80963-52-6; triphenyl(3-butenyl)stannane, 29972-16-5; trimethyl(5-hexenyl)stannane, 73017-74-0; trimethyl(cyclopentylmethyl)stannane, 73017-75-1; triphenyl(cyclopentylmethyl)stannane, 76001-27-9; triphenyl(5-hexenyl)stannane, 73017-73-9; trimethyl(5-hexenyl)germane, 80963-53-7; triphenyl(5-hexenyl)germane, 76001-24-6; trimethyl(6-hepten-2-yl)stannane, 76879-52-2; *cis*-trimethyl(2-methylcyclopentylmethyl)stannane, 76879-57-7; *trans*-trimethyl(2-methylcyclopentylmethyl)stannane, 76879-58-8; dimethylphenyl(6-hepten-2-yl)stannane, 76879-53-3; *cis*-dimethylphenyl(2-methylcyclopentylmethyl)stannane, 76879-59-9; *trans*-dimethylphenyl(2-methylcyclopentylmethyl)stannnane, 76879-60-2; methyldiphenyl-(6-hepten-2-yl)stannane, 76879-54-4; *cis*-methyldiphenyl(2-methylcyclopentylmethyl)stannane, 76879-61-3; *trans*-methyldiphenyl(2-methylcyclopentylmethyl)stannane, 76879-62-4; triphenyl(6-hepten-2-yl)stannane, 76879-55-5; triphenyl(6-hepten-2-yl)germane, 76879-56-6; *cis*-triphenyl(2-methylcyclopentylmethyl)germane, 76900-25-9; *trans*-triphenyl(2-methylcyclopentylmethyl)germane, 76900-26-0; trimethyl(6-hepten-2-yl)germane, 76879-49-7; trimethyl(5(*Z*)-hepten-2-yl)germane, 76879-50-0; trimethyl(5(*E*)-hepten-2-yl)germane, 76879-51-1; *cis*-trimethyl(2-methylcyclopentylmethyl)germane, 76879-63-5; *trans*-trimethyl(2-methylcyclopentylmethyl)germane, 76879-64-6; 2-deuterio-6-heptene, 80963-54-8; *cis*-1-(deuteromethyl)-2-methylcyclopentane, 80963-55-9; *trans*-1-(deuteriomethyl)-2-methylcyclopentane, 80963-56-0; ntrimethylstannyl)lithium, 17946-71-3; (dimethylphenystannyl)lithium, 76879-67-9; (methyldiphenylstannyl)lithium, 4167-85-5; (triphenylstannyl)lithium, 4167-90-2; (trimethylgermyl)lithium, 18489-76-4; (triphenylgermyl)lithium, 3839-32-5.

Supplementary Material Available: Tables of the observed and calculated ^{13}C NMR chemical shifts (and $^{13}C-^{119}Sn$ couplings) for the products of the reactions between substituted cyclohexyl bromides with $Me_{3-x}Ph_xMLi$ (M = Sn, Ge) and also for the corresponding reactions with 6-bromo-1-exene and 6-bromo-1-heptene (Tables VI and VII) (7 pages). Ordering information is given on any current masthead page.

Oxidatively Assisted Nucleophilic Substitution/Elimination of Alkyl Iodides in Alcoholic Media. A Further Study

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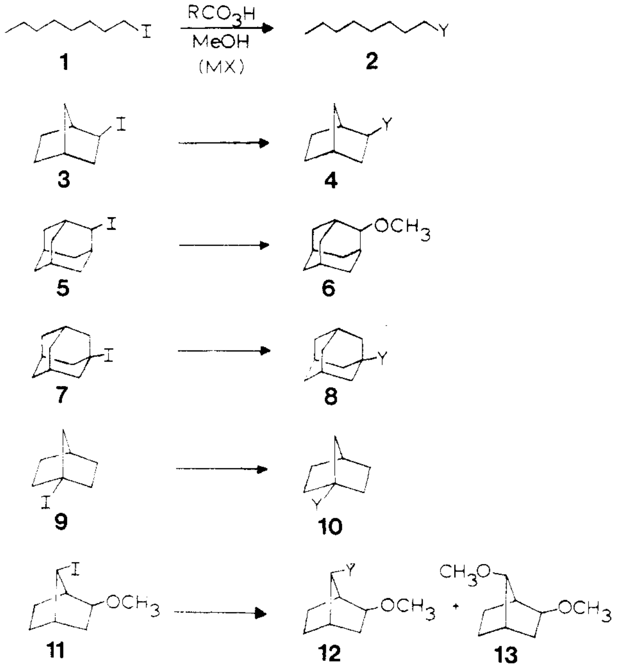
Oxidation of a series of alkyl halides with alcoholic 3-chloroperoxybenzoic acid afforded the results outlined in Charts I–III and Tables I–III. The reaction was found to be a powerful and convenient method for effecting nucleophilic substitution in a variety of systems, including the highly inert 1- and 7-bicyclo[2.2.1]heptyl systems. Qualitatively, the number of molar equivalents of oxidant required varied inversely with the expected ease of substitution for a given system. A mechanism is suggested whereby the iodide is oxidized stepwise to a species RIO_n in which n is an integer sufficiently large that the system in question will undergo nucleophilic substitution or elimination. Reaction in the presence of added chloride or bromide ion usually resulted in a facilitation of reaction rate and a decrease in the number of molar equivalents of oxidant required; the principal product under these conditions was usually the corresponding chloride or bromide.

Treatment of alkyl iodides with peroxy acids has been the subject of several recent papers.[1-5] In nonnucleophilic media simple alkyl iodides are converted principally to the corresponding alcohols, while elimination is the predominant pathway for more complex systems.[3-5] However, when simple alkyl iodides are oxidized in solvents such as methanol or acetic acid, nucleophilic substitution occurs instead.[1,2,4] Iodoso intermediates (RIO) have been proposed to account for this behavior.[2-5] We now report the results of a detailed, systematic study of the oxidation of alkyl iodides with 3-chloroperoxybenzoic acid in alcoholic media which show that this reaction affords an exceptionally mild but powerful, efficient, and selective method for effecting nucleophilic substitution of many systems. Some additional insight into the mechanism of the reaction was also obtained.

Results

The alkyl iodides selected for study, along with the products resulting from their oxidation with 3-chloroperoxybenzoic acid, are shown in Charts I–III. The results from oxidation in methanolic solution are summarized in Table I. Most of the alkyl iodides afforded methyl ether substitution products upon oxidation. (+)-(*S*)-2-Iodooctane (17) which was 76% optically pure[6] afforded (−)-(*R*)-ether 18 (Y = OCH_3) which was 25% optically pure[7] (33% net inversion). One system, 3,3-dimethyl-1-iodopropane (25) underwent accompanying rearrangement, and three systems (14, 19, and 29) apparently underwent initial

Chart I



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0022-3263/82/1947-1904$01.25/0

Table I. Oxidation of Alkyl Iodides with Methanolic 3-Chloroperoxybenzoic Acid[a]

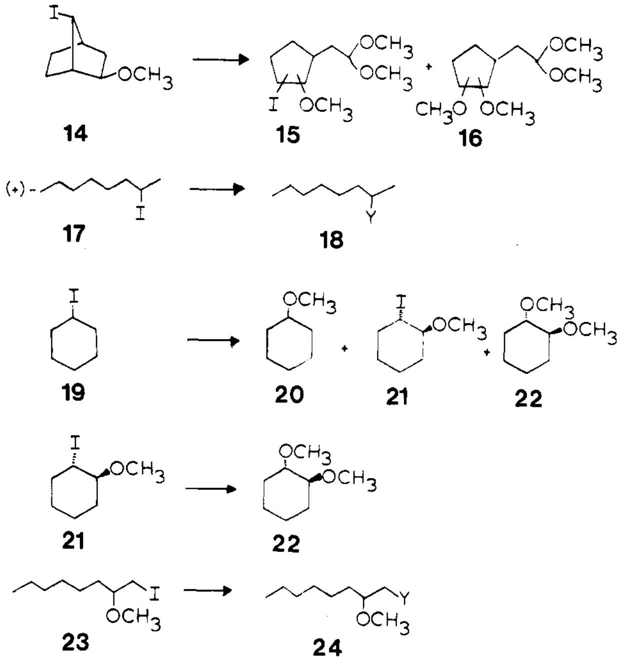
iodide	product	yield,[b] % 2 molar equiv of [O][c]	yield,[b] % sufficient [O] for completion[d]	molar equiv of [O] required for completion
1	2 (Y = OCH_3)	74	99	3
3	4 (Y = OCH_3)	94	98	3
5	6	66	97	3
7	8 (Y = OCH_3)	84		
	8 (Y = OH)	16		
9	10 (Y = OCH_3)	*e*	67	10
	10 (Y = OH)	*e*	16	
11	12 (Y = OCH_3)	*e*	66	7
	13 (Y = OCH_3)	*e*	15	
14	15	12[f]		
	16	23		
17[g]	18 (Y = OCH_3)[h]	53	60	3
19	20	4	4	5
	21	44	*e*	
	22	34	95	
21	22	48	78	3
23	24 (Y = OCH_3)	57	69	3
25	26	54	65	4
27	28 (Y = OCH_3)	60	97	4
29	30	37[f]	*f, i*	4
31	32	65[j,k]	92[j]	4

[a] Conducted as described in the Experimental Section by using 0.05 M methanolic solutions of iodide. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard except where noted. [c] Analysis of aliquots removed from the reaction mixture after treatment with 2 molar equiv of [O] for 3 h as described in the Experimental Section. [d] Analysis of the reaction mixture after treatment with additional 1 molar equiv portions of [O] every 3 h until the iodide was consumed as described in the Experimental Section. [e] None detectable. [f] Additional products present as an inseparable mixture. [g] $[\alpha]^{23}_D$ +43.1°. [h] $[\alpha]^{23}_D$ −2.7°. [i] No detectable amounts of 29 or 30. [j] Yield of isolated product. [k] Product collected after 12 h of oxidation.

elimination or fragmentation to afford alkene intermediates (**33–35**) which reacted further under the oxidation conditions. As shown in Scheme I, independent treatment of each of the suspected alkene intermediates **33–35** under the reaction conditions afforded a mixture of products similar to that obtained from the corresponding iodide. With a fixed amount of oxidant (2 molar equiv) the various iodides went to varying degrees of completion, and differing molar equivalent amounts of oxidant were required for complete oxidation. Interestingly, the 1- and 7-iodobicyclo[2.2.1]heptanes **9** and **11** underwent no detectable reaction until more than 2 molar equiv of oxidant had been added. In contrast with its alkyl analogues, iodobenzene (**31**) afforded none of the substitution product; instead, the iodoxy derivative **32** precipitated from solution.

The results of a detailed study of the oxidation of 1-iodooctane (**1**) in various alcoholic solvents in the presence or absence of various added salts are summarized in Table II. Nucleophilic displacement also occurred in isopropyl and *tert*-butyl alcohols but with reduced efficiency relative

Chart II



Scheme I

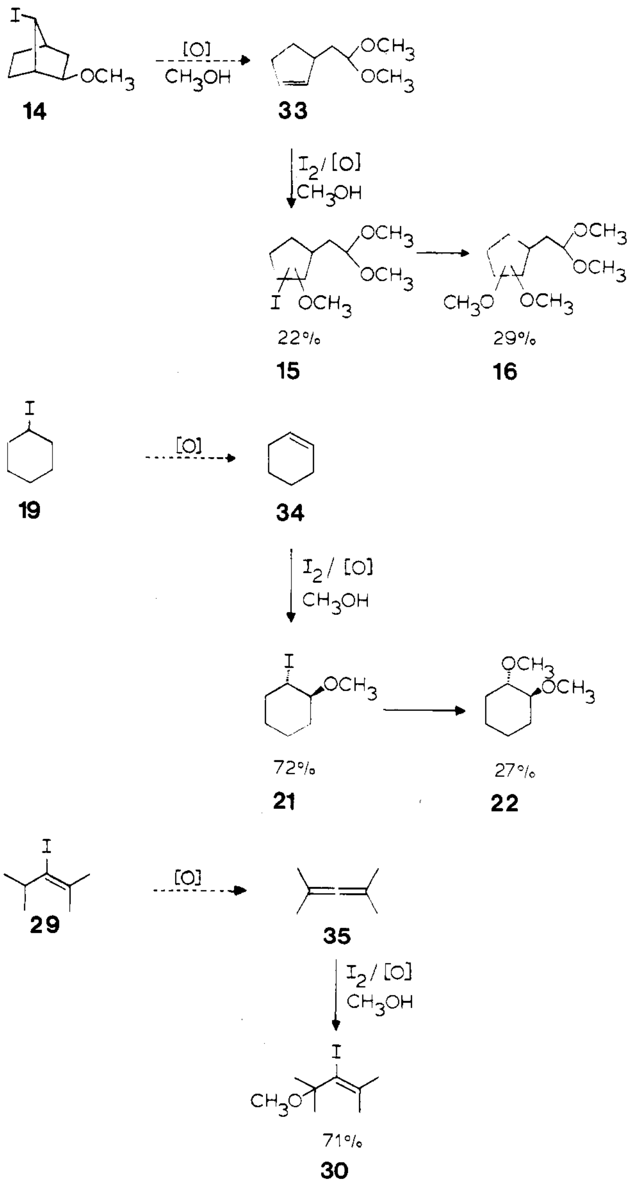
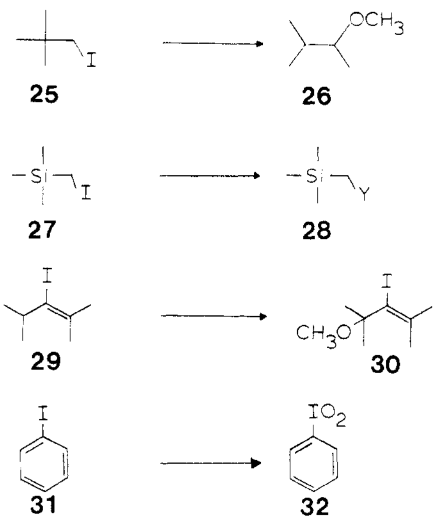


Table II. Oxidation of 1-Iodooctane (1) with 3-Chloroperoxybenzoic Acid[a]

solvent (ROH)	molar equiv of [O]	time, h	salt		yield,[b] %		
						2	
			MX	molar equiv	1	Y = OR	Y = X
CH_3OH	2	3			25	74	
CH_3OH	3	6			1	99	
$(CH_3)_2CHOH$	2	3			49	50	
$(CH_3)_3COH$	2	3			34	12[c]	
CH_3OH	2	3	LiCl	1	42	22	35
CH_3OH	2	3	LiCl	5	21	7	72
CH_3OH	2	3	LiCl	10	18	10	72
CH_3OH	0	3	LiCl	10	98	*d*	*d*
CH_3OH	2	3	LiBr	5	4	14	82
CH_3OH	2	3	NaCl	5	14	24	62
CH_3OH	2	3	KCl	5	13	44	43
CH_3OH	2	3	LiF	5	43	57	*d*
CH_3OH	2	3	$LiClO_4$	5	26	73	*d*
CH_3OH	2	3	NaCN	5	100	*d*	*d*
CH_3OH	2	3	KCN	5	100	*d*	*d*
CH_3OH	2	3	$(C_2H_5)_4NOAc$	5	87	10	*d*
$(CH_3)_2CHOH$	2	3	LiCl	5	19	3	78
$(CH_3)_3COH$	2	3	LiCl	5	23	18	59

[a] Oxidations were conducted as described in the Experimental Section by using 0.05 M solutions of iodide **1**. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the oxidation mixture and quenched as described in the Experimental Section. [c] **2** (Y = OH) formed in 53% yield. [d] None detectable.

Chart III



to methanol. In the latter solvent the principal product was 1-octanol (**2**, Y = OH), with only a small amount of the *tert*-butyl ether **2** [Y = $OC(CH_3)_3$] being formed. In the presence of various chloride salts the corresponding chloride **2** (Y = Cl) was formed in competition with the nucleophilic substitution product **2** (Y = OR). Analogous behavior was exhibited in methanolic lithium bromide; however, other salts either quenched oxidation or had a minimal effect.

The results from oxidation of a number of iodides in the presence of lithium chloride are summarized in Table III. As with 1-iodooctane (**1**), a mixture of the corresponding methyl ether and chloride substitution products was obtained, but the relative amounts varied from system to system. (+)-(*S*)-2-Iodooctane (**17**) which was 76% optically pure[6] afforded (−)-(*R*)-2-chlorooctane (**18**, Y = Cl) which was 62% optically pure[8] (82% inversion) and (−)-(*R*)-ether **18** (Y = OCH_3) which was 34% optically pure[7] (45% inversion). Particularly striking was the effect of the presence of lithium chloride on the 1- and 7-bicyclo[2.2.1]heptyl iodides **9** and **11**, which underwent extensive reaction with 2 molar equiv of oxidant in the presence of lithium chloride but no detectable reaction until more than 2 molar equiv had been added in its absence. In each of the oxidations conducted in the presence of lithium chloride a precipitate formed which had spectral data consistent with those of lithium iodate.

Table III. Oxidation of Alkyl Iodides with Methanolic 3-Chloroperoxybenzoic Acid in the Presence of Lithium Chloride[a]

alkyl iodide	product	yield,[b] %		
		iodide	Y = OCH_3	Y = Cl
1	**2**	21	7	72
3	**4**	12	69	29
9	**10**	48	2	48
11	**12**	32	17[c]	42
17[d]	**18**	12	44[e]	16[f]
23	**24**	22	16	52
27	**28**	*g*	*g*	52

[a] Conducted as described in the Experimental Section by using methanolic solutions 0.05 M in iodide and containing 5 molar equiv of lithium chloride and 2 molar equiv of 3-chloroperoxybenzoic acid. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture after 3 h and quenched as described in the Experimental Section. [c] **13** was also obtained in 5% yield. [d] $[\alpha]^{23}_D$ +43.1°. [e] $[\alpha]^{23}_D$ −3.7°. [f] $[\alpha]^{23}_D$ −22.3°. [g] None detected.

Discussion

As shown by the preceding results, treatment with 3-chloroperoxybenzoic acid in alcoholic solvents is a convenient and exceedingly mild method for effecting the solvolysis of alkyl iodides which has promising synthetic utility. Even such unreactive systems as the 1- and 7-iodobicyclo[2.2.1]heptanes **9** and **11**, which are inert toward silver ion assisted methanolysis,[9,10] afford high yields of

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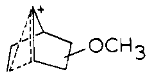
substitution products. Moreover, there is promising potential for effecting selective substitution in the presence of other good leaving groups such as chloride, bromide, or tosylate which are generally inert under the mild conditions required for oxidatively assisted substitution or elimination of alkyl iodides.

A number of interesting contrasts can be seen in the behavior exhibited by various iodides. For example, the 7-syn iodide **11** principally underwent nucleophilic substitution with predominant, but not exclusive, retention of configuration, as expected for the σ-delocalized 7-bicyclo[2.2.1]heptyl cation **36**.[11] The epimeric 7-anti iodide **14** underwent instead extensive fragmentation to **33**, followed by further reaction. This fragmentation, which is novel for the 7-bicyclo[2.2.1]heptyl cation, apparently involves the isomeric delocalized cation **37**, in which an oxygen substituent is available at C-2 to facilitate the fragmentation process.



36

37

Another interesting contrast is provided by iodocyclohexane (**19**), which underwent almost exclusive elimination to cyclohexene (**34**) followed by further reaction, and the β-methoxy derivative **21**, which afforded principally the substitution product **22**. Facile elimination is generally characteristic of the cyclohexyl system.[1,12] Neighboring participation by the methoxyl oxygen in the case of **21** apparently accounts for the difference, since substitution occurred with retention of configuration. Thus, depending on the structure, oxidatively assisted reactions of alkyl iodides involve elimination, fragmentation, or nucleophilic substitution.

It has previously been suggested that reactions of alkyl iodides induced by peroxy acids involve the initial formation of highly labile iodoso intermediates.[2,5] However, it is curious that reaction involves differing numbers of molar equivalents of oxidant depending on the system. Indeed, there is a qualitative correlation between the amount of oxidant required for each system and the expected ease of substitution, with such unreactive systems as the 1- and 7-iodobicyclo[2.2.1]heptanes **9** and **11** requiring the most oxidant. It has been proposed that this variation in stoichiometry is due to a competing catalyzed decomposition of the peroxy acid to carboxylic acid and oxygen.[5] However, it may also be due, at least in part, to a mechanism requiring the formation of a different leaving group IO_n^-, with n increasing from 1 to 3, depending on the ease of substitution for the system in question. That is, stepwise oxidation may occur until the substituent IO_n is a sufficiently good leaving group for substitution or elimination to occur in a given system. Such an interpretation is supported by the observation that the 1- and 7-iodobicyclo[2.2.1]heptanes **9** and **11** showed no detectable reaction on treatment with only 2 molar equiv of oxidant.

Reaction was facilitated by the presence of chloride or bromide salts and required fewer molar equivalents of oxidant under these conditions. Moreover, substitution by chloride or bromide ion generally competed effectively with that by the alcoholic solvent. It is not clear whether these differences simply reflect the greater nucleophilicity of chloride or bromide ion compared with the alcohol or whether there is a change in mechanism in these cases involving a highly reactive $RICl_2$ or $RIBr_2$ intermediate.[13] However, the latter possibility finds support in the 1- and 7-bicyclo[2.2.1]heptyl systems **9** and **11**, which underwent extensive reaction with 2 molar equiv of oxidant in the presence of lithium chloride but no detectable reaction until more than 2 molar equiv had been added in its absence.

Work continues on exploring both the synthetic potential and the mechanistic features of this interesting reaction.

Experimental Section

General Methods. Infrared spectra were obtained by using carbon tetrachloride solutions or potassium bromide pellets with a Beckman 4250 grating spectrophotometer. High-resolution mass spectra were obtained with an AEI MS-902 instrument; the m/e values reported include the parent ion peak and other significantly large peaks appearing above m/e 55. Optical rotations were taken on a Perkin-Elmer 141 polarimeter. Gas chromatographic analyses were performed on a Hewlett-Packard 5750 instrument by using 10 ft × $^1/_8$ in. stainless-steel columns packed with either 20% SF-96 or 20% Carbowax 20M on 60–80-mesh Chromosorb W; the column temperature was increased from 50 to 200 °C at a rate of 8 °C/min following a 4-min postinjection interval. Peak areas were obtained by the cut-and-weigh method and corrected for experimentally determined response factors. Preparative gas chromatography was carried out on either a Varian-Aerograph 90P or 920 instrument using 10 ft × 0.25 in. stainless-steel or nickel columns packed with the materials described above. Nuclear magnetic resonance spectra were obtained on chloroform-*d* solutions with a Varian XL-100 spectrometer; data are reported in the following manner: chemical shift (multiplicity, integration, coupling constant, and assignment). Multiplicity is indicated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = unresolved multiplet, and br s = broadened singlet. All optically active materials were purified by preparative gas chromatography, and their chemical integrity was verified spectroscopically.

Iodides. 1-Iodooctane (**1**), iodomethyltrimethylsilane (**27**), and iodobenzene (**31**) were obtained commercially. 2-*exo*-Iodobicyclo[2.2.1]heptane (**3**),[14] 2-iodoadamantane (**5**),[9] 1-iodoadamantane (**7**),[15] 1-iodobicyclo[2.2.1]heptane (**9**),[16] 7-*anti*-iodo-2-*exo*-methoxybicyclo[2.2.1]heptane (**14**),[10] (+)-(*S*)-2-iodooctane (**17**),[6a] iodocyclohexane (**19**),[17] *trans*-1-iodo-2-methoxycyclohexane (**21**),[18] 2,2-dimethyl-1-iodopropane (**25**),[17] and 2,4-dimethyl-3-iodopent-2-ene (**29**),[19] were prepared as previously reported.

7-*syn*-Iodo-2-*exo*-methoxybicyclo[2.2.1]heptane (11). To a stirred mixture of 6.9 g (73 mmol) of bicyclo[2.2.1]hept-2-ene, 22.9 g (99.8 mmol) of silver oxide, and 300 mL of methanol cooled to 0 °C was added 26.0 g (102 mmol) of iodine over a 1-h period. The resulting mixture was stirred overnight at room temperature, filtered, and distilled at 85–86 °C (2 mm) to afford 13.7 g (54.4 mmol, 74% yield) of iodide **11** as a colorless liquid: IR (CCl_4) ν_{max} 2964, 2941, 2873, 2820, 1467, 1453, 1376, 1301, 1227, 1219, 1194, 1152, 1133, 1121, 1065, 951 cm^{-1}; ^1H NMR δ 3.62 (t, 1, J = 0.8 Hz, CH-7), 3.43 (m, 1, CH-2), 3.31 (s, 3, OCH_3), 2.60 (br s, 1, bridgehead), 2.47 (br s, 1, bridgehead), 2.26–0.86 (m, 6); mass spectrum, m/e (relative intensity) 252.0015 (calcd for $C_8H_{13}IO$ m/e 252.0012), 125 (29), 93 (15), 67 (100).

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[11] Gassman, P. G.; Hornback, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 2487–2488. Miles, F. B. *Ibid.* **1968**, *90*, 1265–1268.

[12] Silver ion assisted solvolysis of iodocyclohexane (**19**) has been reported to afford cyclohexene (**34**) exclusively. See: Tiffeneau, M. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1914**, *59*, 773–775.

[13] Several alkyl iododichlorides have been prepared but are highly unstable. See: (a) Exner, O. *Collect. Czech. Chem. Commun.* **1959**, *24*, 3562–3571. (b) Dence, J. B.; Roberts, J. D. *J. Org. Chem.* **1968**, *33*, 1251.

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[19] McNeely, S. A. Ph.D. Dissertation, University of North Carolina, 1976.

Anal. ($C_8H_{13}IO$) C, H, I.

1-Iodo-2-methoxyoctane (23). To a stirred mixture of 3.0 g (27 mmol) of 1-octene, 3.8 g (31 mmol) of silver oxide, and 150 mL of methanol cooled to 0 °C was added 8.2 g (32 mmol) of iodine over a 30-min period. The resulting mixture was stirred for an additional 6 h at room temperature and then filtered. The methanolic solution was diluted with 100 mL of water and extracted with two 50-mL portions of diethyl ether. The ether layer was washed consecutively with a 50-mL portion of saturated sodium thiosulfate solution and a 100-mL portion of saturated sodium chloride solution, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to yield 5.0 g (18 mmol, 67% yield) of iodine **23** as a pale yellow liquid: IR (CCl_4) ν_{max} 2924, 2856, 2820, 1465, 1456, 1369, 1181, 1151, 1095, 628 cm^{-1}; ^{1}H NMR δ 3.41 (s, 3, OCH_3), 3.29 (d, 2, J = 4 Hz, CH-1), 3.0 (m, 1, CH-7), 1.52–1.09 (m, 10), 1.03–0.70 (m, 3, CH-8); mass spectrum, m/e (relative intensity) 270.0482 (calcd for $C_9H_{19}IO$ m/e 270.0482), 185 (77), 143 (25), 129 (97), 87 (60), 71 (38), 69 (100), and 58 (94).

Anal. ($C_9H_{19}IO$) C, H, I.

Oxidation Procedure. (A) Without Metal Salt. Alkyl iodide (1.00 mmol) and 60 mg of hydrocarbon standard (usually tetradecane or hexadecane) were added to 20 mL of solvent in a 25-mL round-bottomed flask equipped with a magnetic stirring bar. After the solution had been stirred for 10 min, an initial aliquot was withdrawn. At this point, 400 mg (2.00 mmol) of 3-chloroperoxybenzoic acid (Aldrich 80–90%) was added in one portion. After 3 h a second aliquot was withdrawn, placed in a 0.5-dram vial, and quenched by the addition of 3 drops each of 10% sodium sulfite and 10% sodium hydroxide solution. The solution was extracted in the vial with 10 drops of diethyl ether, and the organic layer was used for gas chromatographic analysis. If starting material remained, an additional (1.00 mmol) portion of 3-chloroperoxybenzoic acid was added as a solid. After 3 h another aliquot was removed and the procedure repeated until no further starting material remained. The initial aliquot was then reanalyzed for simple solvolysis.

After the completion of oxidation, the reaction mixture was added to a 100-mL portion of water and extracted with a 100-mL portion of diethyl ether. The ether layer was washed consecutively with 25-mL portions each of 10% sodium sulfite solution, 10% sodium hydroxide solution, and water. The combined aqueous layers were back-extracted with a 25-mL portion of diethyl ether. The combined organic layers were then washed with 50 mL of saturated sodium chloride solution, dried over anhydrous sodium sulfate, and concentrated by distillation of the solvent through a Vigreux column.

(B) With Metal Salt. A modification of the above procedure was used. The metal salt was added with the halide and hydrocarbon standard to the solvent. Two initial aliquots were then removed, and one was quenched and extracted as described above. At the conclusion of the reaction the second initial aliquot was quenched, extracted, and analyzed.

(C) Products. From the oxidations outlined in Tables I–III the following products were obtained.

1-Octanol (2, Y = OH), **1-chlorooctane** (2, Y = Cl), **1-bromooctane** (2, Y = Br), **1-adamantanol** (8, Y = OH), and **(chloromethyl)trimethylsilane** (28, Y = Cl) were characterized by direct comparison with commercial specimens.

1-Methoxyoctane (2, Y = OCH_3),[9] **2-*exo*-methoxybicyclo[2.2.1]heptane** (4, Y = OCH_3),[20] **2-methoxyadamantane (6)**,[21] **1-methoxyadamantane** (8, Y = OCH_3),[22] **1-methoxybicyclo[2.2.1]heptane** (10, Y = OCH_3),[22] **bicyclo[2.2.1]heptan-1-ol** (10, Y = OH),[22] **1-chlorobicyclo[2.2.1]heptane** (10, Y = Cl),[22] **2-*exo*,7-*syn*-dimethoxybicyclo[2.2.1]heptane** (12, Y = OCH_3),[23] **7-*syn*-chloro-2-*exo*-methoxybicyclo[2.2.1]heptane** (12, Y = OCH_3),[10] **2-*exo*,7-*anti*-dimethoxybicyclo[2.2.1]heptane (13)**,[23] **2-chlorooctane** (18, Y = Cl),[24] **2-methoxyoctane** (18, Y = OCH_3),[9] **methoxycyclohexane (20)**,[25] **1,2-dimethoxyoctane** (24, Y = OCH_3),[26] **1-chloro-2-methoxyoctane** (24, Y = Cl),[27] **2-methoxy-2-methylbutane (26)**,[28] **(methoxymethyl)trimethylsilane** (28, Y = OCH_3),[29] and **iodoxybenzene (32)**[30] had spectral properties in agreement with those reported in the literature.

1-(Methylethoxy)octane (2, Y = $OCH(CH_3)_2$) was isolated as a colorless liquid: IR (CCl_4) ν_{max} 2970, 2930, 2854, 1466, 1456, 1380, 1368, 1335, 1172, 1149, 1125, 1081 cm^{-1}; ^{1}H NMR δ 3.40 (t, 2, J = 6.5 Hz, CH_2-1), 3.50 (m, 1, OCH), 1.17 (d, 6, J = 6.5 Hz $C(CH_3)_2$), 1.62–0.70 (m, 15); mass spectrum, m/e (relative intensity) 172.1828 (calcd for $C_{11}H_{24}O$ m/e 172.1827), 157 (56), 113 (31), 73 (58), 71 (98), 69 (23), 61 (21), 57 (100).

1-(Dimethylethoxy)octane (2, Y = $OC(CH_3)_3$) was isolated as a colorless liquid: IR (CCl_4) ν_{max} 2970, 2912, 2852, 1465, 1456, 1388, 1360, 1195, 1075 cm^{-1}; ^{1}H NMR δ 3.33 (t, 2, J = 6 Hz, CH-1), 1.20 (s, 9, $C(CH_3)_3$), 1.59–0.76 (m, 15); mass spectrum, m/e (relative intensity) 186.1986 (calcd for $C_{12}H_{26}O$ m/e 186.1983), 171 (56), 82 (28), 71 (100), 69 (95), 68 (28).

2-*exo*-Chlorobicyclo[2.2.1]heptane (4, Y = Cl) was isolated as a colorless liquid with spectral properties identical with those of an independently prepared specimen:[10] IR (CCl_4) ν_{max} 2958, 2910, 2870, 1452, 1441, 1315, 1255, 946, 896, 695 cm^{-1}.

A mixture consisting of **2-iodo-3-methoxy- and 3-iodo-2-methoxycyclopentane-1-acetaldehyde dimethyl acetal (15)** was isolated as a colorless liquid which was characterized by gas chromatographic retention time and spectral data: IR (CCl_4) ν_{max} 2978, 2930, 2890, 2820, 1456, 1360, 1190, 1120, 1095, 1053 cm^{-1}; the ^{1}H NMR spectrum had a complex multiplet δ 4.12–4.68 consisting of at least three different protons in the region of $CH(OCH_3)$ and CHI and a broad signal at δ 2.98–3.48 representing multiple OCH_3 signals.

A mixture of **2,3-dimethoxycyclopentane-1-acetaldehyde dimethyl acetal** isomers **(16)** was isolated as a colorless liquid: IR (CCl_4) ν_{max} 2989, 2931, 2891, 2811, 1481, 1362, 1187, 1123, 1105, 1091, 1042, 809 cm^{-1}; ^{1}H NMR δ 4.20 (t, 1, J = 6 Hz, $CH(OCH_3)_2$), 3.74–3.06 (m, 14, OCH_3 and CH-2 and CH-3), 2.16–1.22 (m, 7).

***trans*-1,2-Dimethoxycyclohexane (22)** was isolated as a colorless liquid: IR (CCl_4) ν_{max} 2974, 2932, 2859, 2817, 1454, 1192, 1144, 1100 cm^{-1}; ^{1}H NMR δ 3.46 (s, 6, OCH_3), 3.14–3.00 (m, 2, $CHOCH_3$), 2.19–1.11 (m, 8); lit.,[22] no spectral data given. This material was identical with that prepared independently as described below.

2,4-Dimethyl-3-iodo-4-methoxypent-2-ene (30) was isolated as colorless crystals: IR (CCl_4) ν_{max} 2986, 2936, 2830, 1608, 1467, 1456, 1444, 1380, 1365, 1204, 1170, 1145, 1077, 829, 610, 582 cm^{-1}; ^{1}H NMR δ 3.37 (s, 3, OCH_3), 2.12 (s, 3, $=CCH_3$), 2.07 (s, 3, $=CCH_3$), 1.53 (s, 6, $OC(CH_3)_2$); mass spectrum, m/e (relative intensity) 254.0166 (calcd for $C_8H_{15}IO$ m/e 255.0169), 239 (24), 222 (82), 96 (26), 95 (65), 81 (24), and 73 (100).

Lithium iodate was isolated from oxidations in the presence of lithium chloride as a colorless precipitate which had spectral properties in agreement with those previously reported.[32]

Oxidation of Alkenes. (A) 2-Cyclopentene-1-acetaldehyde Dimethyl Acetal (33). To 20 mL of methanol in a 25-mL round-bottomed flask containing a magnetic stirring bar were added 170 mg (1.09 mmol) of alkene **33**,[33] 52 mg of decane, 150 mg (0.59 mmol) of iodine, and 480 mg (2.40 mmol) of 3-chloroperoxybenzoic acid. After being stirred for 3 h, the reaction mixture was worked up as described above. Preparative gas chromatography afforded a mixture of iodides **15** (22%) and a mixture of dimethoxycyclopentanes **16** (22%) as colorless liquids

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having spectral properties consistent with those described above.

(B) Cyclohexene (34). To 20 mL of methanol in a 25-mL round-bottomed flask containing a magnetic stirring bar were added 130 mg (1.60 mmol) of cyclohexene (**34**), 30.4 mg of tetradecane, 300 mg (1.20 mmol) of iodine, and 700 mg (3.50 mmol) of 3-chloroperoxybenzoic acid. After being stirred for 3 h, the reaction mixture was worked up as described above. Preparative gas chromatography afforded iodide **21** (72%) and diether **22** (27%) as colorless liquids having spectral properties consistent with those described above.

(C) 2,4-Dimethyl-2,3-pentadiene (35). To 20 mL of methanol in a 25-mL round-bottomed flask containing a magnetic stirring bar were added 85 mg (0.89 mmol) of diene **35**, 20.6 mg of hexadecane, 120 mg (0.47 mmol) of iodine, and 400 mg (1.97 mmol) of 3-chloroperoxybenzoic acid. After being stirred for 3 h, the reaction mixture was worked up as described above. Preparative gas chromatography afforded iodide **30** (71%) as colorless crystals having spectral properties consistent with those described above.

Independent Synthesis of *trans*-1,2-Dimethoxycyclohexane (22).[34] To a solution of 1.16 g (10.0 mmol) of *trans*-1,2-cyclohexanediol in 20 mL of freshly distilled dimethoxyethane was added 48 mg (20 mmol) of sodium hydride, and resulting mixture was stirred for 4 h at room temperature under an atmosphere of nitrogen. Methyl iodide (2.8 g, 20 mmol) was added in one portion, and the solution was maintained at 40 °C for 24 h. Dilution with an equal volume of water and continuous extraction for 24 h with pentane, followed by distillation of the organic layer, afforded 75 mg of a colorless oil [bp 75 °C (32–34 mm)] which had spectral properties identical with those described above for ether **22**.

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Registry No. 1, 629-27-6; **2** (Y = OCH_3), 929-56-6; **2** (Y = OPr-i), 30983-85-8; **2** (Y = OBu-t), 51323-70-7; **2** (Y = Br), 111-83-1; **2** (Y = Cl), 111-85-3; **3**, 30983-85-8; **4** (Y = OCH_3), 10395-53-6; **4** (Y = Cl), 765-91-3; **5**, 18971-91-0; **6**, 19066-23-0; **7**, 768-93-4; **8** (Y = OCH_3), 6221-74-5; **8** (Y = OH), 768-95-6; **9**, 930-80-3; **10** (Y = OCH_3), 57901-28-7; **10** (Y = OH), 51566-98-4; **10** (Y = Cl), 765-67-3; **11**, 80754-45-6; **12** (Y = OCH_3), 13921-80-7; **12** (Y = Cl), 80754-46-7; **13**, 34300-08-8; **14**, 80754-47-8; **15** (isomer 1), 80754-48-9; **15** (isomer 2), 80754-49-0; **16**, 80754-50-3; **17**, 1809-04-7; 18 (Y = OCH_3), 56711-42-3; 18 (Y = Cl), 18651-57-5; **19**, 626-62-0; **20**, 931-56-6; **21**, 54826-41-4; **22**, 29887-60-3; **23**, 80754-51-4; **24** (Y = OCH_3), 54583-18-5; **24** (Y = Cl), 34786-17-9; **25**, 15501-33-4; **26**, 62016-49-3; **27**, 4206-67-1; **28** (Y = OCH_3), 14704-14-4; **28** (Y = Cl), 2344-80-1; **29**, 35895-37-5; **30**, 80754-52-5; **31**, 591-50-4; **32**, 696-33-3; **33**, 20145-40-8; **34**, 110-83-8; **35**, 1000-87-9; bicyclo[2.2.1]hept-2-ene, 498-66-8; 1-octene, 111-66-0; *trans*-1,2-cyclohexanediol, 1460-57-7.

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[34] We are indebted to P. R. Worsham for this preparation.

Synthesis of Strained Heterobicycles from Alkynes and Heterocumulenes

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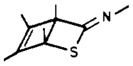
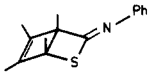
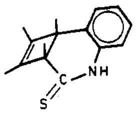
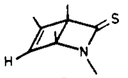
A one-pot synthesis of strained heterobicycles such as 2-thia(or 2-aza)-3-iminobicyclo[2.2.0]hex-5-enes and 2-thia-3-azabicyclo[4.2.0]oct-7-ene 2-oxides from alkynes, aluminum halides, and heterocumulenes (isothiocyanates, carbodiimides, *N*-sulfinylaniline) is described. The thermal and acid-promoted reactions of the permethylated 2-thia-3-iminobicyclo[2.2.0]hex-5-ene **2** to monocyclic isomers are reported.

In addition to the use of aluminum halide σ complexes of cyclobutadienes for the synthesis of four-, five-, and six-membered-ring compounds[1] such as Dewar benzenes, cyclopentadienes, and pyridines, a new method of preparation of Dewar pyridones with these σ complexes and isocyanates[2] was recently introduced. In this paper it will be shown that isothiocyanates, carbodiimides, and *N*-sulfinylaniline react in a similar way with the aluminum halide σ complexes, affording strained heterobicyclic compounds. In the case of isothiocyanates and carbodiimides a difference is observed with comparable reactions involving organotransition-metal complexes, alkynes, and isothiocyanates[3] or carbodiimides:[4] under these circumstances monocyclic six-membered-ring compounds are formed.

Table I. Reactions of Aluminum Halide σ Complexes of Cyclobutadienes with Isothiocyanate

complex	isothiocyanate (RN=C=S)	product(s)	yield,[a] %
1 ($AlCl_3$)	R = Me	 2	66
1 ($AlCl_3$)	R = Ph	 3a  3b	35 (1/1 3a/3b)
4 (Al_2Br_6)	R = Me	 5	70

[a] Yields are based on the amount of alkyne used.

Dewar pyridones are easily converted to 2-pyridones either thermally[2,5] or by acid.[2] A similar investigation of

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