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Surface-Mediated Reactions. 4. Hydrohalogenation of Alkynes[1]

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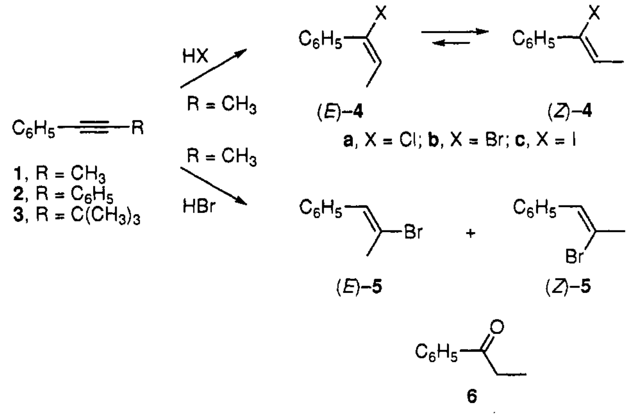
The use of appropriately prepared silica gel and alumina has been found to mediate the addition of hydrogen halides to alkynes. The technique has been rendered even more convenient by the use of various organic and inorganic acid halides that react in the presence of silica gel or alumina to generate hydrogen halides in situ. Treatment in this fashion of 1-propynylbenzene (**1**), which underwent no reaction in CH_2Cl_2 solution saturated with HCl, readily afforded the syn addition product, alkenyl chloride (*E*)-**4a**. On extended treatment (*E*)-**4a** underwent subsequent isomerization to the thermodynamically more stable *Z* isomer. Thus either isomer of **4a** could be obtained in good yield depending on the reaction conditions. In a similar way bromides (*E*)- and (*Z*)-**4b** were obtained without competing formation of the radical products (*E*)- and (*Z*)-**5**, which occurred in solution. In contrast with solution-phase hydriodination of alkyne **1**, which slowly afforded iodide (*E*)-**4c**, surface-mediated addition readily afforded (*E*)-**4c**, followed by isomerization to the *Z* isomer. $E \rightleftharpoons Z$ equilibration of the alkenyl halides **4** was shown to involve, at least in part, addition–elimination via the *gem*-dihalides **13**. Analogous behavior was exhibited by the phenylalkynes **2** and **3** on surface-mediated hydrohalogenation. Surface-mediated addition of HBr and HI to the internal alkylalkyne **14** afforded principally the anti addition products (*Z*)-**15b,c**. Treatment of the terminal alkynes **17** and **22** with $(COBr)_2$ over alumina gave the dibromides **20** and **24**/**25**, respectively, whereas use of acetyl bromide as the HBr precursor afforded the alkenyl bromides **18b** and **23**.

Introduction

Despite numerous implications to the contrary in introductory textbooks, HCl does not add to most alkynes at preparatively useful rates.[2,3] HI adds more readily, but the anhydrous form is difficult to generate and expensive to obtain commercially.[4] HBr also adds readily, but this is often due to competing radical–chain addition to give the anti-Markovnikov product, which predominates unless stringent precautions are taken.[5] Moreover, the generation and transfer of these hygroscopic, gaseous reagents is both inconvenient and difficult to perform stoichiometrically. Recent studies in these laboratories have shown that adsorption of acids to the surfaces of silica gel and alumina greatly enhances their acidities.[6] Use has been made of this to facilitate the addition of hydrogen halides to alkenes.[1] We report here extension of these studies to the surface-mediated hydrohalogenation of alkynes, which both affords a convenient method for the preparation of alkenyl halides and provides further insight into the role of silica gel and alumina surfaces in mediating chemical reactivity.[7]

Results

Phenylalkynes. Our studies began with phenylalkynes **1**–**3**. Although phenyl-substituted, alkyne **1** undergoes addition of HCl only very slowly in solution.[8] Even treatment with a saturated solution of HCl in the presence of the Lewis acid catalyst $ZnCl_2$ in refluxing CH_2Cl_2 solution for 24 h afforded alkenyl chlorides (*E*)- and (*Z*)-**4a** in yields of only 16 and 7%, respectively.[9] Thus treatment of alkyne **1** with a saturated solution of HCl in CH_2Cl_2 afforded no detectable reaction after 1 h (Table 1). However, under identical conditions except for the presence of silica gel, substantial conversion to a mixture of alkenyl chlorides (*E*)- and (*Z*)-**4a** occurred. Even faster conversion occurred in the presence of alumina.



More conveniently, chlorides (*E*)- and (*Z*)-**4a** could be obtained using $SOCl_2$ or $(COCl)_2$ as an HCl precursor in

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(1) Part 3: Kropp, P. J.; Daus, K. A.; Tubergen, M. W.; Kepler, K. D.; Wilson, V. P.; Craig, S. L.; Baillargeon, M. M.; Breton, G. W. *J. Am. Chem. Soc.* **1993**, *115*, 3071–3079.

(2) Commonly cited examples include the internal alkylalkynes, which react "slowly at 25 °C"[3a] and require extended treatment at elevated temperatures,[3b] and the terminal alkylalkynes, which require either a Lewis acid catalyst[3c] or 35–60 days at 25 °C.[3d]

(3) (a) Fahey, R. C.; Lee, D.-J. *J. Am. Chem. Soc.* **1968**, *90*, 2124–2131. (b) Hudrlik, P. F.; Kulkarni, A. K.; Jain, S.; Hudrlik, A. M. *Tetrahedron* **1983**, *39*, 877–882. (c) Hennion, G. F.; Welsh, C. E. *J. Am. Chem. Soc.* **1940**, *62*, 1367–1368. (d) Griesbaum, K.; El-Abed, M. *Chem. Ber.* **1973**, *106*, 2001–2008.

(4) Consequently, alternative approaches to hydriodination have been developed: (a) Irifune, S.; Kibayashi, T.; Ishii, Y.; Ogawa, M. *Synthesis* **1988**, 366–369. (b) Reddy, C. K.; Periasamy, M. *Tetrahedron Lett.* **1990**, *31*, 1919–1920.

(5) For a review of radical addition of HBr to alkynes, see: Stacey, F. W.; Harris, J. F., Jr. *Org. React.* (*N.Y.*) **1963**, *13*, 150–376.

(6) Breton, G. W.; Daus, K. A.; Kropp, P. J. *J. Org. Chem.* **1992**, *57*, 6646–6649.

(7) (a) For a preliminary report see: Kropp, P. J.; Daus, K. A.; Crawford, S. D.; Tubergen, M. W.; Kepler, K. D.; Craig, S. L.; Wilson, V. P. *J. Am. Chem. Soc.* **1990**, *112*, 7433–7434. (b) For use of the surface-mediated hydrochlorination of an alkyne in the undergraduate laboratory, see: Pienta, N. J.; Crawford, S. D.; Kropp, P. J. *J. Chem. Ed.* **1993**, *70*, 682–684.

(8) (a) Fahey, R. C.; Lee, D. J. *J. Am. Chem. Soc.* **1966**, *88*, 5555–5560. (b) Fahey, R. C.; Payne, M. T.; Lee, D.-J. *J. Org. Chem.* **1974**, *39*, 1124–1130.

Table 1. Hydrochlorination of 1-Propynylbenzene (1)[a]

reagent	adsorbent	solvent	time, h	yield, %[b]			
				1	(*E*)-**4a**	(*Z*)-**4a**	*E*/*Z*
HCl[c]		CH_2Cl_2	1	100			
HCl[c]		$(C_2H_5)_2O$	1	100			
HCl[c]	SiO_2	CH_2Cl_2	1	44	39	11[d]	3.5
HCl[c]	SiO_2	$(C_2H_5)_2O$	1	93			
HCl[c]	Al_2O_3	CH_2Cl_2	1		29	71	0.41
$SOCl_2$	SiO_2	CH_2Cl_2	0.3	54	33	3	11
			3	3	76	15[d]	5.1
$SOCl_2$	SiO_2[e]	CH_2Cl_2	3	73	14	1	14
$SOCl_2$	SiO_2[f]	CH_2Cl_2	0.3	12	67	11	6.1
$SOCl_2$	SiO_2[f,g]	CH_2Cl_2	3	58	37	4	9.3
$SoCl_2$	SiO_2	C_5H_{12}[h]	0.3	3	65	16	4.1
$SOCl_2$	SiO_2	C_5H_{12}[h]	3		11	88	0.13
$SOCl_2$	SiO_2	$C_6H_5CH_3$	3	11	79	7	11
$SOCl_2$	SiO_2	$(C_2H_5)_2O$	3	100			
$SOCl_2$	SiO_2	CH_3CN	3	92			
$SOCl_2$	Al_2O_3	CH_2Cl_2	0.3		66	29[d]	2.3
			3		1	82[d]	0.01
$SOCl_2$	Al_2O_3	$(C_2H_5)_2O$	5	97			
$(COCl)_2$	SiO_2	CH_2Cl_2	0.3	42	34	3	11
			3		67	15	4.5
$(COCl)_2$	Al_2O_3	CH_2Cl_2	0.08	28	62	5	12
			0.3		85	14	6.1
			3		3	96	0.03

[a] Conducted with 2.0 mol equiv of reagent according to the standard small-scale procedure,[10] unless otherwise indicated. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. [c] Continuously bubbled through the solution at 25 °C. [d] A small amount of an unidentified product was also obtained. [e] Partially silylated according to the procedure of ref 14. The resulting increase in weight corresponded to 0.68 mmol of derivatized silanol groups per gram. [f] Fisher S-157. [g] Partially silylated according to the procedure of ref 14. The resulting increase in weight corresponded to 0.40 mmol of derivatized silanol groups per gram. [h] Five milliliters of CH_2Cl_2 was added and stirring continued for an additional 5 min before removal of the aliquot.

CH_2Cl_2 solution in the presence of either silica gel or alumina.[10,11] Again, addition occurred more rapidly over alumina. At short reaction times chloride (*E*)-**4a**, resulting from syn addition of HCl, was formed preferentially, whereas at longer times the thermodynamically more stable isomer (*Z*)-**4a** predominated. Thus either isomer could be obtained in good yield depending on the conditions.

Both addition and subsequent $E \rightleftharpoons Z$ isomerization were sensitive to the choice of solvent, following the order $C_5H_{12} > CH_2Cl_2 \approx C_6H_5CH_3$.[12] No addition occurred in $(C_2H_5)_2O$ or CH_3CN, which coordinate with HCl. Reaction occurred more rapidly over Fisher S-157 silica gel, which has a somewhat higher surface area (750 m^2/g) than the Merck grade 40 silica gel normally used in our studies (675 m^2/g).[13] Partial silylation of either type of silica gel by treatment with hexamethyldisilazane[14] resulted in substantially slower reaction, even though only a portion of the surface silanol groups had been modified. Fumed silica and a number of other adsorbents either afforded substantially slower conversion or gave lower material balances than silica gel or alumina (Table 2).

When an excess of alkyne **1** was treated over silica gel with 1.00 mmol of $SOCl_2$, which would afford 2.00 mmol of HCl on total hydrolysis, 1.95 mmol of alkyne **1** was eventually consumed (Table 3). Thus hydrolysis was complete and no HCl was consumed by the silica gel. Similarly, when an appropriate amount of $SOCl_2$ was used with alumina to afford 2.00 mmol of HCl after neutralization of the adsorbent,[15] 2.03 mmol of alkyne **1** was consumed. Under these conditions, with no excess acid, little or no $E \rightleftharpoons Z$ isomerization occurred and a high *E*/*Z* ratio of chlorides **4b** was obtained.

Alkyne **1** reacted rapidly with a saturated solution of HBr in CH_2Cl_2 but afforded a mixture of bromides **4b** and the radical products **5**, with the latter predominating (Table 4). Preventing radical addition of HBr to alkynes has traditionally required the rigorous absence of light, oxygen, and peroxide impurities, along with the use of a radical inhibitor.[16] However, the simple addition of silica gel or alumina to the reaction mixture was found sufficient to effect rapid conversion to the ionic products **4b** in high yield, without any detectable formation of the radical addition products **5**. Even more conveniently, the use of acetyl bromide as an HBr precursor in CH_2Cl_2 solution with silica gel afforded bromides **4b** in excellent yield. By

Table 2. Hydrochlorination of 1-Propynylbenzene (1) over Various Adsorbents[a]

adsorbent	time, h	yield, %[b]		
		1	(*E*)-**4a**	(*Z*)-**4a**
SiO_2 (Cab-O-Sil fumed silica)[c]	48	80	19	
SiO_2 (Celite 512)	3	71	1	
$MgSiO_3$ (Florisil)	3	2	37	4
SiO_2–Al_2O_3 (Strem silica alumina)[d]	3	74	6	*e*
$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]$[f]	3	85	*e*	
Montmorillonite K-10	0.3	*e*	5	2
Montmorillonite KSF	24	42	10	3
TiO_2	3	65	24	*e*
$[-CH_2CH(OH)-]_n$[g]	3	100		

[a] Conducted with 2.0 mol equiv of $SOCl_2$ according to the standard small-scale procedure.[10] [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. [c] 1.0 g in 10 mL of CH_2Cl_2. [d] 87% SiO_2, 13% Al_2O_3. [e] Trace. [f] Linde Type 4A molecular sieves. [g] Poly(vinyl alcohol), 100% hydrolyzed, av MW 106 000–110 000.

Table 3. Hydrochlorination of Excess 1-Propynylbenzene (1) with $SOCl_2$ over Silica Gel and Alumina[a]

adsorbent	$SOCl_2$, mmol	HCl,[c] mmol	yield, mmol[b]			
			1	(*E*)-**4a**	(*Z*)-**4a**	*E*/*Z*
SiO_2	1.00	2.00	0.65	1.59	0.16	10
Al_2O_3	1.25	2.00	0.57	1.79	0.13	14

[a] Conducted for 24 h with 2.60 mmol of alkyne **1** and 1.25 g of adsorbent according to the standard small-scale procedure.[10] [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. [c] Assuming complete hydrolysis and allowing for neutralization of 0.4 mmol of HCl/g of Al_2O_3.

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(9) Marcuzzi, F.; Melloni, G. *J. Am. Chem. Soc.* **1976**, *98*, 3295–3300.

(10) To facilitate a systematic study of the surface-mediated hydrohalogenation of alkynes, a previously optimized small-scale procedure was used, involving addition of a specified amount of an HX precursor to a stirred suspension of 2.5 g of Merck 10181 silica gel or Fisher A540 alumina, which had been equilibrated with the atmosphere at 120 °C for at least 48 h, in 5 mL of CH_2Cl_2 containing 1 mmol of substrate.[1] This procedure was scaled up for the isolation and identification of products. Silica gel and alumina that had been recycled as described previously gave results indistinguishable from those obtained with fresh adsorbent.

(11) The formation of hydrogen halides from acid halide precursors over silica gel and alumina is due principally to hydrolysis by residual physisorbed water: Baillargeon, M. M. Unpublished. Silica gel prepared by our standard procedure hydrolyzed 0.5 mmol of $(COCl)_2$ per gram, whereas alumina hydrolyzed 0.7 mmol/g.[1]

(12) Since chlorides **4a** are strongly adsorbed to the surface from C_5H_{12}, higher material balances were obtained by adding CH_2Cl_2 at the end of reaction to desorb the products.

(13) Sindorf, D. W.; Maciel, G. E. *J. Am. Chem. Soc.* **1983**, *105*, 1487–1493.

(14) Sindorf, D. W.; Maciel, G. E. *J. Phys. Chem.* **1983**, *87*, 5516–5521.

(15) Previous studies have shown that the Fisher A540 alumina used in these studies neutralizes approximately 0.40 mmol of a hydrogen halide per gram.[1]

(16) Walling, C. *Free Radicals in Solution*; Wiley: New York, 1957; pp 291–296.

Table 4. Hydrobromination of 1-Propynylbenzene (1)^a

				yield, %^{b}					
reagent	equiv^c	adsorbent	time, h	1	(*E*)-**4b**	(*Z*)-**4b**	(*E*)-**5**	(*Z*)-**5**	(*E*)-**4b**/(*Z*)-**4b**
HBr	*d*		3		29	8	18	29	3.6
HBr	*d*	SiO_2	0.3		2	79			0.03
HBr	*d*	Al_2O_3	0.3		14	79			0.18
AcBr	1.0	SiO_2	0.3	8	71	21			3.4
AcBr	1.0	SiO_2^{e}	0.3				40	53	
PBr_3	1.0		3	98					
PBr_3	0.33	SiO_2	0.3		76	13			5.9
			3		6	76			0.08
PBr_3	0.67	Al_2O_3	0.3	19	63	6			11
			3	2	82	10			8.2
PBr_3	1.0	Al_2O_3	0.3	9	74	12			6.2
			3		4	80^f			0.05

^{a} Conducted according to the standard small-scale procedure,[10] except that the reagent was added to the reaction mixture as a 1 M solution in CH_2Cl_2. ^{b} Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. ^{c} [Reagent]/[1]. ^{d} Continuously bubbled through the solution at 25 °C. ^{e} $(C_2H_5)_2O$ used as solvent. ^{f} (*E*)-(1,2-Dibromo-1-propenyl)benzene also obtained (6% yield).

Table 5. HBr Adsorption Studies^a

				in solution		
adsorbent	precursor	$[precursor]_{init}$	$[HBr]_{theor}$^{b}	[HBr]	[precursor]	$[HBr]_{ads}$, %
SiO_2	$(COBr)_2$	1.0	2.0	0.2	0	90
SiO_2	AcBr	2.0	2.0	0.6	*c*	70
		4.0	4.0	2.5	0	38
Al_2O_3	$(COBr)_2$	1.0	2.0	0.1	*c*	95
		2.0	4.0	0.3	0	93
Al_2O_3	AcBr	2.0	2.0	0.2	0	90
		4.0	4.0	0.4	0.7	73

^{a} Conducted as described in the Experimental Section; all concentrations are mmol/5 mL. ^{b} Based on total hydrolysis. ^{c} Assumed to be 0 since all of the precursor was hydrolyzed when a higher initial concentration was used.

Table 6. Comparison of Basic, Neutral, and Acidic Alumina for the Hydrobromination of 1-Propynylbenzene (1)^a

			yield, %^{b}		
Al_2O_3	pH^c	equiv of PBr_3^{d}	1	(*E*)-**4b**	(*Z*)-**4b**
CAMAG 5016-A-I	9.5^e	0.33	89		
		0.67^f	66	24	*g*
CAMAG 507-C-I	7.5^e	0.33	89	3	
		0.67^f	*g*	89	10
CAMAG 504-C-I	4.5^e	0.33	95	5	
		0.67^f		7	92
Fisher A540	10.2	0.33	86	8	
		0.67^f	1	84	11

^{a} Conducted for 1 h with 2.5 g of Al_2O_3 according to the standard small-scale procedure.[10] ^{b} Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. ^{c} pH of a 5% aqueous suspension. ^{d} $[PBr_3]/[1]$. ^{e} Value provided by supplier. ^{f} After 1 h an additional 0.33 equiv of PBr_3 was added to the preceding reaction mixture, and stirring was continued for another 1 h. ^{g} Trace.

Table 7. Hydriodination of 1-Propynylbenzene (1)^a

				yield, %^{b}				
reagent	equiv^c	adsorbent	time, h	1	(*E*)-**4c**	(*Z*)-**4c**	6	*E*/*Z*
HI^d			24	33	58	3		19
NaI/TsOH^e			24	6	74	19		3.9
AcI	1.0	SiO_2	0.3	11	57	10		5.7
AcI	4.0	Al_2O_3	0.3	*f*	92	6		15
PI_3	0.67	SiO_2	0.3	6	69	9		7.7
			3	1	21	66	3	0.32
			6	1	12	71	3	0.17
PI_3	1.0	Al_2O_3	0.3	2	82	15		5.5
			3		42	24	10	1.8

^{a} Conducted according to the standard small-scale procedure,[10] unless otherwise indicated. ^{b} Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. ^{c} [Reagent]/[1]. ^{d} 1 mmol of alkyne 1 was treated with 5 mL of 57% aqueous HI. ^{e} 1 mmol of alkyne 1 was treated with 8 mmol of NaI and 4 mmol of *p*-toluenesulfonic acid in 5 mL of CH_2Cl_2. ^{f} Trace.

contrast, in $(C_2H_5)_2O$ solution, which coordinates with HBr, only the radical products **5** were obtained, presumably through reaction in solution. Thus through the appropriate choice of solvent, either the ionic products **4b** or the radical products **5** could be obtained exclusively.

PBr_3 was also found to be a useful HBr precursor. At short reaction times the syn adduct (*E*)-**4b** was formed preferentially, whereas at longer times the thermodynamically more stable isomer (*Z*)-**4b** predominated. Thus through the appropriate choice of conditions either isomer could be obtained in good yield. Addition and subsequent $E \rightleftharpoons Z$ equilibration occurred more slowly over alumina than silica gel, apparently due to an effect of the hydrolysis byproduct H_3PO_3 on alumina.

The deleterious effect of another hydrolysis byproduct, acetic acid, was observed during adsorption studies (Table 5). Up to 3.7 mmol of HBr was adsorbed from CH_2Cl_2 solution on to 2.5 g of silica gel or alumina when generated by hydrolysis of $(COBr)_2$, which affords only the gaseous byproducts CO and CO_2.[17] However, substantially less adsorption occurred when acetyl bromide was used as the HBr precursor, particularly with silica gel, even though hydrolysis was complete.

Comparison of CAMAG basic, neutral, and acidic aluminas with the Fisher A540 alumina, which was used throughout most of our studies, revealed that none, even the acidic form, effected significant addition of HBr to alkyne 1 when treated with the equivalent of 0.4 mmol/g of HBr, presumably due to neutralization of the acid by residual basic sites on the surface (Table 6). The extent of reaction on treatment with a second 0.4 mmol/g of HBr

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(17) For the hydrolysis of $(COCl)_2$, see: Ugi, I.; Beck, F. *Chem. Ber.* 1961, *94*, 1839–1850.

Table 8. Hydrohalogenation of Diphenylethyne (2)[a]

reagent	equiv[c]	adsorbent	time, h	yield, %[b] 2	(E)-7	(Z)-7	8	E/Z	X
HCl	d		48	96					
HCl	e	SiO_2	3	12	77	4		19	Cl
$SOCl_2$	1.0	SiO_2	3	30	60	2		30	Cl
			8	1	79	5		16	Cl
$SOCl_2$	2.0	Al_2O_3	0.3	33	66	f		>66	Cl
			16		5	77		0.06	Cl
HBr	e		0.3	4	13	64		0.20	Br
HBr	e	SiO_2	0.3		59	22		2.7	Br
PBr_3	0.67	SiO_2	0.3	10	71	19		3.8	Br
			24		10	73		0.14	Br
PBr_3	1.0	Al_2O_3	3	5	77	4		19	Br
			24		18	71		0.25	Br
PI_3	0.67	SiO_2	3	2	45	4	16	11	I
			24		7	24	30	0.29	I
PI_3	1.0	Al_2O_3	3	4	76	4		19	I
			24	21	15	18		0.83	I

[a] Conducted according to the standard small-scale procedure,[10] unless otherwise indicated. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. [c] [Reagent]/[2]. [d] Continuously bubbled through the solution at −78 °C for 1 h; the solution was then allowed to stand at 22 °C for 47 h. [e] Continuously bubbled through the solution at 25 °C. [f] Trace.

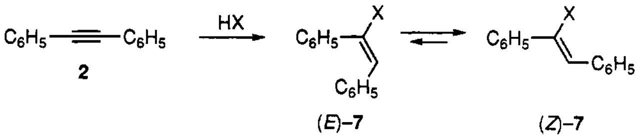
increased on going from basic to neutral and then acidic alumina. Fisher A540 alumina exhibited behavior similar to that of CAMAG neutral alumina.

Alkyne 1 underwent slow addition of HI in solution to afford a mixture of iodides (*E*)- and (*Z*)-**4c** (Table 7). Addition occurred much more rapidly over silica gel or alumina using acetyl iodide or PI_3 as an HI precursor. The syn adduct (*E*)-**4c** was initially formed preferentially, whereas at longer time $E \rightleftharpoons Z$ isomerization afforded the thermodynamically more stable isomer (*Z*)-**4c**. Depending on conditions, either isomer could be obtained in good yield. However, isomerization to the *Z* isomer occurred somewhat more slowly than for chloride (*E*)-**4a** and bromide (*E*)-**4b** and was accompanied by formation of small amounts of the hydrolysis product **6**.

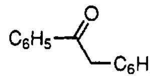
The phenyl and *tert*-butyl analogs **2** and **3** undergo $ZnCl_2$-catalyzed addition of HCl somewhat more rapidly than alkyne **1**, but reflux temperature and an extended reaction time are still required.[9,18,19] Interestingly, they afford only the syn adducts (*E*)-**7a** and (*E*)-**9a**, respectively, under these conditions. Hence, alkyne **2** underwent no detectable addition on prolonged treatment with HCl in CH_2Cl_2 solution (Table 8). However, addition occurred readily under these conditions in the presence of silica gel, or on treatment with $SOCl_2$ over silica gel, to afford the syn adduct (*E*)-**7a**. Addition occurred even more readily over alumina, as did equilibration with the thermodynamically more stable *Z* isomer. Thus either isomer could be obtained preferentially.

Addition of HBr occurred rapidly in solution to afford predominantly bromide (*Z*)-**7b**, whereas the syn adduct (*E*)-**7b** predominated in the presence of silica gel. The use of PBr_3 with silica gel or alumina initially afforded principally bromide (*E*)-**7b**, whereas at longer reaction time equilibration with the *Z* isomer occurred. Thus, once again, either isomer could be obtained predominantly. Treatment with PI_3 in the presence of alumina afforded principally the syn adduct (*E*)-**7c**. However, attempted equilibration with the *Z* isomer on extended reaction afforded only a low material balance. Over silica gel substantial formation of ketone **8** occurred.

Treatment of the *tert*-butyl analog **3** with $SOCl_2$, PBr_3, or PI_3 over silica gel or alumina for short times afforded the syn adducts (*E*)-**9a–c** in good yields (Table 9). However, attempted equilibration to the *Z* isomers occurred slowly and afforded hydrolysis to ketone **11**, along with low material balances, except for bromide (*Z*)-**9b**, which could be obtained in good yield over silica gel.



a, X = Cl; b, X = Br; c, X = I



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$E \rightleftharpoons Z$ Isomerization. In contrast with the $ZnCl_2$-promoted addition of HCl to alkynes **1** and **2**,[9,18] the resulting alkenyl chlorides **4a** and **7a**, respectively, underwent $E \rightleftharpoons Z$ equilibration under surface-mediated conditions. The mechanism of $E \rightleftharpoons Z$ isomerization was explored with chlorides **4a**. No equilibration occurred on treatment of a mixture of (*E*)- and (*Z*)-**4a** with silica gel or alumina alone or with HCl in solution, but equilibration occurred readily over silica gel or alumina in the presence of HCl (Table 10). This would be consistent with a mechanistic scheme involving protonation–deprotonation via cation **12** (Scheme 1). However, equilibration of chlorides **4a** and iodides **4c** in the presence of HBr resulted in substantial halogen interchange (Table 11), indicating that at least some formation of the *gem*-dihalide **13** is involved.[20]

Alkylalkynes. The internal alkyne 4-octyne (**14**) and the terminal alkyne 1-heptyne (**17**), which afforded no reaction with a saturated solution of HCl in CH_2Cl_2, underwent conversion on treatment with $SOCl_2$ over silica gel or alumina (Tables 12 and 13). However, the material balances were low with 4-octyne (**14**), and 1-heptyne (**17**) afforded principally a mixture of rearranged alkenyl chloride **19a** and the dichloride **20a**.

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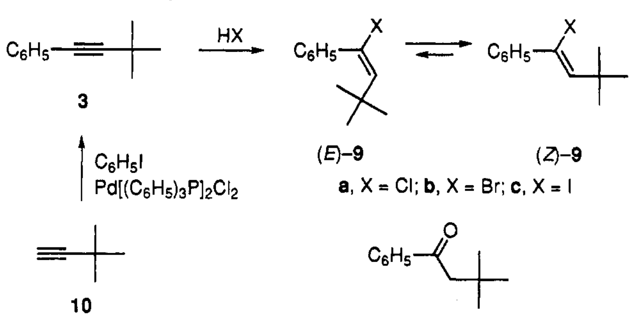
(18) Maroni, R.; Melloni, G.; Modena, G. *J. Chem. Soc., Perkin Trans. 1* **1974**, 353–356.

(19) Maroni, R.; Melloni, G.; Modena, G. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2491–2496.

(20) We are indebted to J. S. Raleigh for this study.

Table 9. Hydrohalogenation of 3,3-Dimethyl-1-phenylbutyne (3)[a]



3

10

(*E*)-9 (*Z*)-9

a, X = Cl; b, X = Br; c, X = I

11

reagent	equiv[c]	adsorbent	time, h	yield, %[b] 3	 (*E*)-9	 (*Z*)-9	 11	*E*/*Z*	X
$SOCl_2$	2.0	SiO_2	3		90	*d*		>90	Cl
$SOCl_2$	2.0	Al_2O_3	0.3		99	*d*		>99	Cl
			24		13	44	2	0.30	Cl
PBr_3	0.33	SiO_2	0.3		86			>86	Br
			24		19	39	2	0.49	Br
PBr_3	0.67	SiO_2	0.3	1	63	20		3.2	Br
			24		20	69	4	0.29	Br
PBr_3	1.0	Al_2O_3	3		94	1		94	Br
			24		51	38		1.3	Br
PI_3	0.67	SiO_2	0.3		77	2		38	I
			24	7	12	9	28	1.3	I
PI_3	1.0	Al_2O_3	0.3		85			>85	I
			24		22	13	11	1.7	I

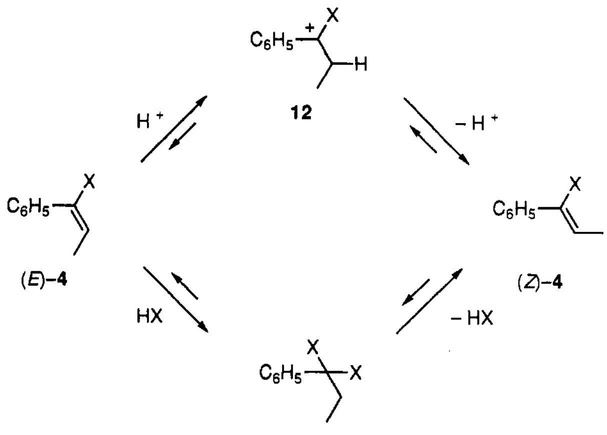
[a] Conducted according to the standard small-scale procedure.[10] [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. [c] [Reagent]/[3]. [d] Trace.

Table 10. Equilibration of (1-Chloro-1-propenyl)benzene (4a)[a]

reagent	equiv[c]	adsorbent	time, h	(*E*)-4a/(*Z*)-4a[b]	mass balance,[b] %
HCl	*d*		3	1.8	93
		SiO_2[e]	6	1.1	87
			27	0.2	84
		SiO_2	3	1.8	96
$(COCl)_2$[e]	1.5		6	0.7	95
			27	0.04	77
		Al_2O_3	3	1.8	99
$(COCl)_2$[e]	1.5		6	0.04	99

[a] Conducted with a 1.8:1 mixture of chlorides (*E*)- and (*Z*)-4a, respectively, according to the standard small-scale procedure.[10] [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. [c] [Reagent]/[4a]. [d] Continuously bubbled through the solution at 25 °C for 30 min; the reaction flask was sealed and stirring continued for an additional 2.5 h. [e] Added to the preceding reaction after 3 h.

Scheme 1



12

(*E*)-4

(*Z*)-4

13

a, X = Cl; b, X = Br; c, X = I

Table 11. Equilibration of Chlorides 4a and Iodides 4c in the Presence of HBr[a]

halide	$COBr_2$, equiv[c]	time, h	yield, %[b] (*E*)-4a/c	 (*Z*)-4a/c	 (*E*)-4b	 (*Z*)-4b
4a	1.5	0	100	0		
		2	0	12	14	74
4c	0.6	0	89	11		
		1	37	38	1	24

[a] Conducted over Al_2O_3 according to the standard small-scale procedure.[10] [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. [c] [Reagent]/[4a].

4-Octyne (**14**) reacted readily with HBr in solution to afford principally bromide (*Z*)-**15** in moderate yield (Table 12), whereas the terminal alkynes **17** and **22** underwent very slow addition in solution (Tables 13 and 14). Treatment of these alkynes with $(COBr)_2$ over alumina afforded principally the dibromides **16b**, **20b**, and **24**/**25**. However, dibromination could be avoided using acetyl bromide as the HBr precursor, affording alkenyl bromides (*Z*)-**15b**, **18b**, and **23** in good yields.[21]

Treatment of 1-heptyne (**17**) with acetyl bromide over silica gel rather than alumina resulted in rapid formation of the radical product **21**, apparently due to reaction in solution. Alkyne **17** can thus be converted principally to either alkenyl bromide **18b** or **21** or to dibromide **20b**, depending on the reaction conditions. In contrast with the phenylalkynes **1**–**3**, 4-octyne (**14**) underwent anti addition of HBr to afford exclusively the *Z* isomer of bromide **15b**. Similarly, treatment with acetyl iodide over

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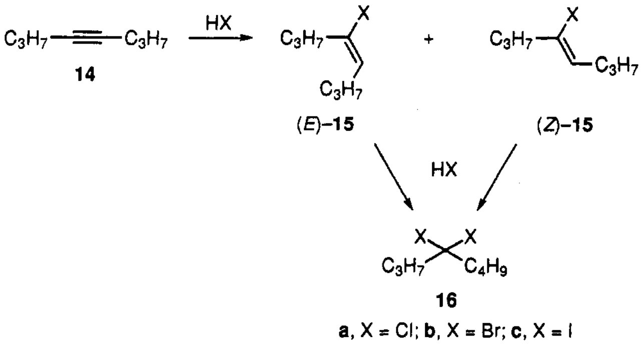
[21] Because of the difficulty of converting terminal alkylalkynes to the corresponding 2-bromo-1-alkenes, a number of indirect methods have previously been employed: (a) Boeckman, R. K., Jr.; Blum, D. M. *J. Org. Chem.* **1974**, *39*, 3307–3308. (b) Cousseau, J. *Synthesis* **1980**, 805–806. (c) Hara, S.; Dojo, H.; Takinami, S.; Suzuki, A. *Tetrahedron Lett.* **1983**, *24*, 731–735.

Table 12. Hydrohalogenation of 4-Octyne (14)[a]

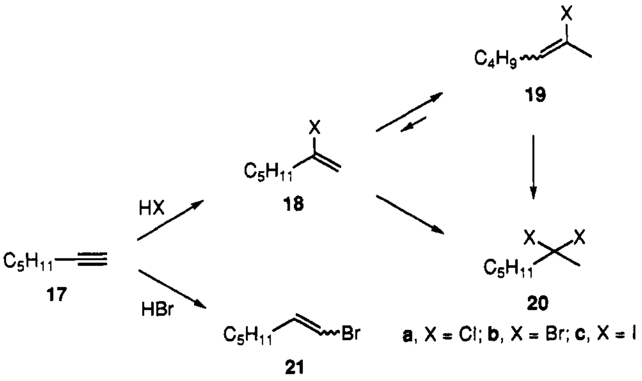


reagent	equiv[c]	adsorbent	time, h	yield, %[b] 14	(*E*)-15	(*Z*)-15	16	X
HCl	*d*		3	93				
$SOCl_2$	2	SiO_2	3	33	2	3		Cl
$SOCl_2$	2	Al_2O_3	1	30	11	6	3	Cl
HBr	*d*		1	8	4	33		Br
$(COBr)_2$	2	Al_2O_3	2				79	Br
AcBr	2	SiO_2	0.3		7	53	7	Br
AcBr	3	Al_2O_3	48	13		72		Br
HI	*e*		24	1		78		I
AcI	2	SiO_2	0.3		21	60		I
AcI	3	Al_2O_3	1	21	16	62		I
			24		18	77		I

[a] Conducted according to the standard small-scale procedure,[10] unless otherwise indicated. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. [c] [Reagent]/[14]. [d] Continuously bubbled through the solution at 25 °C for 0.5 h. [e] 1 mmol of alkyne 14 was treated with 5 mL of 57% hydriodic acid.

silica gel or alumina afforded principally iodide (*Z*)-15c, accompanied by some of the *E* isomer (Table 12).

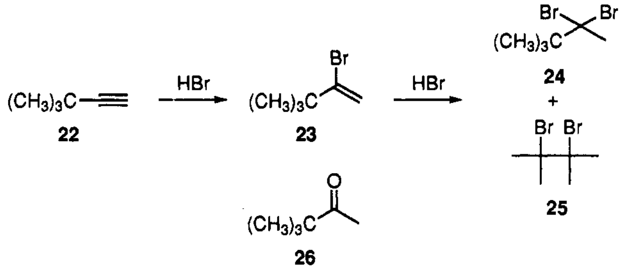
Table 13. Hydrohalogenation of 1-Heptyne (17)[a]



reagent	equiv[c]	adsorbent	time, h	yield, %[b] 17	18	19	20	21	X
HCl	*d*		3	98					
$SOCl_2$	2.0	SiO_2	3	78	3	4	3		Cl
$SOCl_2$	2.0	Al_2O_3[e]	3	2	2	19	54		Cl
HBr	*f*		24	48	6	2		1	Br
$(COBr)_2$	2.0	Al_2O_3	1			5	70	*g*	Br
AcBr	1.0	SiO_2	3	7	4	5	4	80	Br
AcBr	3.0	Al_2O_3	20	19	71	2	*g*	*g*	Br
HI	*h*		24	22	19	3			I
AcI[i]	2.2	Al_2O_3	24	18	45	36			I

[a] Conducted according to the standard small-scale procedure,[10] unless otherwise indicated. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. [c] [Reagent]/[17]. [d] Continuously bubbled through the solution at 25 °C for 30 min; the reaction flask was sealed and stirred for an additional 2.5 h. [e] Aldrich granular, 4–8 mesh. [f] Continuously bubbled through the solution at 25 °C for 30 min; the reaction flask was sealed and stirred for an additional 23.5 h. [g] Trace. [h] 1 mmol of alkyne 17 was treated with 5 mL of 57% hydriodic acid. [i] Acetyl iodide was added to Al_2O_3 10 min prior to the addition of alkyne 17.

Table 14. Hydrobromination of 3,3-Dimethyl-1-butyne (22)[a]



reagent	equiv[c]	adsorbent	solvent	time, h	yield, %[b] 22	23	24 + 25	26
HBr	*d*			24	41	31	10	18
$(COBr)_2$	2.0	Al_2O_3	CH_2Cl_2	1			62	
AcBr	2.5	Al_2O_3	CH_2Cl_2	24	61	39		
AcBr	2.5	Al_2O_3	C_7H_{16}	24	26	67		

[a] Conducted according to the standard small-scale procedure,[10] unless otherwise indicated. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. [c] [Reagent]/[22]. [d] 5 mL of 48% hydrobromic acid was added to neat 22.

Discussion

The use of silica gel and alumina clearly provides a simple means for facilitating additions of hydrogen halides to alkynes that do not occur readily in solution. The results are generally superior to those obtained previously using Lewis acid catalysts, and there is no need to dispose of heavy-metal salts. Moreover, the silica gel or alumina can be easily recycled.[1] In the case of hydrobromination, the use of surface-mediated conditions is a simple, highly effective means of preventing competing radical addition. The subsequent isomerization of the initially formed syn adducts to the thermodynamically more stable *Z* isomers under surface-mediated conditions permits the preparation of either stereoisomer in good yield. Finally, the use of various HX precursors in conjunction with silica gel and alumina eliminates the need to prepare or transfer these corrosive, hygroscopic gases.

Mechanism. The adsorption study showed that hydrogen halides are extensively adsorbed to the surfaces of silica gel and alumina from CH_2Cl_2 solution. Silica gel and alumina surfaces that have been equilibrated with atmospheric moisture at 120 °C, as in our standard procedure, are extensively hydroxylated, with a small amount of residual physisorbed water.[14,22] In the case of silica gel, most of the silanol groups are isolated, having O–O distances beyond the limit for internal hydrogen bonding. However, approximately 15% of the silanol groups are geminal and, hence, sufficiently close to form hydrogen-bonded chains through interaction with adjacent groups.[13] The greatly reduced reactivity of partially silylated silica gel (Table 1) indicates that these latter sites, which undergo preferential derivatization,[23] are principally involved in mediating hydrohalogenation. The

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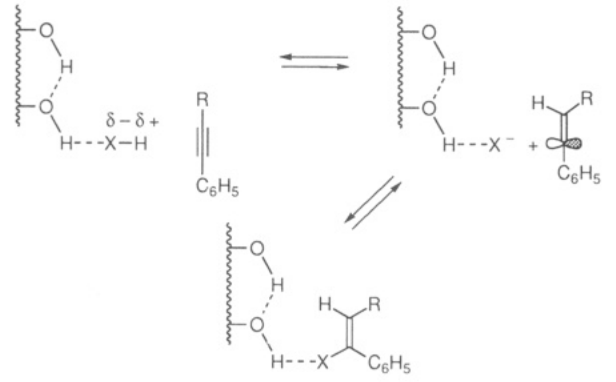
[22] For a review of the surface structures of silica gel and alumina and their mode of interaction with adsorbates, see: Knözinger, H. In *The Hydrogen Bond. III. Dynamics, Thermodynamics and Special Systems*; Schuster, P., Zundel, G., Sandorfy, C., Eds.; North-Holland: Amsterdam, 1976; Chapter 27.

[23] (a) Sindorf, D. W.; Maciel, G. E. *J. Phys. Chem.* **1982**, *86*, 5208–5219. (b) Feher, F. J.; Newman, D. A. *J. Am. Chem. Soc.* **1990**, *112*, 1931–1936.

Scheme 2



low effectiveness of fumed silica (Table 2), which is prepared by hydrolysis of $SiCl_4$ in a dihydrogen flame, is similarly due to the general absence of hydrogen-bonded sites on its surface. By contrast, the surfaces of γ-alumina are terminated by a monolayer of hydroxyl groups separated by ~3.2 Å, within the limit for internal hydrogen bonding.[22,24]

Adsorption of the hydrogen halide thus occurs through a hydrogen-bonding interaction, in which acidic OH groups on the surface serve as hydrogen-bond donors (Scheme 2).[22] This greatly enhances the acidity of the hydrogen halide by disrupting any aggregation that the acid had in solution and polarizing the H–X bond, leading to protonation of the alkyne from the surface.[25,26] As was previously observed with alkenes,[1] transfer of halide ion from the surface to the alkenyl cations derived from the phenylalkynes **1**–**3** is apparently rapid, competing with diffusion and affording predominantly the syn addition products (*E*)-**4**, -**7**, and -**9**.[27] The absence of radical behavior by HBr is due to its adsorption to the surface, rendering it unavailable for radical chain addition.

We continue to explore the rich potential of surface-mediated reactivity.

Experimental Section

General Procedures. All reactions were conducted in oven-dried glassware. Reagents were from commercial suppliers and used without further purification. Gas chromatographic analyses were performed with 3 m × 3 mm stainless steel columns and preparative gas chromatography with 3 m × 6 mm columns packed with (A) 20% SF-96, (B) 20% Carbowax 20M, or (C) 20% DC-550 on 60–80 mesh Chromosorb W. NMR spectra were recorded in $CDCl_3$ solution at 400 MHz (^1H) or 100 MHz (^{13}C). Melting points are uncorrected.

Standard Surface-Mediated Procedures. Except as indicated, the standard small- and preparative-scale procedures previously developed were followed.[1,10]

(*E*)-(1-Chloro-1-propenyl)benzene [(*E*)-4a]. Treatment of 1.16 g (10.0 mmol) of 1-propynylbenzene (**1**) with 2.38 g (20 mmol) of $SOCl_2$ and 25 g of silica gel for 3.5 h according to the standard preparative-scale procedure afforded a mixture of chlorides (*E*)- and (*Z*)-**4a**, which were separated by preparative gas chromatography (column C, 115 °C). Isolation of the lower retention time component afforded chloride (*E*)-**4a** as a colorless liquid: ^1H NMR δ 1.74 (d, J = 7.3 Hz, 3 H, CH_3-3), 6.05 (q, J = 7.3 Hz, 1 H, CH-2), 7.39 (m, 5 H, C_6H_5); ^{13}C NMR δ 15.43, 124.56, 128.19, 128.40, 128.90, 130.86, 137.04; lit.[28] ^1H NMR (CCl_4) δ 1.7 (d, J = 7.2 Hz, 3 H), 5.95 (q, J = 7.2 Hz, 1 H), 7.2 (s).

(*Z*)-(1-Chloro-1-propenyl)benzene [(*Z*)-4a]. Treatment of 2.32 g (20.0 mmol) of alkyne **1** with 4.76 g (40 mmol) of $SOCl_2$ and 25 g of alumina for 4 h according to the standard preparative-scale procedure followed by distillation at 130–135 °C (75 mmHg) afforded 1.81 g (59% yield) of chloride (*Z*)-**4a** as a yellow liquid: ^1H NMR δ 1.96 (d, J = 6.7 Hz, 3 H, CH_3-3), 6.21 (q, J = 6.7 Hz, 1 H, CH-2), 7.34 (m, 3 H, CH-2′, -4′, -6′), 7.56 (m, 2 H, CH-3′, -5′); ^{13}C NMR δ 15.11, 122.36, 126.26, 128.13, 128.29, 133.74, 138.39; lit.[28] ^1H NMR (CCl_4) δ 1.9 (d, J = 6.8 Hz, 3 H), 6.03 (q, J = 6.8 Hz, 1 H), 7.1–7.7 (m).

(*E*)-(1-Bromo-1-propenyl)benzene [(*E*)-4b]. Treatment of 1.16 g (10 mmol) of alkyne **1** with 6.7 mL of a 1 M solution (6.7 mmol) of PBr_3 and 25 g of alumina for 2 h according to the standard preparative-scale procedure afforded 1.79 g of a colorless liquid, which was shown by gas chromatographic analysis to consist of 5% alkyne **1**, 56% bromide (*E*)-**4b**, and 39% bromide (*Z*)-**4b**. Isolation by preparative gas chromatography (column A, 135 °C) afforded bromide (*E*)-**4b** as a colorless liquid: ^1H NMR δ 1.65 (d, J = 7.2 Hz, 3 H, CH_3-3), 6.26 (q, J = 7.2 Hz, 1 H, CH-2), 7.34 (m, 5 H, C_6H_5); ^{13}C NMR δ 16.49, 128.16, 128.29, 128.73, 128.91, 129.04, 150.38; lit.[29] ^1H NMR (CCl_4) δ 1.59 (d, J = 7 Hz, 3 H), 6.19 (q, J = 7 Hz, 1 H), 7.0–7.4 (m).

(*Z*)-(1-Bromo-1-propenyl)benzene [(*Z*)-4b]. Treatment of 1.16 g (10.0 mmol) of alkyne **1** with 2.70 g (10 mmol) of PBr_3 and 25 g of alumina for 18 h according to the standard preparative-scale procedure followed by distillation at 64–65 °C (0.9 mmHg) afforded 1.27 g (64% yield) of bromide (*Z*)-**4b** as a yellow liquid: ^1H NMR δ 1.96 (d, J = 6.5 Hz, 3 H, CH_3-3), 6.28 (q, J = 6.5 Hz, 1 H, CH-2), 7.32 (m, 3 H, CH-2′, -4′, -6′), 7.52 (m, 2 H, CH-3′, -5′); ^{13}C NMR δ 18.10, 126.23, 126.59, 127.43, 128.18, 128.22, 140.09; lit.[29] ^1H NMR (CCl_4) δ 1.9 (d, J = 6 Hz, 3 H), 6.17 (q, J = 6 Hz, 1 H), 7.0–7.4 (m).

(*E*)- and (*Z*)-(1-Iodo-1-propenyl)benzene (4c). Treatment of 2.32 g (20.0 mmol) of alkyne **1** with 20 mL of a 1 M solution (20 mmol) of acetyl iodide and 20 g of silica gel for 0.5 h according to the standard preparative-scale procedure followed by chromatography over alumina and elution with hexanes afforded 4.28 g (87% yield) of a pink liquid, which was determined by ^1H NMR analysis to be an 11:1 mixture of iodides (*E*)- and (*Z*)-**4c**. The major isomer was identified as iodide (*E*)-**4c**: ^1H NMR δ 1.63 (d, J = 7.1 Hz, 3 H, CH_3-3), 6.56 (d, J = 7.1 Hz, 1 H, CH-2), 7.31 (m, 5 H, C_6H_5); lit.[30] ^1H NMR ($CDCl_3$) δ 1.61 (d, J = 6.7 Hz, 3 H), 6.50 (q, J = 6.7 Hz).

The minor isomer was identified as iodide (*Z*)-**4c**: ^1H NMR δ 1.96 (d, J = 6.4 Hz, 3 H, CH_3-3), 5.98 (q, J = 6.4 Hz, 1 H, CH-2), 7.35 (m, 3 H, CH-2′, -4′, -6′) 7.45 (m, 2 H, CH-3′, -5′); lit.[30] ^1H NMR ($CDCl_3$) δ 1.93 (d, J = 6.7 Hz, 3 H), 5.93 (q, J = 6.7 Hz, 1 H), 7.30 (m, 5 H).

(*E*)- and (*Z*)-(2-Bromo-1-propenyl)benzene [(*E*)- and (*Z*)-5]. Treatment of 2.32 g (20 mmol) of alkyne **1** with 2.45 g (20 mmol) of acetyl bromide dissolved in 5 mL of $(C_2H_5)_2O$ and 25 g of silica gel in 50 mL of $(C_2H_5)_2O$ according to the standard preparative-scale procedure followed by distillation at 60–62 °C (0.8 mmHg) afforded 3.13 g (79% yield) of a 39:61 mixture of bromides (*E*)- and (*Z*)-**5** as a yellow liquid. The minor isomer was identified as bromide (*E*)-**5**: ^1H NMR δ 2.48 (d, J = 1.3 Hz, 3 H, CH_3-3), 6.99 (br s, 1 H, CH-1), 7.37 (m, 5 H, C_6H_5); lit.[31] ^1H NMR ($CDCl_3$) δ 2.30 (d, J = 1.5 Hz, 3 H), 6.75 (br s, 1 H), 6.9–7.4 (m, 5 H).

The major isomer was identified as bromide (*Z*)-**5**: ^1H NMR δ 2.51 (d, J = 1.3 Hz, 3 H, CH_3-3), 6.74 (br s, 1 H, CH-1), 7.37

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[24] However, the active sites responsible for mediating hydrohalogenation are not present on the surface of γ-alumina until neutralization with HX has occurred.[1] Apparently Al–X bonds are formed that increase the acidity of adjacent aluminol groups.

[25] The surface also provides an exceptionally polar local environment. See: (a) Lindley, S. M.; Flowers, C. G.; Leffler, J. E. *J. Org. Chem.* **1985**, *50*, 607–610. (b) Spange, S.; Keutel, D.; Simon, F. *J. Chim. Phys.* **1992**, *89*, 1615–1622.

[26] It is not clear what role, if any, is played by adsorption of the alkyne to the surface. This question is currently under study.

[27] By contrast, 4-octyne (**14**) underwent predominantly anti addition, to afford alkenyl halides (*Z*)-**15b**,**c**. The change in mechanism may be due to the difficulty of forming an alkenyl cation lacking stabilization by a phenyl substituent, thereby requiring simultaneous nucleophilic trapping from the opposite side of the alkyne by a molecule of HX in solution (Ad_E3-type addition).

[28] Cousseau, J.; Gouin, L. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1797–1801.

[29] Marcuzzi, F.; Melloni, G. *Gazz. Chim. Ital.* **1975**, *105*, 495–507.

[30] Campbell, J. R.; Pross, A.; Sternhell, S. *Aust. J. Chem.* **1971**, *24*, 1425–1436.

(m, 5 H, C_6H_5); lit.[31] ^{1}H NMR ($CDCl_3$) δ 2.35 (d, J = 1.5 Hz, 3 H), 6.50 (br s, 1 H), 6.9–7.4 (m, 5 H).

(*E*)-(1,2-Dibromo-1-propenyl)benzene. Treatment of 1.16 g (10 mmol) of alkyne 1 with 3.07 g (25 mmol) of acetyl bromide and 25 g of alumina for 32 h according to the standard preparative-scale procedure followed by concentration at 25–40 °C (1.0 mmHg) and isolation by preparative gas chromatography (column A, 170 °C) afforded the dibromide as a yellow liquid: ^{1}H NMR δ 2.59 (s, 3 H, CH_3-3), 7.37 (m, 5 H, C_6H_5); lit.[32] ^{1}H NMR (CCl_4) δ 2.60 (s, 3 H), 7.30 (s, 5 H).

1-Phenyl-1-propanone (6) was also isolated and identified by comparison of its gas chromatographic times with those of a commercial sample on columns A and B.

(*E*)-1,1′-(1-Chloro-1,2-ethenediyl)bisbenzene [(*E*)-7a]. Treatment of 1.78 g (10.0 mmol) of diphenylethyne (**2**) with 1.19 g (10 mmol) of $SOCl_2$ and 25 g of silica gel according to the standard preparative-scale procedure for 12 h followed by distillation at 115–116 °C (4.5 mmHg) gave 1.12 g (52% yield) of chloride (*E*)-**7a** as a yellow liquid: ^{1}H NMR δ 6.96 (s, 1 H, CH-2), 7.00 (m, 2 H), 7.25 (m, 3 H), 7.33 (m, 3 H), 7.39 (m, 2 H); ^{13}C NMR δ 127.43, 128.27, 128.34, 128.60, 128.82, 128.96, 129.23, 133.08, 135.38, 137.76; UV (CH_3OH) λ_{max} 274 nm (ϵ 11 190); lit.[33] UV (CH_3OH) λ_{max} 274 nm.

(*Z*)-1,1′-(1-Chloro-1,2-ethenediyl)bisbenzene [(*Z*)-7a]. Treatment of 1.78 g (10.0 mmol) of alkyne **2** with 2.38 g (20 mmol) of $SOCl_2$ and 15 g of Davisil grade 636 silica gel according to the standard preparative-scale procedure for 72 h afforded a mixture of alkyne **2** and chloride (*E*)-**7a**. Further treatment with 1.67 g (14.0 mmol) of $SOCl_2$ and 10 g of alumina in 20 mL of CH_2Cl_2 for 16 h followed by chromatography over silica gel (elution with hexanes), rotary evaporation, distillation at 128–134 °C (0.7 mmHg), and recrystallization from C_2H_5OH gave 0.55 g (26% yield) of chloride (*Z*)-**7a** as colorless prisms: mp 51–52 °C; ^{1}H NMR δ 7.10 (s, 1 H, CH-2), 7.42 (m, 6 H), 7.75 (m, 4 H); ^{13}C NMR δ 126.07, 126.70, 127.98, 128.26, 128.38, 128.72, 129.44, 132.06, 135.25, 139.26; UV (CH_3OH) λ_{max} 286 nm (ϵ 18 350); lit.[34] mp 52–54 °C, bp 90–92 °C (0.10 mmHg); lit.[33] UV (CH_3OH) λ_{max} 285 nm.

(*E*)-1,1′-(1-Bromo-1,2-ethenediyl)bisbenzene [(*E*)-7b]. Treatment of 1.78 g (10.0 mmol) of alkyne **2** with 12 mL of a 1 M solution (12 mmol) of acetyl bromide and 20 g of silica gel according to the standard preparative-scale procedure for 1.5 h followed by bulb-to-bulb distillation at 135–142 °C (0.9 mmHg) afforded a mixture that was shown by gas chromatographic analysis to consist of 10% alkyne **2**, 70% bromide (*E*)-**7b**, and 20% bromide (*Z*)-**7b**. Isolation by preparative gas chromatography (column A, 185 °C) afforded bromide (*E*)-**7b** as a colorless liquid: ^{1}H NMR δ 6.97 (m, 2 H), 7.14 (m, 3 H), 7.19 (s, 1 H, CH-2), 7.32 (m, 2 H), 7.36 (m, 3 H); ^{13}C NMR δ 136.04, 133.05, 131.65, 129.26, 128.83, 128.68, 128.66, 128.24, 127.49, 123.34; lit.[35] ^{1}H NMR ($CDCl_3$) δ 7.0 (m, 5 H), 7.4 (m, 6 H).

(*Z*)-1,1′-(1-Bromo-1,2-ethenediyl)bisbenzene [(*Z*)-7b]. Treatment of 1.78 g (10.0 mmol) of alkyne **2** with 6.7 mL of a 1 M solution (6.7 mmol) of PBr_3 and 25 g of silica gel according to the standard preparative-scale procedure for 4.5 days followed by filtration through a 5-cm pad of silica gel, washing with 25 mL of fresh CH_2Cl_2, and rotary evaporation afforded 1.7 g (66% yield) of a 12:88 mixture of bromides (*E*)- and (*Z*)-**7b**, respectively. Recrystallization from C_2H_5OH afforded 0.48 g (19% yield) of bromide (*Z*)-**7b** as colorless prisms: mp 34–35 °C; ^{1}H NMR δ 7.22 (s, 1 H, CH-2), 7.41 (m, 6 H), 7.66 (m, 2 H), 7.71 (d, J = 1.3 Hz, 2 H); ^{13}C NMR δ 141.07, 136.32, 130.00, 129.26, 128.79, 128.40, 128.24, 128.11, 127.85, 124.11; UV (C_2H_5OH) λ_{max} 280 nm (ϵ 19 960); lit.[36] mp 31 °C; UV (CH_3OH) λ_{max} 280 nm (ϵ 15 850).

(*E*)-1,1′-(1-Iodo-1,2-ethenediyl)bisbenzene [(*E*)-7c].[37] Treatment of 3.56 g (20.0 mmol) of alkyne **2** with 5.10 g (30 mmol) of acetyl iodide and 25 g of silica gel according to the standard preparative-scale procedure for 1 h followed by chromatography over silica gel and elution with hexanes afforded 4.85 g (79% yield) of iodide (*E*)-**7c** as a brown liquid, which solidified upon standing: mp 46.5–48.5 °C; ^{1}H NMR δ 6.91 (m 2 H), 7.11 (m, 3 H), 7.30 (br, m, 5 H), 7.42 (s, 1 H, CH-2); ^{13}C NMR δ 98.40, 127.54, 128.16, 128.40, 128.70, 128.75, 137.17, 141.34, 143.00; UV (CH_3OH) λ_{max} 266 nm (ϵ 15 000); lit.[38] no physical data.

(*Z*)-1,1′-(1-Iodo-1,2-ethenediyl)bisbenzene [(*Z*)-7c].[37] Treatment of 1.53 g (5.0 mmol) of iodide (*E*)-**7c** with 1.34 g (3.3 mmol) of PI_3 and 12.5 g of silica gel according to the standard preparative-scale procedure for 24 h followed by chromatography over silica gel gave, on elution with hexanes, 0.25 g of a colorless liquid that solidified on standing. Recrystallization from C_2H_5OH afforded 0.04 g of diphenylethyne (**2**). Concentration of the mother liquors afforded a colorless oil, which was found by gas chromatographic analysis to consist of 58% iodide (*Z*)-**7c**, 32% iodide (*E*)-**7c**, and 10% other products. Iodide (*Z*)-**7c** was identified by subtraction of the peaks for (*E*)-**7c** from the ^{1}H and ^{13}C NMR spectra: ^{1}H NMR δ 7.05 (s, 1 H, CH-2), 7.3 (br m, 6 H), 7.59 (m, 4 H), ^{13}C NMR δ 103.26, 128.04, 128.14, 128.26, 128.51, 128.68, 128.74, 137.22, 138.54, 144.14; lit.[38] no spectral data.

1,2-Diphenylethanone (8) was identified by comparison of its gas chromatographic times with those of a commercial sample on columns A and B.

(3,3-Dimethyl-1-butynyl)benzene (3). A modification of the general procedure of Hagihara was used.[39] Into a 50-mL round-bottomed flask were placed 4.08 g (20 mmol) of iodobenzene, 2.46 g (40 mmol) of 3,3-dimethyl-1-butyne (**10**), 10 mL of $(C_2H_5)_3N$, and 10 mL of CH_3CN. The flask was placed under a N_2 atmosphere and cooled to 0 °C in an ice bath. To this solution was added 0.28 g (0.40 mmol) of $Pd[P(C_6H_5)_3]_2Cl_2$ and 0.15 g (0.80 mmol) of CuI. The resulting solution was stirred at 0 °C for 20 min and then at 25 °C for an additional 3 h. The reaction mixture was poured into 50 mL of $(C_2H_5)_2O$ and washed with two 25-mL portions of saturated NH_4Cl solution and one of water. The combined aqueous washings were back-extracted with 25 mL of fresh $(C_2H_5)_2O$ and the combined organic fractions dried over saturated NaCl solution followed by anhydrous Na_2SO_4 and concentrated by rotary evaporation. Chromatography of the crude product over silica gel and elution with petroleum ether afforded 2.8 g (88% yield) of alkyne **3** as a colorless liquid: ^{1}H NMR δ 1.34 (s, 9 H, $(CH_3)_3C$), 7.27 (m, 2 H, CH-3′, -5′), 7.39 (m, 3 H, CH-2′, -4′, -6′); ^{13}C NMR δ 27.90, 31.04, 78.79, 98.50, 124.05, 127.36, 128.08, 131.54; lit.[40] ^{1}H NMR (neat) δ 1.33 (s, 9 H), 7.22 (m, 5 H).

(*E*)-(1-Chloro-3,3-dimethyl-1-butenyl)benzene [(*E*)-9a]. Treatment of 0.79 g (5.0 mmol) of alkyne **3** with 1.19 g (10 mmol) of $SOCl_2$ and 12.5 g of silica gel according to the standard preparative-scale procedure for 19 h followed by chromatography over silica gel and elution with hexanes afforded 0.59 g (61% yield) of chloride (*E*)-**9a** as a colorless liquid: ^{1}H NMR δ 0.91 (s, 9 H, $(CH_3)_3C$), 6.01 (s, 1 H, CH-2) 7.32 (m, 5 H, C_6H_5); lit.[28] ^{1}H NMR δ 0.89 (s, 9 H), 5.92 (s, 1 H) 7.2 (s, 5 H).

(*Z*)-(1-Chloro-3,3-dimethyl-1-butenyl)benzene [(*Z*)-9a]. Treatment of 0.50 g (2.6 mmol) of chloride (*E*)-**9a** with 0.44 g (3.5 mmol) of $(COCl)_2$ and 7.5 g of alumina according to the standard preparative-scale procedure for 48 h afforded 0.42 g (84% yield) of a 43:57 mixture of chlorides (*E*)- and (*Z*)-**9a** as a colorless liquid. The major isomer was identified as chloride (*Z*)-**9a** by subtraction of the ^{1}H NMR peaks for chloride (*E*)-**9a**: ^{1}H NMR δ 1.29 (s, 9 H, $(CH_3)_3C$), 6.11 (s, 1 H, CH-2) 7.32 (m, 3 H, CH-2′,

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(31) Klein, J.; Levene, R. *Tetrahedron Lett.* **1974**, *34*, 2935–2938.

(32) Uemura, S.; Okazaki, H.; Okano, M. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1278–1282.

(33) Favini, G.; Trovato, S.; Gamba, A. *Theor. Chim. Acta* **1967**, *7*, 305–312.

(34) Cristol, S. J.; Whittemore, C. A. *J. Org. Chem.* **1969**, *34*, 705–709.

(35) Gordon, J. E.; Chang, V. S. K. *J. Org. Chem.* **1973**, *38*, 3062–3064.

(36) Drefahl, G.; Zimmer, C. *Chem. Ber.* **1960**, *93*, 505–508.

(37) Configurational assignments for iodides **7c** are based on their relative retention times compared with those of halides **7a,b**, as well as the UV absorption spectrum of the *E* isomer compared with those of halides (*E*)-**7a,b**.

(38) (a) Al-Hassan, M. I. *J. Coll. Sci., King Saud Univ.* **1987**, *18*, 103–105. (b) Al-Hassan, M. I. *Synth. Commun.* **1987**, *17*, 1787–1796.

(39) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627–630.

(40) Suzuki, A.; Miyaura, N.; Abiko, S.; Ito, M.; Midland, M. M.; Sinclair, J. A.; Brown, H. C. *J. Org. Chem.* **1986**, *51*, 4507–4511.

-4′, -6′), 7.52 (m, 2 H, CH-3′, -5′); lit.[28] ^{1}H NMR δ 1.29 (s, 9 H), 6.02 (s, 1 H) 7.1–7.6 (m, 5 H).

(*E*)- and (*Z*)-(1-Bromo-3,3-dimethyl-1-butenyl)benzene [(*E*)- and (*Z*)-9b]. Treatment of 0.79 g (5.0 mmol) of alkyne **3** with 3.4 mL of a 1 M solution (3.4 mmol) of PBr_3 and 12.5 g of silica gel according to the standard preparative-scale procedure for 20 h afforded a mixture of bromides (*E*)- and (*Z*)-**9a**, which were separated by preparative gas chromatography (column B, 140 °C). Isolation of the lower retention time product afforded bromide (*E*)-**9b** as a yellow liquid: ^{1}H NMR δ 0.88 (s, 9 H, $(CH_3)_3C$), 6.22 (s, 1 H, CH-2) 7.28 (m, 5 H, C_6H_5); lit.[29] ^{1}H NMR δ 0.88 (s, 9 H), 6.21 (s, 1 H) 7.25 (s, 5 H).

Isolation of the higher retention time product afforded bromide (*Z*)-**9b** as a yellow liquid: ^{1}H NMR δ 1.29 (s, 9 H, $(CH_3)_3C$), 6.28 (s, 1 H, CH-2) 7.30 (m, 3 H, CH-2′, -4′, -6′), 7.48 (m, 2 H, CH-3′, -5′); lit.[29] ^{1}H NMR δ 1.29 (s, 9 H), 6.25 (s, 1 H) 7.0–7.5 (m, 5 H).

(*E*)-(1-Iodo-3,3-dimethyl-1-butenyl)benzene [(*E*)-9c]. Treatment of 0.50 g (3.2 mmol) of alkyne **3** with 1.32 g (3.2 mmol) of PI_3 and 8.0 g of alumina according to the standard preparative-scale procedure for 0.5 h afforded 0.90 g of a yellow liquid, which was shown to consist of 26% alkyne **3** and 74% iodide (*E*)-**9c** by ^{1}H NMR and gas chromatographic analysis. Iodide (*E*)-**9c** was identified by subtraction of the ^{1}H NMR peaks for alkyne **3**: ^{1}H NMR δ 0.88 (s, 9 H, $(CH_3)_3C$), 6.47 (s, 1 H, CH-2) 7.25 (m, 5 H, C_6H_5); ^{13}C NMR δ 30.58, 38.08, 93.72, 127.75, 127.88, 128.22, 144.17, 152.44; lit.[41] ^{1}H NMR ($CDCl_3$) δ 0.97 (s, 9 H), 6.46 (s, 1 H), 7.20–7.39 (m, 5 H).

(*Z*)-(1-Iodo-3,3-dimethyl-1-butenyl)benzene [(*Z*)-9c]. Treatment of 0.35 g (2.2 mmol) of alkyne **3** with 1.02 g (2.5 mmol) of PI_3 and 7.5 g of alumina according to the standard preparative-scale procedure for 36 h afforded 0.40 g of a yellow liquid, which was shown to consist of iodide (*Z*)-**9c** and ketone **11** by ^{1}H NMR and gas chromatographic analysis. Iodide (*E*)-**9c** was identified by subtraction of the ^{1}H NMR peaks for ketone **11**: ^{1}H NMR δ 1.28 (s, 9 H, $(CH_3)_3C$), 6.23 (s, 1 H, CH-2), 7.25 (m, 5 H, C_6H_5); lit.[41] ^{1}H NMR ($CDCl_3$) δ 1.27 (s, 9 H), 6.23 (s, 1 H), 7.20–7.39 (m, 5 H).

3,3-Dimethyl-1-phenyl-1-butanone (11). Chromatography of the preceding crude product over silica gel and elution with 10:1 hexanes/ethyl acetate afforded 0.07 g (18% yield) of ketone **11** as a colorless liquid: ^{1}H NMR δ 1.04 (s, 9 H, $(CH_3)_3C$), 2.84 (s, 2 H, CH_2-2), 7.51 (br m, 3 H, CH-2′, -4′, -6′), 7.92 (m, 2 H, CH-3′, -5′); lit.[42] ^{1}H NMR ($CDCl_3$) δ 1.05 (s, 9 H), 2.86 (s, 2 H), 7.41–8.00 (m, 5 H).

Hydrochlorination of 4-Octyne (14). Treatment of 1.10 g (10.0 mmol) of octyne **14** with 1.78 g (15 mmol) of $SOCl_2$ and 12.5 g of alumina according to the standard preparative-scale procedure for 16 h followed by chromatography over silica gel afforded, on elution with pentane, 0.60 g of a mixture of three products, which were separated by preparative gas chromatography (column A, 120 °C) to afford colorless liquids:

(*E*)-4-Chloro-4-octene [(*E*)-15a]: ^{1}H NMR δ 0.90 (m, 6 H, CH_3-1, -8), 1.38 (m, 4 H, CH_2-2, -7), 2.00 (q, *J* = 7.6 Hz, 2 H, CH_2-6), 2.29 (t, *J* = 7.3 Hz, 2 H, CH_2-3), 5.59 (t, *J* = 7.6 Hz, 1 H, CH-5); lit.[43] ^{1}H NMR ($CDCl_3$) δ 0.9 (m, 6 H), 1.5 (m, 4 H), 2.0 (q, *J* = 7 Hz, 2 H), 2.29 (t, *J* = 7 Hz, 2 H), 5.62 (t, *J* = 7 Hz, 1 H).

(*Z*)-4-Chloro-4-octene [(*Z*)-15a]: ^{1}H NMR δ 0.88 (m, 6 H, CH_3-1, -8), 1.40 and 1.54 (2 × m, 4 H, CH_2-2, -7), 2.13 (q, *J* = 6.1 Hz, 2 H, CH_2-6), 2.26 (t, *J* = 7.3 Hz, 2 H, CH_2-3), 5.42 (t, *J* = 6.1 Hz, 1 H, CH-5); lit.[43] ^{1}H NMR ($CDCl_3$) δ 0.88 and 0.92 (2 × t, 6 H), 1.5 (m, 4 H), 2.2 (m, 4 H), 5.35 (t, *J* = 7 Hz, 1 H).

4,4-Dichlorooctane (16a): ^{1}H NMR δ 0.93 and 0.96 (2 × t, *J* = 7.3 and 7.4 Hz, 6 H, CH_3-1, -8), 1.35 (m, 2 H, CH_2-7), 1.63 (m, 4 H, CH_2-2, -6), 2.15 (m, 4 H, CH_2-3, -5).

(*E*)- and (*Z*)-4-Bromo-4-octene [(*E*)- and (*Z*)-15b]. Treatment of 1.10 g (10.0 mmol) of alkyne **14** with 15 mL of a 1 M solution (15 mmol) of acetyl bromide and 12.5 g of silica gel according to the standard preparative-scale procedure for 1 h followed by chromatography over alumina gave, on elution with pentane, 1.27 g of a yellow liquid, which was further purified by preparative gas chromatography.

Bromide (*E*)-15b was isolated as a colorless liquid, which was identical by ^{1}H NMR spectrum and gas chromatographic time with a specimen prepared independently as previously described:[3b] ^{1}H NMR δ 0.89 (t, *J* = 7.3 Hz, 6 H, CH_3-1, -8), 1.37 and 1.55 (2 × m, 4 H, CH_2-2, -7), 1.98 (q, *J* = 7.5 Hz, 2 H, CH_2-6), 2.38 (t, *J* = 7.3 Hz, 2 H, CH_2-3), 5.85 (t, *J* = 7.7 Hz, 1 H, CH-5); lit.[3b] no spectral data.

Bromide (*Z*)-15b was isolated as a colorless liquid, which was identical by ^{1}H NMR spectrum and gas chromatographic time with a specimen prepared independently as previously described:[3b] ^{1}H NMR δ 0.87 and 0.91 (2 × t, *J* = 7.3 Hz, 6 H, CH_3-1, -8), 1.40 and 1.54 (2 × m, 4 H, CH_2-2, -7), 2.11 (q, *J* = 7.2 Hz, 2 H, CH_2-6), 2.37 (t, *J* = 7.2 Hz, 2 H, CH_2-3), 5.60 (t, *J* = 6.8 Hz, 1 H, CH-5); lit.[3b] no spectral data.

4,4-Dibromooctane (16b). Treatment of 0.50 g (4.5 mmol) of alkyne **14** with 1.94 g (9.0 mmol) of $(COBr)_2$ and 11.25 g of alumina according to the standard preparative-scale procedure for 2 h followed by chromatography over silica gel afforded, on elution with hexanes, 0.68 g (79% yield) of dibromide **16b** as a colorless liquid: ^{1}H NMR δ 0.94 and 0.98 (2 × t, *J* = 7.4 Hz, 6 H, CH_3-1, -8), 1.37 (m, 2 H, CH_2-7), 1.65 (m, 4 H, CH_2-2, -6), 2.31 (m, 4 H, CH_2-3, -5); ^{13}C NMR δ 13.39, 13.98, 21.03, 22.10, 29.70, 50.62, 52.88, 77.09. Anal. Calcd for $C_8H_{16}Br_2$: C, 35.32; H, 5.93. Found: C, 35.42; H, 5.84.

(*E*)- and (*Z*)-4-Iodo-4-octene [(*E*)- and (*Z*)-15c]. Treatment of 1.10 g (10 mmol) of alkyne **14** with 3.70 g (9.0 mmol) of PI_3 and 25 g of alumina according to the standard preparative-scale procedure for 3 h afforded 1.72 g (72% yield) of a 1:5.4 mixture of iodides (*E*)- and (*Z*)-**15c** as a colorless liquid. Iodide (*E*)-**15c**: ^{1}H NMR δ 0.88 (m, 6 H, CH_3-1, -8), 1.40 and 1.52 (2 × m, 4 H, CH_2-2, -7), 2.01 (q, *J* = 7.3 Hz, 2 H, CH_2-6), 2.33 (t, *J* = 6.8 Hz, 2 H, CH_2-3), 6.17 (t, *J* = 7.3 Hz, 1 H, CH-5); lit.[3b] ^{1}H NMR ($CDCl_3$) δ 0.8–2.5 (m, 14 H), 6.20 (t, 1 H).

Iodide (*Z*)-**15c**: ^{1}H NMR δ 0.85 and 0.91 (2 × t, *J* = 7.4 Hz, 6 H, CH_3-1, -8), 1.40 and 1.52 (2 × m, 4 H, CH_2-2, -7), 2.07 and 2.41 (2 × q, *J* = 6.8 Hz, 4 H, CH_2-3, -6), 5.44 (t, *J* = 6.8 Hz, 1 H, CH-5); lit.[3b] ^{1}H NMR ($CDCl_3$) δ 0.8–2.6 (m, 14 H), 5.48 (t, 1 H).

Hydrochlorination of 1-Heptyne (17). Treatment of 0.96 g (10.0 mmol) of alkyne **17** with 1.59 g (12.5 mmol) of $(COCl)_2$ and 25 g of alumina according to the standard preparative-scale procedure for 48 h followed by preparative gas chromatography (column A, 95 °C) afforded the following products as colorless liquids.

2-Chloro-1-heptene (18a):[44] ^{1}H NMR δ 0.88 (t, *J* = 7.0 Hz, 3 H, CH_3-7), 1.31 (m, 4 H, CH_2-5, -6), 1.54 (m, 2 H, CH_2-4), 2.31 (t, *J* = 7.4 Hz, 2 H, CH_2-3), 5.09 and 5.11 (2 × d, *J* = 1.2 Hz, 2 H, CH_2-1); lit.[45] ^{1}H NMR ($CDCl_3$) δ 2.30 (t, 2 H), 5.05 (d, 2 H).

(*E*)-2-Chloro-2-heptene [(*E*)-19a]: ^{1}H NMR δ 0.88 (t, *J* = 7.0 Hz, 3 H, CH_3-7), 1.31 (m, 4 H, CH_2-5, -6), 1.99 (t, *J* = 7.5 Hz, 2 H, CH_2-4), 2.01 (s, 3 H, CH_3-1), 5.56 (t, *J* = 7.7 Hz, CH-3); lit.[45] ^{1}H NMR (CCl_4) δ 1.99 (t, *J* = 7.5 Hz, 2 H) 1.99 (s, 3 H), 5.46 (t, *J* = 7.5 Hz, 1 H).

(*Z*)-2-Chloro-2-heptene [(*Z*)-19a]: ^{1}H NMR δ 0.88 (t, *J* = 7.0 Hz, 3 H, CH_3-7), 1.31 (m, 4 H, CH_2-5, -6), 2.06 (s, 3 H, CH_3-1), 2.11 (m, 2 H, CH_2-4), 5.41 (t, *J* = 7.0 Hz, 1 H, CH-3); lit.[45] ^{1}H NMR (CCl_4) δ 2.05 (s, 3 H), 2.07 (t, *J* = 6.2 Hz, 2 H), 5.32 (t, *J* = 6.2 Hz, 2 H), 5.32 (t, *J* = 6.2 Hz, 1 H).

2,2-Dichloroheptane (20a) was identified by comparison of its ^{1}H NMR spectrum and gas chromatographic retention time with those of a sample prepared independently as described below.

Independent Synthesis of Dichloride 20a. Into a 100-mL round-bottomed flask with condenser were placed 10.0 mmol of 2-heptanone and 50 mL of CH_2Cl_2. To this solution was added 3.12 g (15.0 mmol) of PCl_5. The addition was slightly exothermic and the reaction mixture refluxed spontaneously for 5 min. After an additional 1.5 h of stirring at 25 °C the reaction solution was transferred to a separatory funnel containing 50 mL of H_2O. The organic layer was separated and the aqueous layer washed with 15 mL of fresh CH_2Cl_2. The combined organic fractions were dried over saturated NaCl solution followed by anhydrous Na_2-

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(41) Curran, D. P.; Kim, D. *Tetrahedron* **1991**, *47*, 6171–6188.

(42) Zadok, E.; Rubinraut, S.; Mazur, Y. *J. Org. Chem.* **1987**, *52*, 385–390.

(43) Tarchini, C.; An, T. D. Jan, G.; Schlosser, M. *Helv. Chim. Acta* **1979**, *62*, 635–640.

(44) Isolated as a mixture with chloride (*E*)-**19a**.

(45) Abudarham, J. P.; Meyet, J.; Smadja, W.; Levisalles, J. *Org. Mag. Reson.* **1977**, *10*, 192–197.

SO_4. Into a 100-mL round-bottomed flask was weighed 15 g of alumina, which had been equilibrated with the atmosphere at 120 °C for at least 48 h. The flask was stoppered, and the contents allowed to cool to 25 °C. The preceding solution was added to this flask and the resulting suspension was stirred for 5 min before 2.38 g (20 mmol) of $SOCl_2$ was added. After continued stirring for 24 h, the suspension was filtered and the filtrate washed with three 25-mL portions of CH_2Cl_2. The combined organic fractions were washed with one 50-mL portion each of saturated Na_2CO_3 solution and water. The combined aqueous washings were back-extracted with 25 mL of CH_2Cl_2 and the combined organic fractions were dried over saturated NaCl solution followed by anhydrous Na_2SO_4 and concentrated by rotary evaporation. Distillation at 63–65 °C (21 mmHg) afforded 0.80 g (47% yield) of dichloride **20a** as a colorless liquid: ^{1}H NMR δ 0.93 (t, J = 7.0 Hz, 3 H, CH_3-7), 1.36 (m, 4 H, CH_2-5, -6), 1.66 (m, 2 H, CH_2-4), 2.15 (s, 3 H, CH_3-1), 2.21 (t, J = 8.1 Hz, 2 H, CH_2-3); ^{13}C NMR δ 13.93, 22.43, 25.34, 31.12, 49.78, 90.94; lit.[46] no spectral data.

2-Bromo-1-heptene (18b). According to the standard preparative-scale procedure, 1.44 g (15.0 mmol) of alkyne **17** in 30 mL of C_5H_{12} was treated with 3.07 g (25 mmol) of acetyl bromide and 10 g of Aldrich granular alumina. After 38 h of stirring at 25 °C, an additional 5.0 g of alumina was added and stirring continued for 2 h. Distillation at 57–61 °C (23 mmHg) afforded 1.23 g (46% yield) of bromide **18b** as a colorless liquid: ^{1}H NMR δ 0.91 (t, J = 6.9 Hz, 3 H, CH_3-7), 1.30 (m, 4 H, CH_2-5, -6), 1.56 (m, 2 H, CH_2-4), 2.42 (t, J = 7.3 Hz, 2 H, CH_2-3), 5.39 and 5.46 (2 × s, 2 H, CH_2-1); ^{13}C NMR δ 13.95, 22.36, 27.57, 30.58, 41.38, 116.16, 134.94; lit[21b] bp 55 °C (17 mmHg); ^{1}H NMR (CCl_4) δ 5.3–5.47 (m, CH_2-1).

(*E*)- and (*Z*)-2-Bromo-2-heptene [(*E*)- and (*Z*)-19b]. Treatment of 0.96 g (10.0 mmol) of alkyne **17** with 8 mL of a 1 M solution (8.0 mmol) of PBr_3 and 25 g of alumina according to the standard preparative-scale procedure for 24 h followed by preparative gas chromatography (column A, 95 °C) afforded the following products as yellow liquids.

Isolation of the lower retention time, major product afforded bromide (*Z*)-**19b**: ^{1}H NMR δ 0.88 (t, J = 6.9 Hz, 3 H, CH_3-7), 1.33 (m, 4 H, CH_2-5, -6), 2.10 (m, 2 H, CH_2-4), 2.25 (d, J = 1.3 Hz, 3 H, CH_3-1), 5.58 (tq, J = 6.9, 1.3 Hz, 1 H, CH-3); lit.[47,48] ^{1}H NMR (CCl_4) δ 1.0 (m, 3 H), 1.5 (m, 4 H), 2.2 (m, 2 H), 2.3 (s, 3 H), 5.56 (tq, J = 7, 1.2 Hz, 1 H).

Isolation of the higher retention time product afforded bromide (*E*)-**19b**: ^{1}H NMR δ 0.88 (t, J = 7.0 Hz, 3 H, CH_3-7), 1.31 (m, 4 H, CH_2-5, -6), 1.99 (m, 2 H, CH_2-4), 2.19 (d, J = 1.3 Hz, 3 H, CH_3-1), 5.80 (tq, J = 7.7, 1.3 Hz, 1 H, CH-3); lit.[47,48] ^{1}H NMR (CCl_4) δ 0.9 (m, 3 H), 1.35 (m, 4 H), 2.0 (m, 2 H), 2.2 (s, 3 H), 5.80 (tq, J = 8, 1 Hz, 1 H).

2,2-Dibromoheptane (20b). According to the standard preparative-scale procedure, 0.96 g (10.0 mmol) of alkyne **17** was treated with 5 mL of a 2.0 M solution (10.0 mmol) of $(COBr)_2$ and 25 g of alumina. After 2 h, an additional 2.15 g (10.0 mmol) of $(COBr)_2$ was added as a neat liquid, and stirring was continued for 3 h. The crude product, in 50 mL of CH_2Cl_2, was filtered through a 2.5-cm pad of Florisil, and the solvent was then removed by rotary evaporation. Distillation of the residue at 50–55 °C (1 mmHg) afforded 1.40 g (52% yield) of dibromide **20b** as a yellow liquid: ^{1}H NMR δ 0.93 (br t, 3 H, J = 7.1 Hz, CH_3-7), 1.35 (m, 4 H, CH_2-5, -6), 1.66 (m, 2 H, CH_2-4), 2.31 (m, 2 H, CH_2-3), 2.50 (s, 3 H, CH_3-1); ^{13}C NMR δ 13.93, 22.42, 27.66, 30.91, 41.20, 52.94, 69.02. Anal. Calcd for $C_7H_{14}Br_2$: C, 32.59; H, 5.47. Found: C, 32.76; H, 5.47.

(*E*)- and (*Z*)-1-Bromo-1-heptene [(*E*)- and (*Z*)-21]. Treatment of 1.44 g (15.0 mmol) of alkyne **17** with 1.84 g (15 mmol) of acetyl bromide and 20 g of silica gel according to the standard preparative-scale procedure for 1.5 h followed by distillation at 60–61 °C afforded 0.31 g (12% yield) of an isomeric mixture of bromides (*E*)- and (*Z*)-**21** as a yellow liquid, which was further purified by preparative gas chromatography (column A, 82–85 °C). Isolation of the lower retention time product afforded bromide (*E*)-**21** as a colorless liquid, which was identical with a specimen synthesized independently as described below: ^{1}H NMR δ 0.89 (br t, J = 6.9 Hz, 3 H, CH_3-7), 1.27 and 1.36 (2 × m, 6 H, CH_2-4, -5, -6), 2.01 (q, J = 7.2 Hz, 2 H, CH_2-3), 5.98 (d, J = 12.0 Hz, 1 H, CH-1), 6.13 (m, 1 H, CH-2); ^{13}C NMR δ 13.96, 22.39, 28.27, 31.12, 32.89, 103.98, 138.29; lit.[49] no spectral data.

Isolation of the higher retention time product afforded bromide (*Z*)-**21** as a colorless liquid: ^{1}H NMR δ 0.89 (br t, J = 7.0 Hz, 3 H, CH_3-7), 1.27 and 1.36 (m, 6 H, CH_2-4, -5, -6), 2.16 (q, J = 7.3 Hz, 2 H, CH_2-3), 6.10 (m, 2 H, CH-1, -2); ^{13}C NMR δ 13.99, 22.44, 27.82, 29.65, 31.31, 107.50, 135.06; lit.[50] ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3 H), 1.33 (m, 4 H), 2.17 (m, 2 H), 6.07 (m, 2 H).

Independent Synthesis of Bromide (*E*)-21. According to the general procedure of Zweifel and Whitney,[51] 1.44 g (15 mmol) of alkyne **17** and 5 mL of hexanes were placed in a 100-mL round-bottomed flask at 25 °C under a N_2 atmosphere. The resulting solution was stirred as 15 mL of a 1 M solution (15 mmol) of $[(CH_3)_2CHCH_2]_4AlH$ (DIBAL-H) in hexanes was added over 5 min, and the solution was then warmed to 50 °C for 2 h. The hexanes were removed with mild heating under aspirator pressure, and 10 mL of anhydrous THF was added to the liquid residue. The reaction mixture was cooled to −78 °C, and a solution of 2.40 g (15 mmol) of Br_2 in 10 mL of CCl_4 was added over 15 min. After the addition was complete, the reaction mixture was warmed to 25 °C, and approximately 1 mL of 20% H_2SO_4 was added dropwise. The reaction mixture was poured into 100 mL of C_5H_{12} and the organic fraction washed with 10% $NaHSO_4$ and 10% $NaHCO_3$ solutions and dried over anhydrous Na_2SO_4. Concentration by rotary evaporation and isolation by preparative gas chromatography (column A, 85 °C) gave bromide (*E*)-**21** as a colorless liquid, which had a ^{1}H NMR spectrum and gas chromatographic retention time identical to those of the material described previously.

2-Iodo-1-heptene (18c) and (*E*)-2-Iodo-2-heptene [(*E*)-19c]. Treatment of 0.48 g (5.0 mmol) of alkyne **17** with 1.87 g (11.0 mmol) of acetyl iodide and 12.5 g of alumina according to the standard preparative-scale procedure for 24 h followed by preparative gas chromatography (column A, 90 °C) afforded the following products as colorless liquids.

Isolation of the lower retention time product afforded iodide **18c**: ^{1}H NMR ($CDCl_3$) δ 0.81 (t, J = 7.0 Hz, 3 H, CH_3), 1.26 (m, 4 H, CH_2-5, -6), 1.49 (m, 2 H, CH_2-4), 2.36 (t, J = 7.3 Hz, 2 H, CH_2-3), 5.66 and 5.99 (2 × s, 2 H, CH_2-1); ^{13}C NMR ($CDCl_3$) δ 14.02, 22.40, 28.78, 30.37, 45.31, 112.88, 125.14; lit.[52] no spectral data.

Isolation of the higher retention time product afforded iodide (*E*)-**19c**: ^{1}H NMR δ 0.87 (t, J = 7.1 Hz, 3 H, CH_3-7), 1.30 (m, 4 H, CH_2-5, -6), 2.00 (q, J = 7.0 Hz, 2 H, CH_2-4), 2.34 (d, J = 1.5 Hz, 3 H, CH_3-1), 6.13 (tq, J = 7.5 Hz, 1.5 Hz, 1 H, CH-3); lit.[47,52,53] no spectral data.

(*Z*)-2-Iodo-2-heptene [(*Z*)-19c]. Treatment of 0.48 g (5.0 mmol) of alkyne **17** with 3.40 g (11.0 mmol) of acetyl iodide and 12.5 g of alumina according to the standard preparative-scale procedure for 72 h followed by preparative gas chromatography (column A, 90–95 °C) gave the following two products.

Isolation of the lower retention time product afforded iodide (*Z*)-**19c** as a pink liquid: ^{1}H NMR δ 0.89 (t, J = 7.1 Hz, 3 H, CH_3-7), 1.33 (m, 4 H, CH_2-5, -6), 2.06 (q, J = 6.7 Hz, 2 H, CH_2-4), 2.47 (d, J = 1.5 Hz, 3 H, CH_3-1), 5.38 (tq, J = 6.7, 1.5 Hz, 1 H, CH-3); lit.[47,52] no spectral data.

The higher retention time product was identified as iodide (*E*)-**19c** by comparison of its ^{1}H NMR spectrum and gas

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(46) Kovarik, P.; Valko, L.; Gatial, A. *Chem. Zvesti.* **1982**, *36*, 611–626; *Chem. Abstr.* **1983**, *98*, 35095k.

(47) Configurational assignments for halides **19b,c** are based on their relative retention times compared with chlorides **19a**, along with the assumption that the alkenyl protons should resonate at higher field in the *Z* isomers as exhibited by chlorides **19a** and the closely related halides **15a–c**. This reverses the assignments previously made for bromides **19b**,[48] based on the substituent shielding constants of Tobey, S. W. *J. Org. Chem.* **1969**, *34*, 1281–1298. These constants have been revised for alkenyl chlorides.[45]

(48) Baird, M. S.; Reese, C. B. *Synthesis* **1976**, 385–386.

(49) Block, R.; Benecou, C.; Guibe-Jampal, E. *Tetrahedron Lett.* **1985**, *26*, 1301–1304.

(50) Brown, H. C.; Hamaoka, T.; Ravindran, N.; Subrahmanyam, C.; Somayaji, V.; Bhat, N. *J. Org. Chem.* **1989**, *54*, 6075–6079.

(51) Zweifel, G.; Whitney, C. C. *J. Am. Chem. Soc.* **1967**, *89*, 2753–2754.

(52) Hara, S.; Takinami, S.; Satoru, H.; Hyuga, S.; Suzuki, A. *Chem. Lett.* **1984**, 345–348.

(53) Kamiya, N.; Chikami, Y.; Ishii, Y. *Synlett* **1990**, 675–676.

chromatographic retention time with those of the previously isolated sample.

2-Bromo-3,3-dimethyl-1-butene (23) and 3,3-Dimethyl-2-butanone (26). Treatment of 0.82 g (10.0 mmol) of 3,3-dimethyl-1-butyne (**22**) with 6.7 mL of a 1 M solution (6.7 mmol) of PBr_3 and 25 g of silica gel according to the standard preparative-scale procedure for 14 h followed by preparative gas chromatography afforded bromide **23** as a yellow liquid: ^1H NMR δ 1.17 (s, 9 H, $(CH_3)_3C$), 5.36 and 5.57 (2 × d, J = 2.1 Hz, 2 H, CH_2-1); lit.[54] ^1H NMR (CCl_4) δ 1.19 (s, 9 H), 5.34 and 5.57 (2 × d, J = 1.9 Hz, 2 H).

Ketone **26** was isolated as a yellow liquid, which was identified by comparison of its ^1H NMR spectrum and gas chromatographic retention time with those of a commercial sample.

2,2-Dibromo-3,3-dimethylbutane (24) and 2,3-Dibromo-2,3-dimethylbutane (25). Treatment of 0.82 g (10.0 mmol) of alkyne **22** with 4.32 g (20.0 mmol) of $(COBr)_2$ and 25 g of alumina according to the standard preparative-scale procedure for 3.5 h followed by recrystallization from C_2H_5OH afforded a mixture of dibromides **24** (63%) and **25** (37%) as a colorless solid. Dibromide **24**: ^1H NMR δ 1.27 (s, 9 H), $(CH_3)_3C$), 2.55 (s, 3 H, CH_3-1); lit.[55] ^1H NMR ($CF_2{=}CCl_2$) δ 1.26 (s 9 H), 2.31 (s, 3 H). Dibromide **25**: ^1H NMR δ 2.00 (s, 12 H); lit.[54] ^1H NMR (CCl_4) δ 2.00 (s, 12 H).

HBr Adsorption Studies. To a slurry of 2.5 g of Merck 10181 silica gel or Fisher A540 alumina, which had been equilibrated with the atmosphere at 120 °C for at least 48 h, in 7 mL of CH_2Cl_2 was added the indicated amount of reagent, and the resulting mixture was stirred for 30 min. Stirring was stopped and two 2-mL aliquots of the supernatant liquid were withdrawn and each added to a solution of 94 mg (1.0 mmol) of 2-bicyclo[2.2.1]heptene in 3 mL of CH_2Cl_2 containing an internal hydrocarbon standard. The first solution was stirred for 1 h and analyzed by gas chromatography to determine the amount of HBr remaining in solution. To the second solution was added 0.10 mL of H_2O, and the solution was stirred for 1 h and analyzed by gas chromatography to determine the total amount of HBr and unhydrolyzed reagent remaining in solution.

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Registry nos. supplied by author: **1**, 673-32-5; **2**, 501-65-5; **3**, 4250-82-2; (*E*)-**4a**, 4541-86-0; (*Z*)-**4a**, 4541-84-9; (*E*)-**4b**, 31076-47-8; (*Z*)-**4b**, 31026-78-5; (*E*)-32780-80-6; (*Z*)-**4c**, 32780-79-3; (*E*)-**5**, 54624-37-2; (*Z*)-**5**, 21453-89-4; **6**, 93-55-0; (*E*)-**7a**, 948-98-1; (*Z*)-**7a**, 948-99-2; (*E*)-**7b**, 14447-41-7; (*Z*)-**7b**, 15022-93-2; (*E*)-**7c**, 119379-68-9; **7c**, 46418-24-0; **8**, 451-40-1; (*E*)-**9a**, 38690-88-9; (*Z*)-**9a**, 38690-89-0; (*E*)-**9b**, 56813-83-3; (*Z*)-**9b**, 56813-84-4; (*E*)-**9c**, 125315-95-9; (*Z*)-**9c**, 125315-96-0; **11**, 31366-07-1; **14**, 1942-45-6; (*E*)-**15a**, 10124-70-6; (*Z*)-**15a**, 7321-48-4; (*E*)-**15b**, 24-291-80-3; (*Z*)-**15b**, 24291-81-4; (*E*)-**15c**, 81793-05-7; (*Z*)-**15c**, 86223-33-8; **16b** (novel); **17**, 628-71-7; **18a**, 65786-11-0; **18b**, 3252-91-3; **18c**, 90496-82-5; (*E*)-**19a**, 67804-46-0; (*Z*)-**19a**, 67804-45-9; (*E*)-**19b**, 60254-59-3; (*Z*)-**19b**, 60254-60-6; (*E*)-**19c**, 90496-83-6; (*Z*)-**19c**, 90496-93-8; **20a**, 65786-09-6; **20b** (novel); (*E*)-**21**, 53434-74-5; (*Z*)-**21**, 39924-57-7; **22**, 917-92-0; **23**, 33693-77-5; **24**, 594-77-4; **25**, 594-81-0; **26**, 75-97-8.

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(54) Pross, A.; Sternhell, S. *Aust. J. Chem.* **1971**, *24*, 1437–1447.

(55) Hawkins, B. L.; Bremser, W.; Borcic, S.; Roberts, J. D. *J. Am. Chem. Soc.* **1971**, *93*, 4472–4479.