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A NOVEL SYNTHESIS OF METHYLCYCLOPROPANES

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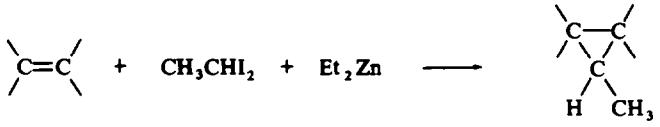
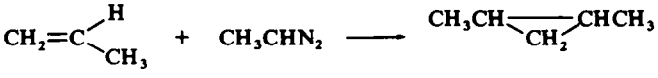
Abstract—Several methylcyclopropanes have been prepared in 32–96% yield by the reaction of olefins with ethylidene iodide and diethylzinc. The reaction is electrophilic, and proceeds stereospecifically.



In the case of the reaction with 1,2-disubstituted olefins, *cis* and *trans* olefins affords cyclopropane derivatives whose configurations with respect to the substituents from original olefins are *cis* and *trans*, respectively.

The reaction yields predominantly the *anti* isomer from olefins containing the hydroxyl group such as allyl alcohol, 2-buten-1-ol and cyclopenten-4-ol. On the other hand, the *syn* isomer is obtained predominantly from other types of olefins. Stereochemistry of the reaction is discussed.

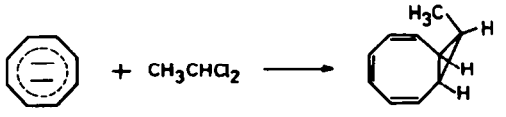
SYNTHESIS of methyl-substituted cyclopropanes from olefins have been reported by several authors.[1–4] Frey[1] prepared *cis*- and *trans*-1,2- dimethylcyclopropane in low yield by the photolysis of diazoethane in the presence of propene, where the reaction showed *syn* selectivity.*



(i)

(*cis*:*trans* = 1·4)

Katz and Garratt[2] prepared *endo*-9-methylbicyclo[6.1.0]nonatriene in 3% yield by the reaction of dilithium or dipotassium cyclooctatetraenide with ethylidene chloride.

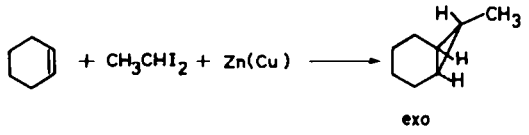


(ii)

(endo)

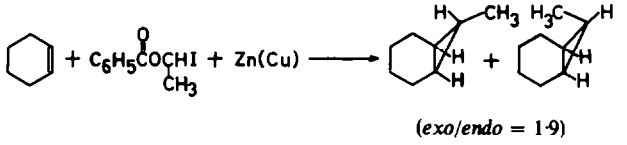
* The terms, *syn* and *anti* selectivity and *syn* and *anti* configuration, are used in the sense defined by R. A. Moss, J. Org. Chem. **30**, 3261 (1965).

These methylcarbene and carbenoid exhibit *syn* selectivity. On the other hand, Simmons *et al.*[3] prepared *exo*-7-methylnorcarane in 3·6% yield from cyclohexene by its reaction with ethylidene iodide and zinc–copper couple.



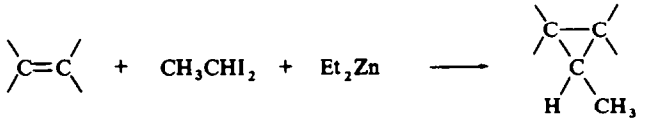
(iii)

Wittig and Jautelat[4] modified this method (iii) by using 1-iodoethyl benzoate instead of ethylidene iodide and prepared *endo*- and *exo*-7-methylnorcarane in 29% yield from cyclohexene.



(iv)

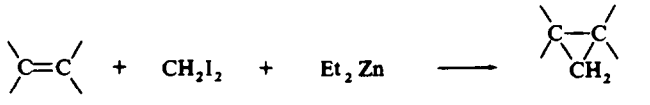
An improved method was proposed previously[5] for preparing methylsubstituted cyclopropanes by the reaction of olefins with ethylidene iodide and diethylzinc. The details of the reaction are described in this paper.



(v)

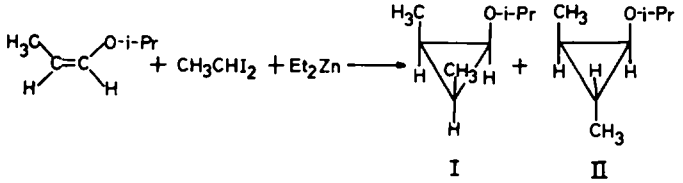
The reaction (v) is exothermic and is controlled to complete within several hours. Results are summarized in Table 1.

Similarly to the case of the reaction with methylene iodide (vi),[6] electron-donating substituents in olefin increase both the yield and rate of the reaction (v). Consequently, the reaction is electrophilic.



(vi)

The reaction (v) produces methylcyclopropanes in a stereospecific way. *Cis*-propenyl isopropyl ether afforded a 9·2:1 mixture of *cis*-1,*cis*-2-(I) and *cis*-1,*trans*-2-dimethyl-3-isopropoxycyclopropane (II) but the *trans-trans* isomer (III) was not



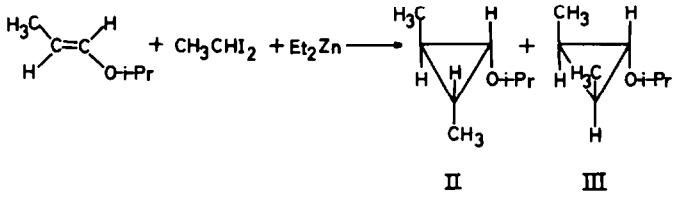
(vii)

TABLE 1. SYNTHESIS OF METHYLCYCLOPROPANES FROM OLEFINS

Olefin	Olefin (mole)	CH_3CHI_2 (mole)	Et_2Zn (mole)	Solvent	Product	Yield (%)*	Isomer ratio
Cyclohexene	0·20	0·40	0·25	Petroleum ether	*endo*/*exo*-7-Methylbicyclo[4.1.0]-heptane	66	1·5
Norbornene	0·20	0·60	0·35	Petroleum ether	*exo*/*endo*-3-Methyltricyclo[3.2.1.$0^{2,4}$]-octane	70	2·2
Vinyl isobutyl ether	0·05	0·10	0·075	Diethyl ether	*cis*/*trans*-1-Methyl-2-isobutoxycyclo-propane	96	2·3
cis-Propenyl isopropyl ether	0·17	0·30	0·16	Diethyl ether	*cis*-1,*cis*-2/*cis*-1,*trans*-2-Dimethyl-3-isopropoxycyclopropane	90	9·2
trans-Propenyl isopropyl ether	0·17	0·30	0·16	Diethyl ether	*cis*-1,*trans*-2/*trans*-1,*trans*-2-Dimethyl-3-iso-propoxycyclopropane	77	3·1
Dihydropyran	0·10	0·20	0·13	Petroleum ether	*endo*/*exo*-7-Methyl-2-*oxa*-bicyclo[4.1.0]-heptane	57	1·4
Furan	0·20	0·40	0·25	Diethyl ether	*endo*-4,*endo*-7/*endo*-4,*exo*-7-Dimethyl-2-*oxa*-*trans*-tricyclo[4.1.0.$0^{3,5}$]heptane	32	3·2
Allyl alcohol	0·20	0·40	0·30	Diisopropyl ether	*trans*/*cis*-2-Methylcyclopropylmethanol	23	5·4
trans-2-Butene-1-ol	0·20	0·40	0·30	Diisopropyl ether	*trans*-2,*trans*-3/*cis*-2,*trans*-3-Dimethyl-cyclopropylmethanol	85	1·7
Cyclopenten-4-ol	0·12	0·20	0·25	Diisopropyl ether	*exo*-6-Methyl-*cis*-bicyclo[3.1.0]hexan-3-ol	45	—

* Based upon olefin.

detected. *Trans*-propenyl isopropyl ether gave a 3·1:1 mixture of II and III but I was not detected in this case.

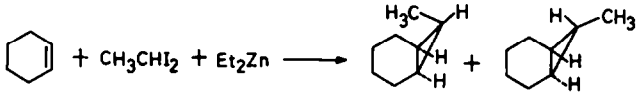


(viii)

II III

The NMR spectra of I, II and III showed the absorptions of the ring proton in the geminal position to the isopropoxyl group at 6·81, 7·10 and 7·44 τ, respectively. These absorptions were assigned to the ring protons of *cis-cis*, *cis-trans* and *trans-trans* isomer, respectively, on the basis that the methyl group linked to the cyclopropane ring shields the *cis* proton more than the *trans* proton.*

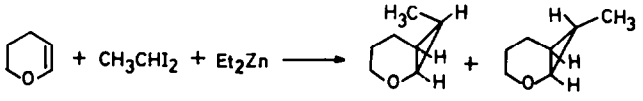
Cyclohexene gave a 1·5:1 mixture of *endo*- and *exo*-7-methylnorcarane, whose structure was determined by comparison with authentic samples.[3,4] Dihydropyran



(ix)

IV V

gave a 1·4:1 mixture of *endo*- (VI) and *exo*-7-methyl-2-*oxa*-bicyclo[4.1.0]heptane (VII).



(x)

VI VII

The structures of VI and VII were determined by NMR spectroscopy. They showed the methyl protons at 8·96 and 9·08 τ, respectively. These absorptions were assigned to the methyl protons of *endo* and *exo* isomer, respectively, on the basis that the etheral oxygen deshields the protons of the *cis* methyl group more than those of the *trans* methyl group.†

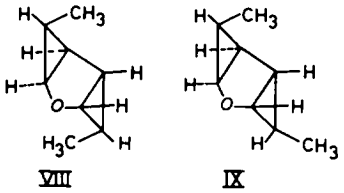
Furan afforded a 3·2:1 mixture of two isomeric compounds *A* and *B*, for which there are five possible structures.

The NMR spectrum of *A* contained a doublet ($J \sim 6{\cdot}0$ c/s) at 8·79 τ due to the methyl protons, while the NMR spectrum of *B* contained two doublets at 8·82 τ ($J \sim 6{\cdot}0$ c/s) and 9·12 τ ($J \sim 3{\cdot}0$ c/s) due to the methyl group. This fact indicates that *A* has two *endo* methyls, while *B* has one *endo* and one *exo* methyl. Therefore *A*

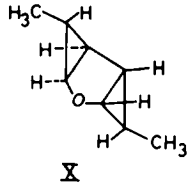
* See Ref. 6*b*, footnote p. 54.

† For example, *cis*- and *trans*-1-methyl-2-isobutoxycyclopropane showed the methyl proton linked to cyclopropane ring at 8·87 and 9·05 τ, respectively.[6b] The shielding effect of the methylene group linked to the cyclopropane ring on the methyl group will not be very significant because methyl protons of *endo*- and *exo*-7-methylnorcarane appeared at 9·05 and 9·02 τ, respectively.

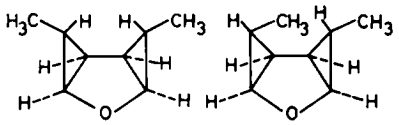
is assigned as VIII, and *B* as IX or XII. However, the strong non-bonding interaction in XII between the *endo* methyl group and the other cyclopropane ring would enable the formation of IX rather than XII. The NMR absorption of ring protons geminal to



VIII IX

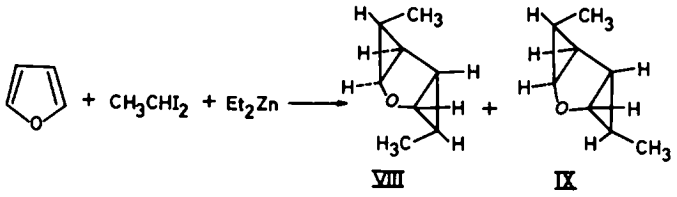


X



XI XII

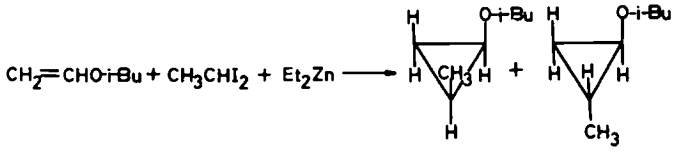
the etheral oxygen of *A* appeared at 6·58 τ as a triplet ($J \sim 5{\cdot}4$ c/s), while that of *B* appeared at 6·54 τ ($J \sim 5{\cdot}4$ c/s) as a triplet and at 6·85 τ as a multiplet.



(xi)

VIII IX

Vinyl isobutyl ether gave a 2·3:1 mixture of *cis*- and *trans*-1-methyl-2-isobutoxy-cyclopropane.



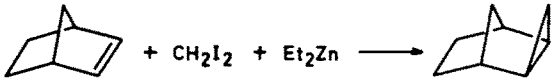
(xii)

XIII XIV

These observations show that reaction (v) favours the formation of *syn* isomer rather than the *anti* one. The conversion of *trans*-propenyl isopropyl ether to 1,2-dimethyl-3-isopropoxycyclopropane (reaction viii) would be an interesting case. The *cis-trans* isomer (II) predominated over the *trans-trans* isomer (III). This fact means that the methyl group introduced from ethylidene iodide is located favouring

the *cis* configuration with respect to the isopropoxyl group rather than to methyl group. In reaction (i), the *cis/trans* isomer ratio is 1·4.[1] Reaction (ii) gives the *syn* isomer exclusively.[2] Thus, reaction (v) shows the same steric preference as reactions (i) and (ii). On the other hand, the Simmons–Smith reaction (iii) and related reaction (iv) give the *exo* isomer exclusively from cyclohexene. The *anti* selectivity of the latter reactions might be due to the presence of zinc metal in the reaction systems, or to the difference of transition state for reactions (iii) and (v).*

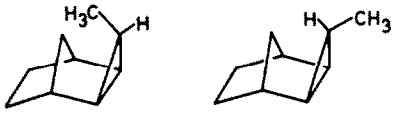
The reaction of methylene iodide and diethylzinc with norbornene is quite similar to the Simmons–Smith reaction[3] to give only *exo*-tricyclo[3.2.1.$0^{2,4}$]octane in nearly quantitative yield. But the reaction of ethylidene iodide and diethylzinc with nor-



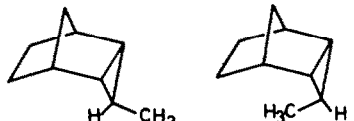
(xiv)

XV

bornene gave a 2·2:1 mixture of two isomeric compounds *C* (b.p. 153°, n_D^{25} 1·4744) and *D* (b.p. 170°, n_D^{25} 1·4824), of which there are four possible structures: XVI, XVII,



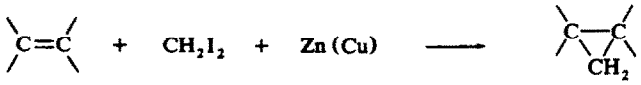
XVI XVII



XVIII XIX

XVIII and XIX. Compound *C* was identified as XVII by the comparison with authentic sample.† The chemical shifts of the methine protons of 1 and 5 positions were of particular interest because of their usefulness in assigning configurations of the other stereoisomer *D*. The NMR absorption due to the methine protons appeared at 7·76 and 7·64 τ, respectively, for (XVII) and *D*. Therefore, we excluded the structure XVI

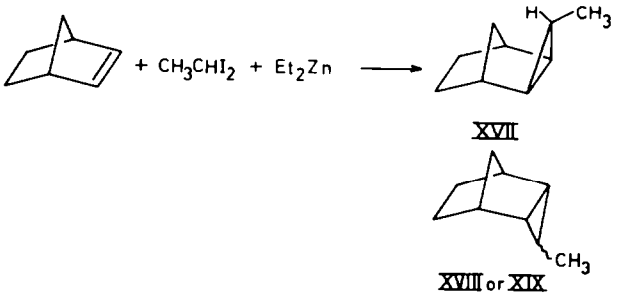
* We reported previously[6b] that essential feature of the reaction (vi) is similar to that of the Simmons–Smith reaction (xiii).



(xiii)

† Authentic *anti*-3-methyl-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (XVII) was synthesized by the lithium aluminum hydride reduction of the crystalline tosylate of *exo*-tricyclo[3.2.1.$0^{2,4}$]octane-*anti*-3-carbinol.

for *D* on the basis that the shielding effect of methyl group on the methine protons is larger in XVI than that in XVII.*

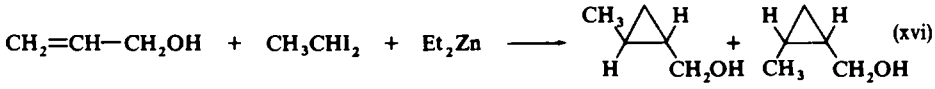


XVII XVIII or XIX (xv)

As we have mentioned before, the *syn* isomer predominates over the *anti* isomer in the cyclopropane formation reaction (v). However, the *syn* isomer of 3-methyl-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (XVI) was not formed in reaction (xv), probably due to strong steric interference between the methyl and bridge methylene groups.

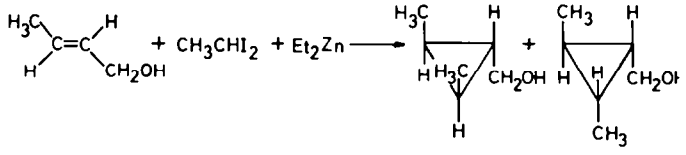
The reaction of diethylzinc and ethylidene iodide with olefin is applicable to unsaturated alcohol, although half of ethylzinc bond is consumed by the reaction with hydroxyl group of alcohol. The cyclopropane formation takes place after unsaturated alcohol is converted to ethylzinc alkoxide.

Reaction of allyl alcohol with diethylzinc and ethylidene iodide gave a 5·4:1 mixture of *trans*- (XX) and *cis*-2-methylcyclopropylmethanol (XXI). Structures were determined by comparison with authentic *trans* isomer (XX).† Crotyl alcohol was



(xvi)

reacted with diethylzinc and ethylidene iodide to give a 1·7:1 mixture of *trans*-2,-*trans*-3-(XXII) and *cis*-2,*trans*-3-dimethylcyclopropylmethanol (XXIII). The NMR



XXII XXIII (xvii)

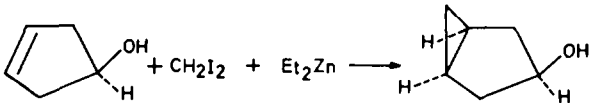
spectrum of XXII showed the absorption of methyl groups at 8·96 τ as a doublet ($J \sim 5{\cdot}0$ c/s), while that of XXIII showed the absorption as two doublets at 8·88 τ

* The authors could not determine whether *D* was XVIII or XIX. However, the strong-non-bonding interaction in XIX between the methyl group and the hydrogens of 6 and 7 positions would enable the formation of XVIII rather than XIX.

† Authentic *trans*-2-methylcyclopropylmethanol (XX) was prepared by the reaction of crotyl alcohol with methylene iodide and diethylzinc.

($J \sim 1{\cdot}6$ c/s) and 8·98 τ ($J \sim 2{\cdot}6$ c/s). Therefore, XXII was assigned to the compound having two *trans* methyl groups, and XXIII that having one *trans* methyl and one *cis* methyl groups, on the basis that the hydroxyl group deshields the protons of the *cis* methyl group more than those of the *trans* methyl group (see footnote on p. 2650).

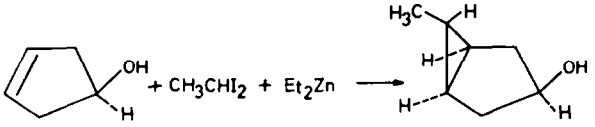
Cyclopenten-4-ol, diethylzinc and methylene iodide were reacted to give *cis*-bicyclo[3.1.0]hexan-3-ol (XXIV),* the structure of which was determined by comparison with authentic sample.†



(xviii)

XXIV

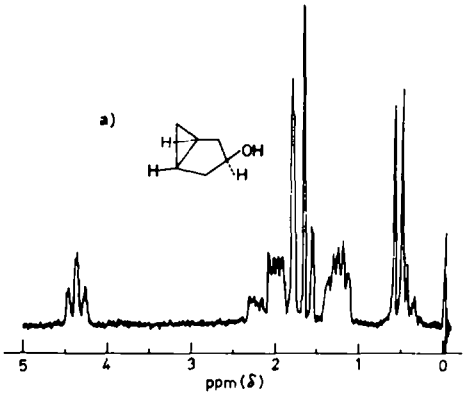
Reaction of cyclopenten-4-ol with ethylidene iodide and diethylzinc afforded *exo*-6-methyl-*cis*-bicyclo[3.1.0]hexan-3-ol (XXV). Assignment of the configuration



(xix)

XXV

of XXV was made as follows: We prepared ketone XXVI by oxidation of XXV with chromic anhydride in pyridine. Reduction of XXVI by sodium borohydride in ethanol gave a 2·8 : 1 mixture of XXV and an isomeric compound XXVII. The major product



* The VPC analysis showed the presence of another product as a shoulder after XXIV. However, the amount of the product was less than 0·8% as compared with XXIV, and the product would be negligible even if it is the *trans* isomer.

† Authentic *cis*-bicyclo[3.1.0]hexan-3-ol (XXIV) was prepared from cyclopenten-4-ol by the reaction with methylene iodide and zinc-copper couple.[7a,b]

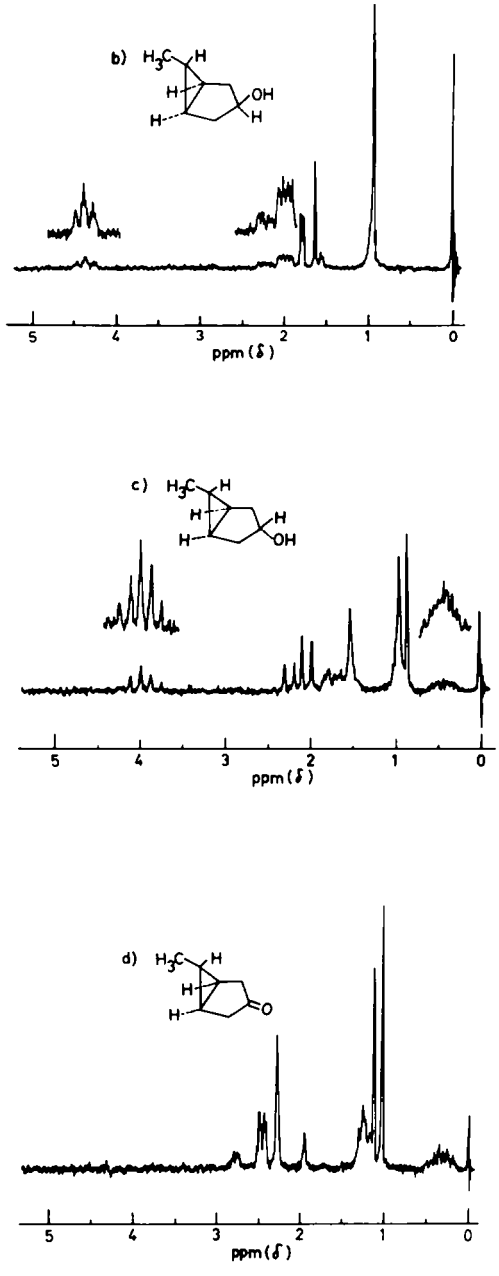
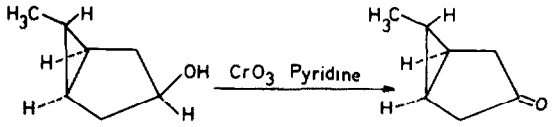


FIG. 1 NMR spectra of bicyclo[3.1.0]hexane derivatives.

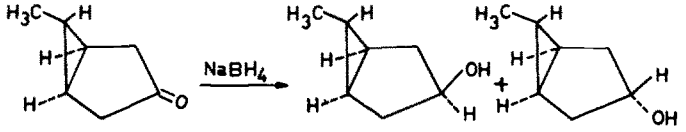
(a) *cis*-Bicyclo[3.1.0]hexan-3-ol (XXIV).
(b) *exo*-6-Methyl-*cis*-bicyclo[3.1.0]hexan-3-ol (XXV)
(c) *exo*-6-Methyl-*trans*-bicyclo[3.1.0]hexan-3-ol (XXVII).
(d) *exo*-6-Methylbicyclo[3.1.0]hexan-3-one (XXVI).

XXV was assigned to the compound with the *cis* configuration based upon the strong kinetic control mechanism for sodium borohydride reduction.[7] The similarity of NMR spectrum of XXIV with that of XXV as is shown in Figure 1 also supports the above assignment. The NMR absorption of the cyclopropane ring proton in the



(xx)

XXV XXVI



(xxi)

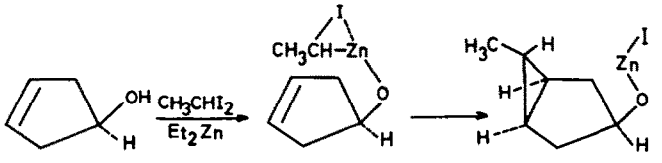
XXVI XXV XXVII

(74 : 26)

geminal position to the methyl group of XXV appeared at 9·07 τ, while that of XXVII appeared at 9·57 τ. This fact indicates that the methyl group of XXV and XXVII has the *anti* configuration, because the hydroxyl group deshields the *endo* proton more than the *exo* proton (see footnote on p. 2650).

The stereospecific formation of *cis* bicyclo alcohols (XXIV and XXV) seems to indicate that reactions (xviii) and (xix) are intramolecular.

In reaction (xix), the *anti* isomer was obtained exclusively. In reaction (xvi), the *anti* isomer predominates over the *syn* isomer. These results make a contrast to the case of the reaction (v) with other types of olefins, i.e. olefins without hydroxyl group. This fact may be ascribed to the intramolecular mechanism for the cyclopropane formation (v) in the case with unsaturated alcohols. In such a transition state as XXVIII[7b] for reaction (xix), the steric interference between the methyl group and the cyclopentene ring would lead the methyl group to the *anti* direction. Reaction (xvii)



(xxii)

XXVIII

produced predominantly the *trans-trans* isomer (XXII), indicating that the methyl group introduced from ethylidene iodide is located in the position favouring the *trans* configuration with respect to the carbinol group. This result would also support the intramolecular mechanism for reaction (v) with unsaturated alcohols.

EXPERIMENTAL

Analyses were performed at the Elemental Analysis Center of Kyoto University. IR spectra were recorded on a Hitachi EPI-G spectrophotometer. NMR spectra were taken on a Varian Model A-60 or Japan Electron Optics Lab. Model C60H spectrometer, in deuterochloroform using tetramethylsilane as internal standard. Vapour-phase chromatograms were obtained on a Shimadzu GC-2C gas chromatograph. All boiling points were uncorrected.

Material

cis- and *trans*-Propenyl ether were prepared according to the procedure of Farina *et al.*[8] Other olefins were commercial products and were purified by distillation before use. Ethylidene iodide was prepared according to the procedure of Neuman.[9] Cyclopenten-4-ol was prepared according to the procedure of Allred *et al.*[10] *Exo*-tricyclo[3.2.1.$0^{2,4}$]octane-*anti*-3-carbinol was prepared according to the procedure of Sauers *et al.*[11] and was converted to its tosylate in pyridine. Commercial samples of methylene iodide, diethylzinc, solvents and nitrogen were purified as in a previous paper.[6b] Other chemicals were commercially available and used without further purification.

Methylcyclopropanes from olefins by the reaction with ethylidene iodide and diethylzinc

General procedure. A 3-necked, round-bottomed flask equipped with thermometer, dropping funnel, 3-way cock and magnetic stirring bar was evacuated and filled with dry N_2. Olefin, solvent and diethylzinc were added via hypodermic syringes. Ethylidene iodide was added through dropping funnel over a period of a $\frac{1}{2}$ hr while stirring at room temp. The exothermic reaction took place immediately. After the addition was completed, the reaction mixture was allowed to stand at room temperature for several hours, and the reaction mixture was successively poured into dilute hydrochloric acid and washed with water and dilute sodium bicarbonate. After drying over sodium sulfate, solvent, ethyl iodide (b.p. 73°), and *sec*-butyl iodide (b.p. 119°) were eliminated by distillation. The residue was fractionally distilled through a packed column. In those cases where epimeric cyclopropanes were formed, the ratios of isomers were determined by VPC on the crude material. Final purification of the analytical and spectral samples was accomplished by distillation though a spinning-band column or by VPC. Yields were based upon the olefins.

7-Methylnorcarane (IV *and* V). From cyclohexene (0·20 mole, 20·3 ml), diethylzinc (0·25 mole, 25 ml) and ethylidene iodide (0·40 mole, 37·6 ml) in light petroleum ether (100 ml) were obtained 14·5 g (66%) of 7-methylnorcarane. The *endo/exo* isomer ratio was 1·5. Anal. Calcd. for C_8H_{14}: C, 87·19; H, 12·81. Found: C, 86·93; H, 12·62. The *exo* isomer has b.p. 132–133° and n_D^{25} 1·4508 (Ref. b.p. 130°,[3] 131°;[4] n_D^{25} 1·4528,[3] 1·4493[4]). The *endo* isomer has b.p. 142–143° and n_D^{25} 1·4636 (Ref. b.p. 144°;[4] n_D^{25} 1·4638[4]).

1-Methyl-2-isobutoxycyclopropane (XIII *and* XIV). Isobutyl vinyl ether (0·05 mole, 5 g), diethylzinc (0·075 mole, 7·5 ml) and ethylidene iodide (0·10 mole, 9·4 ml) were allowed to react in ether (25 ml) producing 6·1 g (96%) of the cyclopropyl ethers. The *cis/trans* isomer ratio was 2·3. Structures were determined by comparison with authentic samples.[6]

1,2-Dimethyl-3-isopropoxycyclopropane (I, II *and* III). *Cis*-propenyl isopropyl ether (0·17 mole, 17 g) was reacted with diethylzinc (0·16 mole, 16 ml) and ethylidene iodide (0·30 mole, 28·2 ml) in 100 ml of ether to produce 19·6 g (90%) of 1,2-dimethyl-3-isopropoxycyclopropane. The *cis-cis/cis-trans* isomer ratio was 9·2. The *cis-cis* isomer (I) has b.p. 130–131° and n_D^{25} 1·4125. Anal. Calcd. for $C_8H_{16}O$: C, 74·94; H, 12·58. Found: C, 74·64; H, 12·62. NMR ($CDCl_3$, τ): 6·38 (1H, μl), 6·81 (1H, triplet, $J \sim 7·0$ c/s), 8·82 (6H, doublet, $J \sim 6·0$ c/s), 9·03 (6H, doublet, $J \sim 7·0$ c/s), 8·9–9·5 (2H, μl). ν_{max}: 1390, 1235, 1178, 1158, 1137, 1038 cm^{-1}. The *cis-trans* isomer (II) has b.p. 121° (microdetermination). NMR ($CDCl_3$, τ): 6·37 (1H, μl), 7·10 (1H, μl), 8·78–9·08 (12H, two triplets, $J \sim 7·5$ c/s, and one doublet, $J \sim 6·0$ c/s), 9·53 (2H, μl).

The same procedure was adopted for *trans*-propenyl isopropyl ether and 1,2-dimethyl-3-isopropoxycyclopropane was obtained in 77% yield. The *cis-trans/trans-trans* isomer ratio was 3·1. The *trans-trans* NMR ($CDCl_3$, τ): 6·31 (1H, μl), 7·44 (1H, μl), 8·84 (6H, doublet, $J \sim 6·0$ c/s), 9·03 (8H, μl).

2-Oxa-bicyclo[4.1.0]*heptane* (VI *and* VII). The reaction of freshly distilled dihydropyran (0·10 mole, 8·4 g) with diethylzinc (0·13 mole, 13 ml) and ethylidene iodide (0·20 mole, 18·8 ml) in light petroleum ether (100 ml) gave the title compound (6·4 g, 57%). The *endo/exo* isomer ratio was 1·4. The *exo* isomer (VI) has b.p. 138° (microdetermination) and n_D^{25} 1·4475. Anal. Calcd. for $C_7H_{12}O$: C, 74·95; H, 10·78. Found: C, 74·39; H, 10·60. NMR ($CDCl_3$, τ): 6·40–7·00 (3H, μl), 7·90–8·30 (2H, μl), 8·40–8·83 (2H, μl), 9·08 (3H, doublet, $J \sim 3·0$), 8·83–9·60 (2H, μl). The *endo* isomer (VII) has b.p. 142° (microdetermination) and n_D^{25} 1·4550. Anal. Calcd. for $C_7H_{12}O$: C, 74·95; H, 10·78. Found: C, 74·94; H, 10·81. NMR ($CDCl_3$, τ): 6·55 (3H, μl), 7·90–8·80 (4H, μl), 8·95 (3H, doublet, $J \sim 5·4$ c/s), 9·05–9·50 (2H, μl).

4,7-*Dimethyl*-2-*oxa*-*bicyclo*[4.1.0.0^{3,5}]*heptane* (VIII *and* IX). Freshly distilled furan (0·30 mole, 21·9 ml) was reacted with diethylzinc (0·25 mole, 25 ml) and ethylidene iodide (0·40 mole, 37 ml) for 15 hr in 200 ml of refluxing ether. A 3·2:1 mixture of *endo*-4,*endo*-7-(VIII) and *endo*-4,*exo*-7-dimethyl-2-*oxa*-*trans*-tricyclo-[4.1.0.0^{3,5}]heptane (IX) was obtained in 32% (11·9 g) yield, although an unknown substance was present in the crude product to the extent of 1% yield (VPC analysis). VPC analysis of the reaction mixture showed that the major product (VII) had the longest and the unknown product had the shortest retention time. A 3·2:1 mixture of VIII and IX was distilled at 104–105° (57 mm Hg). Anal. Calcd. for $C_8H_{12}O$: C, 77·38; H, 9·74. Found: C, 77·23; H, 9·71. The *endo*-*endo* isomer: NMR ($CDCl_3$, τ): 6·58 (2H, triplet, $J \sim 5{\cdot}4$ c/s), 8·79 (doublet, $J \sim 6{\cdot}0$ c/s) and 8·50–8·90 (8H, μl), 9·20–9·70 (2H, μl). The *endo*-*exo* isomer: NMR ($CDCl_3$, τ): 6·57 (1H, triplet, $J \sim 5{\cdot}4$ c/s), 6·85 (1H, μl), 8·10–8·60 (2H, μl), 8·82 (doublet, $J \sim 6{\cdot}0$ c/s), 9·12 (doublet, $J \sim 3{\cdot}0$ c/s) and 8·70–9·60 (9H, contained peaks of impurities, μl).

Tricyclo[3.2.1.0^{2,4}]*octane* (XV). The procedure reported previously[6] was adopted for the reaction of norbornene (0·05 mole, 4·7 g) with methylene iodide (0·15 mole, 12 ml) and diethylzinc (0·08 mole, 8 ml) in 30 ml of benzene, and 5·2 g (96%) of *exo*-tricyclo[3.2.1.0^{2,4}]octane was obtained. B.p. 137° (Ref. 136–137°)[7b] and n_D^{25} 1·4778 (Ref. 1·4778).[7b]

3-*Methyltricyclo*[3.2.1.0^{2,4}]*octane* (XVII, XVIII *and* XIX). From norbornene (0·20 mole, 18·8 g), diethylzinc (0·35 mole, 35 ml) and ethylidene iodide (0·60 mole, 56·4 ml) in light petroleum ether (200 ml), the title compound (17·1 g, 70%) was obtained. The *exo*/*endo* isomer ratio was 2·2. The *exo* isomer has the shorter VPC retention time The *exo* isomer (XVII) has b.p. 153° (micro determination) and n_D^{25} 1·4744. Anal. Calcd. for C_9H_{14}: C, 88·45; H, 11·55. Found: C, 88·57; H, 11·57. NMR ($CDCl_3$, τ): 7·76 (2H, broad singlet), 8·68 (4H, μl), 8·90–9·05 (1H, μl), 9·16 (3H, singlet), 9·10–9·50 (2H, μl), 9·61 (2H, μl). ν_{max}: 1389, 1033 cm^{-1}. The *endo* isomer (XVIII or XIX) has b.p. 170° (microdetermination) and n_D^{25} 1·4824. Anal. Calcd. for C_9H_{14}: C, 88·45; H, 11·55. Found: C, 88·69; H, 11·76. NMR ($CDCl_3$, τ): 7·64 (2H, broad singlet), 8·68 (4H, μl), 8·85 (4H, doublet, $J \sim 5{\cdot}5$ c/s), 9·34 (4H, μl). ν_{max}: 1385, 1029, 1012 cm^{-1}.

2-*Methylcyclopropylmethanol* (XX *and* XXI). Allyl alcohol (0·20 mole, 13·6 ml) was added dropwise to diethyl zinc (0·30 mole, 30 ml) in 100 ml of diisopropyl ether at room temperature. After gas evolution ceased, ethylidene iodide (0·40 mole, 37·6 ml) was added to the reaction mixture through a dropping funnel with refluxing. After 10 hr, the refluxing was ceased. The reaction mixture was poured into 100 ml of dilute hydrochloric acid. The aqueous layer was extracted three times with ether. The combined organic solution was washed with water and aq. $NaHCO_3$, and dried over $MgSO_4$. Solvents were removed and the residue was distilled, and 4·0 g (23%) of 2-methylcyclopropylmethanol was obtained. B.p. 134–135°. The *trans*/*cis* isomer ratio was 5·4. The *trans* isomer has n_D^{25} 1·4291 (Ref. b.p. 133°, n_D^{25} 1·4283 for *cis*, *trans* mixture).[12] Anal. Calcd. for $C_5H_{10}O$: C, 69·72; H, 11·70. Found: C, 69·83; H, 11·67. NMR ($CDCl_3$, τ): 6·54 (2H, doublet, $J \sim 6{\cdot}9$ c/s), 8·43 (1H, singlet), 8·89 (3H, doublet, $J \sim 4{\cdot}8$ c/s), 9·0–9·9 (4H, μl). ν_{max}: 3333, 3068, 1385, 1010, 1030, 650 cm^{-1}. The *cis* isomer: NMR ($CDCl_3$, τ): 6·36 (2H, μl), 8·58 (1H, singlet), 8·90 (3H, doublet, $J \sim 3{\cdot}1$ c/s), 8·9–9·5 (4H, μl).

Authentic *trans*-2-methylcyclopropylmethanol was obtained (5·5 g, 33%) from crotyl alcohol (0·20 mole, 16·9 ml), diethylzinc (0·30 mole, 30 ml) and methylene iodide (0·40 mole, 32 ml) in 100 ml of diisopropyl ether according to the procedure above mentioned.

2,3-*Dimethylcyclopropylmethanol* (XXII *and* XXIII). Crotyl alcohol (0·20 mole, 16·9 ml), diethylzinc (0·30 mole, 30 ml), ethylidene iodide (0·40 mole, 37·6 ml) and 100 ml of diisopropyl ether was reacted to give 17 g (85%) of *trans*-2,*trans*-3- and *cis*-2,*trans*-3-dimethylcyclopropylmethanol in the ratio of 1·7:1; b.p. 77–78°/58 mm Hg, n_D^{25} 1·4359. Anal. Calcd. for $C_6H_{12}O$: C, 71·95; H, 12·08. Found: C, 71·30; H, 12·13. The *trans*-*trans* isomer: NMR ($CDCl_3$, τ): 6·55 (2H, doublet, $J \sim 6{\cdot}3$ c/s), 8·43 (1H, singlet), 8·96 (6H, doublet, $J \sim 5{\cdot}0$ c/s), 9·0–9·7 (3H, μl), ν_{max}: 3335, 1386, 1015, 650 cm^{-1}. The *cis*-*trans* isomer: NMR ($CDCl_3$, τ): 6·36 (2H, μl), 8·65 (1H, singlet), 8·88 (3H, doublet, $J \sim 1{\cdot}6$ c/s), 8·98 (3H, doublet, $J \sim 2{\cdot}6$ c/s), 9·0–9·9 (3H, μl). ν_{max}: 3335, 1384, 1037, 650 cm^{-1}.

cis-*Bicyclo*[3.1.0]*hexan*-3-*ol* (XXIV). Cyclopenten-4-ol (0·12 mole, 10 g), diethylzinc (0·25 mole, 25 ml), methylene iodide (0·20 mole, 16 ml) and 100 ml of diisopropyl ether was reacted in the same way to afford 6·8 g (60%) of *cis*-bicyclo[3.1.0]hexan-3-ol; b.p. 60–62°/13 mm Hg, n_D^{25} 1·4782 (Ref. b.p. 68°/18 mm Hg, n_D^{25} 1·4781).[7a] NMR ($CDCl_3$, τ): 5·62 (1H, triplet, $J \sim 6{\cdot}5$ c/s), 8·32 (1H, singlet), 7·6–8·5 (4H, μl), 8·6–8·9 and 9·3–9·6 (3H, μl). ν_{max}: 3345, 3081, 1047, 650 cm^{-1}.

exo-6-*Methyl*-cis-*bicyclo*[3.1.0]*hexan*-3-*ol* (XXV). *exo*-6-Methyl-*cis*-bicyclo[3.1.0]hexan-3-ol (XXV) was obtained (5·9 g, 45%) in a similar way from cyclopenten-4-ol (0·12 mole, 10 g), ethylidene iodide (0·20 mole, 19 ml), diethylzinc (0·25 mole, 25 ml) and 100 ml of diisopropyl ether. B.p. 71–72°/36 mm Hg, n_D^{25} 1·4711. Anal. Calcd. for $C_7H_{12}O$: C, 74·95; H, 10·78. Found: C, 74·82; H, 10·76. NMR ($CDCl_3$, τ): 5·64 (1H,

triplet, $J \sim 6{\cdot}5$ c/s), 7·67–8·48 (4H, μl), 8·37 (1H, singlet), 9·07 (6H, broad singlet). ν_{max}: 3348· 3023, 2948, 1388, 1075, 1056, 1033, 1023, 959, 868 cm^{-1}.

The compound XXV (1·8 g) was oxidized to *exo*-6-methyl-*cis*-bicyclo[3.1.0]hexan-3-one (XXVI) (1 g, 56%) by the reaction with 9 g of chromic anhydride in 65 ml of pyridine. A sample collected by VPC on PEG 6000 at 110° was analyzed: n_D^{25} 1·4545. Anal. Calcd. for $C_7H_{10}O$: C, 76·32; H, 9·15. Found: C, 76·37; H, 9·35. NMR ($CDCl_3$, τ): 7·1–8·1 (4H, μl), 8·75 (2H, μl), 8·93 (3H, doublet, $J \sim 6{\cdot}0$ c/s), 9·70 (1H, μl). ν_{max}: 3030, 2950, 1742, 1389, 1142, 1055, 1026, 988, 952 cm^{-1}.

To 100 mg of XXVII dissolved in 5 ml of 95% ethanol, 0·5 g of sodium borohydride was added, and the mixture was heated on a steam bath for 1 hr. The cooled mixture was diluted with 50 ml of water and extracted with ether. The combined ether extracts were washed with water, dried, and the solvent was removed to give 90 mg of material, which was later shown to contain 74% of *cis* isomer (XXV) and 26% of *trans* isomer (XXVII) of 6-methylbicyclo[3.1.0]hexan-3-ol. A NMR sample of *exo*-6-methyl-*trans*-bicyclo-[3.1.0]hexan-3-ol (XXVII) was collected from the above mixture by VPC (PEG 6000, 150°). NMR ($CDCl_3$, τ): 6·02 (1H, μl), 7·7–8·4 (4H, μl), 8·48 (1H, singlet), 9·10 (doublet, $J \sim 5{\cdot}5$ c/s) and 8·9–9·1 (5H, μl), 9·57 (1H, μl).

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