Further reactions of coordinated cyclobutadiene and their utility in the synthesis of strained molecules of interest will be discussed in subsequent papers.

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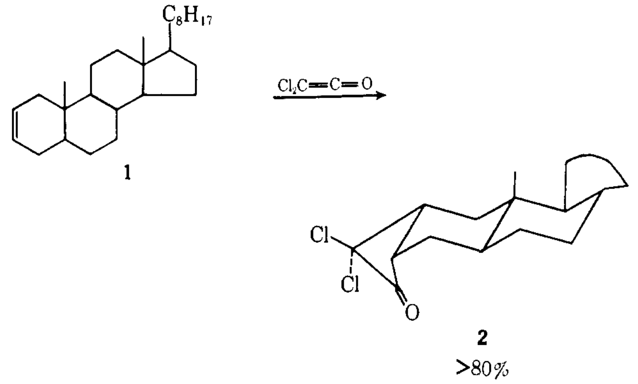
Stereoelectronic Effects in the Cycloaddition of Dichloroketene to Cyclohexenes[1]

Sir:

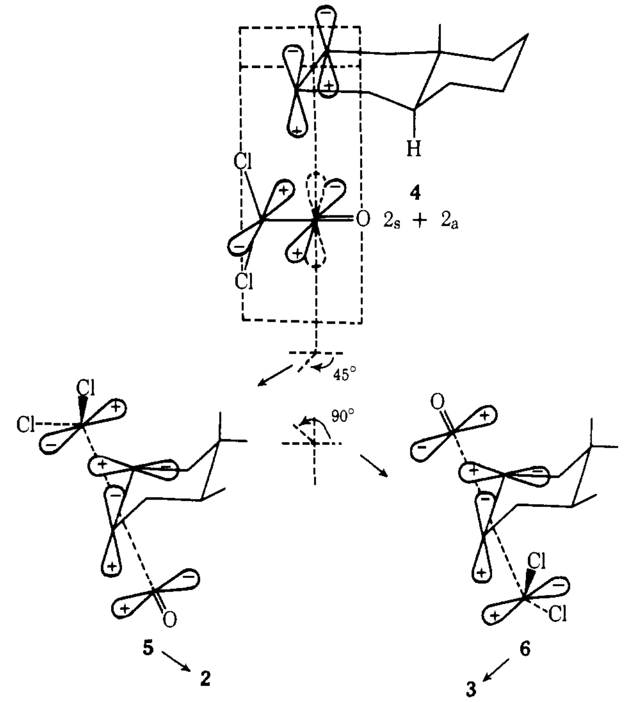
Recently cycloadditions of ketenes to olefins have attracted considerable interest,[2] and the high stereoselectivity of the process has been explained in terms of orbital symmetry.[3] A communication[4] from this laboratory has reported that the addition of dichloroketene to 2-cholestene (1) also exhibited an unusually high degree of regioselectivity[5] (Scheme I).

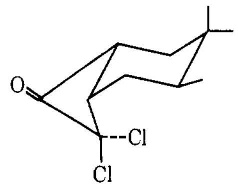
The preferred formation of 2 can be rationalized by considering the conformation of the possible products 2 and 3 as related to the transition state and the orbital overlap involved during the symmetry-allowed $2_s + 2_a$ process.

Scheme I



To complete orbital overlap (bond formation) from the orthogonal complex 4,[6] rotation of the ketene is required. If the transition state (5 or 6) is geometrically similar to the product, which we assume to be somewhat puckered,[7] a rotation of *ca.* 45° is required to afford isomer **2** (*via* transition state **5**). On the other hand, a rotation of the ketene between 90 and 135° is necessary to produce isomer **3** (*via* **6**). Following the principle of least motion,[8] transition state **5** should be favored, leading to the regioisomer **2**. This is equivalent to considering stereoelectronic control[9] in this cycloaddition (preferential axial orbital overlap in a chair conformer of the cyclohexane ring).





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In order to determine the generality of this effect we have studied the addition of dichloroketene to 4-*tert*-butylcyclohexene (7), where either side of the molecule is accessible to reagents (epoxidation gives a 3:2 ratio of cis:trans isomers).[10] If the cycloaddition to this olefin follows the selectivity shown by 2-cholestene, then one would expect predominantly two products (**8** and **9**, R = Cl), resulting from axial bond formation between the carbonyl carbon and the six-membered ring. If the reaction were not regioselective an equal distribution of four isomers (**8**–**11**, R = Cl) is expected.

Reaction of trichloroacetyl bromide with activated zinc[11] in the presence of **7** gave a product (ir 1800 cm^{-1}) which on reduction (Zn–HOAc, 100°) afforded a mixture of cyclobutanones A and B, free from chlorine,

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[1] Cycloadditions. V. Support of this work by the National Science Foundation is gratefully acknowledged.

[2] See, for instance, (a) H. C. Stevens, D. A. Reich, D. R. Brandt, R. R. Fountain, and E. J. Goughan, *J. Amer. Chem. Soc.*, **87**, 5257 (1965); (b) L. Ghosez, R. Montaigue, and P. Mollet, *Tetrahedron Lett.*, 135 (1966); (c) R. Huisgen, L. A. Feiler, and P. Otto, *ibid.*, 4485 (1968); (d) M. Rey, S. Roberts, A. Dieffenbacher, and A. S. Dreiding, *Helv. Chim. Acta*, **53**, 417 (1970); (e) W. T. Brady, E. F. Hoff, R. Roe, Jr., and F. H. Parry, Jr., *J. Amer. Chem. Soc.*, **91**, 5679 (1969); (f) J. E. Baldwin and J. A. Kapecki, *ibid.*, **92**, 4874 (1970).

[3] R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

[4] V. R. Fletcher and A. Hassner, *Tetrahedron Lett.*, 1071 (1970).

[5] Regio is used to describe directional selectivity in bond making or breaking: A. Hassner, *J. Org. Chem.*, **33**, 2686 (1968).

[6] Such a complex formation or transition state has been postulated for cycloadditions: T. Do Minh and O. P. Strausz, *J. Amer. Chem. Soc.*, **92**, 1768 (1970); P. R. Brook, J. M. Harrison, and A. J. Duke, *Chem. Commun.*, 589 (1970).

[7] Evidence for the nonplanar conformation of cyclobutanones is available: J. M. Conia and J. Gore, *Bull. Soc. Chim. Fr.*, 1968 (1964); A. Hassner and V. R. Fletcher, *Tetrahedron Lett.*, in press.

[8] J. Hine, *J. Org. Chem.*, **31**, 1236 (1966).

[9] E. J. Corey and R. A. Sneen, *J. Amer. Chem. Soc.*, **78**, 6269 (1956), see footnote 3.

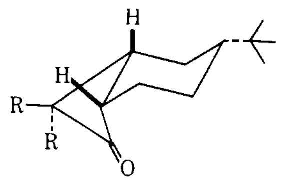
[10] B. Rickborn and J. Quartucci, *J. Org. Chem.*, **29**, 2476 (1964).

[11] W. T. Brady, H. G. Liddell, and W. L. Vaughn, *ibid.*, **31**, 626 (1966).

and in a ratio of 87:13 by glc. Separation by preparative glc yielded the two components A and B (ir 1770 cm^{-1}),[12] each of which was in turn resolved upon analytical glc into two peaks in the ratio of *ca.* 3:2.

Oxidation of the major component A with *m*-chloroperbenzoic acid produced two isomeric lactones[12] (ir 1780 cm^{-1}). Glc indicated two peaks in a ratio of *ca.* 2:1. At 100 MHz the nmr spectrum in the region of the proton next to oxygen was resolved into two multiplets (in a ratio of 2:1) at τ 5.5 and 5.36, each with a half-width of less than 9 Hz,[13] indicating that these protons were in an equatorial configuration. This indicates that both lactones contain the alkyl oxygen atom in an axial configuration relative to the cyclohexane ring, hence they must have structures **12** and **13** and have arisen from ketones **8** and **9** (R = H).

Hydrolysis of the lactone mixture gave hydroxy acids which, on methylation with diazomethane and CrO_3 oxidation, yielded ketoesters[12] **14** and **15** (ir 1740 and 1720 cm^{-1}) in the ratio of 3:2. The major component of the ketoesters was shown to be **14** by glc comparison with an authentic sample prepared by alkylation of the pyrrolidine enamine of 4-*tert*-butylcyclohexanone.



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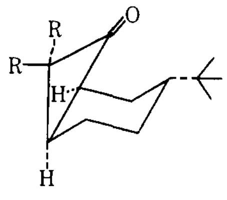

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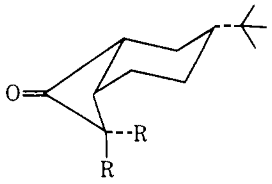

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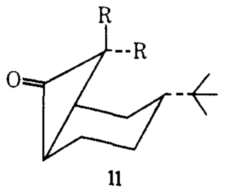

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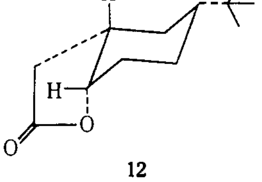
Preliminary attempts to add dichloroketene, generated from dichloroacetyl chloride and triethylamine,[14] to **7** have been unsuccessful. This suggests that possibly the additions we have observed involve a zinc-complexed ketene and therefore have a great deal of electrophilic character, in keeping with the stereoelectronic effects observed.



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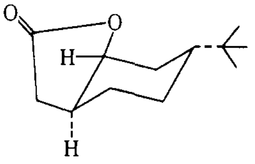

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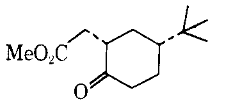

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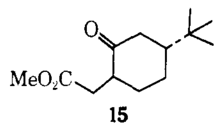

15

It is clear that in cyclohexene systems, unlike in many open-chain olefins,[15] ketene cycloaddition is not only stereospecific but highly regioselective. Namely, *the newly formed bond of the carbonyl carbon will prefer to be axial with respect to the six-membered ring* (chair conformation).

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(12) Consistent elemental analysis and nmr spectra were obtained for all compounds or isomeric mixtures isolated.

(13) For the use of half-width in conformational assignments, see A. Hassner and C. Heathcock, *J. Org. Chem.*, **29**, 1350 (1964).

(14) H. C. Stevens, D. A. Reich, D. R. Brandt, K. R. Fountain, and E. J. Gaughan, *J. Amer. Chem. Soc.*, **87**, 5257 (1965).

(15) Our preliminary results indicate that cycloaddition of 4,4-dimethylcyclohexene with dichloroketene leads predominantly to one regioisomer, as predicted from the orbital considerations discussed above. On the other hand, a most recent report by N. S. Isaacs and P. F. Stanbury, *Chem. Commun.*, 1061 (1970), indicates that ketene cycloaddition to 2-pentene is nonregioselective.

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A New 1:1 Adduct of Trimethylamine and Trichlorosilane, Trimethylammonium Trichlorosilyl

Sir:

Benkeser and coworkers[1] have recently demonstrated the usefulness of trichlorosilane–tertiary amine combinations in both organic and organosilicon chemistry. They postulated that the reactive species was the trichlorosilyl anion. Evidence for the existence of this anion in solution has now been obtained.[2,3] Bis(trichlorosilyl)mercury has also recently been obtained.[4] We wish to describe our results concerning a *new* 1:1 adduct of $N(CH_3)_3$ and $HSiCl_3$ which we believe must be $HN(CH_3)_3{}^+SiCl_3{}^-$.

It has been reported[5,6] that trimethylamine and trichlorosilane form a 1:1 adduct at −70° which decomposes below 0°. We have verified this result with the same quantities used by Burg ($HSiCl_3$, 0.19 mmol; $N(CH_3)_3$, 0.32 mmol). However, when larger quantities of reactants were used (see Table I), a different result was obtained. The trimethylamine and the trichlorosilane were condensed into a reaction tube at −196° (−78°). As the mixture warmed to room temperature, some of the condensate transformed into another white solid. The volatile fraction was recondensed and then allowed to warm to room temperature. This procedure was repeated until all or most of the trichlorosilane was consumed. We propose that the first condensate contained the complex observed by Burg which, in the presence of liquid trimethylamine, transferred a proton to form $(CH_3)_3NH^+SiCl_3{}^-$.

The results in Table I demonstrated that a 1:1 adduct was formed when a 2:1 excess of the amine was used. The solid had a vapor pressure of less than 1 mm at 25°. The infrared spectrum in Nujol contained the following absorptions (cm^{-1}): 2920 (vs), 2860 (vs), 2520 (vw), 2480 (w), 1460 (s), 1380

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(1) R. A. Benkeser and W. E. Smith, *J. Amer. Chem. Soc.*, **90**, 5307 (1968); **91**, 1556 (1969); R. A. Benkeser, J. M. Gaul and W. E. Smith, *ibid.*, **91**, 3666 (1969).

(2) R. A. Benkeser, K. M. Foley, J. B. Grutzner, and W. E. Smith, *ibid.*, **92**, 697 (1970).

(3) S. C. Bernstein, *ibid.*, **92**, 699 (1970).

(4) C. R. Bettler, J. C. Sendra, and G. Urry, *Inorg. Chem.*, **9**, 1060 (1970).

(5) A. B. Burg, *J. Amer. Chem. Soc.*, **76**, 2674 (1954).

(6) H. J. Campbell-Ferguson and E. A. V. Ebsworth, *J. Chem. Soc. A*, 705 (1967).