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# Total Synthesis of *dl*-Chamaecynone, a Termiticidal Norsesquiterpene[1]

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The total synthesis of *dl*-chamaecynone (**1**), which has termiticidal activity, has been accomplished. The key compound (**30a**), which has the same four chiral centers as chamaecynone (**1**), was obtained in a single step by taking advantage of the Diels–Alder reaction of 5-ethynyl-2-methylcyclohex-2-en-1-one (**3**) with 1-methoxy-3-trimethylsiloxy-1,3-pentadiene (**4**). The stereostructure of the major adduct of the Diels–Alder reaction was determined to be the formula (**30a**) by INDOR experiment. The compound (**30a**) was converted in four steps into *dl*-chamaecynone. The preliminary examinations of the Diels–Alder reaction of *trans*-1-methoxy-3-trimethylsiloxy-1,3-butadiene (**2**) with *l*-carvone and the compound (**3**) were also carried out, respectively.

**Keywords**——Diels–Alder reaction; *dl*-chamaecynone; termiticidal activity; 5-ethynyl-2-methylcyclohex-2-en-1-one; 1-methoxy-3-trimethylsiloxy-1,3-pentadiene; stereochemistry; INDOR experiment; conformational analysis

Chamaecynone was isolated from an essential oil of *Chamaecyparis formosensis* MATSUM. (Cupressaceae) and its structure (**1**) possessing a nonsteroidal *cis*-decalin conformation was established,[3] and then this norsesquiterpene has become of interest because of its termiticidal activity.[4] A formal synthesis of chamaecynone starting from α-santonin has been established by Nozoe, *et al.*[5] in 1967 and the present study is undertaken for the total synthesis of *dl*-chamaecynone.

In previous papers, we reported that the Diels–Alder addition of butadiene to 5-alkyl or 2,5-dialkyl-cyclohex-2-en-1-ones such as 5-methyl-cyclohex-2-en-1-one,[6] 2,5-dimethyl-cyclohex-2-en-1-one,[7] and *l*-carvone,[7] in the presence of a Lewis acid took place stereoselectively from the opposite side to the $C_5$-alkyl substituent of the dienophile. It was also suggested that this type of reaction may be useful for the synthesis of some eudesmane type sesquiterpenes and some alkaloids.[7] The instances of synthesis using this type of reaction are now found in the formal synthesis of β-eudesmol by the present authors[7] and total synthesis of luciduline, a lycopodium alkaloid, by Oppolzer, *et al.*[8]

On the other hand, the Diels–Alder reaction in which the functionalized dienes are used, has become of interest in recent years. Using a novel diene, *trans*-1-methoxy-3-trimethylsiloxy-1,3-butadiene (**2**) developed by Danishefsky,[9] the compounds containing the δ-carbonyl-α,β-unsaturated ketone moiety were effectively synthesized.[10]

We presumed that all four chiral centers in the chamaecynone molecule are constructed in a single step by taking advantage of the Diels–Alder reaction of the dienophile (**3**) with a

1) A preliminary communication of a part of this work appeared in *Tetrahedron Lett.*, **1977**, 3273.
2) Location: *Yoshida-Shimoadachi-cho, Sakyo-ku, Kyoto.*
3) T. Nozoe, Y.S. Cheng, and T. Toda, *Tetrahedron Lett.*, **1966**, 3663.
4) I. Saeki, M. Sumimoto, and T. Kondo, *Holzforschung*, **27**, 93 (1973); T. Kondo, Japan Kokai, 7392, 525 (1973) [*C.A.*, **81**, 59351*r* (1974)].
5) T. Nozoe, T. Asao, M. Ando, and K. Takase, *Tetrahedron Lett.*, **1967**, 2821.
6) T. Harayama, H. Cho, M. Ohtani, and Y. Inubushi, *Chem. Pharm. Bull.* (Tokyo), **22**, 2784 (1974).
7) T. Harayama, H. Cho, and Y. Inubushi, *Tetrahedron Lett.*, **1975**, 2693; *idem*, *Chem. Pharm. Bull.* (Tokyo), **25**, 2273 (1977).
8) W. Oppolzer and M. Petrzilka, *J. Am. Chem. Soc.*, **98**, 6722 (1976).
9) S. Danishefsky and T. Kitahara, *J. Am. Chem. Soc.*, **96**, 7807 (1974).
10) S. Danishefsky and T. Kitahara, *J. Org. Chem.*, **40**, 538 (1975).

new diene, 1-methoxy-3-trimethylsiloxy-1,3-pentadiene (4). On the basis of this assumption, total synthesis of *dl*-chamaecynone has now been achieved and details of experiments of this synthesis are reported in this paper.

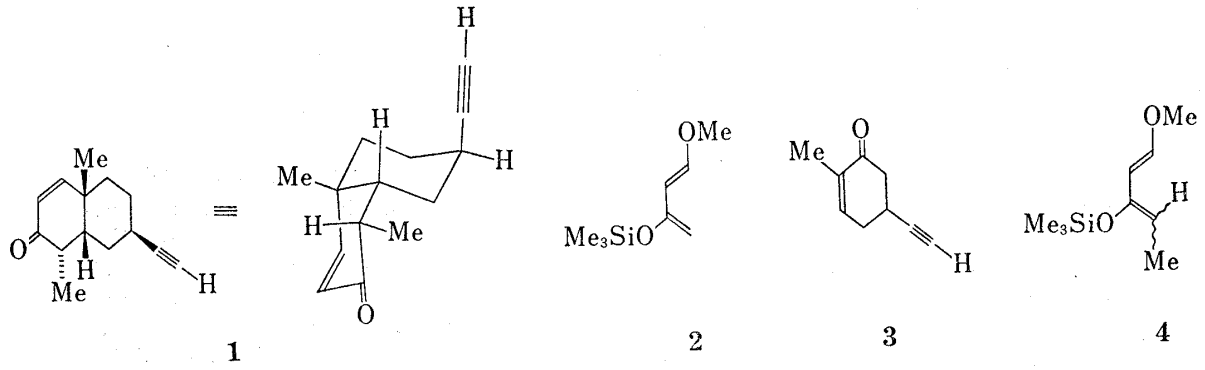


Chart 1

As a preliminary experiment, the stereochemistry of the Diels–Alder adduct of *trans*-1-methoxy-3-trimethylsiloxy-1,3-butadiene (2)[9] with *l*-carvone was examined with the intention of confirming whether addition of the 1,3-dioxygenated diene (2) took place from the opposite side to the $C_5$ isopropenyl substituent of *l*-carvone as that of butadiene,[6,7] or from the same side.

The Diels–Alder reaction of the diene (2) with *l*-carvone in anhyd. xylene was performed in a sealed tube at 190° for 22 hr or at 145° for 8 days. Hydrolysis of the product with aq. HCl–THF provided two kinds of adducts, **5a** and **5b**, in 25% and 14% yields, respectively. The major adduct (**5a**) was then transformed to the ketone (**8**) of the established stereostructure. Thus, the compound (**5a**) was hydrogenated over $PtO_2$ to give the diketone (**6**) which was reacted with 1.4 mol eq. ethanedithiol and 1.1 mol eq. of $BF_3$-ether to provide selectively the monothioketal (**7**) in 89% yield. Reduction of **7** with Raney nickel W-2 furnished the ketone (**8**), a sample of which was identical with an authentic sample.[7]

This result indicates that the configurations of three chiral centers of **5a** are the same as those of **8**. In the nuclear magnetic resonance (NMR) spectrum of **5a**, the signal due to $C_1$–H appeared as a doublet ($\delta$ 6.77, 1H, d, $J$=10 Hz) and no W letter long-range coupling of the $C_1$–H signal [refer to the $C_1$–H signal of the compound (**5b**) (*vide infra*)] was observed, indicating the double bond located at $C_1$–$C_2$ and the steroidal conformation of **5a**. Consequently, the structure of the major product is shown by the formula (**5a**) in which the stereochemical relationship between the angular methyl and the $C_7$-alkyl (isopropenyl group) is *cis* as that in chamaecynone.

Next, the stereochemistry of **5b** was examined. Thus, the minor product (**5b**) was hydrogenated over $PtO_2$ to give quantitatively the diketone (**9**). Since the thioketalization of **9** gave an inseparable mixture in contrast with the compound (**6**), the thioketalization of the compound (**5b**) itself was tried. Separation of the product gave the monothioketal (**10**; $\nu_{C=O}$: 1703 $cm^{-1}$) and the dithioketal (**11**) in 27% and 10% yields, respectively, together with the recovered material in 23% yield. Reduction of **10** with Raney nickel, followed by catalytic hydrogenation, provided the ketone (**12**) in 34% yield, a sample of which was identified with an authentic sample.[7] Consequently, the configurations of three chiral centers of **5b** are the same as those of **12** in which the stereochemical relationship between the angular methyl group and the $C_7$- isopropyl group is *trans*. The position of the double bond estimated from the fact that the Diels–Alder reaction using the 1,3-dioxygenated diene (**2**) proceeds regiospecifically to give the compound containing the $\delta$-carbonyl-$\alpha,\beta$-unsaturated ketone moiety[9,10] after hydrolysis of the adduct. Moreover, the W letter long-range coupling was observed on

the signal due to the $C_1$-H ($\delta$ 6.47, 1H, d.d, $J$=10, 2 Hz) in the NMR spectrum of **5b**, suggesting the nonsteroidal conformation of **5b**. Consequently, the structure of the minor product is shown by the formula (**5b**) in which the stereochemical relationship between the angular methyl group and the isopropenyl group is *trans*.

Next, selective reduction of the $C_9$ carbonyl group of **5a** was examined because a similar selective reduction is required for the chamaecynone synthesis. Thioketalization of **5a** gave the dithioketal (**13**) and the monothioketal (**14**; $\nu_{C=O}$ 1700 $cm^{-1}$) in 4% and 75% yields, respectively. Treatment of **14** with *p*-$TsNHNH_2$ provided the hydrazone, which without purification was reduced with an excess of $NaBH_4$. The reduction product, without separation, in aq. 99% acetone was treated with $CuCl_2 \cdot 2H_2O$–CuO[11] and the product was purified by the preparative thin-layer chromatography (TLC) to furnish the desired $\alpha,\beta$-unsaturated ketone (**15**) and the compound (**16**) in 34% and 8% yields, respectively. The formation mechanism of the latter was uncertain and no further investigation was made. From the results described above, it is obvious that addition of *trans*-1-methoxy-3-trimethylsiloxy-1,3-butadiene (**2**) to *l*-carvone took place predominantly from the opposite side of the $C_5$ isopropenyl group of the latter.

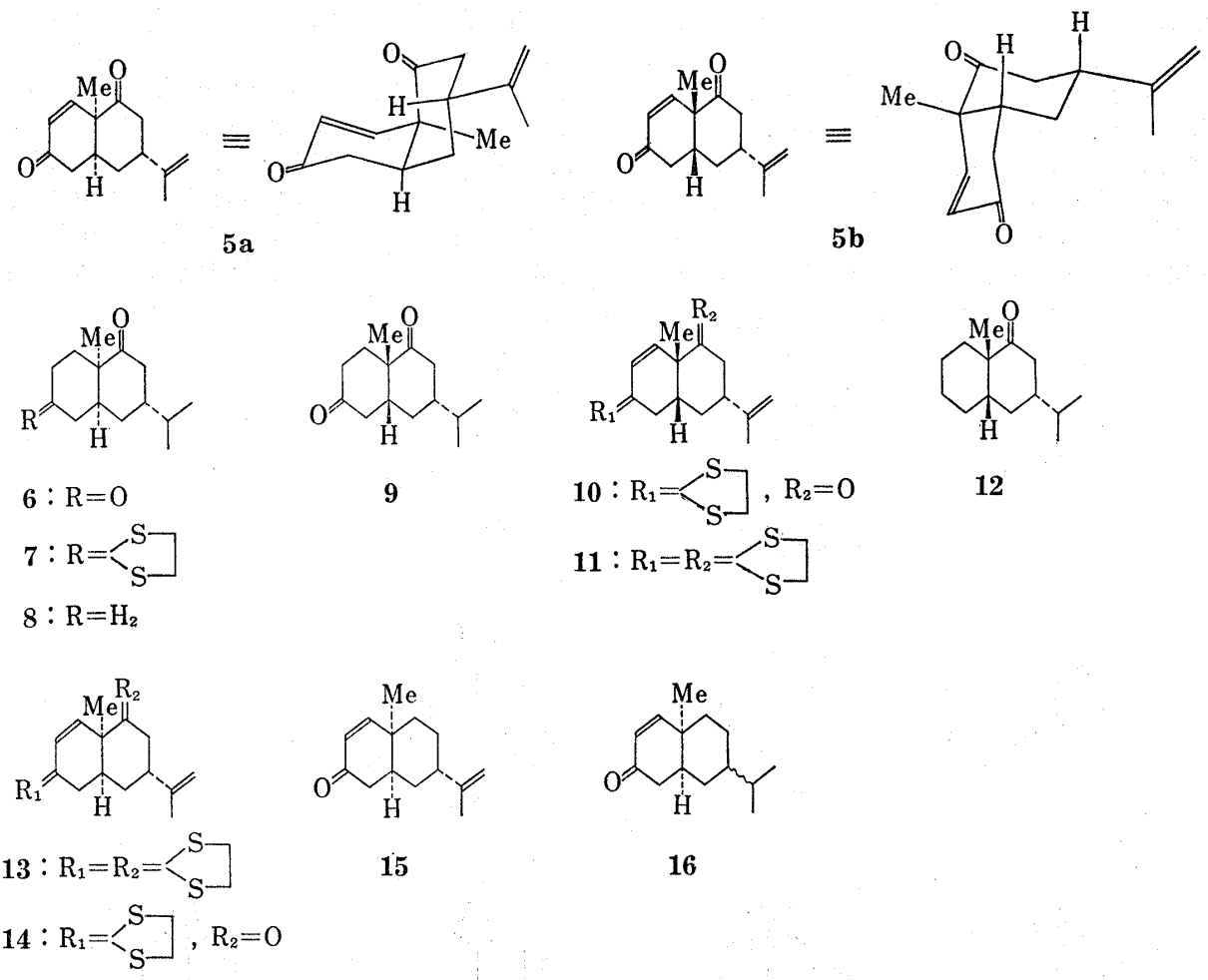


Chart 2

The influence of addition of a Lewis acid on the yield and selectivity of addition direction to the dienophile in the Diels–Alder reaction was studied. In the previous paper,[7] it was reported that yield and selectivity of addition direction are improved by addition of a Lewis

11) T. Mukaiyama, K. Narasaka, and M. Furusato, *J. Am. Chem. Soc.*, **94**, 8641 (1972).

acid compared with those in heating method without catalyst. In the present case, the lower yield and higher selectivity of addition direction were observed and the lower yield should be attributed to the susceptibility of the diene (**2**) to a Lewis acid.

Table I

| Reaction condition | **5a**: **5b** | Total yield |
|---|---|---|
| Heating method | 25 : 14 | 39% |
| 0.3 eq. $ZnCl_2$ at r.t. | 75 : 12 | 6% |
| 0.3 eq. $AlCl_3$ at r.t. | **5a** only | 2% |

The dienophile, 5-ethynyl-2-methylcyclohex-2-en-1-one (**3**) required for the chamaecynone synthesis, was synthesized in a high yield through the following route. It is known that the direct introduction of an ethynyl group at the $\beta$ position of the $\alpha,\beta$-unsaturated ketone moiety with organocopper reagent is impractical. The procedure developed by Corey[12] using the organotin compound is inadequate for a large quantity of material because of expensiveness of the reagent. Then, the indirect introduction procedure was adopted. Reaction of 6-methylcyclohex-2-en-1-one[13] with vinylmagnesium bromide–CuI gave the compound (**17**: *trans*/*cis* =1) in 80% yield. Since selective bromination of the vinyl group of **17** was unfruitful, the compound (**17**) was reduced with $NaBH_4$ to lead to the alcohol which was brominated to give the dibromo-alcohol in 62% yield. Dehydrobromination of the bromide with $NaNH_2$ in liq. $NH_3$ gave 5-ethynyl-2-methylcyclohexan-1-ol (**18a**) in 83% yield. When a series of reactions described above was applied to the acetate (**19**) and the product (**18b**) was hydrolyzed, the yield of **18a** was improved. Jones' oxidation of **18a** gave the compound (**20**) which was subjected successively to bromination and dehydrobromination to provide the desired 5-ethynyl-2-methylcyclohex-2-en-1-one (**3**) in 70% yield.

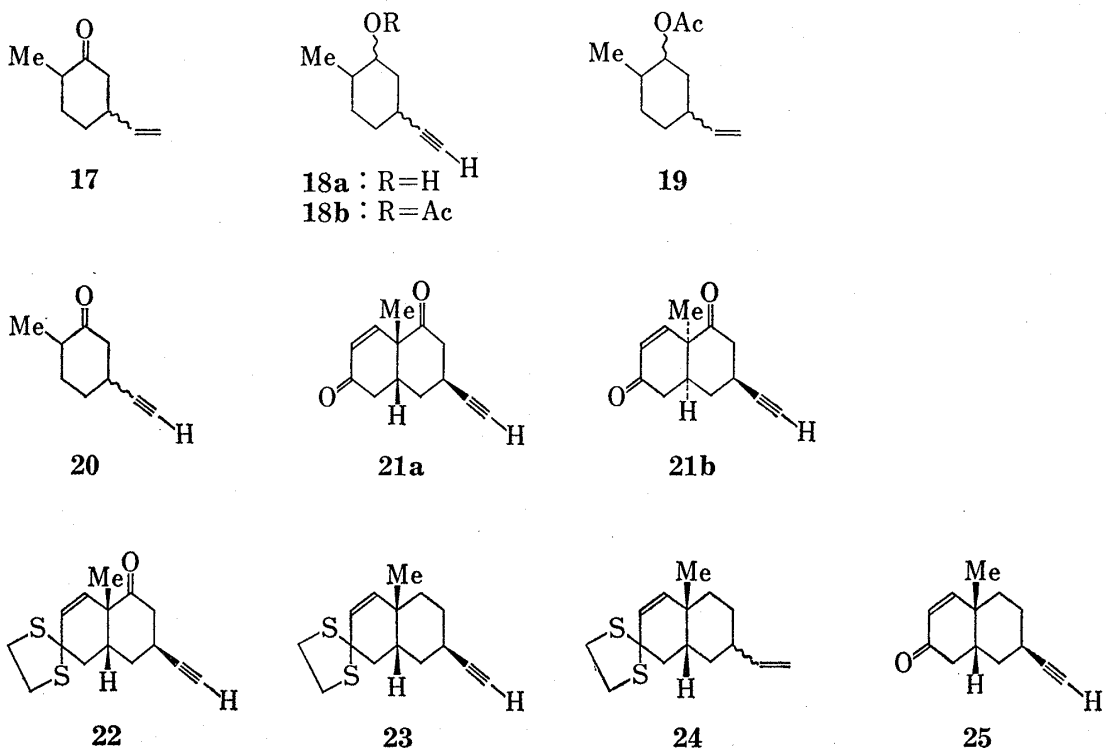


Chart 3

12) E.J. Corey and R.H. Wollenberg, *J. Am. Chem. Soc.*, **96**, 5581 (1974).
13) G. Stork and W.N. White, *J. Am. Chem. Soc.*, **78**, 4604 (1956).

The Diels–Alder reaction of the dienophile (**3**) with *trans*-1-methoxy-3-trimethylsiloxy-1,3-butadiene (**2**) was carried out by heating at 180—200° for 60 hr in anhyd. xylene to give two kinds of adducts, (**21a**) and (**21b**), in 30% and 3% yields, respectively. The stereostructures of these adducts were inferred from the analogy with the Diels–Alder adducts obtained from the diene (**2**) and *l*-carvone (*vide ante*). Selective thioketalization of the major product (**21a**) furnished the monothioketal (**22**) in 91% yield. Reduction of the tosylhydrazone derived from **22** with a large excess of $NaBH_4$ gave the compound (**23**) in only 10% yield. Reduction of the tosylhydrazone with $NaBH_3CN$–TsOH–sulfolane–DMF[14] provided the compound (**23**) together with the compound (**24**) in 22% and 14% yields, respectively. Treatment of **23** with 1.6 mol eq. of $Tl(NO_3)_3 \cdot 3H_2O$[15] gave the $\alpha,\beta$-unsaturated ketone (**25**) in 60% yield. Then, methylation at $C_4$ of **25** with LDA–HMPA/MeI–THF was tried but no satisfactory result was obtained.

An attempt was then made to obtain the Diels–Alder adduct possessing a methyl group at $C_4$ by the reaction of the dienophile (**3**) with a new diene (**4**).

A new diene (**4**) was synthesized as follows. The Friedel–Crafts reaction of vinyl bromide and propionyl chloride in the presence of $AlCl_3$ gave a mixture consisting of the compounds, (**26**) and (**27**), which without separation, was treated with NaOMe–MeOH to give 1,1-dimethoxypentan-3-one (**28**)[16] in 35% overall yield from vinyl bromide. A suspension of NaOMe in the compound (**28**) was heated at 160—170° to give 1-methoxy-pent-1-en-3-one (**29**)[17] in 73% yield. Finally, trimethylsilylation of **29** with $Me_3SiCl$–$ZnCl_2$–$Et_3N$[9] gave the desired 1-methoxy-3-trimethylsiloxy-1,3-pentadiene (**4**) in 70% yield. From the NMR spectrum of **4**, it was estimated that this product is a mixture consisting of the E and Z isomer shown by the formula (**4**).

The Diels–Alder reaction of the dienophile (**3**) with the diene (**4**) in anhyd. xylene was carried out at 190—210° for 3 days under argon atmosphere in a sealed tube. Hydrolysis of the product with 2N HCl–THF, followed by chromatographic separation, gave the adducts (**30a**), (**30b**), and (**30c**) in 16%, 6%, and 4% yields, respectively. In addition, the diene dimer

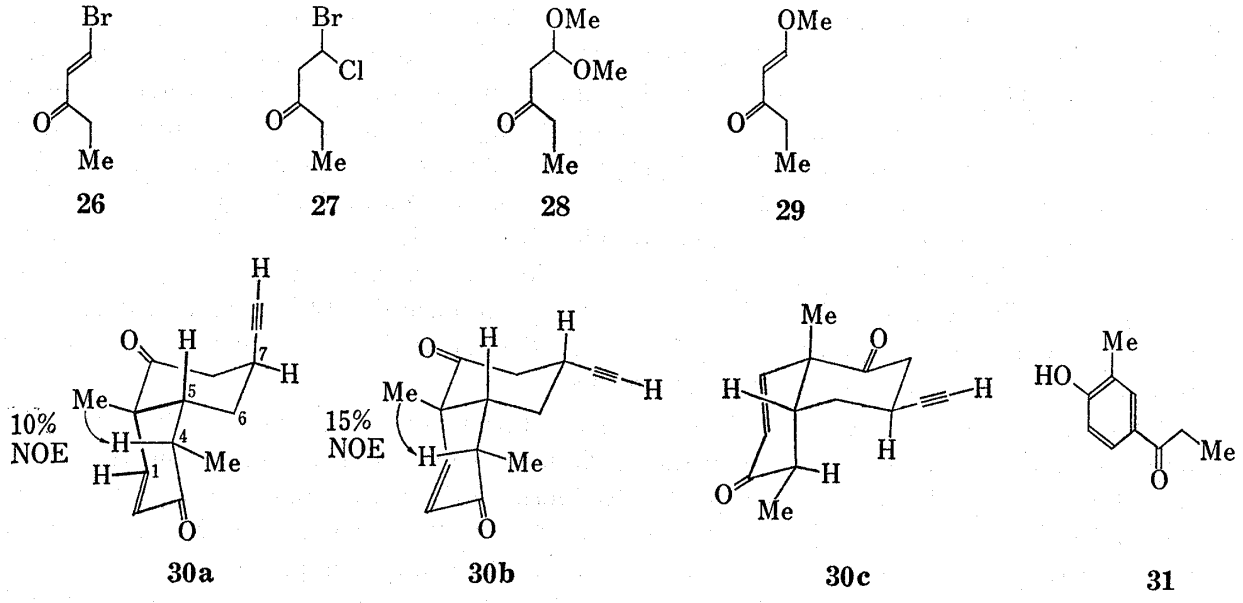


Chart 4

14) R.O. Hutchins, C.A. Milewski, and B.E. Maryanoff, *J. Am. Chem. Soc.*, **95**, 3662 (1973).
15) E. Fujita, Y. Nagao, and K. Kaneko, *Chem. Pharm. Bull.* (Tokyo), **24**, 1115 (1976).
16) P.R. Hills and F. McQuillin, *J. Chem. Soc.*, **1953**, 4060.
17) E.E. Royals and K.C. Brannock, *J. Am. Chem. Soc.*, **76**, 3041 (1954).

(**31**) which may result from the Diels–Alder reaction of the diene (**4**) with its hydrolyzed compound (**29**), was isolated.

The stereostructure of the major product (**30a**) was determined by its NMR spectral examinations. In the INDOR experiment of **30a**, the signal due to $C_5$–H (1H, m) was observed by monitoring the signal due to $C_1$–H ($\delta$ 6.32, 1H, dd, $J$=10, 2 Hz). The W letter long-range coupling ($J$=2 Hz) between $C_1$–H and $C_5$–H suggests the nonsteroidal conformation of **30a** [see formula (**30a**)]. Moreover, the signal due to $C_4$–H was observed at $\delta$ 2.99 (1H, double q, $J$=7, 4.5 Hz) by monitoring the signal of the secondary methyl group. In the NOE measurement of **30a**, the increment (10%) was observed at the signal due to $C_4$–H upon irradiation at the signal of the angular methyl group ($\delta$ 1.46. 3H, s). This observation indicates the $\alpha$ configuration of the secondary methyl group at $C_4$. Moreover, the peak was observed at $\delta$ 3.22 ($C_7$–H, 1H, m) by monitoring the signal of an ethynyl proton at $\delta$ 2.21 (1H, d, $J$=2.5 Hz) and the peaks were observed at $\delta$ 2.73 ($C_5$–H), $\delta$ 1.99 ($C_6$–$H_{eq.}$, 1H, m) and $\delta$ 3.22 ($C_7$–H) by monitoring the signal due to $C_6$–$H_{ax.}$ at $\delta$ 1.63. On the other hand, no peak except the $C_7$–H signal was observed by monitoring the signal due to the $C_8$ methylene protons at $\delta$ 2.58 (2H, m). These observations allowed the identification of the coupled protons. Since the $C_6$–$H_{ax.}$ signal overlapped in part with the signal of the angular methyl protons, the coupling pattern of the former signal at $\delta$ 1.63 ($C_6$–$H_{ax.}$, octet, $J$=14, 13 and 4 Hz) was identified by taking advantage of the solvent effect (in $CDCl_3$: $C_6D_6$=2:1) which permitted the up-field shift of the signal concerned. Because the geminal coupling ($C_6$–$H_{ax.}$–$C_6$–$H_{eq.}$) and the diaxial coupling ($C_5$–$H_{ax.}$–$C_6$–$H_{ax.}$) have the values of 13 Hz and 14 Hz or *vice versa*, the coupling constant value of 4 Hz is allotted to the coupling between $C_6$–$H_{ax.}$–$C_7$–$H_{eq.}$. This suggests the $\beta$ axial conformation of the ethynyl group at $C_7$. The stereostructure of the major product is now shown by the formula (**30a**) and the correctness of these assignments was ultimately shown by identification of the final synthetic product with natural chamaecynone.

The W letter long-range coupling between $C_1$–H ($\delta$ 6.33, 1H, dd, $J$=10 and 2 Hz) and $C_5$–H was observed in the NMR spectrum of the minor product (**30b**), suggesting the nonsteroidal conformation of **30b**. In the NOE experiment, the increment (15%) of the integrated intensity of the $C_4$–H signal ($\delta$ 2.96, 1H, double q, $J$=7 and 3.5 Hz) was observed by irradiation at the signal of the angular methyl protons ($\delta$ 1.43), indicating the $\alpha$ configuration of the secondary methyl group at $C_4$. Consequently, the minor product (**30b**) is a stereoisomer of **30a** with respect to the configuration of the ethynyl group and is shown by the formula (**30b**).

In the NMR spectrum of the other minor product (**30c**), no W letter long-range coupling between $C_1$–H ($\delta$ 6.77, 1H, d, $J$=10 Hz) and $C_5$–H was observed and this suggests its steroidal conformation. The equilibrium experiment of **30c** with $^t$BuOK–$^t$BuOH at room temperature for 2 hr causes epimerization at the $C_4$ position to afford a mixture consisting of **30a** and **30c** in a 2/1 ratio. The stereostructure of **30c** is shown by the formula (**30c**) in which the ethynyl group and the secondary methyl group are both $\beta$-equatorial. Consequently, the major product (**30a**) serves for the chamaecynone synthesis.

Before the chamaecynone synthesis is put forward from the major product (**30a**), selective reduction of the $C_9$ carbonyl function to the methylene group was examined using the minor product (**30b**) as a preliminary experiment. Reduction of **30b** with 0.34 mol eq. of $NaBH_4$ in iso-PrOH–MeOH gave selectively the compound (**32**) in 94% yield. The NMR spectrum of **32** revealed the signal ($\delta$ 3.43, 1H, dd, $J$=12 and 4 Hz) due to a proton geminal to the hydroxyl group and the diaxial coupling constant value ($J$=12 Hz) indicates the $\alpha$-equatorial conformation of the newly generated hydroxyl group. Mesylation of **32** furnished the mesylate (**33**) in 94% yield and reduction of **33** with $LiAlH_4$, followed by $MnO_2$ oxidation regenerated the hydroxyl compound (**32**) and the desired compound possessing the methylene group at $C_9$ was not detected. Then, tosylation of **32** gave the tosylate (**34**) which was reduced with $NaBH_4$ to afford the allyl alcohol. Treatment of the allyl alcohol with Super Hydride

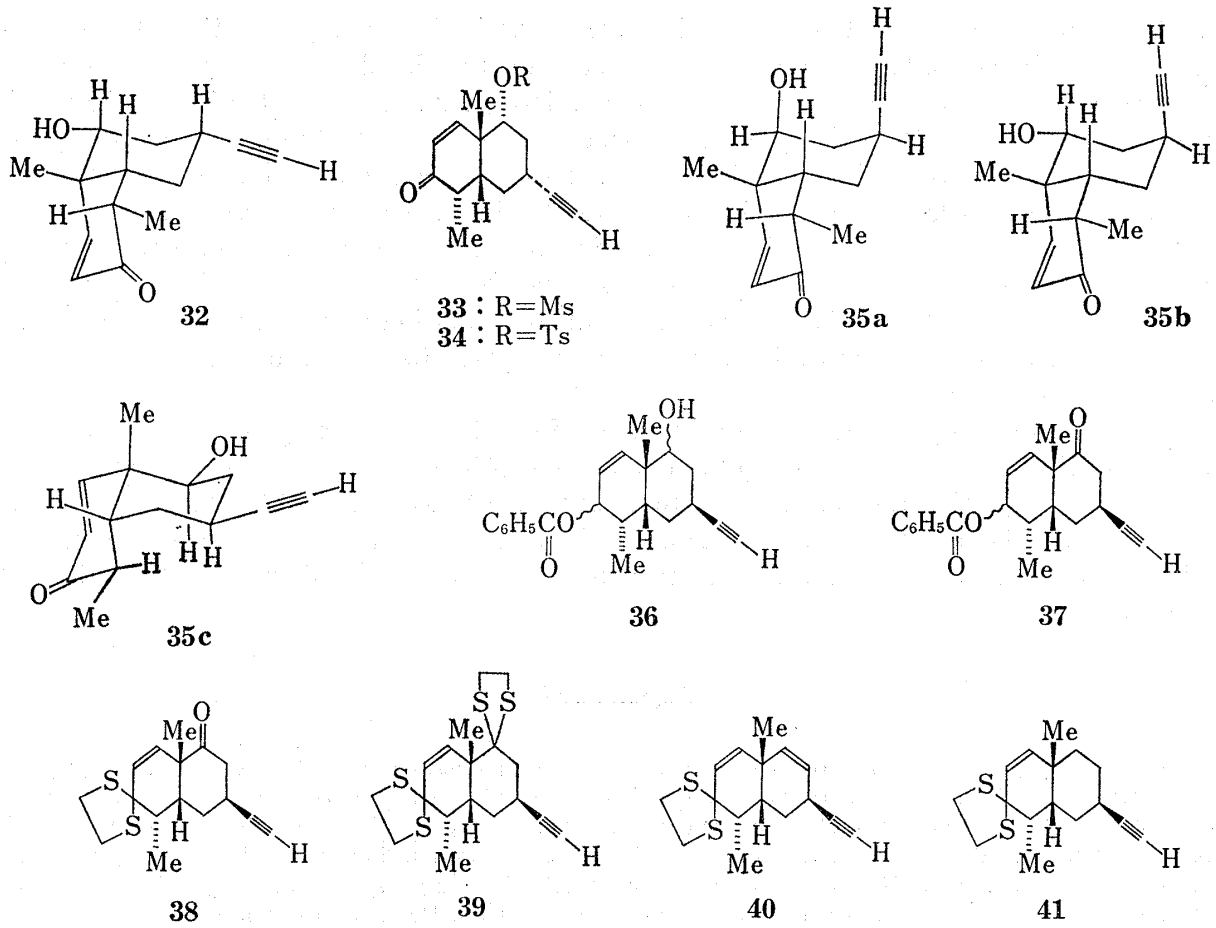


Chart 5

(LiBHEt$_3$–THF),[18] however, furnished no desired compound and treatment of **33** with Zn–NaI–glyme–HMPA[19] also gave no satisfactory result.

On the other hand, reduction of the major product (**30a**) with 0.63 mol eq. of $NaBH_4$ afforded three kinds of alcohols, (**35a**), (**35b**), and (**35c**) in 45%, 27%, and 12% yields, respectively, in contrast to the compound (**30b**). The stereostructures of these alcohols were inferred from their NMR spectral investigations. In reduction of **30b**, the hydride attack took place from the convex face to give selectively the $\alpha$ alcohol, whereas reduction of the major product (**30a**) gave predominantly the $\beta$ alcohol which was formed by the hydride attack from the concave face. This result was rationalized by taking account of the steric hindrance at the $C_9$ carbonyl group by the axial ethyl group. Then, it was presumed that benzoylation of the diol, which is obtained by reduction of **30a** with $NaBH_4$ or $LiAlH_4$, may cause the selective benzoylation of the allylic hydroxyl group. From this assumption, the reduction product of **30a** with $LiAlH_4$ was benzoylated with 1.5 mol eq. of benzoyl chloride to afford mainly the monobenzoate (**36**). Jones' oxidation of **36** gave the monoketone (**37**), $\nu_{max}$ 1708 cm$^{-1}$, in 82% yield, which was hydrolyzed with alkaline to give the allyl alcohol. Reduction of the tosylhydrazone derived from the allyl alcohol with a large excess of $NaBH_4$, however, gave no desired reduction product.

Finally, the chamaecynone synthesis was performed through the following route from the major product (**30a**). Thioketalization of **30a** with 4.9 mol eq. ethanedithiol and 2.9 mol eq. $BF_3$-ether provided the monothioketal (**38**) and the dithioketal (**39**) in 57% and 13% yields, respectively. Treatment of **38** with 1.6 mol eq. $p$-$TsNHNH_2$ gave quantitatively the

18) S. Krishnamurthy and H.C. Brown, *J. Org. Chem.*, **41**, 3064 (1976).
19) Y. Fujimoto and T. Tatsuno, *Tetrahedron Lett.*, **1976**, 3325.

tosylhydrazone. In contrast to the tosylhydrazone derived from **14**, reduction of the tosylhydrazone of **38** with a large excess of $NaBH_4$ gave mainly the olefinic compound (**40**) which was formed by the elimination of the tosylhydrazino group. Next, reduction of the tosylhydrazone from **38** with $NaBH_3CN$–TsOH–DMF–sulfolane[14] was tried. In this case, the olefinic compound (**40**) was also obtained together with the expected reduction product (*vide infra*). The formation of the olefinic compound (**40**) in the case of the hydrazone from **38** in contrast to those from **14** and **22** may be attributed to the different conformation among these compounds. Thus, the hydrazones of **14** and **22**, have the steroidal conformation, whereas the hydrazone of **38** has the nonsteroidal conformation in which the hydride attack at the $C_9$ position is hindered by the $\beta$-axial ethynyl group to cause the unusual elimination of the tosylhydrazino group.

The reduction product of the tosylhydrazone from **38** with $NaBH_3CN$ was separated by the preparative TLC to isolate the desired compound (**41**) and the olefinic compound (**40**) in 10% and 7% yields, respectively. Treatment of **41** with $Tl(NO_3)_3 \cdot 3H_2O$[15] gave *dl*-chamaecynone (**1**) in 73% yield. A sample of synthetic *dl*-chamaecynone was identified with an authentic sample of natural chamaecynone by comparison of their IR (in $CCl_4$) and NMR spectra.

## Experimental

All melting points were taken 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 stated. Low-resolution mass spectra and high-resolution mass spectra were taken with a Hitachi RMU-6C spectrometer with a heated direct inlet system and a JEOL JMS-01SG-2 spectrometer, respectively. Optical rotations were observed with a Rex Photoelectric Polarimeter NEP-2. All extracts were dried over anhyd. $MgSO_4$ and column chromatography was performed on silica gel (Mallinckrodt, Silicic Acid 100 mesh) or on alumina (Merck, neutral Aluminiumoxide). The preparative TLC was performed on silica gel (Merck, Silicic Acid PF-254 containing $CaSO_4$) or on alumina (Merck, Aluminiumoxide $PF_{254}$).

**The Diels-Alder Adducts, (5a) and (5b), by the Heating Method**——To a solution of 14 g of *l*-carvone in 10 ml of anhyd. xylene was added 18 g of *trans*-1-methoxy-3-trimethylsiloxy-1,3-butadiene (**2**) at 0° in a sealed tube. The mixture was heated at 190° for 22 hr or at 145° for 8 days under the argon atmosphere. The reaction mixture was acidified with a 2 N HCl–THF solution (1: 6) and stirred at 0° for 30 min. The mixture was extracted with $CHCl_3$, and the extract was dried and evaporated under reduced pressure to leave 18 g of the residue. The residue was chromatographed on $SiO_2$ and elution of the column with 5% ether in *n*-hexane gave 7 g of the recovered *l*-carvone. Continuous elution with 20% ether in *n*-hexane afforded 1.6 g of the Diels-Alder adduct (**5b**) and changing the eluting solvent to 25% ether in *n*-hexane provided 3.9 g of the adduct (**5a**). Continuous elution with 30% ether in *n*-hexane yielded 3.7 g of the oily compound. A solution of this oily compound in 100 ml of 2 N HCl in THF (1: 6) was refluxed for 40 min and the reaction mixture was extracted with ether. The extract was washed with a 3% $NaHCO_3$ solution, dried and evaporated under reduced pressure to leave 3 g of the residue. The residue was chromatographed on $SiO_2$ in a similar manner as above to yield another crops of **5b** (1.18 g) and **5a** (1.05 g). Total yields of the adducts (**5a**) and (**5b**) were 4.95 g (25%) and 2.78 g (14%), respectively. **5a**: colorless plates (ether–*n*-hexane), mp 62—64°, $[\alpha]_D^{28}$ −84.6° ($c$=1.0, EtOH). IR $cm^{-1}$: $\nu_{C=O}$ 1700, $\nu_{C=O}$ 1678, $\nu_{C=C}$ 1650, $\delta_{C=CH}$ 904. NMR $\delta$: 1.49 (3H, s, angular $CH_3$), 1.79 (3H, m, allyl $CH_3$), 4.75—4.95 (2H, m, terminal methylene protons), 6.04 (1H, d, $J$=10 Hz, olefinic proton, $C_2$–H), 6.75 (1H, d, $J$=10 Hz, olefinic proton, $C_1$–H). *Anal.* Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.03; H, 8.18. **5b**: colorless plates (ether–*n*-hexane), mp 76—78°, $[\alpha]_D^{28}$ +312.2° ($c$=1.0, EtOH). IR $cm^{-1}$: $\nu_{C=O}$ 1710, $\nu_{C=O}$ 1679, $\nu_{C=C}$ 1650, $\delta_{C=CH}$ 904. NMR $\delta$: 1.42 (3H, s, angular $CH_3$), 1.71 (3H, m, allyl $CH_3$), 2.90 (1H, d.d, $J$=17 and 5 Hz, one of methylene protons), 4.68—4.85 (2H, m, terminal methylene protons), 6.05 (1H, d.d, $J$=10 and 1 Hz, olefinic proton, $C_2$–H), 6.47 (1H, d.d, $J$=10 and 2 Hz, olefinic proton, $C_1$–H). *Anal.* Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.07; H, 8.54.

**The Adducts (5a) and (5b) from the Reaction in the Presence of the Lewis Acid**——To a solution of 10 g of *l*-carvone in 100 ml of anhyd. $CH_2Cl_2$ were added 2.6 g of anhyd. $ZnCl_2$ and 15 g of the diene (**2**). The mixture was allowed to stand at room temperature for 5 days. The usual work-up gave the residue which was chromatographed on $SiO_2$ to afford 750 mg of the adduct (**5a**) and 120 mg of the adduct (**5b**). To a solution of 7 g of *l*-carvone in 100 ml of anhyd. $CH_2Cl_2$ were added 2.0 g of anhyd. $AlCl_3$ in place of $ZnCl_2$

and 10 g of the diene (**2**). The mixture was left for 5 days at room temperature. A similar treatment as above yielded 220 mg of **5a** but the compound (**5b**) was not detected by GLC.

**Conversion of the Major Adduct (5a) to the Ketone (8)**——To a solution of 327 mg of the adduct (**5a**) in 10 ml of abs. EtOH was added 100 mg of 10% Pd-C and the mixture was stirred under the hydrogen atmosphere. After the hydrogen uptake had ceased, catalyst was removed by filtration. The filtrate was concentrated under reduced pressure to leave 320 mg (96% yield) of the colorless oil (**6**). IR $cm^{-1}$: $\nu_{C=O}$ 1703. NMR $\delta$: 0.92 (6H, d, $J=7$ Hz, $CH(CH_3)_2$), 1.28 (3H, s, angular $CH_3$). MS *m/e*: 222 ($M^+$). To a solution of 250 mg of the diketone (**6**) in 5 ml of anhyd. MeOH were added dropwise 150 mg of ethanedithiol and 170 mg of $BF_3$·ether. The mixture was allowed to stand for 40 hr at 0°. The reaction mixture was diluted with a 3% NaOH solution and extracted with ether. The extract was washed with water, dried and evaporated under reduced pressure to leave the oily residue. The oil was solidified on trituration with *n*-pentane. Recrystallization from *n*-pentane gave 300 mg (89% yield) of **7** as colorless plates, mp 92—93°. IR $cm^{-1}$: $\nu_{C=O}$ 1698. NMR $\delta$: 0.90 (6H, d, $J=6$ Hz, $CH(CH_3)_2$), 1.20 (3H, s, angular $CH_3$), 3.27 (4H, s, $-S-(CH_2)_2-S-$). *Anal.* Calcd. for $C_{16}H_{26}OS_2$: C, 64.37; H, 8.78. Found: C, 64.08; H, 8.62. A solution of 190 mg of **7** in 10 ml of abs. EtOH was added to 5 ml (the volume of precipitates from EtOH) of Raney Ni (W-2). The mixture was refluxed for 5 hr and extracted with ether. The extract was dried and evaporated under reduced pressure to leave the residue. The residue was chromatographed on $SiO_2$ and elution of the column with *n*-hexane provided 110 mg of the ketone (**8**) in an 83% yield, $[\alpha]_D^{24}$ +56.5° ($c=0.94$, EtOH). The compound (**8**) was identified with an authentic sample,[4] $[\alpha]_D^{28}$ +57.1° ($c=1.0$, EtOH).

**The Ketone (9)**——To a solution of 273 mg of the minor adduct (**5b**) in 15 ml of abs. EtOH was added 150 mg of 10% Pd-C and the mixture was stirred under the hydrogen atmosphere. The usual work-up afforded 273 mg of the diketone (**9**) as colorless flakes (*n*-hexane), mp 96—98°. IR $cm^{-1}$: $\nu_{C=O}$ 1702. NMR $\delta$: 0.89 (6H, d, $J=6$ Hz, $CH(CH_3)_2$), 1.41 (3H, s, angular $CH_3$), 2.79 (1H, d.d, $J=15$ and 6 Hz, one of methylene protons). *Anal.* Calcd. for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.63; H, 10.26.

**Conversion of the Minor Adduct (5b) to the Ketone (12) *via* the Compound (10)**——To a solution of 440 mg of the minor adduct (**5b**) in 6 ml of anhyd. MeOH were added dropwise 200 mg of ethanedithiol and 300 mg of $BF_3$·ether. The mixture was left standing at 0° for 40 hr. The usual work-up gave the residue which was chromatographed on $SiO_2$. Elution of the column with a mixture of *n*-hexane and ether (1: 1) afforded 230 mg of the oily compound. Continuous elution with ether gave 180 mg of the oily compound. The separation of the former oil by the preparative TLC on $SiO_2$ gave 73 mg of the compound (**11**) in a 10% yield from a less polar zone and 140 mg of the monothioketal (**10**) from a more polar zone. The latter oil was similarly separated to give 20 mg of **10** and 100 mg of the starting material. The total yield of **10** was 27%. **10**: colorless plates (*n*-hexane), mp 92—94°. IR $cm^{-1}$: $\nu_{C=O}$ 1703, $\nu_{C=C}$ 1646, $\delta_{C=CH}$ 899. NMR $\delta$: 1.23 (3H, s, angular $CH_3$), 1.75 (3H, m, allyl $CH_3$), 3.28—3.45 (4H, m, $-S-(CH_2)_2-S-$), 4.76 (2H, m, methylene protons), 5.27 (1H, d, $J=10$ Hz, olefinic proton), 5.89 (1H, d.d, $J=10$ and 1 Hz, olefinic proton). *Anal.* Calcd. for $C_{16}H_{22}OS_2$: C, 65.24; H, 7.53. Found: C, 65.48; H, 7.73. **11**: colorless needles (*n*-hexane), mp 95—96°. IR $cm^{-1}$: $\nu_{C=C}$ 1643, $\delta_{C=CH}$ 896. NMR $\delta$: 1.39 (3H, s, angular $CH_3$), 1.71 (3H, m, allyl $CH_3$), 3.23—3.43 (total 8H, m, $-S-(CH_2)_2-S-$), 4.70 (2H, m, methylene protons), 5.66 (2H, m, olefinic protons). *Anal.* Calcd. for $C_{18}H_{26}S_4$: C, 58.33; H, 7.07. Found: C, 58.04; H, 7.04. A solution of 252 mg of **10** in 15 ml of abs. EtOH was added to 6 ml of Raney Ni (W-2) and the mixture was refluxed for 16.5 hr. The usual work-up gave the residue which was separated by the preparative TLC to afford 42 mg of the oily compound from a less polar zone and 85 mg of the oily compound from a more polar zone. To a solution of 85 mg of the latter oil in 5 ml of abs. EtOH was added 30 mg of $PtO_2 \cdot 2H_2O$ and the mixture was stirred under the hydrogen atmosphere. The catalyst was removed by filtration and the filtrate was diluted with water and extracted with ether. The extract was dried and evaporated to leave 80 mg of the residue. The separation of the residue by the preparative TLC provided 60 mg of the colorless oil (**12**) in a 34% yield, $[\alpha]_D^{24}$ +88.8° ($c=1.1$, EtOH). The compound (**12**) was identified with an authentic sample,[4] $[\alpha]_D^{25}$ +84.3° ($c=0.91$, EtOH).

**The Ketone (15) from the Major Adduct (5a) *via* the Compound (14)**——To a solution of 660 mg of the adduct (**5a**) in 10 ml of anhyd. MeOH were added dropwise 330 mg of ethanedithiol and 480 mg of $BF_3$·ether. The mixture was left standing at 0° for 30 hr and the usual work-up gave the residue which was chromatographed on $SiO_2$. Elution of the column with *n*-hexane afforded 40 mg of the compound (**13**) and continuation of elution with 5—10% ether in *n*-hexane provided 670 mg of the compound (**14**) in a 75% yield. **13**: colorless plates (*n*-hexane), mp 155—157°. IR $cm^{-1}$: $\nu_{C=C}$ 1643, $\delta_{C=CH}$ 899. NMR $\delta$: 1.40 (3H, s, angular $CH_3$), 1.75 (3H, m, allyl $CH_3$), 3.00—3.45 (total 8H, m, $-S-(CH_2)_2-S-$), 4.75 (2H, m, methylene protons), 5.84 (2H, br. s, olefinic protons). *Anal.* Calcd. for $C_{18}H_{26}S_4$: C, 58.33; H, 7.07. Found: C, 58.52; H, 7.12. **14**: colorless needles (*n*-hexane), mp 103—104°. IR $cm^{-1}$: $\nu_{C=O}$ 1700, $\nu_{C=C}$ 1645, $\delta_{C=CH}$ 899. NMR $\delta$: 1.33 (3H, s, angular $CH_3$), 1.73 (3H, m, allyl $CH_3$), 3.27—3.42 (4H, m, $-S-(CH_2)_2-S-$), 4.79 (2H, m, methylene protons), 5.64 (1H, d, $J=10$ Hz, olefinic proton), 5.95 (1H, d.d, $J=10$ and 1 Hz, olefinic proton). *Anal.* Calcd. for $C_{16}H_{22}OS_2$: C, 65.24; H, 7.53. Found: C, 64.98; H, 7.58. To a solution of 520 mg of the compound (**14**) in 15 ml of anhyd. MeOH was added 503 mg of *p*-$TsNHNH_2$ and the mixture was refluxed for 8.5 hr. The mixture was cooled at 0° and 10 ml of anhyd. MeOH and 2.2 g of $NaBH_4$ were added alternatively to the mixture in small portions. The mixture was refluxed for 20 hr and extracted with ether. The extract was washed with water, dried and evaporated to leave the residue and purification of the residue by the

preparative TLC yielded 280 mg of the oily material (58% yield). To a solution of this oil in 15 ml of 99% aqueous acetone were added 383 mg of $CuCl_2 \cdot 2H_2O$ and 362 mg of CuO. The mixture was stirred for 22 hr at room temperature and was extracted with $CHCl_3$. The extract was dried and evaporated to leave the residue. The separation of the residue by the preparative TLC gave 108 mg of the recovered starting material from a less polar zone and 42 mg of the crude ketone (**15**) from a more polar zone. A solution of the recovered material (108 mg) in 5 ml of 99% aqueous acetone was refluxed with $CuCl_2 \cdot 2H_2O$ (154 mg) and CuO (138 mg) for 8.5 hr and a similar work-up as above gave the second crop (73 mg) of the crude ketone (**15**). The combined first and second crops of the ketone (**15**) were purified by the preparative TLC on $SiO_2$ impregnated with $AgNO_3$ to provide 16 mg of the compound (**16**) from a less polar zone and 72 mg (20% yield from **14**) of the ketone (**15**) from a more polar zone. **15**: IR $cm^{-1}$: $\nu_{C=O}$ 1670, $\nu_{C=C}$ 1650 (shoulder), $\delta_{C=CH}$ 897. NMR $\delta$: 1.22 (3H, s, angular $CH_3$), 1.75 (3H, m, allyl $CH_3$), 4.75 (2H, m, methylene protons), 5.88 (1H, d.d, $J=10$ and 1 Hz, olefinic proton, $C_2$–H), 6.65 (1H, d, $J=10$ Hz, olefinic proton, $C_1$–H). MS *m/e*: 204 ($M^+$). **16**: IR $cm^{-1}$: $\nu_{C=O}$ 1670. NMR $\delta$: 0.89 (6H, d, $J=6$ Hz, $CH(CH_3)_2$), 1.18 (3H, s, angular $CH_3$), 5.85 (1H, d.d, $J=10$ and 1 Hz, olefinic proton, $C_2$–H), 6.62 (1H, d, $J=10$ Hz, olefinic proton, $C_1$–H). MS *m/e*: 206 ($M^+$).

**5-Vinyl-2-methylcyclohexan-1-one** (**17**)——In a two-necked flask equipped with a dry-ice acetone reflux condenser, a mechanical stirrer, and a rubber stopper were placed a mixture of magnesium (10.5 g) and iodine (5 g) in 180 ml of anhyd. THF. The mixture was stirred for 20 min under the argon atmosphere at 0° and a solution of 51 g of freshly distilled vinyl bromide[20] in 90 ml of THF was injected into the flask with the aid of a syringe through a rubber stopper. The reaction started with violence and the mixture was refluxed for 10 min. After stirring was continued for further 35 min at 0°, the reaction mixture was then cooled at −45° and the dry-ice condenser was removed. To this Grignard reagent was added 9.2 g of dry CuI at once and the mixture was vigorously stirred for 25 min under the argon atmosphere. To the mixture was injected a solution of 24 g of 6-methylcyclohex-2-en-1-one[13] in 105 ml of anhyd. THF with the aid of a syringe. The dry-ice bath temperature was gradually raised from −45° to 0° during 1.5 hr and the mixture was hydrolyzed by the careful addition of an aq. saturated solution with $NH_4Cl$ and then filtrated. The filtrate was extracted with ether and the extract was washed with brine, dried and evaporated. Distillation of the residue gave 24 g (80%) of 5-vinyl-2-methylcyclohexan-1-one (**17**), bp 81—84°/16 mmHg, which was indicated to be an epimeric mixture of *cis* and *trans* isomers in a ratio of 1:1 by its NMR spectrum and GLC. IR $cm^{-1}$: $\nu_{C=O}$ 1705, $\nu_{C=C}$ 1640, $\delta_{CH}$ 995, 920. NMR $\delta$: 1.03 and 1.06 (total 3H, each d, $J=6.5$ Hz, –CH–$CH_3$), 4.80—5.00, 5.00—5.20, and 5.53—6.15 (each 1H, m, vinyl protons). MS *m/e*: 138 ($M^+$).

**5-Ethynyl-2-methylcyclohexan-1-ol** (**18a**)——To a solution of 14.9 g of **17** in 120 ml of 99% EtOH was added 16.4 g of $NaBH_4$ at 0°. The mixture was stirred for 45 min at the same temperature and stirring was continued for further 2 hr at room temperature. The reaction mixture was extracted with ether and the extract was washed with water, dried and evaporated to leave 15.1 g of a mixture of the isomeric alcohols. IR $cm^{-1}$: $\nu_{OH}$ 3600, 3450, $\nu_{C=C}$ 1642, $\delta_{CH}$ 1000, 918. NMR $\delta$: 0.92 and 1.01 (total 3H; d, $J=7$ Hz and d, $J=5$ Hz, –CH–$CH_3$), 2.90—3.38 and 3.58—3.95 (total 1H, br.m, –CH–OH), 4.75—5.15 (2H, m, vinyl protons), 5.50—6.10 (1H, m, vinyl proton). MS *m/e*: 140 ($M^+$). To a solution of 1.37 g of the alcohols in 96 ml of $CHCl_3$ was added dropwise a solution of 10.7 mmol of bromine in 10 ml of $CHCl_3$. After 10 min, the reaction mixture was diluted with water and the organic layer was separated and the aqueous layer was extracted with $CHCl_3$. The organic layer and the extracts were combined and dried. Evaporation of the solvent under reduced pressure gave the residue which was purified by chromatography on $SiO_2$ to afford 1.83 g (62%) of the dibromo-alcohol. A powder of 160 mg of anhyd. $FeCl_3$ was added to 50 ml of liq. $NH_3$ at −78°. After 5 min, 262 mg of sodium was added by portions and the mixture was stirred for 1 hr. A solution of 341 mg of the dibromo-alcohol in 8 ml of anhyd. ether was then added and the mixture was stirred for further 3 hr. After evaporation of ammonia, an aq. saturated solution of $NH_4Cl$ was added and the mixture was extracted with ether. The extract was washed with water, dried and evaporated to leave 131 mg (83%) of 5-ethynyl-2-methylcyclohexan-1-ol (**18a**); bp 98—99°/20 mmHg. IR $cm^{-1}$: $\nu_{OH}$ 3600, 3550, 3450, $\nu_{C\equiv CH}$ 3330, $\nu_{C\equiv C}$ 2125. NMR: $\delta$ 0.85—1.05 (3H, m, –CH–$CH_3$), 2.07 and 2.13 (total 1H, each d, $J=2$ Hz, –C≡CH), 2.80—3.30 and 3.50—3.95 (total 1H, m, –CH–OH). *Anal.* Calcd. for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.93; H, 10.33.

**The Alternative Synthesis of 18a *via* the Compounds (19) and (18b) from 5-Vinyl-2-methylcyclohexan-1-one** (**17**)——To a solution of 11.7 g of the alcohol derived from 5-vinyl-2-methylcyclohexan-1-one (**17**) in 100 ml of anhyd. pyridine was added 100 ml of acetic anhydride. The mixture was allowed to stand for 17 hr at room temperature. The reaction mixture was acidified with an ice-cooled 5% HCl solution and was extracted with $CHCl_3$. The extract was washed with water, dried and evaporated to leave 15.5 g of the compound (**19**), bp 121—122°/32 mmHg. IR $cm^{-1}$: $\nu_{C=O}$ 1720, $\nu_{C=C}$ 1640, $\nu_{C-O}$ 1255, $\delta_{CH}$ 915. NMR $\delta$: 0.90 and 0.93 (total 3H; d, $J=6$ Hz and d, $J=7$ Hz, –CH–$CH_3$), 2.04 (3H, br.s, $OCOCH_3$), 4.78—5.15 (2H, m, vinyl protons), 5.50—6.10 (1H, m, vinyl proton). *Anal.* Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C,

20) Vinyl bromide was washed with an ice-cooled aq. saturated solution of $Na_2SO_3$ twice, with an ice-cooled aq. saturated solution of $NaHCO_3$ once, dried over $K_2CO_3$ and distilled.

72.72; H, 10.09. To a solution of 15.5 g of the compound (**19**) in 200 ml of $CHCl_3$ was added dropwise a solution of 94 ml (94 mmol) of bromine in 85 ml of $CHCl_3$. After 10 min, the usual work-up gave 28.8 g of the crude dibromo-acetate, IR $cm^{-1}$: $\nu_{C=O}$ 1725.

A powder of 3 g of anhyd. $FeCl_3$ was added to 800 ml of liq. $NH_3$ at −78°. After 20 min, 23 g of sodium was added by portions and the mixture was stirred for 1 hr. A solution of 28.8 g of the crude dibromo-acetate in 200 ml of anhyd. ether was added dropwise and the mixture was stirred for 2 hr at −78°. The usual work-up provided 12.8 g (85%) of the compound (**18b**). IR $cm^{-1}$: $\nu_{C\equiv CH}$ 3298, $\nu_{C\equiv C}$ 2100, $\nu_{C=O}$ 1720, $\nu_{C-O}$ 1255. To a solution of 12.8 g of **18b** in 200 ml of MeOH was added an aqueous solution (100 ml) of 11.6 g of KOH. The mixture was refluxed for 30 min and extracted with ether. The extract was washed with water, dried and evaporated to leave 9.0 g of 5-ethynyl-2-methylcyclohexan-1-ol (**18a**) in overall 78% yield from **17**.

**5-Ethynyl-2-methylcyclohexan-1-one** (**20**)——To a solution of 3.55 g of **18a** in 150 ml of acetone was added dropwise 8.74 ml (23.6 mmol) of Jones' reagent at 0° under stirring and the mixture was stirred 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 3.5 g of 5-ethynyl-2-methylcyclohexan-1-one (**20**), bp 87—90°/12 mmHg. IR $cm^{-1}$: $\nu_{C\equiv CH}$ 3320, $\nu_{C\equiv C}$ 2100, $\nu_{C=O}$ 1710. NMR $\delta$: 1.02 and 1.05 (total 3H, each d, $J$=6.5 Hz, $-\overset{|}{C}H-CH_3$), 2.18 (1H, d, $J$=2 Hz, $-C\equiv CH$). *Anal.* Calcd. for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.24; H, 8.87.

**5-Ethynyl-2-methylcyclohex-2-en-1-one** (3)——To a solution of 7 g of **20** in 100 ml of $CHCl_3$ was added dropwise 66 ml (66 mmol) of bromine in $CHCl_3$ at 30°. After a reddish-brown color had faded, the usual work-up gave 11 g of the residue. IR $cm^{-1}$: $\nu_{C\equiv CH}$ 3310, $\nu_{C\equiv C}$ 2130, $\nu_{C=O}$ 1718. To a solution of 11 g of the residue in 200 ml of DMF were added 18.3 g of $LiBr\cdot H_2O$ and 12.9 g of $Li_2CO_3$ under stirring. The mixture was heated at 120—130° for 4 hr with stirring under the argon atmosphere. After cooling, the reaction mixture was acidified with an ice-cooled 5% HCl solution and extracted with ether. The extract was washed with a 3% NaOH solution, with brine, dried and evaporated. Purification of the residue by chromatography on $Al_2O_3$ to give 4.8 g of 5-ethynyl-2-methylcyclohex-2-en-1-one (3) in 70% yield, colorless plates, mp 46° from *n*-hexane–ether. IR $cm^{-1}$: $\nu_{C\equiv CH}$ 3330, $\nu_{C\equiv C}$ 2140, $\nu_{C=O}$ 1675. NMR $\delta$: 1.72—1.85 (3H, m, $=\overset{|}{C}-CH_3$), 2.15 (1H, d, $J$=2 Hz, $-C\equiv CH$), 6.70 (1H, m, $W_{1/2}$=9 Hz). *Anal.* Calcd. for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.44; H, 7.81.

**The Diels-Alder Adducts** (**21a**) **and** (**21b**)—To a solution of 4.7 g of 5-ethynyl-2-methylcyclohex-2-en-1-one (3) in 12 ml of anhyd. xylene was added 16.1 g of *trans*-1-methoxy-3-trimethylsiloxy-1,3-butadiene (**2**). The mixture was heated at 180—200° for 60 hr in a sealed tube. The solvent was removed under reduced pressure to leave the residue which was chromatographed on $SiO_2$. Elution of the column with $CHCl_3$ gave 2.75 g of the crude oil from an earlier fraction. Continuous elution afforded 1.63 g of the crystalline major adduct (**21a**). Rechromatography of the crude oil furnished 0.223 g (3%) of the minor adduct (**21b**) from the earlier eluate and the another crop of the major adduct (**21a**; 0.472 g) from the later eluate. The major adduct was obtained in 30% total yield. **21a**: colorless prisms mp 92—94° from ether. IR $cm^{-1}$: $\nu_{C\equiv CH}$ 3300, $\nu_{C\equiv C}$ 2120, $\nu_{C=O}$ 1710, $\nu_{C=O}$ 1676. NMR $\delta$: 1.48 (3H, s, $CH_3$), 2.26 (1H, d, $J$=2 Hz, $-C\equiv CH$), 6.03 (1H, d, $J$=10.5 Hz, $C_2$–H), 6.60 (1H, d.d, $J$=10.5 and 1 Hz, $C_1$–H). *Anal.* Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 76.92; H, 7.18. **21b**: IR $cm^{-1}$: $\nu_{C\equiv CH}$ 3340, $\nu_{C\equiv C}$ 2180, $\nu_{C=O}$ 1718, $\nu_{C=O}$ 1684. NMR $\delta$: 1.40 (3H, s, $CH_3$), 2.20 (1H, d, $J$=2 Hz, $-C\equiv CH$), 6.07 (1H, d, $J$=10.5 Hz, $C_2$–H), 6.49 (1H, d.d, $J$=10.5 and 1.5 Hz, $C_1$–H). MS *m/e*: 202 ($M^+$).

**The Monothioketal** (**22**)——To a solution of 108 mg of **21a** in 9 ml of anhyd. MeOH were added 60 mg of ethanedithiol and 82 mg of $BF_3\cdot$ether. The mixture was allowed to stand for 20 hr at room temperature. The reaction mixture was extracted with $CHCl_3$ and the extract was washed with a 3% NaOH solution, dried and evaporated under reduced pressure. Purification of the residue by preparative TLC afforded 134 mg (91%) of the monothioketal (**22**); colorless prisms mp 134° from ether. IR $cm^{-1}$: $\nu_{C\equiv CH}$ 3340, $\nu_{C\equiv C}$ 2140, $\nu_{C=O}$ 1702. NMR $\delta$: 1.34 (3H, s, $CH_3$), 2.19 (1H, d, $J$=1.5 Hz, $-C\equiv CH$), 3.28—3.48 (4H, m, $S-(CH_2)_2-S-$), 5.59 and 5.92 (each 1H, d, $J$=10 Hz, olefinic protons). *Anal.* Calcd. for $C_{15}H_{18}OS_2$: C, 64.71; H, 6.52. Found: C, 64.43; H, 6.54.

**The Compounds** (**23**) **and** (**24**)——To a solution of 215 mg of **22** in 8 ml of anhyd. MeOH was added 230 mg of *p*-$TsNHNH_2$. The mixture was refluxed for 9 hr and the solvent was removed under reduced pressure to leave 343 mg of the crude crystals. To a solution of the crystals in 2.5 ml of anhyd. DMF and 2.5 ml of anhyd. sulfolane were added 58 mg of anhyd. *p*-TsOH and 194 mg of $NaBH_3CN$. The mixture was heated at 110° (oil bath temperature) for 5 hr with stirring under the argon atmosphere. To the mixture were further added 194 mg of $NaBH_3CN$ and 58 mg of anhyd. *p*-TsOH. Vigorous stirring was continued for further 16 hr at 110—120°. The reaction mixture was extracted with AcOEt–ether (1: 4) and the extract was washed with water, dried and evaporated under reduced pressure to leave 208 mg of the residue. Separation of the residue by preparative TLC on $SiO_2$ gave 32 mg of the crude oil (A) from the less polar zone, 57.5 mg of the crude oil (B) from the middle zone, and 78 mg of the recovered hydrazone from the most polar zone. Purification of both the oil (A) and (B) by preparative TLC provided 28 mg (14%) of the compound (**24**) and 44 mg (22%) of the compound (**23**), respectively. **23**: colorless prisms, mp 80—82° from *n*-pentane. IR $cm^{-1}$: $\nu_{C\equiv CH}$ 3300, $\nu_{C\equiv C}$ 2140. NMR $\delta$: 1.08 (3H, s, $CH_3$), 2.04 (1H, d, $J$=2 Hz, $-C\equiv CH$), 3.28—3.42 (4H, m, $-S-(CH_2)_2-S-$), 5.33 (1H, d, $J$=10 Hz, $C_1$–H), 5.70 (1H, d.d, $J$=10 and 1 Hz, $C_2$–H). MS *m/e*: 264 ($M^+$).

**24**: IR $cm^{-1}$: $\nu_{C=C}$ 1645, $\delta_{C=CH}$ 1000, 915. NMR $\delta$: 1.05 (3H, s, $CH_3$), 3.27—3.40 (4H, m, $-S-(CH_2)_2-S-$), 4.75—6.05 (3H, m, vinyl protons), 5.37 (1H, d, $J=10$ Hz, $C_1$–H), 5.69 (1H, d.d, $J=10$ and 1.5 Hz, $C_2$–H). MS *m/e*: 266 ($M^+$).

**The α,β-Unsaturated Ketone (25)**——To a solution of 86 mg of **23** in 11 ml of $CHCl_3$ was added 229 mg of $Tl(NO_3)_3 \cdot 3H_2O$ in 9 ml of anhyd. MeOH under stirring at 0°. After 10 min, the reaction mixture was diluted with water and the organic layer was separated. The aqueous layer was extracted with $CHCl_3$ and the washing was combined with the organic layer. After drying, evaporation of the solvent under reduced pressure gave 71 mg of the residue which was purified by preparative TLC on $Al_2O_3$ to yield 37 mg (60%) of the α,β-unsaturated ketone (**25**). IR $cm^{-1}$: $\nu_{C\equiv CH}$ 3300, $\nu_{C\equiv C}$ 2130, $\nu_{C=O}$ 1670. NMR $\delta$: 1.25 (3H, s, $CH_3$), 2.08 (1H, d, $J=2$ Hz, $-C\equiv CH$), 5.90 (1H, d, $J=10$ Hz, $C_2$–H), 6.58 (1H, d.d, $J=10$ and 1 Hz, $C_1$–H). MS *m/e*: 188 ($M^+$).

**1-Methoxy-3-trimethylsiloxy-1,3-pentadiene (4)**——The powder of 150 g of $AlCl_3$ was added to 125 g of propionyl chloride under cooling by the freezing mixture of salt and ice. The mixture was stirred vigorously for 10 min and 140 g of vinyl bromide was added to the mixture in small portions during 15 min. Stirring was continued for 1 hr at 0° and the crushed ice was added to the mixture. The reaction mixture was extracted with $CHCl_3$ and the extract was washed with a large amount of water, dried and evaporated under reduced pressure. The residue was immediately distilled to give 141 g of the pale yellow oil, bp 48—75°/12 mmHg, which was indicated to be a mixture of the compound (**26**) and (**27**) in a ratio of 1:1 by its NMR spectrum. NMR $\delta$: 1.09 and 1.10 (each 3H, t, $J=7$ Hz, $-CH_2-CH_3$), 2.48 and 2.57 (each 2H, q, $J=7$ Hz, $-CH_2-CH_3$), 3.63 (2H, d, $J=6.5$ Hz, $-COCH_2CHBrCl$), 6.01 (1H, t, $J=6.5$ Hz, $-COCH_2CHBrCl$), 6.80 (1H, d, $J=14$ Hz, $-COCH=CHBr$), 7.57 (1H, d, $J=14$ Hz, $-COCH=CHBr$).

A solution of 28 mg of sodium in 700 ml of anhyd. MeOH was added little by little to a solution of 141 g of the oil in 400 ml of anhyd. MeOH at 0° with stirring. The mixture was stirred for further 40 hr at room temperature and the reaction mixture was extracted with ether. The extract was washed with a large amount of water, dried and evaporated under reduced pressure. The residue was immediately distilled to give 67 g of 1,1-dimethoxy-pentan-3-one in overall 35% yield from vinyl bromide, bp 69°/3 mmHg.[16]

The powder of 670 mg of NaOMe was mixed with 67 g of the oil (**28**) and the mixture was heated at 160—170° (oil bath temperature), while methanol was removed by distillation at atmospheric pressure and exhaustively by lowing occasionally the pressure of the reaction flask.[17] Heating was continued for 8 hr and the reaction mixture was distilled under reduced pressure to provide 38 g (73%) of the colorless oil of 1-methoxy-pent-1-en-3-one (**29**),[16] bp 92—93°/30 mmHg. To a suspension of 14 g of anhyd. $ZnCl_2$ in 120 ml of anhyd. $Et_3N$ was added 38 g of the compound (**29**) in 120 ml of anhyd. ether at room temperature. After 10 min, 106 g of trimethylsilyl chloride was added to the mixture little by little at 0° with stirring. The mixture was stirred at 0° for 20 hr and then at room temperature for 3 days. The reaction mixture was filtrated with a glass filter and the filtrate was concentrated under reduced pressure. The residue was immediately distilled to yield 43 g (70%) of 1-methoxy-3-trimethylsiloxy-1,3-pentadiene (**4**), which was indicated to be the E and Z isomers in a ratio of 3—4:1 or *vice versa* by its NMR spectrum, bp 72—76°/9 mmHg. IR $cm^{-1}$: $\nu_{C=C}$ 1658, 1623, $\nu_{Si-C}$ 853. NMR $\delta$: 0.18 and 0.22 (total 9H, m, $-SiMe_3$), 1.60 (total 3H, br.d, $J=7$ Hz, $=CH-CH_3$), 3.55 and 3.65 (total 3H, s, –OMe), 4.62 and 5.15 (total 1H, q, $J=7$ Hz, $=CHCH_3$), 5.35 and 5.60 (total 1H, d, each $J=12.5$ and 12 Hz), 6.65 and 6.80 (total 1H, d, each $J=12.5$ and 12 Hz). MS *m/e*: 186 ($M^+$).

**The Diels-Alder Adducts (30a), (30b) and (30c)**——To a solution of 7.701 g of 5-ethynyl-2-methylcyclohex-2-en-1-one (**3**) in 30 ml of anhyd. xylene was added 32 g of 1-methoxy-3-trimethylsiloxy-1,3-pentadiene (**4**) in 30 ml of anhyd. xylene. The mixture was heated at 190—210° for 3 days in a sealed tube. The solvent was removed under reduced pressure and the residue in 2N HCl–THF (each 320 ml) was refluxed for 2 hr. The reaction mixture was extracted with ether and the extract was washed with water, dried and evaporated under reduced pressure to leave the residue which was chromatographed on $SiO_2$. Elution of the column with *n*-hexane gave the less polar crude oil and continuous elution with 10—25% ether in *n*-hexane afforded 0.546 g of the Diels-Alder adduct (**30b**) in an earlier fraction and then 0.300 g of **30c**, 1.315 g of **30a**, 0.375 g of **31** and the oily compound, respectively, in the later fractions. The oily compound was hydrolyzed and separated in a similar manner to provide additional crops of the compounds, (**30a**), (**30b**), (**30c**), and (**31**), respectively. The total yields of these compounds were 2.014 g (16%) of **30a**, 0.774 g (6%) of **30b**, 0.480 g (4%) of **30c** and 1.375 g (**31**: diene dimer), respectively. **30a**: colorless plates mp 145—146° from ether–$C_6H_6$. IR $cm^{-1}$: $\nu_{C\equiv CH}$ 3330, $\nu_{C\equiv C}$ 2150, $\nu_{C=O}$ 1718, $\nu_{C=O}$ 1683. NMR (100 MHz) $\delta$: 1.16 (3H, d, $J=7$ Hz, $-\overset{1}{C}HCH_3$), 1.46 (3H, s, $CH_3$), 1.63 (1H, octet, $J=14$, 13 and 4 Hz, $C_6-H_{ax.}$), 1.99 (1H, m, $C_6-H_{eq.}$), 2.21 (1H, d, $J=2.5$ Hz, $-C\equiv CH$), 2.58 (2H, m, $C_8$–H), 2.73 (1H, m, $C_5$–H), 2.99 (1H, d.q, $J=7$ and 4.5 Hz, $C_4$–H), 3.22 (1H, m, $C_7$–H), 6.01 (1H, d, $J=10$ Hz, $C_2$–H), 6.32 (1H, d.d, $J=10$ and 2 Hz, $C_1$–H). *Anal.* Calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.85; H, 7.61. **30b**: colorless pillars mp 90° from *n*-hexane–ether. IR $cm^{-1}$: $\nu_{C\equiv CH}$ 3300, $\nu_{C\equiv C}$ 2150, $\nu_{C=O}$ 1710, $\nu_{C=O}$ 1680. NMR $\delta$: 1.17 (3H, d, $J=7$ Hz, $-\overset{1}{C}HCH_3$), 1.43 (3H, s, $CH_3$), 2.18 (1H, d, $J=2$ Hz, $C\equiv CH$), 2.96 (1H, d.q, $J=7$ and 3.5 Hz, $C_4$–H), 6.03 (1H, d, $J=10$ Hz, $C_2$–H), 6.33 (1H, d.d, $J=10$ and 2 Hz, $C_1$–H). *Anal.* Calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.64; H, 7.64. **30c**: colorless pillars mp 75—77° from *n*-hexane–ether. IR $cm^{-1}$: $\nu_{C\equiv CH}$ 3270, $\nu_{C\equiv C}$ 2130, $\nu_{C=O}$ 1700, $\nu_{C=O}$ 1680. NMR $\delta$: 1.14 (3H, m, $-\overset{1}{C}H-CH_3$), 1.52 (3H, s, $CH_3$), 2.22 (1H, d, $J=1.5$ Hz, $-C\equiv CH$), 6.04 (1H, d, $J=10$ Hz, $C_2$–H), 6.77 (1H, d, $J=10$ Hz, $C_1$–H). *Anal.* Calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.97; H, 7.75.

31: colorless prisms mp 85° from *n*-hexane–ether. IR $cm^{-1}$: $\nu_{OH}$ 3560, 3350, $\nu_{C=O}$ 1668. NMR $\delta$: 1.22 (3H, t, $J$=7.5 Hz, $-CH_2CH_3$), 2.29 (3H, s, $CH_3$), 2.96 (2H, q, $J$=7.5 Hz, $-CH_2CH_3$), 6.90 (1H, br.s, aromatic proton), 7.73 (2H, m, aromatic protons). MS *m/e*: 164 ($M^+$).

**The Equilibrium Experiment of 30c**——To a solution of 25 mg of **30c** in 3.2 ml of $^t$BuOH was added 12 mg of $^t$BuOK powder and the mixture was allowed to stand for 2 hr at room temperature. The reaction mixture was extracted with AcOEt and the extract was washed with water, dried and evaporated under reduced pressure to leave 9 mg of the crystalline compounds which were a mixture of **30a** and **30c** in a ratio of 2:1 by its NMR, GLC and TLC.

**The Hydroxyl Compound (32)**——To a solution of 372 mg of the minor adduct (**30b**) in 15 ml of iso-PrOH was added a solution of 23 mg of $NaBH_4$ in 3 ml of EtOH and 6 ml of iso-PrOH under stirring at room temperature. The mixture was stirred for 15 min and extracted with $CHCl_3$. The extract was washed with water, dried and evaporated under reduced pressure to leave 352 mg (94%) of **32**, colorless prisms mp 127—129° from *n*-hexane–ether. IR $cm^{-1}$: $\nu_{OH}$ 3550, 3450, $\nu_{C\equiv CH}$ 3280, $\nu_{C\equiv C}$ 2170, $\nu_{C=O}$ 1672. NMR $\delta$: 1.12 (3H, d, $J$=7 Hz, $-CHCH_3$), 1.40 (3H, s, $CH_3$), 2.07 (1H, d, $J$=2 Hz, $-C\equiv CH$), 3.43 (1H, d.d, $J$=12 and 4 Hz, $-CHOH$), 5.98 (1H, d, $J$=10 Hz, $C_2$–H), 7.00 (1H, d.d, $J$=10 and 2 Hz, $C_1$–H). MS *m/e*: 218 ($M^+$).

**The Mesylate (33)**——To a solution of 73 mg of **32** in 8 ml of anhyd. pyridine was added 152 mg of methanesulfonyl chloride at 0°. The mixture was allowed to stand for 16 hr at room temperature. The reaction mixture was acidified with an ice-cooled 10% HCl solution and extracted with $CHCl_3$. The extract was dried and evaporated to leave 92 mg (94%) of **33**, colorless prisms mp 165—169° from ether–$C_6H_6$. IR $cm^{-1}$: $\nu_{C\equiv CH}$ 3300, $\nu_{C\equiv C}$ 2150, $\nu_{C=O}$ 1678, $\nu_{SO_2}$ 1310—1400, 1178, $\nu_{S-O}$ 935. NMR $\delta$: 1.13 (3H, d, $J$=7 Hz, $-CHCH_3$), 1.43 (3H, s, $CH_3$), 2.07 (1H, d, $J$=2 Hz, $-C\equiv CH$), 3.10 (3H, s, $OSO_2CH_3$), 4.43 (1H, d.d, $J$=12 and 4 Hz, $-CHOMs$), 6.02 (1H, d, $J$=10 Hz, $C_2$–H), 6.77 (1H, d.d, $J$=10 and 2 Hz, $C_1$–H). *Anal.* Calcd. for $C_{15}H_{20}O_4S$: C, 60.78; H, 6.80. Found: C, 60.92; H, 7.01.

**The Tosylate (34)**——To a solution of 157 mg of **32** in 3 ml of anhyd. pyridine was added 1.243 g of *p*-toluenesulfonyl chloride at 0° and the mixture was allowed to stand for 24 hr at room temperature. The reaction mixture was acidified with an ice-cooled 5% HCl solution and extracted with AcOEt. The extract was washed with water, dried and evaporated under reduced pressure. Purification of the residue by preparative TLC on $SiO_2$ yielded 179 mg (67%) of the tosylate (**34**). IR $cm^{-1}$: $\nu_{C\equiv CH}$ 3300, $\nu_{C\equiv C}$ 2130, $\nu_{C=O}$ 1680, $\nu_{SO_2}$ 1370, 1175, $\nu_{S-O}$ 938, 900. NMR $\delta$: 1.09 (3H, d, $J$=7 Hz, $-CHCH_3$), 1.23 (3H, s, $CH_3$), 2.05 (1H, d, $J$=2 Hz, $-C\equiv CH$), 2.47 (3H, s, aromatic $CH_3$), 2.96 (1H, d.q, $J$=7 and 4 Hz, $C_4$–H), 4.35 (1H, d.d, $J$=12 and 4 Hz, $-CHOTs$), 5.97 (1H, d, $J$=10 Hz, $C_2$–H), 6.75 (1H, d.d, $J$=10 and 2 Hz, $C_1$–H), 7.22 and 7.85 (each 2H, d, $J$=8.5 Hz, aromatic protons). MS *m/e* 372 ($M^+$).

**The Hydroxyl Compounds (35a), (35b) and (35c)**——To a solution of 135 mg of the major adduct (**30a**) in 3 ml of abs. EtOH and 6 ml of iso-PrOH was added 8 mg of $NaBH_4$ at room temperature. The mixture was stirred for 25 min and additional 7 mg of $NaBH_4$ was added. After 10 min, the reaction mixture was extracted with AcOEt and the extract was washed with water, dried and evaporated under reduced pressure to leave 136 mg of the residue. Separation of the residue by preparative TLC on $SiO_2$ provided 61 mg (45%) of **35a** from the less polar zone, 37 mg (27%) of **35b** from the middle zone, and 17 mg (12%) of **35c** from the most polar zone. **35a**: colorless plates mp 144—145° from ether. IR $cm^{-1}$: $\nu_{OH}$ 3540, $\nu_{C\equiv CH}$ 3320, $\nu_{C\equiv C}$ 2130, $\nu_{C=O}$ 1675. NMR $\delta$: 1.13 (3H, d, $J$=7 Hz, $-CHCH_3$), 1.41 (3H, s, $CH_3$), 2.30 (1H, d, $J$=2.5 Hz, $-C\equiv CH$), 3.65 (1H, m, $-CHOH$), 5.88 (1H, d, $J$=10 Hz, $C_2$–H), 6.43 (1H, d.d, $J$=10 and 2 Hz, $C_1$–H). MS *m/e*: 218 ($M^+$). **35b**: IR $cm^{-1}$: $\nu_{OH}$ 3630, 3450, $\nu_{C\equiv CH}$ 3300, $\nu_{C\equiv C}$ 2130, $\nu_{C=O}$ 1675. NMR $\delta$: 1.09 (3H, d, $J$=7 Hz, $-CHCH_3$), 1.43 (3H, s, $CH_3$), 2.12 (1H, d, $J$=2.5 Hz, $-C\equiv CH$), 3.93 (1H, d.d, $J$=12 and 4 Hz, $-CHOH$), 5.97 (1H, d, $J$=10 Hz, $C_2$–H), 6.98 (1H, d.d, $J$=10 and 2 Hz, $C_1$–H). MS *m/e*: 218 ($M^+$). **35c**: IR $cm^{-1}$: $\nu_{OH}$ 3630, 3450, $\nu_{C\equiv CH}$ 3300, $\nu_{C\equiv C}$ 2130, $\nu_{C=O}$ 1675. NMR $\delta$: 1.13 (3H, d, $J$=7 Hz, $-CHCH_3$), 1.23 (3H, s, $CH_3$), 2.10 (1H, d, $J$=2 Hz, $-C\equiv CH$), 3.95 (1H, d.d, $J$=11 and 5 Hz, $-CHOH$), 5.98 (1H, d, $J$=10 Hz, $C_2$–H), 6.93 (1H, d, $J$=10 Hz, $C_1$–H). MS *m/e*: 218 ($M^+$).

**The Monobenzoate (36) and the Compound (37)**——To a solution of 71 mg of the major adduct (**30a**) in 7 ml of anhyd. THF was added 125 mg of $LiAlH_4$ at room temperature and the mixture was refluxed for 2 hr. The excess reagent was decomposed by addition of AcOEt and wet ether. The organic layer was decanted and the precipitates were washed thoroughly with three portions of ether and the organic layer and the washings were combined. After drying, evaporation of the solvents under reduced pressure gave 61 mg (86%) of the diol. To a solution of the diol in 1 ml of anhyd. pyridine was added dropwise 58 mg of benzoyl chloride and the mixture was allowed to stand for 18 hr at room temperature. The reaction mixture was made acidic with an ice-cooled 5% HCl solution and extracted with ether. The extract was washed with water, dried and evaporated under reduced pressure to leave 90 mg of the residue. Separation of the residue by preparative TLC on $SiO_2$ yielded 18 mg of the dibenzoate from the less polar zone, 38 mg (42%) of the monobenzoate (**36**) from the more polar zone and 13 mg of another monobenzoate from the most polar zone. Jones' oxidation of the latter monobenzoate did not give the compound (**37**). To a solution of 38 mg of **36** in 2 ml of acetone was added 4 drops of Jones' reagent. After 10 min, the reaction mixture was diluted with MeOH and extracted with $CHCl_3$. The extract was washed with water, dried and evaporated under reduced pressure to afford 31 mg (82%) of the compound (**37**). IR $cm^{-1}$: $\nu_{C\equiv CH}$ 3300, $\nu_{C\equiv C}$ 2150, $\nu_{C=O}$ 1708, $\nu_{C-O}$ 1275. NMR $\delta$: 1.05—1.40 (6H, m, $-CHCH_3$ and $CH_3$), 2.18 (1H, d, $J$=2 Hz, $-C\equiv CH$), 5.32—6.18 (2H, m, olefinic

protons), 7.40—8.18 (5H, aromatic protons). MS *m/e*: 322 ($M^+$).

**The Monothioketal (38) and the Dithioketal (39)**——To a solution of 52 mg of the major adduct (**30a**) in 3.5 ml of anhyd. MeOH were added 110 mg of ethanedithiol and 99 mg of $BF_3$·ether. The mixture was allowed to stand for 43 hr at room temperature and the reaction mixture was then made basic with a 3% $NaHCO_3$ solution and extracted with AcOEt. The extract was washed with water, dried and evaporated under reduced pressure to give 95 mg of the residue. Separation of the residue by preparative TLC on $SiO_2$ provided 11 mg (13%) of the dithioketal (**39**) from the less polar zone and 40 mg (57%) of the monothioketal (**38**) from the more polar zone. **38**: IR $cm^{-1}$: $\nu_{C\equiv CH}$ 3325, $\nu_{C\equiv C}$ 2140, $\nu_{C=O}$ 1708. NMR $\delta$: 1.27 (3H, s, $CH_3$), 1.32 (3H, d, $J$=7 Hz, $-CHCH_3$), 2.15 (1H, d, $J$=2.5 Hz, $-C\equiv CH$), 3.15—3.40 (4H, m, $-S-(CH_2)_2-S-$), 5.13 (1H, d.d, $J$=10 and 1 Hz, $C_1$–H), 5.95 (1H, d, $J$=10 Hz, $C_2$–H). MS *m/e*: 292 ($M^+$). **39**: colorless pillars mp 173—174° from ether–$C_6H_6$. IR $cm^{-1}$: $\nu_{C\equiv CH}$ 3300, $\nu_{C\equiv C}$ 2150. NMR $\delta$: 1.29 (3H, d, $J$=7 Hz, $-CHCH_3$), 1.43 (3H, s, $CH_3$), 2.16 (1H, d, $J$=2.5 Hz, $-C\equiv CH$), 3.25 (8H, br.s, $-S-(CH_2)_2-S-$), 5.53 (1H, d.d, $J$=10 and 2 Hz, $C_1$–H), 5.83 (1H, d, $J$=10 Hz, $C_2$–H). MS *m/e*: 368 ($M^+$).

**The Olefinic Compound (40) and the Thioketal (41) of *dl*-Chamaecynone**——To a solution of 220 mg of **38** in anhyd. MeOH and $CHCl_3$ (each 4 ml) was added 224 mg of *p*-$TsNHNH_2$. The mixture was refluxed for 10 hr and then solvents were removed under reduced pressure to give the crude oil. Separation of the oil by preparative TLC on $SiO_2$ afforded 345 mg of the crystalline tosylhydrazone of **38**. To a solution of 218 mg of the tosylhydrazone in anhyd. sulfolane and DMF (each 1.5 ml) were added 120 mg of $NaBH_3CN$ and 35 mg of anhyd. *p*-TsOH. The mixture was heated at 110—115° (oil bath temperature) under the argon atmosphere for 4.5 hr with stirring and then added with additional 1 ml of anhyd. DMF, 1 ml of sulfolane, 117 mg of $NaBH_3CN$ and 35 mg of anhyd. *p*-TsOH. Stirring was continued at 110—120° for 15.5 hr. The reaction mixture was extracted with AcOEt–ether and the extract was washed with water, dried and evaporated under reduced pressure. Separation of the residue by preparative TLC on $Al_2O_3$ yielded 17 mg of the colorless oil from the less polar zone, 10 mg of the olefinic compound (**40**) from the middle zone, and 54 mg of the tosylhydrazone from the most polar zone. The colorless oil (17 mg) from the less polar zone was further purified by chromatography on neutral $Al_2O_3$ (Merck; activity I). Elution of the column with *n*-pentane furnished 13 mg of the thioketal (**41**) of *dl*-chamaecynone. **40**: IR $cm^{-1}$: $\nu_{C\equiv CH}$ 3300, $\nu_{C\equiv C}$ 2130. NMR $\delta$: 1.13 (3H, s, $CH_3$), 1.33 (3H, d, $J$=7 Hz, $-CHCH_3$), 2.08 (1H, d, $J$=2 Hz, $-C\equiv CH$), 3.25 (4H, br.s, $-S-(CH_2)_2-S-$), 5.15 (1H, d.d, $J$=10 and 1.5 Hz, $C_1$–H), 5.30—5.65 (2H, m, $C_8$ and $C_9$–H), 5.73 (1H, d, $J$=10 Hz, $C_2$–H). MS *m/e*: 276 ($M^+$). **41**: IR $cm^{-1}$: $\nu_{C\equiv CH}$ 3300, $\nu_{C\equiv C}$ 2130. NMR $\delta$: 1.07 (3H, s, $CH_3$), 1.24 (3H, d, $J$=7 Hz, $-CHCH_3$), 2.04 (1H, d, $J$=2.5 Hz, $-C\equiv CH$), 3.05—3.45 (4H, m, $-S-(CH_2)_2-S-$), 5.13 (1H, d.d, $J$=10 and 2 Hz, $C_1$–H), 5.81 (1H, d, $J$=10 Hz, $C_2$–H). MS *m/e*: 278 ($M^+$).

***dl*-Chamaecynone (1)**——To a solution of 15 mg of **41** in 2 ml of $CHCl_3$ was added a solution of 40 mg of $Tl(NO_3)_3 \cdot 3H_2O$ in 1.5 ml of anhyd. MeOH at 0° with stirring. After 10 min, the reaction mixture was diluted with water and the organic layer was separated. The aqueous layer was extracted with $CHCl_3$ and the extract was combined to the organic layer. After drying, the solvent was removed to leave the residue which was purified by preparative TLC on $Al_2O_3$ to yield 8 mg (73%) of the crystalline *dl*-chamaecynone (**1**). Recrystallization from *n*-pentane afforded 3.5 mg of *dl*-chamaecynone (**1**), as colorless prisms, mp 77—80°. IR ($CCl_4$) $cm^{-1}$: $\nu_{C\equiv CH}$ 3300, $\nu_{C\equiv C}$ 2130, $\nu_{C=O}$ 1680. NMR (100 MHz; $CCl_4$) $\delta$: 1.03 (3H, d, $J$=7 Hz, $-CHCH_3$), 1.29 (3H, s, $CH_3$), 1.93 (1H, d, $J$=2 Hz, $-C\equiv CH$), 2.75—3.00 (2H, m), 5.78 (1H, d, $J$=10 Hz, $C_2$–H), 6.30 (1H, d.d, $J$=10 and 2 Hz, $C_1$–H). MS *m/e*: 202 ($M^+$). High mass spectrum; Calcd. for $C_{14}H_{18}O$; 202.1358. Found: 202.1431.

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