chloride, 32115-62-1; 3-trimethylsilylcyclohexene, 40934-71-2; 4-trimethylsilylcyclohexene, 40934-72-3; 3-cyclohexenylmagnesium bromide, 31463-48-6; 4-trichlorosilylcyclohexene, 10137-69-6; methylmagnesium bromide, 75-16-1; 1-trimethylsilylcyclohexene, 17874-17-8; 1-cyclohexenyllithium, 37609-34-0; 1-cyclohexenyldichlorosilane, 69239-02-7; phenylmagnesium bromide, 100-58-3; 4-cyclohexenylsilane, 69239-03-8; chlorodimethylsilane, 1066-35-9; trichlorosilane, 10025-78-2.

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Regio- and Stereochemistry of the Cycloadditions of Dichloroketene to 2-Methyl- and 3-Methyl-2-cholestene[1]

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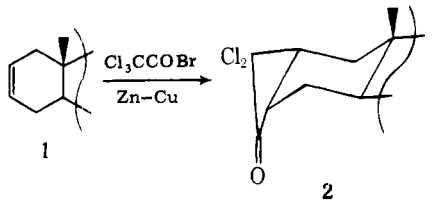
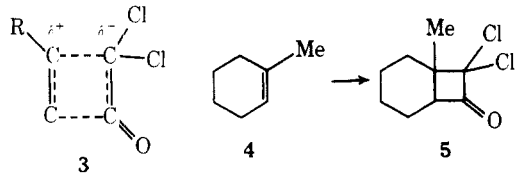
Electronic and stereoelectronic factors governing the cycloaddition of 2-methyl- and 3-methyl-2-cholestene (7 and 8) with dichloroketene were examined. In each case, the reaction was regio- and stereospecific: 2-methyl-2-cholestene (7) afforded 2a,2a-dichloro-2α,3α-ethano-2β-methylcholestan-3a-one (9), while 3-methyl-2-cholestene (8) afforded 3a,3a-dichloro-2α,3α-ethano-3β-methylcholestan-2a-one (13). The results indicate that the cycloaddition proceeds exclusively via attack of the ketene from the α side of the steroid and that the regiochemistry is guided largely by electronic factors. The structures of the cycloadducts were elucidated by chemical means (reduction, Baeyer–Villiger oxidation) and NMR, while circular dichroism proved useful in the conformational analysis of the fused steroidal cyclobutanones and lactones.

The formation of cyclobutanones by addition of dichloroketene[2] to reactive olefins has been the subject of many synthetic and mechanistic studies.[3,4] In cyclohexene systems the cycloaddition has been demonstrated to be highly regioselective[4,5] and occurs for stereoelectronic reasons with preferential axial bond formation between the carbonyl carbon and the cyclohexane chair conformation. Thus, generation of dichloroketene in the presence of 2-cholestene (1) was found[4] to yield almost exclusively **2**.



1 2

On the other hand, olefin substituents exert strong electronic effects that guide the regiochemistry of the cycloaddition. If a substituent R is capable of stabilizing a positive charge, then the reaction can be visualized to proceed via a transition state such as **3**. For instance, 1-methylcyclohexene (**4**) leads to cycloadduct **5**.[9]

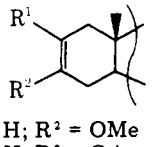


3 4 5

In light of the striking regioselectivity found[4b] in the 2-cholestene–dichloroketene reaction, we were interested in the effect an additional double-bond substituent would have on the regio- and stereochemistry of a dichloroketene cycloaddition. Until recently, the yield of cyclobutanones from the cycloaddition of dichloroketene to tri- and tetrasubstituted olefins has been low or nil.[2b,c] However, we have recently described[6] an improved procedure, using $POCl_3$, which overcomes these old difficulties. With this new method in hand, it was feasible to study the cyloaddition of dichloroketene to trisubstituted steroidal olefins.

Results and Discussion

The steroidal enol derivatives **6a–e** were studied in the re-



6a, R^1 = H; R^2 = OMe
b, R^1 = H; R^2 = OAc
c, R^1 = H; R^2 = $OSiMe_3$
d, R^1 = OAc; R^2 = H
e, R^1 = $OSi(Me_3)$-*t*-Bu; R^2 = H

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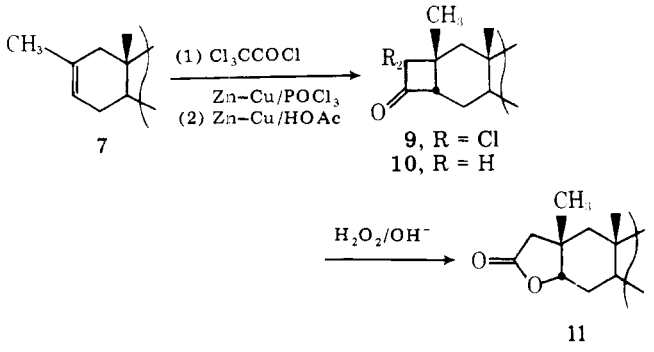
action with dichloroketene, generated either via HCl elimination with Et_3N or via Cl_2 elimination with Zn, in the presence or absence of $POCl_3$. In none of these cases (surprisingly not even with the enol ether **6a**) was an isolable cycloadduct detected. Only hydrolysis to the parent ketone and/or formation of intractable tars was observed.

The methylcholestenes **7** and **8** were unreactive to dichloroketene under normal condition as well, but when dichloroketene was generated in the presence of phosphorus oxychloride TLC examination indicated that olefin **7** has been consumed within ~20 h. The yield of the crude product was very high (98%); the yield of recrystallized material was somewhat lower (72%). The formation of a single product in this reaction was evident by TLC examination of the crude



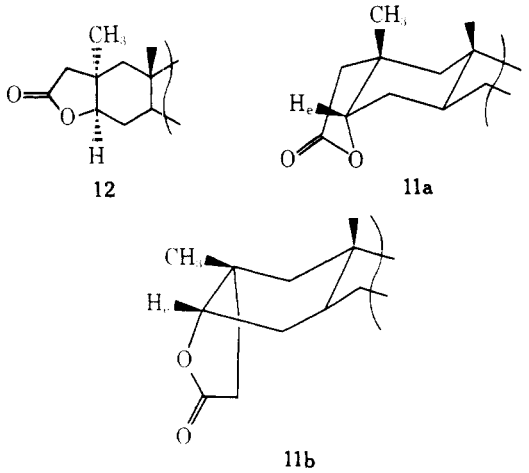
7

9, R = Cl
10, R = H

11

material, recrystallized product, and mother liquors from the recrystallization. The dichlorocyclobutanone was assigned structure **9** on the basis of reduction to **10** and Baeyer–Villiger oxidation to **11**.

The latter displayed a downfield signal at δ 4.91 (integrating for one proton) with a half-width of 6 Hz, indicative of an equatorial proton.[7] This evidence eliminates structure **12** in

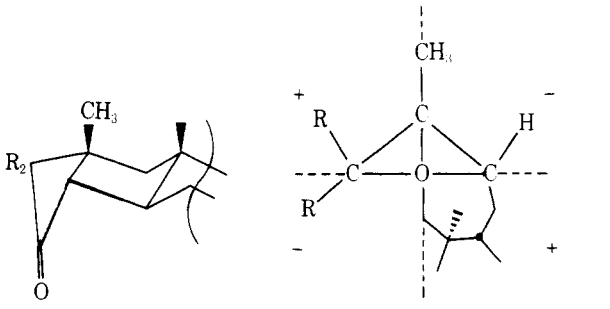


12 **11a**

11b

which an axial (or pseudoaxial) proton H_a would display a broad (12–25 Hz) half-width in the NMR. This leaves only **11** as a possible structure of the lactone which must have arisen from the cyclobutanone **9** rather than from a regioisomeric ketene adduct. Because of the unfavorable 1,3-diaxial interaction which would result if lactone **11** existed in conformation **11a**, the steroidal A ring would probably undergo a conformational flip and prefer to exist in a semi-boat conformation **11b**.[8] In either conformation **11a** or **11b**, H_e occupies an equatorial (or pseudoequatorial) position and would be expected to display a narrow (7–12 Hz) half-width in the NMR spectrum.

The circular dichroism (CD)[9,10] spectra of compounds **9** and **10** also support the assigned structures. These cyclobutanones probably also exist in semi-boat conformations **9b** and **10b** for the reasons discussed for lactone **11**. As indicated by the octant projection for **9** and **10**, compound **10** would be expected to

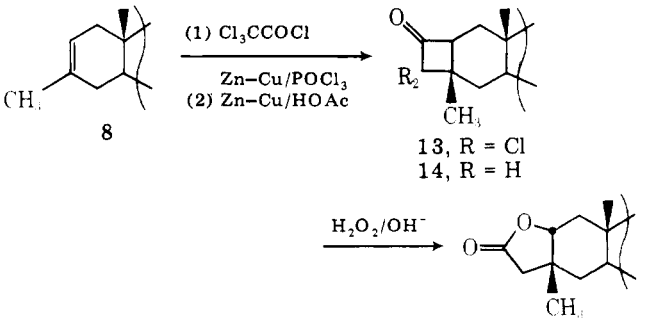


9b, R = Cl
10b, R = H

octant projection for **9**, R = Cl
octant projection for **10**, R = H

display a positive Cotton effect. The Cotton effect was indeed determined to be quite strongly positive ($[\theta]_{297}$ +2200). As expected, the pseudoaxial chlorine substituent in **9** substantially enhances the positive Cotton effect ($[\theta]_{313}$ +8800).

When dichloroketene was generated in the presence of 3-methyl-2-cholestene (**8**), a single product was again formed.



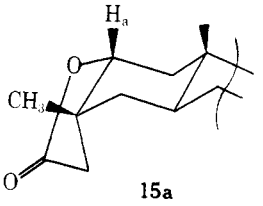
8

13, R = Cl
14, R = H

15

The reaction of this olefin, however, required 3 days for completion, significantly slower than 2-methyl-2-cholestene (**7**) (~20 h). The cycloadduct was smoothly transformed via **13** and **14** to a lactone, assigned structure **15**.[11]

The NMR spectrum of lactone **15** displayed a broad downfield signal (a poorly resolved doublet of doublets) centered at δ 4.21. This signal integrated for one proton and had a half-width of 22 Hz, indicative of an axial proton as in **15a**.



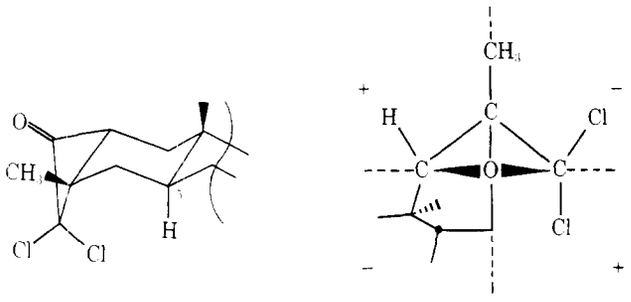
15a

This establishes the dichlorocyclobutanone structure **13** for the product of the dichloroketene reaction with 3-methyl-2-cholestene (**8**).

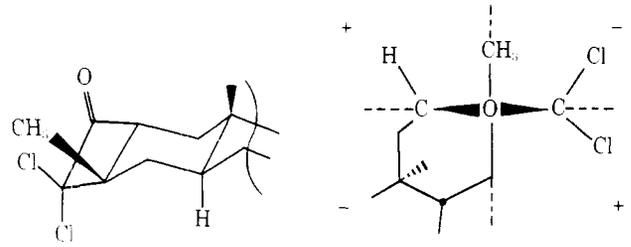
The Cotton effects displayed by this group of compounds are important in establishing their preferred conformation. As shown in Chart I, ketone **13** might be expected to show a positive Cotton effect if it existed in conformation **13a**. However, in **13a** the endo chlorine experiences a severe nonbonded interaction with the 5α-hydrogen, thus forcing the four-membered ring to become more planar, as depicted by **13b**. In the latter case, the effect of the exo chlorine partially cancels the (positive) effect of the endo chlorine while the bulk of the steroid skeleton continues to contribute in the negative octant to the Cotton effect. In fact, the Cotton effect in **13** was found to be quite strongly negative ($[\theta]_{325}$ −6900), indicative of the importance of conformation **13b**.

Reduction of the dichlorocyclobutanone **13** to the cyclobutanone **14** eliminates the unfavorable steric interaction discussed for **13a**, and the four-membered ring in **14** can as-

Chart I

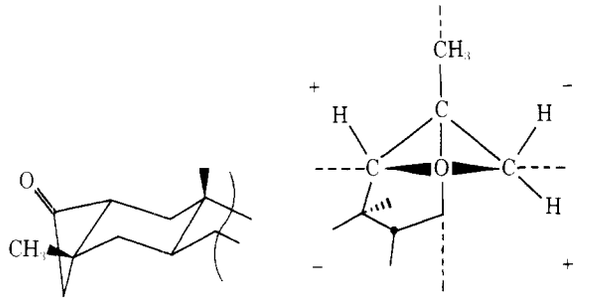


13a octant projection for 13a

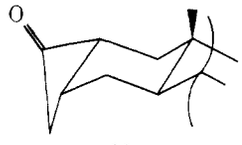


13b octant projection for 13b

sume a more puckered conformation. As shown in the octant projection, this conformation **14** would be expected to exhibit a negative Cotton effect. The Cotton effect for **14** was indeed found to be strongly negative ($[\theta]_{297}$ −15 000). The situation for cyclobutanone **16** (obtained from **2** via carbonyl transposition)[10c] is similar, and indeed **16** also exhibits a strongly negative Cotton effect ($[\theta]_{299}$ −12 000).

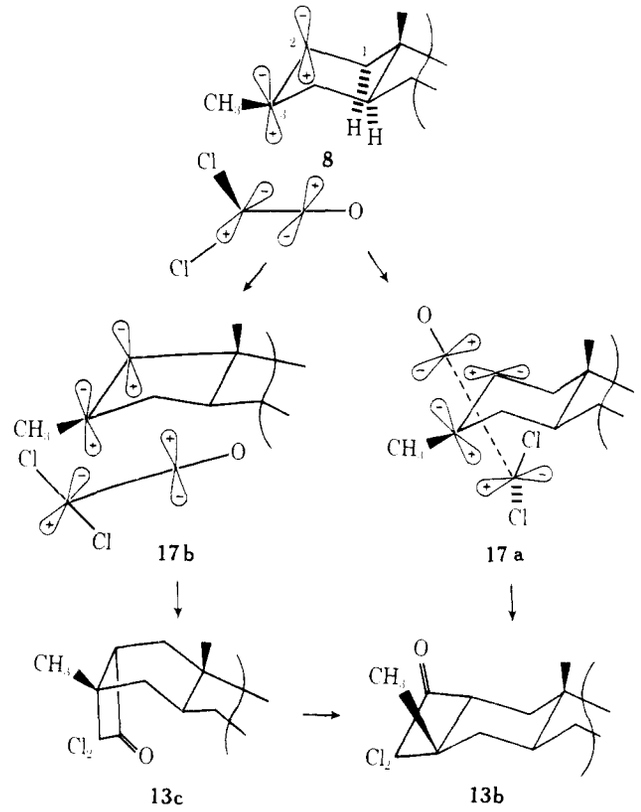


14 octant projection for 14



16

The observation that dichloroketene reacts with 3-methyl-2-cholestene (**8**) to produce **13** and the reaction occurs 4–5 times more slowly than with either 2-cholestene (**1**) or 2-methyl-2-cholestene (**7**) requires an explanation. If electronic factors predominate in a transition state involving a chair-like conformation of the A ring, **17a,** the ketene must rotate almost 135° to complete bond formation through an equatorial bond. This process generates unfavorable steric interactions as a result of the ketene carbonyl interaction with the 1α-hydrogen and the interaction between the chlorine and the 3-methyl group. Alternately, if initial bond formation occurs through a semi-boat transition state, **17b,** then pseudoaxial bonding of the carbonyl is possible and the initial product of the cycloaddition would be the semi-boat conformation **13c,** which would then flip to **13b.** In either case, steric interactions or an energetically unfavorable boat intermediate would make the reaction of dichloroketene with 3-methyl-2-cholestene (**8**) a slow process.



8

17b **17a**

13c **13b**

In conclusion, the addition of dichloroketene to both 2-methyl- and 3-methyl-2-cholestene (**7** and **8**) is stereo- and regiospecific with bond formation occurring at the least hindered α side of the steroid molecule. In the addition to **7** both the electronic and the stereoelectronic factors favor formation of product **9,** but in the case of **8** the methyl substituent directs bond formation between the ketene carbonyl and the least substituted carbon of the olefinic bond in apparent contradiction to expected stereoelectronic control. However, in this case, the overriding electronic effects may still be compatible with axial bond formation by the ketene carbonyl onto a half-boat conformer of the steroid. Such a process avoids both β attack by the ketene from the more hindered side of the steroid and bonding with unfavorable electronic effects.

Experimental Section

Melting points were determined on a Fisher-Johns block and are uncorrected. Infrared spectra were obtained of liquid films or carbon tetrachloride solutions as noted on a Perkin-Elmer 457 instrument. NMR spectra were recorded on a Varian A-60A or EM-360 spectrometer with Me_4Si as an internal standard. Mass spectra were recorded on a Varian MAT CH5 instrument. CD spectra were obtained as chloroform solutions on a Cary 61 spectropolarimeter. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, Ga. Trichloroacetyl chloride and activated zinc were prepared as described[6] unless otherwise noted.

2a,2a-Dichloro-2α,3α-ethano-2β-methylcholestan-3a-one (9). To a stirred mixture of 2.0 g (5.2 mmol) of 2-methyl-2-cholestene (**7**)[12] and 1.05 g (16 mmol) of activated zinc in 75 mL of anhydrous ether was added a solution of 1.14 mL (1.89 g, 10.4 mmol) of Cl_3CCOCl and 0.95 mL (1.59 g, 10.4 mmol) of $POCl_3$ in 35 mL of anhydrous ether. When addition of the solution was complete, the mixture was refluxed with stirring. TLC (silica gel, 3:1 pentane/benzene eluent) indicated that olefin was consumed after 20 h. The usual workup afforded 2.50 g (97%) of a yellow solid. Recrystallization from ethyl formate/methanol afforded 1.85 g (72%) of **9**: mp 128–129 °C; IR (CCl_4) 1800 cm^{-1}; CD ($CHCl_3$) $[\theta]_{313}$ +8760; NMR ($CDCl_3$) δ 3.60–3.33 (1 H) and 1.50 (2β-methyl); MS *m/e* (%) 496 (15.0, M + 2), 494 (21.0, M^+), 468 (18.8), 466 (27.1), 383 (21.2), 329 (37.9), 287 (30.7), 119 (34.0), 107 (43.5), 105 (35.6), 95 (69.0), 81 (58.8), and 42 (100).

Anal. Calcd for $C_{30}H_{48}ClO$: C, 72.70; H, 9.76. Found: C, 72.93; H, 9.88.

2α,3α-Ethano-2β-methylcholestan-3a-one (10). To 2.0 g (4.05

mmol) of dichlorocyclobutanone **9** dissolved in 50 mL of hot acetic acid was added 2.0 g (30.6 mmol) of activated zinc.[13] The mixture was heated on a steam bath for 3 days and filtered through a pad of Celite, and the excess zinc was washed with 25 mL of ether. The solvents were removed in vacuo to leave 1.7 g of a slightly yellow solid. The solid was dissolved in 75 mL of ether, and the solution was washed with a saturated $NaHCO_3$ solution and dried over K_2CO_3. The solvent was removed in vacuo, and recrystallization from acetone afforded 1.44 g (83%) of **10**: mp 111.5–112.5 °C; IR (CCl_4) 1775 cm^{-1}; NMR ($CDCl_3$) δ 3.0–2.55 (3 H) and 1.43 (s, 3 H); CD ($CHCl_3$) $[\theta]_{297}$ +2200; MS *m/e* (%) (no M^+) 384 (33.8), 107 (37.5), 105 (37.4), 93 (47.1), 91 (26.8), 81 (48.1), 79 (32.3), 69 (35.4), 67 (35.9), 57 (45.9), 55 (73.3), and 42 (100).

Anal. Calcd for $C_{30}H_{50}O$: C, 84.44; H, 11.81. Found: C, 84.24; H, 11.93.

3α-Hydroxy-2β-methylcholestan-2α-acetic Acid Lactone (11). To a solution of 0.75 g (1.76 mmol) of cyclobutanone **10** in 25 mL of methanol and 25 mL of THF was added 0.60 g (~5.3 mmol) of a 30% H_2O_2 solution and 2.25 mL of a 1 M NaOH solution. The solution was stirred at room temperature. TLC (silca gel, benzene eluent) indicated that starting material was consumed after 2 h. The solvents were removed in vacuo, and the residue was taken up in 50 mL of ether/hexane (1:1), washed with a 5% HCl solution and water, and dried over K_2CO_3. The solvent was removed in vacuo to leave 0.75 g (96%) of a white solid. Recrystallization from 2-propanol yielded 0.52 g (67%) of **11**: mp 164–165 °C; IR (CCl_4) 1775 cm^{-1}; NMR ($CDCl_3$) δ 4.21 (broad, 1 H, $W_{1/2}$ = 6 Hz), 2.2 (broad, 2 H), and 1.23 (s, 3 H); MS *m/e* (%) 443 (32.1), 442 (100, M^+), 288 (64.5), and 287 (76.1).

Anal. Calcd for $C_{30}H_{50}O_2$: C, 81.39; H, 11.38. Found: C, 81.53; H, 11.50.

3a,3a-Dichloro-2α,3α-ethano-3β-methylcholestan-2a-one (13) was prepared from 8[14] in 61% (recrystallized) yield by a reaction analogous to that described above for **9** (reaction time 3 days). Dichlorocyclobutanone **13** had mp 121–122 °C; IR (CCl_4) 1800 cm^{-1}; CD ($CHCl_3$) $[\theta]_{325}$ −6930; NMR ($CDCl_3$) δ 3.03 (unresolved triplet, J = 10 Hz, 1 H); MS *m/e* (%) 496 (45.7, M + 2), (66.2, M^+), 468 (65.1), 467 (31.5), 466 (93.7), 453 (43.4), 452 (20.7), 451 (63.0), 316 (24.0), 315 (38.7), 314 (41.2), 313 (80.3), 312 (57.5), and 311 (100).

Anal. Calcd for $C_{30}H_{48}Cl_2O$: C, 72.70; H, 9.76. Found: C, 72.47; H, 9.81.

2α,3α-Ethano-3β-methylcholestan-2a-one (14) was prepared in 80% (recrystallized) yield by a reaction analogous to that described above for **11**. It melted at 133.5–134.5 °C; IR (CCl_4) 1777 cm^{-1}; CD ($CHCl_3$) $[\theta]_{297}$ −15 100; NMR ($CDCl_3$) δ 3.40–3.15 (1 H), 2.70–2.25 (2 H), and 1.23 (broadened s, 3 H); MS *m/e* (%) 385 (31.4), 384 (100), and 316 (64.4).

Anal. Calcd for $C_{30}H_{50}O$: C, 84.44; H, 11.81. Found: C. 84.36; H, 11.84.

2α-Hydroxy-3β-methylcholestan-3α-acetic Acid Lactone (15). To a solution of 0.50 g (1.17 mmol) of cyclobutanone **14** in 20 mL of methanol and 25 mL of THF was added 0.40 g (~3.5 mmol) of a 30% H_2O_2 solution and 1.5 mL of a 1 M NaOH solution. The solution was refluxed for 12 h, the solvents were removed in vacuo, and 50 mL of ether was added to the residue. The resulting solution was washed successively with a 5% HCl solution, water, and brine and dried over K_2CO_3. The solvent was removed in vacuo to leave 0.49 g (95%) of a white solid. Recrystallization from acetone yielded 0.36 g (70%) of **15**: mp 192.5–193.5 °C; IR (CCl_4) 1775 cm^{-1}; NMR ($CDCl_3$) δ 4.21 (poorly resolved d of d, J = 6, 12 Hz, 1 H, $W_{1/2}$ = 22 Hz); MS *m/e* (%) 443 (32.9, M + 1), 442 (100, M^+), and 287 (41.0).

Anal. Calcd for $C_{30}H_{50}O_2$: C, 81.39; H, 11.38. Found: C, 81.67; H, 11.56.

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Registry No.—**7**, 22599-90-2; **8**, 1249-78-1; **9**, 69351-08-2; **10**, 69309-28-0; **11**, 69309-29-1; **13**, 69309-30-4; **14**, 69309-31-5; **15**, 69309-32-6; trichloroacetyl chloride, 76-02-8; dichloroketene, 4591-28-0.

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(1) (a) Cycloadditions. 26. For part 25, see L. R. Krepski and A. Hassner, *J. Org. Chem.*, **43**, 3173 (1978). (b) Work performed in part at the University of Colorado, Boulder, Colo.
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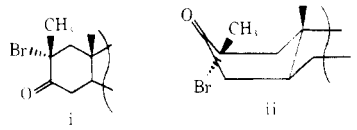

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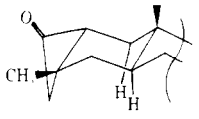

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