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Stereoelectronic and Homoconjugative Effect of Stereoselectivity. The Addition of Dichlorocarbene to 1,5-Dimethyl-6-methylenetricyclo[3.2.1.$0^{2,7}$]oct-3-en-8-one and Its Related Compounds

Makoto NITTA,* Shuji OKADA, and Masami KATO
Department of Chemistry, School of Science and Engineering, Waseda University, Shinjuku-ku, Tokyo 160
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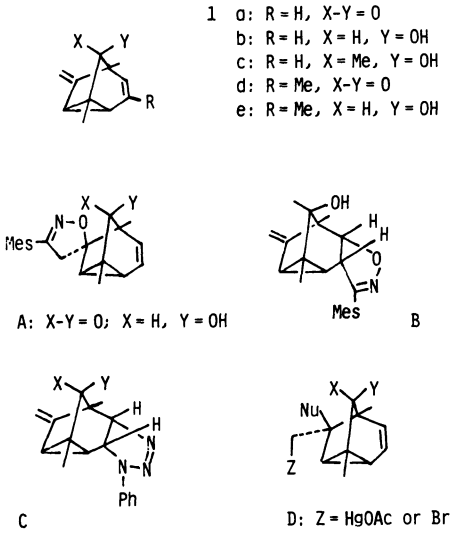
The reaction of dichlorocarbene with 1,5-dimethyl-6-methylenetricyclo[3.2.1.$0^{2,7}$]oct-3-en-8-one, its corresponding alcohol derivative, and 1,5,8-trimethyl-6-methylenetricyclo[3.2.1.$0^{2,7}$]oct-3-en-8-*endo*-ol occurs on the exocyclic double bond to give *exo* and *endo* adducts with preferential formation of the *exo* adduct. Dichlorocarbene addition to 1,3,5-trimethyl-6-methylenetricyclo[3.2.1.$0^{2,7}$]oct-3-en-8-one (**1d**) occurs on the endocyclic double bond from the *exo* side, while the reaction occurs on the exocyclic double bond from both the *exo* and *endo* sides in the case of the corresponding alcohol derivative. The stereoselectivity or site selectivity was discussed on the basis of the stereoelectronic and homoconjugative effects as well as the steric effect of the reaction. Several chemical transformations, along with the derivation of bis adducts of dichlorocarbene, were also studied for confirmation of the structure of mono adducts. 1,3-Dipolar cycloaddition of **1d** and its dichlorocarbene adduct with mesitonitrile oxide, giving the adducts on the exocyclic double bond, was also studied to suggest a possible causative factor to control the electrophilic addition in the indicated direction.

Recently the stereoselectivities and/or site selectivities of electrophilic reactions or cycloadditions of molecules containing proximal π-bonds have been investigated.[1] In a previous paper,[2] we have shown that the 1,3-dipolar cycloadditions of mesitonitrile oxide (MNO) or phenyl azide (PA) to 1,5-dimethyl-6-methylenetricyclo-[3.2.1.$0^{2,7}$]oct-3-en-8-one (**1a**), its alcohol derivative (**1b**), and 1,5,8-trimethyl-6-methylenetricyclo[3.2.1.$0^{2,7}$]oct-3en-8-*endo*-ol (**1c**) exhibit a remarkable stereoselectivity and site selectivity to give the products of **A**, **B**, and **C**. The stereoselectivity giving *exo* adduct **A** could be ascribed to the preferential MNO(LUMO)-**1a**,**b**(HOMO) interaction. When the *exo* attack on the exocyclic double bond is sterically hindered by the methyl group at 8-position of **1c**, the addition occurs on the endocyclic double bond to give **B**. In the dipolar cycloaddition of PA, PA(LUMO)-**1a**, **b**(HOMO) interaction giving the type **A** adduct could be prohibited by the large van der Waals nonbonded interaction of the phenyl group with the C_1–C_5 bridge of **1a**,**b**, thus the adduct **C** could be obtained.

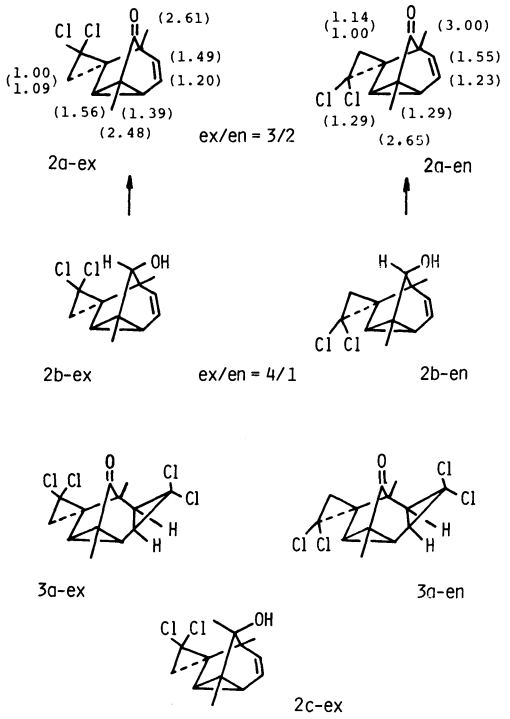


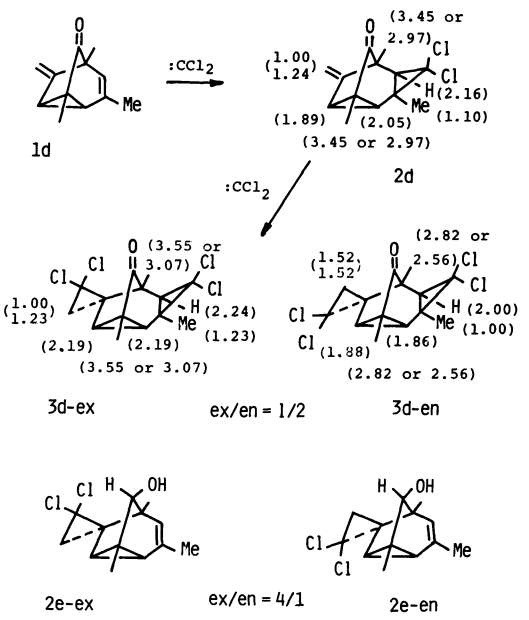
The prohibited *endo* attack of MNO and PA on the exocyclic double bond of **1a**,**b** or **1c** could be ascribed to the repulsive orbital interaction, which would be experienced with the endocyclic double bond. Similar stereoselection of electrophilic reactions such as solvomercuration, bromination and its related reaction on the exocyclic double bond of **1a**—**c** have been found to give the type D products.[3] In order to gain insight into the correlation for stereoselectivity of various electrophiles, the cheletropic reactions of dichlorocarbene with **1a**—**c** and its trimethyl analogue **1d**,**e** were investigated. In addition, 1,3-dipolar cycloadditions of **1d** and its dichlorocarbene adduct **2d** with MNO were also studied to find a plausible factor to control the stereoselectivity of 1,3-dipolar cycloaddition and dichlorocarbene addition.

Results and Discussion

The reaction of **1a**[4] with dichlorocarbene, generated by the usual phase transfer method,[5] occurred on the exocyclic double bond to give *exo* adduct **2a-ex** (48%) and *endo* adduct **2a-en** (31%) in a ratio of 3/2. A similar reaction of **1b**[6] with dichlorocarbene also afforded a mixture of two adducts, **2b-ex** (66%) and **2b-en** (16%), in a ratio of 4/1. The mixture was not separable. On oxidation with pyridinium chlorochromate, however, the mixture was converted to a mixture of **2a-ex** and **2a-en** (in a ratio of 4/1) in a 63% yield. Thus the correlation of **2a-ex** with **2b-ex** as well as **2a-en** with **2b-en** was clarified.

The structural proof for **2a-ex** and **2a-en** was based on the analytical and spectroscopic data. The stereochemical arrangement of the dichlorocarbene moiety of **2a-ex** and **2a-en** was deduced from the pseudo-contact NMR spectra obtained by using Eu(fod)$_3$. The relative downfield shifts of δ's are given in parentheses in the structural formulae.[7] The relatively large value of 1.14 for one of the methylene protons of the spirocyclopropane ring of **2a-ex**, as compared to the value of 1.01 for that of **2a-en**, could support the stereochemistry of the dichlo-





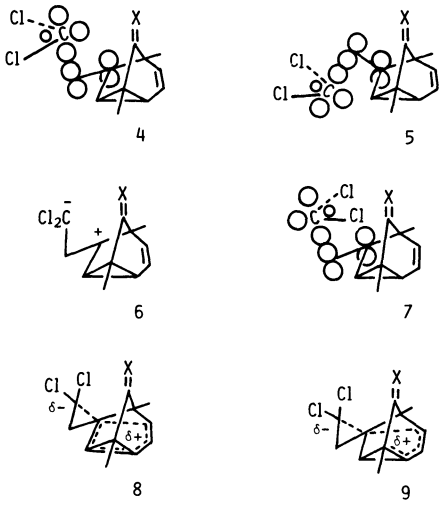
rocarbene moiety. Furthermore, in the reaction of **2a-ex** and **2a-en** with dichlorocarbene, the addition occured on the endocyclic double bond from the *exo* side giving **3a-ex** and **3a-en** respectively. The structures were deduced from the elemental analyses and the spectral data. Regarding the NMR spectra of **3a-ex** and **3a-en**, the noteworthy results include the chemical shifts of two hydrogens of dichlorocyclopropane moiety incorporated on the endocyclic double bond of **2a-ex** and **2a-en**. In the case of **3a-ex**, the key proton absorptions were seen at δ 2.37 and δ 2.50 (see Experimental). In the case of **3a-en**, however, the corresponding proton absorptions appeared at higher fields of δ 1.82 and δ 2.23. These trends are also observed for similar adducts, **2d-ex** and **2d-en** (*vide infra*). The *endo* orientation of chlorine ligand of spirocyclopropane moiety seems to cause a substantial change in long-range shielding. Assuming the *endo* attack of dichlorocarbene on the endocyclic double bond of **2a-ex** and **2a-en**, a chlorine atom comes very close to the spirocyclopropane carbon atom and the van der Waals nonbonded interaction would be very large. Consequently the *exo* attack giving **3a-ex** and **3a-ex** would be observed.

The reaction of **1c**,[8] which has a methyl group at 8-position, with dichlorocarbene afforded only **2c-ex**. This compound was also derived from the reaction of **2a-ex** with iodomethylmagnesium; thus the structure as well as the stereochemical arrangement of dichlorocyclopropane moiety could be assigned.

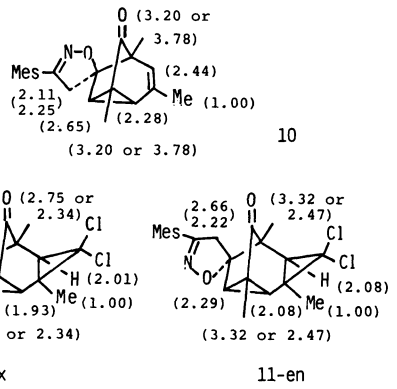
In contrast to the behavior of **1a**, reaction of the trimethyl analogue **1d**[4] with dichlorocarbene occurred on the endocyclic double bond from the *exo* side to give **2d**. In dichlorocarbene addition of cyclopropylethylenes, the rate enhancement caused by the methyl group has been observed.[9] The reaction of 2-cyclopropyl-1-propene proceeds 14 times faster than that of simple cyclopropylethylene itself. The methyl group at 3-position of **1d** could enhance the reactivity of the endocyclic double bond; thus only **2d** could be obtained. Furthermore the *exo* selectivity observed in the formation of **2d** may be ascribed to the steric effect of methyl group at 1- and 3-positions: the latter methyl group should come very close to the former one in the transition state.[10] The independent reaction of isolated **2d** with dichlorocarbene gave bis adducts, **3d-ex** and **3d-en** in a ratio of 1/2. The structural proof was based on elemental analyses and the spectroscopic data as well as on the pseudo-contact NMR spectra.[7]

Contrary to the reaction of **1d**, the reaction of the corresponding alcohol **1e**[6] with dichlorocarbene afforded a mixture of **2e-ex** and **2e-en** (in a ratio of 4/1) in a 60% yield. The *exo/endo* ratio is similar to that of the reaction of **1b**. The prohibited *exo* attack of dichlorocarbene on the endocyclic double bond (*cf.* the reaction of **1d**) could be explained by a steric effect of the chlorine ligand of the incorporating dichlorocarbene and OH group at 8-position. The mixture was not separable; however, the correct elemental analysis and mass spectral data were obtained. In the comparison of the NMR spectra of **2e-ex** and **2e-en**, particularly noteworthy are the chemical shifts of a hydrogen and a methyl group on the endocyclic double bond. In the case of **2e-ex**, the key proton absorptions were seen at δ 5.15 and δ 2.02, respectively (see Experimental). In the case of **2e-en**, however, these proton absorptions appeared at the higher fields of δ 4.79 and δ 1.92. This phenomenon is observed also for two protons on the endocyclic double bond in the pairs of NMR spectra of **2a-ex** (δ 6.20, 6.76) and **2a-en** (δ 5.08, 6.26). The difference of the stereochemical arrangement of chlorine atoms of the spirocyclopropane moiety may cause a substantial change in long-range shielding. Thus the structures of **2e-ex** and **2e-en** were deduced.

Regarding the stereoselection of the dichlorocarbene addition on the exocyclic double bond, *exo* adducts such as **2a,b,c-ex**, and **2e-ex**, were obtained preferentially as compared to the corresponding *endo* adducts. The



4 5 6 7 8 9



10

11-ex 11-en

LUMO (p orbital) of the dichlorocarbene approaches the exocyclic double bond along the π axis closer to the least substituted carbon atom to form loose charge-transfer type complexes **4** and **5**, as illustrated. These could correspond closely in geometry to the valence structure **6**. The above approach was originally proposed on the basis of experimental data[12] and later on the basis of the theoretical calculations.[13] The approach of dichlorocarbene in the way illustrated as **7** could be unlikely because of a steric destabilization experienced with the chlorine ligand and the carbon skeleton in the present case. The complex **4** then collapses with rotation of the CCl_2 group to give an *exo* adduct, and **5** collapses to give an *endo* adduct.

Considering the *endo* approach **5** giving an *endo* adduct, interaction of the HOMO (carbene)with the appropriate occupied orbital of endocyclic double bond could cause a destabilizing effect in the transition state, as compared to that derived from **4** giving an *exo* adduct. Consequently an *exo* adduct could be favored over an *endo* adduct for **1a-c** and **1e**.

The additional explanation for the *exo* prevalence for **1a-c** and **1e** could be a homoconjugative stabilization of the transition state. Considering the developing-charge delocalization derived from **4** giving an *exo* adduct, an interaction of type **8** is bishomocyclopentadienyl cation, which is bishomoantiaromatic in nature and undoubtedly disfavored energetically.[14] However, interaction in the way of **9** removes the energetic disadvantage present in **8** and provides for intervention of a stabilized transition state.[15] This stabilizing effect seems to be reflected in the value of *exo/endo* ratio of products derived from **1b,d** (4/1) being larger than that from **1a** (3/2), the carbonyl group in which electrons from the cyclopropane ring could be released. The high stereoselectivity for **1c** giving **2c-ex** is still ambiguous.

In the reaction of **2d**, the product ratio of **3d-ex/3d-en** is 1/2, which is almost a reversed value of 3/2 for **2a-ex/2a-en**. The *endo* prevalence for the reaction of **2d** could be explained by a low degree of intervention of the dichlorocyclopropane into the stabilising effect on the developing cationic center illustrated as **9**. Furthermore the destabilizing effect arising from the interaction of HOMO(carbene) with an occupied orbital of endocyclic double bond for **1a-c**, and **1e** seems to be large, compared to that of **2d**, in which the double bond is replaced by the cyclopropane ring. This reduced repulsive interaction for **2d** also prefers **3d-en** over **3d-ex**.

The 1,3-dipolar cycloaddition of **1d** with MNO afforded only an *exo* adduct **10** as in the case of **1a, b**.[2] However, a similar reaction of **2d** with MNO gave two adducts, **11-ex** and **11-en**, in 71 and 6% yields. The structures of these adducts were deduced from the elemental analyses and from their spectroscopic data.[7] Thus the postulated repulsive interaction of MNO with the endocyclic double bond seems also to be larger than that of MNO with the cyclopropane bent bond.

Experimental

The melting points are uncorrected. The IR spectra were recorded on a Shimadzu IR-400 spectrometer. The mass spectral studies were conducted using a Hitachi RMU-60 spectrometer. All of the NMR spectra were recorded on a Hitachi R-25 or JEOL PS-100 spectrometer, using tetramethylsilane as the internal standard. The shift data were obtained by adding small increments of $Eu(fod)_3$ to the sample and then noting the extent to which each peak was shifted. The relative shift slopes were obtained by dividing each slope by the slope of the least shifted signal.

General Procedure for the Addition of Dichlorocarbene. To a stirred mixture of substrate, an adequate amount of chloroform, and triethylbenzylammonium chloride (TEBA), 50% (w/w) aqueous sodium hydroxide solution were added dropwise at 0 °C. In several cases, an adequate amount of dichloromethane was added to dilute the reaction mixture. After stirring for 1 h at 0 °C and 15 h at the ambient temperature, the resulting reaction mixture was poured into water and extracted with dichloromethane. After the removal of the dichloromethane, the resulting residue was purified as follows.

Reaction of 1a with Dichlorocarbene. The reaction was carried out using **1a** (1.0 g, 6.25 mmol), chloroform (1.49 g, 12.5 mmol) TEBA (30 mg), and sodium hydroxide solution (42 cm^3). The products were purified by column chromatography on Florisil using benzene as the eluent to give a mixture (1.75 g, 78%) of **2a-ex** (47%) and **2a-en** (31%) in a ratio of 3/2, which was determined by NMR spectroscopy. Repeated separation of the above mixture by TLC on silica gel using benzene–hexane (1/1) gave pure **2a-ex**. For **2a-ex**: mp 87—89 °C; IR CCl_4), 1742 cm^{-1}; NMR (CCl_4), δ=1.16 (3H, s), 1.41 (3H, s), 1.90 (2H, s), 2.17 (1H, d, J=7.5 Hz), 2.41 (1H, dxdxd, J=7.5, 5.0, 2.0 Hz), 6.20 (1H, dxd, J=7.2, 2.0 Hz), 6.76 (1H, dxd, J=7.2, 5.0 Hz); MS, m/z (rel intensity), 244 (M^+, 1),

242 (M^+, 2), 179 (100). The product **2a-en** was contaminated with **2a-ex** and the pure sample was not obtained; but the NMR spectrum was assigned as follows. For **2a-en**: NMR (CCl_4), δ=1.23 (3H, s) 1.45 (3H s), 1.54 (1H, d, J=7.5 Hz), 1.69 (1H, d, J=7.5 Hz), 1.87 (2H, m), 5.90 (1H, dxd, J=7.2, 2.0 Hz), 6.62 (1H, dxd, J=7.2, 5.0 Hz).

*Reaction of **1b** with Dichlorocarbene.* The reaction was carried out using **1b** (500 mg, 3.1 mmol), chloroform (740 mg, 6.2 mmol), TEBA (30 mg), and sodium hydroxide solution (2.1 cm^{-3}). The products were purified by distillation to give 619 mg (82%) of a mixture of **2b-ex** (66%) and **2b-en** (16%). For **2b-ex**: NMR (CCl_4), δ=1.11 (3H, s), 1.31 (3H, s), 1.13—1.52 (2H, m), 1.55 (1H, d, J=7.2 Hz), 1.68 (1H, d, J=7.2 Hz), 3.33 (1H, s), 5.44 (1H, dxd, J=8.4, 1.7 Hz), 6.40 (1H, dxd, J=8.4, 5.4 Hz). For **2b-en**: NMR (CCl_4), δ=1.21 (3H, s), 1,39 (3H, s), 1.13—1.52 (4H, m), 3.65 (1H, s), 5.08 (1H d, J=8.2Hz) 6.26 (1H, d, J=8.2, 5.4 Hz).

*Oxidtation of a Mixture of **2b-ex** and **2b-en**.* To a stirred soltion of pyridinium chlorochromate (681 mg, 3.17 mmol) and anhydrous sodium acetate (58 mg, 0.7 mmol) in 30 cm^3 of anhydrous dichloromethane, a 4/1 mixture of **2b-ex** and **2b-en** (516 mg, 2.11 mmol) in 1 cm^3 of dichloromethane was added, followed by stirring for 10 h under a nitrogen stream. The reaction mixture was chromatographed on Florisil using dichloromethane as the eluent. The dichloromethane was evaporated and the resulting residue was distilled [bp 115—120 °C/792 Pa (bath temp)] to give a mixture (63%) of **2a-ex** and **2a-en** in a ratio of 4/1. The NMR spectrum of the mixture was identical with the authentic specimen, which was obtained from the reaction of **1a** with dichlorocarbene.

*Reaction of **2a-ex** with Dichlorocarbene.* The reaction was carried out using **2a-ex** (150 mg, 0.62 mmol), chloroform (740 mg, 6.2 mmol), dichloromethane (0.5 cm^3), TEBA (20 mg), and sodium hydroxide solution (2.2 cm^3). The product was recrystallized from ethanol to give 144 mg (71%) of **3a-ex**: mp 149—151 °C; IR (CCl_4), 1742 cm^{-1}; NMR ($CDCl_3$), δ=1.18 (3H, s), 1.31 (3H, s), 1.52 (1H, d, J=8.3 Hz), 1.66 (1H, d, J=8.3 Hz), 1.91 (1H, d, J=6.7 Hz), 2.24 (1H, dxdxd, J=6.7, 3.3, 2.0 Hz), 2.37 (1H, dxd, J=11.1, 3.3 Hz), 2.50 (1H, dxd, J=11.1, 2.0 Hz); MS, m/z (rel intensity), 328 (M^+, 1), 326(M^+, 3), 322 (M^+, 2), 291 (100). Found: C, 47.76; H, 3.66%. Calcd for $C_{13}H_{12}OCl_4$: C, 47.89; H, 3.71%.

*Reaction of the Mixture of **2a-ex** and **2a-en** with Dichlorocarbene.* The reaction was carried out using a mixture of **2a-ex** and **2a-en** in a ratio of 3/2 (1.372 g, 5.65 mmol), chloroform (7.24 g, 60.5 mmol), TEBA (60 mg), and sodium hydroxide solution (10 cm^3). The products were separated by TLC on silica gel using benzene–hexane (1/1) to give **3a-ex** (632 mg, 34%), **3a-en** (452 mg, 25%), and a mixture of **2a-ex** and **2a-en** in a ratio of 5/2 (495 mg, 36%). For **3a-en**: mp 163—164 °C (from ethanol); IR (CCl_4), 1739 cm^{-1}; NMR ($CDCl_3$), δ=1.25 (3H, s), 1.31 (3H, s), 1.54 (1H, d, J=6.0 Hz), 1.63 (1H, d, J=6.0 Hz), 1.82 (1H, dxd, J=9.6, 2.6 Hz), 2.19 (1H, dxdxd, J=7.4, 2.6, 2.0 Hz), 2.23 (1H, dxd, J=9.6, 2.0 Hz), 2.24 (1H, d, J=7.4 Hz); MS, m/z (rel intensity), 332 (M^+, 80), 330 (M^+, 9), 328 (M^+, 9), 326 (M^+, 3), 324 (M^+, 3), 291 (100). Found: C, 47.95; H, 3.80%. Calcd for $C_{13}H_{12}OCl_2$: C, 47.89; H, 3.71%.

*Reaction of **1c** with Dichlorocarbene.* The reaction was carried out using **1c** (300 mg, 1.7 mmol), chloroform (405 mg, 3.4 mmol), TEBA (20 mg), and sodium hydroxide solution (1.2 cm^3). The product was purified by distilation to give 315 mg (71%) of **2c-ex**: bp 118—122 °C/528 Pa (bath temp); NMR (CCl_4), δ=1.07 (3H, s), 1.09 (3H, s), 1.23 (3H, s), 1.26—1.65 (2H, m), 1.46—1.78 (2H, m), 5.52 (1H, dxd, J=8.5, 1.9 Hz), 6.42 (1H, dxd, J=8.5, 5.5 Hz); MS, m/z (rel intensity), 260 (M^+, 4), 258 (M^+, 5), 162 (100). Found: C, 59.76; H, 5.93%. Calcd for $C_{13}H_{16}OCl_2$: C, 60.25; H, 6.22%.

*Independent Preparation of **2c-ex**.* To a stirred ethereal solution of iodomethylmagnesium, which was prepared from iodomethane (1.20 g, 8.5 mmol) and magnesium (48 mg, 1.98 mmol), a solution of **2a-ex** (120 mg, 0.49 mmol) in 5 cm^3 of ether was added dropwise over 20 min. After the addition was completed, the mixture was refluxed for 15 min. The reaction mixture was cooled and followed by addition of water and aqueous ammonium chloride. The mixture was extracted with ether and the extract was evaporated to give 106 mg (83%) of **2c-ex**: its spectral data were identical with the authenic specimen.

*Reaction of **1d** with Dichlorocarbene.* The reaction was carried out using **1d** (507 mg, 2.91 mmol), chloroform (522 mg, 4.37 mmol), dichloromethane (1 cm^3), TEBA (30 mg), and sodium hydroxide solution (1.5 cm^3). The product was purified by TLC on silica gel using benzene as the eluent to give 664 mg (89%) of **2d**: mp 145—147 °C (from ethanol); IR (CCl_4), 1748 cm^{-1}; NMR ($CDCl_3$), δ=1.21 (3H, s), 1.24 (3H, s), 1.54 (3H, s), 1.33 (1H, d, J=2.8 Hz), 2.02 (1H, dxd, J=7.3, 2.8 Hz) 2.57 (1H, d, J=7.3 Hz), 4.73 (1H, s), 4.91 (1H, s); MS, m/z (rel intensity), 258 (M^+, 2), 256 (M^+, 3), 193 (100). Found: C, 60.48; H, 5.30%. Calcd for $C_{13}H_{17}OCl_2$: C, 60.72; H, 5.49%.

*Reaction of **2d** with Dichlorocarbene.* The reaction was carried out using **2d** (257 mg, 1 mmol), chloroform (598 mg, 5 mmol), TEBA (20 mg), dichloromethane (1 cm^3), and sodium hydroxide solution (1.7 cm^3). The products were separated by TLC on silica gel using benzene as the eluent to give **3d-en** (160 mg, 47%) and **3d-ex** (78 mg, 22%). For **3d-ex**: mp 112—113 °C (from ethanol); IR (CCl_4), 1745 cm^{-1}; NMR (CCl_4), δ=1.10 (3H, s), 1.22 (3H, s), 1.72 (3H, s), 1.48 (1H, d, J=7.4 Hz), 1.59 (1H, d, J=7.4 Hz), 1.80 (1H, s), 1.85 (2H, broad s); MS, m/z (rel intensity), [M^+] is absent; 207 (100). Found: C, 49.45; H, 4.16%. Calcd for $C_{14}H_{14}OCl_2$: C, 49.45; H, 4.15%. For **3d-en**: mp 139—142 °C; IR (CCl_4), 1748 cm^{-1}; NMR (CCl_4), δ=1.15 (3H, s), 1.22 (3H, s), 1.53 (3H, s), 1.29 (1H, d, 8.6 Hz), 1.46 (1H, d, J=8.6 Hz), 2.21 (1H, d, J=6.8 Hz), 1.75 (1H, dxd, J=6.8, 2.4 Hz), 1.26 (1H, d, J=2.4 Hz); MS, m/z (rel intensity), [M^+] is absent; 207 (100). Found: C, 49.53; H, 3.90%. Calcd for $C_{14}H_{14}OCl_4$: C, 49.45; H, 4.15%.

*Reaction of **1e** with Dichlorocarbene.* The reaction was carried out using **1e** (822 mg, 4.67 mmol), chloroform (837 mg, 7.0 mmol), dichloromethane (4 cm^3), TEBA (20 mg), and sodium hydroxide solution (2.3 cm^3). The purification by TLC on silica gel using benzene as the eluent gave a mixture (728 mg, 60%) of **2e-ex** (48%) and **2e-en** (12%). For a mixture of **2e-ex** and **2e-en**: MS, m/z (rel intensity), 260 (M^+, 3), 258 (M^+, 6), 106 (100). Found: C, 60.44; H, 6.43%. Calcd for $C_{13}H_{16}OCl_2$: C, 60.25; H, 6.22%. For **2e-ex**: NMR (CCl_4), δ=1.08 (3H, s), 1.33 (3H, s), 1.12—1.15 (2H, overlapping with methyl group), 1.55 (1H, d, J=7.0 Hz), 1.68 (1H, d, J=7.0 Hz), 2.02 (3H, d, J=1.4 Hz), 3.32 (1H, s), 5.15 (1H, broad s). For **2e-en**: NMR (CCl_4), δ=1.17 (3H, s), 1.41 (3H, s), 1.12—1.51 (4H, overlapping with methyl group), 1.92 (3H, d, J=1.4 Hz), 3.64 (1H, s), 4.79 (1H, broad s).

*1,3-Dipolar Cycloaddition of **1d** with Mesitonitrile Oxide.* A solution of **1d** (174 mg, 1 mmol) and mesitonitrile oxide (161 mg, 1 mmol) in 3 cm^3 of anhydrous benzene was refluxed for 5 h. After the solvent removal *in vacuo*, the resulting residue was separated by TLC on silica gel using benzene–dichloromethane (1/1) as the eluent. The first band from the TLC plates contained 30 mg (17%) of **1d**. The second band from the TLC plates gave 271 mg (81%) of **4**: mp 123—124 °C; IR (CCl_4), 1742 cm^{-1}; NMR ($CDCl_3$), δ= 1.10 (3H, s), 1.32 (3H, s), 1.79 (3H, d, J=1.8 Hz), 1.89 (1H, dxd, J=7.5, 3.5 Hz), 2.23 (9H, broad s), 2.30 (1H, d, J=7.5 Hz), 2.94 (1H, d, J=18.5 Hz), 3.01 (1H, d, J=18.5 Hz), 5.11 (1H, dxd, J=3.5, 1.5 Hz), 6.84 (2H, s); MS, m/z (rel intensity), 335 (M^+, 19), 159 (100). Found: C, 78.58; H, 7.45; N, 3.89%. Calcd for $C_{22}H_{25}NO_2$: C,

78.77; H, 7.51; N, 4.17%.

1,3-Dipolar Cycloaddition of **2d** *with Mesitonitrile Oxide.* A solution of **2d** (257 mg, 1 mmol) and mesitonitrile oxide (161 mg, 1 mmol) in 3 cm^3 of anhydrous benzene was refluxed for 5 h. After the solvent was evaporated, the resulting residue was separated by TLC on silica gel using benzene as the eluent. The first band from the TLC plates contained 51 mg (20%) of **2d**. The second band from the TLC plates gave 27 mg (6%) of **11-en**: mp 148—149 °C; IR ($CHCl_3$), 1730 cm^{-1}; NMR ($CDCl_3$), δ=1.24 (3H, s), 1.28 (3H, s), 1.63 (1H, d, J=2.4 Hz), 1.73 (3H, s), 2.01 (1H, dxd, J=6.7, 2.4 Hz), 2.21 (6H, s), 2.24 (3H, s), 2.30 (1H, d, J=6.7 Hz), 2.89 (1H, d, J=18.4 Hz), 3.05 (1H, d, J=18.4 Hz), 6.85 (2H, s); MS, *m/z* (rel intensity), 421 (M^+, 1), 419 (M^+, 5), 417 (M^+, 6), 159 (100). Found: C, 65.85; H, 5.94; N, 3.55%. Calcd for $C_{23}H_{25}NO_2Cl_2$: C, 66.03; H, 6.02; N, 3.35%. The third band from the TLC plates gave 297 mg (71%) of **11-ex**: mp 186—187 °C; IR ($CHCl_3$), 1742 cm^{-1}; NMR ($CDCl_3$), δ=1.26 (3H, s), 1.29 (3H, s), 1.31 (1H, d, J=3.8 Hz), 1.58 (3H, s), 1.91 (1H, dxd, J=6.6, 3.8 Hz), 2.26 (9H, broad s), 2.35 (1H, d, J=6.6 Hz), 3.13 (1H, d, J=16.5 Hz), 3.18 (1H, d, J=16.5 Hz), 6.90 (2H, s); MS, *m/z* (rel intensity), 419 (M^+, 2), 417 (M^+, 3), 159 (100). Found: C, 66.09; H, 5.81; N, 3.41%. Calcd for $C_{23}H_{25}NO_2Cl_2$: C, 66.03; H, 6.02; N, 3.35%.

References

1) K. Okada and T. Mukai, *J. Am. Chem. Soc.*, **100**, 6509 (1978); L. A. Paquette, L. W. Hartel, R. Gleiter, and M. C. Bohm, *J. Am. Chem. Soc.*, **100**, 6510 (1978); L. A. Paquette and L. W. Hartel, *J. Am. Chem. Soc.*, **101**, 7620 (1979); L. A. Paquette, L. W. Hartel, R. Gleiter, M. C. Bohm, M. A. Beno, and G. G. Christoph, *J. Am. Chem. Soc.*, **101**, 7106 (1981); T. Sasaki, K. Hayakawa, and S. Nishida, *J. Am. Chem. Soc.*, **103**, 565 (1981); K. E. Green and L. A. Paquette, *J. Org. Chem.*, **48**, 1849 (1983).

2) M. Nitta, A. Omata, and S. Okada, *Bull. Chem. Soc. Jpn.*, in press.

3) M. Nitta, A. Omata, and H. Sugiyama, *Bull. Chem. Soc. Jpn.*, **55**, 569 (1982); Epoxidation reaction of **1a,d** also occurs on the exocyclic double bond from the *exo* side: M. Nitta, A. Omata, and H. Nakatani, *Bull. Chem. Soc. Jpn.*, **56**, 2009 (1983).

4) J. Zsindely and H. Schmid, *Helv. Chim. Acta*, **51**, 1510 (1968).

5) M. Makosza and M. Wawrzyniewicz *Tetrahedron Lett.*, **1969**, 4659 E. V. Dehmlow, *Angew. Chem. Int. Ed. Engl.*, **13**, 170 (1974); **16**, 493 (1977).

6) J. P-Katalinic, J. Zsindely, and H. Schmid, *Helv. Chim. Acta*, **57**, 223 (1974).

7) The numerical values presented in parentheses in the structural formulae in this paper are relative dowfield shifts of δ's obtained by using $Eu(fod)_3$.

8) G. M-Muller, P. Gilgen, J. Zsindely, and H. Schmid, *Helv. Chim. Acta*, **60**, 1758 (1977).

9) E. V. Dehmlow and A. Eulenberger, *Angew, Chem. Int. Ed. Engl.*, **17**, 674 (1978).

10) The cycloaddition of phenyl azide (PA) with **1a** gave an *endo* adduct of type **C**.[2] However, in the reaction of **1d** with PA, both *endo* and *exo* adducts were obtained in a ratio of 1/1. Thus the methyl group of 3-position of **1d** seems to affect the *endo-exo* selectivity, possibly using a steric reason.[11]

11) M. Nitta, S. Okada, and T. Kobayashi, unpublished results.

12) P. S. Skell and M. S. Chold, *J. Am. Chem Soc.*, **91**, 7131 (1969).

13) R. Hoffmann, D. W. Hayes, and P. S. Skell, *J. Phys. Chem.*, **76**, 664 (1972).

4) A. F. Diaz, M. Sakai, and S. Winstein, *J. Am. Chem. Soc.*, **92**, 7477 (1970); R. Breslow and J. M. Hoffman Jr., *J. Am. Chem. Soc.*, **94**, 2110 (1972).

15) H. Hart and M. Kuzuya, *J. Am. Chem. Soc.*, **98**, 1545 (1976).