Anal. Calcd. for $C_{20}H_{28}N_4O_4$: M_r, 388.2104. Found: M_r, 388.2132.

Mixtures of hydrazone **22** with each of the isomeric hydrazones **18**, **20**, and **23** exhibited depressed and broadened melting ranges. The hydrazones were separated by TLC analysis (silica gel coating with an ethyl acetate–hexane eluent, 1:4, v/v) and exhibited the following R_f values: **18**, 0.32; **22**, 0.31; **20**, 0.28, **23**, 0.26. A crystal of the hydrazone **22** was used for X-ray crystallography.

Preparation of Hydrazones 21 and 24. Solutions of 18.1 mg (0.072 mmol) of p-$BrC_6H_4SO_2NHNH_2$ and 1 μL of HOAc in 5 mL of EtOH were treated with solutions of 15.0 mg (0.072 mmol) of one of the ketones **4** or **6** in 2 mL of EtOH. After the resulting solutions had been stirred at 25 °C for 1 h, they were concentrated and the derivatives were collected on a filter and washed with cold (0 °C) EtOH. The crude derivative **21** (24.1 mg or 77%, mp 141–145 °C) was recrystallized from MeOH to separate 21.0 mg (67%) of the hydrazone **21** as colorless prisms: mp 155–156 °C; IR ($CHCl_3$) 3360, 3300 cm^{-1} (NH); ^1H NMR ($CDCl_3$, 300 MHz), δ 9.98 (1 H, s, NH), 7.6–7.8 (4 H, m, aryl CH), 2.55 (1 H, m, 764.3 Hz), 1.2–2.3 (14H, m, aliphatic CH), 0.86 (9 H, s, t-Bu).

Anal. Calcd for $C_{20}H_{29}BrN_2O_2S$: C, 54.41; H, 6.62; Br, 18.10; N, 6.35; S, 7.26. Found: C, 54.38; H, 6.62; Br, 18.13; N, 6.35; S, 7.22.

The crude derivative **24** (27.0 mg or 95%, mp 148–151 °C) was recrystallized from MeOH to separate 18.2 mg (56%) of the hydrazone **24** as colorless prisms: mp 152–153 °C; IR ($CHCl_3$) 3200 cm^{-1} (NH); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.5–7.8 (4 H, m, aryl CH), 3.24 (1 H, m, 970.8, 959.6 Hz), 2.40 (1 H, m, 730.6, 711.5 Hz), 1.0–2.2 (13 H, m, aliphatic CH), 0.87 (9 H, s, t-Bu).

Anal. Calcd for $C_{20}H_{29}BrN_2O_2S$: C, 54.41; H, 6.62; Br, 18.10; N, 6.35; S, 7.26. Found: C, 54.18; H, 6.62; Br, 18.03; N, 6.29; S, 7.15.

Registry No. **3**, 85283-13-2; **4**, 85283-14-3; **5**, 85283-15-4; **6**, 85283-16-5; **7**, 120-92-3; **8**, 57205-03-5; **9**, 1121-66-0; **10**, 24301-22-2; **11a**, 85283-17-6; **11b**, 85283-18-7; (*E*)-**12**, 85283-19-8; (*Z*)-**12**, 85283-20-1; (*E*)-**13**, 85283-21-2; (*Z*)-**13**, 85283-22-3; *cis*-**14**, 5365-37-7; *trans*-**14**, 5365-38-8; **15**, 85283-23-4; *cis*-**16**, 85283-24-5; *trans*-**16**, 85283-25-6; **18**, 85283-26-7; **20**, 85283-27-8; **21**, 85283-28-9; **22**, 85283-29-0; **23**, 85283-30-3; **24**, 85283-31-4; **25**, 85283-32-5; **26**, 85283-33-6; **27**, 85283-34-7; **28**, 15144-12-4; **29**, 85283-35-8; *cis*-**30**, 85283-36-9; *trans*-**30**, 85283-37-0; **31**, 594-56-9; **32**, 85283-38-1; **33**, 16112-10-0; *cis*-**34**, 85283-39-2; *trans*-**34**, 85283-40-5; **35**, 762-72-1; **36**, 17891-78-0; **37**, 85283-41-6; phenylselenyl chloride, 5707-04-0; trimethylsilyl chloride, 75-77-4; methyllithium, 917-54-4; pinacolone, 75-97-8.

Supplementary Material Available: Descriptions of determination of crystal structures for the ketone derivatives **11a** and **22**, including tables of atomic coordinates for each compound (8 pages). Ordering information is given on any current masthead page.

Interhalogen-Catalyzed Cleavages of Ethers and Esters with Trimethylsilyl Bromide or Chloride

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The cleavages of various dialkyl ethers, trimethylsilyl alkyl ethers, and alkyl esters by trimethylsilyl bromide are strongly catalyzed by iodine monobromide. This catalyzed cleavage procedure using iodine monobromide makes possible synthetic applications for trimethylsilyl bromide which were previously ruled out by problems with its low reactivity. Cleavages of benzylic and tertiary alkyl ethers and esters by trimethylsilyl chloride are feasible when catalyzed by iodine monochloride. However, other systems are essentially unreactive toward trimethylsilyl chloride even in the presence of iodine monochloride.

We recently reported[1] that small amounts of molecular iodine catalyze the reactions of trimethylsilyl iodide with alkyl chlorides or bromides to give the corresponding alkyl iodides and trimethylsilyl chloride or bromide. The mechanism proposed[1] to explain the catalytic behavior involves initial formation of an alkyl(trimethylsilyl)halonium iodide species in an equilibrium process (Scheme I). The action of the catalyst is to shift this equilibrium to the right by formation of triiodide.

Scheme I

$$R\text{-}X + Me_3SiI \rightleftarrows R\text{-}X^+\text{-}SiMe_3 + I^-$$

$$I^- + I_2 \rightleftarrows I_3^-$$

$$R\text{-}X^+\text{-}SiMe_3 + I_3^- \xrightarrow[\text{or } S_N2]{S_N1} R\text{-}I + XSiMe_3 + I_2$$

The present paper reports a brief study of the application of the molecular halogen catalysis to the cleavage of ethers and esters with trimethylsilyl bromide or chloride.[2]

It was envisioned that the halogen catalysis with the ethers and esters would be similar to that given in Scheme I, except involving a (trimethylsilyl)oxonium intermediate. In earlier investigations[3] of uncatalyzed cleavages of ethers and esters with trimethylsilyl bromide, only low to no reactivity was exhibited, depending on the specific substrate being examined.

Results and Discussion

Halogen Catalysis of Cleavages with Trimethylsilyl Bromide. Small-scale reactions of trimethylsilyl bromide with selected ethers and esters were initially carried out to determine if their catalysis by halogens was actually possible. Also, it was of considerable interest to determine

(1) Friedrich, E. C.; De Lucca, G. *J. Organomet. Chem.* **1982**, *226*, 143.

(2) Benkeser, R. A.; Mozdzen, E. C.; Muth, C. L. *J. Org. Chem.* **1979**, *44*, 2185. Olah, G. A.; Narang, S. C.; Gupta, G. B.; Malhotra, R. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 612. These authors have reported iodine catalysis of the reactions of trimethylsilyl iodide but not trimethylsilyl bromide or chloride with ethers and esters.

(3) (a) Ho, T. L.; Olah, G. A. *Synthesis* **1977**, 417. (b) Jung, M. E.; Hatfield, G. L. *Tetrahedron Lett.* **1978**, 4483. (c) Kricheldorf, H. R.; Mörber, G.; Regel, W. *Synthesis* **1981**, 383.

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Table I. Molecular-Halogen-Catalyzed Cleavages of Several Alkyl Ethers and Esters with Trimethylsilyl Bromide at 50 °C[a]

substrate	catalyst	est time for 50% reaction, h
c-$C_6H_{11}OCH_3$	none	*b*
	I_2	20
	Br_2	20
	IBr	18
c-$C_6H_{11}OCH_2C_6H_5$	none	*c*
	I_2	1
	Br_2	2
	IBr	<0.5
$CH_3C(O)OCH_3$	none	*b*
	I_2	30
	Br_2	70
	IBr	16
$CH_3C(O)OCH_2C_6H_5$	none	*d*
	I_2	<0.5
	Br_2	<0.5
	IBr	<0.5

[a] All reactions were run neat on a millimole scale in 1:1 molar ratios in NMR tubes at 50 °C by using 10 mol % of the halogen catalyst. [b] No reaction observed after 100 h. [c] With a 1:2 molar ratio of ether to Me_3SiBr, 50% cleavage was observed after 85 h at 50 °C. [d] After 120 h at 50 °C only 15% cleavage was observed.

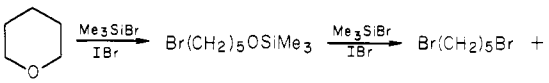
if the nature of the specific halogen used as the catalyst was important. From literature information which was available concerning trihalide formation constants,[4] it was anticipated that the interhalogen iodine monobromide might prove to be the best catalyst.[5]

For this investigation methyl and benzyl cyclohexyl ethers and acetates were selected as examples of representative slow and fast reacting substrates, respectively. Jung and Lyster[6] had found in their studies with trimethylsilyl iodide that uncatalyzed cleavages of methyl cyclohexyl ether and methyl acetate in CCl_4 solvent required 2 and 6 h, respectively, at 50 °C for high conversions. On the other hand, benzyl cyclohexyl ether and benzyl acetate in CCl_4 solvent at 25 °C required less than 0.1 and 0.5 h, respectively, for high conversions.

The results in Table I reveal that all of the halogen catalysts strongly accelerate the ether and ester cleavages by trimethylsilyl bromide with both the methyl and benzyl derivatives. Similar to the behavior observed previously with trimethylsilyl iodide by Jung and Lyster[6], the benzyl derivatives react considerably faster with trimethylsilyl bromide than do the methyl derivatives. It would appear in general that the order of catalytic activity for the various halogens investigated is IBr > I_2 > Br_2. However, the differences are not striking. In cases where there are other functionalities present in the molecules, such as double bonds which would react with IBr, I_2 would clearly be the catalyst of choice.

Cleavage of Dialkyl Ethers with Trimethylsilyl Bromide. To learn more of the synthetic potential of the halogen catalyzed cleavages of dialkyl ethers with trimethylsilyl bromide, we investigated the reactions summarized in Table II. Some of these were done on a small scale to obtain information regarding the effects of structural changes in the ethers on reactivity. However, others were carried out on a preparative scale, and the products were isolated.

The results clearly illustrate the strong catalytic activity of IBr in the dialkyl ether cleavages. It is of special interest to note in the reactions of dibenzyl ether and of tetrahydropyran that only bromide products and no trimethylsilyl ether products were found. This indicates that with these systems the initially formed trimethylsilyl ethers react further with trimethylsilyl bromide to give bromides faster than do the starting ethers (eq 1).



(1)

Finally, in a run which is not included in Table II, anisole was also found to react rapidly with trimethylsilyl bromide and iodine monobromide. However, liberated hydrogen halide and not trimethylsilyl bromide must actually be involved in the cleavage in this system. Thus, there was evidence of some concomitant ring halogenation.

Cleavages of Trimethylsilyl Alkyl Ethers with Trimethylsilyl Bromide. Jung and Hatfield[3] have reported that in the absence of a catalyst the reactions of trimethylsilyl bromide with simple primary, secondary, and tertiary trimethylsilyl alkyl ethers are exceedingly slow. However, Kricheldorf and co-workers[3c] found the cleavages of secondary and tertiary benzylic trimethylsilyl alkyl ethers to be almost quantitative within 12 h under reflux. The results from the present work (Table III) reveal that use of an iodine monobromide catalyst enables simple primary alkyl as well as primary and secondary benzylic trimethylsilyl alkyl ethers to be cleaved readily. Also, with iodine as a catalyst, crotyl trimethylsilyl ether reacted rapidly at room temperature to give an 80:20 mixture of crotyl and α-methylallyl bromides. On the other hand, cyclohexyl trimethylsilyl ether was unreactive even on using the iodine monobromide catalyst. This indicates that for cleavage to occur readily either a system which gives a stabilized carbocation intermediate or one which is unhindered toward nucleophilic backside displacement is required.

Cleavages of Esters with Trimethylsilyl Bromide. Previous workers[3c] have shown that uncatalyzed cleavages of acyclic esters with trimethylsilyl bromide are exceedingly slow. However, the ring opening of lactones proceeds more rapidly.[7] In the present work (Table IV) it has been found that use of an iodine monobromide catalyst enables the cleavages of all but simple secondary alkyl esters to proceed at reasonable rates. With benzyl and *tert*-butyl esters, the cleavages are rapid and quantitative even at room temperature. Also, the ring opening of γ-butyrolactone to give γ-bromobutyric acid proceeded rapidly when the iodine monobromide catalyst was used.

Cleavages Using Trimethylsilyl Chloride. Having been successful in our attempts to catalyze the reactions of trimethylsilyl bromide with ethers and esters, we examined briefly the scope of corresponding cleavages using trimethylsilyl chloride. In preliminary small-scale studies with benzyl acetate as a model substrate, it was of considerable interest to note that the range of catalytic behaviors with various halogen or interhalogen catalysts was quite large. Thus, with a 1:1 molar ratio of benzyl acetate to trimethylsilyl chloride at 50 °C, use of 10 mol % of molecular iodine resulted in only about 7% cleavage to benzyl chloride and trimethylsilyl acetate after 17 h.

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(5) See also: Ibaraki, T.; Katsuko, I. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3235.
(6) (a) Jung, M. E.; Lyster, M. A. *J. Org. Chem.* **1977**, *42*, 3761. (b) Jung, M. E.; Lyster, M. A. *J. Am. Chem. Soc.* **1977**, *99*, 968.
(7) Kricheldorf, H. R. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 689.

Table II. Cleavages of Dialkyl Ethers Using Trimethylsilyl Bromide and IBr Catalyst in the Absence of Solvent

substrate	molar ratio of substrate/ Me_3SiBr/IBr	temp, °C	time, h	products	yield, %
$CH_3OC_6H_{11}$	1:1:0.1	50	54	c-$C_6H_{11}OSiMe_3$ + CH_3Br	75[a,b]
$C_6H_5CH_2OCH_2CH_3$	1:1:0.1	[g]	1	$CH_3CH_2OSiMe_3$ + $C_6H_5CH_2Br$	66[a,c]
$C_6H_5CH_2OC_6H_{11}$	1:1:0.1	[g]	1	$C_6H_{11}OSiMe_3$ + $C_6H_5CH_2Br$	50[a]
$C_6H_5CH_2OCH_2C_6H_5$	1:1:0.1	[g]	1	$C_6H_5CH_2Br$	77[d]
	1:1.3:0.06	[g]	1	$Br(CH_2)_4OSiMe_3$	59[d,e]
	1:1.3:0.1	100	2	$Br(CH_2)_5Br$	71[d,f]

[a] By NMR. [b] Jung and Hatfield[3b] reported 20–25% demethylation of cholestanyl methyl ether after 150 h at 25 °C without a catalyst. [c] Kricheldorf and co-workers[3c] reported that 7 days of reflux were required to bring about 40–50% conversion in the absence of a catalyst. [d] By isolation. Attempts to maximize yields were not carried out. [e] Kricheldorf and co-workers[3c] reported obtaining an 82% yield after 40 h of reflux in the absence of a catalyst. [f] Kricheldorf and co-workers[3c] reported no reaction after 7 days reflux in the absence of a catalyst. [g] Room temperature.

Table III. Reactions of Trimethylsilyl Alkyl Ethers with Trimethylsilyl Bromide Using a Halogen Catalyst in the Absence of a Solvent

substrate	X_2	molar ratio of substrate/ Me_3SiBr/X_2	temp, °C	time, h	product	yield, %
$CH_3(CH_2)_7OSiMe_3$	IBr	1:1.4:0.1	100	6	$CH_3(CH_2)_7Br$	85[a-c]
c-$C_6H_{11}OSiMe_3$	IBr	1:2.0:0.1	100	24		0[b,d]
$C_6H_5CH_2OSiMe_3$	IBr	1:1.4:0.1	[f]	0.5	$C_6H_5CH_2Br$	80[a-c]
$C_6H_5CH(CH_3)OSiMe_3$	IBr	1:1.1:0.1	[f]	0.2	$C_6H_5CH(CH_3)Br$	100[d,e]
$CH_3CH{=}CHCH_2OSiMe_3$	I_2	1:1.1:0.1	[f]	0.2	$CH_3CH{=}CHCH_2Br$	80[d]
					$CH_3CHBrCH{=}CH_2$	20[d]

[a] By isolation. No attempts were made to maximize yields. [b] Jung and Hatfield[3b] reported no evidence for bromide formation on treatment of the trimethylsilyl ether with 2 equiv of Me_3SiBr at 50 °C without a catalyst for 2–4 days. [c] Kricheldorf and co-workers[3c] reported that a 7-day reflux with excess Me_3SiBr but without a catalyst was required to bring about 40–50% conversion of the trimethylsilyl ether. [d] By NMR. [e] Kricheldorf and co-workers[3c] reported that the trimethylsilyl ether was cleaved almost quantitatively within 12 h by refluxing with excess Me_3SiBr in the absence of a catalyst. [f] Room temperature.

Table IV. Cleavages of Esters Using Trimethylsilyl Bromide and IBr Catalyst in the Absence of a Solvent

substrate	molar ratio of substrate/Me_3SiBr/IBr	temp, °C	time, h	product	yield, %
CH_3COOCH_3	1:1:0.1	50	42	$CH_3COOSiMe_3$	80[a,b]
$CH_3COOCH_2CH_3$	1:1:0.1	50	54	$CH_3COOSiMe_3$	50[a]
$CH_3COOC_6H_{11}$	1:1:0.1	50	48	$CH_3COOSiMe_3$	<5[a]
$CH_3COOCH_2C_6H_5$	1:1:0.1	[e]	0.5	$C_6H_5CH_2Br$	82[a]
$CH_3COOC(CH_3)_3$	1:1:0.1	[e]	0.1	$(CH_3)_3CBr$	100[a]
$C_6H_5COOCH_3$	1:1:0.1	50	18	$C_6H_5COOSiMe_3$	46[a]
$C_6H_5COOCH_2C_6H_5$	1:1.3:0.1	[e]	0.3	C_6H_5COOH	85[c]
$(CH_2CH_2COOCH_3)_2$	1:2.6:0.1	100	17	$(CH_2CH_2COOH)_2$	68[c]
	1:1:0.05	[e]	12	$Br(CH_2)_3COOH$	73[c,d]

[a] By NMR. [b] Jung and Hatfield[3b] reported that treatment of methyl acetate with Me_3SiBr at 25 °C for 150 h in the absence of a catalyst resulted in <5% demethylation. [c] By isolation. Attempts to maximize the yield were not carried out. [d] Kricheldorf[7] has reported, for his uncatalyzed reactions with trimethylsilyl bromide, the effect of ring size on lactone reactivity falls in the order 4 > 6 ≃ 7 > 5. With ϵ-caprolactone 20% excess Me_3SiBr 10 h at 100 °C and ca. 30 h at 120 °C were required to give a 96% yield of trimethylsilyl 6-bromohexanoate. [e] Room temperature.

However, with 10 mol % of iodine monochloride, 60% cleavage took place in 17 h. With molecular bromine or with iodine monobromide as catalysts, some benzyl bromide was formed as a side product along with the benzyl chloride. Entirely analogous behavior was observed with benzyl trimethylsilyl ether. Thus, iodine monochloride would appear to be the catalyst of choice for use with trimethylsilyl chloride.

A summary of various cleavages of ethers and esters studied by using trimethylsilyl chloride and iodine monochloride catalyst is given in Table V. The data reveal that these cleavage reactions are all very much slower than those using trimethylsilyl bromide and iodine monobromide catalyst. In fact, with trimethylsilyl chloride only benzyl or tertiary alkyl systems exhibit any reactivity.

Since cleavages of ethers or esters to give chloride products do possess some potential synthetic utility, we examined whether use of dichlorodimethylsilane or trichloromethylsilane instead of trimethylsilyl chloride offered any advantages in reactivity. Thus, with benzyl cyclohexyl ether and with benzyl acetate at 50 °C in 1:1 molar ratios with 10 mol % of iodine monochloride catalyst, dichlorodimethylsilane and trichloromethylsilane were found to be approximately 2 and 4 times as reactive, respectively, as trimethylsilyl chloride. However, with these reagents cyclohexyl methyl ether and methyl acetate still showed no detectable reactivity even after 100 h at 50 °C. Therefore, dichlorodimethylsilane and trichloromethylsilane do not offer any major practical advantages in reactivity over trimethylsilyl chloride.

Table V. Attempted Cleavages of Some Ethers and Esters Using Trimethylsilyl Chloride and ICl Catalyst in a 1:1:0.1 Molar Ratio and in the Absence of a Solvent

substrate	temp, °C	time, h	product	yield,[a] %
$CH_3OC_6H_{11}$	50	66		0
$C_6H_5CH_2OC_6H_{11}$	50	60	$C_6H_5CH_2Cl$	40
$C_6H_5CH_2OSiMe_3$	c	1	$C_6H_5CH_2Cl$	75[b]
CH_3COOCH_3	50	70		0
$CH_3COOCH_2C_6H_5$	50	17	$C_6H_5CH_2Cl$	60
$CH_3COOC(CH_3)_3$	c	0.1	$(CH_3)_3CCl$	75

[a] By NMR. [b] In a reaction carried out on a larger scale for 0.5 h at 100 °C, a 65% isolated yield of benzyl chloride was obtained. [c] Room temperature.

Experimental Section

General Methods. Melting and boiling points are uncorrected. NMR spectra were run on a Varian Associates EM360 or EM390 instrument. All chemical shifts are reported in parts per million downfield from Me_4Si. Unless otherwise noted, all reagents and starting materials were obtained commercially and purified if necessary before use.

Trimethylsilyl Bromide. This material was prepared by two different procedures. For method 1,[8] 10 mL (50 mmol) of hexamethyldisilane was placed into a 25-mL round-bottomed flask fitted with a drying tube and cooled in an ice bath. Bromine (about 8 g, 50 mmol) was then added dropwise until the bromine color persisted. Note that the reaction is extremely exothermic, so it must be carried out with suitable precautions. The reaction mixture was then distilled directly through a short-path distilling head to give 12 g (80% yield) of the trimethylsilyl bromide as a clear, colorless liquid, bp 80 °C (1 atm) [lit.[9] bp 79.9 °C (754 mm)].

For method 2,[10] 30 mL (0.14 mol) of hexamethyldisiloxane and 6.4 g of aluminum powder were added to a 100-mL, three-necked, round-bottomed flask equipped with a reflux condenser, nitrogen inlet, pressure-equalized dropping funnel, and magnetic stirrer. The reaction mixture was heated in an oil bath to 70–80 °C, the oil bath was removed, and with vigorous stirring 12 mL (0.24 mol) of bromine was added dropwise over a period of several hours at a rate such that refluxing was maintained without any external heating. The resulting mixture was then heated under reflux for an additional 2 h and distilled directly under atmospheric pressure through a short-path apparatus. The crude distillate collected (34 g) was redistilled through a short Vigreux column to give 26 g (61% yield) of pure trimethylsilyl bromide as a clear, colorless liquid, bp 80 °C (1 atm) [lit.[9] bp 79.9 °C (755 mm)].

Ethers and Esters. All ethers and esters except those noted below were obtained commercially and purified if necessary before use. Cyclohexyl benzyl ether was prepared in 78% yield by reaction of the sodium alkoxide of cyclohexanol with benzyl bromide in ether: bp 125 °C (8 mm); n^{22}_D 1.5151 [lit.[11] bp 146 °C (17 mm); n^{20}_D 1.5178]. Cyclohexyl methyl ether was prepared similarly in 75% yield except that methyl iodide was used: bp 60–61 °C (64 mm); n^{22}_D 1.4322 [lit.[12] bp 134 °C (762 mm); n^{20}_D 1.4355]. Benzyl trimethylsilyl ether was prepared in 74% yield by reaction of benzyl alcohol, trimethylsilyl chloride, and pyridine: bp 62 °C (3.5 mm); n^{24}_D 1.4738 [lit.[13] bp 90 °C (20 mm); n^{20}_D 1.4749]. Cyclohexyl trimethylsilyl ether was similarly prepared in 65% yield by the reaction of cyclohexanol, trimethylsilyl chloride, and pyridine: bp 78 °C (33 mm); n^{24}_D 1.4289 [lit.[14] bp 168–169 °C (1 atm); n^{20}_D 1.4307]. *n*-Octyl trimethylsilyl ether was obtained in 82% yield: bp 62 °C (2 mm); n^{25}_D 1.4146 [lit.[13] bp 214 °C (1 atm); n^{20}_D 1.4134]. 1-Phenylethyl trimethylsilyl ether was prepared in 80% yield: bp 62 °C (4.1 mm); n^{24}_D 1.4695 [lit.[15] bp 94 °C (16.5 mm); n^{20}_D 1.4707]. But-2-enyl trimethylsilyl ether was synthesized in 60% yield from crotyl alcohol, trimethylsilyl chloride, and *N,N*-dimethylaniline in ether; bp 60 °C (65 mm) [lit.[16] bp 45–47 °C (30 mm)].

General Procedure for Small-Scale Runs. All small scale runs were carried out in tightly capped or sealed NMR tubes by using millimolar quantities of reactants which were weighed or measured by volume directly into the tubes. The reactions were followed by periodic examination by using ^1H NMR techniques.

Cleavage of Dibenzyl Ether with Trimethylsilyl Bromide. Into a 50-mL, round-bottomed flask were added 15 g (76 mmol) of dibenzyl ether and 1.2 g (7.7 mmol) of iodine monochloride.[17] Then, with stirring at room temperature, 12 g (76 mmol) of trimethylsilyl bromide was added dropwise over a 15-min period through an addition funnel. The reaction mixture became slightly warm during the addition. After the mixture was allowed to cool to room temperature, it was decolorized by passing it through a 2 cm × 15 cm column of neutral activity grade 1 alumina with *n*-hexane as the eluent. The *n*-hexane was removed on a rotary vacuum evaporator and the residue distilled through a 50-cm tantalum spiral column to yield 10 g (77% yield) of benzyl bromide: bp 53 °C (3 mm); n^{24}_D 1.5719 [lit.[18] bp 55 °C (2 mm); n^{25}_D 1.5728].

By use of a similar procedure as above except with 10 g (50 mmol) of dibenzyl ether, 0.64 g (2.5 mmol) of iodine, 0.40 g (2.5 mmol) of bromine, and 19 g (120 mmol) of trimethylsilyl bromide, there was obtained 13 g (75% yield) of benzyl bromide, bp 83 °C (15 mm) [lit.[19] bp 82 °C (11 mm)].

Cleavage of Tetrahydrofuran with Trimethylsilyl Bromide. To a mixture of 9.2 g (60 mmol) of trimethylsilyl bromide, 0.38 g (1.5 mmol) of iodine, and 0.24 g (1.5 mmol) of bromine was added 3.5 g (48 mmol) of tetrahydrofuran over a period of 50 min with stirring at room temperature. The workup and distillation gave 6.5 g (59% yield) of 4-bromobutyl trimethylsilyl ether: bp 80–81 °C (12 mm); n^{28}_D 1.4410 [lit.[3c] bp 82–84 °C (12 mm); n^{20}_D 1.4483]; NMR ($CDCl_3$) δ 0.1 (s, 9 H, $Si(CH_3)_3$), 1.5–2.1 (m, 4 H, CH_2CH_2), 3.4 (t, 2 H, CH_2Br), 3.7 (t, 2 H, CH_2O). Note that if the order of addition of the trimethylsilyl bromide and tetrahydrofuran is reversed, mainly high-boiling polymeric products are obtained.

Cleavage of Tetrahydropyran with Trimethylsilyl Bromide. The reaction of 8.6 g (100 mmol) of tetrahydropyran, 1.3 g (5 mmol) of iodine, 0.80 g (5 mmol) of bromine, and 20 g (130 mmol) of trimethylsilyl bromide at reflux for 2 h gave after workup and distillation 9.9 g (71% yield) of 1,5-dibromopentane: bp 77 °C (4 mm); n^{21}_D 1.5139 [lit.[20] bp 95.5 °C (10 mm); n^{20}_D 1.5136].

Cleavage of *n*-Octyl Trimethylsilyl Ether with Trimethylsilyl Bromide. A mixture of 20 g (130 mmol) of trimethylsilyl bromide, 19 g (94 mmol) of *n*-octyl trimethylsilyl ether, 1.2 g (4.7 mmol) of iodine, and 0.78 g (4.8 mmol) of bromine was heated at reflux for 6 h. The workup and distillation gave 15 g (85% yield) of *n*-octyl bromide: bp 71 °C (7 mm); n^{24}_D 1.4526 [lit.[21] bp 79 °C (9 mm); n^{20}_D 1.4527].

Cleavage of Benzyl Trimethylsilyl Ether with Trimethylsilyl Bromide. With stirring at room temperature, 16 g (110 mmol) of trimethylsilyl bromide was added over a 15-min period to 14 g (80 mmol) of benzyl trimethylsilyl ether, 1.0 g (3.9 mmol) of iodine, and 0.62 g (3.9 mmol) of bromine. After being allowed to react at room temperature for 15 min, the reaction mixture was worked up and distilled to give 11 g (80% yield) of benzyl bromide: bp 50 °C (2 mm); n^{24}_D 1.5700 [lit.[18] bp 55 °C (2 mm); n^{25}_D 1.5728].

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Cleavage of Benzyl Benzoate with Trimethylsilyl Bromide. To a mixture of 11 g (50 mmol) of benzyl benzoate, 0.63 g (2.5 mmol) of iodine, and 0.40 g (2.5 mmol) of bromine was added, with stirring with a magnetic stirrer, 10 g (65 mmol) of trimethylsilyl bromide over a 10-min period. After being stirred for 10 min, the mixture was distilled at reduced pressure to give 6.4 g of a dark liquid [bp 80–90 °C (9 mm)] which appeared to consist of a mixture of iodine monobromide and benzyl bromide, 5.0 g of trimethylsilyl benzoate [bp 95 °C (8.5 mm)], and 3.5 g of a pot residue which solidified on cooling. The pot residue and the fraction which boiled at 95 °C (8.5 mm) were combined and stirred with 20 mL of water at room temperature for 30 min. The solid formed was filtered off and dissolved in 50 mL of ether, and the ether layer was extracted with three 25 mL-portions of saturated aqueous $NaHCO_3$. Acidification of the bicarbonate extract with concentrated HCl gave benzoic acid as a white solid which was filtered and air dried: 5.2 g (85% yield); mp 121–122 °C (lit.[22] mp 122 °C).

Cleavage of Dimethyl Adipate with Trimethylsilyl Bromide. Into a 100-mL, round-bottomed flask were added 8.7 g (50 mmol) of dimethyl adipate, 1.6 g (6.5 mmol) of iodine, 1.1 g (6.8 mmol) of bromine, and 20 g (130 mmol) of trimethylsilyl bromide. The mixture was refluxed for 17 h, cooled to room temperature, and treated with 10 mL of concentrated hydrochloric acid. The solid which formed was filtered, washed with a little aqueous sodium sulfite, dissolved in 100 mL of boiling water, and decolorized with Norite and Celite. Acidification of the resulting light yellow solution to pH 2 with concentrated hydrochloric acid gave adipic acid as a white solid which was allowed to air dry: 5.0 g (68% yield); mp 152–153 °C (lit.[23] mp 151–152 °C).

Cleavage of γ-Butyrolactone with Trimethylsilyl Bromide. A mixture of 4.3 g (50 mmol) of γ-butyrolactone, 0.63 g (2.5 mmol) of iodine, 0.40 g (2.5 mmol) of bromine, and 7.7 g (50 mmol) of trimethylsilyl bromide was allowed to stir overnight at room temperature. The workup and distillation gave 6.0 g (73% yield) of 4-bromobutanoic acid: bp 106–109 °C (3.9 mm); n^{24}_D 1.4825 [lit.[24] bp 124–127 °C (7 mm)]; NMR ($CDCl_3$) δ 2.2 (m, 2 H, $CH_2CH_2CH_2$), 2.5 (m, 2 H, CH_2COOH), 3.4 (t, 2 H, CH_2Br), 11.9 (s, 1 H, COOH).

Cleavage of Benzyl Trimethylsilyl Ether with Trimethylsilyl Chloride. A mixture of 16 g (87 mmol) of benzyl trimethylsilyl ether, 1.3 g (8.1 mmol) of iodine monochloride, and 13 g (120 mmol) of trimethylsilyl chloride was heated at reflux for 30 min. The workup and distillation gave 5.3 g (65% yield) of benzyl chloride: bp 83 °C (29 mm) [lit[25] bp 83.6 °C (29 mm)]; NMR (neat) δ 4.3 (s, 2 H, CH_2Cl), 7.1 (s, 5 H, aromatic).

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Registry No. Me_3SiBr, 2857-97-8; c-$C_6H_{11}OCH_3$, 931-56-6; c-$C_6H_{11}OCH_2C_6H_5$, 16224-09-2; $CH_3C(O)OCH_3$, 79-20-9; $CH_3C(O)OCH_2C_6H_5$, 140-11-4; I_2, 7553-56-2; Br_2, 7726-95-6; IBr, 7789-33-5; $C_6H_5CH_2OCH_2CH_3$, 539-30-0; $C_6H_5CH_2OCH_2C_6H_5$, 103-50-4; $CH_3(CH_2)_7OSiMe_3$, 14246-16-3; c-$C_6H_{11}OSiMe_3$, 13871-89-1; $C_6H_5CH_2OSiMe_3$, 14642-79-6; $C_6H_5CH(CH_3)OSiMe_3$, 14856-75-8; $CH_3CH{=}CHCH_2OSiMe_3$, 18269-32-4; $CH_3COOCH_2CH_3$, 141-78-6; $CH_3COOC_6H_{11}$, 622-45-7; $CH_3COOC(CH_3)_3$, 540-88-5; $C_6H_5COOCH_3$, 93-58-3; $C_6H_5COOCH_2C_6H_5$, 120-51-4; $(CH_2CH_2COOCH_3)_2$, 627-93-0; Me_3SiCl, 75-77-4; ICl, 7790-99-0; $Me_3SiSiMe_3$, 1450-14-2; $Me_3SiOSiMe_3$, 107-46-0; $C_6H_5CH_2Br$, 100-39-0; CH_3I, 74-88-4; $C_6H_5CH_2OH$, 100-51-6; tetrahydrofuran, 109-99-9; tetrahydropyran, 142-68-7; γ-butyrolactone, 96-48-0; cyclohexanol sodium salt, 22096-22-6; cyclohexanol, 108-93-0; crotyl alcohol, 6117-91-5.

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Twin Annulation of Naphthalene via a 1,5-Naphthodiyne Synthon. New Syntheses of Chrysene and Dibenzo[*b*,*k*]chrysene

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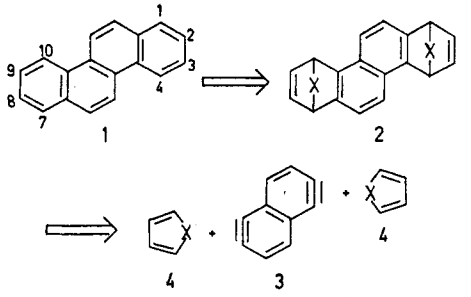
New, efficient syntheses of chrysene (**1**), dibenzo[*b*,*k*]chrysene (**16**), and derivatives are described that feature, as the key step, the formal cycloaddition between 1,5-naphthodiyne (**3**) and a heterocyclic diene (furan, pyrroles, isoindoles). Subsequent manipulation affords the arene in 26–49% overall yield from commercially available 2,6-dibromo-1,5-dihydroxynaphthalene (**5**). The latter is easily converted to ditosylate **6**, which, with phenyllithium, serves as a synthon for **3**.

Chrysene (**1**) and the methylchrysenes are ubiquitous, carcinogenic polycyclic aromatic hydrocarbons[1] (PAH) that are under active investigation by cancer researchers.[2]

Scheme I



These PAH are especially prevalent in tobacco smoke[1a] and various foodstuffs[1c,d] (e.g., spinach, smoked ham), and at least one such derivative, 5-methylchrysene, is highly carcinogenic, having activity comparable to that of ben-

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