permethylated methyl α-D-mannopyranoside is slower than the acetolysis of either permethylated methyl α-D-gluco- or α-D-galactopyranosides.

Therefore, it can be concluded that the conversion of the ground-state chair into the transition-state half-chair conformation of a glycopyranose derivative involves counterclockwise rotation about the C(2)–C(3) and the C(1)–O(5) bonds, analogous to the conversion of a cyclohexane chair into the C_2 half-chair conformation.

The faster acetolysis of permethylated methyl β-D-mannopyranoside as compared to β anomers of both permethylated methyl D-gluco- and D-glactopyranosides is probably due to a much higher ground-state energy of the former.

Registry No. 1, 605-81-2; 2, 3149-65-3; 3, 3149-64-2; 4, 2296-47-1; 5, 3149-62-0; 6, 3445-71-4; 7, 3554-77-6; 8, 3554-78-7; 9, 38986-86-6; 10, 38982-49-9; 11, 38986-87-7; 12, 54307-88-9; 13, 84580-16-5.

Reactions of Haloketenes with Allyl Ethers and Thioethers: A New Type of Claisen Rearrangement[1]

Roger Malherbe,*[2] Guenther Rist, and Daniel Belluš*

Central Research Laboratories, CIBA-GEIGY AG, CH-4002 Basel, Switzerland

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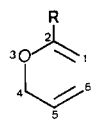
A new reaction of dichloroketene (2) with allylic ethers, sulfides, and selenide 1 has been observed. A [3,3] sigmatropic rearrangement takes place at room temperature, leading to α,α'-dichloro-γ,δ-unsaturated esters 3. The scope of this reaction was further investigated with dibromoketene (16), difluoroketene (17), electron-deficient chloroketenes, and different allylic systems. In the course of these studies, total syntheses of two naturally occurring macrolides, phoracantholide I and phoracantholide J, were achieved. Medium-ring conformations are discussed.

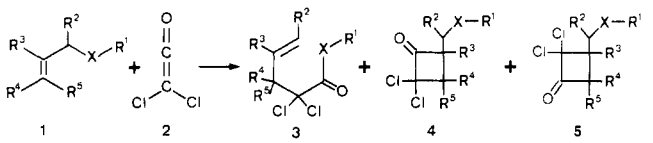
The utility of Claisen rearrangement in the synthesis of complex molecules has recently been reviewed.[3] This rearrangement has value because it proceeds through a highly ordered transition state, leading to unsaturated carbonyl compounds with high regio- and stereospecificity. Unfortunately, the desired transformation often requires temperatures too high for the survival of sensitive functional groups.

One solution to this problem has been to change the rate of Claisen rearrangement through appropriate substituents. Thus, with π-donor substituents at position C-2, the



temperatures for Claisen rearrangement can range from 200 °C to ambient temperature. The rates follow the usual order of donor strength: sodium or lithium enolates (R = $O^{-+}Na$[4] or $O^{-+}Li$[5]) > zinc enolate (R = $O^{-+}ZnBr$[6]) > amide acetal (R = NMe_2[7]) > ortho ester (R = OMe[8]) ≫ vinyl ether (R = H, Me[9]).

Scheme I



X = O, S, Se

Table I. Yields of Competitive Reactions of Allyl Sulfides 1a-f and Selenide 1g with Dichloroketene (2)

entry	X	R^1	R^2	R^3	R^4	R^5	% yield[a] of 3	% yield[b] of 4
a	S	Et	H	H	Me	Me	38	
b	S	Et	H	H	Me	H	45	
c	S	Et	H	Me	H	H	21	
d	S	Me	H	CN	H	H	26	
e	S	Me	H	H	H	H	25	
f	S	Ph	H	H	Me	Me	26	19
g	Se	Ph	H	H	Me	Me	38	19

[a] Yields of isolated products. [b] Yields calculated from integrated ^1H NMR spectra.

A positively charged heteratom at position 3 also lowers the activation energy of the rearrangement. For the Claisen rearrangement of allyl aryl ethers in the presence of boron trichloride, Schmid et al.[10] report that the "charge induction" causes an increase in the reaction rate of 10^{10}. The acceleration factors (k_{H^+}/k_Δ) calculated from the activation parameters of the acid-catalyzed rearrangement of *N*-allylaniline are also very large: 10^5–10^7.[11,12]

(1) Presented at the Second Chemical Congress of the North American Continent, Las Vegas, NV, Aug 1980; Abstr. ORGN 157. Preliminary results in: Malherbe, R.; Belluš, D. *Helv. Chim. Acta* **1978**, *61*, 3096.
(2) Present address: CIBA-GEIGY Corp., Plastics & Additives Research, Ardsley, NY 10502.
(3) Ziegler, F. E. *Acc. Chem. Res.* **1977**, *10*, 227. Bennett, G. B. *Synthesis* **1977**, 589.
(4) Arnold, R. T.; Searles, S., Jr. *J. Am. Chem. Soc.* **1949**, *71*, 1150.
(5) Ireland, R. E.; Mueller, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 5897. Ireland, R. E.; Mueller, R. H.; Willard, A. K. *Ibid.* **1976**, *98*, 2868.
(6) Baldwin, J. E.; Walker, J. A. *J. Chem. Soc., Chem. Commun.* **1973**, 117.
(7) Felix, D.; Gschwend-Steen, K.; Wick, A. E.; Eschenmoser, A. *Helv. Chim. Acta* **1969**, *52*, 1030.
(8) Johnson, W. S.; Werthemann, L.; Bartlett, W. R.; Brocksom, T. J.; Li, Ti.; Faulkner, D. J.; Petersen, M. R. *J. Am. Chem. Soc.* **1970**, *92*, 741.
(9) Burgstahler, A. W.; Nordin, I. C. *J. Am. Chem. Soc.* **1961**, *83*, 198. Marbet, R.; Saucy, G. *Helv. Chim. Acta* **1967**, *50*, 1158, 2091.
(10) Borgulya, J.; Madeja, R.; Fahrni, P.; Hansen, H. J.; Schmid, H.; Barner, R. *Helv. Chim. Acta* **1973**, *56*, 14 and references therein.
(11) Jolidon, S.; Hansen, H. J. *Helv. Chim. Acta* **1977**, *60*, 978 and references therein.

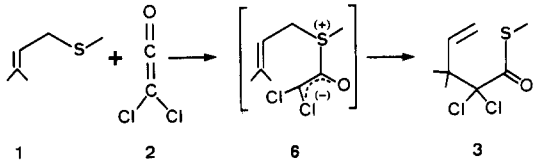
0022-3263/83/1948-0860$01.50/0

Table II. Yields of Competitive Reactions of Allyl Ethers 1k-r with Dichloroketene (2)

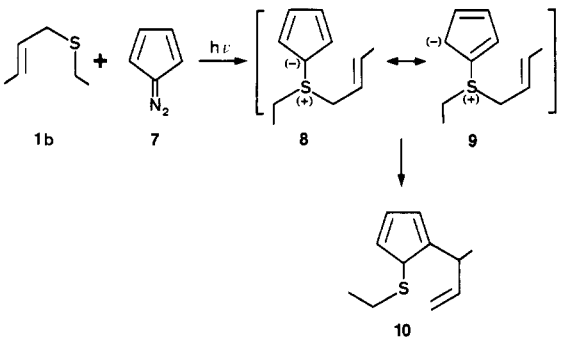
entry	X	R^1	R^2	R^3	R^4	R^5	% yield[a] of 3	% yield[b] of 4	% yield[a] of 5
k	O	Me	H	H	Me	Me	48	25	
l	O	Me	H	H	Me	H	63		
m	O	Me	H	H	Ph	H	48		
n	O	Me	H	Me	Ph	H	42		
o	O	Me	Me	H	Me	H	45		
p	O	Me	H	Me	H	H			56
q	O	Ph	H	H	H	H			47
r	O	$SiMe_3$	H	H	Me	H	36[c]		

[a] Yields of isolated products. [b] Yield calculated from the integrated ^1H NMR spectrum. [c] Yield of the free carboxylic acid (3r, R^1 = H).

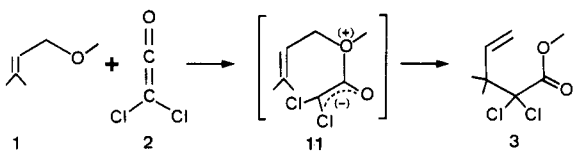
Scheme II



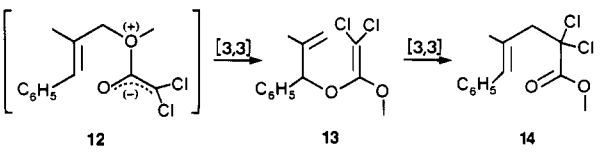
Scheme III



Scheme IV



Scheme V



We have found that the combination of both accelerating factors in one reactive 1,3-dipolar intermediate allows a very facile reaction to take place. The reacting intermediate is easily formed from allylic ethers, sulfides, or selenides and in situ prepared haloketenes. Target molecules were chosen in the field of naturally occurring macrolides.

Results and Discussion

Reaction of Allyl Sulfides and Selenide with Dichloroketene. Dichloroketene (2), which was prepared in situ by dehalogenation of trichloroacetyl chloride with activated zinc powder in absolute ether, was allowed to react with 1 at 25–30 °C (Scheme I).[13] Esters 3 were isolated in 20–45% yield (Table I). Different attempts were made to improve the conversion of 1 to products, with limited success;[14] in most cases the unreacted olefin 1 was recovered by distillation.

In the reaction of the phenyl sulfide **1f**, we isolated two main products: the [2 + 2] cycloadduct **4f** ($\nu_{C=O}$ 1808 cm^{-1}) along with the *S*-phenyl ester **3f** ($\nu_{C=O}$ 1704 cm^{-1}). The reaction with the phenyl selenide **1g** was very similar: we obtained the cyclobutanone **4g** ($\nu_{C=O}$ 1815 cm^{-1}) along with the *Se*-phenyl ester **3g** ($\nu_{C=O}$ 1725 cm^{-1}). With **1f**, **1g**, and **1k**, a side reaction was observed: ionic intermediates such as **6** must undergo a cleavage, which leads to dichloroacetic acid esters (identified by GC, NMR) and the remaining isoprenyl unit. Methyl benzyl sulfide gave no isolable ring substitution product.

The results indicate that the electrophilic dichloroketene (2) attacks a divalent sulfur (or selenium) atom in preference to an olefin. A mechanism for the formation of rearranged products involves the formation of a 1,3-dipolar intermediate **6**, capable of [3,3] sigmatropic rearrangement leading to **3** (Scheme II). This type of [3,3] rearrangement is closely related to the [2,3] rearrangements of sulfonium ylides, derived by attack of a carbene on allylic sulfide.[15,16]

Although some ylides resulting from the photolysis of diazomalonate and olefinic sulfides have been isolated as stable intermediates,[17] we have not been able to observe the dipolar intermediate **6**.

Diazocyclopentadiene (**7**) was reported[18] to give with but-2-enyl ethyl sulfide (**1b**) 23% of insertion product **10** (Scheme III), which could result from a [3,3] rearrangement of the dipolar intermediate **9**.[19] The proposed 1,3-dipole **6** is isoelectronic with **9**; therefore, they sould exhibit similar reactivity.

Allyl ethers were found to give with **2** rearranged products **3** and/or cycloadducts **4** and **5** in yields shown in Table II. We assume that the products **3** are formed by the way of a [3,3] rearrangement of an oxonium dipolar intermediate **11** (Scheme IV). Although the oxygen in-

(12) A qualitative explanation for the influence of substituents on pericyclic reactivity would emphasize the role of charged heteratoms at position 3 (Carpenter, B. K. *Tetrahedron* **1978**, *24*, 1877. Burrows, C. J.; Carpenter, B. K. *J. Am. Chem. Soc.* **1981**, *103*, 6984). For a semiempirical treatment, see: Ahlgren, G. *Tetrahedron Lett.* **1979**, 915.

(13) In this work, dichloroketene (2) was generated exclusively by zinc-reductive elimination of chlorine; see: Krepski, L. R.; Hassner, A. *J. Org. Chem.* **1978**, *43*, 2879.

(14) Sulfides or the products of some side reaction could possibly act as poison for the activated zinc, even when a large excess is added.

(15) The reaction of carbene with divalent sulfur compounds has been reviewed; see: Ando, W. *Acc. Chem. Res.* **1977**, *10*, 179.

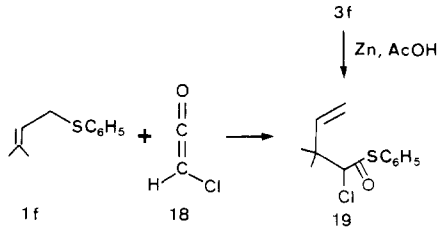
(16) It is interesting to note that in the photolysis or thermolysis of diazo compounds in the presence of allyl sulfide, the electrophilic carbene reacts with both nucleophilic sites, i.e., sulfur atom and carbon–carbon double bond. Dichlorocarbene adds exclusively to the sulfur of allyl sulfide to form insertion products; see: Parham, W. E.; Groen, S. H. *J. Org. Chem.* **1964**, *29*, 2214; **1965**, *30*, 728; **1966**, *31*, 1694.

(17) Ando, W.; Kondo, S.; Nakagama, K.; Ichibori, K.; Kohoda, H.; Yamato, H.; Imai, I.; Nakaido, S.; Migita, T. *J. Am. Chem. Soc.* **1972**, *94*, 3870.

(18) Ando, W.; Saiki, Y.; Migita, T. *Tetrahedron* **1973**, *29*, 3511.

(19) A [2,3] rearrangement of the ylide 8 followed by two Cope rearrangements would give the same product and cannot be excluded. In Scheme III, the fast 1,5 proton shifts are not considered.

Scheme VI



termediate **11** is expected to be less stable than the sulfur analogue **6** (via stabilization through d orbitals), the yields of *O*-esters are surprisingly better than those of *S*-esters.

Some contrasting features can be seen in the comparison of Tables I and II. While 2-methylprop-2-enyl ethyl sulfide (**1c**) gave only the *S*-ester **3c**, the corresponding ether **1p** gave exclusively the cyclobutanone **5p**. In this case the difference of nucleophilicity between oxygen and sulfur atoms is interesting from a synthetic point of view, when a change of regioselectivity is desired.

α-Methylcinnamyl ether (**1n**) gave a 7:1 mixture of two esters **3n** and **14**, which could not be separated by preparative TLC but were characterized by NMR. **3n** results from a normal [3,3] rearrangement via **12**; **14** seems to result from a sequence of rearrangements (Scheme V).[20]

When 2,5-dihydrofuran was reacted with **2**, the cycloadduct **14** was obtained in 33% yield. The rearrangement of an oxonium ion such as **11** via a preferred chair transition state[21] is precluded by the geometry of the system.

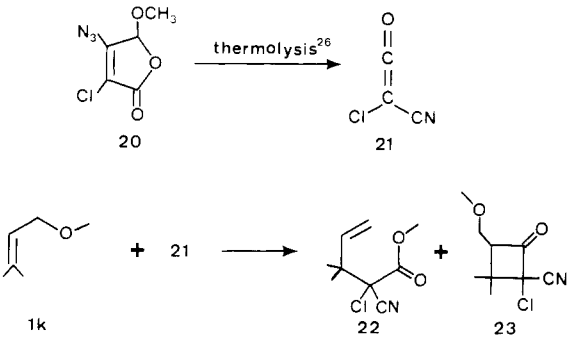
Cleavage of alkoxysilanes with acid chlorides is one of the well-documented reactions in the organosilicon chemistry.[22] Therefore we were interested to see how allyl silyl ethers would behave under our reaction conditions. Silylated crotyl alcohol (**1r**) when reacted with **2** and subsequently hydrolyzed gave the free 2,2-dichloro-3-methylpent-4-enoic acid (**3r**).[6] The [3,3] sigmatropic rearrangement might proceed directly, but a 1,3 shift of the trimethylsilyl group, giving the same type of enol silyl ether used in the procedure of Ireland,[5] cannot be excluded.

Reactions with Electrophilic Ketenes. In order to compare the reactivity of the dichloroketene (**2**) with other electrophilic ketenes, we tested different haloketenes. When dibromoketene[23] (**16**) was generated in the presence of **1b** or **1k**, tribromoacetyl bromide was consumed, but the olefins were recovered unchanged: the bulky bromo substituents near the reaction centers as well as a lower electrophilic character of **16** could explain the lack of reactivity.

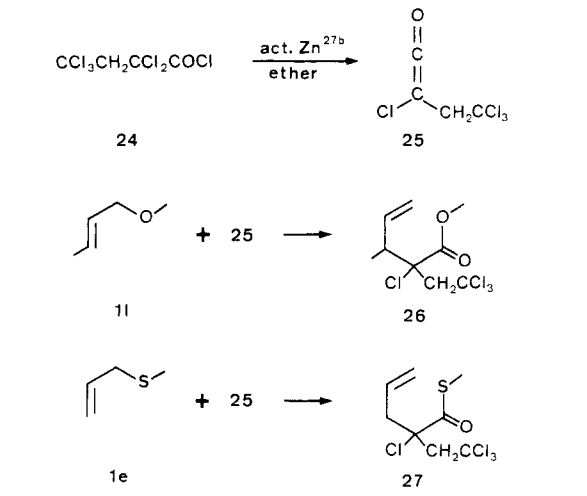
The elusive difluoroketene (**17**) was prepared by dehalogenation of bromodifluoroacetyl fluoride:[24] even under very mild conditions (10 °C, diluted solution of **1k**), we could not avoid the partial decomposition of **17** into carbon monoxide and difluorocarbene. Spectral data of the isolated material showed no evidence of carbonyl or olefinic groups but suggested difluorocarbene adducts.

When **1f** was subjected to monochloroketene (**18**; prepared from zinc wool and dichloroacetyl chloride in diisobutyl ketone),[25] the *S*-phenyl ester **19** was isolated in only 6% yield. This same compound was prepared independently by zinc monodechlorination of **3f** (Scheme VI).

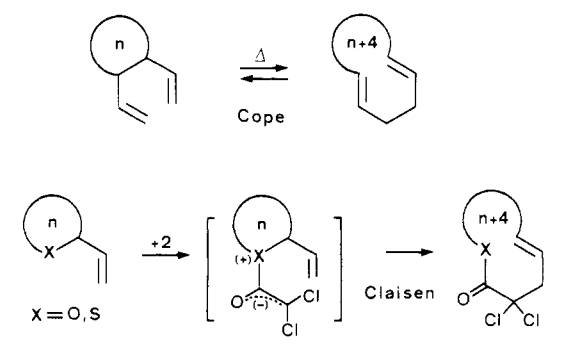
Scheme VII



Scheme VIII



Scheme IX

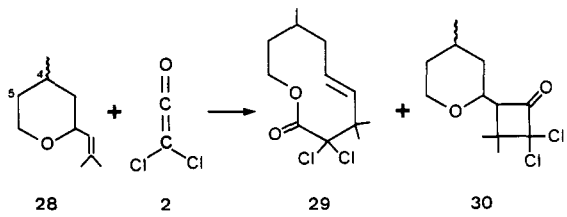


The thermal cleavage of 4-azido-3-chloro-5-methoxy-2-(5*H*)-furanone (**20**) has been reported to give chlorocyanoketene (**21**), which readily undergoes stereospecific cycloadditions, e.g., with imines.[26] Thus when **20** was thermolyzed (toluene) in the presence of methyl 3-methyl-2-butenyl ether (**1k**), the ester **22** (3%) and the cyclobutanone **23** (15%) were obtained (Scheme VII). The thermolysis in propionitrile gave the ester **22** (5%) and less cyclobutanone **23** (2%).

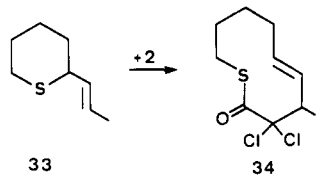
Chloro(trichloroethyl)ketene (**25**) is easily obtained by zinc dechlorination of 2,2,4,4,4-pentachlorobutanoyl chloride (**24**; Scheme VIII).[27] Its propensity for [2 + 2] cycloaddition is very close to that of **2**. The reaction of **25** with methyl allyl sulfide (**1e**) gave rise to the *S*-ester **27**

(20) The examples of Tables I and II show nevertheless a very facile reaction path. The rearrangement of allyl β,β-dichlorovinyl ethers, which are related to the proposed intermediate **13**, takes place only at 130 °C; see: Normant, J. F.; Reboul, O.; Sauvêtre, R.; Deshayes, H.; Masure, D.; Villeras, *J. Bull. Soc. Chim. Fr.* **1974**, 2072.
(21) Hansen, H. J.; Schmid, H. *Tetrahedron* **1974**, *30*, 1959.
(22) Ladenburg, A. *Chem. Ber.* **1871**, *4*, 726.
(23) Brady, W. T. *J. Org. Chem.* **1966**, *31*, 2676.
(24) England, D. C.; Krespan, C. G. *J. Org. Chem.* **1968**, *33*, 816.
(25) Van den Brink, J. M.; Austermuhle-Bertola, H.; Kramer, P. A. Ger. Offen. 2539 048 (Shell Int.), 1974; *Chem. Abstr.* **1976**, *85*, 20680e.
(26) Moore, H. W.; Hernandez, L.; Sing, A. *J. Am. Chem. Soc.* **1976**, *98*, 3728. Moore, H. W.; Hernandez, L.; Chambers, R. *Ibid.* **1978**, *100*, 2245.
(27) (a) Martin, P.; Greuter, H.; Belluš, D. *J. Am. Chem. Soc.* **1979**, *101*, 5853. (b) *Helv. Chim. Acta* **1981**, *64*, 64.

Scheme X



Scheme XI

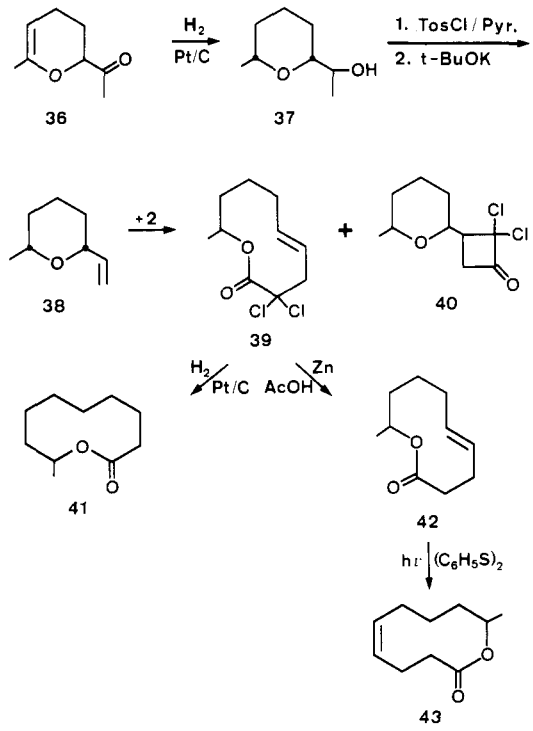


(50% yield), with methyl crotyl ether (11) to **26** (46% yield) as a mixture of diastereomeric esters.

Ring Enlargement Reactions. The results with open-chain allyl ethers prompted us to apply the reaction to cyclic unsaturated ethers. The insertion of a four-carbon unit in one sequence, through a Cope rearrangement, is well-documented.[28] An analogue irreversible Claisen rearrangement was not practicable before, as the methodology for making the reactive oxonium salt was not available. But now by suitable choice of heterocyclic systems with an α-vinyl substituent, synthesis of medium-size lactones could be, in principle, achieved with an electrophilic haloketene (Scheme IX). A general problem in the lactonization reactions is associated with intra- vs. intermolecular cyclization. Stoll's classical work concerning formation of lactones from straight-chain aliphatic ω-hydroxyl acids has shown that 8–11-membered rings are formed in minimal yields.[29,30] Novel approaches involving the intramolecular acylation of an aromatic ring led to improved yields.[31]

Our strictly intramolecular ring expansion reaction was tested on the model compound rose oxide (**28**),[32] producing a 7:3 mixture of two isomers (76% yield; Scheme X).[33] The major compound was separated by chromatography on silica gel and the structure of the 10-membered lactone **29** was fully confirmed by NMR (vide supra). An interesting feature is the high specificity for the *E* isomer (>95% by NMR), which was not affected by this rather strained system.[34] **30** was labile to chromatography and we had to rely on IR and NMR spectra of the mixture **29/30** for the identification. When nerol oxide (**31**) (**28**, with an additional double bond between C(4) and C(5)) was subjected to the same reaction as rose oxide, a product was obtained (22% yield), which crystallized from pentane. Of the number of possible diastereomeric cyclobutanones, we isolated only one as a crystalline compound **32** (mp 55–56 °C). It resulted from an addition of **2** to the 2-vinyl group of nerol oxide. Thus a change in the conformation of the starting material results in a considerably different reactivity.

Scheme XII



In contrast to the various procedures available for the synthesis of lactones,[35] the first preparation of sulfur analogues was reported only recently.[36] Our success in ring expansion prompted further investigation of an alternative route for this class of compounds.[37]

The reaction of 2-propenylthian (**33**)[38] with **2** gave rise to the thiolactone **34** in only 8% yield (Scheme XI).[14,39] Typical for **34** are the carbonyl absorption ($\nu_{C=O}$ 1690 cm^{-1}) and the trans C=C double bond (J = 16 Hz).

Synthesis of Two Naturally Occurring 10-Membered Lactones: (±)-Phoracantholides I and J. The very facile rearrangement of rose oxide (**28**) allowed us to design a simple synthesis of (±)-phoracantholide I (**41**) and (±)-phoracantholide J (**43**),[40,41] which is outlined in Scheme XII.

(28) For a review of the Cope rearrangement, see: Roads, S. J.; Raulins, N. R. *Org. React.* **1975**, *22*, 1.

(29) Stoll, M.; Rouvé, A.; Stoll-Comte, G. *Helv. Chim. Acta* **1934**, *17*, 1289. Stoll, M.; Rouvé, A. *Ibid.* **1935**, *18*, 1087.

(30) In other substrates too, the kinetics of cyclization reactions over wide ranges of ring sizes show minimal rates for medium-ring regions; see: Illuminati, G.; Mandolini, L.; Masci, B. *J. Am. Chem. Soc.* **1977**, *99*, 6308. Mandolini, L. *Ibid.* **1978**, *100*, 550.

(31) (a) Gerlach, H.; Thalmann, A. *Helv. Chim. Acta* **1974**, *57*, 2261. (b) *Ibid.* **1977**, *60*, 2866. (c) Gerlach, H.; Kunzler, P.; Oertle, K. *Ibid.* **1978**, *61*, 1226.

(32) We thank Dr. G. Ohloff, Firmenich SA, Geneva, for the generous gift of rose oxide and nerol oxide.

(33) In this experiment, we introduced with trichloroacetyl chloride an equivalent quantity of $POCl_3$, as complexing agent of $ZnCl_2$ (see ref 13). It seems to have little influence on the yield, but the workup is more convenient.

(34) The *Z* olefin is more stable in the case of cyclooctene, cyclononene, and cyclodecene, as shown by the heat of hydrogenation and the equilibrium constants: Turner, R. B.; Meador, W. R.; Winkler, R. E. *J. Am. Chem. Soc.* **1957**, *79*, 4116. Turner, R. B.; Meador, W. R. *Ibid.* **1957**, *79*, 4133. Cope, A. C.; Moore, P. T.; Moore, W. R. *Ibid.* **1959**, *81*, 3153.

(35) (a) Nicolaou, K. C. *Tetrahedron* **1977**, *33*, 683. (b) Masamune, S.; Bates, G. S.; Corcoran, J. W. *Angew. Chem.* **1977**, *89*, 602.

(36) Araujo, H. C.; Mahajan, J. R. *Synthesis* **1978**, 228; **1980**, 64.

(37) Since this work was done, an interesting application of this procedure for ring expansion of unsaturated cyclic thioketals was reported: Rosini, G.; Spineti, G. G.; Foresti, E.; Pradella, G. *J. Org. Chem.* **1981**, *46*, 2228.

(38) Tuleen, D. L.; Bennett, R. H. *J. Heterocycl. Chem.* **1969**, *6*, 115. Cerè, V.; Bolucci, C.; Pollicino, S.; Sandri, E.; Fava, A. *J. Org. Chem.* **1981**, *46*, 3315.

(39) The persistent stench of **33** discouraged further investigation.

(40) Compounds **41** and **43** have been isolated from the metasternal secretion of the eucalypt longicorn, *Phoracantha synonyma*: Moore, B. P.; Brown, W. W. *Aust. J. Chem.* **1976**, *29*, 1365.

(41) For reported syntheses of phoracantholides, see ref 31c and the following: (a) Wakamatsu, T.; Akasaka, K.; Ban, Y. *Tetrahedron Lett.* **1977**, 2755. (b) Tsuji, J.; Mandai, T. *Ibid.* **1978**, *1817*. (c) Petrzilka, M. *Helv. Chim. Acta* **1978**, *61*, 3075. (d) Nicolau, K. C.; Claremon, D. A.; Barnette, W. E.; Seitz, S. P. *J. Am. Chem. Soc.* **1979**, *101*, 3704. (e) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1979**, *101*, 1595; **1980**, *102*, 4743. (f) Mahajan, J. R.; Araujo, H. C. *Synthesis* **1981**, *49*.

Table III. Some ^{1}H Vicinal Coupling Constants of Lactones 29, 34, 39, 42, and 43[a]

compd	$J_{4,5}$, Hz	$J_{5,6}$, Hz	$J_{6,7}$, Hz	$J_{9,10}$, Hz[b]
29		16.0	11.5	10.0
(conformation A)				(4.10)
			3.5	1.0
				6.0
				(3.49)
				1.2
29		16.0	8.0	11.0
(conformation B)				(3.23)
			6.0	3.0
				5.5
				(4.30)
				3.5
34		16.0		
39	10.5	16.0	10.5	7
				(4.88)
	4.5		4.0	1
42	10.5	16.0	10.5	7
				(4.88)
	4.5		4.0	1
43		11.2		

[a] Zero-order coupling constants from 360-MHz spectra. [b] In parentheses are given chemical shift values of H_2-C(10).

The dimer **36** of 3-buten-2-one (**35**), resulting from a hetero Diels–Alder reaction, was a convenient starting material. Catalytic hydrogenation of **36** under pressure produced a 1:1 epimeric mixture of alcohols **37** (85% yield).[42] The tosylate of **37** was prepared by a standard procedure and the low-melting solid obtained was used without purification for the elimination to **38** (68% overall yield). The vinylpyran **38** was subjected to the usual conditions of the ketene Claisen rearrangement and a clean 6:1 mixture of lactone **39** and cyclobutanone **40** could be distilled. Separation by column chromatography on silica gel gave pure **39** (55% yield) as an oil. Dechlorination of **39** with zinc powder in glacial acetic acid proceeded stepwise: of the two isomeric monochloro lactones, one reacted rather slowly to **42**. For an optimal yield, it was found preferable to stop the reduction before completion and separate **42** by column chromatography (65% yield). Spectral data show that **39** and **42** are isomerically pure *E* lactones (see Experimental Section). Trace analysis on a capillary column revealed the presence of less than 1% of the *Z* isomer **43** in the isolated product **42**, which demonstrates the high stereospecificity (>99%) of the successive steps. Catalytic hydrogenation of **39** or of mixtures of monochlorolactones gave rise to **41** (85% yield), whose properties (IR, NMR, GC) agreed with those of an authentic sample of the natural macrolide (±)-phoracantholide I.[43] Compound **42** was irradiated in the presence of 0.05 equiv diphenyl disulfide,[44a] and after 7 h, a photostationary state was reached, consisting of 4% of *E* lactone **42** and 96% of the desired isomer **43**. Pure (±)-phoracantholide J (**43**) was separated on a $AgNO_3$-pretreated column[44b] in 85% yield.[43]

Discussion of Conformations of 29, 39, and 42. Conformations of medium-sized rings have attracted much attention during the last decade. The spatial arrangement of these compounds is sensitive to both torsional and transannular strain. A discussion of the conformations of monocyclic medium-ring ketones in solution has been given by Anet et al.[45] as well as by Dunitz and Ibers.[46] Another conformation relevant to the present discussion is the one of (*E*)-3β-hydroxy-5,10-seco-1(10)-cholesten-5-one.[47]

Chart I

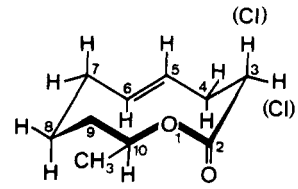
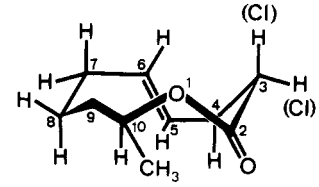


Chart II



Conformation of 39 and 42. The coupling constants of **39** and **42** listed in Table III are identical. This together with the similarity in chemical shift values implies that the two compounds do assume identical ground-state conformations. It is well-established[47,48,49] for this class of compounds that dihedral angles of 180° and 0° correspond to vicinal vinylic–allylic coupling constants of 11.5 and 8.0 Hz. The experimental vicinal coupling constants H–C(5),H_{axial}–C(4) and H–C(6),H_{axial}–C(7) are the same for both compounds **39** and **42**, with an intermediate value of 10.5 Hz. We interpret this coupling as average value due to rapid interconversion between two conformations. In these conformations the dihedral angle between H–C(5) and one of the protons on C(4) as well as between H–C(6) and one of the protons on C(7) is either 180° (conformation A; see Chart I) or 0° (conformation B; see Chart II). With the assumption that deviations from these spatial arrangements would lead to strong transannular interactions,[47,48] the two 10.5-Hz couplings may be rationalized by the major conformation A and the minor conformation B with relative weights of roughly 0.7 and 0.3. The conformation of fragment C(9) to C(2) is speculative. In both conformations the ring oxygen is thought to be directed slightly into the 10-membered ring in order to relieve transannular strain between H–C(10) and H–C(6) and to give CH_3–C(10) an almost equatorial orientation. This model would lead to dihedral angles of approximately 150° and 90° for H–C(10) in the main conformation A in agreement with the experimental values. The major conformation can be characterized as a slightly distorted crown (chair–chair–chair) spatial arrangement. The minor conformation is related to the major one by a 180° rotation of the double bond.[47]

(42) By ^{13}C NMR, it was possible to confirm the cis arrangement of the substituents on the pyran ring. The epimers at C(1^1) are of no importance for the sequence, as the asymmetric center at C(1^1) disappears later.

(43) An authentic sample was generously supplied by Prof. H. Gerlach, ETH, Zurich.

(44) (a) Schulte-Elte, K. H.; Ohloff, G. *Helv. Chim. Acta* **1968**, *51*, 548. (b) Chapman, L. R.; Kuemmel, D. F. *Anal. Chem.* **1965**, *37*, 1598.

(45) Anet, F. A. L.; Jaques, M. St.; Henrichs, P. M.; Cheng, A. K.; Krane, J.; Wong, L. *Tetrahedron* **1974**, *30*, 1629.

(46) "Perspectives in Structural Chemistry", Dunitz, J. D., Ibers, J. A., Ed.; Wiley: New York, 1968; Vol. 2, pp 1–70.

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(48) For conformations of related 10-membered rings in some other secosteroids, see: Fuhrer, H.; Lorenc, L.; Pavlović, V.; Rhis, G.; Rist, G.; Kalvoda, J.; Mihailović, M. L. *Helv. Chim. Acta* **1979**, *62*, 1770; **1981**, *64*, 703.

(49) Karplus equations relating the vicinal vinylic–allylic coupling constants with dihedral angles are given in the following: Garbisch, E. W. *J. Am. Chem. Soc.* **1964**, *86*, 5561. Becker, E. "High resolution NMR"; Academic Press: New York, 1969; p 104.

Conformation of Compound 29. Two sets of NMR resonances in thermal equilibrium were observed for compound **29**. The two additional substituents at C(4) lock the two conformations within the characteristic time of the NMR experiment. The intensity ratio of approximately 4:1 corresponds to an energy difference of 0.8 kcal between the two respective conformations. From ^{13}C line width experiments in the temperature range of −10–70 °C in perdeuterated toluene solvent, an activation energy of 13 ± 2 kcal was estimated.

In the major conformation, the vicinal coupling constant of 11.5 Hz corresponds to a dihedral angle H–C(6),H_{axial}–C(7) of 180°. This angle is compatible with a conformation similar to conformation A given in Chart I. Double-resonance experiments have shown that H_{axial}–C(7) exhibits three coupling constants with values between 10 and 13 Hz. This result establishes the equatorial orientation of CH_3–C(7). The conformation of the ring fragment O=C(2)–C(5) remains speculative, since C(3) and C(4) are fully substituted and no dihedral angles for this fragment can be deduced from the ^1H NMR spectra.

In the minor conformation, the dihedral angle H–C(6),H_{axial}–C(7) is 0°. This value is compatible with a conformation of the type B given in Chart I. Comparison of the chemical shift values of H_2–C(10) in both major and minor conformation of **29** (see Table III) gives strong indication for an axial orientation of the carbonyl group in the major and an equatorial orientation of the carbonyl group in the minor conformation, as drawn in Chart I also for lactones **39** and **42**.

Conclusions

The merits of the new ketene Claisen rearrangement are obvious: (a) neither high temperature nor exotic reagents are needed to create the reactive intermediate; (b) for the first time, the ring enlargement by four carbon atoms (transformation of a cyclic ether into a lactone) can be accomplished by means of a Claisen rearrangement; (c) the chlorine atoms in the α position of products such as **3** or **39** can be conveniently removed by metals (Zn, Fe) reduction; and (d) as far as dichloroketene (**2**) is concerned, this rearrangement represents a new exciting reaction mode of this well-investigated ketene.[50,51]

Experimental Section

General Procedures. All reactions were run under a positive pressure of dry nitrogen or argon (irradiation). Melting points were determined on a Buchi–Tottoli apparatus and are not corrected. Spectral measurements were performed by the analytical department: ^1H NMR, Varian HA-100 or Bruker HX-360 instrument; ^{13}C NMR, Varian XL-100 instrument; chemical shifts are reported in δ units, parts per million (ppm) downfield from tetramethylsilane. Infrared spectra were determined on a Perkin-Elmer 157 spectrophotometer. Mass spectra were obtained at an ionizing voltage of 70 eV, on a Varian MAT CH-7 spectrometer. Preparative chromatography was carried out on silica gel (E. Merck silica gel 60 (0.063–0.200 mm)). Thin-layer chromatography (TLC) was run on E. Merck precoated silica gel 60-F 254 plates with the indicated solvent mixtures. The spots were detected by (a) spraying with an aqueous solution of $KMnO_4$, heating, (b) spraying with 0.1 N $AgNO_3$ and heating, and (c) treating the plates with dimethylamine before exposing them to daylight. The halogenated cyclobutanones develop black spots and the esters dark-gray spots. GC analyses were obtained with Varian Aerograph Model 90P and Perkin-Elmer 900 instruments.

Materials. Allyl methyl sulfide (Aldrich) and allyl phenyl ether (EGA) were dried over molecular sieve (4 Å) before use. Alkyl sulfides **1a,b,c,f** were prepared as described by Parham,[16] **1d** by the method of Stewart,[52] and selenide **1g** according to Sharpless.[53]

The alkyl ethers **1k**,[54] **1m**,[55] and **1n** were prepared by methylation of the alcohol under phase-transfer conditions,[56] **1l**[57] and **1p**[58] from the corresponding alkyl chloride and sodium methoxide, and **1o** as described by Hills.[59] Crotyl alcohol was silylated by *N,O*-bis(trimethylsilyl)acetamide to give **1r**. Zinc dust was activated as reported by Krepski.[13]

Ethyl Thioester of 2,2-Dichloro-3,3-dimethyl-4-pentenoic Acid (3a). A 750-mL, five-necked flask equipped with a condenser, addition funnel, stirrer, thermometer, and N_2 inlet was flame-dried. When cool, the flask was charged with 13.0 g (0.10 mol) of sulfide **1a**, 7.2 g (0.11 mol) of activated zinc, and 200 mL of anhydrous ether. To the stirred suspension was added dropwise a solution of 11.5 mL (18.5 g, 0.105 mol) of Cl_3CCOCl in 100 mL of anhydrous ether over a 4-h period.

When addition of the solution was complete, a second portion of activated zinc (3.5 g, 0.05 mol) was added and the mixture stirred for 1 h. Pentane (200 mL) was added to precipitate the zinc salts, and the solution was decanted from the residue. The residue was washed twice with ether–pentane (50 mL), and the collected solution was washed successively with water, a cold solution of 10% $NaHCO_3$, and brine and then dried over $MgSO_4$. The solvent was removed in vacuo to leave 17.2 g of crude product.

Distillation afforded 9.1 g (38%) of **3a**: bp 66 °C (0.25 mm); IR (neat) 1692 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.30 (t, J = 7 Hz, 3 H, CH_3CH_2S–C(1)), 1.40 (s, 6 H, $2CH_3$–C(3)), 2.89 (q, J = 7 Hz, 2 H, CH_3CH_2S–C(1)), 5.12 (d, J_{trans} = 17 Hz, J_{gem} = 1 Hz, 1 H, H–C(5)), 5.16 (d, J = 11 Hz, 1 H, H–C(5)), 6.13 (dd, J = 17 Hz, J' = 11 Hz, 1 H, H–C(4)); mass spectrum, m/e 240 (M^+, 1), 89 ($M^+ - C_6H_9Cl_2$, 100). Anal. Calcd for $C_9H_{14}Cl_2OS$: C, 44.82; H, 5.85; S, 13.30. Found: C, 44.02; H, 5.85; S, 13.45.

Ethyl Thioester of 2,2-Dichloro-3-methyl-4-pentenoic Acid (3b). The reaction of 11.6 g (0.10 mol) of sulfide **1b** by the general procedure (see preparation of **3a**) gave 10.3 g (45%) of **3b** (distilled twice): bp 98 °C (13 mm); IR (neat) 1703, 1689 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.29 (t, J = 7 Hz, 3 H, CH_3CH_2S–C(1)), 1.33 (d, J = 7 Hz, 3 H, CH_3–C(3)), 2.93 (q, J = 7 Hz, 2 H, CH_3CH_2S–C(1)), 3.27 (m, J = 7 Hz, H–C(3)), 5.17 (m, 2 H, H_2–C(5), 5.80 (m, 1 H, H–C(4)); mass spectrum, m/e 226 (M^+, 2), 89 ($M^+ - C_5H_7Cl_2$, 100). Anal. Calcd for $C_8H_{12}Cl_2OS$: C, 42.30; H, 5.33; S, 14.11. Found: C, 42.0; H, 5.1; S, 14.4.

Ethyl Thioester of 2,2-Dichloro-4-methyl-4-pentenoic Acid (3c). The reaction of 23.2 g (0.20 mol) of sulfide **1c** by the general procedure (see preparation of **3a**) afforded 9.72 g (21%) of **2f**: bp 110–114 °C (14 mm) (purity 95% by GC). An analytical sample was purified by column chromatography (hexane–toluene): IR (neat) 1689 cm^{-1} (C=O); ^{1}NMR ($CDCl_3$) δ 1.33 (t, J = 7 Hz, 3 H, CH_3CH_2S–C(1)), 1.84 (br s, 3 H, CH_3–C(4)), 2.94 (q, J = 7 Hz, 2 H, CH_3CH_2S–C(1)), 3.20 (s, 2 H, H_2–C(3)), 4.90 and 5.00 (2 m, 2 H, H_2–C(5)). Anal. Calcd for $C_8H_{12}Cl_2OS$: C, 42.30; H, 5.33; S, 14.11; Cl, 31.22. Found: C, 42.54; H, 5.48; S, 14.15; Cl, 31.51.

Methyl Thioester of 4-Cyano-2,2-dichloro-4-pentenoic Acid (3d). From 11.3 g (0.10 mol) of sulfide **1d**, one obtained by the general procedure (see preparation of **3a**), on bulb-to-bulb distillation (oven 90 °C, 0.03 mm), 5.81 g (26%) of **3d** and 4.42 g of **1d**, bp 68 °C (13 mm), recovered unchanged; IR (neat) 2272 (CN), 1700 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.42 (s, 3 H, CH_3S–C(1)), 3.32 (s, 2 H, H_2–C(3)), 5.91 (d, J_{gem} = 1 Hz, 1 H, H–C(5)), 6.20 (d, 1 H, H–C(5)); mass spectrum, m/e 223 (M^+, 15), 195 (13), 160 (17), 148 (13), 112 (19) 75 (100), 61 (40).

(50) For some recent reviews, see: Patai, S. "The Chemistry of Allenes, Ketenes and Related Compounds"; Wiley: New York, 1980. Brady, W. T. *Tetrahedron* **1981**, *37*, 2949.

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Methyl Thioester of 2,2-Dichloro-4-pentenoic Acid (3e). By the procedure described above for the preparation of **3a**, 8.8 g (0.10 mol) of **1c** afforded 4.95 g (25%) of **3e**, bp 100 °C (20 mm). An analytical sample was chromatographed (hexane–toluene) to remove polar impurities: IR (neat) 1689 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.36 (s, 3 H, CH_3S–C(1)), 3.14 (m, J_{vic} = 7 Hz, 2 H, H_2–C(3)), 5.25 (d, J_{trans} = 16 Hz, 1 H, H–C(5)), 5.22 (d, J_{cis} = 11 Hz, 1 H, H–C(5)), 5.60–6.03 (m, 1 H, H–C(4)). Anal. Calcd for $C_6H_8Cl_2OS$: C, 36.20; H, 4.05; Cl, 35.61; S, 16.10. Found: C, 35.97; H, 4.02; Cl, 35.99; S, 16.36.

Phenyl Thioester of 2,2-Dichloro-3,3-dimethyl-4-pentenoic Acid (3f). To a stirred mixture of 35.7 g (0.20 mol) of sulfide **1f** and 13.7 g (0.21 mol) of activated zinc in 500 mL of anhydrous ether was added dropwise a solution 23.0 mL (37.3 g, 0.205 mol) of Cl_3CCOCl in 100 mL of anhydrous ether (4 h). The mixture was refluxed with stirring for 2 h and worked up in usual manner (see preparation of **3a**). Distillation afforded, after recovering 16.0 g of unreacted **1f**, 26.5 g (45%) of a mixture of **3f** and **4f** (58:42), bp 117–122 °C (0.001 mm). A pure sample of **3f** was separated by chromatography (hexane–toluene, 4:1): IR (neat) 1704 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.43 (s, 6 H, $2CH_3$–C(3)), 5.15 (d, J_{trans} = 17 Hz, 1 H, H–C(5)), 5.17 (d, J_{cis} = 11 Hz, 1 H, H–C(5)), 6.15 (dd, J = 17 Hz, 11 Hz, 1 H, H–C(4), 7.5 (m, 5 aromatic H). Anal. Calcd for $C_{13}H_{14}Cl_2OS$: C, 53.99; H, 4.88; Cl, 24.52; S, 11.09. Found: C, 54.05; H, 4.97; Cl, 24.22; S, 10.87. Attempted chromatographic isolation of **4f** led to partial decomposition. The cyclobutanone **4f** was therefore characterized by spectra of the distilled mixture: IR (neat) 1808 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.31 and 1.56 (2 s, 6 H, $2CH_3$–C(3)), 2.90 and 3.30 (2 dd, 2 H, J_{gem} = 13 Hz, J_{vic} = 5, 10 Hz, respectively, SCH_2–C(4)), 3.60 (dd, J_{vic} = 5, 10 Hz, 1 H, H–C(4)), 7.40 (5 aromatic H).

2-Methylbut-2-enyl Phenyl Selenide (1g). **1g** was prepared according ref 53 in 80% yield, as a yellow oil: bp 40 °C (0.006 mm); ^1H NMR ($CDCl_3$) δ 1.68 (s, 6 H, $2CH_3$–C(3)), 3.53 (d, J = 7 Hz, 2 H, H_2–C(1)), 5.40 (br t, J = 7 Hz, 1 H, H–C(2)), 7.1 (5 aromatic H). Anal. Calcd for $C_{11}H_{12}Se$: C, 58.67; H, 6.27. Found: C, 58.8; H, 6.2.

Phenyl Selenoester of 2,2-Dichloro-3,3-dimethyl-4-pentenoic Acid (3g). The reaction of 13.5 g (0.06 mmol) of **1g** by the general procedure afforded 11.4 g (57%) of a mixture (65:35) of **3g** and **4g**, bp 104 °C (0.03 mm). **3g** was purified by chromatography (hexane eluent) on silica gel: IR (neat) 1725 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.42 (s, 6 H, $2CH_3$–C(3)), 5.15 (d, J_{trans} = 17 Hz, 1 H, H–C(5)), 5.18 (d, J_{cis} = 11 Hz, 1 H, H–C(5)), 6.14 (dd, J = 17, 11 Hz, 1 H, H–C(4)), 7.4 (5 aromatic H). Anal. Calcd for $C_{13}H_{14}Cl_2OSe$: C, 46.46; H, 4.20; Cl, 21.10. Found: C, 46.50; H, 4.26; Cl, 20.92.

The cyclobutanone **4g** had the following spectra (from a mixture): IR (neat) 1815 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.28 (s, 3 H), 1.55 (s, 3 H), 2.72 (dd, J = 12, 10 Hz, 1 H), 3.23 (dd, J = 12, 10 Hz, 1 H), 3.59 (dd, J = 10, 5 Hz, 1 H), 7.4 (5 aromatic H).

Methyl Ester of 2,2-Dichloro-3,3-dimethyl-4-pentenoic Acid (3k). To 10.0 g (0.10 mol) of ether **1k** and 7.8 g (0.12 mol) of activated zinc in 200 mL of anhydrous ether was added a solution of 12.4 mL (20.0 g, 0.11 mol) of Cl_3CCOCl in 50 mL of anhydrous ether. The rate of the addition was adjusted in order to keep the temperature at ca. 30 °C (4 h). The mixture was refluxed for 1 h and the usual workup followed by distillation gave 15.3 g (73%) of a mixture of **3k** and **4k** (73:27), bp 75–80 °C (13 mm). Analytical samples were separated by preparative GC (SE 30 3% on Chromosorb G a/w dmcs 60/80, 180 °C). Ester **3k**: IR (neat) 1760 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.39 (s, 6 H, $2CH_3$–C(3)), 3.84 (s, 3 H, CH_3O), 5.16 (d, J_{trans} = 17 Hz, 1 H, H–C(5)), 5.18 (d, J_{cis} = 11 Hz, 1 H, H–C(5)), 6.16 (dd, J = 17, 11 Hz, 1 H, H–C(4)). Anal. Calcd for $C_8H_{12}Cl_2O_2$: C, 45.52; H, 5.73; Cl, 33.59. Found: C, 45.66; H, 5.74; Cl, 33.35.

Cyclobutanone **4k** (contaminated by 3% of HCl_2CCO_2Me): IR (neat) 1808 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.30, 1.55 (s, 6 H, $2CH_3$–C(3)), 3.32 (s, 3 H, CH_3O), 3.45–3.85 (m, 3 H, CH_2O, H–C(4)); mass spectrum, m/e 210 (M^+, 1), 175 (4), 143 (4), 124 (M^+ – $(CH_3OCH_2)CH{=}C{=}O$, 100), 86 (M^+ – $(CH_3)_2C{=}CCl_2$, 64).

Methyl Ester of 2,2-Dichloro-3-methyl-4-pentenoic Acid (3l). From 31.9 g (0.37 mol) of **1l**, 26.6 g (0.41 mol) of activated zinc in 500 mL of anhydrous ether and addition of 39.8 mL (64.0 g, 0.35 mol) of Cl_3CCOCl in 200 mL of anhydrous ether (3 h), after 1 h of reflux, one obtained by distillation 43.5 g (63%) of pure (98% by GC) **3l**: bp 75 °C (12 mm); IR (neat) 1779, 1760 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.36 (d, J = 7 Hz, 3 H, CH_3–C(3)), 3.35 (m, J = 7 Hz, 1 H, H–C(3)), 3.92 (s, 3 H, CH_3O), 5.20 (dd, J_{trans} = 17 Hz, $J_{allylic}$ = 2 Hz, 1 H, H–C(5)), 5.27 (dd, J_{cis} = 11 Hz, $J_{allylic}$ = 2 Hz, 1 H, H–C(5)), 5.87 (m, J = 17, 11, 7 Hz, 1 H, H–C(4)). Anal. Calcd for $C_7H_{10}Cl_2O_2$: C, 42.67; H, 5.12; Cl, 35.98. Found: C, 42.8; H, 5.2; Cl, 36.0.

Methyl Ester of 2,2-Dichloro-3-phenyl-4-pentenoic Acid (3m). A 35.2-g (0.24 mol) sample of **1m**, 14.4 g (0.22 mol) of activated zinc, and 22.6 mL (36.4 g, 0.2 mol) of Cl_3CCOCl in anhydrous ether (400 and 200 mL), followed by fractionation, yielded 25.0 g (48%) of **3m**: bp 96 °C (0.3 mm); IR (neat) 1764, 1748 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 3.74 (s, 3 H, CH_3O), 4.32 (d, J = 8 Hz, 1 H, H–C(3), 5.22 (d, J_{trans} = 17 Hz, 1 H, H–C(5)), 5.30 (m, J = 17, 9, 8 Hz, 1 H, H–C(4)), 7.3 (5 aromatic H). Anal. Calcd for $C_{12}H_{12}Cl_2O_2$: C, 55.62; H, 4.67; Cl, 27.36. Found: C, 55.77; H, 4.71; Cl, 27.28.

Methyl Ester of 2,2-Dichloro-4-methyl-3-phenyl-4-pentenoic Acid (3n) and 5-Phenyl-Substituted 14. A 35.7-g (0.22 mol) sample of *E* ether **1n**, 14.4 g (0.22 mol) of activated zinc, and 23.0 mL (37.0 g, 0.21 mol) of Cl_3 CCOCl in anhydrous ether (200 and 100 mL), followed by distillation, afforded 25.3 g (42%) of an oil, bp 93 °C (0.1 mm). NMR showed a mixture (88:12) of **3n** and an isomer, with a very close R_f on TLC (toluene–hexane, 1:1).

3n: IR (neat) 1770, 1754 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.70 (s, 3 H, CH_3–C(4)), 3.84 (s, 3 H, CH_3O), 4.35 (s, 1 H, H–C(4)), 5.07 (br s, 1 H, H–C(5)), 5.30 (s, 1 H, H–C(5)), 7.2–7.6 (5 aromatic H).

14: ^1H NMR ($CDCl_3$) 1.97 (s, 3 H, CH_3–C(4)), 3.34 (br s, 2 H, CH_2CCl_2), 3.86 (s, 3 H, CH_3O), 6.45 (br s, 1 H, H–C(5)), 7.2–7.6 (5 aromatic H). Anal. Calcd for $C_{13}H_{14}Cl_2O_2$: C, 57.16; H, 5.17; Cl, 25.96. Found: C, 57.32; H, 5.03; Cl, 26.10.

Methyl Ester of 2,2-Dichloro-3-methyl-(*E*)-4-hexenoic Acid. A 5.1-g (50.0 mmol) sample of ether **1o**, 3.6 g (55.0 mmol) of activated zinc, and 5.75 mL (93 g, 52.5 mmol) of Cl_3CCOCl in anhydrous ether (100 and 40 mL), followed by distillation, gave 4.85 g (50%) of an oil, bp 85 °C (13 mm). A cyclobutanone ($\nu_{C=O}$ 1818 cm^{-1}), which contaminated the main product, was removed by chromatography on silica gel (10:1 hexane–ether eluent) to give pure (99% by GC) **3o**: IR (neat) 1764, 1754 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.24 (d, J = 7 Hz, 3 H, CH_3–C(3)), 1.68 (d, J = 5 Hz, 3 H, CH_3–C(5)), 3.17 (m, J = 8, 7 Hz, 1 H, H–C(3)), 3.85 (s, 3 H, CH_3O), 5.35 (m, J_{trans} = 15, J_{vic} = 8 Hz, 1 H, H–C(4)), 5.71 (dq, J = 15, 5 Hz, 1 H, 1H–C(5)). Anal. Calcd for $C_8H_{12}Cl_2O_2$: C, 45.52; H, 5.73; Cl, 33.59. Found: C, 45.53; H, 5.67; Cl, 33.83.

2,2-Dichloro-3-(methoxymethyl)-3-methylcyclobutanone (5p). To 17.4 g (0.20 mol) of **1p** and 14.4 g (0.22 mol) of activated zinc in 400 mL of anhydrous ether was added a solution of 23.7 mL (38.2 g, 0.21 mol) of Cl_3CCOCl and 19.2 mL (32.2 g, 0.21 mol) of $POCl_3$ in 200 mL of anhydrous ether (3 h). The mixture was refluxed for 3 h and the usual workup gave ca. 31 g of an oil, which was distilled. One obtained 22.1 g (56%) of pure **5p**: bp 56 °C (0.2 mm); IR (neat) 1821 cm^{-1} (C=O). ^1H NMR ($CDCl_3$) δ 1.45 (s, 3 H, CH_3–C(3)), 3.00, 3.28 (d, J_{gem} = 16 Hz, 2 H, H–C(4)), 3.38 (s, 3 H, CH_3O), 3.52, 3.62 (d, J_{gem} = 10 Hz, 2 H, CH_2OCH_3). Anal. Calcd for $C_7H_{10}Cl_2O_2$: C, 42.67; H, 5.12; Cl, 35.98. Found: C, 42.9; H, 5.2; Cl, 35.7.

2,2-Dichloro-3-(phenoxymethyl)cyclobutanone (5q). The reaction of 26.8 g (0.20 mol) of **1q** following the procedure described for **1p** yielded by distillation 23.0 g (47%) of **5q**: bp 115 °C (0.3 mm); IR (neat) 1818 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 3.1–3.6 (m, 3 H, H–C(3), H_2–C(4)), 4.8–4.45 (m, 2 H, CH_2OPh), 7.1 (5 aromatic H). Anal. Calcd for $C_{11}H_{10}Cl_2O_2$: C, 53.90; H, 4.11; Cl, 28.93. Found: C, 53.59; H, 4.13; Cl, 28.70.

7-Oxo-6,6-dichloro-3-oxabicyclo[3.2.0]heptane (15). From 14.0 g (0.20 mol) of 2,5-dihydrofuran, one obtained by the procedure described for **1p** 11.9 g (33%) of **15**: bp 51 °C (0.25 mm); IR (neat) 1808 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 3.56 (dd, J_{gem} = 9, $J_{1,2}$ = 6 Hz, 1 H, H_{exo}–C(2)), 3.61 (dd, J = 8, 6 Hz, 1 H, H–C(5)), 3.76 (dd, J = 10, 6 Hz, 1 H, H_{exo}–C(4)), 4.22 (dd, J = 8, 6 Hz, 1 H, H–C(1)), 4.43 (d, J_{gem} = 9 Hz, 1 H, H_{endo}–C(2)), 4.56 (d, J_{gem} = 10 Hz, 1 H, H_{endo}–C(4)). Anal. Calcd for $C_6H_6Cl_2O_2$: C, 39.81; H, 3.34; Cl, 39.17. Found: C, 39.41; H, 3.34; Cl, 39.10.

Trimethylsilyl But-2-enyl Ether (1r). To a solution of 52 mL (0.21 mol) of *N,O*-bis(trimethylsilyl)acetamide in 100 mL of acetonitrile was added 28.8 g (0.40 mol) of crotyl alcohol over 30 min at 5 °C. The mixture was stirred for 1 h at 40 °C and then diluted with water. The product, extracted with pentane, was dried over $CaCl_2$ and the solvent removed in vacuo. Distillation afforded 37.6 g (65%) of **1r**: bp 35 °C (25 mm); n^{20}_D = 1.4075.

2,2-Dichloro-3-methyl-4-pentenoic Acid (3r). A mixture of 14.4 g (0.10 mol) of silyl ether **1t** and 7.2 g (0.11 mol) of activated zinc in 200 mL of anhydrous ether was stirred and a solution of 11.9 mL (19.1 g, 0.105 mol) of Cl_3CCOCl in 100 mL of anhydrous ether was added during 2 h. After the mixture was stirred for 4 h, the usual workup gave ca. 17 g of an oil, which was taken up in 100 mL of THF. Hydrolysis of the trimethylsilyl group was accomplished by adding 10 mL of 10 N HCl and stirring the solution for 3 h. The solution was then brought to pH 12 with 30% NaOH, the two phases were separated, and the aqueous phase was washed with ether. The aqueous phase was acidified with 2 N HCl and extracted with ether. The solution was dried over $MgSO_4$, the solvent removed in vacuo, and acid **3t** purified by distillation: 6.6 g (36%), bp 72 °C (0.6 mm); n^{20}_D = 1.4794; IR (neat) 1754 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.40 (d, J = 7 Hz, 3 H, CH_3–C(3)), 3.26 (m, J = 7 Hz, 1 H, H–C(3)), 5.2 (m, 2 H, H–C(5)), 5.8 (m, 1 H, H–C(4)), 11.3 (s, OH). Anal. Calcd for $C_8H_8Cl_2O_2$: C, 39.38; H, 4.41; Cl, 38.74. Found: C, 39.5; H, 4.4; Cl, 38.4.

Phenyl Thioester of 2-Chloro-3,3-dimethyl-4-pentenoic Acid (19). To a suspension of 16.3 g (0.25 mol) of zinc wool, 320 mg (6 mmol) of NH_4Cl, 110 mg (6.7 mmol) of NaI in 17.8 g (0.10 mol) of **1f**, and 30 mL of diisobutyl ketone was added at 40–45 °C 18.4 g (0.125 mol) of $Cl_2CHCOCl$. After an induction time, the reaction started vigorously and the external heating was removed. After 2 h, the flask was cooled, the unreacted zinc was decanted, and the residue was washed with hexane. The solution was washed successively with water, 10% $NaHCO_3$, and brine and dried over $CaCl_2$, and the solvent was removed in vacuo. Distillation of the residue gave 3.6 g of an oil, bp 74–92 °C (0.001 mm), which was chromatographed on a column of silica gel (hexane–toluene, 3:1).

One obtained 1.5 g (6%) of pure **19**, identical in each respect with the product of the reduction of **3f** (zinc powder, glacial acetic acid, 15 °C): IR (neat) 1718, 1695 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.22 (s, 6 H, $2CH_3$–C(3)), 4.24 (s, 1 H, H–C(2)), 5.07 (d, J_{trans} = 17 Hz, 1 H, H–C(5)), 5.10 (d, J_{cis} = 11 Hz, 1 H, H–C(5)), 5.95 (dd, J = 17, 11 Hz, 1 H, H–C(4)), 7.35 (5 aromatic H). Anal. Calcd for $C_{13}H_{15}ClOS$: C, 61.28; H, 5.93; Cl, 13.91; S, 12.58. Found: C, 61.4; H, 6.0; Cl, 13.9; S, 12.6.

Generation of Chlorocyanoketene in the Presence of 1k. A 9.5-g (50 mmol) sample of lactone **20** (21) and 15.0 g (150 mmol) of ether **1k** were dissolved in 100 mL of dry toluene, and the solution was heated at 85–90 °C for 3 h. The cold solution was washed with 10% $NaHCO_3$ and brine and dried over $MgSO_4$ and the solvent evaporated in vacuo. Bulb-to-bulb distillation (oven 90 °C, 0.1 mm) of the residue (ca. 7.7 g) afforded 4.26 g of an oil shown to contain mainly the ester **22** and the cyclobutanone **23** (11:89) by GC (SE 30 3%, 180 °C). At least four minor products were present in the mixture (ca. 8%).

When the reaction was repeated in propionitrile (100 mL) at 75–80 °C for 3 h, one obtained by distillation 1.39 g of an oil that contained **22** and **23** (73:27) and volatile unknown products (ca. 20%), as shown by analytical GC. The isomers were separated by preparative GC (SE 30 3%, 180 °C). **22** and **23** are not stable: a brown untractable material is formed upon standing at room temperature.

Compound **22**: IR (neat) 2180 (C≡N), 1779, 1754 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.40 (s, $2CH_3$–C(3)), 3.84 (s, CH_3O), 5.20 (d, J_{trans} = 17 Hz, H–C(5)), 5.23 (d, J_{cis} = 11 Hz, H–C(5)), 5.99 (dd, J_{trans} = 17 Hz, J_{cis} = 11 Hz, H–C(4)); mass spectrum, m/e 186 (M^+ – CH_3, 0.5), 95 ($C_6H_9N^+$, 0.4), 79 ($C_5H_5N^+$, 5), 69 ($C_5H_9^+$, 100).

Compound **23**: IR (neat) 2245 (CN), 1814 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.24, 1.69 (s, 6 H, $2CH_3$–C(3)), 3.32 (s, 3 H, CH_3O), 3.55 (m, 2 H, CH_2O), 3.66 (m, 1 H, H–C(4)); mass spectrum, m/e 181 (M – HCN, 1), 169 (M – OCH_3, 1), 100, 85.

Methyl Ester of 2-Chloro-2-(2,2,2-trichloroethyl)-3-methyl-4-pentenoic Acid (26). From 10.0 g (116 mmol) of ether **11**, 7.0 g (107 mmol) of activated zinc, and 27.9 g (100 mmol) of $Cl_3CCH_2CCl_2COCl$ (**24**) in 300 mL of anhydrous ether was obtained 13.6 g (46%) of **26**, bp 71 °C (0.01 mm). An analytical sample was chromatographed on silica gel (hexane–Et_2O, 20:1). **26**: IR (neat) 1776, 1745 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) (mixture of diastereomers, ca. 2:1) (major compound) δ 1.09 (d, J = 7 Hz, 3 H), 2.73 (m, 1 H), 3.38 (d, J_{gem} = 16 Hz, 1 H), 3.69 (d, J_{gem} = 16 Hz, 1 H), 3.80 (s, 3 H), 4.92–5.28 (m, 2 H), 5.6–6.0 (m, 1 H); (minor compound) 1.22 (d, J = 7, 3 H), 2.73 (m, 1 H), 3.31 (d, J_{gem} = 16 Hz, 1 H), 3.69 (s, 3 H), 3.80 (d, J_{gem} = 16 Hz, 1 H), 4.92–5.28 (m, 2 H), 5.6–6.0 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 15.8, 15.5 (CH_3–C(3)), 49.3, 48.7 (**C**HCH$_3$)), 53.6, 53.3 (OCH_3), 60.9, 59.9 (CH_2CCl_3), 73.8, 73.6 (C(2)), 95.5 (CCl_3), 119.2, 117.7 (=CH_2), 137.4, 137.0 (=CH), 169.9, 169.4 (CO_2Me). Anal. Calcd for $C_6H_{12}Cl_4O_2$: C, 36.77; H, 4.12; Cl, 48.24. Found: C, 36.62; H, 4.13; Cl, 48.48.

Methyl Thioester of 2-Chloro-2-(2,2,2-trichloroethyl)-4-pentenoic Acid (27). A 8.8-g sample (100 mmol) of sulfide **1e**, 7.2 g (110 mmol) of activated zinc, and 29.2 g (105 mmol) of $Cl_3CCH_2CCl_2COCl$ in 360 mL of anhydrous ether afforded 14.9 g (50%) of **27**, bp 87 °C (0.1 mm). An analytical sample was chromatographed on silica gel (hexane–ether, 20:1) to remove polar impurities. **27**: IR (neat) 1675 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.30 (s, 3 H, CH_3S), 2.64 (dd, J = 15, 6 Hz, 1 H, H–C(3), 2.86 (dd, J = 15, 6 Hz, 1 H, H–C(3)), 3.30, 3.92 (d, J_{gem} = 15 Hz, 2 H, CH_2CCl_3), 5.00–5.35 (m, 2 H, H–C(5)), 5.60–6.05 (m, 1 H, H–C(4)). Anal. Calcd for $C_8H_{10}Cl_4OS$: C, 32.46; H, 3.41; Cl, 47.91; O, 5.41; S, 10.83. Found: C, 32.13; H, 3.37; Cl, 48.38; O, 5.45; S, 10.63.

2,2-Dichloro-3,3,7-trimethyl-(*E*)-4-nonen-9-olide (29). From 15.4 g (0.10 mol) of rose oxide (**28**) and 7.85 g (0.12 mol) of activated zinc in 300 mL of anhydrous ether and addition of a solution of 12.4 mL (20.0 g, 0.11 mol) of Cl_3CCOCl and 10.1 mL (16.9 g, 0.11 mol) of $POCl_3$ in 80 mL of anhydrous ether (3 h, 30 °C) was obtained 24.7 g of an oil. Distillation gave 1.1 g of unreacted **28** and 20.1 g (76%) of a mixture containing **29** and **30** (70:30): bp 75–77 °C (0.002 mm). A solution of 7.96 g (0.03 mol) of distillate and 5 mL of Et_3N in 100 mL of $CHCl_3$ was stirred for 4 h at 60 °C. The solvent was evaporated in vacuo and the residue filtered over silica gel (10:1 hexane–ether eluent), giving 5.3 g of pure lactone **29**, as shown by TLC (hexane–ether, 5:1): IR (neat) 1751 (C=O), 983 cm^{-1} (C=C trans); ^1H NMR ($CDCl_3$) (conformation I) δ 1.02 (d, J = 7 Hz, 3 H, CH_3–C(7)), 1.31, 1.41 (s, 6 H, $2CH_3$–C(3)), 1.5–1.7 (m, 2 H, H–C(7), H_{ax}–C(8)), 1.7–1.9 (m, 2 H, H_{ax}–C(6), H_{eq}–C(8)), 2.32 (br d, J = 13, 1 H, H_{eq}–C(6)), 4.06 (ddd, J = 12, 6, 1 Hz, 1 H, H–C(9)), 4.42 (dd, J = 12, 10 Hz, 1 H, H_{ax}–C(9)), 5.39 (ddd, J = 16, 11, 3 Hz, 1 H, H–C(5)), 5.66 (dd, J = 16, 2 Hz, 1 H, H–C(4)); (conformation II) 1.05 (d, J = 7 Hz, 3 H, CH_3–C(7)), 1.36, 1.41 (s, 6 H, $2CH_3$–C(3)), 1.5–1.9 (m, 4 H), 2.13 (ddd, J = 13, 7, 4 Hz, 1 H, H_{eq}–C(6)), 3.85 (ddd, J = 11, 5, 3 Hz, 1 H, H_{eq}–C(9)), 4.61 (ddd, J = 11, 5, 3 Hz, 1 H, H_{ax}–C(9)), 5.39 (dddd, J = 16, 6, 3 Hz, 1 H, H–C(5)), 5.72 (br d, J = 15 Hz, 1 H, H–C(4)); ^{13}C NMR ($CDCl_3$) δ 21.5, 23.2, 24.9 ($3CH_3$); (conformation I) 36.8 (t, C(9)), 37.1 (d, C(8)), 42.2 (t, C(7)), 47.8 (s, C(3)), 67.8 (t, C(10)), 95.0 (s, C(3)), 130.7 (d, C(6)), 135.1 (d, C(5)), 165.7 (s, C(2)); (conformation II) 32.8 (C(9)), 33.3 (C(8)), 42.2 (C(7)), 47.9 (C(4)), 65.1 (C(10)), 94.3 (C(3)), 130.7 (C(6)), 136.1 (C(5)). Anal. Calcd for $C_{12}H_{18}Cl_2O_2$: C, 54.35; H, 6.84; Cl, 26.74. Found: C, 54.44; H, 6.94; Cl, 26.49.

Cyclobutanone 30 (spectra extracted from the mixture with 29): IR (neat) 1811 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.97 (d, 3 H, CH_3–C(4)), 1.38, 1.53 (2 s, 6 H, $2CH_3$–C(3)), 1.2–2.0 (m, 5 H), 3.2–3.7 (m, 4 H).

2,2-Dichloro-3,3-dimethyl-4-(4-methyl-2,3-dihydro-6*H*-pyran-2-yl)cyclobutanone (32). The reaction of 15.2 g (0.10 mol) of nerol oxide (**31**) by the usual procedure (see **3a**) afforded 5.9 g of an oil, bp 66 °C (0.03 mm). Recrystallization from pentane yielded a first crop, 1.9 g, and a second crop, 1.6 g, (combined yield 13%) of **32**: mp 54–55 °C; IR ($CHCl_3$) 1812 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.34, 1.57 (2 s, 6 H, $2CH_3$–C(3)), 1.72 (br s, 3 H, CH_3C=C), 2.14 (m, 2 H, H_2–C(3′)), 3.48 (d, J = 10.5 Hz, H–C(4)), 3.76 (m, J = 10.5, 8.0, 4.0 Hz, 1 H, H–C(2′)), 4.06 (m, 2 H, H_2–C(6′)), 5.36 (br s, 1 H, CH=C); ^{13}C NMR ($CDCl_3$) δ 20.8, 22.9, 25.0 (q, $3CH_3$), 34.8 (t, C(3′)), 45.2 (s, C(3)), 65.1 (t, C(6′)), 69.9, 68.0 (d, C(4), C(2′)), 91.9 (s, C(2)), 119.4 (d, C(5)), 131.1 (s, C(4′)), 193.4 (s, CO). Anal. Calcd for $C_{12}H_{16}Cl_2O_2$: C, 54.77; H, 6.13; Cl, 26.94. Found: C, 54.7; H, 6.3; Cl, 26.7.

2-Prop-2-enylthiane (33):[35] bp 68–70 °C (13 mm); 42% yield.

2,2-Dichloro-3-methyl-(*E*)-4-nonene-9-thiolide (34). A 6.83-g (50 mmol) sample of thiane **33**, 3.6 g (and 3 × 1.2 g, total 110 mmol) of activated zinc, and 5.75 mL (9.25 g, 52.5 mmol) of Cl_3CCOCl in 150 mL of anhydrous ether gave after standard procedure (see **3a**) and after chromatography on silica gel (20:1 hexane–ether eluent) 1.05 g (8%) of **34**: IR (neat) 1690 (C=O), 997 cm^{-1} (C=C trans); ^1H NMR (toluene-d_8) δ 1.35 (d, J = 7 Hz, 3 H, CH_3–C(3)), 1.1–1.8 (m, 6 H), 2.73 (m, 1 H, H–C(3)), 2.78 (dd, J = 10, 6 Hz, 1 H, H_{ax}–C(9)), 2.88 (br d, J = 10 Hz, 1 H, H_{eq}–C(9)), 4.95 (br dd, J = 16, 10 Hz, 1 H, H–C(4)), 5.23 (ddd, J = 16.0, 7.8, 8.1 Hz, 1 H, H–C(5)). Anal. Calcd for $C_{10}H_{14}Cl_2OS$: C, 47.44; H, 5.58; O, 6.32; Cl, 28.01; S, 12.66. Found: C, 48.09; H, 5.61; O, 6.29; Cl, 27.39; S, 12.91.

2-(1-Hydroxyethyl)-6-methyltetrahydro-2*H*-pyran (37). Catalytic hydrogenation of 140.2 g (1.0 mol) of **36**[60] in ethyl acetate (1.4 L) in the presence of 14 g of 5% Pt–C (P = 150 bar, T = 25 °C) yielded 122.4 g (85%) of **37**, bp 70 °C (15 mm). GC (capillary column, 80 °C) showed an epimeric mixture (60:40), and NMR established a 2,6 cis configuration of epimeric alcohols. **37**: IR (neat) 3450 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ 1.14 (d, J = 7 Hz, 3 H, CH_3–C(6)), 1.20 (d, J = 7 Hz, 3 H, CH_3–C(1′)), 1.2–2.0 (m, 6 H), 2.9–3.8 (m, 3 H); ^{13}C NMR ($CDCl_3$) (epimer I) δ 18.2 (q, CH_3–C(1′)), 22.1 (q, CH_3–C(6)), 23.2 (t, C(4)), 27.0 (t, C(3)), 33.2 (t, C(5)), 70.6 (d, C(1′)), 73.9 (d, C(6)), 82.4 (d, C(2)); (epimer II) 17.8 (q, CH_3–C(1′)), 22.2 (q, CH_3–C(6)), 23.2, 24.5 (t, C(3), C(4)), 33.5 (t, C(5)), 69.6 (d, C(1′)), 74.1 (d, C(6)), 81.0 (d, C(2)). Anal. Calcd for $C_8H_{16}O_2$: C, 66.64; H, 11.19. Found: C, 66.4; H, 10.9.

***cis*-2-Vinyl-6-methyltetrahydro-4*H*-pyran (38).** From 144.2 g (1.0 mol) of **37**, by a standard procedure (pyridine, *p*-toluenesulfonyl chloride), one obtained 262.0 g (88%) of the corresponding tosylate as a low-melting solid.

The crude tosylate was dissolved in 500 mL of Me_2SO and 105 g (0.93 mol) of potassium *tert*-butoxide was added by portions. The mixture was stirred for 3 h at 50 °C,[61] cooled, and poured onto ice. The product was extracted with 300 mL of ether and 2 × 300 mL of pentane, and the organic phase was washed successively with water and brine and dried over $CaCl_2$. Distillation afforded 85.9 g (68%, global yield) of **38**: bp 73 °C (75 mm); ^1H NMR ($CDCl_3$) δ 1.12 (d, J = 7 Hz, 3 H, CH_3–C(6)), 1.1–2.0 (m, 6 H, $3CH_2$), 3.35 (m, 1 H, H–C(6)), 3.68 (m, 1 H, H–C(2)), 4.7–5.3 (m, 2 H, CH_2=CH) 5.78 (ddd, J = 15, 10, 5 Hz, 1 H, CH_2=CH); ^{13}C NMR ($CDCl_3$) 22.3 (CH_3–C(6)), 23.6 (C(4)), 31.3, 33.2 (C(3), C(5)), 73.8 (C(6)), 78.5 (C(2), 114.5 (C(2′)), 139.8 (C(1′)). Anal. Calcd for C, 76.14; H, 11.18. Found: C, 76.06; H, 11.31.

2,2-Dichloro-9-methyl-(*E*)-4-decen-9-olide (39). A mixture of 63.1 g (0.5 mol) of pyran **38** and 45.0 g (0.7 mol) of activated zinc in 500 mL of anhydrous ether was stirred and a solution of 68.0 mL (109.0 g, 0.6 mol) of Cl_3CCOCl in 200 mL of anhydrous ether was added dropwise during 8 h at 28–31 °C. When the addition was complete, the mixture was refluxed for 20 min and then cooled in on ice bath. After addition of 400 mL of petroleum ether, the solution was decanted, the residue was washed with ether–hexane. The exact was washed successively with iced water (3 × 200 mL), 10% $NaHCO_3$ (2 × 100 mL) and brine (100 mL) and dried over $MgSO_4$. The solvent was removed in vacuo, some unreacted pyran **38** (15.1 g) was trapped at −78 °C under low pressure (0.1 mm), and the product was distilled: 80.6 g (68%), bp 60 °C (0.02 mm). NMR and TLC (toluene–hexane, 1:1) show a simple mixture of lactone **39** and cyclobutanone **40** (85:15).

The pure lactone **39** was separated by preparative chromatography on silica gel (hexane–ether, 20:1); **40** was completely retained on the column. **39**: IR (neat) 1751 (C=O), 970 cm^{-1} (C=C trans); ^1H NMR ($CDCl_3$) δ 1.30 (d, J = 7 Hz, 3 H, CH_3–C(9)), 1.48, 1.64 (m, 2 H, H_{ax}–C(7), H_{ax}–C(8)), 1.79–1.90 (m, 2 H, H_{eq}–C(7), H_{eq}–C(8)), 1.95 (m, J = 13.0, 10.5, 10, 2.5 Hz, 1 H, H_{ax}–C(6)), 2.26 (br s, 1 H, H_{eq}–C(6)), 2.93 (dd, J = 13.0, 10.5 Hz, 1 H, H_{ax}–C(3)), 3.15 (br dd, J = 13.0, 4.5 Hz, 1 H, H_{eq}–C(3)), 4.88 (m, J = 7, 6, 2 Hz, 1 H, H–C(9)), 5.42 (ddd, J = 16.0, 10.5, 4.0 Hz, 1 H, H–C(5)), 5.62 (splitted ddd, J = 16.0, 10.5, 4.5 Hz, 1 H, H–C(4)); ^{13}C NMR ($CDCl_3$) δ 21.7 (q, CH_3–C(10)), 28.1 (t, C(8)), 33.0 and 35.0 (t, C(7), C(9)), 51.7 (t, C(4)), 77.1 (d, C(10)), 86.1 (s, C(3)), 124.8 (d, C(5)), 138.1 (d, C(6)), 165.7 (s, C(2)). Anal. Calcd for $C_{10}H_{14}Cl_2$: C, 50.65; H, 5.95; Cl, 29.92. Found: C, 50.54; H, 6.09; Cl, 2 9.95.

Cyclobutanone 40 (spectra of isomeric mixtures): IR (neat) 1821 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.25 (d, J = 7 Hz, 3 H, CH_3–C(6)), 1.2–2.3 (m, 7 H), 2.8–3.6 (m, 4 H).

(±)-9-Decanolide (Phoracantholide I; 41). A 7.11-g (30.0 mmol) sample of lactone **40** was hydrogenated catalytically (5% Pd–C) in the presence of 6.06 g (60.0 mmol) of triethylamine, under normal pressure. Distillation afforded 4.3 g (85%) of **41**, bp 92 °C (14 mm), which was found identical (IR, NMR, TLC) with an authentic sample.[43]

Zinc Reduction of 39. Zinc powder (18.0 g, 0.27 mol) was added in six portions over 6 h to a stirred solution of 6.9 g (0.03 mol) of lactone **39** in 120 mL of acetic acid. The first chlorine atom was removed easily at 40 °C, whereas the second one required 85 °C. After the indicated time, the mixture was cooled, poured onto ice, and partially neutralized with 30% NaOH (ca. 200 mL). The product was taken in ether, and the organic phase was washed with $NaHCO_3$ 10% and dried over $MgSO_4$.

Two products were separated by chromatography (toluene eluent): the first eluted compound (1.34 g, 22%) was identified as the monochloro derivative of **39** (one isomer): IR (neat) 1754 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.25 (d, J = 7 Hz, 3 H, CH_3–C(9)), 1.2–2.3 (m, 5 H), 2.1–2.9 (m, 3 H), 4.19 (dd, J = 12, 5 Hz, H_{ax}–C(2)), 4.90 (br m, J = 7, 6 Hz, 1 H, H–C(9)), 5.2–5.6 (m, 2 H, CH=CH). Anal. Calcd for $C_{10}H_{15}ClO_2$: C, 59.26; H, 7.46; Cl, 17.49. Found: C, 59.24; H, 7.32; Cl, 17.31.

The second eluted compound (3.28 g, 65%) was the pure lactone **42**: IR (CCl_4) 1727 (C=O), 980, 961 cm^{-1} ((*E*)-C=C); ^1H NMR ($CDCl_3$) δ 1.18 (d, J = 7 Hz, 3 H, CH_3–C(9)), 1.35–1.6 (n, 2 H), 1.65 (m, 3 H), 2.24 (br, signal, 3 H), 2.40 (br, signal, 2 H), 4.83 (m, J = 7 Hz, 6, 1 H, H–C(9)), 5.28 (ddd, J = 15.5, 10.2, 4 Hz, 1 H, H–C(5)), 5.46 (ddd, J = 15.5, 9.5, 4.5 Hz, 1 H, H–C(4)); ^{13}C NMR ($CDCl_3$) δ 22.1 (q, CH_3–C(10)), 28.3 (t, C(8)), 30, 6 (t, C(4)), 33.0 and 35.4 (t, C(7)), C(9)), 37.6 (t, C(3)), 72.3 (d, C(10)), 129.5 (d, C(5)), 132.8 (d, C(6)), 173.1 (s, C(2)). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.52; H, 9.55.

(±)-(*Z*)-Dec-4-en-9-olide (Phoracantholide J; 43). A 1.00-g (6.0 mmol) sample of *Z* lactone **42** and diphenyl disulfide (87 mg) in 200 mL of benzene–hexane (1:7, v/v) were irradiated at 25 °C under argon, with a UV lamp (Philips HPK 125; Pyrex vessel). The isomerization process could be conveniently followed by capillary GC: a plot of percent of *E* vs. time gave half-lifes $t_{1/2}$ = 40 min for the isomerization. After 7 h, a photostationary state was reached, consisting of 4% *E* and 96% of the desired *Z* isomer. The reaction solution was filtered over neutral Al_2O_3 and the solvent removed in vacuo.

The residue was chromatographed on a $AgNO_3$-coated silica gel column[44] (hexane–ethyl acetate, 9:1, v/v), to afford 0.85 g (85%) of pure **43**. The spectral data (IR, NMR) and GC of **43** were identical with those of an authentic sample[43] of phoracantholide J. Our products **42** and **43** showed the same retention times on a capillary column (80 °C) as the sample prepared independently by Petrzilka.[41c] **43**: IR (CCl_4) 1735 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.26 (d, J = 7 Hz, 3 H, CH_3–C(9)), 1.3–1.5 (m, 2 H, H_{ax}–C(7), H_{ax}–C(8)), 1.8–2.0 (m, 4 H, H_{eq}–C(7), H_{eq}–C(8), CH_2CO), 2.23 (ddd, J = 16.0, 13.0, 4.5 Hz, 1 H, H_{ax}–C(7), H_{eq}–C(8), CH_2CO), 2.23 (ddd, J = 16.0, 13.0, 4.5 Hz, 1 H, H_{ax}–C(3)), 2.54 (dt, J = 16, 4 Hz, 1 H, H_{eq}–C(3)), 2.68 (br q, 1 H, J = 12, 11 Hz, H_{ax}–C(6)), 2.73 (ddd, J = 12.0, 11.5, 5.0 Hz, 1 H, H_{eq}–C(6)), 5.10 (br q, 1 H, H–C(9)), 5.36 (td, J = 11, 4 Hz, 1 H, H–C(5)), 5.47 (tdd, J = 11.0, 5.5, 2.0 Hz, 1 H, H–C(4)).

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Registry No. **1a**, 10276-06-9; **1b**, 35976-82-0; **1c**, 5296-62-8; **1d**, 84473-36-9; **1e**, 10152-76-8; **1f**, 10276-04-7; **1g**, 69690-81-9; **1k**, 22093-99-8; **1l**, 18408-99-6; **1m**, 16277-67-1; **1n**, 57051-05-5; **1o**, 27125-91-3; **1p**, 22418-49-1; **1q**, 1746-13-0; **1r**, 18269-32-4; **2**, 4591-28-0; **3a**, 84473-37-0; **3b**, 84473-38-1; **3c**, 84473-39-2; **3d**,

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(61) A large excess of potassium *tert*-butoxide and a prolonged reaction time isomerize the double bond in **38** from an exo- to an endocyclic one.

84473-40-5; **3e**, 84473-41-6; **3f**, 69690-79-5; **3g**, 69690-88-6; **3k**, 69690-84-2; **3l**, 69690-82-0; **3m**, 69690-85-3; **3n**, 84473-42-7; **3o**, 69690-83-1; **3r** (R′ = H), 40630-94-2; **4f**, 69862-37-9; **4g**, 69690-90-0; **4k**, 69690-89-7; **5p**, 84473-43-8; **5q**, 84473-44-9; **13**, 84473-45-0; **15**, 84473-46-1; **19**, 84473-47-2; **20**, 60010-88-0; **22**, 84498-68-0; **23**, 84473-48-3; **24**, 72060-97-0; **26** (isomer 1), 84473-49-4; **26** (isomer 2), 84473-56-3; **27**, 84473-50-7; **28**, 16409-43-1; **29**, 84473-51-8; **30**, 84473-52-9; **31**, 1786-08-9; **32**, 84473-53-0; **33**, 77744-03-7; **34**, 84473-54-1; (±)-**36**, 84498-69-1; (±)-**37** (isomer 1), 82335-15-7; (±)-**37** (isomer 2), 82335-14-6; (±)-**38**, 82293-67-2; (±)-**39**, 69690-91-1; **39** (monochloro derivative), 84473-55-2; **40**, 69690-92-2; (±)-**41**, 65371-24-6; (±)-**42**, 69447-14-9; (±)-**43**, 67400-99-1.

Photohydration of Aromatic Alkenes. Catalytic Phenomena and Structure–Reactivity Studies

Peter Wan and Keith Yates*

Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1

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The photohydrations of aromatic alkenes **3–14** have been studied in aqueous sulfuric acid. Aromatic alkenes with substituents that have electron-donating effects equal to or greater than that of hydrogen (**3–7** and **14**) undergo photohydration via S_1 if other photoprocesses do not compete favorably. The electron-donating or -withdrawing abilities of substituents in S_1 do not necessarily reflect their ground-state σ values. For example, the meta-fluoro group is strongly electron withdrawing ($\sigma^+ = 0.35$) in the ground state, but evidence presented in this work suggests it is much less electron withdrawing (or in fact even becomes electron donating) in S_1. The opposite appears to be true for the para-fluoro substituent. It is shown that photohydration can be water, hydronium ion, or general acid catalyzed. The observation of general acid catalysis supports the proposed mechanism involving rate-limiting proton transfer to S_1. The individual catalytic rate constants for photoprotonation obey the Brønsted catalysis law, with an α value of ~0.15, suggesting early transition states in these photoprotonations.

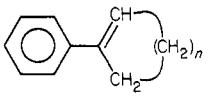
The photochemistry of alkenes has been a topic of continued interest to organic photochemists, offering a rich and fruitful area for study. A recent review[1] summarizes the present understanding of the photobehavior of this functional group in solution.

Of special interest to us is the photoprotonation of alkenes (eq 1). The photoprotonation process for aliphatic

$$>C{=}C< \xrightarrow[H^+]{h\nu} >HC{-}C^+< \xrightarrow{H_2O} >CHC(OH)< \quad (1)$$

photoprotonation; photohydration

alkenes is reasonably well understood. For those aliphatic alkenes that undergo observed photohydration, it has been proposed that the mechanism involves nucleophilic trapping of the Rydberg state of the molecule by the solvent.[2] For nonaromatic cyclic alkenes, the mechanism is believed to involve nucleophilic trapping both of the Rydberg state and of the highly reactive *trans*-alkene intermediate, the mechanism followed depending on the ring size.[3] The situation for aromatic alkenes is less well understood. Phenylcycloalkenes **1** where n = 3–5 undergo photoprotonation via a mechanism involving the reactive trans intermediate (from either direct or sensitized excitation).[4] 1-Phenylcyclopentene (**1**, n = 2), being incapable of undergoing cis to trans isomerization, does not undergo photoprotonation.[4] To our knowledge, there have been no attempts at a systematic study of the protonation process for acyclic styrenes (**2**), although several styryl systems with



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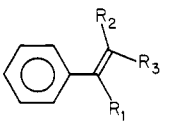

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electron-releasing substituents have been found to undergo Markovnikov addition of methanol and acetic acid.[5] We recently reported[6] our initial exploratory results on the

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