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SYNTHESIS OF Z- AND E-POLYUNSATURATED ISOPRENOIDS WITH FUNCTIONAL GROUPS INITIATING ELECTROPHILIC CYCLIZATION

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An acyclic polyene subjected to electrophilic cyclization must contain an initiating and a terminating group [1]. Effective initiating groups have been found among ω-substituted isoprenoid ketones [1-3] leading to a chromene structure [4]. Isoprenoid α,ω-dicarbonyl compounds, which are products of partial ozonolysis of regular cyclic oligomers of isoprene [5, 6], are of interest for the preparation of polycyclic systems.

The separate olefination of the carbonyl groups of Z- and E,E-unsaturated ketoaldehydes (I) and (IX) has been effected by us. For this purpose the aldehyde group was selectively protected [6]. Subsequent interaction with triphenylmethylenephosphorane gave the methylene-containing compounds (II) and (X). Aldehydes (III and (XI), obtained by the hydrolysis of acetals (II) and (X). Aldehydes (III) and (XI), obtained by the hydrolysis of acetals (II) and (X), were subjected to olefination with various reagents, which led to compounds (IV)-(VIII) and (XII) possessing the skeletal and terminal functional groups necessary for electrophilic crystallization.

The formation of triene (V) is evidently explained by the appearance of phosphorane (XIII) in the reaction mixture which is a product of the exchange between n-butyllithium and triphenylmethoxymethanephosphonium chloride [7]

$$[Ph_3PCH_2OMe]^+Cl^- \xrightarrow[-CH_3OCH_2Li]{n\text{-BuLi}} [Ph_3P{-}Bu\text{-}n]^+Cl^- \to \xrightarrow{n\text{-BuLi}} \underset{(XIII)}{Ph_3P{=}CHC_3H_7} \xrightarrow{(III)} (V)$$

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*Deceased.

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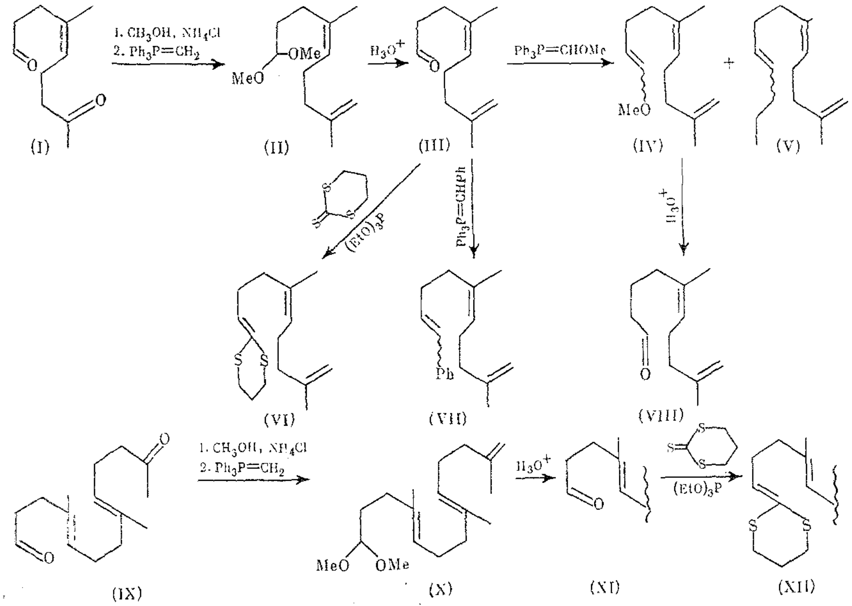

EXPERIMENTAL

GLC was carried out on an LKhM-7A chromatograph with a 2 m × 4 mm column of 5% SE-30 on Chromaton N-AW-DMCS (0.16-0.2 mm) at 150-200°C; the carrier gas was He. IR spectra were obtained on a UR-20 instrument (film), PMR spectra on a Tesla-487B spectrometer (80 MHz) in CCl_4 relative to HMDS, UV spectra on a Specord UV-Vis spectrometer in ethanol, and mass spectra on an MKh-1303 instrument at 150°C and an ionizing voltage of 70 eV.

1,1-Dimethoxy-4,8-dimethyl-4Z,8-nonadiene (II). A solution of t-BuOK (8.5 g, 76 mmole) in THF (70 ml) was added to a suspension of methyltriphenylphosphonium bromide (27 g, 76 mmole) in THF (Ar) (250 ml) stirred at −30°C. The mixture was kept for 30 min at −30°C, then a solution of the dimethylacetal (9 g, 38 mmole) obtained from ketoaldehyde (I) by the method in [6] in THF (50 ml) was added, kept 1 h at −30°C, and left for 15 h at ~25°C. The mixture was then diluted with petroleum ether, Ph_3PO filtered off, the filtrate washed with saturated aqueous NaCl, dried over $MgSO_4$, and evaporated. Compound (II) (7 g, 86%) was extracted from the residue (12.2 g) with hexane and had n_D^{20} 1.4579 [8], R_f 0.46 (Al_2O_3, hexane–ether, 3:1). IR spectrum (ν, cm^{-1}): 840, 895, 1380, 1655, 3070. PMR spectrum (δ, ppm): 1.2 m (2H, CH_2), 2.0 m (6H, $CH_2C=C$), 1.65 s (6H, $CH_3C=C$), 3.16 s (6H, OCH_3), 4.22 t (1H, OCHO, J = 5.5 Hz), 4.6 s (2H, $CH_2=C$), 5.03 t (1H, CH=C, J = 6.5 Hz). Mass spectrum (m/z, %): 212 (M^+, 0.13), 179 ($M^+ - CH_3OH$, 7.23), 165 (1.2), 149 (14.46), 148 ($M^+ - 2CH_3OH$, 8.43), 133 (7.23), 125 (20.48), 107 (20.48), 93 (86.75), 81 (36.14), 75 (100). Found: C 73.3; H 11.3; C=C 23.0; OCH_3 28.5%. $C_{13}H_{24}O_2$. Calculated: C 73.5; H 11.4; C=C 22.6; OCH_3 29.1%.

4,8-Dimethyl-1-keto-4Z,8-nonadiene (III). A solution of (II) (7.8 g) and TosOH (0.1 g) in 80% aqueous acetone (100 ml) was boiled for 1 h, concentrated in vacuum, extracted with ether, dried over $MgSO_4$, and evaporated. Compound (III) (5.7 g, 90%) was obtained, R_f 0.38 (Al_2O_3, hexane–ether, 3:1). IR spectrum (ν, cm^{-1}): 895, 1650, 1720, 2730, 3050. PMR spectrum (δ, ppm): 1.67 s (3H, $CH_3C^4=C$), 1.69 s (3H, $CH_3C^8=C$), 2.0-2.1 m (4H, C^6H_2, C_7H_2), 2.35 m (4H, C^2H_2, C^3H_2), 4.63 s (2H, $CH_2=C$), 5.0-5.1 m (1H, CH=C), 9.6 s (1H, CHO).

1-Methoxy-5,9-dimethyl-1ξ5Z,9-decatriene (IV) and 8,12-Dimethyl-4ξ8Z,12-tridecatriene (V). A 0.8 N solution (40 ml, 32 mmole) of n-BuLi in n-hexane was added at −10°C to a stirred suspension of triphenylmethoxymethylphosphonium chloride (10 g, 29 mmole) in THF (Ar) (20 ml). After 10 min the mixture was cooled to −20°C, a solution of (III) (2 g, 12 mmole) in THF (20 ml) was added, kept at −20°C for 0.5 h, heated to ~25°C, diluted with moist ether, washed with water (20 ml), with 5% HCl (15 ml), and dried over $MgSO_4$. After evaporation the residue was treated with petroleum ether, Ph_3PO filtered off, the solution evaporated, and the residue chromatographed on silica gel (hexane). Compound (IV) (1.21 g, 52%) was obtained, R_f 0.28 (hexane). IR spectrum (ν, cm^{-1}): 890, 1650, 1660, 3050. PMR spectrum (δ, ppm): 1.6 s and 1.7 s (6H, $CH_3C=C$), 1.9-2.4 m (8H, $CH_3C=C$), 3.4 s and 3.5 s (3H, OCH_3), 4.0-4.6 m (1H, $C^2H=C$), 4.61 s (2H, $CH_2=C$), 5.06 t (1H, $C^6H=C$, J = 6.5 Hz), 6.2 d (1H, C'H=C, J = 13 Hz). Yield of compound (V) was 0.82 g (30%), R_f 0.65 (hexane). PMR spectrum (δ, ppm): 0.7-1.1 m (3H, C^1H_3), 1.1-1.5 m (2H, C^2H_2), 1.6 s and 1.7 s (3H, $CH_3C=C$), 1.9-2.1 m (10H, $CH_2C=C$), 4.59 s (2H, $CH_2=C$), 5.04 t (1H, $C^9H=C$, J = 6 Hz), 5.1-5.3 m (2H, $C^4H=C^5H$). Mass spectrum (m/z): 206 (M^+).

1-Keto-5,9-dimethyl-5Z,9-decadiene (VIII). A mixture of (IV) (0.86 g), TosOH (0.04 g), acetone (17 ml), and water (8 ml) was boiled for 0.5 h, evaporated, the residue extracted with ether, the ether solution washed with water, and dried over $MgSO_4$. After evaporation the residue was chromatographed on silica gel. Compound (VIII) (0.57 g, 80%) was obtained, R_f 0.3 (benzene). IR spectrum (ν, cm^{-1}): 895, 1650, 1720, 2725, 3050. PMR spectrum (δ, ppm): 1.3-2.5 m (10H, $CH_2C{=}C$), 1.63 s and 1.7 s (6H, $CH_3C{=}C$), 4.62 s (2H, $H_2C{=}C$), 9.65 s (1H, CHO).

1-(2,6-Dithiacyclohexylidene)-5,9-dimethyl-1,5Z,9-decatriene (VI). A mixture of triethyl phosphite (11.6 g, 7 mmole), trimethylenetrithiocarbonate (0.36 g, 2.4 mmole) (obtained as in [9]) and (III) (0.36 g, 2.2 mmole) was stirred for 2.5 h at 50°C, cooled to ~25°C, and left for 24 h. It was then treated with a 1:1 aqueous methanolic solution of KOH, methanol was distilled off under vacuum, the residue was diluted with water, and extracted with ether. The ether solution was washed with water and dried over K_2CO_3. After evaporation of the solvent the residue was chromatographed on Al_2O_3 (benzene–ether, 1:1). Compound (VI) (0.23 g, 40%) was obtained, R_f 0.8 (benzene–ether, 1:1). IR spectrum (ν, cm^{-1}): 890, 1660, 1670, 3050. PMR spectrum (δ, ppm): 1.63 s and 1.73 s (6H, $CH_3C{=}C$), 1.9-2.6 m (10H, CH_2), 2.65-2.9 m (4H, CH_2S), 4.61 s (2H, $CH_2{=}C$), 5.08 t (1H, C^6H, J = 6 Hz), 5.78 t (1H, $C^2H{=}C$, J = 7 Hz). UV spectrum (λ, nm, ε): 255 (6200).

1-Phenyl-5,9-dimethyl-1,ξ5Z,9-decatriene (VII). A 1-N solution (8 ml, 8 mmole) of n-BuLi in hexane was added to a stirred suspension of triphenylbenzylphosphonium chloride (3.15 g, 8 mmole) in ether (Ar) (60 ml). The mixture was kept for 30 min at ~25°C, cooled to 10°C, a solution of (III) (1.16 g, 7 mmole) in ether (8 ml) was added dropwise, the mixture kept at 10°C for 30 min, and then boiled for 6 h. After cooling to 15°C water (20 ml) was added slowly, then 5% HCl (15 ml), the solution was extracted with hexane, the extract dried over $MgSO_4$, and evaporated in vacuum. The residue was chromatographed on silica gel (benzene). Compound (VII) (1.2 g, 72%) was obtained with a ratio Z/E = 1:3 (GLC), R_f 0.64 (benzene). IR spectrum (ν, cm^{-1}): 890, 1650, 3050. PMR spectrum (δ, ppm): 1.6 s and 1.7 s (6H, $CH_3C{=}C$), 1.9-2.4 m (8H, $CH_2C{=}C$), 4.59 s (2H, $CH_2{=}C$), 5.08 t (1H, $C^6H{=}C$, J = 6.5 Hz), 6.0-6.5 m (2H, $C^1H{=}C^2H$), 6.9-7.3 m (5H, C_6H_5). UV spectrum (λ, nm, ε): 225 (4620), 248 (1820). Found: C 89.9; H 10.1%. $C_{18}H_{24}$. Calculated: C 89.9; H 10.1%.

1,1-Dimethoxy-4,8,12-trimethyl-4E,8E,12-tridecatriene (X). Triene (X) was obtained from (IX) as described above for (II). Yield was 53%, n_D^{20} 1.4652. IR spectrum (ν, cm^{-1}): 840, 895, 1380, 1650, 3080. PMR spectrum (δ, ppm): 1.2 m (2H, CH_2), 1.55 s (6H, $CH_3C{=}C$), 1.62 s (3H, $CH_3C^{12}{=}C$), 2.0 m (10H, $CH_2C{=}C$), 3.2 s (6H, OCH_3), 4.2 t (1H, OCHO, J = 5.5 Hz), 4.6 s (2H, $CH_2{=}C$), 5.1 t (2H, CH=C, J = 6.5 Hz). Mass spectrum (m/z, %): 280 (M^+ 0.06), 249 ($M^+ - OCH_3$ 0.43), 248 (1.48), 217 (1.53), 216 ($M^+ - 2CH_3OH$, 1.4), 201 (1.0), 161 (5.33), 125 (30.0), 93 (100). Found: C 76.7; H 11.2; C=C 25.2; OCH_3 21.7%. $C_{18}H_{32}O_2$. Calculated: C 77.1; H 11.5; C=C 25.7; OCH_3 22.1%.

1-Keto-4,8,12-trimethyl-4E,8E,12-tridecatriene (XI). Triene (XI) was obtained by the hydrolysis of (X) as described above for (III). Yield was 75%, R_f 0.43 (hexane–ether, 3:1). IR spectrum (ν, cm^{-1}): 840, 890, 1380, 1655, 1720, 2725, 3050. PMR spectrum (δ, ppm): 1.56 s (6H, $CH_3C{=}C$), 1.62 s (3H, $CH_3C^{12}{=}C$), 2.0 m (8H, $CH_2C{=}C$), 2.35 m (4H, C^2H_2, C^3H_2), 4.63 s (2H, $CH_2{=}C$), 5.05 m (1H, CH=C), 9.6 s (1H, CHO).

1-(2,6-Dithiacyclohexylidene)-5,9,13-trimethyl-1,5E,9E,13-tetradecatetraene (XII). Tetraene (XII) was obtained from (XI) as described above for (VII). Yield was 30%. IR spectrum (ν, cm^{-1}): 895, 1650, 1665, 3050. PMR spectrum (δ, ppm): 1.62 s (6H, $CH_3C{=}C$), 1.72 s (3H, $CH_3C^{13}{=}C$), 1.7-2.4 m (14H, CH_2), 2.81 t (4H, CH_2–S, J = 6 Hz), 4.65 s (2H, $CH_2{=}C$), 5.05 m (2H, CH=C), 5.8 m (1H, $C^2H{=}C$). UV spectrum (λ, nm, ε): 254 (3200).

SUMMARY

Separate olefination has been carried out for the carbonyl groups of 1,8-diketo-4-methyl-4Z-nonene and 1,12-diketo-4,8-dimethyl-4E,8E-tridecadiene into 1,5-polyenes which were prepared for electrophilic cyclization.

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