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STEREOSELECTIVITIES OF DICHLOROKETENE CYCLOADDITIONS TO BRIDGED BICYCLIC OLEFINS

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Abstract Dichloroketene cycloadditions to bicyclic olefins **1** - **4** are described. Some interesting regio- and stereoselectivities are observed for **2** and **3** yielding **8** and **10** predominantly. Rationalizations are based upon previously reported arguments.

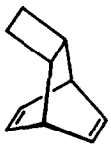
Norbornene and many of its derivatives are attacked by a variety of cycloaddends preferentially on the exo face of the double bond [1] Because of the uncertain origin of this effect Huisgen[2] named it factor "X". Recently K. N. Houk[3] et al. offered as a consistent explanation of both reactivity and stereoselectivity phenomena observed in such electrophilic additions that only exo attack on norbornene can occur with nearly ideal staggering of the partially formed new bonds with respect to the CC and CH bonds on the bridgehead carbon. Attack on the endo face of norbornene involves greater eclipsing with the bond to the bridging carbon. Accordingly, norbornene and norbornadiene are known to react with dichloroketene to give exclusively the respective exo dichlorocyclobutanones.[4] To the best of our knowledge, reactivities of bicyclo[2.2.2]octenes and other bicyclic compounds with larger bridges towards dichloroketene have not previously been reported. Herein we describe the first examples of dichloroketene cycloadditions to bicyclo[2.2.2]-octenes.

Dichloroketene, generated in situ from trichloroacetyl chloride and activated zinc in refluxing diethylether[5] reacted smoothly with the bicyclic olefins **1** - **4** to give the respective 2,2-dichlorocyclobutanone derivatives **7**, **8** and **9** (86 14), **10** and **11** (82.18) and **12** (table I). All adducts were purified by TLC (SiO_2, n-pentane/CH_2Cl_2 95 5) and fully characterized by satisfactory elemental analyses, IR, ^1H and ^{13}C NMR spectral data (see table I). Stereochemical assignments were made on the basis of NMR spectra and their comparison with those of suitable model compounds.

It is noteworthy that bicyclo[2.2.2]octene (**5**) and benzobicyclo[2.2.2]octadiene (**6**) failed to react with dichloroketene under identical conditions as employed for **1**, **2**, **3** and **4**. Although a complete rationalization of the stereoselectivities observed for **1** and **4** and the failure of the cycloadditions to **5** and **6** can not yet be offered, it is evident

1

2



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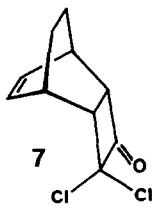

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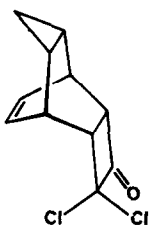

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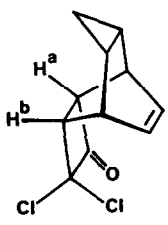

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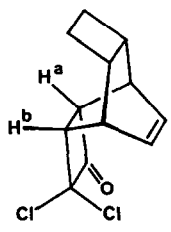

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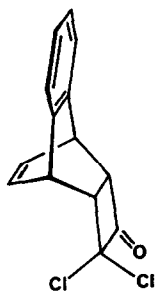

12

that steric factors might be operative, as molecular models reveal, approach of dichloroketene to the exo face of one of the double bonds in **1** should lead to a strong steric interaction with the hydrogens of the saturated bridge, there is less steric interaction upon an approach to the endo face, which is syn to the etheno bridge. In **4** the exclusive endo attack of dichloroketene, which occurs on the face distal to the benzene ring, might likewise be due to increased steric interaction in the exo approach, i e. proximal to the benzene ring Failure of dichloroketene to react with **6** under the conditions employed for **4** suggests that attack from both directions is kinetically unfavorable except at higher temperatures at which polymerization of dichloroketene competes with cycloaddition. In analogy, the electrophilic cycloaddition of chlorosulfonylisocyanate (CSI) to benzobarre-

lene (**4**) has been reported by Paquette et al.[6] to occur with exclusive attack of CSI distal to the benzene ring. In the case of homobarrelene (**2**) and tricyclo[4.2.2.0]deca-7,9-diene (**3**), mixtures of exo,exo (from exo distal) and exo,endo isomers (from endo distal approach) (86 14 and 82 18, respectively) were formed. This same stereoselectivity was observed upon cyclopropanation and epoxidation of **2** and **3**[7,8]. While the endo proximal

Table I. Cycloadditions of dichloroketene to bicyclic olefins **1** - **4**. Physical and spectroscopic data of the products **7** - **12**.

Compd. (Yield)	Physical data

7 (86%) Mp 84-85°C (n-hexane), ^{1}H-NMR (100 MHz, $CDCl_3$) δ_{TMS} = 1.42(m, 4H), 3.02(m, 1H), 3.09 (m, 2H), 3.90(dd, ^3J = 4.80, 12.40 Hz, 1H), 6.22(m, 1H), ^{13}C-NMR (25.1 MHz, $CDCl_3$) δ_{TMS} = 21.84, 24.03, 29 30, 31.34, 50.11, 61.64, 86.94, 132.14, 133.17, 195.29, IR (KBr) 3050, 2950, 2850, 1805, 1420, 1370, 1260, 1200, 1050, 950, 780 cm^{-1}.

8 + **9** (72%) ^{1}H-NMR (100 MHz, $CDCl_3$) **8** δ_{TMS} = 0.28(m, 2H), 0.98(m, 2H), 3.23(m, 3H), 4.03(dd, ^3J = 4.90, 8.54 Hz, 1H), 5.77(m, 2H), **9** δ_{TMS} = 3.03(m, H^b), 3.72(dd, ^3J = 4.90, 8.54 Hz, H^a), 6.47(m, 2H, olefinic). ^{13}C-NMR (25.1 MHz, $CDCl_3$) **8** δ_{TMS} = 3.58, 8.13, 9 46, 31.18, 32.70, 51.81, 62.79, 84.82, 126.92, 126.68, 195.23, **9**.δ_{TMS} = 137 24, 135.66 (olefinic C), IR (KBr) **8** + **9**. 3050, 3000, 2920, 1805, 1380, 1190, 1045, 820, 730 cm^{-1}.

10 + **11** (76%) Mp. 77 - 79°C (n-hexane), ^{1}H-NMR (100 MHz, $CDCl_3$) **10** δ_{TMS} = 1.51(m, 2H), 2.02(m, 2H), 2.46(m, 2H), 2.84(dd, ^3J = 3.35, 8.86 Hz, 1H), 3.02(m, 2H), 3.75(dd, ^3J = 4.58, 8.55 Hz, 1H), 6.36(m, 2H), **11** δ_{TMS} = 3 61(dd, ^3J = 3.34, 8.90 Hz, H^b), 4.27(dd, ^3J = 4.58, 8.56 Hz, H^a), 6.23(m, 2H, olefinic), ^{13}C-NMR (25.1 MHz, $CDCl_3$) **10**·δ_{TMS} = 22.02, 22.39, 33.55, 35.37, 36.65, 49.08, 60.06, 86.76, 131.47, 132.75, 195.29, **11**·δ_{TMS} = 136.66, 135.23 (olefinic C), IR (KBr) **10** + **11** 3050, 2970, 2930, 1805, 1390, 1210, 900, 780 cm^{-1}.

12 (89%) Mp 112 - 113°C (n-hexane), ^{1}H-NMR (100 MHz, $CDCl_3$) δ_{TMS} = 3.20(dd, ^3J = 3.36, 8.55 Hz, 1H), 4 08 (dd, ^3J = 4 58, 8.55 Hz, 1H), 4.30(m, 1H), 4 44(m, 1H), 6.56(m, 2H), 7.16(m, 4H), ^{13}C-NMR (25 1 MHz, $CDCl_3$) δ_{TMS} = 39.92, 42.29, 52.78, 82.39, 123.58, 124.01, 126 07, 126 19, 133.11, 136.14, 141.36, 142.70, 193.05, IR (KBr) 3050, 3000, 2950, 1800, 1470, 1350, 1050, 1030, 960, 940 cm^{-1}.

attack is prevented in both cases by steric hindrance, the other two modes of attack (exo distal and endo distal) of dichloroketene as of any other electrophile[8] must be determined mainly by electronic effects that the cyclopropyl and cyclobutyl groups exert on the two π-systems. In addition, the transition states leading to the respective exo,endo adducts **9** and **11** involves a change of hybridization at positions C^8,C^9 and C^9,C^{10} respectively, bringing the hydrogens in these positions closer to the cyclobutyl and cyclopropyl groups respectively. Although the resulting steric interaction must be smaller in the case of **2** than of **3**, the observed endo distal preference is larger for **2**. This steric effect therefore must be overruled by the differentiating through space interactions of the cyclopropyl and cyclobutyl groups with the two π-bonds in **2** and **3**, respectively[8,9].

We are currently studying dichloroketene additions to other bridged bicyclic ring systems in order to gain more insight into the factors controlling the variations observed in facial selectivities.

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9. Although our rationalization is somewhat detailed we realize that the differences in the free energies of activation are $\sim$1 kcal/mol.

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