Bull. Chem. Soc. Jpn., 56, 514—519 (1983) [Vol. 56, No. 2

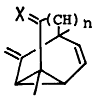
Electrophilic Additions of Rigid Methylenecyclohexane. A Correlation of the Stereochemical Course of the Methoxymercuration-demercuration and the 1,3-Dipolar Cycloaddition[1)]

Makoto Nitta,* Akihiko Omata, Setsuko Hirayama, and Yuji Yajima
Department of Chemistry, School of Science and Engineering, Waseda University, Shinjuku-ku, Tokyo 160

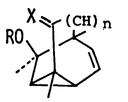
(Received June 10, 1982)

The stereochemical course of the methoxymercuration-demercurations and the 1,3-dipolar cycloadditions of mesitonitrile oxide on the exocyclic double bonds of 2,4-dimethyl-7-methylenetetracyclo[3.3.0.0.^{2,8}0^{4,6}]octan-3-one (**4a**), its corresponding *exo*-3-ol (**4b**), *endo*-3-ol (**4c**), and 2,3,4-trimethyl-7-methylenetetracyclo[3.3.0.0.^{2,8}0^{4,6}]octan-3-*exo*-ol (**4d**) were investigated. In the methoxymercurations of **4a** and **4b**, the methoxyl group was incorporated in the *exo* and *endo* positions, with *endo* preferred over *exo*. On the other hand, **4c** and **4d** underwent the stereospecific incorporation of the methoxyl group in the *endo* position. In the 1,3-dipolar cycloadditions, **4a** or **4b** afforded *exo*- and *endo*-adducts, with the *exo*-adduct preferred. These results seem to imply similar stereochemical course of the formation of the mercurinium-ion intermediates and the 1,3-dipolar cycloadditions. The results are discussed on the basis of the steric hindrance of the molecular framework and the substituents which are located at the C-3 position.

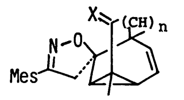
Recently, stereoselectivities of electrophilic additions of molecules containing proximal π-bonds have been explored.[2—5)] Previously, we have also shown that the solvomercuration-demercuration and its related reactions on the exocyclic double bond of 1,5-dimethyl-6-methylenetricyclo[3.2.1.0^{2,7}]oct-3-en-8-one and its related compounds, such as **1**, exhibit a remarkable stereoselectivity to give **2**.[6)] This stereoselectivity is explained by the steric hindrance and/or electronic factor[7)] of the mercurinium-ion formation and the stereoelectronic control of the subsequent incorporation of the nucleophile. The initial addition of $^{+}$Hg(OAc) to **1** was supposed to give the mercurinium ions, M-*exo* and M-*endo*, which may exist in equilibrium with each other. The *trans* addition of the nucleophile to M-*exo* is hindered by the repelling interaction of the nucleophile with the π-electron lobe of the endocyclic double bond. Therefore, the nucleophile is incorporated into M-*endo* to give **2**. A similar stereoselectivity is also obtained in the 1,3-dipolar cycloaddition of mesitonitrile oxide (2,4,6-trimethylbenzonitrile oxide) with **1** to lead **3**.[8)]



1

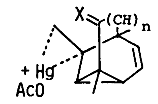


2

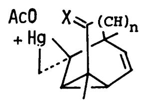


3

n = 0 or 1 ; X = 0 or H, OH

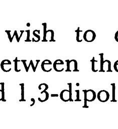


M-endo

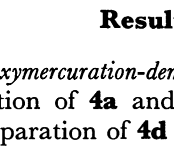


M-exo

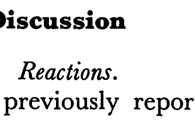
Regarding the mechanistic aspect of the solvomercuration-demercuration of olefins, it has been of further interest to explore the various controlling factor of the stereoselectivities.[9)] In this connection, methoxymercuration and 1,3-dipolar cycloadditions, using mesitonitrile oxide, with 2,4-dimethyl-7-methylenetetracyclo[3.3.0.0.^{2,8}0^{4,6}]octan-3-one (**4a**), its corresponding *exo*-3-ol (**4b**), *endo*-3-ol (**4c**), and 2,3,4-trimethyl-7-methylenetetracyclo[3.3.0.0.^{2,8}0^{4,6}]octan-3-*exo*-ol (**4d**) were investigated. The compounds, **4a**—**d**, contain a boat methylenecyclohexane ring and various degrees of steric hindrance at C-3. Furthermore, **4a**—**d** also contain a bishomofulvene moiety. Therefore, the methoxymercuration-demercuration sequences should proceed *via* a mercurinium ion intermediate (**A**), because of the bishomoantiaromatic nature of the opened cation (**B**).[10)] Consequently, it might be possible to assess how the steric hindrance affects the stereochemical courses of the methoxymercuration and 1,3-dipolar cycloadditions.



4 a: X-Y = O
b: X = H, Y = OH
c: X = OH, Y = H
d: X = CH$_3$, Y = OH



A



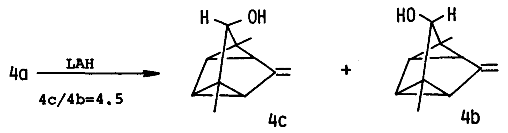
B

We wish to discuss here the stereochemical correlation between the solvomercuration reactions and the concerted 1,3-dipolar cycloadditions of mesitonitrile oxide.

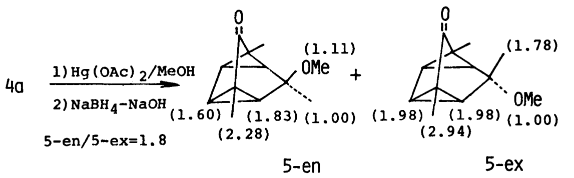
Results and Discussion

Methoxymercuration-demercuration Reactions. The preparation of **4a** and **4b** was previously reported.[11)] The preparation of **4d** was also achieved by the photoirradiation of 1,5,8-trimethyl-6-methylenetricyclo[3.2.1.0^{2,7}]oct-3-en-8-*endo*-ol[12)] (see Experimental section). The *endo* alcohol derivative **4c** was prepared by the reduction of **4a** with lithium aluminium hydride (LAH), along with *exo* alcohol **4b**. The ratio of **4c**/**4b** (4.5) would indicate the stereochemical preference of the *exo*-attack of the hydride ion.

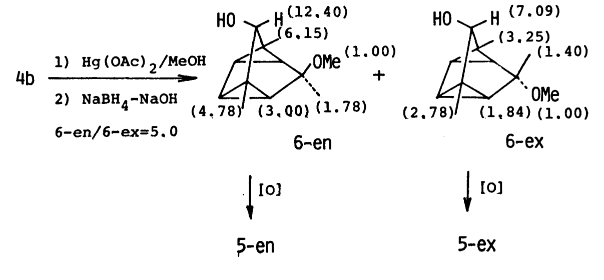
A solution of **4a** in anhydrous methanol was allowed to react with 1.2 molar equivalent of mercury(II) acetate. The reaction proceeded very slowly, and, after a total reaction time of 6 h, *in situ* reduction[13)] by sodium



borohydride gave a 58% overall yield of two products, along with a recovery of **4a** in a 26% yield. The methoxyl group was incorporated preferentially at the more hindered site (see the ratio of **4c**/**4b** in the reduction of **4a** with LAH), giving the *endo* and *exo* isomer, **5**-en and **5**-ex, in a ratio of 1.8/1.0. The structural assignment to **5**-en and **5**-ex follows convincingly from their spectral properties. The carbonyl absorption band at 1710 cm^{-1} of **4a** was shifted to 1721 cm^{-1} and 1713 cm^{-1} for **5**-en and **5**-ex respectively. The NMR spectra of **5**-en and **5**-ex exhibited five signals, suggesting the symmetric structures (see Experimental section). These facts clearly indicate that the methoxymercuration-demercuration occurred on the exocyclic double bond. The protons of the methoxyl group and the methyl group at C-7 of **5**-en appear as singlets at δ 3.16 and δ 1.46 respectively. For **5**-ex, these signals appear at δ 3.34 and δ 1.23. These characteristics suggest that the methoxyl group of **5**-en and the methyl group of **5**-ex are much shielded by the σ-bond in the molecular framework. Therefore, the orientations of the methoxyl group of **5**-en and **5**-ex were determined as depicted. Furthermore, supportive evidence for the stereochemistries of the methoxyl group was also obtained from the pseudo-contact NMR spectra obtained by using Eu(fod)$_3$.[14] The relative downfield shifts of δ's are given in parentheses in the structural formulae **5**-en and **5**-ex. The relatively small shifts of the methoxyl groups of **5**-en and **5**-ex suggest that the coordination of Eu(fod)$_3$ does not occur on methoxyl oxygen, but on the carbonyl oxygen. The small shift (1.00) of the methyl group of **5**-en as compared to that (1.78) of **5**-ex suggests that the methyl group of **5**-ex is located syn to the carbonyl group. Consequently, the stereochemistry of **5**-en and **5**-ex was clarified.

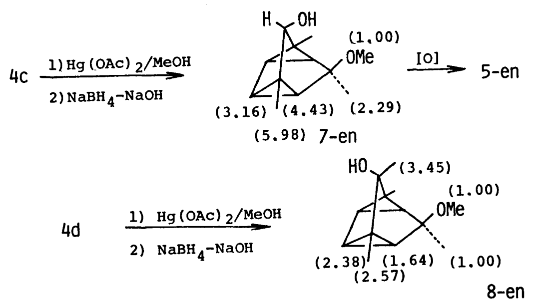


The reaction of **4b** with mercury(II) acetate and subsequent reduction afforded two products, **6**-en and **6**-ex, in a ratio of 5.0/1.0 and in a 73% yield, along with the starting material, **4b**, in a 25% yield. The structures of **6**-en and **6**-ex were deduced from the spectral data (see Experimental section). The pseudo-contact NMR spectra obtained by using Eu(fod)$_3$,[14] however, could not reveal the stereochemistry of the methoxyl group.

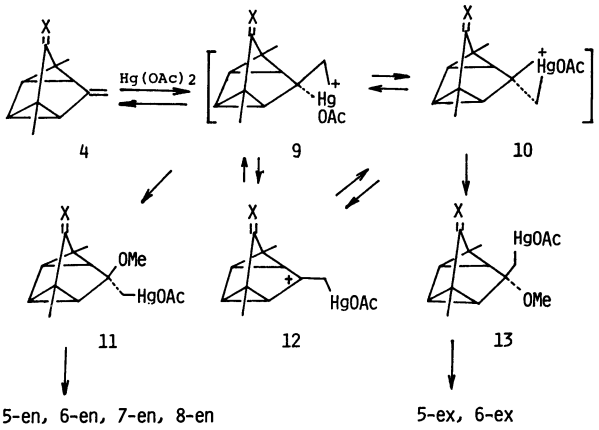


On the oxidation of **6**-en or **6**-ex with pyridinium chlorochromate,[15] **5**-en or **5**-ex was obtained in a fairly good yield. Therefore, the stereochemistry of **6**-en and **6**-ex was confirmed. In this case, the methoxyl group is also incorporated preferentially at the more hindered site.

On the other hand, the reaction of **4c** or **4d** with 1.2 molar equivalents of mercury(II) acetate and the subsequent reduction afforded a single product, **7**-en or **8**-en, in a 70% or in a 60% yield respectively, along with the starting material, **4c** (21%) or **4d** (20%). The structures of **7**-en and **8**-en were deduced from the spectral data (see Experimental section). The large coupling constant ($J=12.0$ Hz) between the protons at C-3 and the hydroxyl proton for **7**-en indicates the intramolecular hydrogen bonding of the hydroxyl hydrogen with methoxyl oxygen. Furthermore, on oxidation with pyridinium chlorochromate, **7**-en was converted to **5**-en in a fairly good yield. Consequently, the stereochemistry of the methoxyl group was assessed. In this case, the methoxyl group was also introduced at the more hindered site. The stereochemistry of the methoxyl group in **8**-en is not clear from its pseudo-contact NMR spectra obtained by using Eu(fod)$_3$,[14] however, the orientation can tentatively be assigned as *endo* on the basis of the similarities of the preferential *endo* orientation in the reactions of **4a**—**c**.

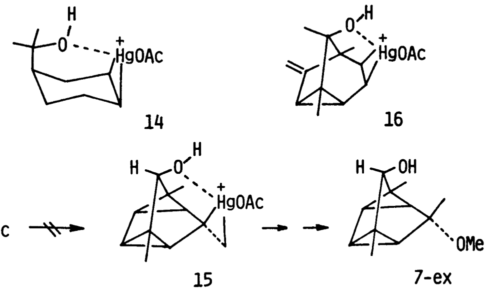


In all of the presented reactions, methanol was incorporated preferentially from the much-hindered site on the exocyclic double bond (see the ratio of **4c**/**4b** in the reduction of **4a** with LAH), and the original tetracyclic skeleton did not undergo rearrangement. These results seems to suggest the formation of such mercurinium ions as **9** and **10**, as is shown in the scheme.[16–19] Such cationic species[20–22] as **12** should be energetically unfavorable because of an antiaromatic nature of the bishomocyclopentadienyl cation,[10] which would be expected to undergo rearrangement.[23] Recently it has been shown that 3-methyltetracyclo[3.3.0.0.^{2,8}0^{4,6}]octan-3-yl cation rearranges to another compound at −95 °C.[24] Previously, we have shown that the stabilization of the cationic center of the cyclopropylmethyl cation by the mercury moiety adjacent to the cationic center is preferable over the resonance-electron donation of the cyclopropane ring.[6] Therefore the cationic center would be stabilized by making such mercurinium ions as **9** and **10**. In the initial addition of $+Hg(OAc)$[25] to the exocyclic double bond, the formation of **9** seems to be faster than the formation of **10** because of the steric hindrance of the molecular framework and the substituent at C-3. Furthermore, **9** should also be thermodynamically more stable than **10**, because of the nonbonded interaction of the substituent with the mercury moiety. If the rapid equilibrium between **9** and **10** *via* the possible short-lived intermediate **12** or *via* the mercuration-demercuration sequence is thought to participate in the present reaction, the equilibrium between **9** and **10** should be shifted to **9** as well. Consequently, the *trans* addition of methanol, affording **11** or **13**, and the subsequent reaction should give **5**-en, **6**-en, **7**-en, and **8**-en or **5**-ex and **6**-ex.



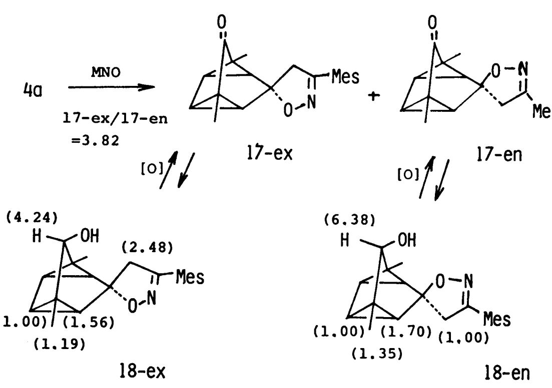
The *endo-exo* ratio in the case of **4a** is 1.8, while that in the case of **4b** is 5.0. These values probably reflect the large steric hindrance of the hydrogen at C-3 with the mercury moiety, as compared to that of the carbonyl group in **4a**. Furthermore, in the case of **4c** and **4d**, the hydroxyl group and the methyl group are larger than hydrogen, so such mercurinium ion as **10** should be absent, and only **7**-en or **8**-en could be obtained *via* **9**.

The stereocontrol by a neighboring hydroxyl group in oxymercuration has been demonstrated to proceed *via* an intermediate such as **14**, which includes a favorable interaction of the hydroxyl group with the mercury moiety.[26] In the reaction of **4c**, however, no expected product, such as **7**-ex *via* **15**, could be obtained. In **14**, the hydroxyl group, which is located close to the bisected plane including the mercurinium ion, should coordinate to the mercury moiety in such a way as to make a tetrahedral arrangement. In **15**, however, the hydroxyl group is located on the plane including the postulated mercurinium ion. Therefore, it can be suggested that the interaction of hydroxyl oxygen with the mercurinium ion is not possible in a planar arrangement such as **15**. Also indicated is a favorable interaction of the mercury moiety with the hydroxyl oxygen, which is located on the bisected plane of a postulated mercurinium ion such as **16**.[8]



1,3-Dipolar Cycloaddition of Mesitonitrile Oxide. As has been described above, the solvomercuration of **4a**—**d** seemed to be much affected by the steric hindrance of various substituents at C-3 in the step of mercurinium-ion formation. A study dealing with the steric hindrance is of interest in order to gain insight into the correlation between the mercurinium-ion formation and the 1,3-dipolar cycloaddition, in which two bonds are formed in a concerted manner. For this reason, the steric effect of substituents located at C-3 was investigated. Less is known about the influence of the steric hindrance in concerted 1,3-dipolar cycloadditions. However, it has been shown that the relative rates of the cycloaddition of aromatic nitrile oxide with substituted ethylenes are influenced by the steric factor.[27]

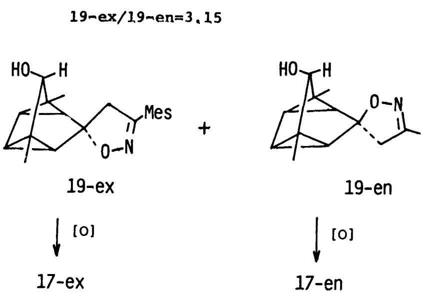
The cycloaddition of **4a** with mesitonitrile oxide (MNO) in dichloromethane gave **17**-ex and **17**-en in 42 and 11% yields respectively. The structural assignment of **17**-ex and **17**-en follows convincingly from their physical properties and the chemical transformations. The carbonyl absorption bands at 1711 cm^{-1} for **17**-ex and, at 1706 cm^{-1} for **17**-en suggest the existence of the tetracyclic skeleton. The mass spectral data, as well as the analytical data, suggest that **17**-ex and **17**-en are one-to-one adducts of **4a** and MNO. The NMR spectra suggested the symmetric structures (see Experimental section), and the addition occurred on the exocyclic double bond of **4a**. The chemical shifts of the protons of the isoxazoline moiety of **17**-ex (δ 3.09) and of **17**-en (δ 3.27) are suggestive of the regiochemistry of the C=N–O moiety, as is depicted.[28] On the reduction of **17**-ex or **17**-en with sodium borohydride, **18**-ex and **18**-en were obtained in good yields. On the oxidation of **18**-ex and **18**-en with pyridinium chlorochromate, **17**-ex and **17**-en were regenerated. The skeletons of **17**-ex and **17**-en are not changed in these chemical



transformations.

The stereochemical arrangements of the C=N–O moiety in **18**-ex and **18**-en were obtained from pseudocontact NMR spectra obtained by using Eu(fod)$_3$.[14] The relative downfield shifts of δ's of hydrogens for the isoxazoline moiety are 2.48 for **18**-ex and 1.00 for **18**-en. Therefore, it is clarified that the coordination of Eu(fod)$_3$ occurs on the hydroxyl oxygens and that the C=N–O moieties are exo for **18**-ex and endo for **18**-ex. Consequently, the stereochemical arrangements of **17**-ex and **17**-en are assessed.

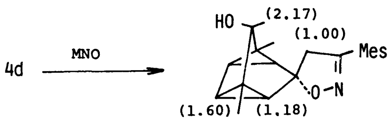
Similarly, **4b** and MNO gave two adducts, **19**-ex and **19**-en, in 63 and 20% yields respectively. On oxidation with pyridinium chlorochromate, **19**-ex and **19**-en were converted to **17**-ex and **17**-en respectively.



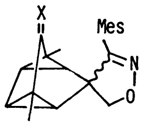
This chemical transformation and the results of a comparison of the spectral data with those of **17**-ex, **17**-en, **18**-ex, and **18**-en revealed the structures of **19**-ex and **19**-en convincingly.

On the other hand, **4d** and MNO gave a single adduct, **20**-ex, in an 80% yield, along with 10% of the starting material, **4d**. The structure was deduced from the spectral data. The stereochemical arrangement of the C=N–O moiety is not clarified from the pseudocontact NMR spectra, however, it should be *exo* because of the large steric effect of the methyl group on C-3.

The regiochemistry of the present cycloadditions seems to suggest the electrophilic nature of MNO, since the unsubstituted terminus of dicyclopropylethylene (large HOMO coefficient) was bound to the carbon terminus of MNO (larger LUMO coefficient).[29] The regiochemistry observed here is also favorable for a steric reason: the van der Waals non-bonded interaction energies should be very large in such material as **21** as compared to the above products. Recently, theoretical as well as experimental studies of the 1,3-dipolar cycloadditions of nitrile oxide with methyleneadamantane have been shown to exhibit a regiochemistry similar to that of the present reactions.[28]



20-ex



21

In the case of the reaction of **4a**, **17**-ex/**17**-en is 3.82, while in that of **4b**, **19**-ex/**19**-en is 3.5. The reaction of **4d**, which has the methyl group at C-3 position, gave only **20**-ex. Previously, the degree of polarization of the exocyclic double bonds of **4a** and **4b** has been ascertained from the ^{13}C-NMR values, in which the electron-withdrawing carbonyl group seems to reduce the polarization through two cyclopropane rings.[30] Therefore, the possible π-orbital distortion of the exocyclic double bond may also conceivably affect the exo, endo-selectivity.[31] However, the increase in the *exo*-adduct **20**-ex upon the introduction of the bulky group on C-3, like the decrease in the *endo* products observed for mercuration reactions of **4a**—**d**, can be classified as a steric effect. The value of **5**-en/**5**-ex (1.8), which could correspond to the ratio of the mercurinium-ion formation of **9**/**10** for the ketone **4a**, is smaller than that of **17**-ex/**17**-en (3.82). The much suppressed **17**-en formation, as compared to that of **17**-ex, may be attributable to the coulombic repulsion of mesitonitrile oxide with the π-electron of the carbonyl function at C-3. Since similar trends for the *exo-endo* ratios of the postulated mercurinium ion formation and the 1,3-dipolar cycloaddition are obtained here, the steric effect seems to affect the reaction pathways in a similar manner. The stereochemical courses of the mercuration reactions of various kinds of compounds may be clarified in comparison with the reaction such as 1,3-dipolar cycloadditions, which involve a two-bond-forming process in the reaction sequences.

Experimental

The IR spectra were recorded on a Shimadzu IR-400 spectrometer. The mass spectral studies were conducted using a Hitachi RMU-60 spectrometer. All NMR spectra were recorded on a JEOL PS-100 high resolution spectrometer, using tetramethylsilane as the internal standard. The shift data were obtained by adding small increments of Eu(fod)$_3$ to the sample and by 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. VPC separations were performed on a Varian model-920 chromatograph, using a column packed with 5% FFAP on Chromosorb W at 110 °C. The analyses were performed by the Science and Engineering Research Laboratory, Waseda University.

Methoxymercuration-demercuration of ***4a***. A solution of **4a** (400 mg, 2.5 mmol) and mercury(II) acetate (960 mg, 3.0 mmol) in 8 cm^3 of anhydrous methanol was stirred for 6 h at room temperature. To this reaction mixture, was added 2.6 cm^3 of 3 mol dm^{-3} aqueous sodium hydroxide. After stirring for 15 min, 10 cm^3 of brine was added to the reaction mixture and mercury precipitated was filtered through Celite. The filtrate was extracted with ether, and the ether extract was dried over sodium sulfate. The removal of the ether *in vacuo* gave an oily material, which was separated by TLC on silica gel, using dichloromethane as the eluent, to give 99 mg (25%) of **4a** and a mixture of **5**-en and **5**-ex in a ratio of 177 mg (37%)/99 mg (21%). This mixture was separated by VPC to give pure **5**-en and **5**-ex. For **5**-en: IR (CCl_4), 2974, 2930, 1721, 1138, 873 cm^{-1}; NMR (CCl_4), δ 1.05 (6H, s), 1.46 (3H, s), 1.53 (2H, d, J=6.0 Hz), 2.10 (2H, d, J=6.0 Hz), 3.16 (3H, s); MS, *m/e* (rel intensity), 192 (M$^+$, 63), 161 (100). Found: C, 74.78; H, 8.17%. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39% For **5**-ex: IR (CCl_4), 2983, 2939, 1713, 1068, 869 cm^{-1}; NMR ($CDCl_3$), δ 1.05 (6H, s), 1.23 (3H, s), 1.52 (2H, d, J=6.0 Hz), 2.24 (2H, d, J=6.0 Hz), 3.34 (3H, s); MS, *m/e* (rel intensity), 192 (M$^+$, 63), 161 (100). Found: C, 74.99; H, 8.70%. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39%.

Methoxymercuration-demercuration of ***4b****.* A solution of **4b** (452 mg, 2.79 mmol) and mercury(II) acetate (1.069 g, 3.35 mmol) in 10 cm^3 of anhydrous methanol was stirred at room temperature for 8 h, followed by the addition of 5 cm^3 of 3 mol dm^{-3} aqueous sodium hydroxide and then sodium borohydride (127 mg, 3.35 mmol) in 5 cm^3 of aqueous sodium hydroxide. A workup similar to that described above gave 502 mg of an oil, which was revealed by VPC analysis and NMR spectroscopy to contain **4b** (112 mg, 25%), **6**-en (328 mg, 61%), and **6**-ex (63 mg, 12%). For **6**-en: IR (CCl_4), 3515—3294 (broad band), 2939, 1136, 1059, 1024 cm^{-1}; NMR (CCl_4), δ 1.11 (6H, s), 1.28 (3H, s), 1.28 (2H, d, J=5.7 Hz, overlapping with methyl signal), 1.59 (2H, d, J=5.7 Hz), 2.75 (1H, s), 3.15 (3H, s), 3.93 (1H, s). For **6**-ex: IR (CCl_4), 3561—3393 (broad band), 2939, 1076, 1061, 1023 cm^{-1}; NMR (CCl_4), δ 1.11 (6H, s), 1.18 (3H, s), 1.18 (2H, d, J=5.7 Hz, overlapping with methyl signal), 1.71 (2H, d, J=5.7 Hz), 1.8—2.0 (1H, broad s), 3.26 (3H, s), 3.56 (1H, s).

Oxidation of ***6****-en.* A suspension of pyridinium chlorochromate (141 mg, 0.65 mmol), anhydrous sodium acetate (11 mg, 0.14 mmol), and **6**-en (70 mg, 0.36 mmol) in 5 cm^3 of dichloromethane was stirred for 6 h under a nitrogen atmosphere. The reaction mixture was then chromatographed on Florisil, using dichloromethane as the eluent, to give a quantitative yield of **5**-en, which was identical with the authentic specimen.

Oxidation of ***6****-ex.* A suspension of pyridinium chlorochromate (50 mg, 0.22 mmol), anhydrous sodium acetate (4 mg, 0.04 mmol), and **6**-ex (24 mg, 0.12 mmol) in 2 cm^3 of dichloromethane was stirred for 6 h under a nitrogen atmosphere. The reaction mixture was then chromatographed on Florisil, using dichloromethane as the eluent, to give 18 mg (76%) of **5**-ex, which was identical with the authentic specimen.

Methoxymercuration-demercuration of ***4c****.* A solution of **4c** (300 mg, 1.85 mmol) and mercury(II) acetate (709 mg, 2.23 mmol) in 5 cm^3 of anhydrous methanol was stirred for 11 h at room temperature, followed by the addition of 2 cm^3 of 3 mol dm^{-3} aqueous sodium hydroxide and sodium borohydride (85 mg, 2.23 mmol) in 2 cm^3 of 3 mol dm^{-3} aqueous sodium hydroxide. A workup similar to that described above gave 312 mg of an oil, which was revealed by VPC and NMR spectroscopy to contain **4c** (63 mg, 21%) and **7**-en (251 mg, 70%). This mixture was separated by VPC to afford pure **4c** and **7**-en. For **7**-en: IR (CCl_4), 3422, 2956, 1461, 1128, 1045 cm^{-1}; NMR (CCl_4), δ 1.06 (6H, s), 1.12 (2H, d, J=6.0 Hz), 1.38(3H, s), 1.46 (2H, d, J=6.0 Hz), 3.02 (3H, d, J=12.0 Hz) ,3.28 (3H, s), 3.83 (1H, d, J=12.0 Hz).

Oxidation of ***7****-en.* A mixture of pyridinium chlorochromate (141 mg, 0.65 mmol), anhydrous sodium acetate (11 mg, 0.14 mmol), and **7**-en (69 mg, 0.36 mmol) in 5 cm^3 of dichloromethane was stirred for 5 h at room temperature under a nitrogen atmosphere. The reaction mixture was then chromatographed on Florisil, using dichloromethane as the eluent, to give 53 mg (78%) of **5**-en, which was identified with the authentic specimen.

Methoxymercuration-demercuration of ***4d****.* A solution of **4d** (500 mg, 2.84 mmol) and mercury(II) acetate (1.008 g, 3.42 mmol) in 10 cm^3 of anhydrous methanol was stirred for 11 h at 40 °C, followed by the addition of 5 cm^3 of 3 mol dm^{-3} aqueous sodium hydroxide and sodium borohydride (130 mg, 3.42 mmol) in 5 cm^3 of 3 mol dm^{-3} aqueous sodium hydroxide. A workup similar to that described above gave 424 mg of an oil, which was revealed to contain **4d** (102 mg, 20%) and **8**-en (321 mg, 64%). This oil was separated by VPC to afford pure **8**-en: IR (CCl_4), 3586, 3451, 2965, 2939, 1383, 1130, 1065, 919 cm^{-1}; NMR (CCl_4), δ 1.00 (6H, s), 1.24 (3H, s), 1.29 (3H, s), 1.08 (2H, d, J=6.0 Hz), 1.43 (2H, d, J=6.0 Hz). Found: C, 74.86; H, 9.29%. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68%.

Reduction of ***4a*** *with Lithium Aluminium Hydride (LAH).* A solution of **4a** (875 mg, 5.47 mmol) and LAH (208 mg, 5.47 mmol) in 10 cm^3 of anhydrous tetrahydrofuran was refluxed for 5 h. The usual workup afforded 735 mg (83%) of a mixture of **4b** (133 mg, 15%) and **4c** (602 mg, 68%). This mixture was separated by VPC to afford pure **4b** and **4c**. For **4c**: NMR (CCl_4), δ 1.10 (6H, s), 1.58 (2H, d, J=6.0 Hz), 1.82 (2H, d, J=6.0 Hz), 3.97 (1H, broad s), 4.83 (2H, s); MS, *m/e* (rel intensity), 162 (M$^+$, 23), 58 (100).

*Irradiation of 1,5,8-Trimethyl-6-methylenetricyclo[3.2.1.0^{2,7}]oct-3-en-8-*endo*-ol.* A solution of the tricyclic alcohol (1.0 g, 5.68 mmol) in 200 cm^3 of anhydrous acetonitrile was irradiated using RPR-254 nm lamps for 48 h under a nitrogen atmosphere. After the removal of the solvent, the residue was chromatographed on alumina (30 g), using benzene as the eluent, to give **4d**, which was then recrystallized from hexane to give 582 mg (58%) of pure **4b**: IR (CCl_4), 3595, 3437, 2974, 1653, 1443, 1379, 1342, 1131, 925, 862 cm^{-1}; NMR (CCl_4), δ 1.02 (3H, s), 1.05 (6H. s), 1.45 (2H, d, J=6.0 Hz), 1.77 (2H, d, J=6.0 Hz), 4.76 (2H, s). Found: C, 81.57; H, 9.17%. Calcd for $C_{12}H_{16}O_2$: C, 81.77; H, 9.15%.

Cycloaddition of ***4a*** *with Mesitonitrile Oxide (2,2,6-Trimethylbenzonitrile Oxide).* A solution of **4a** (160 mg, 1 mmol) and mesitonitrile oxide (161 mg, 1 mmol) in 4 cm^3 of dichloromethane was refluxed for 4 d. After solvent removal *in vacuo*, the resulting residue was separated by TLC on silica gel, using dichloromethane as the eluent. The first band from the TLC plates gave 12 mg (8%) of **4a**. The second band from the TLC plates gave 134 mg (42%) of colorless crystals of **17**-ex: mp 164—165 °C (from ethanol); IR (KBr) 1711, 1609, 1333, cm^{-1}; NMR ($CDCl_3$), δ 1.12 (6H, s), 1.97 (2H, d, J=6.0 Hz) 2.20 (9H, s), 2.48 (2H, d, J=6.0 Hz), 3.09 (2H, s), 6.80 (2H broad s); MS, *m/e* (rel intensity), 321 (M$^+$, 61), 159 (100). Found: C, 78.62; H, 7.14; N, 4.28%. Calcd for $C_{21}H_{23}O_2N$: C, 78.47; H, 7.21; N, 4.36%. The third band from the TLC plates gave 34 mg (11%) of **17**-en: mp 288—289 °C (from ethanol); IR (KBr), 1706, 1610, 1332 cm^{-1}; NMR ($CDCl_3$), δ 1.15 (6H, s), 1.75 (2H, d, J=6.0 Hz), 2.23 (9H, s), 2.26 (2H, d, J=6.0 Hz), 3.27 (2H, s), 6.83 (2H, s); MS, *m/e* (rel intensity), 321 (M$^+$, 27), 159 (100). Found: C, 78.41; H, 7.21; N, 4.18%. Calcd for $C_{21}H_{23}O_2N$: C, 78.47; H, 7.21; N, 4.36%.

Reduction of ***17****-ex.* A solution of **17**-ex (70 mg, 0.22 mmol) and sodium borohydride (9 mg, 0.22 mmol) in 11 cm^3 of benzene–ethanol (10/1) was stirred overnight. This reaction mixture was concentrated and extracted with dichloromethane, and then the extract was dried over sodium sulfate. After solvent removal *in vacuo*, the residue was recrystallized from ethanol to give 56 mg (80%) of **18**-ex: mp 230—231 °C; IR (KBr), 3309, 1601, 1333, 1067 cm^{-1}; NMR ($CDCl_3$), δ 1.13 (6H, s), 1.63 (2H, d, J=6.0 Hz), 1.82 (2H, d, J=6.0 Hz), 2.27 (9H, s), 3.37 (2H, s), 4.17 (1H, d, J=3.7 Hz), 6.85 (2H, s).

Oxidation of ***18****-ex.* To a suspension of pyridinium chlorochromate (20 mg, 0.093 mmol) and anhydrous sodium acetate (2 mg), was added **18**-ex (17 mg, 0.052 mmol) in 0.5 cm^3 of dichloromethane under a nitrogen atmosphere. This mixture was stirred for 3 h. Reaction mixture was then chromatographed on Florisil, using dichloromethane as the eluent, to give 14 mg (84%) of **17**-ex.

*Reduction of **17**-en.* The reduction was carried out as has been described above using 48 mg (0.3 mmol) of **17**-en and 6 mg (0.15 mmol) of sodium borohydride. The product was recrystallized from ethanol to give 39 mg (80%) of **18**-en: mp 193—194 °C; IR (KBr), 3468, 1609, 1321, 1043 cm^{-1}; NMR ($CDCl_3$), δ 1.17 (6H, s), 1.35 (2H, d, $J=6.0$ Hz), 1.68 (2H, d, $J=6.0$ Hz), 2.26 (9H, s), 3.02 (1H, d, $J=11.6$ Hz), 3.17 (2H, s), 4.15 (1H, d, $J=11.6$ Hz), 6.90 (2H, s).

*Oxidation of **18**-en.* The reaction was carried out using **18**-en (30 mg, 0.09 mmol), pyridinium chlorochromate (30 mg, 0.14 mmol), and anhydrous sodium acetate (3 mg). A workup similar to that described above afforded **17**-en (26 mg, 82%).

*Cycloaddition of **4b** with Mesitonitrile Oxide.* A solution of **4b** (324 mg, 2 mmol) and mesitonitrile oxide (322 mg, 2 mmol) in 6 cm^3 of dichloromethane was refluxed for 56 h. The reaction was monitored by TLC (silica gel, dichloromethane). After solvent removal *in vacuo*, the resulting residue was separated by TLC on silica gel, using dichloromethane as the eluent. The first band from the TLC plates afforded 404 mg (63%) of **19**-ex: mp 158—159 °C (from ethanol); IR (KBr), 3307, 1609, 1062 cm^{-1}; NMR ($CDCl_3$), δ 1.13 (6H, s), 1.65 (2H, d, $J=6.0$ Hz), 1.95 (2H, d, $J=6.0$ Hz), 2.21 (9H, s), 3.00 (2H, s), 3.50 (1H, d, $J=8.0$ Hz), 6.86 (2H, s). Found: C, 77.80; H, 7.82; N, 4.24%. Calcd for $C_{21}H_{25}O_2N$: C, 77.98; H, 7.79; N, 4.33%. The second band from the TLC plates gave 127 mg (20%) of **19**-en: mp 205—206 °C (from ethanol); IR (KBr), 3386, 1604, 1331 cm^{-1}; NMR ($CDCl_3$), δ 1.23 (6H, s), 1.38 (2H, d, $J=6.0$ Hz), 1.84 (2H, d, $J=6.0$ Hz), 2.27 (9H, s), 3.15 (2H, s), 4.26 (1H, d, $J=7.8$ Hz), 6.09 (2H, s). Found: C, 77.82; H, 7.78; N, 4.66%. Calcd for $C_{21}H_{25}O_2N$: C, 77.98; H, 7.79; N, 4.38%.

*Oxidation of **19**-ex.* The reaction was carried out using **19**-ex (100 mg, 0.31 mmol), pyridinium chlorochromate (100 mg, 0.31 mmol), and anhydrous sodium acetate (20 mg, 0.24 mmol). A workup similar to that described above afforded 83 mg (83%) of **17**-ex, which was characterized by the spectral data.

*Oxidation of **19**-en.* The oxidation was carried out as has been described above, using 50 mg (0.15 mmol) of **19**-en, pyridinium chlorochromate (60 mg, 0.08 mmol), and anhydrous sodium acetate (6 mg, 0.08 mmol). Exactly the same workup as has been described above afforded 28 mg (57%) of **17**-en, which was identified by a mixed-melting-point determination and by a comparison of the spectral data.

*Cycloaddition of **4d** with Mesitonitrile Oxide.* A solution of **4d** (176 mg, 1 mmol) and mesitonitrile oxide (161 mg, 1 mmol) in 3 cm^3 of benzene was refluxed for 7 h. After solvent removal *in vacuo*, the resulting residue was separated by TLC on silica gel, using dichloromethane as the eluent. The first band from the TLC plates contained 17 mg (10%) of **4d**. The second band from the TLC plates afforded 279 mg (82%) of the adduct, **20**-ex: mp 163—164 °C; IR ($CHCl_3$), 3340—3210, 1611 cm^{-1}; NMR ($CDCl_3$), δ 1.11 (6H, s), 1.16 (3H, s), 1.62 (2H, d, $J=6.0$ Hz), 1.86 (2H, d, $J=6.0$ Hz), 2.24 (6H, s), 2.25 (3H, s), 3.15 (2H, s), 6.84 (2H, s); MS, m/e (rel intensity), 337 (M^+, 21), 294 (100). Found: C, 78.07; H, 7.83; N, 3.95%. Calcd for $C_{22}H_{27}O_2N$: C, 78.30; H, 8.07; N, 4.15%.

References

1) This paper was presented at the National Meeting of Chemical Society of Japan, October 1981.

2) K. Okada and T. Mukai, *J. Am. Chem. Soc.*, **100**, 6509 (1978).

3) L. A. Paquette, L. W. Hartel, R. Gleiter, and M. C. Bohm, *J. Am. Chem. Soc.*, **100**, 6510 (1978).

4) L. W. Hartel and L. A. Paquette, *J. Am. Chem. Soc.*, **101**, 7620 (1979).

5) L. A. Paquette, L. W. Hartel, R. Gleiter, M. C. Bohm, M. A. Beno, and G. G. Christoph, *J. Am. Chem. Soc.*, **103**, 7106 (1981).

6) M. Nitta, A. Omata, and H. Sugiyama, *Chem. Lett.*, **1980**, 1615; *Bull. Chem. Soc. Jpn.*, **55**, 569 (1982).

7) M. Nitta, A. Omata, and H. Nakatani, in submission to *Bull. Chem. Soc. Jpn.*

8) M. Nitta, A. Omata, and S. Okada, to be published.

9) Y. Senda, S. Kamiyama, and S. Imaizumi, *J. Chem. Soc., Perkin Trans. 1*, **1978**, 530; H, C, Brown and W. J. Hammer, *Tetrahedron*, **34**, 3405 (1978), and the references cited therein.

10) A. F. Diaz, M. Makai, and S. Winstein, *J. Am. Chem. Soc.*, **92**, 7477 (1970).

11) M. Nitta, O. Inoue, and M. Tada, *Chem. Lett.*, **1977**, 59.

12) G. Muherjee-Müller, P. Gilgen, J. Zsindely, and H. Schmid, *Helv. Chim. Acta*, **60**, 1758 (1977).

13) H. C. Brown and P. Geoghegan, Jr., *J. Am. Chem. Soc.*, **89**, 1522 (1967).

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

15) E. J. Corey and A. S. Suggs, *Tetrahedron Lett.*, **1975**, 2647.

16) M. C. Cabaleiro, A. D. Araya, and M. D. Johnson, *J. Chem. Soc., Perkin Trans. 2*, **1973**, 1207; D. Dodd and M. D. Johnson, *J. Chem. Soc., B*, **1971**, 662.

17) R. D. Bach and R. F. Richter, *Tetrahedron Lett.*, **1973**, 4099; *J. Org. Chem.*, **38**, 3442 (1976).

18) S. J. Christol, J. S. Perry, Jr., and R. S. Beckley, *J. Org. Chem.*, **41**, 1912 (1976).

19) H. C. Brown and J. H. Kawakami, *J. Am. Chem. Soc.*, **95**, 8665 (1973).

20) T. J Taylor and A. W. Baker, *J. Am. Chem. Soc.*, **85**, 2746 (1963).

21) F. T. Bond, *J. Am. Chem. Soc.*, **90**, 5326 (1968).

22) J. F. Galle and A. Hassner, *J. Am. Chem. Soc.*, **94**, 3930 (1972).

23) W. Lotsh and A. S. Kende, *Angew. Chem.*, **83**, 581 (1971).

24) H. Volz, J-H. Shin, and H. Hettel, *Liebigs Ann. Chem.*, **1982**, 480.

25) H. C. Brown and P. Geoghegan, Jr., *J. Org. Chem.*, **37**, 9937 (1972).

26) H. B. Henbest and R. S. McElhinney, *J. Chem. Soc.*, **1959**, 1834.

27) K. Bast, M. Christl, R. Huisgen, and W. Mack, *Chem. Ber.*, **106**, 3313 (1973); A. Battaglia, S. M. Shaw, C-S. Hsue, and K. N. Houk, *J. Org. Chem.*, **44**, 2800 (1979).

28) T. Sasaki, S. Eguchi, T. Esaki, and T. Suzuki, *Tetrahedron*, **35**, 1073 (1979).

29) K. N. Houk, *Acc. Chem. Res.*, **8**, 361 (1975).

30) M. Nitta and T. Kuroki, *Bull. Chem. Soc. Jpn.*, **55**, 1323 (1982).

31) J. Klein, *Tetrahedron Lett.*, **1973**, 4307.