# Strategic Synthesis based on Cyclohexadienes: Preparation of 2-, 2,3- and 2,4-Substituted Cyclohexenones; Synthesis of (*Z*)-Heneicosa-6-en-11-one

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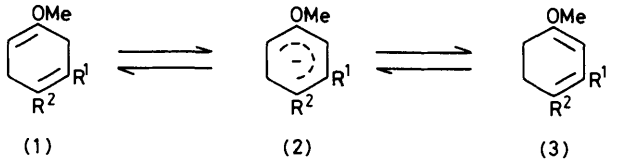
The mesomeric anions, generated from 1-methoxycyclohexa-1,4-diene, 1-methoxy-5-methylcyclohexa-1,4-diene, and 1-methoxy-4-methylcyclohexa-1,4-diene with potassium amide in liquid ammonia, have been readily alkylated and the resulting dienes were hydrolysed to yield 2-alkyl-, 2,3-dialkyl- and 2,4-dialkyl-cyclohex-2-enones in good yield. Arylation of the above mesomeric anions followed by hydrolysis afforded 2-arylcyclohex-2-enones in addition to substituted biphenyls. A new and efficient synthesis of the male sex attractant of the Douglas Fir Tussock Moth, (*Z*)-heneicosa-6-en-11-one is described using the above methodology.

A strategy frequently employed [1] in the synthesis of natural products is the construction, functionalisation, and fragmentation of cyclic compounds to build the carbon framework of the target molecule. This concept has been successfully employed in the synthesis [2,3] of several insect pheromones. Substituted cyclohex-2-enones are potential synthetic intermediates in the above strategy. In connection with the synthesis of some sex pheromones, we required an efficient method for the preparation of 2-substituted, 2,3-disubstituted, and 2,4-disubstituted cyclohexenones. While several procedures were employed for the preparation of these compounds, recent methods of Taber,[4] Piers,[5] Sutherland,[6] and Mander [7] were notable and are generally based on an earlier work of Birch [8] involving the base-catalysed alkylation of dihydroanisoles. We have reinvestigated the original alkylation procedure of Birch and describe here, the detailed conditions for an efficient alkylation and arylation of methoxycyclohex-1,4-dienes, acid hydrolysis of which lead to the formation of substituted cyclohexenones. Based on this strategy a new and efficient synthesis of the male sex attractant, (*Z*)-heneicosa-6-en-11-one (12) [9] isolated from Douglas Fir Tussock Moth, *Orgiya pseudosugata*, is reported.

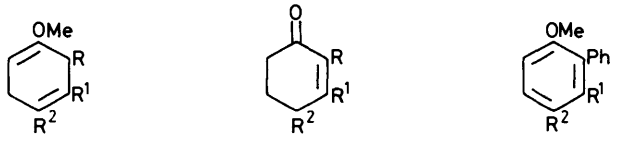
Reaction of 1-methoxycyclohex-1,4-diene (1a) with potassium amide results in the regiospecific formation of the mesomeric anion (2a) which is protonated with methanol to the conjugated 1-methoxycyclohexa-1,3-diene (3a) in 80% yield. Quenching the mesomeric anion (2a) with alkyl or aryl halides affords the 6-alkyl- or 6-aryl substituted cyclohexa-1,4-dienes (4) in good yield. The alkylated compounds are obtained as unconjugated dienes (4) as indicated from their u.v. and $^1$H n.m.r. spectral data. This is not unexpected, since protonation of such anions normally favours [10] the middle carbon. Hydrolysis of these dienes under mild acidic conditions afforded the 2-alkyl- or 2-aryl-cyclohex-2-en-1-ones (5). Thus the dienes (1a—c) have been alkylated with n-butyl bromide, n-pentyl bromide; the diene (1b) was also alkylated with n-hexyl bromide to the compounds (4a—g) which were hydrolysed to the unsaturated ketones (5a—g) (overall yield 70—80%). Arylation of the dienes (1a—c) with bromobenzene afforded a mixture which could not be obtained pure. Hydrolysis of this mixture with dilute acid afforded a 2 : 1 mixture of 2-phenylcyclohexenones (5h—j) and the biphenyl derivatives (6a—c) (overall yield 50%). The structure of these compounds were assigned from their analytical and spectral data and comparison with an authentic specimen.

Although the equilibrium between the dienes (1) and (3) can be initiated [11] with a catalytic amount of potassium amide in liquid ammonia, we have observed that alkylations require



(1) (2) (3)

a; $R^1 = R^2 = H$ c; $R^1 = H$, $R^2 = Me$
b; $R^1 = Me$, $R^2 = H$ d; $R^1 = Decyl$, $R^2 = H$



(4) (5) (6)

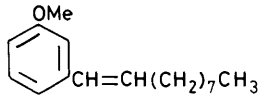
a; R = Bu, $R^1 = R^2 = H$
b, R = Bu, $R^1 = Me$; $R^2 = H$
c, R = Bu, $R^1 = H$, $R^2 = Me$
d; R = Pentyl, $R^1 = R^2 = H$
e; R = Pentyl, $R^1 = Me$, $R^2 = H$
f; R = Pentyl, $R^1 = H$, $R^2 = Me$
g; R = Hexyl, $R^1 = Me$, $R^2 = H$
h; R = Ph, $R^1 = R^2 = H$
i; R = Ph, $R^1 = Me$, $R^2 = H$
j; R = Ph, $R^1 = H$, $R^2 = Me$
k; R = Pentyl, $R^1 = Decyl$, $R^2 = H$

a; $R^1 = R^2 = H$
b; $R^1 = Me$, $R^2 = H$
c; $R^1 = H$, $R^2 = Me$

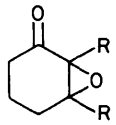
stoicheiometric amounts of the amide. Further arylation of these dienes proceeds through the initial formation of the benzyne since larger amounts of the amide are required for completion of the reaction. This method of alkylation appears to be general and can be applied to a variety of systems.

Smith *et al.*[9] have isolated a potent male sex attractant (*Z*)-heneicosa-6-en-11-one (12) from the Douglas Fir Tussock Moth, *Orgyia pseudosugata*, the structure of which was deduced from its spectral data and confirmed [2,12-14] by synthesis. We describe a new and efficient synthesis of this sex attractant (12) from 2-phenylcyclohex-2-en-1-one [4] (5d) and 3-decyl-2-pentylcyclohex-2-enone [13] (5k).

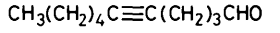
The ketone (5d) was epoxidised to the α,β-epoxy-compound (8a) with alkaline hydrogen peroxide and subjected to



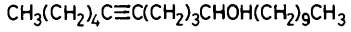
(7)



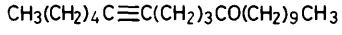
(8) a; R = Pentyl ; $R^1$ = H
b; R = Pentyl ; $R^1$ = Decyl



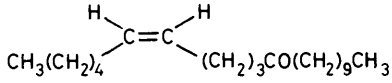
(9)



(10)



(11)



(12)

Eschenmoser's fragmentation [15] *via* the tosylhydrazone to the acetylenic aldehyde (9). Further elaboration of the chain was accomplished through the Grignard addition with decylmagnesium bromide and the resulting alcohol (10) was oxidised to the acetylenic ketone (11). Partial hydrogenation of the ketone (11) with Pd–$BaSO_4$ gave the pheromone (12) in good yield (overall 22%), the spectral data of which were identical with the published data.

In an alternative approach, 3-decyl-2-pentylcyclohex-2-enone (5k) was prepared by the pentylation of the diene (1d), obtained from 3-deca-9-enylanisole (7) followed by hydrolysis. This ketone (5k) was subjected to epoxidation and the resulting epoxy-ketone (8b) was fragmented to the acetylenic ketone which was subsequently transformed into the pheromone (12) in an overall yield of 25%.

## Experimental

B.p.s and m.p.s are uncorrected. I.r. spectra of liquids were measured as liquid films and those of solids were taken in Nujol on a Perkin-Elmer model 397 spectrometer. $^1H$ N.m.r. spectra (chemical shifts in p.p.m. from $SiMe_4$) were recorded in $CDCl_3$ solution on a Varian T-60 (60 MHz) spectrometer. All the compounds were routinely checked for homogeneity on t.l.c. using silica gel (Acme's India). Liquid ammonia was distilled from sodium before use. All the alkylations were done at liquid ammonia temperature. Whenever a mixture of compounds were obtained, separation was effected either by short-path distillation or by column chromatography. 2,4-Dinitrophenylhydrazones were prepared in the usual way and unless otherwise stated, were crystallised from ethanol.

*Alkylation of* 1-*Methoxycyclohexa*-1,4-*dienes* (1a—c).—To potassamide in liquid ammonia [prepared from liquid ammonia (80 ml), $FeCl_3$ (catalytic quantity) and potassium (500 mg)] cyclohexa-1,4-diene (20 mmol) was added with stirring. A dark red solution was formed. After 10 min of vigorous stirring, the reaction mixture was quenched with alkyl bromide (excess). Ammonia was slowly evaporated off, water added and the organic matter was thoroughly extracted with ether. The ethereal solution was washed until neutral with water, brine, and dried ($Na_2SO_4$). The solvent was evaporated and the residual oil was distilled under reduced pressure (yields 75—85%).

*Arylation of* 1-*Methyoxycyclohexa*-1,4-*dienes* (1a—c).—To the potassamide in liquid ammonia (prepared from liquid ammonia (80 ml), $FeCl_3$ (catalytic quantity) and potassium (740 mg)], 1-methoxycyclohexa-1,4-diene (20 mmol) was added with stirring. A dark red solution was formed. After 10 min of vigorous stirring, bromobenzene (1.5 g) was added to give a reaction. The mixture was then stirred for a further 20 min. It was then quenched with solid $NH_4Cl$. After evaporation of the liquid ammonia the mixture was diluted with water and extracted with ether (3 × 50 ml). The ethereal layer was washed until neutral with water and the solvent evaporated to give an oil which was subjected to hydrolysis with 10% aqueous $H_2SO_4$ (30 ml) and methanol (20 ml) and stirring at room temperature for 30 min. The reaction mixture was poured into water and thoroughly extracted with ether (3 × 100 ml); the ethereal layer was then washed until neutral with water and brine and finally dried ($Na_2SO_4$). Evaporation of the solvent gave a brown oil, which on chromatographic separation with ether–hexane (1 : 1) gave pure products (yields 50—60%).

*Hydrolysis of Alkylated Cyclohexa*-1,4-*dienes* (4a—g).—To the alkylated cyclohexadiene (5 mmol) in methanol (15 ml) 10% aqueous $H_2SO_4$ (20 ml) was added and stirred at room temperature for 1 h. The reaction mixture was poured into water and extracted with ether (3 × 40 ml). The ethereal layer was washed until neutral with water and brine and then dried ($Na_2SO_4$). Evaporation of the solvent gave the following alkylated dienes (96—98%) as colourless oils on short-path distillation.

6-Butyl-1-methoxycyclohexa-1,4-diene (4a), b.p. 70—72 °C/3 mmHg; $\nu_{max.}$ 3 040, 2 950, 1 660, 1 620, and 1 210 $cm^{-1}$; δ 0.9 (3 H, t, Me), 1.0—1.35br (6 H, aliphatic), 2.1—2.6br (3 H, m, doubly allylic), 3.45 (3 H, s, OMe), 4.6br (1 H, MeOC=C*H*), and 5.6br (2 H, m, *HC*=C*H*).

6-Butyl-1-methoxy-5-methylcyclohexa-1,4-diene (4b), b.p. 75—77 °C/3 mmHg; $\nu_{max.}$ 3 040, 2 950, 1 660, 1 615, and 1 210 $cm^{-1}$; δ 0.9 (3 H, t, Me), 1.0—1.35br (6 H, m, aliphatic), 1.72 (3 H, s, =CMe), 2.1—2.6br (3 H, m, doubly allylic), 3.45 (3 H, s, OMe), 4.6br (1 H, MeOC=C*H*), and 5.45 (1 H, =CH). 6-Butyl-1-methoxy-4-methylcyclohexa-1,4-diene (4c), b.p. 77—79 °C/3 mmHg; $\nu_{max.}$ 3 030, 2 950, 1 660, 1 615, and 1 210 $cm^{-1}$; δ 0.9 (3 H, t, Me), 1.0—1.4br (6 H, m, aliphatic), 1.75 (3 H, s, =CMe), 2.1—2.5br (3 H, m, doubly allylic), 3.45 (3 H, s, OMe), 4.6br (1 H, MeOC=CH), and 5.75 (1 H, br, =CH).

1-Methoxy-6-pentylcyclohexa-1,4-diene (4d), b.p. 76—77 °C/3 mmHg; $\nu_{max.}$ 3 040, 2 950, 1 660, 1 620, and 1 210 $cm^{-1}$; δ 0.9 (3 H, t, Me), 1.0—1.4br (11 H, m, aliphatic), 2.1—2.6br (3 H, m, doubly allylic), 3.45 (3 H, s, OMe), 4.6br (1 H, MeOC=C*H*), and 5.6br (2 H, m, C*H*=C*H*). 1-Methoxy-5-methyl-6-pentylcyclohexa-1,4-diene (4e), b.p. 80—82 °C/3 mmHg; $\nu_{max.}$ 3 040, 2 950, 1 660, 1 615, and 1 210 $cm^{-1}$; δ 0.9 (3 H, t, Me), 1.0—1.5br (8 H, m, aliphatic) 1.72 (3 H, s, =CMe), 2.1—2.6br (3 H, m, doubly allylic), 3.45 (3 H, s, OMe), 4.6br (1 H, MeO–C=C*H*), and 5.4br (1 H, =CH). 1-Methoxy-4-methyl-6-pentylcyclohexa-1,4-diene (4f), b.p. 83—84 °C/3 mmHg; $\nu_{max.}$ 3 040, 2 950, 1 660, 1 615, and 1 210 $cm^{-1}$; δ 0.9 (3 H, t, Me), 1.0—1.4br (8 H, m, aliphatic), 1.75 (3 H, s, =CMe), 2.1—2.5br (3 H, m, doubly allylic), 3.45 (3 H, s, OMe), 4.6br (1 H, MeOC=C*H*), and 5.75br (1 H, =C*H*). 6-Hexyl-1-methoxy-5-methylcyclohexa-1,4-diene (4g), b.p. 88—90 °C/3 mmHg; $\nu_{max.}$ 3 040, 2 950, 1 660, 1 615, and 1 210 $cm^{-1}$; δ 0.9 (3 H, t, Me), 1.0—1.4br (10 H, m, aliphatic), 1.75 (3 H, s, =CMe), 2.1—2.6br (3 H, m, doubly allylic), 3.45 (3 H, s, OMe), 4.55br (1 H, MeO–C=C*H*), and 5.4br (1 H, =C*H*).

The following cyclohexenones (5a—j) were obtained as colourless oils or solids. 2-Butylcyclohex-2-enone (5a), b.p.

97—98 °C/3 mmHg; $\nu_{max.}$ 3 000 1 675, and 1 630 $cm^{-1}$; δ 0.95 (3 H t, Me), 1.3—1.8br, (4 H, m, aliphatic), 2.0—2.4br (8 H, m, allylic and $COCH_2$), and 6.7br (1 H, t, olefinic) (Found: C, 78.8; H, 10.45. Calc. for $C_{10}H_{16}O$: C, 78.90; H, 10.59%). 2,4-DNP, m.p. 132 °C. 2-Butyl-3-methylcyclohex-2-enone (5b), b.p. 82—83 °C/3 mmHg; $\nu_{max.}$ 2 950, 1 665, and 1 620 $cm^{-1}$; δ 0.95 (3 H, t, $CH_2$*Me*), 1.2—1.8br (6 H, m, aliphatic), 1.9 (3 H, s, =CMe), and 2.0—2.4br (8 H, m, allylic and C−$CH_2$) (Found: C, 79.3; H, 10.85. Calc. for $C_{11}H_{18}O$: C, 79.46; H, 10.91%); 2,4-DNP, m.p. 142 °C. 2-Butyl-4-methylcyclohex-2-enone (5c), b.p. 85—87 °C/3 mmHg; $\nu_{max.}$ 2 950, 1 675, and 1 625 $cm^{-1}$; δ 0.95 (3 H, t, $CH_2$*Me*), 1.15 (3 H, d, CH*Me*), 1.2—1.8br (4 H, m, aliphatic), 2.1—2.5br (7 H, m, allylic and $COCH_2$), and 6.75br (1 H, d, olefinic) (Found: C, 79.3; H, 10.9. Calc. for $C_{11}H_{18}O$: for C, 79.46; H, 10.91%); 2,4-DNP, m.p. 142 °C. 2-Pentylcyclohex-2-enone (5d), b.p. 99—100 °C/3 mmHg; $\nu_{max.}$ 3 000, 1 675, and 1 630 $cm^{-1}$; δ 0.95 (3 H, t, Me), 1.3—1.5br (6 H, m, aliphatic), 2.1—2.4br (8 H, m, allylic and $COCH_2$), and 6.7br (1 H, t, olefinic) (Found: C, 79.35; H, 10.85. Calc. for $C_{11}H_{18}O$: C, 79.46; H, 10.91%); 2,4-DNP, m.p. 113 °C. 3-Methyl-2-pentylcyclohex-2-enone (5e), b.p. 80—81 °C/2.5 mmHg; $\nu_{max.}$ 2 950 and 1 665 $cm^{-1}$; δ 0.92br (3 H, t, $CH_2$*Me*), 1.2—1.45br (6 H, m, aliphatic), 1.9 (3 H, s, =CMe), 2.0—2.4br (8 H, m, allylic and $CH_2$) (Found: C, 79.8; H, 10.05. Calc. for $C_{12}H_{20}O$: C, 79.94; H, 11.18%); 2,4-DNP, m.p. 111 °C. 4-Methyl-2-pentylcyclohex-2-enone (5f), b.p. 92—93 °C/3 mmHg; $\nu_{max.}$ 2 950, 1 675, and 1 625 $cm^{-1}$; δ 0.95 (3 H, t, $CH_2$*Me*), 1.17 (3 H, d, CH*Me*), 1.2—1.5br (6 H, m, aliphatic), 2.1—2.5br (7 H, m, allylic and $COCH_2$), and 6.75br (1 H, d, olefinic) (Found: C, 79.75; H, 10.0. $C_{12}H_{20}O$ requires C, 79.94; H, 11.18%); 2,4-DNP, m.p. 126 °C. 2-Hexyl-3-methylcyclohex-2-enone (5g), b.p. 97—98 °C/3 mmHg; $\nu_{max.}$ 2 950 and 1 665 $cm^{-1}$; δ 0.92 (3 H, t, $CH_2$*Me*), 1.0—1.35br (8 H, m, aliphatic), 1.85 (3 H, s, =C*Me*), and 2.0—2.4 (8 H, m, allylic and $COCH_2$) (Found: C, 80.2; H, 11.35. Calc. for $C_{13}H_{22}O$: C, 80.35; H, 11.41%); 2,4-DNP, m.p. 124 °C. 2-Phenylcyclohex-2-enone (5h), m.p. 93 °C; $\nu_{max.}$ 3 000 and 1 680 $cm^{-1}$; δ 1.7—2.7 br (6 H, m), 6.91 (1 H, t, olefinic), and 7.3 (5 H, s, aromatic) (Found: C, 83.55; H, 6.9. Calc. for $C_{12}H_{12}O$: C, 83.69; H, 7.02%); 2,4-DNP, m.p. 164 °C. 3-Methyl-2-phenylcyclohex-2-enone (5i), m.p. 89 °C; $\nu_{max.}$ 3 030, 2 900, 1 675, 750, and 690 $cm^{-1}$; δ 1.7—2.65br (6 H, m), 1.87 (3 H, s, =CMe), and 7.25 (5 H, s, aromatic) (Found: C, 83.75; H, 7.5. Calc. for $C_{13}H_{14}O$: C, 83.83; H, 7.58%); 2,4-DNP, m.p. 159 °C. 4-Methyl-2-phenylcyclohex-2-en-1-one (5j), m.p. 98 °C; $\nu_{max.}$ 3 030, 2 900, 1 675, 750, and 690 $cm^{-1}$; δ 1.15 (3 H, d, CH*Me*), 1.7—2.6br (5 H, m), 6.9br (1 H, d, olefinic), 7.3 (5 H, s, aromatic) (Found: C, 83.7; H, 7.45. $C_{13}H_{14}O$ requires C, 83.83; H, 7.58%); 2,4-DNP, m.p. 170 °C.

The following biphenyls were obtained as colourless yellow oils. 2-Methoxybiphenyl (6a) (20%), b.p. 119—120 °C/3 mmHg; $\nu_{max.}$ 3 050, 2 950, 1 600, 1 500, 1 240, 760, and 700 $cm^{-1}$; δ 3.5 (3 H, s, OMe) and 6.9—7.4 (9 H, complex m, aromatic) (Found: C, 84.6; H, 6.5. Calc. for $C_{13}H_{12}O$: C, 84.75; H, 6.5%). 2-Methoxy-6-methylbiphenyl (6b) (17%), b.p, 140 °C/3 mmHg; $\nu_{max.}$ 3 030, 1 600, 1 500, 1 245, 760, and 690 $cm^{-1}$; δ 2.35 (3 H, s, Me), 3.52 (3 H, s, OMe), and 6.7—7.3 (8 H, complex m, aromatic) (Found: C, 84.75; H, 7.05. $C_{14}H_{14}O$ requires C, 84.84; H, 7.12%). 2-Methoxy-5-methylbiphenyl (6c) (18%), b.p. 134 °C/1.5 mmHg; $\nu_{max.}$ 3 030, 1 600, 1 500, 1 250, 760, and 690 $cm^{-1}$; δ 2.34 (3 H, s, Me), 3.5 (3 H, s, OMe), and 6.75—7.3 (8 H, complex m, aromatic) (Found: C, 84.8; H, 7.0. $C_{14}H_{14}O$ requires C, 84.81; H, 7.12%).

*Epoxide of 2-Pentylcyclohex-2-enone* (8a).—2-Pentylcyclohex-2-enone (5d) (20 g) was dissolved in methanol (200 ml) and the solution cooled to 15 °C. Hydrogen peroxide solution (30%, 15 ml) was then added to it and the whole stirred vigorously. Potassium hydroxide (4 g) in water (10 ml) was then added during 1 h, to the above mixture at 15 °C. The mixture was diluted with water (1 000 ml) and extracted with ether (3 × 100 ml). The combined ether extract was thoroughly washed with water and brine, dried, and the solvent removed to afford the crude epoxide (19.5 g, 90%), $\nu_{max.}$ 1 720 $cm^{-1}$. This was directly used in the next step.

*Undec-5-yn-1-al* (9).—The above crude epoxide (10.2 g) dissolved in a mixture of acetic acid (60 ml) and dichloromethane (100 ml) was cooled <0 °C; tosyl hydrazine (16 g) was then added during 10 min and the mixture stirred at room temperature for 8 h. It was then diluted with water (500 ml) and extracted with dichloromethane (2 × 100 ml). The combined extracts were washed sequentially with sodium hydroxide (5%), hydrochloric acid (5%), water, and brine and then dried. Removal of the solvent afforded the crude acetylenic aldehyde (9) (7.8 g), which was chromatographed on neutral alumina. Elution with benzene–chloroform (4 : 1) afforded the pure aldehyde (9), $\nu_{max.}$ 2 890 and 1 720 $cm^{-1}$; δ 0.9br (3 H, t, $CH_3$), 1.4—2.0 (8 H, m, $CH_2$), 2.1—2.5 (6 H, m), and 9.8 (1 H, t, CHO) (Found: C, 79.4; H, 10.8. $C_{11}H_{18}O$ requires C, 79.5 and H, 10.9%).

*Heneicosa-6-yn-11-ol* (10).—A solution of decylmagnesium bromide was prepared in dry tetrahydrofuran from magnesium (0.24 g) and 1-bromodecane (2.2 g). To a stirred solution of the above Grignard reagent under nitrogen was added dropwise a solution of undec-5-yn-1-al (9) (1.78 g) in dry THF (25 ml). After 3 h at room temperature the mixture was hydrolysed with saturated aqueous ammonium chloride acidified with dilute hydrochloric acid, and extracted with ether (3 × 50 ml). The organic extract was washed with water and brine and then dried. Removal of the solvent afforded a crude product which was chromatographed to give the alcohol (10) (2.2 g), $\nu_{max.}$ 3 460 $cm^{-1}$.

*Heneicosa-6-yn-11-one* (11).—Heneicosa-6-yn-11-ol (10) (1.8 g) in dichloromethane (15 ml) was added to a solution of pyridine–chromic anhydride complex [from $CrO_3$ (5 g) and pyridine (8 ml)]. After 15 min at room temperature, the organic layer was decanted and the residue was washed with dichloromethane (3 × 10 ml). The organic extract was washed with water and brine and then dried. Removal of the solvent afforded a liquid (1.62 g) which was distilled, b.p. 150 °C (bath)/0.5 mmHg [lit.,[15] b.p. 125 °C (bath) at 0.35 mmHg], $\nu_{max.}$ 1 720 $cm^{-1}$; δ 0.9 (6 H, m, 2 × $CH_3$), 1.1—1.4br (24 H, s, aliphatic H), and 1.9—2.3 (8 H, m, 2 × $COCH_2$, 2 × C$H_2$-C=C) (Found: C, 82.3; H, 12.5; Calc. for $C_{21}H_{38}O$: C, 82.3 and H, 12.5%).

3-*Deca-9-enylanisole* (7).—To a suspension of magnesium turnings (10 g) in dry THF (200 ml) was added dropwise nonyl bromide (38 g) in dry ether (75 ml). The mixture was initially warmed to initiate the Grignard reaction and then cooled to 0 ° and stirred until all the magnesium dissolved. 3-Methoxybenzaldehyde (20 g) in dry ether (75 ml) was then added to the above mixture and the whole stirred for a further period of 45 min at 10 °C. The mixture was then allowed to attain room temperature after which it was worked up by cautious addition of dilute sulphuric acid (0.5M; 200 ml). The product mixture was extracted with ether (2 × 100 ml) and the extract washed with water and brine and dried. Removal of the solvent gave the crude product (7) which was distilled, b.p. 179 °C/1.5 mmHg; $\nu_{max.}$ 1 620, 1 600, and 1 500 $cm^{-1}$; δ 0.9br (3 H, t, $CH_3$), 1.1—2.0 (14 H, m, aliphatic-$CH_2$), 3.9 (3 H, s, $OCH_3$), 6.0—6.2 (2 H, m, vinylic H), and 7.0—7.4 (4 H, m,

aromatic) (Found: C, 82.6; H, 10.85; $C_{17}H_{26}O$ requires C, 82.9 and H, 10.6%).

3-*Decyl*-1-*methoxycyclohexa*-1.4-*diene* (1d).—Lithium (4 g) was added to a mixture of the anisole (7) (10 g) in dry THF (50 ml), t-butyl alcohol (50 ml), and distilled ammonia (400 ml). The mixture was stirred for 24 h, and then quenched with methanol to destroy the excess of the metal. Ammonia was evaporated and the residue extracted with light petroleum (b.p. 40—60 °C) (3 × 100 ml); the extract was washed with water, dried, and the solvent removed to afford the dihydro-compound (1d) (9.2 g) g), $\nu_{max.}$ 1 690 and 1 660 $cm^{-1}$; δ 0.9br (3 H, t, $CH_3$), 1.12—1.8 (16 H, m, aliphatic), 2.2—2.8 (6 H, m), 3.6 (3 H, s, $OCH_3$), 4.8 (1 H, m, vinylic H at the enol ether), and 5.8 (1 H, vinylic H at the double bond) (Found: C, 81.2: H, 12.4. $C_{17}H_{30}O$ requires C, 81.5 and H, 12.1%).

3-*Decyl*-2-*pentylcyclohex*-2-*enone* (5k).—The diene (1d) (5 g) in dry THF (10 ml) was added to potassium amide in anhydrous ammonia (200 ml) [prepared from potassium (2 g)] and the mixture stirred under nitrogen for 30 min; it was then quenched with an excess of pentyl bromide (10 g) .The reaction was worked up by evaporation of ammonia and extraction with light petroleum (b.p. 40—60 °C). The crude product (14) (6.2 g) obtained on evaporation of the organic extract was hydrolysed with aqueous methanolic hydrochloric acid (5% 30 ml). The hydrolysate was worked up by extraction with ether (3 × 50 ml); the extract was washed with water, dried, and the solvent removed to afford the conjugated ketone (5k) which was purified by column chromatography on alumina Elution with benzene–light petroleum (1 : 1) afforded 3-decyl-2-pentylcyclohexa-2-en-1-one (5k) (3.8 g), b.p. 160 °C/0.5 mmHg (bath) (lit.,[15] b.p. 125 °C/0.18 mmHg (bath) $\nu_{max.}$ 1 665 and 1 610 $cm^{-1}$; δ 0.9 (6 H, m, 2 × $CH_3$), 1.1—1.4br (24 H, s, aliphatic H), and 1.9—2.3 (8 H, m, $CH_2CO$ and allylic $CH_2$) (Found: C, 82.1; H, 12.2; Calc. for $C_{21}H_{38}O$: C, 82.3 and H, 12.5%).

*Heneicosa*-6-*yn*-11-*one* (11).—Hydrogen peroxide (30%) (2 ml) was added dropwise to a stirred and ice-cold solution of the enone (5k) (2 g) in methanol (10 ml). The mixture was cooled to 10 °C and potassium hydroxide (500 mg) in water (5 ml) was added during 10 min. The mixture was stirred at room temperature for 38 h and then poured into water (50 ml) and extracted with ether (3 × 50 ml). The dried extract was evaporated to yield the epoxy-ketone (8b) (1.6 g), $\nu_{max.}$ 1 720 $cm^{-1}$.

The crude epoxy-ketone (16) (1.5 g) in a mixture of acetic acid (5 ml) and dichloromethane (10 ml) was stirred with tosyl hydrazine (1.5 g) for 12 h. The reaction mixture on worked up as before to afford heneicosa-6-yn-11-one (11) (1.2 g) as an oil which was purified by column chromatography followed by short-path distillation. This was identical with the sample obtained earlier.

(Z)-*Heneicos*-6-*en*-11-*one* (12).—Heneicos-6-yn-11-one (11) (2 g) in ethyl acetate was added to a suspension of palladium on barium sulphate (10%, 0.12 g) in ethyl acetate (15 ml) containing a drop of pyridine. The mixture was stirred under a hydrogen atmosphere until the rapid absorption of hydrogen ceased. The catalyst was then filtered and the solvent removed to give the product which was distilled, bath temp. 130 °C/0.5 mmHg (lit., b.p. 118 °C/0.4 mmHg bath). (*Z*)-Heneicos-6-en-11-one (12) (1.6 g) was obtained as a colourless oil, $\nu_{max.}$ 3 025, 2 010, and 1 718 $cm^{-1}$; δ 0.9—1.1 (6 H, m, 2 × $CH_3$), 1.1—1.8 (24 H, m), 1.9—2.2 (4 H, m), 2.4 (4 H, t), and 5.0—5.4 (2 H, m) (Found: C, 81.5; H, 13.3; Calc. for $C_{71}H_{40}O$: C, 81.75 and H, 13.1%).

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