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The Revised Stereostructures of the Diels-Alder Adducts of *l*-Carvone with Butadiene[1]

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The detailed studies on the stereochemistry of the Diels-Alder adducts of 2,5-dialkyl-cyclohex-2-en-1-one with butadiene in the presence of Lewis acid were made. The experimental results indicated that addition of butadiene to the dienophile took place stereoselectively opposite to the 5-alkyl side. This fact is in conflicting with the former results [see ref. 4)] that addition of butadiene in the Diels-Alder reaction of carvone with butadiene occurred predominantly from the same side as that of the 5-isopropenyl group. The reported reaction, therefore, was re-investigated. It was concluded from the results of experiments that addition of butadiene took place predominantly opposite to the 5-isopropenyl side in a similar manner as our deduction. Consequently, the reported stereostructures [see ref. 4)] should be revised in such a way that the structure (**3b**) for the major product is replaced by the formula (**3a**) and the structure (**3a**) for the minor product by the formula (**3b**). The reaction condition was also examined and the yield of the major product (**3a**) was much improved in the presence of 0.11 eq $AlCl_3$ to the dienophile at room temperature under vigorous stirring.

Keywords——2,5-dimethyl-cyclohex-2-en-1-one; butadiene; β-eudesmol; Diels-Alder reaction condition; stereoselective addition of butadiene; stereochemistry of Diels-Alder adducts

Only a few papers[3,4] have been recorded on the Diels-Alder reaction of 5-alkyl-cyclohex-2-en-1-one with butadiene and no detailed studies on the stereochemistry of the adducts have been made. This type of the Diels-Alder reaction seems to be an effective synthetic way for the construction of the carbon skeleton of certain sesquiterpenes and alkaloids. To this end the stereochemical problems regarding the adducts should be clearly solved.

In a previous paper[5], we reported that the Diels-Alder reaction of 5-methyl-cyclohex-2-en-1-one with butadiene provided two kinds of adducts, (**1a**) and (**1b**), in a 1:5 ratio and a 46% yield. This result suggested that addition of butadiene to the dienophile took place stereoselectively from the opposite side to that of the 5-methyl group to give initially the *cis* adduct (**1a**) which then epimerizes mostly to the *trans* isomer (**1b**).

We now carried out the Diels-Alder reaction of 2,5-dimethyl-cyclohex-2-en-1-one with butadiene in which no epimerization of the product is predictable. In this case, a single adduct was stereoselectively obtained in a 55% yield and the structure was established as shown by the formula (**2**) on the basis of the experimental result stated later. This fact revealed that addition of butadiene to 2,5-dimethyl-cyclohex-2-en-1-one occurred opposite to the 5-methyl side as suggested in our previous paper.[5] On the other hand, Nerdel, *et al.*[4] reported that the stereostructure of the major product obtained from the Diels-Alder reaction of carvone with butadiene was represented by the formula (**3b**) and that of the minor product by the formula (**3a**). This assignment indicates that addition of butadiene to carvone took place predominantly from the same side as that of the 5-isopropenyl group. This fact, therefore,

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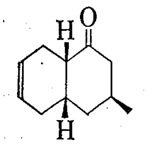
[1] A part of this work was reported in *Tetrahedron Lett.*, **1975**, 2693.
[2] Location: *Shimoadachi-cho, Sakyo-ku, Kyoto.*
[3] K. Yamamoto, I. Kawasaki, and T. Kaneko, *Tetrahedron Lett.*, **1970**, 4859.
[4] F. Nerdel and H. Dahl, *Ann. Chem.*, **710**, 90 (1967).
[5] T. Harayama, H. Cho, M. Ohtani, and Y. Inubushi, *Chem. Pharm. Bull.* (Tokyo), **22**, 2784 (1974).

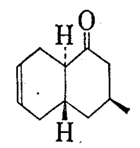
is in conflicting with our suggestion on addition direction of butadiene to dienophiles, prompting us to re-examine the stereostructures of adducts reported in the literature.[4] This contradiction has now been resolved by revision of the reported formulas in such a way that the structure (**3b**) for the major product is replaced by the formula (**3a**) and the structure (**3a**) for the minor product by the formula (**3b**). In the present paper, we wish to report detailed experimental results from which our conclusion was drawn.

The reaction of 2,5-dimethyl-cyclohex-2-en-1-one with butadiene was carried out in the presence of 0.15 eq $AlCl_3$ to the dienophile at room temperature for 8 days to give a single product (**2**) in a 55% yield. Catalytic hydrogenation of **2** over Pd–C catalyst gave the ketone (**4**) and bromination of **4** afforded the bromoketone (**5**). Dehydrobromination of **5** with LiBr-Li_2CO_3 provided the α,β-unsaturated ketone (**6**) in a high yield from the compound (**2**). Catalytic hydrogenation of **6** over Pd–C catalyst provided the ketone (**7**), whose spectral data and gas–liquid chromatography (GLC) behavior were distinct from those of the ketone (**4**). As it is well known that hydrogen attacks a double bond of *cis* decalin derivatives from the less hindered "convex" face, the stereostructure of the adduct (**2**) will be represented by the formula (**2**). This result suggests that addition of butadiene to 2,5-dimethyl-cyclohex-2-en-1-one took place stereoselectively from the opposite side to that of 5-methyl group.

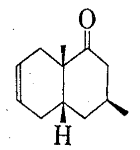
Next, the Diels-Alder reaction of *l*-carvone with butadiene was performed under heating condition (180°, 60 hr) as described in the literature[4] and two kinds of adducts, (**3a**) and (**3b**), were obtained in the same yield and the same ratio as those reported. In order to improve the yield of this reaction, the same reaction was examined in the presence of $AlCl_3$. Thus, the reaction of *l*-carvone with butadiene was carried out in the presence of 0.1 eq $AlCl_3$ to *l*-carvone at room temperature for 7 days in a sealed tube to give the adduct (**3a**, 16% yield) corresponding to the major product described in the literature together with its isomer (**3c**, a few %), respectively. Furthermore, the same reaction was performed in the presence of 0.11 eq $AlCl_3$ to the dienophile at room temperature for 10 days under vigorous stirring in an autoclave to afford two kinds of adducts, (**3a**) and (**3c**), in a 40% and a 3% yield, respec-



1a



1b



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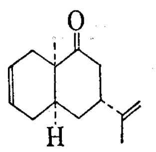
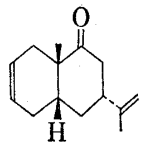
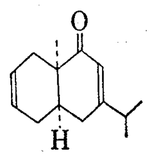


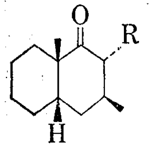
3a



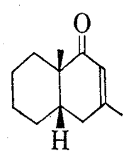
3b



3c



4 : R=H
5 : R=Br



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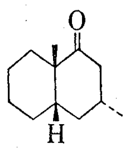

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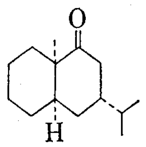

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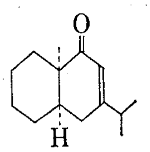

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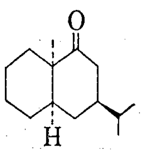

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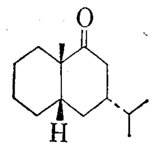

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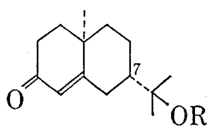

12a : R=Ac
12b : R=H

tively. In both cases, the compound (**3b**) obtained from the heating method as a minor product was not detected.

Catalytic hydrogenation of the major product (**3a**) over PtO_2 catalyst gave the ketone (**8**) in an 80% yield. Bromination of **8**, followed by dehydrobromination with $LiBr$–Li_2CO_3 afforded the α,β-unsaturated ketone (**9**) in a 61% yield which on catalytic reduction over PtO_2 gave the ketone (**10**) in a good yield. The spectral data of **8** was clearly distinct from those of **10**. On the other hand, the minor product (**3b**) was catalytically hydrogenated over PtO_2 to yield quantitatively the ketone (**11**) which was proved to be an antipode of the ketone (**10**). Since hydrogen attacks a double bond of the *cis* decalin derivatives from the less hindered "convex" face, the stereostructure of the ketone (**10**) is represented by the formula (**10**). From this finding, it seems reasonable to assume that the stereostructure of the major product is represented by the formula (**3a**) and that of the minor product by the formula (**3b**) on the contrary to the reported assignments.[4] Furthermore, the absolute stereostructure of **3c** was established by its conversion to the ketone (**10**). When hydrogenated over 10% Pd–C catalyst, not PtO_2, the major product (**3a**) gave two kinds of ketones, (**8**) and (**10**), in an 11 : 3 ratio and an 81% yield. This result will be explained by assuming partial isomerization of a double bond[6] of an isopropenyl group during the hydrogenation process.

In order to confirm more definitely the above deduction, an attempt was made to convert the major product (**3a**) to the compound (**12a**) of established stereostructure. As a model experiment, we examined first the conversion of the compound (**2**) to the diketone (**18**). Thus, treatment of **2** with NBS–$HClO_4$–aq. dioxane gave the bromohydrins, (**13**) and (**14**). That the compound (**14**) contains two bromine atoms was suggested by its elemental analysis. Jones' oxidation of the compound (**13**) and (**14**) yielded quantitatively the compound (**15**) and (**16**), respectively. On reduction with Zn–AcOH, the compound (**15**) and (**16**) afforded the same diketone (**17**) in a good yield. In the nuclear magnetic resonance (NMR) spectrum of the diketone (**17**), a doublet (J=15 Hz, one component of an AB quartet signal) corresponding to one proton of methylene protons adjacent to a carbonyl group was observed at δ 2.90, indicating that a carbonyl group is situated at C_3 position as shown by the formula (**17**). The structures of bromohydrins, (**13**) and (**14**), and bromoketones, (**15**) and (**16**) are, therefore, represented by the formulas (**13**), (**14**), (**15**), and (**16**), respectively. We next tried the conversion *via* an epoxide. Thus, epoxidation of **2** with MCPBA gave the epoxy-ketone (**19**) in an 81% yield. Cleavage of the epoxide ring of **19**, however, with aq. 47% HBr afforded the diol-ketone and treatment of **19** with BF_3–ether also did not provide the desired compound (**18**).

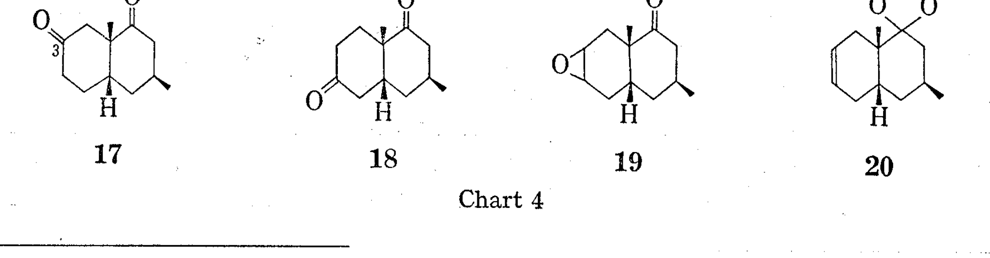

Chart 4

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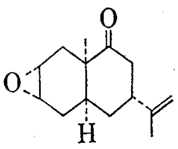
[6] H.O. House, "Modern Synthetic Reactions," 2 nd. edition, Chapter 1, W.A. Benjamin, INC. California, 1972, pp. 20—23.

Ketalization of the compound (**2**) yielded the compound (**20**) which was successively treated with MCPBA, $LiAlH_4$, Jones' reagent and conc. HCl–aq. dioxane to give the desired diketone (**18**). The spectral data of **18** were distinct from those of the diketone (**17**).

With reference to this chemical conversion of the compound (**2**), transformation of the compound (**3a**) into the compound (**12a**) was undertaken. Ketalization or thioketalization of **3a**, however, gave unsatisfactory results. Then, treatment of **3a** in dry CH_2Cl_2 with 1.1 mol eq. MCPBA to **3a** at room temperature or with 0.8 mol eq MCPBA to **3a** at $-70°$ gave epoxyketones (**21**) and (**22**), and the diepoxy-ketone (**23**) with unsatisfactory yield. Epoxidation of **3a** with 3.0 mol eq MCPBA to **3a** at room temperature provided the diepoxy-ketone (**23**) in a 67% yield which on treatment with $LiAlH_4$ gave mainly the unexpected diol-ether (**24**) in a 45% yield and Jones' oxidation of **24** afforded the compound (**25**). The stereostructure of **24** was inferred from the diaxial cleavage of **23**, being presumably in the steroidal conformation. Then, reduction of **3a** with $NaBH_4$ gave the alcohol (**26**). Treatments of **26** with tosylchloride, mesylchloride, N,N,N',N'-tetramethyldiamidophosphorochloridate[7] and diethylphosphorochloridate[7] provided the compounds, (**27**), (**28**), (**29**), and (**30**), in a good yield, respectively. However, reduction of **27** and **28** with $LiAlH_4$ or $LiCuH_2$ was unfruitful. Reduction of **29** and **30** with Li–liq. NH_3 (or $EtNH_2$) gave also no satisfactory result. These routes for transformation of **3a** into **12a** did not serve to our purpose.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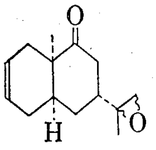
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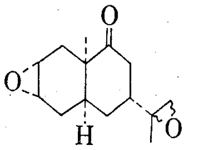
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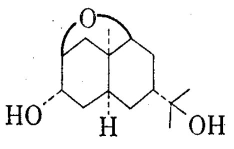
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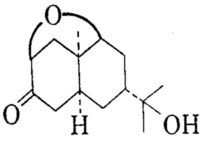
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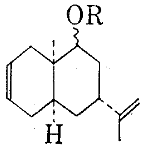
26 : R=H
27 : R=Ts
28 : R=Ms
29 : R=$\underset{\overset{\|}{O}}{P}$(N-Me$_2$)$_2$
30 : R=$\underset{\overset{\|}{O}}{P}(OEt)_2$

Successive treatments of **3a** with *p*-tosylhydrazine, a large excess of $NaBH_4$[8] and MCPBA afforded the diepoxide (**31**) and the isopropyl-epoxide (**32**) in a 25% and a 7% yield from **3a**, respectively. The epoxy-ring opening of **31** with $LiAlH_4$ gave a sole diol (**33**) in a 60% yield, the stereostructure of which was inferred from the reductive diaxial cleavage of the epoxy-ring of **31** being presumably in the steroidal conformation. Jones' oxidation of **33** gave the hydroxy-ketone (**34**). Acetylation of **34** with isopropenyl acetate–anhyd. *p*-TsOH at room temperature gave the acetoxy-ketone (**35**) in a 78% yield which on bromination with Br_2–$MgCO_3$ afforded the bromo-ketone (**36**) in a 53% yield. In the NMR spectrum of **36**, a doublet (J=12.5 Hz) due to a methine proton at C_1 was observed at δ 4.83 and the α configuration of the C_1–Br bond was suggested by the J value. Thus, the structure of the bromo-ketone is represented by the formula (**36**), from which the structures of the diol, the hydroxy-ketone, and the acetoxy-ketone are deduced to be represented by the formulas, (**33**), (**34**), and (**35**), respectively. Finally, dehydrobromination of **36** with LiBr–Li_2CO_3 provided the desired α,β-unsaturated keto-acetate (**12a**) in a 59% yield. The 2,4-dinitrophenylhydrazone of **12a**, mp 180—181°, was identical with an authentic sample.[9] Thus, this

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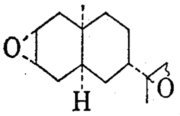
[7] R.E. Ireland, D.C. Muchmore, and U. Hengartner, *J. Amer. Chem. Soc.*, **94**, 5098 (1972).

[8] L. Caglioti, *Tetrahedron*, **22**, 487 (1966).

transformation provided conclusive proof that the structures of the major product and the minor product obtained from the Diels-Alder reaction of *l*-carvone with butadiene are represented by the formula (**3a**) and (**3b**), respectively. Consequently, the Diels-Alder reaction of 2,5-dialkyl-cyclohex-2-en-1-one with butadiene will serve as an effective route for the synthesis of the eudesmane sesquiterpenes and certain alkaloids,[10] in which an angular alkyl group and a secondary alkyl group at C_7 bear a *cis* relationship. Moreover, synthesis of the α,β-unsaturated keto-acetate (**12a**) amounts to a formal synthesis of (−)-β-eudesmol since the α,β-unsaturated keto-acetate (**12a**) was converted to the α,β-unsaturated ketone (**12b**),[9] an antipode of which was transformed to (+)-β-eudesmol.[11]



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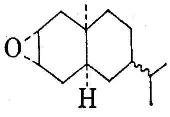

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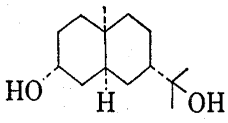

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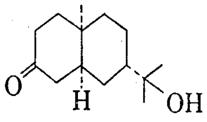

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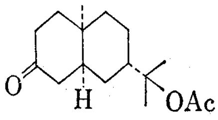

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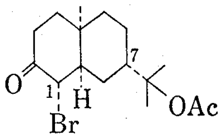

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Experimental

All melting points were observed on a microscopic hot stage (Yanagimoto melting point apparatus) and uncorrected. All NMR spectra were obtained in $CDCl_3$ solution with tetramethylsilane as an internal standard on a Varian A-60 spectrometer, and IR spectra were measured for a solution in $CHCl_3$ with a Hitachi EPI spectrometer, unless otherwise noted. MS were taken with a Hitachi RMU-6C spectrometer with a heated direct inlet system. UV spectra were measured with a Hitachi EPS-2U spectrometer and GLC was carried out with a Hitachi gas chromatography model 063 equipped with a hydrogen flame ionization detector, using nitrogen as a carrier gas (30 ml/min). All extracts were dried over anhyd. $MgSO_4$. Column chromatography was performed on silica-gel (Mallinckrodt silicic acid, 100 mesh) or alumina (Aluminium Oxyd. G. Brockmann, Activity, II–III).

2,5-Dimethyl-cyclohex-2-en-1-one from 2,5-Dimethyl-cyclohexanone——Although 2,5-dimethyl-cyclohex-2-en-1-one had been synthesized,[12] we synthesized this compound through an alternative route. To a solution of 52 g of 2,5-dimethylcyclohexanone in 800 ml of $CHCl_3$ was added dropwise a solution of 72 g of bromine in 104 ml of $CHCl_3$ at 0° under stirring. After 30 min, the brown color of reaction mixture faded away. The mixture was washed with water, dried and evaporated. To a solution of the oily residue in 320 ml of N,N-dimethylformamide (DMF) were added 116 g of LiBr and 111 g of Li_2CO_3 under stirring. The mixture was heated at 115° under an argon atmosphere for 3.5 hr with stirring. After cooling, the mixture was made acidic with dil. HCl and extracted with ether. The extract was dried and evaporated. Distillation of the residue gave 24 g of 2,5-dimethyl-cyclohex-2-en-1-one, bp 85—91°/40 mmHg. The melting points of the 2,4-dinitrophenylhydrazone and the oxime of the compound were the same as those of the reported compounds.[12] IR cm^{-1}: $\nu_{C=O}$ 1665. NMR δ: 1.05 (3H, m, $W_{1/2}=6$ Hz, $>CH-CH_3$), 1.78 (3H, m, $W_{1/2}=4$ Hz, allyl CH_3), 6.72 (1H, m, $W_{1/2}=8$ Hz, olefinic proton).

The Diels-Alder Adduct (2)——To a solution of 12.2 g of 2,5-dimethyl-cyclohex-2-en-1-one in 18 ml of dry benzene were added 2 g of anhyd. $AlCl_3$ powder and 16 g of butadiene at −30°. The mixture was allowed to stand at room temperature in a sealed tube for 8 days. The reaction mixture was extracted with ether. The extract was dried and evaporated. Distillation of the oily residue provided the starting material as a first run and 9.6 g (55%) of the Diels-Alder adduct (2), bp 77—80°/1 mmHg as a second run. IR cm^{-1}: $\nu_{C=O}$ 1695 and $\nu_{C=C}$ 1660. NMR δ: 1.02 (3H, d, $J=6$ Hz, $>CH-CH_3$), 1.18 (3H, s, CH_3), 5.61 (2H, m, $W_{1/2}=4$ Hz, olefinic protons). GLC: PEG 20 M, 200°, retention time 7 min 15 sec. MS *m/e*: 178 (M^+).

Using 0.4 eq BF_3–ether for the dienophile instead of 0.15 eq $AlCl_3$, the same Diels-Alder reaction was carried out to give the adduct (2) in a 21% yield.

The Diels-Alder Adducts (3a) **and** (3c) **by using the Lewis Acid in a Sealed Tube**——To a solution of 15 g

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[9] F. Fringuelli, A. Taticchi, and G. Traverso, *Gazz. Chim. Ital.*, **99**, 231 (1969); F. Fringuelli, A. Taticchi, F. Fernandez, D.N. Kirk, and M. Scopes, *J. Chem. Soc. Perkin I*, **1974**, 1103; The provided authentic sample melted at 171—173°. The sample purified by several recrystallizations from EtOH showed mp 180—181°, $UV_{max}^{CHCl_3}$ 393 nm ($\varepsilon=27600$) and $[\alpha]_D^{15}-296°$ ($c=0.14$, $CHCl_3$).

[10] W. Oppolzer and M. Petrzilka, *J. Amer. Chem. Soc.*, **98**, 6722 (1976).

[11] D.C. Humber, A.R. Pinder, and R.A. Williams, *J. Org. Chem.*, **32**, 2335 (1967).

[12] O. Wallach, *Ann. Chem.*, **396**, 269 (1913); *idem*, *ibid.*, **397**, 190 (1913).

of *l*-carvone in 10 ml of dry benzene were added 1.3 g of anhyd. $AlCl_3$ powder and 16 g of butadiene at $-30°$. The mixture was left at room temperature in a sealed tube for 7 days. The reaction mixture was extracted with ether and the extract was dried and evaporated to leave the residue, distillation of which gave 7.9 g of *l*-carvone as a first run and 5.6 g of the mixture of the Diels-Alder adducts (**3a**) and (**3c**). The latter was chromatographed on SiO_2. Elution of the column with *n*-hexane gave 3.3 g (16%) of **3a** and a trace of **3c**.

The Diels-Alder Adducts (3a) and (3c) by using the Lewis Acid in an Autoclave with Vigorous Stirring——To a solution of 100 g of *l*-carvone in 100 ml of dry CH_2Cl_2 were added 10 g of anhyd. $AlCl_3$ powder and 108 g of butadiene at $-30°$. The mixture was vigorously stirred at room temperature in an autoclave for 10 days. After the same work-up above, distillation of the residue afforded *l*-carvone as a first run and 92 g of the mixture of the adducts (**3a**) and (**3c**) as a second run. The second run was chromatographed on SiO_2 and elution of the column with *n*-hexane gave 49 g of the adduct (**3a**) and the following fractions were re-chromatographed. The total yields of **3a** and **3c** were 54 g (40%) and 4 g (3%), respectively. **3a**: IR cm^{-1}: $\nu_{C=O}$ 1695, $\nu_{C=C}$ 1645, $\delta_{C=CH}$ 1800 and 900. NMR δ: ($CDCl_3$): 1.20 (3H, s, CH_3), 1.75 (3H, br.s, allyl CH_3), 4.72 and 4.82 (each 1H, br.s, methylene proton), 5.62 (2H, br.s, olefinic protons). $[\alpha]_D^{24}$ $-5.3°$ ($c=1.0$, EtOH). MS *m/e*: 204 (M^+). GLC: 10% PEG 20 M, 200°, retention time 14 min 36 sec. The 2,4-dinitrophenylhydrazone of **3a** melted at 129—131°, yellow needles (MeOH), $[\alpha]_D^{31}$ $-20.6°$ ($c=0.5$, $CHCl_3$). *Anal.* Calcd. for $C_{20}H_{24}N_4O_4$: C, 62.49; H, 6.29. Found: C, 62.32; H, 6.38. **3c**: IR cm^{-1} $\nu_{C=O}$ 1655. NMR δ: 1.10 (6H, d, $J=7$ Hz, $-CH(CH_3)_2$), 1.20 (3H, s, CH_3), 5.55—5.85 (3H, m, olefinic protons). MS *m/e*: 204 (M^+). GLC: 10% PEG 20 M, 200°, retention time 16 min 20 sec.

Diels-Alder Adducts, (3a) and (3b) by the Heating Method——The reaction was carried out according to the reported reaction condition (180°, 60 hr).[4] The work-up in the same manner described in the literature gave **3a** and **3b** in a 6% and a 2% yield, respectively. **3b**: IR cm^{-1} $\nu_{C=O}$ 1693, $\nu_{C=C}$ 1645, $\delta_{C=C-H}$ 1800, $\delta_{C=C-H}$ 900. NMR ($CDCl_3$) δ: 1.12 (3H, s, angular CH_3), 1.74 (3H, br. s, allyl CH_3), 4.75 (2H, m, $W_{1/2}=3$ Hz, methylene protons), 5.65 (2H, m, $W_{1/2}=5$ Hz, olefinic protons). $[\alpha]_D^{20}$ $+132.4°$ ($c=0.5$, EtOH). The 2,4-dinitrophenylhydrazone of **3b** melted at 143.5—144.5°, yellow needles (from MeOH–AcOEt). $[\alpha]_D^{29}$ $-24.0°$ ($c=0.25$, $CHCl_3$). *Anal.* Calcd. for $C_{20}H_{24}N_4O_4$: C, 62.49; H, 6.29. Found: C, 62.30; H, 6.07.

The Ketone (7) from the Adduct (2) *via* (4), (5) and (6)——A solution of 1.04 g of the adduct (**2**) in 50 ml of 99% EtOH was added to 200 mg of 10% Pd-C catalyst and stirred under the hydrogen atmosphere. After the hydrogen uptake had ceased, the catalyst was removed by filtration. The filtrate was concentrated under reduced pressure to leave 800 mg of colorless oil (**4**) in a 79% yield. IR cm^{-1}: $\nu_{C=O}$ 1690. NMR δ: 0.98 (3H, m, $W_{1/2}=7$ Hz, $>CH-CH_3$), 1.17 (3H, s, angular CH_3). GLC: PEG 20 M, 200°, retention time 5 min. MS *m/e*: 180 (M^+).

To a solution of 180 mg of the ketone (**4**) in 2 ml of $CHCl_3$ was added dropwise a solution of 160 mg of Br_2 in 1 ml of $CHCl_3$ at 0° under stirring. The mixture was washed with water, dried, and evaporated to leave 240 mg of the oily substance (**5**) which was solidified on trituration with *n*-pentane. Recrystallization from *n*-pentane gave the crystalline bromoketone (**5**) as colorless prisms, mp 54—57°. IR cm^{-1}: $\nu_{C=O}$ 1720. NMR δ: 1.25 (3H, s, angular CH_3), 1.26 (3H, d, $J=6$ Hz, $>CH-CH_3$), 4.62 (1H, d, $J=11$ Hz, $>CH-Br$). *Anal.* Calcd. for $C_{12}H_{19}BrO$: C, 55.60; H, 7.39. Found: C, 55.62; H, 7.54.

To a solution of 400 mg of the compound (**5**) in 15 ml of DMF were added 426 mg of LiBr and 404 mg of Li_2CO_3 under stirring. The mixture was heated at 130° under an argon atmosphere for 5 hr with stirring. After cooling, the mixture was made acidic with dil. H_2SO_4 and extracted with ether. The extract was dried and evaporated to give 274 mg of the α,β-unsaturated ketone (**6**) as an oil. IR cm^{-1}: $\nu_{C=O}$ 1655. NMR δ: 1.09 (3H, s, CH_3), 1.90 (3H, m, $W_{1/2}=3$ Hz, $>CH-CH_3$), 5.77 (1H, m, $W_{1/2}=5$ Hz, olefinic proton). MS *m/e*: 178 (M^+). To a solution of 150 mg of the compound (**6**) in 10 ml of 99% EtOH was added 200 mg of 10% Pd-C catalyst and the mixture was stirred under the hydrogen atmosphere. The usual work-up gave the ketone (**7**: 106 mg) in a 70% yield. IR cm^{-1}: $\nu_{C=O}$ 1690. NMR δ: 1.02 (3H, m, $W_{1/2}=7$ Hz, $>CH-CH_3$), 1.19 (3H, s, CH_3). GLC: PEG 20M, 200°, retention time 6 min. MS *m/e*: 180 (M^+).

The Ketone (10) from the Major Adduct (3a) *via* the Compound (8) and (9)——A solution of 507 mg of the major adduct (**3a**) in 50 ml of 99% EtOH was added to 392 mg of PtO_2 and stirred under the hydrogen atmosphere. The usual work-up gave an oil which was purified by chromatography on SiO_2 to give the colorless oil (**8**, 453 mg) in an 88% yield. **8**: IR cm^{-1} $\nu_{C=O}$ 1690. NMR δ: 0.90 (6H, d, $J=7$ Hz, $-CH(CH_3)_2$), 1.17 (3H, s, angular CH_3). GLC: 10% PEG 20M, 220°, retention time 5 min 24 sec. MS *m/e*: 208 (M^+). $[\alpha]_D^{23}$ $+57.1°$ ($c=1.0$, EtOH). 2,4-DNP of **8**: mp 107.5—109.5°, yellow needles (from EtOH). $[\alpha]_D^{20}$ $+6.6°$ ($c=0.167$, EtOH). *Anal.* Calcd. for $C_{20}H_{28}N_4O_4$: C, 61.84; H, 7.27. Found: C, 61.61; H, 7.31.

To a solution of 394 mg of the compound (**8**) in 10 ml of $CHCl_3$ was added dropwise a solution of 3.18 mmol Br_2 in 3.18 ml of $CHCl_3$ under stirring. The usual work-up gave 469 mg of the oily compound. IR cm^{-1} $\nu_{C=O}$ 1715 and 1705. Without separation of the epimeric mixture, the oily residue in 14 ml of DMF was mixed with 582 mg of Li_2CO_3 and 509 mg of LiBr under stirring. The mixture was heated at 120° under an argon atmosphere for 5 hr and then the mixture was made acidic with dil. HCl and extracted with ether. The extract was washed with water, dried, and evaporated. The residue was purified by chromatography on SiO_2 to give 245 mg (71% yield) of the α,β-unsaturated ketone (**9**) as an oil. IR cm^{-1} $\nu_{C=O}$ 1655. NMR δ: 1.10 (6H, d, $J=6.5$ Hz, $-CH(CH_3)_2$), 1.11 (3H, s, angular CH_3) and 5.77 (1H, d, $J=2.5$ Hz, olefinic proton). $[\alpha]_D^{26}$ $-31.6°$ ($c=1.0$, EtOH). MS *m/e*: 206 (M^+). To a solution of 49 mg of the α,β-unsaturated ketone (**9**) in 10 ml of 99% EtOH was added 38 mg of PtO_2 catalyst. The mixture was stirred under the hydrogen atmosphere. The usual work-up gave the residue which was purified by chromatography on SiO_2 to give 33 mg of the ketone (**10**) in a 67% yield. IR cm^{-1}: $\nu_{C=O}$ 1690. NMR δ: 0.90 (6H, d, $J=7$ Hz, $CH(CH_3)_2$), 1.18 (3H, s, angular CH_3). GLC: 10% PEG 20M, 220°, retention time 6 min 18 sec. $[\alpha]_D^{23}$ $-79.8°$ ($c=1.0$, EtOH). MS *m/e*: 208 (M^+). 2,4-DNP of **10**: mp 103.5—106°, yellow needles (EtOH). $[\alpha]_D^{30}$ $-75.0°$ ($c=0.2$, EtOH). *Anal.* Calcd. for $C_{20}H_{28}N_2O_4 \cdot 1/4H_2O$: C, 61.12; H, 7.18. Found: C, 60.95; H, 7.31. Catalytic hydrogenation of 285 mg of the major adduct (**3a**) with 1 g of 10% Pd-C afforded 237 mg (81% yield) of the oily mixture. That the mixture consists of the compound (**8**) and (**10**) in an 11 : 3 ratio was detected by GLC.

The Ketone (11) from the Minor Adduct (3b)——To a solution of 60 mg of **3b** in 10 ml of 99% EtOH was added 26 mg of PtO_2 catalyst and the mixture was stirred under the hydrogen atmosphere. The usual work-up gave 60 mg of the ketone (**11**), an antipode of the compound (**10**). $[\alpha]_D^{25}$ $+84.3°$ ($c=0.91$, EtOH). The IR and NMR spectral data and the retention time of GLC were completely identical with those of the ketone (**10**).

The Ketone (11) from the Compound (3c)——Catalytic hydrogenation of 74 mg of **3c** in 10 ml of 99% EtOH was performed on 57 mg of PtO_2 catalyst and the usual work-up gave 66 mg of the oily compound which was completely identical with the compound (**10**) including the specific rotation.

Bromohydrins (13) and (14)——To a solution of 3.56 g of the Diels-Alder adduct (**2**) in 50 ml of dioxane were added 40 drops of $HClO_4$, 4.58 g of NBS and 60 drops of water at room temperature under stirring for 1 day. The reaction mixture was extracted with $CHCl_3$ and the extract was washed with water, dried and evaporated to leave 6 g of the residue. Chromatography of the residue on SiO_2 gave 3.06 g of the bromohydrin (**13**, 56%) from an earlier fraction and continuation of elution provided 0.56 g (8%) of the compound (**14**). **13**: mp 93—94.5°, colorless prisms (*n*-hexane). IR cm^{-1}: ν_{OH} 3450, $\nu_{C=O}$ 1690. NMR δ: 1.05 (3H, m, $W_{1/2}=7$ Hz, $>CH-CH_3$), 1.30 (3H, s, CH_3), 4.00 (1H, d.d, $J=8$, 3.5 Hz), 4.32 (1H, m, $W_{1/2}=12$ Hz). *Anal.* Calcd. for $C_{12}H_{19}BrO_2$: C, 51.38; H, 6.96. Found: C, 51.61; H, 7.16. The Beilstein test was positive. **14**: mp 213—215°, colorless plates (ether–acetone). IR cm^{-1} (Nujol): ν_{OH} 3500, $\nu_{C=O}$ 1715. NMR δ: 1.04 (3H, d, $J=7$ Hz, $>CH-CH_3$), 1.38 (3H, s, CH_3), 4.00 (2H, m, HO–$\dot{C}$H–$\dot{C}$H–Br), 5.00 (1H, d, $J=5$ Hz, H–$\underset{|}{\overset{|}{C}}$–Br). MS *m/e*: 356 ($M^+$+2), 354 ($M^+$), 352 ($M^+$−2). *Anal.* Calcd. for $C_{12}H_{18}Br_2O_2$: C, 40.70; H, 5.13. Found: C, 40.91; H, 5.12. The Beilstein test was positive.

The Diketone (17) from the Compounds (13) and (14) *via* the Compounds (15) and (16)——To a solution of 138 mg of the compound (**13**) in 10 ml of acetone was added dropwise 0.2 ml of Jones' reagent at room temperature under stirring. After 1 hr, the reaction mixture was diluted with MeOH and extracted with $CHCl_3$. The extract was washed with water, dried and evaporated to leave 130 mg of the compound (**15**), colorless pillars (benzene), mp 129—133°. IR cm^{-1}: $\nu_{C=O}$ 1720 and 1700 (shoulder). NMR δ: 1.03 (3H, br. d, $W_{1/2}=7$ Hz, $>CH-CH_3$), 1.40 (3H, s, CH_3), 2.72 (2H, s, $COCH_2$-), 4.33 (1H, t, $J=3.5$ Hz, -CO$\underset{|}{C}$HBr). *Anal.* Calcd. for $C_{12}H_{17}BrO_2$: C, 52.75; H, 6.27. Found: C, 52.90; H, 6.32.

Similarly, the compound (**16**, 320 mg) was obtained quantitatively from 320 mg of the compound (**14**). Recrystallization from ether–acetone gave colorless pillars, mp 153°. IR cm^{-1}: $\nu_{C=O}$ 1725. NMR δ: 1.14 (3H, d, $J=7$ Hz, $>CH-CH_3$), 1.50 (3H, s, CH_3), 2.52 [1H, d, $J=15$ Hz, -COCH(H)], 3.02 [1H, d.d, $J=15$ Hz, and 1 Hz, COCH(H)], 4.58 (1H, br. t, $J=5$ Hz, CO$\dot{C}$HBr), 4.72 (1H, d, $J=5$ Hz, COC$\underline{H}$Br–$\dot{C}$HCH$_3$). *Anal.* Calcd. for $C_{12}H_{16}Br_2O_2$: C, 40.93; H, 4.58. Found: C, 40.91; H, 4.59.

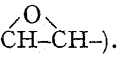
To a solution of 136 mg of the compound (**15**) in 10 ml of glacial AcOH was added 100 mg of Zn-powder. The mixture was refluxed for 30 min and was made basic with aq. $NaHCO_3$ and extracted with $CHCl_3$. The extract was washed with water, dried and evaporated to give 84 mg (87%) of the diketone (**17**), colorless plates (ether), mp 51—52°. IR cm^{-1}: $\nu_{C=O}$ 1710. NMR δ: 1.05 (3H, br. d, $W_{1/2}=7$ Hz, $>CH-CH_3$), 1.34 (3H, s, CH_3), 2.90 (1H, d, $J=15$ Hz, COCH(H)). MS *m/e*: 194 (M^+).

To a solution of the compound (**16**) in 10 ml of glacial AcOH was added 244 mg of Zn-powder. The mixture was refluxed for 40 min, and the similar work-up above afforded 91 mg of the diketone (**17**).

The Epoxy-ketone (19)——To a solution of 178 mg of the adduct (**2**) in 6 ml of dry CH_2Cl_2 was added 207 mg of MCPBA. The mixture was stirred at room temperature overnight and then an aqueous $Na_2S_2O_3$ solution was added. The mixture was extracted with $CHCl_3$. The extract was washed with an aq. $NaHCO_3$ solution, dried and evaporated to leave 157 mg (81%) of the epoxy-ketone (**19**), colorless pillars (*n*-pentane), mp 60—61°. IR cm^{-1}: $\nu_{C=O}$ 1695, ν_{epoxy} 1210—1220, 900, 815. NMR δ: 1.03 (3H, m, $W_{1/2}=7$ Hz, $>CH-CH_3$), 1.20 (3H, s, CH_3), 3.10—3.22 (2H, m, $\underset{\diagdown O \diagup}{\text{-CH-CH-}}$). *Anal.* Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.36; H, 9.21.

The Diketone (18) from the Adduct (2) *via* the Ketal (20)——To a solution of 1.1 g of the adduct (**2**) in 45 ml of benzene were added 2 g of ethylene glycol and catalytic amounts of *p*-toluenesulfonic acid. The mixture was refluxed for 10 hr, while water was separated in a Dean-Stark apparatus. After cooling, the mixture was neutralized with aq. $NaHCO_3$ and extracted with ether. The extract was dried and evaporated to leave the residue which was chromatographed on Al_2O_3 to give 1.32 g (95%) of the ketal (**20**). IR cm^{-1}: $\nu_{C=C}$ 1660, ν_{C-O} 1098. NMR δ: 0.96 (3H, s, CH_3), 1.04 (3H, d, $J=7$ Hz, $>CH-CH_3$), 3.92 (4H, m, $W_{1/2}=2$ Hz, $-O-CH_2-CH_2-O-$), 5.58 (2H, m, $W_{1/2}=4$ Hz, olefinic protons). MS *m/e*: 222 (M^+). To a solution of 1.32 g of the ketal (**20**) in 30 ml of dry CH_2Cl_2 was added 1.2 g of MCPBA. The mixture was stirred at room temperature overnight and then an aqueous solution of 5 g of $Na_2S_2O_3$ was added. The usual work-up gave 1.5 g of the residue. To a solution of the crude product in 35 ml of dry ether was added 1.3 g of $LiAlH_4$ and the mixture was refluxed for 4 hr. After cooling, the mixture was allowed to stand at room temperature overnight. To the reaction mixture were carefully added dropwise AcOEt and then wet ether at 0°. The organic layer was separated by decantation and the residue was washed with $CHCl_3$ two times. The organic layer and the washing were combined, dried and evaporated to give 1.3 g of the ketal-alcohol. To a solution of 400 mg of the ketal-alcohol in 10 ml of acetone was added dropwise 0.6 ml of Jones' reagent under stirring. The reaction mixture was stirred for 1 hr at room temperature and excess reagent was decomposed by addition of methanol, and the mixture was extracted with ether. The extract was washed with water, dried and evaporated to leave 300 mg of the ketal-ketone. To a solution of the ketal-ketone in 15 ml of aq. dioxane was added 3 drops of conc. HCl and the mixture was refluxed for 1 hr and the reaction mixture was extracted with ether. The extract was dried and evaporated under reduced pressure. The residue was chromatographed on SiO_2 to provide 150 mg of the diketone (**18**) in a 40% yield from the compound (**2**). IR cm^{-1}: $\nu_{C=O}$ 1706. NMR δ: 1.05 (3H, m, $W_{1/2}=7$ Hz, $>CH-C\underline{H}_3$), 1.30 (3H, s, CH_3). MS *m/e*: 194 (M^+).

Monoepoxides (21) and (22)——To a solution of 320 mg of the adduct (**3a**) in 12 ml of CH_2Cl_2 was added 299 mg of MCPBA at 0° under stirring. Stirring was continued for further 1 day at room temperature and an aq. $Na_2S_2O_3$ solution was added to the mixture. The mixture was extracted with $CHCl_3$ and the extract was washed with an aq. $KHCO_3$ solution, water, dried and evaporated to afford 332 mg of the residue. The residue was chromatographed on SiO_2 with $CHCl_3$ to yield 13 mg of **21** and 41 mg of **22**. **21**: IR cm^{-1}: $\nu_{C=O}$ 1700, $\nu_{C=C}$ 1645, $\delta_{C=CH}$ 1800, ν_{epoxy} 900 and 815. NMR δ: 1.25 (3H, s, CH_3), 1.75 (3H, br.s, allyl methyl), 3.17 (2H, m, $W_{1/2}=6$ Hz, epoxy protons), 4.78 (2H, m, $W_{1/2}=4$ Hz, methylene protons). GLC: SE 30, 150°, retention time 8 min 12 sec. MS *m/e*: 220 (M^+). The epimeric mixture **22**: IR cm^{-1}: $\nu_{C=O}$ 1700, $\nu_{C=C}$ 1660, ν_{epoxy} 900 and 830. NMR δ: 1.25 and 1.10 (total 3H, s, angular CH_3), 1.35 and 1.30 (total 3H, s, tertiary CH_3), 5.62 (2H, m, $W_{1/2}=4$ Hz, olefinic protons). GLC: SE 30, 150°, retention time 8 min 30 sec. MS *m/e*: 220 (M^+).

The Diepoxy-ketone (23)——To a solution of 1.313 g of the adduct (**3a**) in 25 ml of dry CH_2Cl_2 was added 3.356 g of MCPBA at 0° under stirring and the mixture was stirred at room temperature for 3.5 hr. The usual work-up gave the residue which was chromatographed on SiO_2. The column was eluted with $CHCl_3$ to leave 1.02 g (67%) of the diepoxy-ketone (**23**). IR cm^{-1}: $\nu_{C=O}$ 1702, ν_{epoxy} 1230, 900 and 816. NMR δ: 1.22 (3H, s, angular CH_3), 1.32 (3H, s, tertiary CH_3), 3.16 (2H, m, $W_{1/2}=6$ Hz,  $-\overset{\diagup O \diagdown}{CH-CH}-$). MS *m/e*: 236 ($M^+$).

The Compounds (24) and (25)——To a solution of 876 mg of the diepoxy-ketone (**23**) in 80 ml of dry ether was added 844 mg of $LiAlH_4$ at 0° under stirring and the mixture was refluxed for 3 hr. After cooling, excess reagent was decomposed by addition of AcOEt and wet ether and the organic layer was decanted, dried and evaporated to leave the residue which was chromatographed on SiO_2. Elution of the column with $CHCl_3$ and then 1—20% MeOH in $CHCl_3$ gave 400 mg (45%) of the compound (**24**). IR cm^{-1}: ν_{OH} 3600, 3400, ν_{C-O} 1050. NMR δ: 1.08 (3H, s, angular CH_3), 1.14 and 1.17 (each 3H, s, tertiary CH_3), 3.60 (1H, m, $>C\underline{H}-OH$), 3.75—4.12 (2H, m, $-\underset{|}{C}H-O-\underset{|}{C}H-$). MS *m/e*: 240 ($M^+$), 222 ($M^+-18$). To a solution of 70 mg of the compound (**24**) in 3 ml of acetone was added dropwise 0.5 ml of Jones' reagent at 0° under stirring. The mixture was stirred for 10 min and the usual work-up left the residue which was chromatographed on SiO_2. Elution of the column with 0.5% MeOH in $CHCl_3$ gave 45 mg (66%) of the colorless oil (**25**). IR cm^{-1}: ν_{OH} 3550, 3450, $\nu_{C=O}$ 1720. NMR δ: 1.16 (3H, s, angular CH_3), 1.20 (6H, s, tertiary CH_3), 3.86 (1H, m, $W_{1/2}=7$ Hz, $>CH-O-$), 4.10 (1H, d, $J=6$ Hz, $-O-\underset{|}{C}H-$). MS *m/e*: 238 (M^+).

The Alcohol (26)——To a solution of 1.645 g of the adduct (**3a**) in 20 ml of 99% EtOH was added little by little 1.224 g of $NaBH_4$ at room temperature with stirring and stirring was continued for further 5 hr. The reaction mixture was extracted with $CHCl_3$ and the extract was washed with water, dried and evaporated to afford 1.645 g of the alcohol (**26**), which was indicated to be the epimeric mixture in a 4.5 : 1.0 ratio by its NMR spectrum. IR cm^{-1}: ν_{OH} 3600, 3500, $\delta_{C=CH}$ 1800, 895, $\nu_{C=C}$ 1645. NMR δ: 0.98 and 1.03 (total 3H, s, CH_3), 1.74 (3H, br.s, allyl CH_3), 3.60 and 3.77 (total 1H, d.d, $J=10$, 5 Hz, $>C\underline{H}-OH$), 4.74 and 4.84 (each 1H, m, $W_{1/2}=3$ Hz and 5 Hz, methylene proton), 5.64 (2H, m, $W_{1/2}=3$ Hz, olefinic protons). MS *m/e*: 206 (M^+).

The Tosylate (27)——To a solution of 510 mg of the alcohol (**26**) in 20 ml of dry pyridine was added 1.890 g of *p*-TsCl at 0°. The mixture was left for 20 hr at room temperature and the reaction mixture was acidified with an aq. 10% H_2SO_4 solution and extracted with $CHCl_3$. The extract was washed with a $NaHCO_3$ solution and water, dried and evaporated under reduced pressure. The residue was chromatographed on SiO_2 to give 676 mg (76%) of the tosylate (**27**). The tosylate (**27**) was suggested to be the epimeric mixture by its NMR spectrum. IR cm^{-1}: $\nu_{C=C}$ 1640, ν_{SO_2} 1355, 1170, ν_{S-O} 908, 895. NMR δ: 0.80 and 1.00 (total 3H, s, CH_3), 1.70 (3H, br.s, allyl CH_3), 2.43 (3H, s, $-C_6H_4-CH_3$), 4.55 and 4.72 (total 1H, m, $>CH-O-Ts$), 4.90 (2H, m, $W_{1/2}=4$ Hz, methylene protons), 5.53 (2H, m, $W_{1/2}=4$ Hz, olefinic protons), 7.33 and 7.80 (each 2H, m, aromatic protons). MS *m/e*: 360 (M^+).

The Mesylate (28)——To a solution of 3.036 g of the alcohol (**26**) in 90 ml of dry pyridine was added dropwise 6.762 g of methanesulfonyl chloride at 0°. The mixture was allowed to stand at room temperature for 18 hr. The reaction mixture was made acidic with an ice-cooled 10% H_2SO_4 solution and extracted with ether. The ether extract was washed with water, dried and evaporated under reduced pressure to leave 4.068 g (98%) of the mesylate (**28**) as a colorless oil. This oil was indicated to be the epimeric mixture by its NMR spectrum. IR cm^{-1}: $\nu_{C=C}$ 1643, ν_{SO_2} 1335—1355, 1174, ν_{S-O} 915. NMR δ: 1.08 (3H, s, CH_3), 1.75 (3H, m, allyl CH_3), 2.98 and 3.00 (total 3H, s, $-OSO_2-CH_3$), 4.50—4.70 and 4.70—5.00 (total 2H, m, methylene protons), 5.50—5.70 (2H, m, olefinic protons). MS *m/e*: 284 (M^+).

The Compound (**29**)——A solution of 443 mg of **23** in a mixture of 1,2-dimethoxyethane (DME, 7 ml) and tetramethylethylenediamine (TMEDA, 2 ml) was placed in a flask and the atmosphere was replaced by an argon gas. A solution of 4.3 mmol of *n*-BuLi in 2 ml of *n*-hexane was then injected into the flask with the aid of a syringe through a rubber stopper at 0°. After the mixture was stirred at room temperature for 30 min, a solution of 1.833 g of N,N,N′,N′-tetramethyldiamidophosphorochloridate in 1 ml of DME was added. Stirring was continued at room temperature for 3 hr. To the reaction mixture was added carefully water and the mixture was extracted with $CHCl_3$. The extract was dried and evaporated under reduced pressure to leave the residue which was chromatographed on SiO_2. Elution of the column with $CHCl_3$ provided 580 mg (80%) of **29**. IR cm^{-1}: $\nu_{C=C}$ 1640, ν_{P-O} 985, $\delta_{C=CH}$ 890. NMR δ: 1.02 (3H, s, CH_3), 1.72 (3H, br.s, allyl CH_3), 2.57 and 2.70 (each 6H, s, $-N-(CH_3)_2$), 4.75 and 4.95 (each 1H, m, $W_{1/2}=4$ Hz, methylene proton), 5.60 (2H, m, $W_{1/2}=7$ Hz, olefinic protons). MS *m/e*: 340 (M^+).

The Compound (**30**)——To a solution of 1.720 g of **26** in the mixture of DME (20 ml) and TMEDA (4 ml) was added at 0° 16.7 mmol *n*-BuLi in 7.6 ml of *n*-hexane as described previously. The mixture was stirred at 0° for 15 min and then stirring was continued at room temperature for 15 min. To the mixture was added 2.156 g of diethylphosphorochloridate in the mixture of DME (4 ml) and TMEDA (2 ml). The mixture was stirred for further 2 hr and extracted with $CHCl_3$. The extract was dried and evaporated under reduced pressure. The chromatography of the residue on SiO_2 gave 2.532 g (89%) of **30**. IR cm^{-1}: $\delta_{C=CH}$ 1800, $\nu_{C=C}$ 1638, $\nu_{P=O}$ 1258, ν_{P-OEt} 1160, $\nu_{P-O-C-R}$ 1040—980, and $\delta_{C=CH}$ 892. NMR δ: 1.08 (3H, br.s, CH_3), 1.34 and 1.35 (each 3H, t, $J=7$ Hz, CH_2CH_3), 1.75 (3H, m, $W_{1/2}=3$ Hz, allyl CH_3), 4.06 and 4.18 (each 2H, q, $J=7$ Hz, $-CH_2CH_3$), 4.75 and 4.94 (each 1H, m, $W_{1/2}=4$ Hz, methylene proton) 5.61 (2H, m, $W_{1/2}=6$ Hz, olefinic protons). MS *m/e*: 342 (M^+).

The Diepoxide (31) **and the Monoepoxide** (**32**) **from the Adduct** (**3a**)——To a solution of 17.9 g of the Diels-Alder major adduct (**3a**) in 150 ml of dry MeOH was added 25 g of *p*-$TsNHNH_2$ and the mixture was refluxed for 10.5 hr. The reaction mixture was cooled to 0° and added into 500 ml of dry MeOH. To this solution was added alternatively 90 g of $NaBH_4$ and 500 ml of MeOH little by little during 4 hr at 0°. The mixture was refluxed for 14 hr and extracted with ether. The extract was washed with water, dried and concentrated to 250 ml. The concentrated extract was cooled at 0° and 95 g of Na_2HPO_4 and 46 g of MCPBA were added. The mixture was stirred at room temperature for 2 hr and then the reaction mixture was extracted with $CHCl_3$. The extract was successively washed with an aq. $Na_2S_2O_3$ solution, a 3% aq. NaOH solution, and water, dried, and evaporated to leave the residue which was chromatographed on SiO_2. Elution of the column with $CHCl_3$ afforded 1.3 g (overall yield 7%) of the monoepoxide (**32**) from an earlier fraction. Continuation of elution provided 4.9 g (overall yield 25%) of the diepoxide (31). **31**: IR cm^{-1}: ν_{epoxy} 1230, 900—885 and 830—810. NMR δ: 0.94 (3H, s, angular CH_3), 1.26 (3H, s, tertiary CH_3), 2.53—2.62 (2H, m, $-\overset{\diagup O \diagdown}{C-CH_2}$), 2.95—3.30 (2H, m, $\underset{\diagdown O \diagup}{-CH-CH-}$). MS *m/e*: 222 ($M^+$). **32**: IR cm^{-1}: ν_{epoxy} 1235, 890, 835 and 810. NMR δ: 0.85 (6H, d, $J=5$ Hz, $-CH(CH_3)_2$), 0.91 (3H, s, angular CH_3), 2.95—3.30 (2H, m, $\underset{\diagdown O \diagup}{-CH-CH-}$). MS *m/e*: 208 ($M^+$).

The Diol (33)——To a solution of 129 mg of the diepoxide (**31**) in 16 ml of dry ether was added 176 mg of $LiAlH_4$ at 0° under stirring and the mixture was then refluxed for 1 hr. After cooling, the organic layer was separated by decantation. The usual work-up gave the residue which was chromatographed on SiO_2 to provide the crystalline mass. Recrystallization of the solid mass from benzene gave 78 mg (59%) of the diol (33) as colorless pillars, mp 141—142°. IR cm^{-1}: ν_{O-H} 3550, 3400. NMR δ: 0.99 (3H, s, angular CH_3), 1.15 (6H, s, tertiary CH_3), 4.11 (1H, m, $W_{1/2}=7$ Hz, $>C\underline{H}-OH$). $[\alpha]_D^{23}$ $-10.0°$ ($c=0.2$, benzene). *Anal.* Calcd. for $C_{14}H_{26}O_2$: C, 74.28; H, 11.58. Found: C, 74.28; H, 11.88.

The Hydroxy-ketone (**34**)——To a solution of 55 mg of the diol (33) in 15 ml of acetone was added dropwise 0.09 ml of Jones' reagent at room temperature under stirring and stirring was continued for 10 min. The reaction mixture was diluted with MeOH and extracted with $CHCl_3$. The extract was washed with water, dried and evaporated to give 54 mg of the compound (34). IR cm^{-1}: ν_{OH} 3558, 3450, $\nu_{C=O}$ 1705. NMR δ: 1.05 (3H, s, angular CH_3), 1.20 (6H, s, tertiary CH_3). $[\alpha]_D^{23}$ $-51.9°$ ($c=1.0$, EtOH). MS *m/e*: 224 (M^+).

The Acetoxy-ketone (**35**)——To a solution of 255 mg of the hydroxy-ketone (**34**) in 12 ml of isopropenylacetate was added 40 mg of anhyd. *p*-TsOH. The mixture was stirred for 15 hr at room temperature and was made alkaline with a 3% NaOH solution and extracted with ether. The extract was dried and evaporated to leave the oily residue which was crystallized on trituration with *n*-pentane. Recrystallization from *n*-pentane afforded 236 mg (78%) of the acetoxy-ketone (**35**) as colorless plates, mp 75—76°. IR cm^{-1}:

$\nu_{C=O}$ 1710, ν_{C-O} 1200—1280. NMR δ: 1.04 (3H, s, angular CH_3), 1.41 (3H, s, tertiary CH_3), 1.43 (3H, s, tertiary CH_3), 1.95 (3H, s, $COCH_3$). $[\alpha]_D^{21}$ $-44.0°$ ($c=0.5$, EtOH). *Anal.* Calcd. for $C_{16}H_{26}O_3$: C, 72.14; H, 9.84. Found: C, 71.86; H, 9.68.

The Acetoxy-bromoketone (36)——To a solution of 233 mg of the compound (35) in 10 ml of $CHCl_3$ were added 704 mg of $MgCO_3$ powder and 0.97 mmol of Br_2 in 0.97 ml of $CHCl_3$ at 35° under sunlight. The reaction mixture was extracted with $CHCl_3$ and the extract was washed with water, dried and evaporated. On trituration with *n*-hexane, the residue was crystallized and several recrystallizations from *n*-hexane gave 161 mg (53%) of the acetoxy-bromoketone (36) as colorless needles, mp 122—125°. IR cm^{-1}: $\nu_{C=O}$ 1720, ν_{C-O} 1265. NMR δ: 1.11 (3H, s, angular CH_3), 1.41 (3H, s, tertiary CH_3), 1.47 (3H, s, tertiary CH_3), 1.98 (3H, s, $-COCH_3$), 4.83 (1H, d, $J=12.5$ Hz, >CH–Br). $[\alpha]_D^{31}$ $-48.7°$ ($c=1.0$, EtOH). *Anal.* Calcd. for $C_{16}H_{25}BrO_3$: C, 55.65; H, 7.30. Found: C, 55.41; H, 7.01.

The *α,β*-Unsaturated Keto-acetate (12a)——To a solution of 109 mg of the compound (36) in 7 ml of DMF were added 71 mg of Li_2CO_3 and 83 mg of LiBr under stirring. The mixture was heated at 110—120° for 13 hr under stirring. After cooling, the reaction mixture was acidified with a 5% H_2SO_4 solution, and extracted with ether. The extract was washed with water, dried, and evaporated under reduced pressure to leave the residue. The residue was chromatographed on SiO_2 (dry packed column) and elution of the column with a mixture of $CHCl_3$ and benzene (6: 1) gave 49 mg (59%) of a colorless oil (**12a**). IR cm^{-1}: $\nu_{C=O}$ 1720, $\nu_{C=O}$ 1662, $\nu_{C=C}$ 1620, ν_{C-O} 1200—1270. NMR δ: 1.23 (3H, s, angular CH_3), 1.49 (6H, s, tertiary CH_3), 1.99 (3H, s, $COCH_3$), 5.76 (1H, br.s, $W_{1/2}=2$ Hz, olefinic proton). $[\alpha]_D^{28}$ $-94.3°$ ($c=2.0$, benzene).

The 2,4-Dinitrophenylhydrazone of 12a——To a solution of 8 mg of **12a** in 1 ml of dry EtOH were added 1 drop of conc. H_2SO_4 and a solution of 8.5 mg of 2,4-dinitrophenylhydrazine in 1 ml of dry EtOH. The mixture was stirred at room temperature for 15 hr. The precipitated red crystals were collected by filtration and washed with dry EtOH. Several recrystallizations from EtOH afforded 5.5 mg of the 2,4-dinitrophenylhydrazone of **12a** as red needles, mp 180—181°. $[\alpha]_D^{25}$ $-288°$ ($c=0.25$, $CHCl_3$). UV $\lambda_{max}^{CHCl_3}$ 393 mμ ($\varepsilon=29600$), IR (nujol) cm^{-1}: ν_{NH} 3300, $\nu_{C=O}$ 1722, $\nu_{C=C}$ 1620. These data were identical with those of an authentic sample [see 9) foot note].

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