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.

Acknowledgment. We thank Professor D. N. Kevill and Dr. G. Schrumpf for stimulating discussions and the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for support of this work.

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

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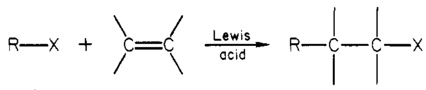
Lewis acid catalyzed addition reactions of alkyl halides **1** with unsaturated hydrocarbons **2** have been studied. 1:1 addition products **3** are formed if the addends **1** dissociate faster than the corresponding products **3**; otherwise, polymerization of **2** takes place. For reaction conditions 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]



(1)

1 **2** **3**

Prins[4] found that polychloroalkanes alkylate chlorinated alkenes readily in the presence of aluminum chloride (eq 2). Schmerling showed that monohaloalkanes, particularly

$$CHCl_3 + CH_2{=}CHCl \xrightarrow[AlCl_3]{} Cl_2CHCH_2CHCl_2 \quad (2)$$

$$(CH_3)_3CCl + CH_2{=}CH_2 \xrightarrow[AlCl_3]{} (CH_3)_3CCH_2CH_2Cl \quad (3)$$

tert-alkyl halides, also undergo Lewis acid catalyzed addition reactions with halogenated as well as nonhalogenated 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
$(CH_3)_2CHCl$ (**1a**)	2×10^{-9}	8a
$CH_2{=}CHCH(CH_3)Cl$ (**1b**)	5×10^{-7}	8b
$CH_3CH{=}CHCH_2Cl$ (**1c**)	$\sim 1 \times 10^{-6}$	*a*
$(CH_3)_3CCl$ (**1d**)	9×10^{-6}	8b,d
$PhCH(CH_3)Cl$ (**1e**)	1×10^{-5}	8e
$(CH_3)_2C{=}CHCH_2Cl$ (**1f**)	$\sim 4 \times 10^{-4}$	*a*
$PhC{\equiv}CC(CH_3)_2Cl$ (**1g**)	2×10^{-3}	8f
$PhC(CH_3)_2Cl$ (**1h**)	$\sim 2 \times 10^{-3}$	*b*
Ph_2CHCl (**1i**)	2×10^{-3}	8b
CH_3OCH_2Cl (**1j**)	15	8h
Ph_3CCl (**1k**)	$\sim 2 \times 10^{2}$	8i
$CH_3OCH(CH_3)Cl$ (**1l**)	>15	
$CH_3OCH(Ph)Cl$ (**1m**)	$\gg 15$	

[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 $(\Delta G^{\ddagger}_2)_R$ are reflected by the relative dis-

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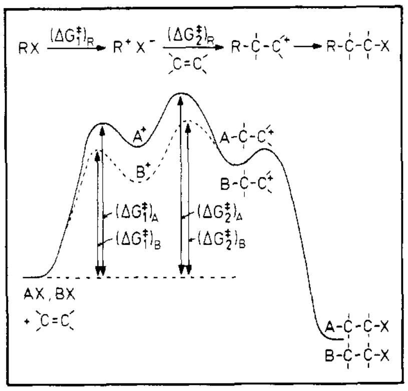
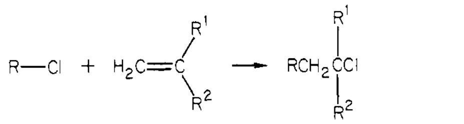


Figure 1. Energy profiles for the Lewis acid catalyzed reactions of alkyl halides AX and BX with a common alkene.

sociation rates of AX and BX $(\Delta G^\ddagger_1)_R$. Noncrossing of the reaction profiles in Figure 1 (i.e., applicability of the Leffler–Hammond postulate[9]) 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



(4)

1a–m **2a–g** **3a–ff**

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

$(CH_3)_3CCH_2CH(CH_3)Cl$ **3a** $(CH_3)_2CClCH(CH_3)CH_2CH_3$ **4**

$(CH_3)_2CHC(CH_3)ClCH_2CH_3$ **5**

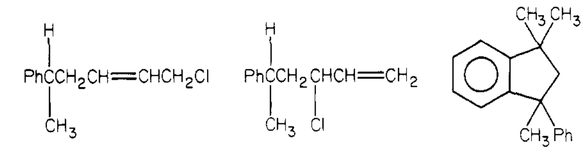
variable yields.[11,12] When we used $ZnCl_2$–Et_2O in dichloromethane to catalyze this reaction, **4** and **5** were not detectable in the ^1H NMR spectrum, indicating predominant formation of **3a**.

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

$(CH_3)_3CCH_2CH{=}CHCH_2Cl$ **3b**

chloride (**1d**) and butadiene (**2b**), while **1d** and isoprene (**2e**) give oligomers of the general formula $[C_4H_9\text{–}(C_5H_8)_{2.3}\text{–}Cl]_{1.9}$ 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.

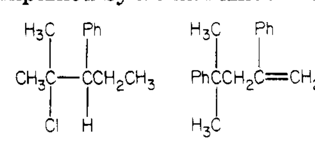
The data on (α-chloroethyl)benzene (**1e**) additions in Table II are contradictory. Previous workers reported the formation of 1:1 products by $ZnCl_2$-catalyzed reactions of **1e** with **2a–f**.[14] The products were identified by their boiling points or the boiling points of their HCl elimination 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.



3d **3d′** **6**

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 $ZnCl_2$–Et_2O 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



7 **8**

successive 1,2 hydride and phenyl shifts in the intermediate carbenium ions. $ZnCl_2$–Et_2O 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 $ZnCl_2$–Et_2O 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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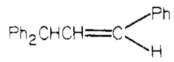
Table II. Lewis Acid Catalyzed Reactions of Alkyl Halides with Alkenes

R-Cl	alkene[d]	catalyst	temp, °C	time	products (yield, %)	ref
$(CH_3)_2CHCl$ (1a)	2a	$ZnCl_2$-Et_2O	−78	36 days	no reaction	*a*
		$ZnCl_2$-Et_2O	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_2O	20	10 days	oligomers	*a*
	2e	$ZnCl_2$, $SnCl_4$			polymers	10
$(CH_3)_3CCl$ (1d)	2a	$AlCl_3$	−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		$C_7H_{15}Cl$ (70)	12
		$ZnCl_2$-Et_2O	0	17 h	3a (major) (41)	*a*
	2b	$ZnCl_2$	20		3b (20–35)	10, 13
		$ZnCl_2$-Et_2O	−30	48 h	3b (20)	*a*
	2c	$ZnCl_2$-Et_2O	0	15 h	oligomers	*a*
	2d	$ZnCl_2$-Et_2O	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_2O	0	15 h	3c (52)	*a*
	2b	$ZnCl_2$	20–70	1 h	3d (45)	14a
		$ZnCl_2$-Et_2O	−30	22 h	3d (39), 3d′ (12)	*a*
	2c	$ZnCl_2$	20–50	1 h	3e (95)[b]	14a,b
		$ZnCl_2$-Et_2O	−78	4 days	3e (71)	*a*
	2d	$ZnCl_2$	45–60	1 h	3f (70)	14a,b
		$ZnCl_2$			polymers	15
		$ZnCl_2$-Et_2O	0	22 h	3f (72)	*a*
	2e	$ZnCl_2$	20–30		3g (56)[c]	14a
		$ZnCl_2$	variable		polymers	*a*
		$ZnCl_2$-Et_2O	conditions		polymers	*a*
	2f	$ZnCl_2$	45–60		3h (57)[b]	14a,b
		$ZnCl_2$	50	4 h	6 (80)	*a*
$PhC(CH_3)_2Cl$ (1h)	2a	$ZnCl_2$-Et_2O	−78	18 h	decomp of 1h	*a*
		BCl_3	−78	6 h	3i (43), 7 (15)	*a*
	2b	$ZnCl_2$-Et_2O	−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_2O	−78	4 h	3k (71)	*a*
	2d	$ZnCl_2$-Et_2O	−78	15 h	3l (71)	*a*
	2e	$ZnCl_2$-Et_2O	−78	4 h	3m (64)	*a*
	2f	$ZnCl_2$-Et_2O	−78	17 h	8 (58)	*a*
	2g	$ZnCl_2$-Et_2O	−78	4 h	polyvinyl ether	*a*
Ph_2CHCl (1i)	2a	$ZnCl_2$-Et_2O	−78 to +2		3n (92)	*a*
	2b	$ZnCl_2$-Et_2O	−78	4 days	3o (48), 3o′ (37)	*a*
	2c	$ZnCl_2$-Et_2O	−78	15 h	3p (97)	*a*
	2d	$ZnCl_2$	40	6 h	3q (54), 9 (8)	15
		$ZnCl_2$-Et_2O	−78	15 h	3q (88)	*a*
	2e	$ZnCl_2$-Et_2O	−78	6 h	3r (82)	*a*
	2f	$ZnCl_2$-Et_2O	−78	1 h	3s (75)	*a*
		$ZnCl_2$-Et_2O	−78	18 h	10 (47)	*a*
	2g	$ZnCl_2$-Et_2O	−78	3 h	polyvinyl ether	*a*
CH_3OCH_2Cl (1j)	2a	$ZnCl_2$	30	3 h	3t (47)	16
	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_2O	−78	21 h	3y (37)	*a*
	2g	$ZnCl_2$-Et_2O	−78	4 h	oligomers	*a*
Ph_3CCl (1k)	2c	$ZnCl_2$-Et_2O	−78	19 h	no reaction	*a*
		$ZnCl_2$-Et_2O	0	15 h	13 (21), 12 (8)	*a*
	2e	$ZnCl_2$-Et_2O	−78	15 h	polymers	*a*
	2f	$ZnCl_2$-Et_2O	−78	16 h	no reaction	*a*
	2g	$ZnCl_2$-Et_2O	−78	17 h	polyvinyl ether	*a*
$PhCH(OCH_3)Cl$ (1m)	2a	$ZnCl_2$-Et_2O	−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_2O	−78	2 h	3bb (90)	*a*
	2d	$ZnCl_2$-Et_2O	20	1 day	3cc (57)	20
	2e	$ZnCl_2$	20	10 days	3dd (52)	21
	2f	$ZnCl_2$-Et_2O	−78	2 h	3ee (69)	*a*
	2g	$ZnCl_2$-Et_2O	−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.



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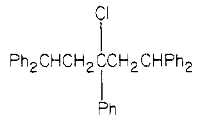

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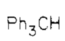
3q can be obtained by carrying out the reaction at −78 °C with $ZnCl_2$–Et_2O as a catalyst. Adduct **3s**, formed from benzhydryl chloride (**1i**) and α-methylstyrene (**2f**), decomposed to give the 2:1 product **10** when exposed to $ZnCl_2$–Et_2O for several hours. This reaction can be rationalized 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 $ZnCl_2$–Et_2O 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 $ZnCl_2$–Et_2O-catalyzed reaction of **1k** with isobutene (**2c**).



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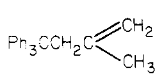

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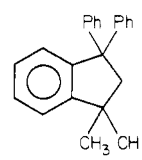

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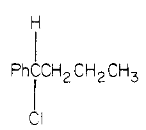
α-Methoxybenzyl chloride (**1m**) was the only alkylating agent in this series which gave 1:1 products with all alkenes **2a–g**. Reaction with propene gives addition products **3z,z′** as a 31:69 mixture of two diastereomers (62%) with 16% **14**. The mechanism of formation of the latter product is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



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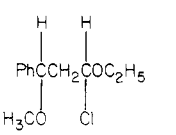

3ff

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 prediction[7]—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 $ZnCl_2$–Et_2O, 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 $(\Delta G^{\ddagger}_2)_A$ and $(\Delta G^{\ddagger}_2)_B$ 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 $(\Delta G^{\ddagger}_1)_A$ and $(\Delta G^{\ddagger}_1)_B$ 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 $(\Delta G^{\ddagger}_2)_A$ and $(\Delta G^{\ddagger}_2)_B$ will be. It can be derived that the above rules even have to be reversed if dissociation of RX becomes exothermic (stable ion conditions).

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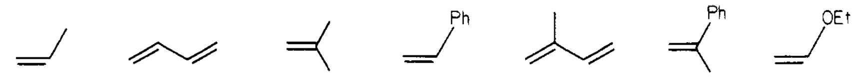
Table III. Yields of 1:1 Products from Lewis Acid Catalyzed Addition Reactions of Alkyl Halides with Alkenes (Predictions in Parentheses)



RCl	alkene 2a	2b	2c	2d	2e	2f	2g
$(CH_3)_2CHCl$ (1a)	0	0	0	(0)	0	0	(0)
$(CH_3)_3CCl$ (1d)	41	35	0	0	0	(0)	(0)
$PhCH(CH_3)Cl$ (1e)	52	50	71	72	0	0	(0)
$(CH_3)_2C{=}CHCH_2Cl$ (1f)	32[22]	27[23]	65[22]	75[22]	10[24]	0[22]	0[22]
$PhC{\equiv}CC(CH_3)_2Cl$ (1g)	67[25]	46[26]	93[27]	91[28]	67[26]	0[28]	0[28]
$PhC(CH_3)_2Cl$ (1h)	58	65	71	71	64	58	0
Ph_2CHCl (1i)	92	85	97	88	82	75	0
CH_3OCH_2Cl (1j)	47	70	60	75	64	37	0
$CH_3OCH(Ph)Cl$ (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 $(\Delta G^{\ddagger}{}_2)_R$ 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 ^{13}C NMR spectra on a JEOL JNM-PS-100 spectrometer. Chemical shifts (δ) were recorded relative to $(CH_3)_4Si$ as an internal standard.

It was advantageous to use $ZnCl_2$ in a homogeneous solution. For this purpose 50 g of $ZnCl_2$ (commercial quality, Merck) was dissolved in 60 mL of ether. This solution (referred to as $ZnCl_2$–Et_2O in the following) can be diluted with CH_2Cl_2. 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 CH_2Cl_2 was added to a solution of 4 mL of $ZnCl_2$–Et_2O and 1.68 g (39.9 mmol) of **2a** in 45 mL of CH_2Cl_2 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 $C_7H_{15}Cl$: 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 CH_2Cl_2 reacted at −30 °C in the presence of 4 mL of $ZnCl_2$–Et_2O 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 = 6Hz, 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 $C_8H_{15}Cl$: 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 CH_2Cl_2 was added to a solution of 4 mL of $ZnCl_2$–Et_2O and 2.5 g (59 mmol) of **2a** in 35 mL of CH_2Cl_2 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 $C_{11}H_{15}Cl$: 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 $ZnCl_2$–Et_2O in 65 mL of CH_2Cl_2 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 $C_{12}H_{15}Cl$: 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 $ZnCl_2$–Et_2O (4 mL) catalyzed reaction of **2c** (1.1 g, 20 mmol) with **1e** (2.8 g, 20 mmol) in 45 mL of CH_2Cl_2 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 $C_{12}H_{17}Cl$: 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 CH_2Cl_2 was added to a solution of **2d** (4.2 g, 40 mmol) and $ZnCl_2$–Et_2O (8 mL) in 80 mL of CH_2Cl_2 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 $C_{16}H_{17}Cl$: 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 $ZnCl_2$ (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 NMR[30] 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 BCl_3 solution in CH_2Cl_2 (2 mL) was added to a solution of **2a** (2.1 g, 50 mmol) in 30 mL of CH_2Cl_2 at −78 °C. **1h** (3.1 g, 20 mmol) dissolved in 20 mL of CH_2Cl_2 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) 48–60 °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}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}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 $C_{12}H_{17}Cl$: 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) 65–80 °C (0.01 mmHg); ^{1}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 $C_{13}H_{17}Cl$: 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 $ZnCl_2$–Et_2O (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) 64–69 °C (0.1 mmHg); ^{1}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 $C_{13}H_{19}Cl$: 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 $ZnCl_2$–Et_2O (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) 82–98 °C (0.001 mmHg); ^{1}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 $C_{17}H_{19}Cl$: C, 78.90; H, 7.40. Found: C, 78.45; H, 7.16.

Cumyl Chloride (1h) and Isoprene (2e). $ZnCl_2$–Et_2O (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) 55–62 °C (0.001 mmHg); ^{1}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 $C_{14}H_{19}Cl$: 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 $ZnCl_2$–Et_2O (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) 75–82 °C (10^{-4} mmHg); ^{1}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 $C_{18}H_{20}$: 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 $ZnCl_2$–Et_2O (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}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 $C_{16}H_{17}Cl$: 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 $ZnCl_2$–Et_2O 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) 115–130 °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 $ZnCl_2$–Et_2O (9 h, 0 °C). **3o**: mp 40–45 °C (petroleum ether) ^{1}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 $C_{17}H_{17}Cl$: C, 79.52; H, 6.67. Found: C, 79.90; H, 6.91. **3o′**: ^{1}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, =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 $ZnCl_2$–Et_2O (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 44–45 °C (ether–petroleum ether); ^{1}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 $C_{17}H_{19}Cl$: 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 $ZnCl_2$–Et_2O (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 95–96 °C (ether) (lit.[15] mp 97–98 °C); ^{1}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 $ZnCl_2$–Et_2O (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) 120–135 °C (10^{-4} mmHg); ^{1}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 $C_{18}H_{19}Cl$: 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 $ZnCl_2$–Et_2O 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}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) 150–160 °C (0.03 mmHg); ^{1}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 $C_{22}H_{20}$: 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 $ZnCl_2$–Et_2O (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 146–150 °C (ether); ^{1}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 $C_{35}H_{31}Cl$: 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 $ZnCl_2$–Et_2O (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) 45–50 °C (0.01 mmHg); ^{1}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 $C_{11}H_{15}ClO$: C, 66.49; H, 7.61. Found: C, 66.19; H, 7.26.

Trityl Chloride (1k) and Isobutene (2c). Solutions of $ZnCl_2$–Et_2O (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-diphenylindan [**13**:[31] ^{1}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}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 $ZnCl_2$–Et_2O 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) 50–60 °C (0.03 mmHg); ^{1}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}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) 44–48 °C (0.03 mmHg); ^{1}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}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 $C_{11}H_{15}ClO$: C, 66.49; H, 7.61. Found: C, 66.58; H, 7.39.

2-Chloro-4-methoxy-4-phenylbutane (isomer 2, 3z′): bp (bath) 44–48 °C (0.03 mmHg); ^{1}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}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).

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 $ZnCl_2$–Et_2O 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) 52–65 °C (0.02 mmHg); ^{1}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 $C_{12}H_{17}ClO$: C, 67.75; H, 8.06. Found: C, 67.88; H, 7.74.

α-Methoxybenzyl Chloride (1m) and α-Methylstyrene (2f). $ZnCl_2$–Et_2O (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 diasteromers (~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}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}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 $C_{17}H_{19}ClO$: C, 74.30; H, 6.97. Found: C, 74.59; H, 6.89.

α-Methoxybenzyl Chloride (1m) and Ethyl Vinyl Ether (2g). $ZnCl_2$–Et_2O (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.

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