however, and eliminates HCl to give 8 under reaction conditions. Attempts, adding 1h to ethyl vinyl ether led to polyvinyl ether.

With the exception of ethyl vinyl ether, all alkenes examined (2a–f) gave 1:1 addition products 3n–s with benzhydryl chloride (1i) under $\text{ZnCl}_2\text{-Et}_2\text{O}$ catalysis. Only the thermodynamically more stable 1,4-addition product 3r was formed with isoprene (2e) while butadiene (2b) gave a mixture of 1,4- (3o) and 1,2-addition products (3o'), which were not interconverted under the reaction conditions. When the reaction of 1i with styrene (2d) catalyzed by ZnCl_2 in refluxing dichloromethane, the addition product 3q was accompanied by the condensation product 9;¹⁵ pure

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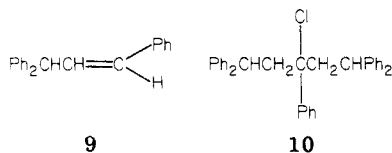
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Table II. Lewis Acid Catalyzed Reactions of Alkyl Halides with Alkenes

R-Cl	alkene ^d	catalyst	temp, °C	time	products (yield, %)	ref	
(CH ₃) ₂ CHCl (1a)	2a	ZnCl ₂ -Et ₂ O	-78	36 days	no reaction	a	
		ZnCl ₂ -Et ₂ O	20	36 days	oligomers	a	
		AlCl ₃	20	0.15 h	oligomers	a	
	2b	ZnCl ₂ , FeCl ₃	20		polymers	10	
	2c	ZnCl ₂ -Et ₂ O	20	10 days	oligomers	a	
(CH ₃) ₃ CCl (1d)	2a	ZnCl ₂ , SnCl ₄			polymers	10	
		AlCl ₃	-40 to -32		3a, 4, 5 (43)	11	
		FeCl ₃	-15 to -10		3a, 4, 5 (43)	11	
		BiCl ₃	22		3a, 4, 5 (28)	11	
		ZnCl ₂	23		3a, 4, 5 (21)	11	
		ZrCl ₄	22		3a, 4, 5 (18)	11	
		TiCl ₄	50		3a, 4, 5 (29)	11	
		BF ₃	10		3a, 4, 5 (63)	11	
		AlCl ₃	-30		C ₇ H ₁₅ Cl (70)	12	
		ZnCl ₂ -Et ₂ O	0	17 h	3a (major) (41)	a	
		ZnCl ₂	20		3b (20-35)	10, 13	
		ZnCl ₂ -Et ₂ O	-30	48 h	3b (20)	a	
		ZnCl ₂ -Et ₂ O	0	15 h	oligomers	a	
		ZnCl ₂ -Et ₂ O	0	20 h	polystyrene	a	
	2e	ZnCl ₂ , SnCl ₄			oligomers	10	
PhCH(CH ₃)Cl (1e)	2a	ZnCl ₂	20-80		3c (40) ^b	14b	
		ZnCl ₂ -Et ₂ O	0	15 h	3c (52)	a	
	2b	ZnCl ₂	20-70	1 h	3d (45)	14a	
	ZnCl ₂ -Et ₂ O	-30	22 h	3d (39), 3d' (12)	a		
	2c	ZnCl ₂	20-50	1 h	3e (95) ^b	14a,b	
	ZnCl ₂ -Et ₂ O	-78	4 days	3e (71)	a		
	2d	ZnCl ₂	45-60	1 h	3f (70)	14a,b	
	ZnCl ₂			polymers	15		
	ZnCl ₂ -Et ₂ O	0	22 h	3f (72)	a		
	2e	ZnCl ₂	20-30		3g (56) ^c	14a	
	ZnCl ₂	variable conditions		polymers	a		
	ZnCl ₂ -Et ₂ O	45-60		polymers	a		
2f	ZnCl ₂	45-60		3h (57) ^b	14a,b		
ZnCl ₂	50	4 h	6 (80)	a			
PhC(CH ₃) ₂ Cl (1h)	2a	ZnCl ₂ -Et ₂ O	-78	18 h	decomp of 1h	a	
		BCl ₃	-78	6 h	3i (43), 7 (15)	a	
	2b	ZnCl ₂ -Et ₂ O	-78	4 h	decomp of 1h	a	
	BCl ₃	-78	18 h	3j (65)	a		
	2c	ZnCl ₂	20-50		3k (80) ^b	14a,b	
	ZnCl ₂ -Et ₂ O	-78	4 h	3k (71)	a		
	2d	ZnCl ₂ -Et ₂ O	-78	15 h	3l (71)	a	
	2e	ZnCl ₂ -Et ₂ O	-78	4 h	3m (64)	a	
	2f	ZnCl ₂ -Et ₂ O	-78	17 h	8 (58)	a	
	2g	ZnCl ₂ -Et ₂ O	-78	4 h	polyvinyl ether	a	
Ph ₂ CHCl (1i)	2a	ZnCl ₂ -Et ₂ O	-78 to +2		3n (92)	a	
		ZnCl ₂ -Et ₂ O	-78	4 days	3o (48), 3o' (37)	a	
	2c	ZnCl ₂ -Et ₂ O	-78	15 h	3p (97)	a	
	2d	ZnCl ₂	40	6 h	3q (54), 9 (8)	15	
	ZnCl ₂ -Et ₂ O	-78	15 h	3q (88)	a		
	2e	ZnCl ₂ -Et ₂ O	-78	6 h	3r (82)	a	
	2f	ZnCl ₂ -Et ₂ O	-78	1 h	3s (75)	a	
	ZnCl ₂ -Et ₂ O	-78	18 h	10 (47)	a		
	2g	ZnCl ₂ -Et ₂ O	-78	3 h	polyvinyl ether	a	
	2a	ZnCl ₂	30	3 h	3t (47)	16	
CH ₃ OCH ₂ Cl (1j)	2b	ZnCl ₂	0	24 h	3u,u' (70)	17	
	2c	HgCl ₂	20	4 days	3v (60)	17	
	2d	ZnCl ₂	20	3 h	3w (75)	18	
	2e	ZnCl ₂	10	3 h	3x,x' (30)	19a	
		SnCl ₄ -ROH	0	80 min	3x (64)	19b	
	2f	ZnCl ₂ -Et ₂ O	-78	21 h	3y (37)	a	
	2g	ZnCl ₂ -Et ₂ O	-78	4 h	oligomers	a	
	Ph ₃ CCl (1k)	2c	ZnCl ₂ -Et ₂ O	-78	19 h	no reaction	a
			ZnCl ₂ -Et ₂ O	0	15 h	13 (21), 12 (8)	a
		2e	ZnCl ₂ -Et ₂ O	-78	15 h	polymers	a
2f		ZnCl ₂ -Et ₂ O	-78	16 h	no reaction	a	
2g		ZnCl ₂ -Et ₂ O	-78	17 h	polyvinyl ether	a	
PhCH(OCH ₃)Cl (1m)	2a	ZnCl ₂ -Et ₂ O	-30 to 0	3 h	3z (19), 3z' (43), 14 (16)	a	
	2b	HgCl ₂	20	6 days	3aa (65)	17	
	2c	ZnCl ₂ -Et ₂ O	-78	2 h	3bb (90)	a	
	2d	ZnCl ₂ -Et ₂ O	20	1 day	3cc (57)	20	
	2e	ZnCl ₂	20	10 days	3dd (52)	21	
	2f	ZnCl ₂ -Et ₂ O	-78	2 h	3ee (69)	a	
	2g	ZnCl ₂ -Et ₂ O	-78	0.5 h	3ff (48)	a	

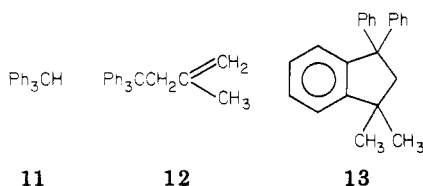
^a This work. ^b Products not isolated. ^c Products not characterized spectroscopically. ^d See Table III for structures.



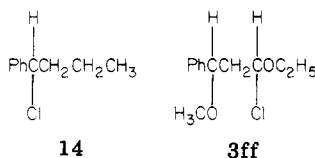
3q can be obtained by carrying out the reaction at -78°C with $\text{ZnCl}_2\text{-Et}_2\text{O}$ as a catalyst. Adduct **3s**, formed from benzhydryl chloride (**1i**) and α -methylstyrene (**2f**), decomposed to give the 2:1 product **10** when exposed to $\text{ZnCl}_2\text{-Et}_2\text{O}$ for several hours. This reaction can be rationalized by regeneration of **1i** via retro addition of **3s** and addition of **1i** to 2,4,4-triphenyl-1-butene, the HCl elimination product of **3s**.

Chlorodimethyl ether (**1j**) reacts with **2a-f** under mild conditions to produce the 1:1 products **3t-y**. Both dienes **2b** and **2e** yield mixtures of 1,4- and 1,2-addition products when ZnCl_2 was used as a catalyst. When the addition of **1j** to isoprene (**2e**) was catalyzed by SnCl_4 , a stronger Lewis acid, the 1,4-product **3x** was formed selectively.

Trityl chloride (**1k**) did not react with isobutene (**2c**) or α -methylstyrene (**2f**) under $\text{ZnCl}_2\text{-Et}_2\text{O}$ catalysis at -78°C . Isoprene (**2e**) and ethyl vinyl ether (**2g**) were polymerized under these conditions. At 0°C a mixture of **11-13** was formed from $\text{ZnCl}_2\text{-Et}_2\text{O}$ -catalyzed reaction of **1k** with isobutene (**2c**).



α -Methoxybenzyl chloride (**1m**) was the only alkylating agent in this series which gave 1:1 products with all alkenes **2a-g**. Reaction with propene gives addition products **3z,z'** as a 31:69 mixture of two diastereomers (62%) with 16% **14**. The mechanism of formation of the latter product is



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not completely clear. Addition of **1m** to ethyl vinyl ether (**2g**) must be a reversible process since the concentration of **1m** in the reaction mixture goes through a minimum at short reaction times. Addition product **3ff**, which was not isolated in substance but degraded to cinnamaldehyde, was accompanied by a variety of side products, which have not been identified since they were formed in small quantities.

Discussion

The matrix presentation in Table III summarizes the above results and the 1:1 product yields of addition reactions with prenyl chloride (**1f**) and 1,1-dimethyl-3-phenylpropargyl chloride (**1g**). When the alkyl halides **1** are arranged vertically according to increasing solvolysis rates (Table I) and the alkenes are ordered horizontally in a way that solvolysis rates of the 1:1 addition products increase from left to right, a diagonal results which correlates addends and products of equal solvolysis rates. This diagonal separates Table III into a lower left section where the formation of 1:1 products is observed and an upper right section where polymerization of the alkenes takes place. Our prediction⁷—formation of 1:1 products only if educts dissociate faster than products—is thus verified.








However, the impressive presentation in Table III is only possible when the addition reactions of trityl chloride are not included. From solvolysis rates, one would derive that trityl chloride (**1k**) is more reactive than **1a-j** and therefore should yield 1:1 products with **2a-f**. In contrast to this expectation, isoprene (**2e**) polymerizes when treated with **1k** and $\text{ZnCl}_2\text{-Et}_2\text{O}$, indicating that allyl chlorides of the prenyl type are more reactive than **1k**. The observation that trityl chloride (**1k**), in contrast to **1h** or **1i**, does not react with isobutene (**2c**) or α -methylstyrene (**2f**) at -78°C also indicates that solvolysis rates are not the only factor determining relative addition rates. We attribute the low reactivity of trityl chloride (**1k**) to steric hindrance in the addition transition state. Resonance stabilization of the trityl cation cannot be the determining factor, since α -methoxybenzyl chloride (**1m**), which forms an even more electronically stabilized carbenium ion, reacts readily with all alkenes **2a-g**.

The operation of steric effects is also realized in other cases. The 10% solvolysis rate difference between *tert*-butyl chloride (**1d**) and α -phenylethyl chloride (**1e**) can hardly explain that **1e** gives good yields of 1:1 products with isobutene and styrene whereas **1d** does not. More plausible is the assumption that the attack of the secondary 1-phenylethyl cation at an olefin is sterically less hindered than the attack of the *tert*-butyl cation.

However, the clear diagonal dividing Table III indicates that steric effects can often be neglected. The reason is that solvolysis rates in Table I span a range of ~ 12 powers of 10, corresponding to 11 kcal/mol at -78°C . Therefore, steric effects have only to be considered if very bulky systems are involved or if systems with closely similar solvolysis rates are compared.

Besides steric effects we have to consider another factor which limits the scope of our predictions. The approximation that the relative magnitudes of $(\Delta G^*_2)_A$ and $(\Delta G^*_2)_B$ are reflected by the energy ordering of A^+ and B^+ will be valid if A^+ and B^+ are high-energy intermediates (Figure 1). The smaller $(\Delta G^*_1)_A$ and $(\Delta G^*_1)_B$ become, either by going into highly ionizing reaction media or by going to better stabilized carbenium ions, the less reliable solvolysis data for estimating the relative magnitudes of $(\Delta G^*_2)_A$ and $(\Delta G^*_2)_B$ will be. It can be derived that the above rules even have to be reversed if dissociation of RX becomes exothermic (stable ion conditions).

Table III. Yields of 1:1 Products from Lewis Acid Catalyzed Addition Reactions of Alkyl Halides with Alkenes (Predictions in Parentheses)

RCl	alkene						
							
	2a	2b	2c	2d	2e	2f	2g
(CH ₃) ₂ CHCl (1a)	0	0	0	(0)	0	0	(0)
(CH ₃) ₃ CCl (1d)	41	35	0	0	0	(0)	(0)
PhCH(CH ₃)Cl (1e)	52	50	71	72	0	0	(0)
(CH ₃) ₂ C=CHCH ₂ Cl (1f)	32 ²²	27 ²³	65 ²²	75 ²²	10 ²⁴	0 ²²	0 ²²
PhC=CC(CH ₃) ₂ Cl (1g)	67 ²⁵	46 ²⁶	93 ²⁷	91 ²⁸	67 ²⁶	0 ²⁸	0 ²⁸
PhC(CH ₃) ₂ Cl (1h)	58	65	71	71	64	58	0
Ph ₂ CHCl (1i)	92	85	97	88	82	75	0
CH ₃ OCH ₂ Cl (1j)	47	70	60	75	64	37	0
CH ₃ OCH(Ph)Cl (1m)	78	65	90	57	52	69	68

Generally, reliable predictions are possible for those addition reactions where the dissociation step is the main contributor to the activation energy of the overall process. If the addition products undergo rapid sequence reactions (e.g., eliminations and cyclizations), application of the above rules is not possible.

In order to include steric effects as well as widely dissociated reaction systems, we are going to directly determine relative magnitudes of $(\Delta G^\ddagger)_R$ for various alkyl halides. Until these new data become available, we recommend solvolysis rates as a guide for synthesis planning with aliphatic Friedel-Crafts reactions.

Experimental Section

General Methods. Infrared spectra were recorded on a Beckmann Acculab 1 IR spectrophotometer. ¹H NMR spectra were taken in carbon tetrachloride on a JEOL JNM-C-60-HL spectrometer and ¹³C NMR spectra on a JEOL JNM-PS-100 spectrometer. Chemical shifts (δ) were recorded relative to (CH₃)₄Si as an internal standard.

It was advantageous to use ZnCl₂ in a homogeneous solution. For this purpose 50 g of ZnCl₂ (commercial quality, Merck) was dissolved in 60 mL of ether. This solution (referred to as ZnCl₂-Et₂O in the following) can be diluted with CH₂Cl₂. Precipitates, sometimes formed at 20 °C, are mostly dissolved at low temperature.

tert-Butyl Chloride (1d) and Propene (2a). A solution of 1.85 g (20.0 mmol) of 1d in 10 mL of CH₂Cl₂ was added to a solution of 4 mL of ZnCl₂-Et₂O and 1.68 g (39.9 mmol) of 2a in 45 mL of CH₂Cl₂ at -78 °C. The mixture was allowed to stand at 0 °C for 17 h, washed with aqueous ammonia and dried. The solvent was evaporated and the remaining oil was distilled to give 2-chloro-4,4-dimethylpentane 3a: 1.1 g (41%); bp (bath) 45-50 °C (40 mmHg) [lit.²⁹ bp 45 °C (39 mmHg)]; ¹H NMR δ 0.99 (s, 9 H), 1.4-2.1 (m, 5 H), 4.06 (m, 1 H). Anal. Calcd for C₇H₁₅Cl: C, 62.44; H, 11.23. Found: C, 62.58; H, 11.32.

tert-Butyl Chloride (1d) and 1,3-Butadiene (2b). Compounds 1d (5.0 g, 54 mmol) and 2b (3.0 g, 55 mmol) dissolved in 60 mL of CH₂Cl₂ reacted at -30 °C in the presence of 4 mL of ZnCl₂-Et₂O to give 1.6 g (20%) 1-chloro-5,5-dimethyl-2-hexene (3b): bp (bath) 50-65 °C (4 mmHg) [lit.¹⁰ bp 47-47.5 (10 mmHg)]; ¹H NMR δ 0.92 (s, 9 H), 1.95 (br d, *J* = 6.0 Hz, 2 H), 3.99 (br d, *J* = 6 Hz, 2 H), 5.68 (m, 2 H); IR (neat) 965 cm⁻¹ (trans olefin); mass spectrum (70 eV), *m/e* (relative intensity) 146, 148 (10, 3, M⁺), 95 (98), 57 (100). Anal. Calcd for C₈H₁₆Cl: C, 65.51; H, 10.31. Found: C, 65.71; H, 10.58.

1-Chloro-1-phenylethane (1e) and Propene (2a). A solution of 2.8 g (20 mmol) of 1e in 10 mL of CH₂Cl₂ was added to a solution of 4 mL of ZnCl₂-Et₂O and 2.5 g (59 mmol) of 2a in 35 mL of CH₂Cl₂ at -78 °C and warmed up to 0 °C. After 15 h the mixture was worked up as above to give 2-chloro-4-phenylpentane

(3c): 1.9 g (52%); bp (bath) 50-62 °C (0.003 mmHg). The mixture of two diastereomers was not separated: ¹H NMR δ 0.7-1.6 (m, 6 H), 1.65-2.3 (m, 2 H), 2.94 (br sextet, 1 H), 3.9 (m, 1 H), 7.18 and 7.20 (2 s, 5 H); mass spectrum (96 eV), *m/e* (relative intensity) 182, 184 (33, 10, M⁺), 105 (100). Anal. Calcd for C₁₁H₁₅Cl: C, 72.31; H, 8.28. Found: C, 72.95; H, 8.50.

1-Chloro-1-phenylethane (1e) and 1,3-Butadiene (2b). Compounds 2b (2.16 g, 39.9 mmol) and 1e (5.60 g, 40.0 mmol) were added to 4 mL of ZnCl₂-Et₂O in 65 mL of CH₂Cl₂ and kept at -30 °C for 22 h. An ordinary workup yielded 3.88 g (50%) of 1-chloro-5-phenyl-2-hexene (3d) and 3-chloro-5-phenyl-1-hexene (3d') (77:23): bp (bath) 55-65 °C (0.01 mmHg) [lit.^{14a} bp 100-110 °C (4 mm Hg)]. Fractionated distillation yielded pure 3d as the higher boiling isomer: bp (bath) 60-65 °C (0.01 mmHg); ¹H NMR δ 1.24 (d, *J* = 7 Hz, 3 H), 2.15-2.50 (m, 2 H), 2.5-3.0 (m, 1 H), 3.89 (split d, *J* = 6 Hz, 2 H), 5.6 (m, 2 H); mass spectrum (96 eV), *m/e* (relative intensity) 194 (1, M⁺), 158 (3), 143 (3), 105 (100). Anal. Calcd for C₁₂H₁₅Cl: C, 74.03; H, 7.77. Found: C, 73.96; H, 7.64.

3d': ¹H NMR δ 1.24 (d, *J* = 7 Hz), 1.8-2.4 (m), 3.8-4.3 (m), 4.9-5.3 (m), other signals masked by 3d absorptions.

1-Chloro-1-phenylethane (1e) and Isobutene (2c). 2-Chloro-2-methyl-4-phenylpentane (3e; 2.8 g, 71%) was obtained from the ZnCl₂-Et₂O (4 mL) catalyzed reaction of 2c (1.1 g, 20 mmol) with 1e (2.8 g, 20 mmol) in 45 mL of CH₂Cl₂ at -78 °C (4 days): bp (bath) 32-34 °C (10⁻⁴ mmHg); ¹H NMR δ 1.29 (d, *J* = 7 Hz, 3 H), 1.36 (s, 3 H), 1.47 (s, 3 H), 2.13, 2.14 (2 d, *J* = 6, 7 Hz, 2 H), 3.08 (br sextet, *J* \approx 7 Hz, 1 H), 7.18 (s, 5 H); mass spectrum (70 eV), *m/e* (relative intensity) 196, 198 (4.3, 1.3, M⁺), 145 (100). Anal. Calcd for C₁₂H₁₇Cl: C, 73.26; H, 8.71. Found: C, 73.75; H, 8.80.

1-Chloro-1-phenylethane (1e) and Styrene (2d). A solution of 1e (5.6 g, 40 mmol) in 20 mL of CH₂Cl₂ was added to a solution of 2d (4.2 g, 40 mmol) and ZnCl₂-Et₂O (8 mL) in 80 mL of CH₂Cl₂ at -78 °C. The mixture was warmed to 0 °C and after 22 h washed with aqueous ammonia. Distillation yielded 7.0 g (72%) 1-chloro-1,3-diphenylbutane (3f), a mixture of two diastereomers: bp (bath) 78-85 °C (0.001 mmHg); ¹H NMR δ 1.23, 1.30 (2 d, *J* = 8 Hz, 3 H), 2.3 (m, 2 H), 3.1 (m, 1 H), 4.5 (m, 1 H), 7.2 (m, 10 H); mass spectrum (96 eV), *m/e* (relative intensity) 244, 246 (3, 1, M⁺), 105 (100). Anal. Calcd for C₁₆H₁₇Cl: C, 78.51; H, 7.00. Found: C, 78.34; H, 6.93.

1-Chloro-1-phenylethane (1e) and α -Methylstyrene (2f). Compound 1e (11 g, 78 mmol) was added to a mixture of 2f (9.4 g, 80 mmol) and ZnCl₂ (120 mg) and kept at 50 °C for 4 h. A workup as described in the literature^{14a} gave 0.7 g of 1e, 7.5 g (80%) of 6, and polymeric material. 1,1,3-Trimethyl-3-phenylindan (6): bp (bath) 100-120 °C (0.05 mmHg); ¹H NMR³⁰ δ 1.03 (s, 3 H), 1.32 (s, 3 H), 1.63 (s, 3 H), 2.15 and 2.40 (AB system, *J* = 13 Hz, 2 H).

Cumyl Chloride (1h) and Propene (2a). A 1 M BCl₃ solution in CH₂Cl₂ (2 mL) was added to a solution of 2a (2.1 g, 50 mmol) in 30 mL of CH₂Cl₂ at -78 °C. 1h (3.1 g, 20 mmol) dissolved in 20 mL of CH₂Cl₂ was added dropwise and the resulting solution

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kept at -78°C for 6 h. The solution was poured onto water, washed (2×25 mL of H_2O), and dried (CaCl_2). Distillation yielded 3.0 g of a colorless oil, bp (bath) $48\text{--}60^{\circ}\text{C}$ (0.02 mmHg). HPLC (silica gel, petroleum ether) gave 1.7 g (43%) of **3i** and 0.6 g (15%) of 7. 2-Chloro-4-methyl-4-phenylpentane (**3i**): $^1\text{H NMR}$ δ 1.26 (d, $J = 7$ Hz, 3 H), 1.33 (s, 3 H), 1.44 (s, 3 H), 2.13 (d, $J = 6$ Hz, 2 H), 3.74 (sextet, $J = 6.3$ Hz, 1 H), 7.24 (br s, 5 H); mass spectrum (70 eV), m/e (relative intensity) 198, 196 (8, 25, M^+), 160 (10), 145 (29), 119 (100).

2-Chloro-2-methyl-3-phenylpentane (**7**): $^1\text{H NMR}$ δ 0.73 (t, $J = 7$ Hz, 3 H), 1.44 (s, 3 H), 1.49 (s, 3 H), 1.6–2.3 (m, 2 H), 2.65 (dd, $J = 11.4$, 3.4 Hz, 1 H), 7.24 (s, 5 H); mass spectrum (70 eV), m/e (relative intensity) 198, 196 (4, 12, M^+), 160 (59), 145 (65), 131 (96), 119 (100). Anal. Calcd for $\text{C}_{12}\text{H}_{17}\text{Cl}$: C, 73.27; H, 8.71. Found: C, 72.86; H, 8.65.

Cumyl Chloride (1h) and 1,3-Butadiene (2b). A 1 M BCl_3 solution in CH_2Cl_2 (2 mL) was added to a solution of **2b** (1.6 g, 30 mmol) in 30 mL of CH_2Cl_2 at -78°C . After dropwise addition of **1h** (3.1 g, 20 mmol) the mixture was allowed to stand at -78°C for 17 h, and the reaction was stopped with water as described above. Distillation yielded 2.7 g (65%) of (*E*)-1-chloro-5-methyl-5-phenyl-2-hexene (**3j**): bp (bath) $65\text{--}80^{\circ}\text{C}$ (0.01 mmHg); $^1\text{H NMR}$ δ 1.30 (s, 6 H), 2.33 (m, 2 H), 3.83 (m, 2 H), 5.45 (m, 2 H), 7.18 (br s, 5 H); IR (neat) 968 cm^{-1} (*trans*-alkene); mass spectrum (96 eV), m/e (relative intensity) 208, 210 (0.7, 0.2, M^+), 172 (2), 157 (3), 119 (100). Anal. Calcd for $\text{C}_{13}\text{H}_{17}\text{Cl}$: C, 74.80; H, 8.21. Found: C, 75.03; H, 7.81.

Cumyl Chloride (1h) and Isobutene (2c). A solution of **1h** (3.1 g, 20 mmol) in 10 mL of CH_2Cl_2 was added dropwise within 0.5 h to a cooled (-78°C) solution of **2c** (2.2 g, 39 mmol) and $\text{ZnCl}_2\text{-Et}_2\text{O}$ (4 mL) in 35 mL of CH_2Cl_2 . After 4 h at -78°C the mixture was worked up as described to give 3.0 g (71%) 2-chloro-2,4-dimethyl-4-phenylpentane (**3k**): bp (bath) $64\text{--}69^{\circ}\text{C}$ (0.1 mmHg); $^1\text{H NMR}$ δ 1.29 (s, 6 H), 1.46 (s, 6 H), 2.36 (s, 2 H), 7.0–7.5 (m, 5 H); mass spectrum (96 eV), m/e (relative intensity) 210 (1.3, M^+), 119 (100). Anal. Calcd for $\text{C}_{13}\text{H}_{19}\text{Cl}$: C, 74.09; H, 9.09. Found: C, 74.56; H, 9.09.

Cumyl Chloride (1h) and Styrene (2d). A solution of **1h** (3.1 g, 20 mmol) and **2d** (2.1 g, 20 mmol) in 20 mL of CH_2Cl_2 was added dropwise to a solution of $\text{ZnCl}_2\text{-Et}_2\text{O}$ (4 mL) in 35 mL of CH_2Cl_2 at -78°C . After 15 h at -78°C the mixture was worked up as described to give 3.68 g (71%) 1-chloro-3-methyl-1,3-diphenylbutane (**3l**): bp (bath) $82\text{--}98^{\circ}\text{C}$ (0.001 mmHg); $^1\text{H NMR}$ δ 1.14 (s, 3 H), 1.41 (s, 3 H), 2.52 (d, $J = 6$ Hz, 2 H), 4.51 (t, $J = 6$ Hz, 1 H), 7.14 (s, 5 H), 7.22 (s, 5 H); mass spectrum (70 eV), m/e (relative intensity) 258, 260 (10, 3, M^+), 207 (53), 119 (100). Anal. Calcd for $\text{C}_{17}\text{H}_{19}\text{Cl}$: C, 78.90; H, 7.40. Found: C, 78.45; H, 7.16.

Cumyl Chloride (1h) and Isoprene (2e). $\text{ZnCl}_2\text{-Et}_2\text{O}$ (4 mL) was dissolved in 30 mL of CH_2Cl_2 and cooled to -78°C . Solutions of **1h** (3.1 g, 20 mmol) in 10 mL of CH_2Cl_2 and **2e** (1.4 g, 20 mmol) in 10 mL of CH_2Cl_2 were successively added, each within 20 min. After being allowed to stand 4 h at -78°C , the mixture was worked up as described to give 2.83 g (64%) of (*E*)-1-chloro-3,5-dimethyl-5-phenyl-2-hexene (**3m**): bp (bath) $55\text{--}62^{\circ}\text{C}$ (0.001 mmHg); $^1\text{H NMR}$ δ 1.24 (d, $J = 1$ Hz, 3 H), 1.32 (s, 6 H), 2.34 (s, 2 H), 3.91 (d, $J = 8$ Hz, 2 H), 5.30 (br t, $J = 8$ Hz, 1 H), 7.0–7.4 (m, 5 H); mass spectrum (70 eV), m/e (relative intensity) 222, 224 (0.7, 0.2, M^+), 186 (16), 119 (100). Anal. Calcd for $\text{C}_{14}\text{H}_{19}\text{Cl}$: C, 75.48; H, 8.60. Found: C, 75.82; H, 8.87.

Cumyl Chloride (1h) and α -Methylstyrene (2f). Compound **1h** (3.9 g, 25 mmol) dissolved in 10 mL of CH_2Cl_2 was added (10 min) to a precooled (-78°C) solution of $\text{ZnCl}_2\text{-Et}_2\text{O}$ (10 mL) in 40 mL of CH_2Cl_2 . Subsequently, a solution of **2f** (2.95 g, 25 mmol) in 10 mL of CH_2Cl_2 was added within 30 min, and the resulting mixture was kept at -78°C for 17 h to give 4-methyl-2,4-diphenyl-1-pentene (**8**): 3.4 g (58%); bp (bath) $75\text{--}82^{\circ}\text{C}$ (10^{-4} mmHg); $^1\text{H NMR}$ δ 1.22 (s, 6 H), 2.80 (s, 2 H), 4.75 (br s, 1 H), 5.08 (br s, 1 H), 7.16 (m, 10 H); mass spectrum (70 eV), m/e (relative intensity) 236 (87, M^+), 119 (100). Anal. Calcd for $\text{C}_{18}\text{H}_{20}$: C, 91.47; H, 8.53. Found: C, 90.99; H, 8.73.

Chlorodiphenylmethane (1i) and Propene (2a). A solution of **1i** (4.04 g, 19.9 mmol) in 10 mL of CH_2Cl_2 was added dropwise to a solution of $\text{ZnCl}_2\text{-Et}_2\text{O}$ (4 mL) and **2a** (2.04 g, 48.5 mmol) in 35 mL of CH_2Cl_2 at -78°C . The solution was allowed to warm to 2°C within 18 h, was washed with aqueous ammonia, and was

dried. Removal of solvent and recrystallization from ether-petroleum ether gave 4.50 g (92%) of 2-chloro-4,4-diphenylbutane (**3n**): mp 71°C ; $^1\text{H NMR}$ δ 1.49 (d, $J = 7$ Hz, 3 H), 2.35 (t, $J = 7$ Hz, 2 H), 3.72 (sextet, $J = 7$ Hz, 1 H), 4.27 (t, $J = 7$ Hz, 1 H), 7.23 (br s, 10 H); mass spectrum (70 eV), m/e (relative intensity) 244, 246 (12, 4, M^+), 167 (100). Anal. Calcd for $\text{C}_{18}\text{H}_{17}\text{Cl}$: C, 78.51; H, 7.00. Found: C, 78.83; H, 7.18.

Chlorodiphenylmethane (1i) and 1,3-Butadiene (2b). A solution of **1i** (4.04 g, 19.9 mmol) in 10 mL of CH_2Cl_2 was added dropwise to a solution of **2b** (3.24 g, 59.9 mmol) and 4 mL $\text{ZnCl}_2\text{-Et}_2\text{O}$ in 45 mL CH_2Cl_2 at -78°C . After being allowed to stand 4 days at -78°C , the solution was washed with aqueous ammonia and dried. Evaporation of the solvent and distillation yielded 4.35 g (85%) of 1-chloro-5,5-diphenyl-2-pentene (**3o**) and 3-chloro-5,5-diphenyl-1-pentene (**3o'**) (57:43), bp (bath) $115\text{--}130^{\circ}\text{C}$ (10^{-4} mmHg). Pure **3o** was obtained when 1.0 g of the **3o/3o'** mixture in 12 mL of CH_2Cl_2 was treated with 3 mL of $\text{ZnCl}_2\text{-Et}_2\text{O}$ (9 h, 0°C). **3o**: mp $40\text{--}45^{\circ}\text{C}$ (petroleum ether) $^1\text{H NMR}$ δ 2.74 (m, 2 H), 3.7–4.15 (m, 3 H), 5.55 (m, 2 H), 7.18 (s, 10 H); mass spectrum (96 eV), m/e (relative intensity) 256, 258 (3, 1, M^+), 165 (100). Anal. Calcd for $\text{C}_{17}\text{H}_{17}\text{Cl}$: C, 79.52; H, 6.67. Found: C, 79.90; H, 6.91. **3o'**: $^1\text{H NMR}$ δ 2.46 (t, $J = 7.5$ Hz, 2 H), 4.21 (t, $J = 7.5$ Hz, 1 H), 4.9–5.3 (m, $=\text{CH}_2$), 5.88 (ddd, $J = 17, 10, 8$ Hz, 1 H), other signals masked.

Chlorodiphenylmethane (1i) and Isobutene (2c). Compound **1i** (4.4 g, 22 mmol) was dissolved in 10 mL of CH_2Cl_2 and added slowly to a solution of **2c** (1.2 g, 22 mmol) and $\text{ZnCl}_2\text{-Et}_2\text{O}$ (4 mL) in 45 mL of CH_2Cl_2 at -78°C . A workup after 15 h at -78°C gave 5.5 g (97%) of 2-chloro-2-methyl-4,4-diphenylbutane (**3p**): mp $44\text{--}45^{\circ}\text{C}$ (ether-petroleum ether); $^1\text{H NMR}$ δ 1.38 (s, 6 H), 2.58 (d, $J = 6$ Hz, 2 H), 4.32 (t, $J = 6$ Hz, 1 H), 7.22 (m, 10 H); mass spectrum (96 eV), m/e (relative intensity) 258, 260 (15, 5, M^+), 167 (100). Anal. Calcd for $\text{C}_{17}\text{H}_{19}\text{Cl}$: C, 78.90; H, 7.40. Found: C, 79.02; H, 7.31.

Chlorodiphenylmethane (1i) and Styrene (2d). A solution of **2d** (2.08 g, 20.0 mmol) in 10 mL of CH_2Cl_2 was slowly added to a solution of **1i** (4.04 g, 19.9 mmol) and $\text{ZnCl}_2\text{-Et}_2\text{O}$ (4 mL) in 45 mL of CH_2Cl_2 at -78°C . After 15 h at -78°C the mixture was worked up to give 5.38 g (88%) of 1-chloro-1,3,3-triphenylpropane (**3q**): mp $95\text{--}96^{\circ}\text{C}$ (ether) (lit.¹⁵ mp $97\text{--}98^{\circ}\text{C}$); $^1\text{H NMR}$, see ref 15.

Chlorodiphenylmethane (1i) and Isoprene (2e). A solution of **2e** (2.04 g, 30.0 mmol) in 10 mL of CH_2Cl_2 was added dropwise to a solution of $\text{ZnCl}_2\text{-Et}_2\text{O}$ (4 mL) and **1i** (6.06 g, 29.9 mmol) in 25 mL of CH_2Cl_2 and allowed to stand 6 h at -78°C . The solution was washed with aqueous ammonia, dried, and distilled to give (*E*)-1-chloro-3-methyl-5,5-diphenyl-2-pentene (**3r**): 6.60 g (82%); bp (bath) $120\text{--}135^{\circ}\text{C}$ (10^{-4} mmHg); $^1\text{H NMR}$ δ 1.63 (br s, 3 H), 2.74 (br d, $J = 8$ Hz, 2 H), 3.83 (d, $J = 8$ Hz, 2 H), 4.09 (t, $J = 8$ Hz, 1 H), 5.26 (br t, $J = 8$ Hz, 1 H), 7.1 (s, 10 H); mass spectrum (96 eV), m/e (relative intensity) 270 (1, M^+), 234 (38), 167 (100). Anal. Calcd for $\text{C}_{18}\text{H}_{19}\text{Cl}$: C, 79.83; H, 7.07. Found: C, 80.17; H, 7.12.

Chlorodiphenylmethane (1i) and α -Methylstyrene (2f). (a) A solution of **2f** (2.36 g, 20.0 mmol) in 10 mL of CH_2Cl_2 was added slowly (1 h) to a solution of 2 mL of $\text{ZnCl}_2\text{-Et}_2\text{O}$ and **1i** (4.04 g, 19.9 mmol) in 50 mL of CH_2Cl_2 at -78°C . After 10 min the solution was washed with aqueous ammonia and dried and the solvent evaporated to give 2-chloro-2,4,4-triphenylbutane (**3s**) contaminated by some **1i**: $^1\text{H NMR}$ δ 1.67 (s, 3 H), 2.97 (d, $J = 6$ Hz, 2 H), 3.99 (t, $J = 6$ Hz, 1 H), 6.8–7.5 (mc). **3s**, which was formed in 75% yield according to NMR, was identified by the following elimination reaction.

The crude product and 6.0 g (53 mmol) of KO-*t*-Bu in 40 mL of *tert*-butyl alcohol were heated at reflux for 6 h. H_2O (20 mL) was added and the mixture extracted with 40 mL of CH_2Cl_2 . The organic layer was dried over CaCl_2 , the solvent evaporated, and the residue distilled to give 2,4,4-triphenyl-1-butene: 4.1 g (72%); bp (bath) $150\text{--}160^{\circ}\text{C}$ (0.03 mmHg); $^1\text{H NMR}$ δ 3.19 (br d, $J = 7.5$ Hz, 2 H), 4.01 (br t, $J = 7.5$ Hz, 1 H), 4.79 (br s, 1 H), 5.07 (br s, 1 H), 7.12 (s, 10 H), 7.23 (s, 5 H); mass spectrum (70 eV), m/e (relative intensity) 284 (8, M^+), 269 (3), 193 (8), 167 (100). Anal. Calcd for $\text{C}_{22}\text{H}_{20}$: C, 92.91; H, 7.09. Found: C, 93.30; H, 7.12.

(b) Solutions of **2f** (2.36 g, 20.0 mmol) in 10 mL of CH_2Cl_2 and **1i** (4.04 g, 19.9 mmol) in 10 mL of CH_2Cl_2 were subsequently added

to $\text{ZnCl}_2\text{-Et}_2\text{O}$ (4 mL) in 35 mL of CH_2Cl_2 at -78°C . After 18 h the mixture was worked up as described and gave 2.29 g (47%) of 3-chloro-1,1,3,5,5-pentaphenylpentane (10): needles; mp $146\text{--}150^\circ\text{C}$ (ether); $^1\text{H NMR}$ δ 2.87, 2.83 (2 d, $J = 6$ Hz, 4 H), 4.05 (br t, $J = 6$ Hz, 2 H), 6.7–7.5 (m, 25 H); mass spectrum (70 eV), m/e (relative intensity) 486 (0.2, M^+), 450 (44), 284 (39), 283 (29), 282 (21), 270 (64), 269 (100). Anal. Calcd for $\text{C}_{35}\text{H}_{31}\text{Cl}$: C, 86.30; H, 6.42. Found: C, 86.20; H, 6.28.

Chloromethyl Methyl Ether (1j) and α -Methylstyrene (2f). A solution of 2f (4.7 g, 40 mmol) in 20 mL of CH_2Cl_2 was added dropwise to a solution of $\text{ZnCl}_2\text{-Et}_2\text{O}$ (2 mL) and 1j (6.4 g, 80 mmol) in 70 mL of CH_2Cl_2 . After being allowed to stand 21 h at -78°C , the mixture was worked up to give 2.9 g (37%) of 2-chloro-2-phenyl-4-methoxybutane (3y): bp (bath) $45\text{--}50^\circ\text{C}$ (0.01 mmHg); $^1\text{H NMR}$ δ 1.94 (s, 3 H), 2.38 (t, $J = 7$ Hz, 2 H), 3.19 (s, 3 H), 3.40 (t, $J = 7$ Hz, 2 H), 7.1–7.7 (m, 5 H); mass spectrum (70 eV), m/e (relative intensity) 198 (2, M^+), 162 (30), 147 (59), 132 (100). Anal. Calcd for $\text{C}_{11}\text{H}_{15}\text{ClO}$: C, 66.49; H, 7.61. Found: C, 66.19; H, 7.26.

Trityl Chloride (1k) and Isobutene (2c). Solutions of $\text{ZnCl}_2\text{-Et}_2\text{O}$ (4 mL) in 4 mL of CH_2Cl_2 and 1k (4.96 g, 17.8 mmol) in 10 mL of CH_2Cl_2 were added successively to a solution of 2c (1.00 g, 17.8 mmol) in 40 mL of CH_2Cl_2 at -78°C . The mixture was warmed up slowly, kept at 0°C for 15 h, and worked up as described to give 5.3 g of crude product. Chromatographic separation (silica gel; CH_2Cl_2 /petroleum ether, 1:3) yielded 1.1 g (21%) 1,1-dimethyl-3,3-diphenylindane [13:³¹ $^1\text{H NMR}$ δ 1.17 (s, 6 H), 2.88 (s, 2 H), 7.14 (s, ~ 10 H), 7.19 (s, ~ 4 H)], 0.95 g (22%) of triphenylmethane, 0.44 g (8%) of 2-methyl-4,4,4-triphenyl-1-butene [12: $^1\text{H NMR}$ δ 1.41 (s, 3 H), 3.32 (s, 2 H), 4.24 (br s, 1 H), 4.62 (br s, 1 H), 6.0–7.3 (m, 15 H)], and triphenylmethanol contaminated by high molecular weight compounds.

α -Methoxybenzyl Chloride (1m) and Propene (2a). When a solution of 1m (3.1 g, 20 mmol) in 20 mL of CH_2Cl_2 was added dropwise to a solution of 2a (2.1 g, 50 mmol) and 2 mL of $\text{ZnCl}_2\text{-Et}_2\text{O}$ in 30 mL of CH_2Cl_2 at -30°C , a colorless precipitate formed. After 2 h the mixture was warmed to 0°C ; the precipitate dissolved, and the mixture turned brownish. After 1 h the reaction was stopped by pouring it onto aqueous ammonia. The organic layer was washed with NaHSO_3 solution and water and dried, and the solvent was evaporated to give 3.0 g of crude product. HPLC (silica gel; ether/petroleum ether, 7.5:92.5) yielded 535 mg (16%) of 14, 743 mg (19%) of 3z, and 1.69 g (43%) of 3z' (increasing retention times).

1-Chloro-1-phenylbutane (14): bp (bath) $50\text{--}60^\circ\text{C}$ (0.03 mmHg); $^1\text{H NMR}$ (100 MHz) δ 0.92 (t, $J = 7$ Hz, 3 H), 1.5 (m, 2 H), 2.0 (m, 2 H), 4.77 (t, $J = 7$ Hz, 1 H), 7.28 (m, 5 H); $^{13}\text{C NMR}$ δ 13.4, 20.3, 42.0, 63.5, 126.9 (double intensity), 128.1, 128.5 (double intensity), 141.9; mass spectrum (70 eV), m/e (relative intensity) 168, 170 (27, 8, M^+), 133 (100), 125 (87), 91 (90), 77 (22).

2-Chloro-4-methoxy-4-phenylbutane (isomer 1, 3z): bp (bath) $44\text{--}48^\circ\text{C}$ (0.03 mmHg); $^1\text{H NMR}$ (100 MHz) δ 1.47 (d, $J = 7$ Hz, 3 H), 1.5–2.1 (m, 2 H), 3.16 (s, 3 H), 4.2–4.4 (m, 2 H), 7.27 (br s, 5 H); $^{13}\text{C NMR}$ δ 25.7, 49.4, 55.5, 56.8, 80.6, 126.3 (double intensity), 127.6, 128.5 (double intensity), 141.8; mass spectrum (70 eV), m/e (relative intensity) 198, 200 (0.3, 0.1, M^+), 162 (0.2), 161 (0.2), 147 (0.3), 121 (100). Anal. Calcd for $\text{C}_{11}\text{H}_{15}\text{ClO}$: C, 66.49; H, 7.61. Found: C, 66.58; H, 7.39.

2-Chloro-4-methoxy-4-phenylbutane (isomer 2, 3z'): bp (bath) $44\text{--}48^\circ\text{C}$ (0.03 mmHg); $^1\text{H NMR}$ (100 MHz) δ 1.44 (d, $J = 6.5$ Hz, 3 H), 1.8 (m, 1 H), 2.25 (m, 1 H), 3.08 (s, 3 H), 3.69 (m, 1 H), 4.24 (br t, $J = 7$ Hz, 1 H), 7.20 (s, 5 H); $^{13}\text{C NMR}$ δ 25.2, 48.1, 54.8, 56.3, 81.3, 126.8 (double intensity), 127.9, 128.5 (double intensity), 140.8; mass spectrum (70 eV), m/e (relative intensity) 198, 200 (0.3, 0.1, M^+), 162 (0.2), 161 (0.2), 147 (0.3), 121 (100).

(31) Richey, H. G., Jr.; Lustgarten, R. K.; Richey, J. M. *J. Org. Chem.* 1968, 33, 4543.

α -Methoxybenzyl Chloride (1m) and Isobutene (2c). At -78°C 2c (2.7 g, 50 mmol) was added to a solution of 2.5 mL of $\text{ZnCl}_2\text{-Et}_2\text{O}$ in 40 mL of CH_2Cl_2 . Subsequently, a solution of 1m (3.1 g, 20 mmol) in 10 mL of CH_2Cl_2 was added dropwise. A yellow precipitate, which was formed during this procedure, dissolved when the reaction mixture was stirred for 2 h at -78°C . The reaction mixture was poured onto aqueous ammonia solution, washed with NaHSO_3 solution and water, dried, and distilled to give 2-chloro-4-methoxy-2-methyl-4-phenylbutane (3bb): 3.8 g (90%); bp (bath) $52\text{--}65^\circ\text{C}$ (0.02 mmHg); $^1\text{H NMR}$ δ 1.58 (s, 3 H), 1.69 (s, 3 H), 2.04 (d, $J = 4$ Hz, 1 H), 2.09 (d, $J = 7.5$ Hz, 1 H), 3.18 (s, 3 H), 4.45 (dd, $J = 7.5, 4$ Hz, 1 H), 7.27 (s, 5 H); mass spectrum (70 eV), m/e (relative intensity) 214, 212 (1, 4, M^+), 176 (23), 121 (100). Anal. Calcd for $\text{C}_{12}\text{H}_{17}\text{ClO}$: C, 67.75; H, 8.06. Found: C, 67.88; H, 7.74.

α -Methoxybenzyl Chloride (1m) and α -Methylstyrene (2f). $\text{ZnCl}_2\text{-Et}_2\text{O}$ (2 mL) was added to a solution of 1m (3.1 g, 20 mmol) in 40 mL of CH_2Cl_2 at -78°C . A solution of 2f (2.4 g, 20 mmol) in 20 mL of CH_2Cl_2 was added dropwise. After 2 h at -78°C , the solution was washed with aqueous ammonia, NaHSO_3 solution, and water and dried, and the solvent was evaporated. Since distillation resulted in decomposition of the addition product, the crude material was purified by HPLC (silica gel; petroleum ether/ether, 82:18) to give 3.8 g (69%) of 3ee as a mixture of two diastereomers ($\sim 5:4$). HPLC of this mixture resulted in partial decomposition of the products, and only the major isomer could be obtained as a pure sample. 2-Chloro-4-methoxy-2,4-diphenylbutane (3ee): $^1\text{H NMR}$ (major isomer) δ 2.08 (s, 3 H), 2.53 (d, $J = 4$ Hz, 1 H), 2.60 (d, $J = 8$ Hz, 1 H), 2.88 (s, 3 H), 3.73 (dd, $J = 8, 4$ Hz, 1 H), 7.0–7.7 (m, 10 H); $^1\text{H NMR}$ (minor isomer) δ 2.03 (s, 3 H), 2.37 (d, $J = 4$ Hz, 1 H), 2.40 (d, $J = 7$ Hz, 1 H), 3.18 (s, 3 H), 4.55 (dd, $J = 7, 4$ Hz, 1 H), 7.0–7.7 (m); mass spectrum (both isomers, 96 eV) m/e (relative intensity) 274 (0.1, M^+), 238 (4), 206 (2), 121 (91), 118 (100), 117 (68). Anal. Calcd for $\text{C}_{17}\text{H}_{19}\text{ClO}$: C, 74.30; H, 6.97. Found: C, 74.59; H, 6.89.

α -Methoxybenzyl Chloride (1m) and Ethyl Vinyl Ether (2g). $\text{ZnCl}_2\text{-Et}_2\text{O}$ (1.4 mL) was added to a solution of 1m (4.1 g, 26 mmol) in 40 mL of CH_2Cl_2 at -78°C . A colorless precipitate formed, which dissolved when 2g (1.9 g, 26 mmol) in 20 mL of CH_2Cl_2 was added dropwise within 30 min. The mixture was stirred for another 15 min, poured onto water, and extracted with concentrated NaHSO_3 solution. The organic layer was dried and the solvent evaporated to give 1.2 g (20%) of an oil, a mixture of six 1:1 addition products (HPLC). Acidification of the NaHSO_3 solution and extraction with ether yielded 0.50 g of benzaldehyde. The bisulfite solution was then treated with 2 N NaOH to give pH 12 and stirred for 4 h at 25°C . Extraction with ether yielded a mixture of 0.33 g of benzaldehyde and 1.67 g (48%) of cinnamaldehyde.

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Registry No. 1a, 75-29-6; 1b, 507-20-0; 1e, 672-65-1; 1h, 934-53-2; 1i, 90-99-3; 1j, 107-30-2; 1k, 76-83-5; 1m, 35364-99-9; 2a, 115-07-1; 2b, 106-99-0; 2c, 115-11-7; 2d, 100-42-5; 2e, 78-79-5; 2f, 98-83-9; 2g, 109-92-2; 3a, 33429-72-0; (E)-3b, 84803-15-6; 3c (isomer 1), 84803-16-7; 3c (isomer 2), 84803-17-8; 3d, 84803-18-9; 3d', 84803-19-0; 3e, 33484-99-0; 3f (isomer 1), 84803-20-3; 3f (isomer 2), 84803-21-4; 3i, 33484-54-7; (E)-3j, 84803-22-5; 3k, 84803-23-6; 3l, 84803-24-7; (E)-3m, 84803-25-8; 3n, 36317-61-0; 3o, 84803-26-9; 3o', 84803-27-0; 3p, 84803-28-1; 3q, 70550-48-0; (E)-3r, 84803-29-2; 3s, 84803-30-5; 3y, 84803-31-6; 3z, 84803-32-7; 3z', 84803-33-8; 3bb, 71375-49-0; 3ee (isomer 1), 84803-34-9; 3ee (isomer 2), 84803-35-0; 3ff, 84803-36-1; 6, 3910-35-8; 7, 84803-37-2; 8, 6362-80-7; 9, 5424-75-9; 10, 84803-38-3; 12, 84803-39-4; 13, 84803-40-7; 14, 27059-40-1; 2,4,4-triphenyl-1-butene, 84803-41-8; ZnCl_2 , 7646-85-7; BCl_3 , 10294-34-5.