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Stereochemical Control Exerted by Methoxyl Group on the Diiodomethane-Copper Methylenation of Cyclic Olefins Containing Methoxyl Group

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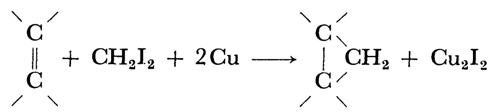
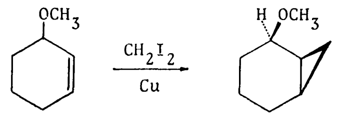
Synopsis. In the diiodomethane-copper methylenation of 3- and 4-methoxycyclopentenes and 3-methoxycyclohexene, the cis isomers of the cyclopropane derivatives predominated over the corresponding trans isomers, the trans isomer of cyclopropane derivatives being predominantly obtained from 3-methoxycyclooctene.

Reports have been given on the synthesis of cyclopropane derivatives from olefins by the reaction with diiodomethane and copper.[1,2] The reaction gave



$$>C=C< + CH_2I_2 + 2Cu \longrightarrow >C(CH_2)C< + Cu_2I_2$$

cyclopropane derivatives in good yields as in the corresponding Simmons-Smith reaction.[3] The reaction proceeded stereospecifically, *i.e.*, cis and trans olefins afforded cyclopropane derivatives whose configurations with respect to the olefin substituents were cis and trans, respectively. Moreover, the ether functions controlled the stereochemistry of the cycloaddition, *cis*-2-methoxybicyclo[4.1.0]heptane being exclusively obtained from 3-methoxycyclohexene.[2] This type of

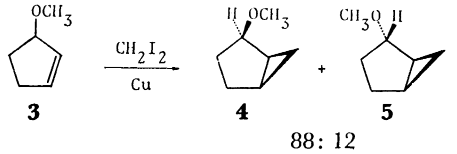


1 **2**

stereospecific synthesis of cyclopropane derivatives in the Simmons-Smith reaction has been widely used in synthesis.[4] The present work deals with an investigation of the stereochemistry of the diiodomethane-copper methylenation with olefins containing oriented ether functions.

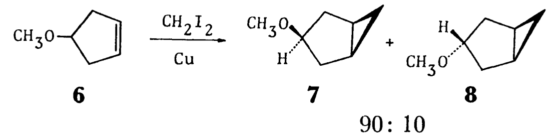
Results and Discussion

Reaction of 3-methoxycyclopentene with diiodomethane and copper powder gave an 88: 12 mixture of *cis*- and *trans*-2-methoxybicyclo[3.1.0]hexane in 75% yield. Reaction of 4-methoxycyclopentene with diiodomethane and copper powder gave a 90: 10 mixture of



3 **4** **5**

88: 12

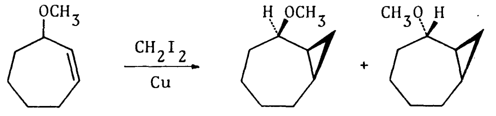


6 **7** **8**

90: 10

cis- and *trans*-3-methoxybicyclo[3.1.0]hexane in 70% yield. The structures of these cyclopropane derivatives were determined by comparison of their spectral data with those of authentic materials.[5]

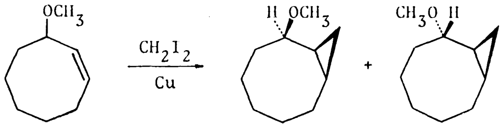
Reaction of 3-methoxycycloheptene with diiodomethane and copper powder gave a 57: 43 mixture of *cis*- and *trans*-2-methoxybicyclo[5.1.0]octane in 77% yield. The relative configurations of these cyclopropane derivatives were assigned on the basis of their ^{1}H NMR spectra. The cis isomer **10** and the trans isomer **11** showed absorptions due to the protons geminal to the methoxyl group at δ 3.65 with a width at half-height of 13 Hz and δ 2.70 with a width at half-height of 17 Hz, respectively. This is in line with the cis and trans configurations of the cyclopropane ring to the methoxyl group, respectively. In the case of 2-hydroxybicyclo[5.1.0]octanes, the peak due to the hydrogen atom geminal to the hydroxyl group of the trans isomer appears at δ 3.3 with a width at half-height of 15 Hz, the corresponding peak of the cis isomer appearing at δ 4.2 with a width at half-height of 10 Hz.[6]



9 **10** **11**

57: 43

The reaction of 3-methoxycyclooctene with diiodomethane and copper powder gave an 18: 82 mixture of *cis*- and *trans*-2-methoxybicyclo[6.1.0]nonane in 83% yield. The relative configurations of these cyclopropane derivatives were also determined on the basis of their ^{1}H NMR spectra. The cis isomer **13** and the trans isomer **14** showed absorption due to the protons geminal to the methoxyl group at δ 3.78 with a width at half-height of 11 Hz, and δ 2.72 with a width at half-height of 18 Hz, respectively. This is in line with the cis and trans configurations of the cyclopropane ring to the methoxyl group, respectively.[6]



12 **13** **14**

18: 82

In brief, preferential cis-directive addition was observed in reactions with the methoxycyclopentenes and the methoxycyclohexene, and preferential trans-directive addition being observed in the reaction with the methoxycyclooctene. Stereochemical control of the methoxyl group was weak in the reaction with the methoxycycloheptene.

The stereospecific synthesis in the Simmons-Smith reaction with cyclic allylic alcohols was explained in terms of the attack of organozinc reagent on the nearest face of the neighboring double bond after coordination to the oxygen atom of the substrate.[7] Models of the 3- and 4-methoxycyclopentenes and 3-methoxycyclohexene indicate that the methoxyl group can only function as a cis-director. The model of 3-methoxycyclooctene shows that addition in the trans-direction is favored. On the other hand, the model of 3-methoxycycloheptene is less useful for determining which face of the double bond is more accessible.

In the Simmons-Smith reaction with cyclic allylic alcohols,[7] the cis isomers of the corresponding cyclopropane derivatives were exclusively obtained from 2-cyclopenten-1-ol and 2-cyclohexen-1-ol, the trans isomers of the cyclopropane derivatives being exclusively obtained from 2-cycloocten-1-ol and 2-cyclononen-1-ol. A 90: 10 mixture of the cis and trans isomers of the cyclopropane derivatives was obtained from cyclohepten-1-ol.[7]

The methoxyl group shows a tendency in stereochemical control in the cycloaddition of copper carbenoid to cyclic olefins containing the methoxyl group similar to that in the Simmons-Smith reaction with cyclic allylic alcohols, although the control was weak in the diiodomethane–copper methylenation. This can be interpreted in terms of the weaker interaction of the methoxyl group with copper carbenoid in the transition state than that of the hydroxyl group with the organozinc intermediate in the Simmons-Smith reactions, since copper halides are weaker Lewis acids than zinc halides.

Experimental

Elemental analyses were performed at the Elementary Analyses Center of Kyoto University. ^{1}H NMR spectra were taken on a Varian T-60-A spectrometer in carbon tetrachloride using tetramethylsilane as an internal standard, IR spectra on a Hitachi 215 grating spectrophotometer, and mass spectra on a Hitachi Model RMU-6 mass spectrometer. VPC analyses were performed on a Shimadzu GC-4C gas chromatograph.

Materials. 3-Methoxycyclopentene was prepared according to the conventional procedure.[8] 4-Methoxycyclopentene, 3-methoxycycloheptene, and 3-methoxycyclooctene were prepared by the conventional method[9] from 3-cyclopenten-1-ol,[10] 2-cyclohepten-1-ol,[11] and 2-cycloocten-1-ol,[12] respectively. Commercial copper powder was used without further purification. Diiodomethane and benzene were purified by distillation. Other chemicals were used without further purification.

Procedure. Reactions of cyclic olefins containing methoxyl group with diiodomethane and copper powder were carried out as reported.[1,2] Yields were determined by VPC analysis of the reaction mixture on the basis of olefin. Products were isolated by collection from the reaction mixture by VPC, and analyzed.

2-Methoxybicyclo[3.1.0]hexane. Reaction of 3-methoxycyclopentene (0.20 g, 2.05 mmol), diiodomethane (1.05 g, 3.97 mmol), copper powder (0.58 g, 9.16 mmol), and iodine (0.015 g, 0.12 mmol) in 1.5 ml of benzene at 75 °C for 72 h gave an 88: 12 mixture of *cis*- (**4**) and *trans*-2-methoxybicyclo[3.1.0]hexane (**5**) in 75% yield based on the olefin.

2-Methoxybicyclo[3.1.0]hexane. Reaction of 4-methoxycyclopentene (0.18 g, 1.85 mmol), diiodomethane (1.07 g, 4.00 mmol), copper powder (0.58 g, 9.13 mmol), and iodine (0.017 g, 0.14 mmol) in 1.5 ml of benzene at 75 °C for 72 h gave a 90: 10 mixture of *cis*- (**7**) and *trans*-3-methoxybicyclo[3.1.0]hexane (**8**) in 70% yield based on the olefin.

2-Methoxybicyclo[5.1.0]octane. From 3-methoxycycloheptene (0.25 g, 1.95 mmol), diiodomethane (1.03 g, 3.86 mmol), copper powder (0.58 g, 9.16 mmol) and iodine (0.015 g, 0.12 mmol) in 1.5 ml of benzene at 75 °C for 96 h was obtained a 57: 43 mixture of *cis*- (**10**) and *trans*-2-methoxybicyclo[5.1.0]octane (**11**) in 77% yield based on the olefin. Found: C, 77.00; H, 11.62%. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50%. The cis isomer (**10**): ^{1}H NMR (CCl_4) δ 0.2—2.5 (m, 12H), 3.20 (s, 3H), 3.65 (m, 1H, width at half-height= 13 Hz). The trans isomer (**11**): ^{1}H NMR (CCl_4) δ 0.2—2.5 (m, 12H), 2.70 (m, width at half-height= 17 Hz), 3.35 (s, 3H).

2-Methoxybicyclo[6.1.0]nonane. From 3-methoxycyclooctene (0.25 g, 1.81 mmol), diiodomethane (1.04 g, 3.90 mmol), copper powder (0.61 g, 9.53 mmol), and iodine (0.015 g, 0.12 mmol) in 1.5 ml of benzene at 75 °C for 96 h was obtained an 18: 82 mixture of *cis*- (**13**) and *trans*-2-methoxybicyclo[6.1.0]nonane (**14**) in 83% yield based on the olefin. The cis isomer (**13**): n_D^{30}= 1.4705; ^{1}H NMR (CCl_4) δ 0.2—2.3 (m, 14H), 3.21 (s, 3H), 3.78 (m, 1H, width at half-height= 11 Hz); MS *m/e* (rel intensity) 154 (1.0, M^+), 93 (59), 81 (65), 80 (74), 79 (100). Found: C, 78.12; H, 11.83%. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76%. The trans isomer (**14**): n_D^{30}= 1.4665; ^{1}H NMR (CCl_4) δ 0.0—2.3 (m, 14H), 2.72 (m, 1H, width at half-height= 18 Hz), 3.29 (s, 3H); MS *m/e* (rel intensity) 154 (1.0, M^+), 93 (59), 81 (67), 80 (50), 79 (100); Found: C, 77.75; H, 11.79%. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76%.

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