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REGIO- AND STEREOSELECTIVE CYCLOADDITIONS OF DICHLOROKETENE TO BRIDGED BICYCLIC OLEFINS

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Summary: Dichloroketene cycloadditions to selected bridged bicyclic compounds are described. The regio- and stereochemical course of these cycloadditions is discussed.

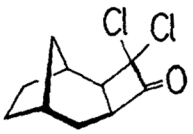
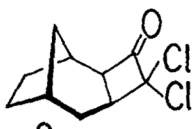
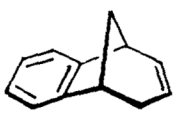
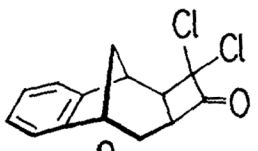
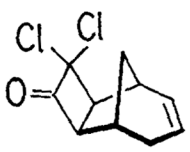
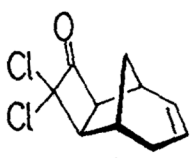
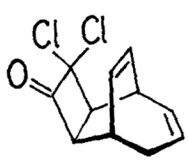
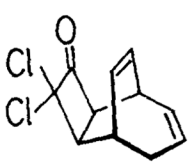
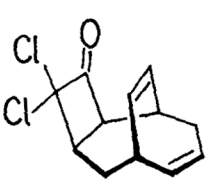
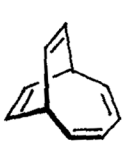
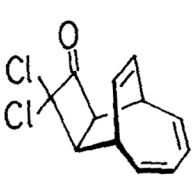
The annelation of a cyclopropane ring to a bridged bicyclic system is an exceptionally simple task.[1] Cyclobutane annelation to such compounds is considerably more difficult. We recently reported that cyclobutane-fused bicyclo[2.2.2]octenes could be conveniently prepared by addition of dichloroketene to the appropriate dienes.[2] This procedure has previously been limited to strained systems such as norbornene, norbornadiene, and α-pinene.[3,4]

Further studies indicate that this method is generally applicable to a wide variety of bridged bicyclic olefins and that the stereochemistry of the cycloadditions is readily predictable.

In this communication we report the cycloaddition of dichloroketene[5,6,7] to the bicyclic olefins 1-6 as well as the regio- and stereoselectivities observed for these systems. All adducts were purified by TLC (SiO_2, n-pentane/CH_2Cl_2 95:5) and characterized by elemental analyses, as well as IR and ^1H NMR spectral data.[8] The stereochemistry of the adducts was assigned on the basis of the ^1H chemical shifts of the appropriate methine protons. Our results are presented in Table 1.

The exclusive formation of exo-adducts from 1 and 2 parallels the stereoselectivities observed for the bicyclo[2.2.2]octadienes. Approach of dichloroketene (DCK) from the endo face in 1 (syn to the ethano bridge) apparently is sterically hindered. Attack of dichloroketene syn to the benzene ring is likewise impeded by steric interaction with the benzene ring with the result that only exo adducts are obtained. Whereas two regioisomers, 7 and 8, are obtained from the reaction of 1 with dichloroketene only one regioisomer, 9, is formed in the corresponding reaction of DCK with 2. We suggest that this latter result is due to electronic effects that the benzene ring exerts on the remote π-bond.

Table I. [2+2]Cycloadditions of Dichloroketene with Bridged Bicyclic Olefins.

Olefin	Cycloadduct	Ratio	% Yield
 1	 7  8	1:1	68
 2	 9		77
 3	 10  11	5:1	84
 4	 12  13	6:1	81
 5	 14		86
 6	 15		95

Bicyclo[3.2.1]octa-2,6-diene (3) reacted with dichloroketene exclusively on its cyclopentene moiety to give the two regioisomers, 10 and 11 in a ratio of 5:1. This corresponds to the previously reported[9] dipolar cycloadditions of chlorosulfonyl isocyanate and tetracyanoethylene to 3. We feel that in the case of the dichloroketene addition the preferential attack at the cyclopentene double bond in 3 is not due to the strain factor only. Inspection of Dreiding models indicates that the orthogonal approach of dichloroketene[10] to the cyclohexene part of 3 is sterically more hindered than the approach to the etheno bridge.

Bicyclo[3.2.2]nona-2,6,8-triene (4) afforded upon reaction with dichloroketene a mixture of the two regioisomers, 12 and 13, in a ratio of 6:1. The facial selectivity observed for 4 can be attributed to diminished steric interaction of dichloroketene upon an attack to the etheno bridge syn to the second etheno bridge. Similarly, bicyclo [3.3.2]deca-2,6,9-triene (5) gave under the same conditions with dichloroketene a single adduct, 14. Examination of space-filling molecular models indicates that approach of DCK to the etheno bridge in 5 causes greater steric interaction with the propeno bridge than an attack at C2-C3 on the face syn to the etheno bridge.

Finally, bicyclo[4.2.2]deca-2,4,6,9-tetraene (6) reacted with dichloroketene to give 15 as the sole cycloadduct. It is noteworthy that 15 showed no tendency to undergo an intramolecular [4+2]cycloaddition. This is in contrast to the dibromocarbene adduct of 6 which exists in an equilibrium with its pentacyclic valence isomer.[11]

Our results show that bridged bicyclic olefins readily react with dichloroketene to give [2+2] cycloadducts. Approach of dichloroketene occurs distal to the ethano and benzeno bridges and syn to methano bridges. In systems with larger bridges, attack of dichloroketene occurs syn to the etheno bridge. Steric factors appear to dictate the facial selectivities of dichloroketene cycloadditions. Remote π-systems (etheno or benzeno bridges) have a strong directing effect on the regioselectivity of the cycloaddition. Clearly, dichloroketene cycloadditions to bridged bicyclic olefins offer a convenient entry into several new cyclobutyl annelated hydrocarbons. We are currently studying dichloroketene cycloadditions to other bridged alicyclic olefins which contain the cis-divinyl cyclopropane moiety and will report our results shortly.

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5) In this study dichloroketene was generated in situ by the zinc-promoted reductive dechlorination of trichloroacetylchoride, as recommended by Brady[4] and Hassner.[6]

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7) Brady, W. T., Tetrahedron Report No. 113, Tetrahedron, 37, 2949 (1981); b) Patai, S., "The Chemistry of Ketenes, Allenes and Related Compounds", Interscience, N.Y. (1980).

8) Spectral data of the adducts: 7+8: IR (film): 2920, 2850, 1805, 1460 cm^{-1}. ^1H NMR ($CDCl_3$, TMS): δ 3.75 (dt, 1H); 2.89 (d, 1H); 3.83 (dm, 1H): 3.05 (dt, 1H); 2.42 (m, 1H); 2.13 (m, 1H); 2.05-1.24 (m, 8H). Signals at 3.83 and 3.05 ppm were assigned to H(2) and H(5) in 8. Adduct 9 (mp. 128-129°, n-hexane): IR (KBr): 3070, 3020, 2960, 2930, 1800, 1480, cm^{-1}. ^1H NMR ($CDCl_3$, TMS): δ: 7.21 (m, 4H); 3.75 (dt, ^3J = 10.37, 1.5 Hz, 1H); 3.57 (d, ^3J = 4.89, 1H); 3.15 (t, ^3J = 6.11 Hz, 1H); 3.01 (d, ^3J = 10.37 Hz, 1H); 2.56 (m, 1H); 2.20 (m, 1H); 2.12-1.76 (m, 2H). Adducts 10+11: IR (film); 3015, 2945, 2875, 2825, 1805, 1455, 1440 cm^{-1}. ^1H NMR ($CDCl_3$ TMS): δ: 5.99 (m, 1H); 5.49 (m, 1H); 4.13 (d, ^3J = 7.01 Hz, 1H); 3.85 (d, ^3J = 7.33 Hz, 1H); 3.42 (d, ^3J = 7.33 Hz, 1H); 3.16 (d, ^3J = 7.01 Hz, 1H); 2.78 (m, 2H); 2.48 (dm, A part of an AB system, 1H); 1.90 (dm, B part, 1H); 1.83 (br.s, 1H). Signals at 4.13 and 3.16 ppm were assigned to H(5) and H(2) in 11. Adducts 12+13 (mp. 78-84°, n-hexane): IR (KBr): 3035, 2980, 2950, 2900, 2840, 1815, 1430, 1390, 1380, 1265 cm^{-1}. ^1H NMR ($CDCl_3$ TMS): δ: 6.31 (m, 1H); 6.10 (m, 1H); 5.96 (m, 1H); 5.66 (m, 1H); 4.43 (dd, ^3J = 9.44, 3.35 Hz, 1H); 4.12 (dd, ^3J = 9.46 , 3.05, Hz, 1H); 3.64 (ddd, ^3J = 9.46, 2.13, 0.61 Hz, 1H); 3.40 (d, ^3J = 9.44, Hz, 1H); 3.09 (m, 1H); 2.92 (m, 1H); 2.31 (m, 2H); signals at 4.43 and 4.12 ppm were assigned to H(2) and H(5) in 13. Adduct 14: IR (film): 3040, 2990, 2920, 1815, 1450, 1435, 1410, 1355, 1310 cm^{-1}. 360 MHz ^1H NMR ($CDCl_3$, TMS): δ: 6.08 (t, ^3J = 9.76 Hz, 1H); 5.92 (t, ^3J = 9.76 Hz, 1H); 5.74 (m, 1H); 5.62 (m, 1H); 4.06 (dd, ^3J = 10.99, 2.44 Hz, 1H); 3.40 (q, ^3J = 10.99 Hz, 1H); 2.97 (q, ^3J = 7.32 Hz, 1H); 2.90 (m, 1H); 2.47 (dd, ^2J = 18.31, ^3J = 2.34 Hz, 1H); 2.23-2.07 (m, 2H); 1.80 (dd, ^2J = 12.42, ^3J = 10.99 Hz, 1H).

Adduct 15 (mp. 98-99.5°, n-hexane): IR (KBr): 3040, 2925, 1800, 1400, 1280, 1240 cm^{-1}. 360 MHz ^1H NMR ($CDCl_3$, TMS). δ: 6.08 (dt, ^3J = 9.76, 3.66 Hz, 1H); 5.98 (dt, ^3J = 9.76, 3.66 Hz, 1H); 5.83 (m, 3H); 5.70 (dd, ^3J = 9.76, 7.32 Hz, 1H); 4.21 (d, ^3J = 10.99 Hz, 1H); 3.45 (d, ^3J = 10.99 Hz, 1H); 3.25 (dd, ^3J = 7.32, 6.10 Hz, 1H); 3.15 (ddd, ^3J = 9.76, 7.32, 2.44 Hz, 1H).

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