Peroxide as a Source of Alkyl Radicals. In a typical procedure Co(phen)$_3$(PF$_6$)$_3$ (0.41 g, 400 μmol) was placed in a 50-mL tube and a calculated amount of BrCCl$_3$ in CH$_3$CN added, followed by 50 mmol of butyryl peroxide dissolved in CH$_3$CN. The volume was brought up to 10 mL, the solution degassed by a freeze–pump–thaw cycle, and the tube sealed in vacuo. After the tubes were left sitting in the bath for 8 h at 70 °C, they were opened and filled with argon. After GC analysis of CO$_2$ on a Porapak Q column, hexane and n-propyl bromide were analyzed on a Carbowax 20 M column. The cobalt complex was collected by concentrating the solution in vacuo and then adding ether. The recovered complex was analyzed directly for its *n*-Prphen content (12.7 μmol for 200 μmol of BrCCl$_3$). Analysis: *n*-propyl bromide (45.1 μmol), *n*-propylacetamide (1.0 μmol), *N*-isopropylacetamide (2.2 μmol). The latter resulted from the ionic decomposition of the peroxide.

The direct competition between (phen)$_3$Fe^{3+} (500 μmol) and phenH$^+$ for methyl radical was carried out with 0.25, 0.50, and 1.00 mmol of phenH$^+$ OTf$^-$, using Me$_4$Pb (98 μmol) in 20 mL of CH$_3$CN. After 1 h, the solution was analyzed and then concentrated in vacuo. The phenanthroline complexes were precipitated with ether, and the protonated derivative was separated by extraction with successive portions of ethanol.

Cyclic Voltammetry. The standard reduction potentials of the ML$_3{}^{3+,2+}$ couples were measured by cyclic voltammetry on a Princeton Applied Research model 173 potentiostat/galvanostat equipped with a Houston Instrument Series 2000 Omnigraphic X-Y recorder, as previously described.[11] The measurements were carried out at 25 °C in CH$_3$CN containing 0.1 M tetraethylammonium perchlorate as the supporting electrolyte. A platinum microelectrode was employed with a saturated NaCl calomel reference electrode.

Acknowledgment. We wish to thank the National Science Foundation for financial support, and R. J. Klingler for the writing of the Fortran program for the digital simulation of the kinetics using Feldberg's method.

Registry No. Methyl, 2229-07-4; ethyl, 2025-56-1; *n*-propyl, 2143-61-5; isopropyl, 2025-55-0; isobutyl, 4630-45-9; *tert*-butyl, 1605-73-8; neopentyl, 3744-21-6; benzyl, 2154-56-5; cyclohexyl, 3170-58-9; Fe(phen)$_3{}^{3+}$, 13479-49-7; Os(phen)$_3{}^{3+}$, 47837-53-6; Ru(phen)$_3{}^{3+}$, 23633-32-1; Co(phen)$_3{}^{3+}$, 18581-79-8; Cr(phen)$_3{}^{3+}$, 15276-16-1; Fe(5-NO$_2$phen)$_3{}^{3+}$, 22327-24-8; Fe(4,7-Me$_2$phen)$_3{}^{3+}$, 17378-76-6; Fe(bpy)$_3{}^{3+}$, 18661-69-3; Fe(4,7-Ph$_2$phen)$_3{}^{3+}$, 53204-05-0; Fe(5-Cl(phen))$_3{}^{3+}$, 22327-23-7; Me(phen), 31301-28-7; Et(phen), 80206-19-5; *n*-Pr(phen), 80186-77-2; *i*-Pr(phen), 80186-78-3; *i*-Bu(phen), 80186-79-4; neopentyl(phen), 80186-80-7.

Generation of 2-(Trimethylsiloxy)allyl Cations and Their Reactions with 1,3-Dienes. Change in Mechanism of 3 + 4 → 7 Cycloaddition with Solvent[1]

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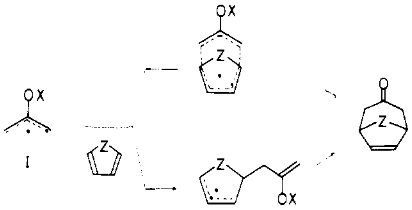
Abstract: A series of 12 different 2-(trimethylsiloxy)allyl cations **34a–l** is generated from various 2-(trimethylsiloxy)allyl chlorides (**3–5**) with silver perchlorate. In nitromethane solution, all the cations smoothly react with furan and cyclopentadiene in a 3 + 4 → 7 manner to give a comprehensive series of 8-oxabicyclo[3.2.1]oct-6-en-3-ones and bicyclo[3.2.1]oct-6-en-3-ones in good yields. The cycloaddition with furan proceeds in a stereospecific manner with the retention of allyl cation configurations, in accord with a concerted mechanism. The 3 + 4 → 7 reactions in THF/ether contrast with those in nitromethane in the following ways. (1) The yield of the adducts strongly depends on the structure of the allyl cations. (2) The reaction with furan is nonstereospecific. (3) An electrophilic substitution reaction strongly competes with the cycloaddition. (4) The cycloaddition between the cation **34a** and 2-methylfuran is highly regioselective (**11**/**12** = 19) as compared to that in nitromethane (the ratio being only 1.9). These findings in THF/ether are reasonably explained by a stepwise mechanism via an intermediate **40**. Reactions with acyclic dienes (isoprene and 2,3-dimethylbutadiene), naphthalene, anisole, and methanol are also described.

The chemistry of 2-oxyallyl species (I) has increasingly received wide attention from synthetic and mechanistic interests.[2-9] One of the characteristic reactions of the oxyallyls is a 3 + 4 → 7 cycloaddition with a conjugated diene, providing a unique and important route to seven-membered rings in organic synthesis.[2,3,10]



Mechanistically, this cycloaddition has been classified as either a concerted $2_\pi + 4_\pi$ pericyclic reaction[2,11-13] or a stepwise reaction initiated by an electrophilic addition followed by cyclization of an intermediate.[14,15] However, details are not yet fully understood.

In connection with our study on the reactions of 2-functionalized allyl halides, we have found that 1,1-dimethyl-2-(trimethylsil-

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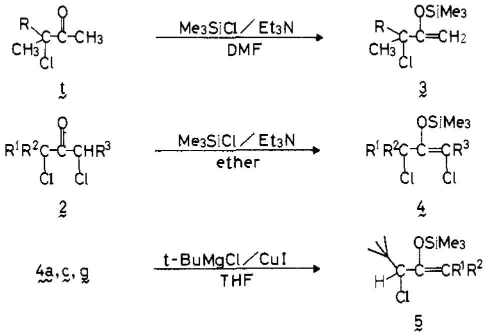
oxy)allyl chloride reacts with various 1,3-dienes in a 3 + 4 → 7 manner in the presence of silver perchlorate to give seven-membered ketones in excellent yields.[1,16] This new route to an oxyallyl species seems to be of synthetic value[17] and particularly useful for a mechanistic study on the 3 + 4 → 7 reaction in the following ways. First, the reactive species—probably a 2-(trimethylsiloxy)allyl cation (I: $X = SiMe_3$)—is structurally much less ambiguous than metal oxyallyls obtained from α,α′-dihalo ketones with the aid of reducing agents.[5] Second, the oxyallyl species of a given configuration is readily obtainable from geometrically pure 2-siloxyallyl chlorides. Third, the species must be more electrophilic than metal oxyallyls and hence would have a greater chance to take a stepwise cycloaddition route.[15] Fourth, structural modification of the species is easy as compared to that of related oxyallyls such as 2-methoxyallyl cation.[7]

Here we describe the details of the silver perchlorate promoted reactions of various 2-(trimethylsiloxy)allyl chlorides **3**–**5** with 1,3-dienes and with nucleophiles and show that the 3 + 4 → 7 reaction of 2-(trimethylsiloxy)allyl cations proceeds in two different manners, one concerted and the other stepwise, depending on the solvent.

Results and Discussion

Two 1,1-dialkyl-2-(trimethylsiloxy)allyl chlorides, **3a**,**b**, and a series of 3-chloro-2-(trimethylsiloxy)allyl chlorides, **4a**–**g**, were prepared by silylation of α-chloro ketones (**1**) and α,α′-dichloro ketones (**2**) by use of trimethylchlorosilane and triethylamine.[18] 1-*tert*-Butyl-2-(trimethylsiloxy)allyl chlorides **5a**–**c** were prepared by the coupling reaction of the chlorides **4a**, **4c**, and **4g** with *tert*-butylmagnesium chloride in the presence of cuprous iodide.



1, **3**
a, $R = $ Me
b, $R = $ Et

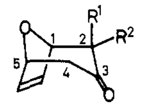
5
a, $R^1 = R^2 = $ Me
b, $R^1 = $ H; $R^2 = $ Me
c, $R^1 = R^2 = $ H

2, **4**
a, $R^1 = R^2 = $ Me; $R^3 = $ H
b, $R^1 = $ Me; $R^2 = $ Et; $R^3 = $ H
c, $R^1 = R^3 = $ H; $R^2 = $ Me
d, $R^1 = R^3 = $ H; $R^2 = $ i-Pr
e, $R^1 = $ H; $R^2 = R^3 = $ Me
f, $R^1 = $ H; $R^2 = R^3 = $ Et
g, $R^1 = R^2 = R^3 = $ H

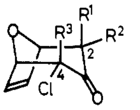
GLC and spectral (IR and NMR) analyses indicated the chlorides **4a**–**d** and **4g** to be geometrically pure. The *Z* configuration was assigned for these chlorides from the fact that the silylation of the related chloro carbonyls, chloroacetaldehyde and phenacyl chloride, under the same conditions used for **4**, gave only (*Z*)-trimethylsilyl enol ethers.[19] The chlorides **4e**, **4f**, and **5b** were mixtures of *Z* and *E* isomers in the ratios of 58:42, 75:25, and 67:33, respectively. The stereochemical assignment was deduced from the NMR characteristic that the allylic protons (CH_3 or CH_2) cis to $OSiMe_3$ group generally resonate at 0,05–0.15 ppm higher field than the trans protons.[20]

Silver Perchlorate Promoted Reactions of 2-(Trimethylsiloxy)allyl Chlorides 3–5. We used silver perchlorate because it has good solubility in organic solvents such as nitromethane and THF and low nucleophilicity of perchlorate ion. Most reactions were carried out at 0 °C under homogeneous conditions by adding the chloride to a stirred mixture of silver perchlorate (1.5–2 equiv) in nitromethane or THF/ether (1/1–3) in the presence of a reactant (a diene or a nucleophile, 5 equiv) and calcium carbonate. The chlorides **5a**–**c** were not freely soluble in pure nitromethane, so a small amount of ether (ca. 5%) was added in these cases. Reactions under heterogeneous conditions were also examined in several cases. Silver perchlorate on alumina (13% by weight) suspended in benzene was used for this purpose. Major experimental results are given in Tables I, III, and IV.

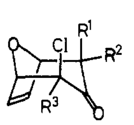
1. Reactions with Furan Derivatives. A. In Nitromethane. All the allyl chlorides **3**–**5** smoothly reacted with furan in the presence of silver perchlorate in nitromethane to give a comprehensive series of 8-oxabicyclo[3.2.1]oct-6-en-3-ones **6**–**10** in good to high yields, as shown in Table I. Methylfuran could be used as well; **3a** formed two regioisomeric adducts, **11** and **12** (65:35), in a combined 92% yield while **4a** gave a single regioisomer, **13**. A side reaction yielding the ketone **14** occurred in a few sterically crowded systems such as **4f**–furan and **4a**–2-methylfuran.



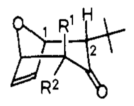
6a, $R^1 = R^2 = $ Me
b, $R^1 = $ Me; $R^2 = $ Et
c, $R^1 = $ Et; $R^2 = $ Me



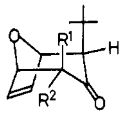
7a, $R^1 = R^2 = $ Me; $R^3 = $ H
b, $R^1 = $ Me, $R^2 = $ Et; $R^3 = $ H
c, $R^1 = $ Et; $R^2 = $ Me; $R^3 = $ H
d, $R^1 = R^3 = $ H, $R^2 = $ Me
e, $R^1 = $ Me; $R^2 = R^3 = $ H
f, $R^1 = R^3 = $ H; $R^2 = $ i-Pr
g, $R^1 = $ i-Pr; $R^2 = R^3 = $ H
h, $R^1 = $ H; $R^2 = R^3 = $ Me
i, $R^1 = $ H; $R^2 = R^3 = $ Et
j, $R^1 = R^2 = R^3 = $ H



8a, $R^1 = R^2 = $ Me; $R^3 = $ H
b, $R^1 = $ H, $R^2 = R^3 = $ Me
c, $R^1 = $ H, $R^2 = R^3 = $ Et
d, $R^1 = R^2 = R^3 = $ H

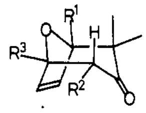


9



10

9, 10a, $R^1 = R^2 = $ Me
b, $R^1 = $ H; $R^2 = $ Me
c, $R^1 = $ Me; $R^2 = $ H
d, $R^1 = R^2 = $ H



11, $R^1 = R^2 = $ H; $R^3 = $ Me
12, $R^1 = $ Me; $R^2 = R^3 = $ H
13, $R^1 = $ H; $R^2 = $ Cl; $R^3 = $ Me

As in a typical S_N1-like reaction, the tertiary chlorides reacted more rapidly than the secondary ones which in turn were more reactive than the primary one, **4g**. For example, the reaction of **3a** finished almost instantaneously even at −70 °C whereas the reaction of **4g** took more than 7 h at 0 °C.

A characteristic feature is the stereochemistry of the adducts with respect to the groups at C_4. Regarding the numbering of the adduct skeleton, it is defined throughout this paper that α and γ carbons of the allyl chloride are respectively transferred to C_2 and C_4 of the adduct. A geometrically pure (*Z*)-allyl chloride,

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(16) A closely related work using 1,1-dimethyl-2-(trimethylsiloxy)allyl bromide and zinc chloride has been reported by Sakurai's group; Sakurai, H.; Shirahata, A.; Hosomi, A. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 163.

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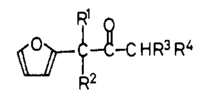
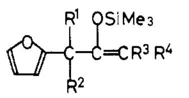
(18) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324.

(19) House has suggested earlier that the silylation of phenacyl chloride with trimethylchlorosilane and triethylamine gives a single stereoisomer of the silyl enol ether [House, H. O.; Fisher, W. E.; Gall, M.; McLaughlin, T. E.; Peet, N. P. *J. Org. Chem.* **1971**, *36*, 3429.]. We characterized both the geometrical isomers. The *E* isomer was successfully prepared photochemically from the *Z* isomer.

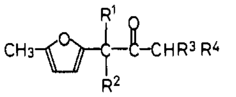
(20) We found this characteristic by examining the reported data and our own data for various types of enoxysilanes. The stereochemical assignment based on the chemical shifts of the olefinic protons is unreliable in sterically crowded enoxysilanes such as **5b** (see ref 18). Predominant formation of *Z* isomer in the case of **5b** is reasonable, judging from the fact that alkylation of allyl acetates and halides by alkylcopper reagents produces preferentially trans olefins: Anderson, R. J.; Henrick, H. A.; Siddall, J. B. *J. Am. Chem. Soc.* **1970**, *92*, 735.



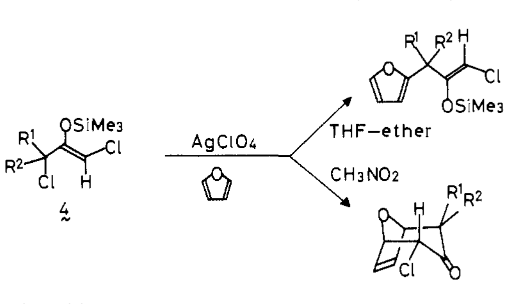
14a, $R^1=R^2=H$; $R^3=Me$; $R^4=Et$
b, $R^1=R^2=Me$; $R^3=H$; $R^4=Cl$
c, $R^1=Me$; $R^2=R^3=H$; $R^4=Cl$
d, $R^1=R^3=Me$; $R^2=H$; $R^4=Cl$
e, $R^1=R^3=Et$; $R^2=H$; $R^4=Cl$
f, $R^1=R^2=R^3=H$; $R^4=Cl$
g, $R^1=Me$; $R^2=R^3=H$; $R^4=t\text{-}Bu$
h, $R^1=t\text{-}Bu$; $R^2=R^3=H$; $R^4=Me$
i, $R^1=R^2=R^3=H$; $R^4=t\text{-}Bu$



15a, $R^1=R^2=Me$; $R^3=H$; $R^4=Cl$
b, $R^1=Me$; $R^2=R^3=H$; $R^4=Cl$
c, $R^1=H$; $R^2=R^3=Me$; $R^4=Cl$
d, $R^1=Me$; $R^2=R^3=H$; $R^4=t\text{-}Bu$
e, $R^1=t\text{-}Bu$; $R^2=R^3=H$; $R^4=Me$



16, $R^1=R^2=H$; $R^3=R^4=Me$
17, $R^1=R^2=Me$; $R^3=R^4=H$
18, $R^1=R^2=Me$; $R^3=H$; $R^4=Cl$

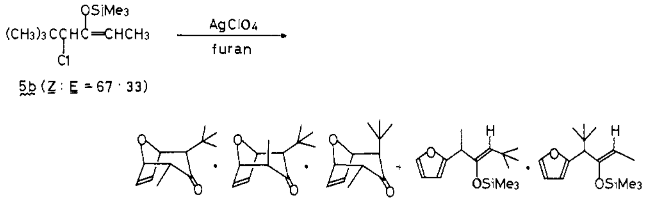


4a, gave a single adduct, **7a**, in which the Cl group at C_4 is in the equatorial position. The axial isomer was not formed at all. The reaction with 2-methylfuran gave the same stereochemical result. The stereospecific formation of C_4-equatorial adduct was also true for other (*Z*)-allyl chlorides **4b–d**, although the adducts in these cases were mixtures of two stereoisomers at C_2. These findings indicate that the 3 + 4 → 7 reaction with furan proceeds in such a stereospecific manner that a substituent cis (or trans) to $OSiMe_3$ group in the allyl chloride is transferred to a C_4-equatorial (or axial) group in the product. One exception appeared to be the case *Z*-**4g** which gave the axial isomer, **8d** (11%), as well as the equatorial one, **7j** (89%). However, the formation of **8d** was ascribable to an acid-catalyzed isomerization of **7j** during the reaction because the ratio **7j**/**8d** decreased as the reaction progressed, e.g., more than 20 after 3 h of reaction but 7.8 after 8 h. The acid-catalyzed isomerization of **7j** was confirmed by a separate experiment. The stereochemical course of the reactions for **4e**, **4f**, and **5b** cannot be analyzed straightforwardly, since these chlorides include both geometrical isomers. However, good agreement between the isomeric ratio (equatorial/axial) of the adduct and the *Z*/*E* ratio of the allyl chloride within an experimental error in each case—**7h**/**8b** = 59/41 vs. *Z*/*E* = 58/42 for **4e**, **7i**/**8c** = 78/22 vs. *Z*/*E* = 75/25 for **4f**, and **9b**/**9c** = 63/37 vs. *Z*/*E* = 67/33 for **5b**—strongly suggests a highly stereoselective nature for the reaction. It can be therefore said that the 3 + 4 → 7 reaction with furan derivatives in nitromethane proceeds with almost perfect retention of stereochemical integrity of the starting allyl chloride.

The stereochemical assignment of the furan adducts **6–13** was deduced from the following NMR characteristics.[5a,e,6a] First, the C_2 and C_4 axial protons resonate at 0.3–0.7 ppm lower field than the equatorial protons. Second, the signals of the C_2 and C_4 axial methyl protons appear at 0.3–0.4 ppm lower field than those of the equatorial protons. Third, the bridgehead protons couple to the C_2 and C_4 axial protons with J = 4.2–4.6 Hz but to the equatorial protons with J = 0–1 Hz.[21]

B. In THF/Ether. Table I includes the results in THF/ether. The reactions in this solvent were completed within 1 h at 0 °C except for **4g** and **5c**. The reaction of the former chloride was very slow; therefore, the reaction was carried out in dimethoxyethane/ether (1:1) under reflux. The results contrasted with those in nitromethane in several ways. First of all, an electrophilic substitution reaction strongly competed with the cycloaddition in most cases. Especially 3-chloroallyl chlorides (**4a**, **4c**, and **4e**) underwent the substitution exclusively. Most of the ketones **14** could be isolated as silyl enol ethers **15** when a careful workup was made. This eliminates an alternative route to **14** via a thermal or an acid-catalyzed rearrangement of the 3 + 4 → 7 adducts.[5b,22] In fact, the adducts **6–13** were stable under the reaction conditions (0 °C, within 1 h). Table II shows a comparison of the reaction selectivity (3 + 4 → 7 reaction vs. substitution) in the two solvents. In THF/ether, the selectivity changes drastically from 3 + 4 → 7 reaction to substitution with the chlorides from **3a**, **3b**, to **5b**, to **4a–e**. All these chlorides, however, undergo the 3 + 4 → 7 reaction overwhelmingly in nitromethane. Replacement of furan by 2-methylfuran in the reaction of **3a** also causes a remarkable increase of substitution in THF/ether but not in nitromethane. Clearly, the reaction course in THF/ether strongly depends on the steric circumstances of an allyl chloride–diene pair, as well as the electronic effects of the substituent at the terminal sp^2 carbon of the allyl chloride.

Second, in contrast to the stereoselective formation of the two adducts **9b** and **9c** (63:37) in the reaction of **5b** with furan in nitromethane, the same reaction in THF/ether led to the formation of three adducts, **9b**, **9c**, and a new isomer, **10b**, in the ratio of 33:46:21 together with the two substitution products **15d** and **15e**.



	9b	9c	10b	15d	15e
THF—ether	16%	22%	10%	40%	12%
CH_3NO_2	63%	37%	—	—	—

Apparently, there is no significant relation between the stereochemistry of the adducts and the geometry of **5b**. The reaction of **4a** with furan also appeared to be nonstereospecific in THF/ether, although the yield of the adducts was very low.

Third, the reaction of **3a** with 2-methylfuran proceeded in a highly regioselective manner in THF/ether as compared to nitromethane. Table III shows the effects of various solvents on this reaction. The two regioisomers **11** and **12** were formed in comparable amounts in nitromethane whereas **11** was formed overwhelmingly in THF/ether. Both regioselectivity and reaction selectivity did not change with the solvents, ether, THF, THF/ether, or even benzene, in which the reaction was heterogeneous. Acetonitrile showed intermediate effects between nitromethane and THF/ether on both selectivities. These observations are interestingly compared with the cycloaddition of 2,2-dimethylcyclopropanone and 2-methylfuran, yielding **11** and **12** without significant selectivity.[23]

2. Reactions with Cyclopentadiene and with Acyclic Dienes. The reactive species generated in nitromethane also reacted with cyclopentadiene in a 3 + 4 → 7 manner to give a series of bicyclo[3.2.1]oct-6-en-3-ones, **19–23**, in good yields irrespective of the structure of the allyl chlorides, as shown in Table IV. An attempted reaction of **4g** (0 °C, 6 h), however, resulted in recovery of the chloride.

A marked difference between the reactions with furan and with cyclopentadiene is the stereochemistry of the adducts. For example, the reaction of *Z*-**4a** gave both the C_4 equatorial and axial adducts **20a** and **21a** (71:29); however, only the equatorial isomer **7a** was formed in the case of furan. Likewise the two stereoisomers (**22** and **23**) with respect to the *tert*-butyl group at C_2 were formed

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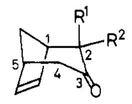
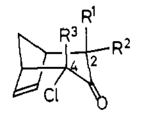
[21] A six-membered chair conformation was assumed for all adducts. Contribution of a boat conformation might be important for the adducts **10** and **23**.

[22] Hill, A. E.; Greenwood, G.; Hoffmann, H. M. R. *J. Am. Chem. Soc.* **1973**, *95*, 1338.

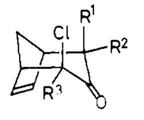
[23] Turro, N. J.; Edelson, S. S.; Darling, J. R.; Hammond, W. B. *J. Am. Chem. Soc.* **1969**, *91*, 2283.



19a, $R^1 = R^2 = Me$
b, $R^1 = Me$; $R^2 = Et$
c, $R^1 = Et$; $R^2 = Me$

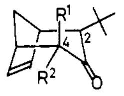


20

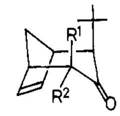


21

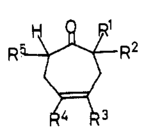
20, 21a, $R^1 = R^2 = Me$; $R^3 = H$
b, $R^1 = R^3 = H$; $R^2 = Me$
c, $R^1 = Me$; $R^2 = R^3 = H$
d, $R^1 = H$; $R^2 = R^3 = Me$
e, $R^1 = R^3 = Me$; $R^2 = H$



22



23



22, 23a, $R^1 = R^2 = Me$
b, $R^1 = H$; $R^2 = Me$
c, $R^1 = Me$; $R^2 = H$
d, $R^1 = R^2 = H$

24, $R^1 = R^2 = R^4 = Me$; $R^3 = R^5 = H$
25, $R^1 = R^2 = R^3 = Me$; $R^4 = R^5 = H$
26, $R^1 = R^2 = R^3 = R^4 = Me$; $R^5 = Cl$
27, $R^1 = R^3 = R^4 = Me$; $R^2 = H$; $R^5 = Cl$

in equal amounts for the chlorides **5a–c** whereas these chlorides reacted with furan to yield the C_2-equatorial isomer (**9**) exclusively.

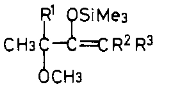
In THF/ether, the yield of the adduct depended on the type of the chloride. For instance, **3a** afforded **19a** in 91% yield, but **4a** gave the adducts only in 8% yield. In addition, the stereoselectivity in the reaction of **4a** was lower in this solvent (**20a**/**21a** = 54/46) than in nitromethane (the ratio being 71:29). These findings in THF/ether are parallel to the results in furan.

The stereochemical assignment of the cyclopentadiene adducts **19–23** was deduced from the following NMR characteristics.[5b,e,6a] First, the signal of the C_2 or C_4 axial methyl protons appears at 0.1–0.37 ppm downfield relative to that of the equatorial methyl protons. Second, the C_4 axial proton in the adducts **20** and **21** resonates at 0.7–0.8 ppm lower field than the equatorial proton. Third, the bridgehead proton at C_5 couples to the C_4 axial proton (CHCl) with $J = 3.2$–3.8 Hz but to the equatorial proton with $J = 1$–2.5 Hz. Fourth, the axial *tert*-butyl group at C_2 appears at 0.5 ppm lower field than the equatorial one.[21]

The relative reactivity of cyclopentadiene to furan was determined by a competition experiment using **4a** in nitromethane. In contrast to reports that cyclopentadiene is more reactive than furan toward iron oxyallyls[24] and cyclopropanones,[23] furan was 1.42 times more reactive than cyclopentadiene. This probably arises from the effective complexation between cyclopentadiene and silver ion. Such complexation must reduce the nucleophilicity of cyclopentadiene as well as the concentration of free cyclopentadiene.

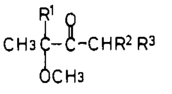
Table IV also includes several reactions with acyclic dienes. **3a** reacted with isoprene to give a mixture of karahanaenone **24** and its regioisomer **25** in good yield irrespective of the reaction conditions. The regioselectivity was slightly higher in THF/ether or benzene than in nitromethane. On the other hand, the 3 + 4 → 7 reactions of 3-chloroallyl chlorides **4a** and **4c** with 2,3-dimethylbutadiene did not proceed well either in nitromethane or in THF/ether.

3. Reactions with Other Substrates. In the presence of silver perchlorate, the chlorides **3a**, **4a**, and **4e** reacted with methanol to give α-methoxy ketones **29a–c** regioselectively.[25,26] The primary product, however, was not **29** but silyl enol ether **28**. This was confirmed by the experiments carried out at low temperatures in THF/ether and in nitromethane. The NMR and GLC analyses of the crude product indicated the formation of **28** as the sole product. The enol ethers **28a–c** were isolated almost quantitatively in the reactions undertaken in the presence of 1 equiv of triethylamine (used as a quencher of perchloric acid).



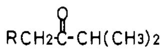
$CH_3C(R^1)(OCH_3)–C(OSiMe_3)=CR^2R^3$

28



$CH_3C(R^1)(OCH_3)–C(=O)–CHR^2R^3$

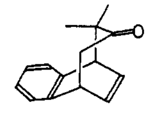
29



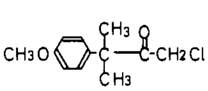
$RCH_2C(=O)CH(CH_3)_2$

31, R = 1-naphthyl
32, R = anisyl

28, 29a, $R^1 = Me$; $R^2 = R^3 = H$
b, $R^1 = Me$; $R^2 = H$; $R^3 = Cl$
c, $R^1 = H$; $R^2 = Me$; $R^3 = Cl$



30



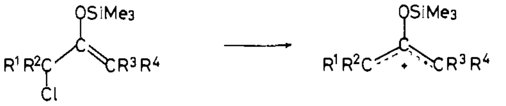
$CH_3O–C_6H_4–C(CH_3)_2–C(=O)–CH_2Cl$

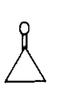
33

The relative reactivity of furan to methanol toward the species obtained from **3a** was determined by a competition technique at −30 °C (Scheme I). The detectable products were only the adduct **6a** and the silyl ether **28a**. Interestingly, the product ratio depended on the solvent; furan was less reactive than methanol by a factor of 3.6 in nitromethane but by a factor of 27 in THF/ether.

The reactive species obtained from **3a** reacted with naphthalene to give a small amount of 1,4-addition product **30** (1.9%) together with substitution product **31** (1,9%).[27] The species also reacted with anisole, giving a mixture of para- and ortho-substituted anisoles **32** (para/ortho = 2.94) in 82% yield. Noteworthy is the fact that this aromatic substitution occurred exclusively with the rearrangement of the allylic double bond. The reaction of **4a** with anisole, however, furnished a poor result (**33**, 2%).

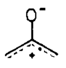
Reactive Species. The formation of the 3 + 4 → 7 adducts and the substitution products, as well as a typical S_N1-like reactivity of the allyl chlorides **3–5**, is consistent with the intervention of 2-(trimethylsiloxy)allyl cations **34a–l**. Other candidates capable of undergoing a 3 + 4 → 7 cycloaddition include cyclopropanones **35**, allene oxides **36**, and pure oxyallyls **37**. The first two species could be formed by an intramolecular cyclization of the cation **34**. In order to examine the possibility of such a process, we first treated **3a** with silver perchlorate at −70 °C and then added 2-methylfuran. A principal product in this case was furan derivative **39**, which could be formed neither from a cyclopropanone nor from an allene oxide;[8,9] however, it could be formed from diene **38**. Furthermore, the fact that **29a** was not formed at all in the





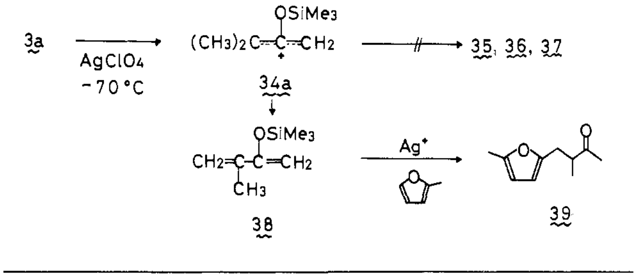
35

36



37

34a, $R^1 = R^2 = Me$; $R^3 = R^4 = H$
b, $R^1 = Me$; $R^2 = Et$; $R^3 = R^4 = H$
c, $R^1 = R^2 = Me$; $R^3 = H$; $R^4 = Cl$
d, $R^1 = Me$; $R^2 = Et$; $R^3 = H$; $R^4 = Cl$
e, $R^1 = R^3 = H$; $R^2 = Me$; $R^4 = Cl$
f, $R^1 = R^3 = H$; $R^2 = i\text{-}Pr$; $R^4 = Cl$
g, $R^1 = H$; $R^2 = R^3 = Me$; $R^4 = Cl$
h, $R^1 = H$; $R^2 = R^3 = Et$; $R^4 = Cl$
i, $R^1 = R^2 = R^3 = H$; $R^4 = Cl$
j, $R^1 = H$; $R^2 = t\text{-}Bu$; $R^3 = R^4 = Me$
k, $R^1 = R^3 = H$; $R^2 = t\text{-}Bu$; $R^4 = Me$
l, $R^1 = R^3 = R^4 = H$; $R^2 = t\text{-}Bu$



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(25) Hoffmann, H. M. R.; Nouv, T. A.; Smithers, R. J. *J. Chem. Soc., Chem. Commun.* **1972**, 963.

(26) Ong, B. S.; Chan, T. H. *Tetrahedron Lett.* **1976**, 3257.

(27) 2-Methoxyallyl cation has been shown to cycloadd to arenes to give bicyclo[3.2.1]nona-6,8-dien-3-ones: Hill, A. E.; Hoffmann, H. M. R. *J. Am. Chem. Soc.* **1974**, *96*, 4597.

Table I. Silver Perchlorate Promoted Reactions of 2-(Trimethylsiloxy)allyl Chlorides with Furan Derivatives

chloride	reaction conditions[a]	products (yield, %)[c]	
		3 + 4 → 7 adducts [rel %]	others
		With Furan	
3a	A, 0.5 h	6a (92)	
3a	B (1/5), 0.8 h	6a (85)	
3a	C, 3 h	6a (91)	
3b	A, 0.5 h	6b + 6c [62:38] (81)	
3b	B (1/3), 1 h	6b + 6c [60:40] (61)[d]	14a (7)[i]
Z-4a	A, 0.5 h	7a (89)	
Z-4a	B (1/3), 1 h	7a + 8a [86:14] (3)[d]	15a (61)[d]
Z-4b	A, 0 4 h	7b + 7c [55:45] (89)	
Z-4c	A, 0.5 h	7d + 7e [50:50] (87)	
Z-4c	B (1/2), 1 h		15b (52)[d]
Z-4d	A, 0.5 h	7f + 7g [50:50] (76)	
4e (*Z*/*E* = 58/42)	A, 0.5 h	7h + 8b [59:41] (78)	14d (6)[d]
4c (*Z*/*E* = 58/42)	B (1/2), 1 h		15c (70)
4f (*Z*/*E* = 75/25)	A, 0.5 h	7i + 8c [78:22] (66, 74[d])	14e (21)
Z-4g	A, 7h	7j + 8d [89:11] (80)[e]	
Z-4g	D, 25 h	7j + 8d [80:20] (45)[d,f]	14f (10)[d]
5a	A,[b] 0.5 h	9a (86)	
5a	B (1/3), 0.5 h	9a (34)	
5b (*Z*/*E* = 67/33)	A,[b] 1 h	9b + 9c [63:37] (84)	
5b (*Z*/*E* = 67/33)	B (1/3), 1 h	9b + 9c + 10b [33:46:21] (35)[d]	15d + 15e [77:23] (38)[d]
5c	A,[b] 1 h	9d + 10d [90:10] (49, 76[g])	
5c	B (1/3), 1 h	9d + 10d [85:15] (8)[d,h]	14i (5)[d]
		With 2-Methylfuran	
3a	A, 0.5 h	11 + 12 [65:35] (92)	
3a	B (1/2), 0.5 h	11 + 12 [95:5] (28)	16 + 17 [80:20] (43)
Z-4a	A, 0.5 h	13 (57, 66[d])	18 (22)[d]

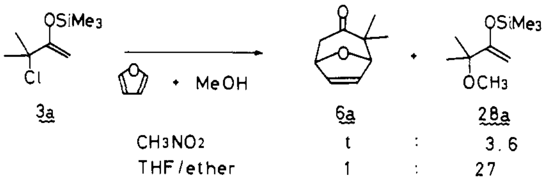
[a] Reaction conditions are abbreviated as follows: A, in nitromethane at 0 °C; B, in THF/ether at 0 °C; C, in benzene at room temperature using $AgClO_4$ on alumina; D, in dimethoxyethane/ether (1:1) at 40 °C. [b] A small amount of ether (ca. 5%) was added. [c] Isolated yield. [d] Determined by GLC. [e] 4g was recovered (10%). [f] 4g was recovered (29%). [g] After correction of the recovery of 5c (27%). [h] 5c was recovered (43%). [i] 3-Methyl-2-(trimethylsiloxy)-1,3-pentadiene (20%) was also obtained.

Table II. 3 + 4 → 7 Cycloaddition vs. Substitution in Silver Ion Assisted Reaction of 2-(Trimethylsiloxy)allyl Chlorides with Furan or 2-Methylfuran

chloride	cycloaddition vs. substitution[a]	
	in nitromethane	in THF/ether
	Reaction with Furan	
3a	~100:0	95 > 5 (95 > 5)[b]
3b	~100:0	89.7:10.3
4a	~100:0	4:96
4b	~100:0	
4c	~100:0	~0:100
4d	~100:0	
4e	91.4:8.6	~0:100
4f	88.0:22.0	
4g	~100:0	(83:17)[c]
5a	94 > 6[d]	
5b	92 > 8[d]	48:52
5c	~100:0[d]	61:39
	Reaction with 2-Methylfuran	
3a	99.6:0.4	39.9:60.1
4a	75:25	

[a] Determined by GLC or NMR. [b] In benzene under heterogeneous conditions. [c] In dimethoxyethane/ether (1:1). [d] In nitromethane containing 5% ether.

Scheme I. Competition between Furan and Methanol



Scheme II. Concerted 3 + 4 → 7 Cycloaddition

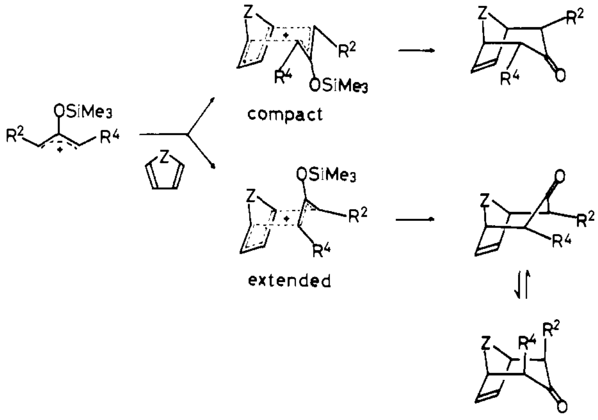


Table III. Effects of Various Solvents on Silver Ion Promoted Reaction of 3a with 2-Methylfuran

solvent	products, rel %[a]				regioselectivity 11:12	cycloaddition vs. substitution
	11	12	16	17		
benzene[b]	38.0	1.9	47.4	12.6	95:5	39.9:60.1
ether	37.5	2.1	47.5	12.9	95:5	39.6:60.4
THF/ether (1:2)	37.8	2.1	47.6	12.5	95:5	39.9:60.1
THF	37.6	1.5	47.2	13.7	96:4	39.1:60.9
acetonitrile	55.9	5.4	22.2	16.5	91:9	61.3:38.7
nitromethane	65.2	34.4	~0.3	~0.1	65:35	99.6:0.4

[a] Determined by GLC. [b] Under heterogeneous conditions using $AgClO_4$ on alumina.

Table IV. Silver Perchlorate Promoted Reactions of 2-(Trimethylsiloxy)allyl Chlorides with Cyclopentadiene, Isoprene, and 2,3-Dimethylbutadiene

chloride	reaction conditions[a]	3 + 4 → 7 adducts [rel %]	yield, %[e]
		With Cyclopentadiene	
3a	B (1/2), 1 h	19a	91
3b	B (1/2), 1 h	19b + 19c [50:50]	71
Z-4a	A, 1 h	20a + 21a [71:29]	80
Z-4a	B (1/1), 1 h	20a + 21a [54:46]	8[f]
Z-4c	A, 1 h	20b + 20c + 21b + 21c [54:16:4:26]	76
4e (*Z*/*E* = 58/42)	A, 1 h	20d + 20e + 21d + 21e [47:15:17:21]	64
Z-4g	A, 6 h		[g]
5a	A,[b] 1 h	22a + 23a [50:50]	82
5b (*Z*/*E* = 67/33)	A,[b] 1 h	22b + 23c [50:50]	60
5c	A,[b] 1 h	22d + 23d [50:50]	9, 60[h]
		With Isoprene	
3a	A, 1 h	24 + 25 [62:38]	58[i]
3a	B (1/1), 1 h	24 + 25 [71:29]	65[i]
3a	C, 2.5 h	24 + 25 [73:27]	71
		With 2,3-Dimethylbutadiene	
Z-4a	A,[c] 1.5 h	26	32[f]
Z-4a	B (1/1),[c] 1 h	26	10[f]
Z-4c	A,[d] 1.5 h	27	10[f]

[a] Reaction conditions are abbreviated as follows: A, in nitromethane at 0 °C; B, THF/ether at 0 °C; C, in benzene at room temperature. [b] A small amount of ether (ca. 5%) was added. [c] At −20 °C. [d] At −15 °C. [e] Isolated yield. [f] Determined by GLC. [g] Almost all 4g was recovered. [h] After correction for the recovery of 5c (85%). [i] A small amount of an unidentified product was involved.

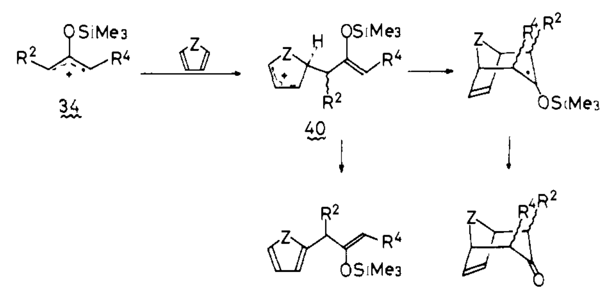
competition experiment between furan and methanol eliminates the participation of the pure oxyallyl **37** as well as the neutral species **35** and **36**. If these Si-free species are really responsible for the cycloadduct, they should be trapped by methanol to give **29** instead of **28**, which was actually formed. It is therefore concluded that cation **34** is the sole species in the present reactions both in nitromethane and in THF/ether.

The regiospecific formation of **28a–c** from **34a**, **34c**, and **34g** is puzzling, although it is in accord with the idea that the most positive site of the allyl cation preferentially reacts with a nucleophile.[28] There might be an interaction between the most positive carbon site and the oxygen at the central carbon of the allyl cation **34**. However, it is obvious that the regioselectivity of **34** also depends on the type of nucleophile, as shown by the reaction with anisole. It seems that a small but strong nucleophile such as methanol prefers the most positive site whereas a weak and bulky nucleophile such as a carbon–carbon double bond prefers the least hindered site to yield a thermodynamically more favorable product.

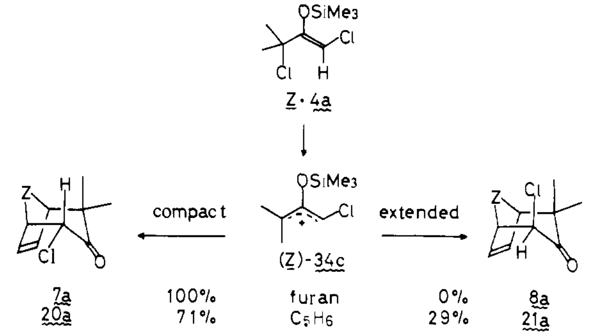
In the cations **34j,k,l**, a neopentyl-type rearrangement is possible.[29] However, the results indicate that the cations are trapped by furan or cyclopentadiene prior to such a skeletal rearrangement.

Mechanism for Formation of Cycloadducts in Nitromethane. Schemes II and III show two possible mechanisms, one concerted and the other stepwise, for the 3 + 4 → 7 cycloaddition of the present oxyallyl species **34**. A characteristic feature in nitromethane solution is the stereospecific formation of the furan adducts. This is most simply explained by the concerted mechanism. The reaction selectivity (Table II) for 3-chloroallyl chlorides is instructive as well. These chlorides produced **15** as the principal product in THF/ether. This means that intermediate **40** (R^4 = Cl), formed by stepwise addition, terminates overwhelmingly by deprotonation. Therefore, the reaction sequence via **40** hardly accounts for the selective formation of the cycloadducts from these chlorides in nitromethane, even if solvent basicity is taken into account. Furthermore, lower stereospecificity for cyclopentadiene than for furan is inconsistent with the stepwise formation of the adducts because intermediate **40** should be more stabilized when Z = O than when Z = CH_2 and should have a greater chance to loosen the stereochemical integrity of the allyl chloride. Thus it is concluded that the furan and cyclopentadiene adducts are formed concertedly in nitromethane.

Scheme III. Stepwise 3 + 4 → 7 Cycloaddition



Scheme IV



Since the silver ion promoted ionization of the allyl chlorides **3–5** must proceed with retention of configuration in the allylic double bond, *Z*-**4a** should produce (*Z*)-3-chloro-1,1-dimethyl-2-(trimethylsiloxy)allyl cation **34c**. Consequently, the stereospecific formation of **7a** indicates that the cation cycloadds to furan via a 100% compact transition state whereas the formation of **20a** and **21a** (2.45:1) shows that the cation reacts with cyclopentadiene via a 71% compact and 29% extended transition state, as shown in Scheme IV.

The reaction course for the chloride *Z*-**4c** is visualized in Scheme V. In this case, the allyl cation **34e** can be produced in two isomeric forms which are represented as *Z,Z* and *E,Z*. In this description, the first and the second letters represent the configuration of the groups at C_α and C_γ of the allyl cation, respectively. The absence of any C_4 axial furan adducts (**8**) clearly shows that the cycloaddition with furan proceeds in a compact manner. Consequently, the formation of the two C_4 equatorial isomers **7d** and **7e** (1:1) indicates that the *Z,Z* and the *E,Z* cations are involved in equal quantities. Of the four stereoisomeric cyclopentadiene adducts, the pair **20b** and **21c** should be formed from the *Z,Z* cation, and the other pair, **20c** and **21b**, from the *E,Z* cation.

The cycloaddition reactions for other geometrically pure chlorides (**4b**, **4d**, and **4g**) are analyzed in a similar way. The chlorides **4e**, **4f**, and **5b** are mixtures of geometrical isomers, so the reaction course for the individual isomers is not determined precisely. Nevertheless, probable reaction sequences can be depicted, owing to the relatively simple stereochemical results for furan. For example, the highly stereoselective formation of the furan adducts **7h** and **8b** from **4e** (*Z*/*E* = 58/42) is most reasonably explained by the stereospecific generation of the allyl cation **34g**—namely, *Z,Z* from *Z*-**4e** and *Z,E* from *E*-**4e**—followed by a compact cycloaddition. Therefore, the pair of the cyclopentadiene adducts **20d** and **21e** can be classified as the products from *Z,Z*-**34g** whereas the pair **20e** and **21d** can be classified as

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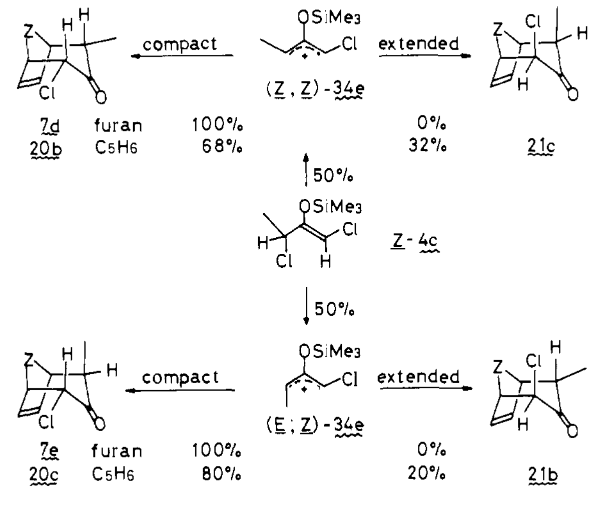
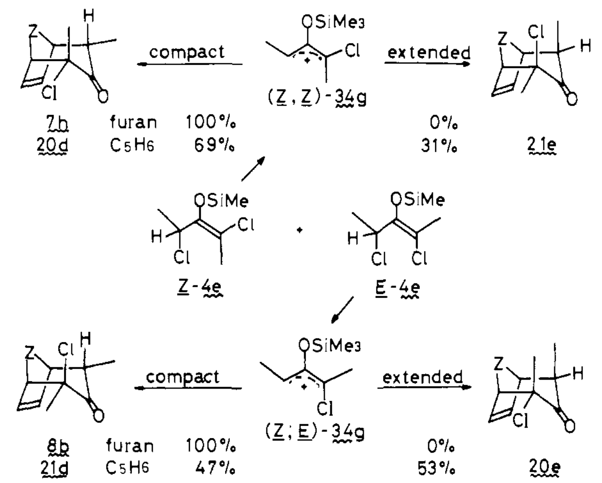
(28) DeWolfe, R. H.; Young, W. G. "The Chemistry of Alkenes"; Patai, S., Ed.; Interscience: New York, 1964; p 681.

(29) Noyori, R.; Hayakawa, Y.; Takaya, H.; Murai, S.; Kobayashi, R.; Sonoda, N. *J. Am. Chem. Soc.* **1978**, *100*, 1759.

Scheme V



Scheme VI



the products from Z,E-**34g**, as shown in Scheme VI.

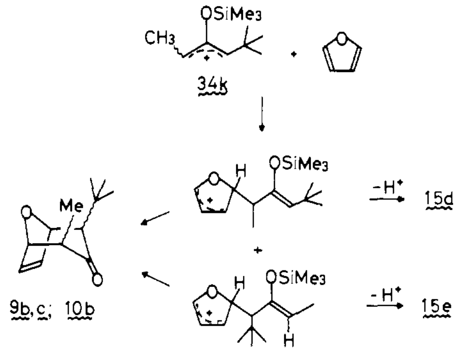
Table V summarizes the stereochemical results for the cycloaddition in nitromethane. It is clear that the configuration induced at C_α of the cation **34** depends on the structure of the precursory allyl chloride. Two major factors must be involved: the 1,3-steric interactions and the cis interactions between the $OSiMe_3$ group and the terminal groups.[30] The formation of the Z,Z and the E,Z cations in equal amounts in the cases of **34e** and **34f** can be interpreted in terms of a balance between these two factors. On the other hand, the 1,3-interactions appear to predominate in the ionization of the terminally trisubstituted allyl chlorides (**4e** and **4f**) and the 1-*tert*-butylallyl chlorides (**5a–c**), both of which afford the cations of the Z configuration at C_α.

The table also shows the difference in the orientational selectivity (compact vs. extended) between furan and cyclopentadiene. Compact cycloaddition is the exclusive course for furan whereas both compact and extended cycloadditions occur in the case of cyclopentadiene in a variable ratio depending on the type (chlorinated vs. nonchlorinated cations) and configuration of the allyl cations (Z,Z-**34g** vs. Z,E-**34g**). Several factors, including secondary orbital interactions[31,32] and conformational differences between six-membered oxa- and carbocycles,[33] may be involved. Polarization of the diene seems to be also worthy of consideration.[34] Furan has a dipole moment ($\mu = 0.71$ D) in the direction so that the oxygen is at the negative end, while cyclopentadiene is a less and oppositely polarized molecule ($\mu = 0.41$ D). Therefore, the dipole–dipole interactions between the oxyallyl species and the diene must favor a compact orientation for furan but an extended orientation for cyclopentadiene. Since the six-membered chairlike transition state is considered to be conformationally lower in energy than the boatlike alternative, the contribution from the dipole-dipole interactions would reinforce the preference for the compact cycloaddition in furan but reduce the preference in cyclopentadiene. This seems to account well for the observation, although only qualitatively.

Table V. Stereochemical Course of 3 + 4 → 7 Cycloadditions in Nitromethane

chloride		allyl cation 34	% compact route for	
			furan	C_5H_6
3b	→	Z-34b, 62%		
		E-34b, 38%		
Z-4a	→	Z-34c	100	71
Z-4b	→	Z,Z-34d, 55%	100	
		E,Z-34d, 45%	100	
Z-4c	→	Z,Z-34e, 50%	100	68
		E,Z-34e, 50%	100	80
Z-4d	→	Z,Z-34f, 50%	100	
		E,Z-34f, 50%	100	
Z-4e, 58%	→	Z,Z-34g	~100	69
E-4e, 42%	→	Z,E-34g	~100	47
Z-4f, 75%	→	Z,Z-34h	~100	
E-4f, 25%	→	Z,E-34h	~100	
Z-4g	→	Z-34i	>95	
5a	→	Z-34j	100	50
Z-5b, 67%	→	Z,Z-34k	~100	50
E-5b, 33%	→	Z,E-34k	~100	
5c	→	Z-34l, 90%	~100	50
		E-34l, 10%	~100	50

Scheme VII



The mechanism of the cycloaddition with acyclic dienes in nitromethane is not clear. The results—regioselectivity (**24**/**25**) and dependence of the reaction on the structure of the allyl chlorides (e.g., **3a** vs. **4a**)—are rather close to those in THF/ether.

Change in Mechanism with Solvent. The formation of **14** and **15** in THF/ether provides good evidence for intermediate **40**. A question is whether the cycloadducts are formed from **40**. The following findings in THF/ether are instructive. (1) The furan adducts are formed with loss of configuration of the allyl chloride in the cases of **5b** and probably **4a**. (2) The selectivity (cycloaddition vs. substitution) strongly depends on the allyl cation–diene pair. (3) The regioselectivity (**11**/**12**) is very high. First of all, finding 1 is obviously against the concerted formation of the adducts. Since Z,Z and E,Z-**34k** are formed from **5b** in nitromethane, the same species must be involved in THF/ether. If the reaction is concerted, then it must proceed via a compact route since the C_2,C_4 diaxial adduct (**10c**) was not formed at all. Therefore, the two adducts **9b** and **9c** were expected to form in a ratio close to the initial Z/E ratio, as was observed in nitromethane. Clearly this is not the case. The result is well explained in terms of the stepwise mechanism shown in Scheme VII.

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(30) Mayer, H.; Förner, W.; Schleyer, P. von R. *J. Am. Chem. Soc.* **1979**, *101*, 6032.

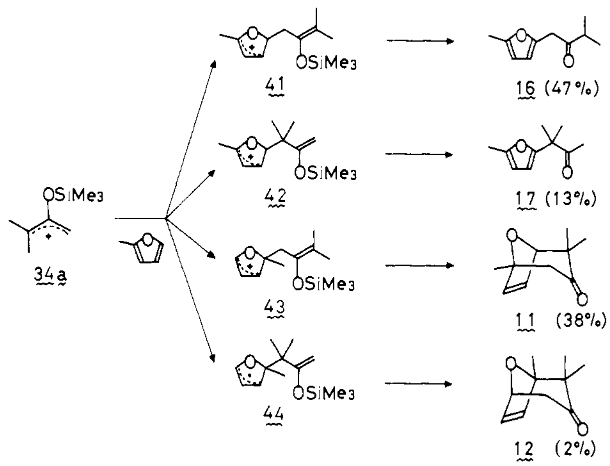
(31) Hoffmann, H. M. R.; Joy, D. R. *J. Chem. Soc. B* **1968**, 1182.

(32) Ito, S.; Ohtani, H.; Amiya, S. *Tetrahedron Lett.* **1973**, 1737.

(33) Vinter, J. G.; Hoffmann, H. M. R. *J. Am. Chem. Soc.* **1974**, *96*, 5466.

(34) Sargent, P. B. *J. Am. Chem. Soc.* **1969**, *91*, 3061.

Scheme VIII



Finding 2 is also consistent with the stepwise formation via **40**. A dramatic change in the selectivity between **3a** and **4a** is reasonable because the nucleophilicity of the enolic double bond in **40** must be reduced substantially by the replacement of a hydrogen terminal group with electronegative chlorine. A strong dependence on steric circumstances is also an expected property of the intermediate. In addition, if the cycloaddition and the substitution occur independently, the latter reaction might occur more easily in nitromethane than in a less polar media such as THF/ether.

The regioselectivity in the concerted 3 + 4 → 7 cycloaddition has been interpreted in terms of the LUMO–HOMO interactions of an oxyallyl–diene pair.[13] Since the shape of both molecular orbitals may not change with the solvent properties, a **11**/**12** ratio similar to the one in nitromethane might be observed in THF/ether if the reaction is concerted. Finding 3 is clearly more in accord with the stepwise mechanism via intermediates **41–44** (Scheme VIII). The high **11**/**12** ratio is reasonable because both possible pathways leading to **12** by way of **41** and **44** involve a very sterically unfavorable process, a bond formation between two trisubstituted sp^2 carbons. The dominant formation of **16** is understandable, since intermediate **41** must be sterically, as well as electronically, the most favorable of all. The adduct **11** can be formed from either **42** or **43**. If only **42** were involved, the relative reactivity of the primary vs. the tertiary carbon sites of the cation **34a** would be near unity [(**16** + **12**)/(**11** + **17**) or **16**/(**11** + **12** + **17**)]. This is unlikely, judging from the fact that the primary carbon site preferentially adds to anisole and to an aromatic olefin.[17] So the adduct **11** must be formed predominantly from **43**. From these considerations, it is concluded that the cycloaddition with furan in THF/ether proceeds in a stepwise manner. The following observations, which are parallel to the results for furan, suggest the stepwise mechanism for the reactions with cyclopentadiene and with acyclic dienes. First, the reaction occurred effectively for **34a** but not for chlorinated cations. Second, the reaction between **34c** and cyclopentadiene was less stereoselective in THF/ether than in nitromethane.

A simple explanation for the mechanistic change caused by solvent is to say that different species are involved in the two solvent systems. However, this is unreasonable because the competition experiment (Scheme I) strongly suggests that cation **34** is the only species responsible for the products in both solvent systems. It seems necessary to take into account the association between the cation and its counteranion (ClO_4^- or Cl^-). If the ionization of the present system can be represented by Winstein's scheme going from an intimate ion pair through a solvent-separated ion pair to a free allyl cation, the dissociation must progress more easily in nitromethane than in THF/ether. The electrostatic interaction with the counteranion not only reduces the positive charge density of the cation but also may cause an increase in the steric bulkiness of the oxyallyl species and a decrease in delocalization of the positive charge, since the interaction is more or less unsymmetrical. These effects, especially on the size and the delocalization of the cation, certainly disfavor the concerted cycloaddition. It seems that a highly dissociated species acts as a dienophile undergoing cycloaddition; otherwise, the species acts as a simple electrophile. In this connection, the nucleophile selectivity, k_{MeOH}/k_{furan}, is interesting, and since in THF/ether **34a** is considered to react with furan and methanol as an electrophile, the ratio of 27 is simply related to the difference in nucleophilicity between methanol and furan. According to the reactivity–selectivity relationship, the cation generated in nitromethane should show a similar or higher selectivity ratio, if it were an electrophile. Actually, the selectivity is only 3.6. This suggests that in nitromethane, **34a** reacts with furan more rapidly than expected for an electrophile by a factor of more than eight. This result is in accord with the idea that the cation reacts with furan as a dienophile in nitromethane. It should be noted, however, that this preference for concerted addition over stepwise addition is energetically very small (less than 1.5 kcal/mol). In fact, the reaction with furan is accompanied by the concomitant formation of the substitution products even in nitromethane in several sterically crowded cases. It is therefore conceivable that a stepwise addition occurs as a competitive or a predominant course even in nitromethane when certain factors disfavoring the concerted cycloaddition—e.g., steric effects of the substituents and the transoid conformation of a diene—are involved.[35]

Summary. Reactions of 2-(trimethylsiloxy)allyl chlorides with 1,3-dienes in the presence of silver perchlorate provide a useful route to seven-membered ketones. 2-(Trimethylsiloxy)allyl cations (**34**) are involved as a reactive species. Marked differences in reaction course and stereochemistry (stereo- and regioselectivities) between the reactions in nitromethane and in THF/ether indicate that the mechanism for the 3 + 4 → 7 cycloaddition of the cation **34** changes with solvent. It is suggested that the cation cycloadds to furan or cyclopentadiene concertedly in nitromethane but in a stepwise manner in THF/ether.

Experimental Section

General. Infrared spectra were recorded on a Hitachi R-215 spectrophotometer. NMR spectra were taken in carbon tetrachloride on a Hitachi R-20B spectrometer at 60 MHz. The chemical shifts were recorded (δ) relative to Me_4Si as an internal standard. Analytical and preparative GLC were performed by a Yanagimoto G-8 gas chromatograph equipped with glass columns (6 mm × 0.75, 1.0, 1.2, 1.5, or 3 m) packed with 25% Apiezon grease L on Chamelite CK (AGL), 10% SE-30 on Chamelite CS (SE), 15% Carbowax 20 M on Chromosorb W (CW), or 10% diethylene glycol succinate polyester on Chamelite CS (DGS). IR and NMR spectra of new compounds obtained in this work are given in supplemental Tables VI, VII, and VIII. Microanalytical data are summarized in Table IX.

Preparation of 2-(Trimethylsiloxy)allyl Chlorides 3–5. The general procedure is given by the following three examples. The spectral data of the allyl chlorides **3–5** are shown in Table VI (supplementary material).

1,1-Dimethyl-2-(trimethylsiloxy)allyl Chloride (3a). A mixture of 3-chloro-3-methyl-2-butanone (**1a**) (35 g), trimethylchlorosilane (35 g), and triethylamine (66 g) in *N*,*N*-dimethylformamide (DMF) (100 mL) was heated at 85–90 °C for 18 h.[18] The mixture was diluted with petroleum ether (bp 35–50 °C) (300 mL), washed with cold water, and dried. Solvent was evaporated and the remaining oil was fractionated under reduced pressure to give **3a** (28 g, 52%), bp 74–75 °C (90 mmHg). 2-Methyl-3-(trimethylsiloxy)-1,3-butadiene (**38**) was obtained as an early fraction (4.1 g), bp 54–55 °C (95 mmHg); IR 1592 cm^{-1}; NMR δ 0.18 (s, 9 H), 1.95 (br s, 3 H), 4.23 (br s, 1 H), 4.40 (s, 1 H), 4.87 (br s, 1 H), 5.30 (m, 1 H).

Similarly, 1-ethyl-1-methyl-2-(trimethylsiloxy)allyl chloride (**3b**), bp 48–50 °C (5 mmHg), was prepared in 31% yield by heating 3-chloro-3-methyl-2-pentanone (**1b**, 6.0 g) with trimethylchlorosilane (5.4 g) and triethylamine (8.8 g) in DMF (20 mL) at 90–95 °C for 17 h.

3-Chloro-2-(trimethylsiloxy)allyl Chloride (4g). A solution of 1,3-dichloro-2-propanone (**2a**) (10 g, 79 mmol) in ether (20 mL) was added to a mixture of trimethylchlorosilane (9.4 g) and triethylamine (9.6 g) in ether (40 mL) during a period of 30 min at room temperature. The resulting mixture was stirred under reflux for 7 h. The mixture was washed with cold water and dried. Solvent was removed and the re-

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[35] The reaction of **34a** and isoprenyltrimethylsilane in nitromethane has been shown to proceed in a stepwise manner: Araki, Y.; Shirahata, A.; Hosomi, A.; Sakurai, H. "Abstracts", 43rd National Meeting of the Chemical Society of Japan, Tokyo, April 1981, No. 1D25.

maining oil was distilled to give **4g** (14.8 g, 92%), bp 55–55.5 °C (4 mmHg).

The following 3-chloro-2-(trimethylsiloxy)allyl chlorides were prepared from appropriate α,α'-dichloro ketones by use of the procedure used to prepare **4g**: 3-chloro-1,1-dimethyl-2-(trimethylsiloxy)allyl chloride (**4a**), bp 50–52 °C (2 mmHg) (85%); 3-chloro-1-ethyl-1-methyl-2-(trimethylsiloxy)allyl chloride (**4b**), bp 70–76 °C (2 mmHg) (74%); 3-chloro-1-methyl-2-(trimethylsiloxy)allyl chloride (**4c**), bp 54.5–55.5 (5 mmHg) (83%); 3-chloro-1-isopropyl-2-(trimethylsiloxy)allyl chloride (**4d**), bp 60–61 °C (1 mmHg) (91%); 3-chloro-1,3-dimethyl-2-(trimethylsiloxy)allyl chloride (**4e**) (Z/E = 1.36), bp 68–72 °C (6 mmHg) (73%); 3-chloro-1,3-diethyl-2-(trimethylsiloxy)allyl chloride (**4f**) (Z/E = 3.00), bp 68–70 °C (0.5 mmHg) (79%).

1-*tert*-Butyl-3,3-dimethyl-2-(trimethylsiloxy)allyl Chloride (5a). To a mixture of **4a** (2.75 g, 12 mmol) and CuI (2.1 g) in THF (10 mL) was added dropwise a solution of *tert*-butylmagnesium chloride (55 mmol) in THF (25 mL) during a period of 30 min at 0 °C under nitrogen. The resulting mixture was stirred for 3 h at 0 °C and worked up. The crude oil was distilled to give **5a**, bp 50–54 °C (2 mmHg) (2.25 g, 74%).

Similarly, **4c** (3.0 g, 14 mmol) was treated with *tert*-butylmagnesium chloride (70 mmol) in the presence of CuI (1.0 g) in THF (0 °C, 3 h). There was obtained a colorless oil (3 g), bp 85–87 °C (16 mmHg), which was a mixture of 1-*tert*-butyl-3-methyl-2-(trimethylsiloxy)allyl chloride (**5b**) (Z/E = 2.03) and 2,2,5,6,6-pentamethyl-4-(trimethylsiloxy)-3-heptene (**45a**) in the ratio 77:23. The latter compound was inactive toward silver perchlorate, so the mixture was used directly for further reactions. The reaction of **4g** (4.0 g, 20 mmol) with *tert*-butylmagnesium chloride (80 mmol) in the presence of CuI (2.1 g) at 0 °C for 3 h gave a mixture of 1-*tert*-butyl-2-(trimethylsiloxy)allyl chloride (**5c**) and 2,2,6,6-tetramethyl-4-(trimethylsiloxy)-3-heptene (**45b**) (55:45, 2.6 g), bp 67–68 °C (12 mmHg). The mixture was used without further purification.

Silylation of Chloroacetaldehyde and Phenacyl Chloride. Aqueous chloroacetaldehyde (30% solution, 8 g) was extracted with ether. The ethereal solution was dried and added to a mixture of trimethylchlorosilane (5 g) and triethylamine (5.6 g) in ether (20 mL) at room temperature. The mixture was stirred for 5 h at ambient temperatures and worked up. There was obtained (*Z*)-1-chloro-2-trimethylsiloxyethylene, bp 42–45 °C (25 mmHg) [lit.[36] bp 45–50 °C (30 mmHg)] as a colorless oil (0.8 g): NMR δ 0.25 (s, 9 H), 5.16 (d, 1 H, J = 4.0 Hz), 6.39 (d, 1 H, J = 4.0 Hz). Silylation of phenacyl chloride using trimethylchlorosilane and triethylamine under the same condition used to prepare **4g** gave (*Z*)-2-chloro-1-phenyl-1-(trimethylsiloxy)ethylene in 86% yield: IR 1612, 1323, 1257, 1230, 1085, 920, 898, 840, 770, 690 cm^{-1}; NMR δ 0.20 (s, 9 H), 5.84 (s, 1 H), 7.2–7.5 (m, 5 H).[19] The product (0.5 g) was irradiated by a 500-W mercury lamp through a Pyrex filter in benzene solution in the presence of benzophenone (0.5 g) for 1 h under nitrogen. Evaporation of solvent left an oil which was a mixture of the *Z* and *E* isomers (1:1.5). Pure *E* isomer was isolated by GLC [1.5 m AGL, 180 °C; retention time (t_R) 12.8 min for *E* and 16.0 min for *Z* isomers]: IR 1600, 1495, 1442, 1328, 1250, 1200, 1115, 900, 845, 780, 770, 750, 690 cm^{-1}; NMR δ 0.13 (s, 9 H), 5.70 (s, 1 H), 7.1–7.8 (m, 5 H). The stereochemical assignment was deduced from the NMR characteristic of styrene derivatives that the olefinic proton cis to the phenyl group resonates at lower field than the trans proton.[37]

Reactions of 2-(Trimethylsiloxy)allyl Chlorides with 1,3-Dienes in the Presence of Silver Perchlorate. General. Procedure A. To a well-stirred mixture of silver perchlorate (10 mmol), calcium carbonate (2 g), and a diene (25 mmol) in nitromethane (20 mL) was added a solution of an allyl chloride (**3–5**) (5 mmol) in nitromethane (5 mL) in a period of 15 min at 0 °C. In the case of the chlorides **5a–c**, the chloride was dissolved in nitromethane/ether (4:1, 5 mL) instead of pure nitromethane. The resulting mixture was stirred for 15 min at 0 °C. The mixture was diluted with ether (50 mL). Then a sodium chloride solution was added until the inorganic materials aggregated. Organic layer was separated by decantation, washed with a sodium bicarbonate solution, and dried. Evaporation of solvent left a crude product mixture. In the case of cyclopentadiene, the excess diene was removed by evaporation prior to workup. Products were isolated from the crude mixture by alumina chromatography, by distillation, or by preparative GLC. The spectral data are summarized in Tables VII (for 3 + 4 → 7 adducts **6–13**, **19–23**, **26**, and **27**) and VIII (for substitution products **14–18**) (supplementary material).

Procedure B. Silver perchlorate (10 mmol) was dissolved in THF (5 mL). The solution was diluted with ether (10 mL), which was followed by addition of a diene (25 mmol) and calcium carbonate (2 g). To the stirred mixture was added an allyl chloride (5 mmol) in ether (5 mL) during a period of 15 min at 0 °C. The resulting mixture was stirred for 45 min at 0 °C and worked up.

Procedure C. Silver perchlorate on alumina was prepared by addition of activated alumina (300 mesh, 15 g) to a solution of silver perchlorate (1.95 g) in THF/ether (1:5, 250 mL) followed by removing solvent on a rotary evaporator in the dark. The residue was further dried under vacuum (1 mmHg) for 1 h in the dark. To a well-stirred mixture of this silver perchlorate on alumina (13% by weight, 2 equiv) and a diene (25 mmol) in benzene (10 mL) was added a solution of an allyl chloride (5 mmol) in benzene (5 mL) during a period of 15 min. The resulting mixture was stirred for 3 h at ambient temperatures. The mixture was filtered through a column packed with alumina (2 g). After the organic layer had been eluted, the column was eluted with 10% ether in petroleum ether (50 mL). The combined eluents were evaporated to give a crude product mixture.

Reaction of 3a with Furan. A. Procedure A was followed, and from 1.00 g (5.2 mmol) of **3a** there was obtained 2,2-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (**6a**) as colorless crystals (727 mg, 92%), mp 46–47 °C. The spectral data were superimposable with those reported.[24]

B. According to procedure B, **3a** (1.2 g) was treated with $AgClO_4$ (1.8 g) in the presence of furan (5 g) in THF/ether (1:5, 25 mL) (45 min). A yellow oil obtained after workup was crystallized in pentane to give **6a** (801 mg, 85%).

C. Procedure C was followed, and from 0.60 g of **3a** there was obtained **6a** (432 mg) in 91% yield.

Reaction of 3b with Furan. A. Procedure A was followed, and from 1.03 g (5.0 mmol) of **3b** there was obtained a mixture of 2-ethyl-2-methyl-8-oxabicyclo[3.2.1]oct-6-en-3-ones **6b** and **6c** (1.6:1 by NMR) as a colorless oil (680 mg, 81%).

B. According to procedure B, **3b** (1.02 g) was treated with $AgClO_4$ (1.5 g) in the presence of furan (3 g). A colorless oil (560 mg) obtained after workup was analyzed by GLC (1.2 m AGL, 160 °C, diphenyl ether as a standard), indicating the formation of 3-methyl-2-(trimethylsiloxy)-1,3-pentadiene (20%, t_R 2.0 min), 1-(2-furyl)-3-methyl-2-pentanone (**14a**) (5%, t_R 9.7 min), and a mixture of **6b** and **6c** (1.5:1 by NMR) (43%, t_R 18.3 min). **14a** was isolated by GLC.

Reaction of 4a with Furan. A. Procedure A was followed, and from 2.00 g (8.78 mmol) of **4a** there was obtained 4-chloro-2,2-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (**7a**) (1.45 g, 89%) as colorless crystals, mp 89–90 °C (from hexane).

B. According to procedure B, **4a** (2.28 g) was treated with $AgClO_4$ (2.5 g) in the presence of furan (3.7 g). GLC analysis (75 cm SE, 160 °C, benzophenone as a standard) of the crude mixture obtained after workup indicated the formation of 1-chloro-3-(2-furyl)-3-methyl-2-(trimethylsiloxy)-1-butene (**15a**) (61%, t_R 4.5 min), the bicyclic ketone (3%, t_R 3.2 min), and three other unidentified products. The first two products were isolated by preparative GLC. Treatment of **15a** with methanol gave the corresponding ketone **14b** quantitatively. The bicyclic product was shown to be a mixture of equatorial and axial isomers **7a** and **8a** in the ratio 6:1 by NMR.

Reaction of 4b with Furan. Procedure A was followed, and from 130 mg (0.54 mmol) of **4b** there was obtained a mixture of 4-chloro-2-ethyl-2-methyl-8-oxabicyclo[3.2.1]oct-6-en-3-ones **7b** and **7c** (1.2:1 by NMR) as a colorless oil (96 mg, 89%).

Reaction of 4c with Furan. A. Procedure A was followed, and from 1.00 g (4.68 mmol) of **4c** there was obtained a mixture of 2-chloro-4-methyl-8-oxabicyclo[3.2.1]oct-6-en-3-ones **7d** and **7e** (1:1) as a colorless oil (702 mg, 87%). **7d** and **7e**, mp 83–84 °C, were isolated by preparative GLC (1.2 m DGS, 190 °C, t_R 18.7 min for **7e** and 20.6 min for **7d**).

B. **4c** (2.0 g) was treated with $AgClO_4$ (1.95 g) in the presence of furan (3.2 g) in THF/ether (1:2, 15 mL) (0 °C, 2 h). GLC analysis (75 cm SE, 110 °C) of the crude oil obtained after workup indicated the formation of 1-chloro-3-(2-furyl)-2-(trimethylsiloxy)-1-butene **15b** (52%, t_R 21.2 min). **15b** was isolated by GLC. Treatment of **15b** with methanol gave the corresponding ketone **14c** quantitatively.

Reaction of 4d with Furan. Procedure A was followed, and from 1.00 g (4.15 mmol) of **4d** there was obtained a mixture of 2-chloro-4-isopropyl-8-oxabicyclo[3.2.1]oct-6-en-3-ones **7f** and **7g** (1:1) as a colorless oil (630 mg, 76%). Each isomer was isolated by preparative GLC (1.2 m DGS, 190 °C, t_R 18.7 min for **7g** and 20.3 min for **7f**).

Reaction of 4e with Furan. A. According to procedure A, **4e** (2.0 g, 8.8 mmol) was treated with $AgClO_4$ (2.5 g) in the presence of furan (3 g). GLC analysis (1.2 m SE, 160 °C) of the crude oil (1.39 g) obtained after workup indicated the formation of 2-chloro-4-(2-furyl)-3-pentanone **14d** (t_R 2.2 min) and a mixture of 2-chloro-2,4-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-ones **7h** and **8b** (t_R 4.4 min, 1.42:1 by NMR) in the ratio 1:10.6. The oil was chromatographed over alumina, eluting with

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5% ether in petroleum ether to give a mixture of **7h** and **8b** as a colorless oil (1.28 g, 78%). Each isomer was isolated by preparative GLC (1.2 m DGS, 190 °C, t_R 14.3 min for **7h** and 15.2 min for **8b**).

B. **4e** (2.21 g) was treated with $AgClO_4$ (2.1 g) in the presence of furan (3.3 g) in THF/ether (1:2, 25 mL). A yellow oil obtained after workup was distilled to give 2-chloro-4-(2-furyl)-3-(trimethylsiloxy)-2-pentene (**15c**) (1.15 g), bp 73–74 °C (3 mmHg), along with **14d** (197 mg), bp 44–45 °C (3 mmHg).

Reaction of 4f with Furan. According to procedure A, **4f** (1.00 g, 3.92 mmol) was treated with $AgClO_4$ (1.5 g) in the presence of furan (2 g). GLC analysis (1.2 m DGS, 190 °C) of the crude oil obtained after workup indicated the formation of 3-chloro-5-(2-furyl)-4-heptanone (**14e**) (t_R 4.5 and 5.6 min as a diastereoisomeric mixture in the ratio 2.3:1) and 2-chloro-2,4-diethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (**7l**) (t_R 17.7 min) and its stereoisomer **8c** (t_R 20.5 min) in 21, 59, and 15% yields, respectively. **14e** was isolated by GLC. A mixture of **7l** and **8c** (556 mg) was obtained from the mixture by alumina chromatography. Separation of the stereoisomers was performed by GLC.

Reaction of 4g with Furan. A. According to procedure A, **4g** (2.0 g, 10 mmol) was treated with $AgClO_4$ (2.9 g) in the presence of furan (3 g) (7 h). GLC analysis (1.2 m DGS, 190 °C) of the crude oil obtained after workup indicated the formation of a mixture of 2-chloro-8-oxabicyclo[3.2.1]oct-6-en-3-ones **7j** and **8d** (8.1:1 by NMR, t_R 22.2 min for both isomers) besides the unchanged **4g** (10%). A mixture of **7j** and **8d** was isolated by alumina chromatography as a colorless oil (1.28 g, 80%). The isomer ratio **7j**/**8d** determined by NMR was 20 after 3 h of reaction and 7.8 after 8 h. When a mixture of **7j** and **8d** (12:1) was allowed to stand for 8 h at room temperature in the presence of a catalytic amount of perchloric acid, there were recovered the isomers in the ratio **7j**/**8d** = 2.5.

B. A mixture of **4g** (1.44 g), $AgClO_4$ (1.5 g), and $CaCO_3$ (2 g) in dimethoxyethane/ether (1:1, 25 mL) was stirred under reflux for 25 h. GLC analysis (1.2 m AGL, 140 °C) of the crude oil obtained after workup indicated the formation of 1-chloro-3-(2-furyl)-2-propanone (**14f**) (10%, t_R 9.5 min) and a mixture of **7j** and **8d** (3.9:1 by NMR, t_R 19.6 min for both isomers, 45%) besides the unchanged **4g** (29%). **14f** was isolated by GLC.

Reaction of 5a with Furan. A. Procedure A was followed, and from 801 mg (3.21 mmol) of **5a** there was obtained 2,2-dimethyl-4-*tert*-butyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (**9a**) as a colorless oil (576 mg, 86%).

B. Procedure B was followed, and from 500 mg of **5a** there was obtained **9a** (125 mg) in 34% yield.

Reaction of 5b with Furan. A. According to procedure A, a mixture of **5b** and **45a** [727 mg, 548 mg (2.33 mmol) as **5b**] was treated with $AgClO_4$ (1.1 g) in the presence of furan (1.2 g) (1 h). The crude oil obtained after workup was chromatographed over alumina. Elution with petroleum ether gave 2,2,3,6,6-pentamethyl-4-heptanone (**46a**) (118 mg). Elution with 5% ether in petroleum ether gave a mixture of 2-*tert*-butyl-4-methyl-8-oxabicyclo[3.2.1]oct-6-en-3-ones **9b** and **9c** (1.70:1, 389 mg). Each isomer was isolated by preparative GLC (1.5 m AGL, 175 °C, t_R 17.6 min for **9c** and 21.2 min for **9b**).

B. Procedure B was followed. GLC analysis of the crude oil obtained from a mixture of **5b** and **45a** (800 mg, 603 mg as **5b**) indicated the formation of 2-(2-furyl)-5,5-dimethyl-3-(trimethylsiloxy)-3-hexene (**15d**), 4-(2-furyl)-5,5-dimethyl-3-(trimethylsiloxy)-2-hexene (**15e**), and three isomeric 2-*tert*-butyl-4-methyl-8-oxabicyclo[3.2.1]oct-6-en-3-ones (**9b**, **9c**, and **10b**) [1.5 m AGL, 172 °C, t_R relative to diphenylmethane 0.40, 0.46, 0.69, 0.53, and 0.58, respectively] in 29.2, 8.8, 16.1, 11.7, and 7.3% yields, respectively. **15d** and **15e** were isolated by GLC. They were converted into the corresponding ketones **14g** and **14h** on treatment with methanol. **10b** was partially separated from the other stereoisomers by preparative GLC.

Reaction of 5c with Furan. A. According to procedure A, a mixture of **5c** and **45b** [750 mg, 397 mg (1.80 mmol) as **5c**] was treated with $AgClO_4$ (1 g) in the presence of furan (1.5 g) (1 h). The crude oil obtained after workup was chromatographed over alumina by eluting with 5% ether in petroleum ether to give a mixture of 3-chloro-4,4-dimethyl-2-pentanone and 2,2,6,6-tetramethyl-4-heptanone (**46b**) (1:3, 420 mg) and a mixture of 2-*tert*-butyl-8-oxabicyclo[3.2.1]oct-6-en-3-ones **9d** and **10d** (9:1 by NMR, 159 mg, 48%) in order of elution. **9d** and **10d** were isolated by GLC (1.5 m AGL, 160 °C, t_R 18.4 min for **10d** and 23.6 min for **9d**).

B. Procedure **B** was followed. GLC analysis (1.5 m AGL, 160 °C, diphenylmethane as a standard) of the crude oil obtained from 397 mg of **5c** (containing 353 mg of **45b**) indicated the formation of 3-chloro-4,4-dimethyl-2-pentanone (43%), **46b** (96%), 1-(2-furyl)-4,4-dimethyl-2-pentanone (**14i**) (5%), **10d** (2.9%), and **9d** (5.1%) (t_R relative to Ph_2CH_2 0.06, 0.10, 0.22, 0.44, and 0.47, respectively). **14i** was isolated by GLC.

Reaction of 3a with 2-Methylfuran. A. Procedure A was followed, and from 1.00 g of **3a** there was obtained a mixture of 1,4,4-trimethyl- and 1,2,2-trimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-ones **11** and **12** (1.90:1) as a colorless oil (794 mg, 92%). **11** and **12**, mp 120–128 °C, were isolated by GLC. Their spectral data were in agreement with those reported.[24]

B. **3a** (746 mg, 3.89 mmol) was treated with $AgClO_4$ (1 g) in the presence of 2-methylfuran (1.6 g) in THF/ether (1:2, 15 mL) (1 h). The crude oil obtained after workup was chromatographed over alumina eluting with 5% ether in petroleum ether to give a mixture of 3-methyl-1-(5-methyl-2-furyl)-2-butanone (**16**) and 3-methyl-3-(5-methyl-2-furyl)-2-butanone (**17**) (4:1, 277 mg, 43%) and a mixture of **11** and **12** (19:1, 183 mg, 28%) in order of elution. **16** and **17** were isolated by GLC.

Reaction of 4a with 2-Methylfuran. According to procedure A, **4a** (1.00 g, 4.4 mmol) was treated with $AgClO_4$ (1.6 g) in the presence of 2-methylfuran (2 g). GLC analysis (1.2 m DGS, 190 °C) of the crude oil indicated the formation of 2-chloro-1,4,4-trimethyl-8-oxabicyclo-[3.2.1]oct-6-en-3-one (**13**) (66%, t_R 7.7 min) and 1-chloro-3-methyl-3-(5-methyl-2-furyl)-2-butanone (**18**) (22%, t_R 5.2 min). The latter product was isolated by GLC. **13** was isolated from the mixture by alumina chromatography as colorless crystals (502 mg), mp 104–105 °C.

Reaction of 3a with Cyclopentadiene. According to the procedure B, **3a** (1.0 g, 5.2 mmol) was treated with $AgClO_4$ (1.5 g) in the presence of cyclopentadiene (3 g) in THF/ether (1:1.5, 25 mL) (45 min). Workup followed by alumina chromatography gave 2,2-dimethylbicyclo[3.2.1]-oct-6-en-3-one (**19a**) as colorless crystals (709 mg, 91%), mp 49–50 °C. The spectral data were superimposable with those reported.[24]

Reaction of 3b with Cyclopentadiene. Procedure B was followed, and from 1.03 g (5.0 mmol) of **3b** there was obtained a mixture of 2-ethyl-2-methylbicyclo[3.2.1]oct-6-en-3-ones **19b** and **19c** (1:1 by NMR) as a colorless oil (582 mg, 71%).

Reaction of 4a with Cyclopentadiene. A. According to procedure A, **4a** (1.0 g, 4.4 mmol) was treated with $AgClO_4$ (1.6 g) in the presence of cyclopentadiene (2 g) (1 h). Workup followed by alumina chromatography gave a mixture of 4-chloro-2,2-dimethylbicyclo[3.2.1]oct-6-en-3-ones **20a** and **21a** (2.46:1, 650 mg, 80%). Each isomer was isolated by preparative GLC (1.2 m DGS, 190 °C, t_R 6.8 min for **21a** and 14.5 min for **20a**).

B. **4a** (2.64 g) was treated with $AgClO_4$ (2.4 g) in the presence of cyclopentadiene (3.5 g) in THF/ether (1:1, 25 mL). GLC analysis of the crude oil obtained after workup indicated the formation of many products including **20a** (4.4%) and **21a** (3.2%).

Reaction of 4c with Cyclopentadiene. Procedure A was followed, and from 1.00 g (4.69 mmol) of **4c** there was obtained a mixture of 2-chloro-4-methylbicyclo[3.2.1]oct-6-en-3-ones **20b**, **20c**, **21b**, and **21c** as a colorless oil (605 mg, 76%). **20b**, **20c**, and a mixture of **21b** and **21c** were isolated by preparative GLC (1.2 m DGS, 190 °C, t_R 6.8 min for **21b, c**, 14.3 min for **20c**, and 16.3 min for **20b**). The following ratio was determined by combination of GLC and NMR analyses: **20b**:**20c**:**21b**:**21c** = 54:16:4:26.

Reaction of 4e with Cyclopentadiene. Procedure A was followed, and from 1.0 g (4.4 mmol) of **4e** there was obtained a mixture of 2-chloro-2,4-dimethylbicyclo[3.2.1]oct-6-en-3-ones **20d**, **20e**, **21d**, and **21e** as a colorless oil (520 mg, 64%). **20d**, **20e**, and a mixture of **21d** and **21e** were isolated by GLC (1.5 m CW, 190 °C, t_R 6.0 min for **21d, e**, 10.3 min for **20e**, and 12.9 min for **20d**). The following ratio was determined by combination of GLC and NMR analyses: **20d**:**20e**:**21d**:**21e** = 47:15:17:21.

Reaction of 5a with Cyclopentadiene. Procedure A was followed, and from 435 mg of **5a** there was obtained a mixture of 2,2-dimethyl-4-*tert*-butylbicyclo[3.2.1]oct-6-en-3-ones **22a** and **23a** (1:1, 296 mg, 82%) as a colorless oil. Separation of the isomers was performed by GLC.

Reaction of 5b with Cyclopentadiene. Procedure A was followed, and from 364 mg of **5b** (containing 119 mg of **45a**) there was obtained a mixture of 2-*tert*-butyl-4-methylbicyclo[3.2.1]oct-6-en-3-ones **22b** and **23c** (1:1, 191 mg, 60%), along with **46a** (80 mg). **22b** and **23c** were isolated by GLC (1.5 m AGL, 150 °C, t_R 46.8 min for **22b** and 48.8 min for **23c**).

Reaction of 5c with Cyclopentadiene. Procedure A was followed, and from 582 mg of **5c** (containing 428 mg of **45b**) there was obtained a mixture of 2-*tert*-butylbicyclo[3.2.1]oct-6-en-3-ones **22d** and **23d** (1:1, 43 mg, 9%) along with a mixture of 3-chloro-4,4-dimethyl-2-pentanone and **46b** (1:1.18, 836 mg). **22d**, mp 43–46 °C, and **23d** were isolated by GLC (1.5 m AGL, 170 °C, t_R 22.4 min for **22d** and 23.2 min for **23d**).

Reaction of 3a with Isoprene. A. Procedure A was followed, and from 1.0 g of **3a** there was obtained a mixture of karahanaenone **24**, its regioisomer **25**, and an unidentified product (55:33:12) as a colorless oil (418 mg). The last compound may be a 3 + 2 → 5 cycloadduct,[14] but we did not examine it further.

B. According to procedure B, **3a** (1.4 g) was treated with $AgClO_4$ (2.3 g) in the presence of isoprene (5.9 g) in THF/ether (1:1, 25 mL) (1 h). Workup followed by alumina chromatography gave a mixture of **24** and **25** (71:29, 678 mg). The mixture contained an unidentified product (5%).

C. Procedure C was followed, and from 0.5 g of **3a** there was obtained a mixture of **24** and **25** (73:27, 281 mg). The spectral data of the products were superimposable with those reported.[14]

Reaction of 4a with 2,3-Dimethylbutadiene. A. According to procedure A, **4a** (1.0 g) was treated with $AgClO_4$ (2.0 g) in the presence of 2,3-dimethylbutadiene (2 mL) at -20 °C (1.5 h). GLC analysis (1.2 m DGS, 180 °C) of the crude oil obtained after workup indicated that 7-chloro-2,2,4,5-tetramethyl-4-cycloheptenone (**26**) (t_R 11.4 min) was formed in 32% yield besides many other minor products. An analytical sample of **26** was obtained by GLC: mass spectrum *m/e* (rel intensity) 202 (8), 200 (M^+ 27), 123 (100).

B. According to procedure B, **4a** (0.51 g) was treated with $AgClO_4$ (1 g) in the presence of 2,3-dimethylbutadiene (1 mL) in THF/ether (1:1) at -20 °C (1 h). GLC analysis indicated the formation of **26** in 10% yield.

Reaction of 4c with 2,3-Dimethylbutadiene. According to procedure A, **4c** (1.0 g, 4.6 mmol) was treated with $AgClO_4$ (2.0 g) in the presence of 2,3-dimethylbutadiene (2 mL) at -15 °C (1.5 h). GLC analysis (1.2 m DGS, 100 °C) of the crude oil obtained after workup indicated that 2-chloro-4,5,7-trimethyl-4-cycloheptenone (**27**) (t_R 20.3 min) was formed in 10% yield. An analytical sample of **27** was obtained by GLC.

Reactions of 2-(Trimethylsiloxy)allyl Chlorides with Methanol, Naphthalene, and Anisole in the Presence of Silver Perchlorate. Reactions of 3a, 4a, and 4e with Methanol. A. A solution of **3a** (1.04 g) in ether (5 mL) was added to a mixture of $AgClO_4$ (2 g), methanol (2 mL), and triethylamine (0.56 g) in THF/ether (1:4, 15 mL) at -30 °C. The resulting mixture was stirred for 15 min at -30 °C and worked up. GLC analysis (1.5 m AGL, 120 °C) of the crude oil (960 mg) indicated the formation of 3-methoxy-3-methyl-2-(trimethylsiloxy)-1-butene (**28a**) (t_R 6.6 min) as the sole product (94%). Treatment of the oil with methanol gave the corresponding ketone, **29a**, bp 50–52 °C (100 mmHg), quantitatively.

The reactions of the chlorides **4a** and **4e** under the same condition used for **3a** gave trimethylsilyl enol ethers **28b** and **28c** (Z/E = 1.3) in 97 and 91% yields, respectively. They were converted into the corresponding methoxy ketones **29b** and **29c** quantitatively on treatment with methanol. The spectral data for **28** and **29** are given in Table VIII (supplementary material).

B. **3a** (0.50 g) was treated with $AgClO_4$ (1 g) in the presence of methanol (1 mL) and $CaCO_3$ (1 g) in nitromethane (8 mL) at -30 °C (10 min). The mixture was directly analyzed by GLC, indicating the formation of **28a** as the sole product; however, the crude oil obtained after workup was a mixture of **28a** and **29a** (1:1).

Reaction of 3a with Naphthalene. **3a** (1.93 g, 10 mmol) was treated with $AgClO_4$ (3.0 g) in the presence of naphthalene (5 g) and $CaCO_3$ (2 g) in THF (10 mL) at 0 °C (1 h). Excess naphthalene was removed by sublimation under reduced pressure. The remaining oil was chromatographed over alumina eluting with 5% ether in petroleum ether to give a mixture of 2,2-dimethyl-6,7-benzobicyclo[3.2.2]nona-6,8-dien-3-one (**30**) and 3-methyl-1-(1-naphthyl)-2-butanone (**31**) (1:1) as a colorless oil (82 mg, 3.9%). Each product was isolated by GLC (1.2 m AGL, 200 °C, t_R 13.6 min for **30** and 19.4 min for **31**). **30**: IR 1685 cm^{-1}; NMR δ 0.89 (s, Me), 1.21 (s, Me), 2.55 (d of d, 2 H, J = 5.1 and 2.0 Hz, H_4), 3.35 (d of d, J = 4.2 and 3.0 Hz, H_1), 3.63 (m, 1 H, H_5), 6.55 (d of d, 2 H, J = 4.2 and 3.0 Hz, $H_{8,9}$), 7.10 (almost s, 4 H, aromatic). Anal: ($C_{15}H_{16}O$) C, H. **31**: IR 1705 cm^{-1}; NMR 0.97 (d, 2Me, J = 6.5 Hz), 2.64 (septet, 1 H), 4.03 (s, 2 H), 7.25–7.95 (m, 7 H).

Reaction of 3a with Anisole. **3a** (0.60 g, 3.1 mmol) was treated with $AgClO_4$ (870 mg) in the presence of anisole (1.9 g) and $CaCO_3$ (1 g) in THF/ether (1:3, 15 mL) at 20 °C (20 h). GLC analysis (1.2 m DGS, 180 °C) of the crude oil obtained after workup indicated the formation of a mixture of para and ortho isomers (2.94:1) of 1-methoxyphenyl-3-methyl-2-butanone (**32**) (82%, t_R 15.6 min for para and 10.1 min for ortho isomers). Each isomer was isolated by GLC. The spectral data are given in Table VIII (supplementary material).

Reaction of 4a with Anisole. **4a** (2.17 g) was treated with $AgClO_4$ (1.8 g) in the presence of anisole (4.7 g) in THF/ether (1:1, 20 mL) at 0 °C (1 h). GLC analysis of the crude oil indicated the formation of 1-chloro-3-(4-methoxyphenyl)-3-methyl-2-butanone (**33**) in 2.4% yield.

Reaction of 2-Methyl-3-(trimethylsiloxy)butadiene (38) with 2-Methylfuran in the Presence of Silver Perchlorate. A. **3a** (1.8 g) in ether (10 mL) was added to a cold (-70 °C) mixture of $AgClO_4$ (2.8 g) and $CaCO_3$ (1 g) in THF/ether (1:1, 15 mL) during a period of 15 min. 2-Methylfuran (5 g) was added. The resulting mixture was allowed to warm up to room temperature and worked up. GLC analysis (3 m DGS, 135 °C) of the crude oil indicated that 4-(5-methyl-2-furyl)-3-methyl-2-butanone (**39**) (t_R 20 min) was formed in 58% yield. An analytical sample of **39** was obtained by GLC: IR 1715 cm^{-1}; NMR δ 1.08 (d, 3 H, J = 6.5 Hz), 2.05 (s, 3 H), 2.24 (s, 3 H), 2.4–3.0 (m, 1 H), 5.77 (almost s, 2 H). Anal: ($C_{10}H_{14}O_2$) C, H.

B. A mixture of **38** (250 mg), 2-methylfuran (700 mg), $AgClO_4$ (0.6 g), and $CaCO_3$ (0.5 g) in THF/ether (1:1, 8 mL) was stirred for 2 h at room temperature and worked up. GLC analysis of the crude oil indicated the formation of **39** in 65% yield.

Treatment of 4a with a Mixture of Furan and Cyclopentadiene in the Presence of Silver Perchlorate. To a stirred mixture of $AgClO_4$ (1.50 g), furan (1.12 g, 16.5 mmol), cyclopentadiene (1.23 g, 18.6 mmol), and $CaCO_3$ (1.0 g) in nitromethane (20 mL) was added a solution of **4a** (1.00 g, 4.4 mmol) in nitromethane (5 mL) during a period of 15 min at 0 °C. The resulting mixture was stirred for another 15 min at 0 °C and worked up. GLC analysis (1.2 m DGS, 190 °C) of the crude oil indicated that **7a**, **20a**, and **21a** were formed in the ratio 55.8:30.2:14.0. This product ratio indicated the following relative reactivity: $k_{\text{furan}}/k_{\text{cyclopentadiene}} = 1.42$.

Treatment of 3a with a Mixture of Furan and Methanol in the Presence of Silver Perchlorate. A. **3a** (540 mg, 2.8 mmol) was added to a stirred mixture of $AgClO_4$ (1.7 g), furan (2.25 g, 33.1 mmol), methanol (550 mg, 17.3 mmol), and $CaCO_3$ (1 g) in nitromethane (8 mL) at -30 °C in a period of 10 min. The reaction mixture was directly analyzed by GLC (1.5 m AGL, 120 °C) indicating that **6a** and **28a** were formed in the ratio 1:1.91. This product ratio indicated the following relative reactivity: $k_{\text{methanol}}/k_{\text{furan}} = 3.64$.

B. **3a** (0.50 g, 2.6 mmol) was treated with $AgClO_4$ (1.7 g) in the presence of furan (2.34 g, 34.5 mmol), methanol (0.792 g, 24.7 mmol), and $CaCO_3$ (1 g) in THF/ether (1:2, 10 mL) at -30 °C (10 min). GLC analysis of the reaction mixture indicated that **6a** and **28a** were formed in the ratio 1:19.4. This ratio indicated the following relative reactivity: $k_{\text{methanol}}/k_{\text{furan}} = 27$.

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Registry No. **1a**, 5950-19-6; **1b**, 30718-05-9; **2a**, 57539-84-1; **2b**, 57539-85-2; **3a**, 69875-71-4; **3b**, 80422-52-2; (*Z*)-**4a**, 80422-53-3; (*Z*)-**4b**, 80422-54-4; (*Z*)-**4c**, 80422-55-5; (*Z*)-**4d**, 80422-56-6; (*Z*)-**4e**, 80422-57-7; (*E*)-**4e**, 80422-58-8; (*Z*)-**4f**, 80422-59-9; (*E*)-**4f**, 80422-60-2; (*Z*)-**4g**, 80422-61-3; **5a**, 80422-62-4; (*E*)-**5b**, 80422-63-5; (*Z*)-**5b**, 80422-64-6; **5c**, 80422-65-7; **6a**, 22940-28-9; **6b**, 80422-66-8; **6c**, 80422-67-9; **7a**, 80422-68-0; **7b**, 80422-69-1; **7c**, 80446-98-6; **7d**, 80422-70-4; **7e**, 80446-99-7; **7f**, 80422-71-5; **7g**, 80447-00-3; **7h**, 80422-72-6; **7i**, 80422-73-7; **7j**, 80422-74-8; **8a**, 80422-75-9; **8b**, 80447-01-4; **8c**, 80447-02-5; **8d**, 80422-76-0; **9a**, 80422-77-1; **9b**, 80422-78-2; **9c**, 80447-03-6; **9d**, 80422-79-3; **10b**, 80447-04-7; **10d**, 80422-80-6; **11**, 10360-53-9; **12**, 10386-03-5; **13**, 80422-81-7; **14a**, 55107-02-3; **14d**, 80422-82-8; **14e**, 80422-83-9; **14f**, 39056-65-0; **14i**, 80422-84-0; **15a**, 80422-85-1; **15b**, 80422-86-2; **15c**, 80422-87-3; **15d**, 80422-88-4; **15e**, 80422-89-5; **16**, 69875-69-0; **17**, 69875-70-3; **18**, 80422-90-8; **19a**, 22940-29-0; **19b**, 80422-91-9; **19c**, 80422-92-0; **20a**, 80422-93-1; **20b**, 80422-94-2; **20c**, 80447-05-8; **20d**, 80422-95-3; **20e**, 80447-06-9; **21a**, 80422-96-4; **21b**, 80447-07-0; **21c**, 80422-97-5; **21d**, 80447-08-1; **21e**, 80422-98-6; **22a**, 80422-99-7; **22b**, 80423-00-3; **22d**, 80423-01-4; **23a**, 80423-02-5; **23c**, 80423-03-6; **23d**, 80423-04-7; **24**, 19822-67-4; **25**, 65395-75-7; **26**, 80423-05-8; **27**, 80423-06-9; **28a**, 80423-07-0; **28b**, 80423-08-1; **28c**, 80423-09-2; **29a**, 36687-98-6; **29b**, 57539-98-7; **29c**, 80423-10-5; **30**, 80423-11-6; **31**, 80423-12-7; *p*-**32**, 61173-96-4; *o*-**32**, 75508-72-4; **33**, 80423-13-8; **34a**, 80423-14-9; **34b**, 80423-15-0; **34c**, 80423-16-1; **34d**, 80423-17-2; **34e**, 80423-18-3; **34f**, 80423-19-4; **34g**, 80423-20-7; **34h**, 80423-21-8; **34i**, 80423-22-9; **34j**, 80423-23-0; **34k**, 80423-24-1; **34l**, 80423-25-2; **39**, 80423-26-3; **45a**, 80423-27-4; **45b**, 80423-28-5; **46a**, 32834-08-5; **46b**, 4436-99-1; *tert*-butyl chloride, 507-20-0; chloroacetaldehyde, 107-20-0; (*Z*)-1-chloro-2-trimethylsiloxyethylene, 80423-29-6; phenacyl chloride, 532-27-4; (*E*)-2-chloro-1-phenyl-1-(trimethylsiloxy)ethylene, 80423-30-9; (*Z*)-2-chloro-1-phenyl-1-(trimethylsiloxy)ethylene, 80423-31-0; furan, 110-00-9; 3-methyl-2-(trimethylsiloxy)-1,3-pentadiene, 80423-32-1; 2-methylfuran, 534-22-5; cyclopentadiene, 542-92-7; 2,3-dimethylbutadiene, 513-81-5; methanol, 67-56-1; naphthalene, 91-20-3; anisole, 110-66-3; **38**, 54781-31-6; isoprene, 78-79-5.

Supplementary Material Available: Tables of IR and NMR spectra for 2-(trimethylsiloxy)allyl chlorides, 3 + 4 → 7 cycloadducts, and substitution products and microanalytical data (12 pages). Ordering information is given on any current masthead page.