−0.86° (c 6). The literature values are as follows: bp 98-99°C (0.5 mm) and $[\alpha]_D^{24}$ −1.64°. The GLC (at 150°C) was characterized as τ_R 11.3 min. The IR spectrum (ν, cm^{-1}) was as follows: 2960, 2930, 2860, 1720, 1460, 1360, and 1160. The PMR spectrum (δ, ppm; J, Hz) was as follows: 0.85 d (3H, J = 6, CH_3—C^{10}), 0.90 t (3H, J = 6, 13-CH_3), 1.0-1.7 (17H, CH_2 and CH), 2.14 s (3H, 1-CH_3), and 2.41 t (2H, J = 6, CH_2CO). Found, %: C 78.95, H 13.18. $C_{14}H_{28}O$. Calculated, %: C 79.18, H 13.29.

Conclusions

The synthesis of (R)-10-methyl-2-tridecanone from the chiral (S)-3,7-dimethyl-1,6-octadiene was accomplished with the total yield of 24-26% in the 13-14 stages of the synthesis.

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CONVERSION OF UBIQUINONE-9 TO UBIQUINONE-10 BY USE OF THE WITTIG REACTION

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The coenzyme ubiquinone-10 (I) is widely used in the therapy of cardiovascular diseases and immune system disorders, for lowering the toxicity of anthracyclic antibiotics, and for other purposes [1]. Because of the scarcity of (I) in natural sources, a simple method for obtaining this compound is needed. We have investigated the conversion of the readily available ubiquinone-9 (II) [2] to quinone (I) by attaching the missing C_5-group of the isoprenoid side chain by means of the Wittig reaction. This approach involved the use of quinone (II) and its O,O'-dibenzyl ether (III), first obtained by the reduction of quinone (II) with $NaBH_4$ and subsequent O-alkylation of the bis-Na salt of the hydroquinone intermediate with $PhCh_2Br$ under the conditions used for the synthesis of the O,O'-dibenzyl ether of ubiquinone-7 [3].

The attachment of the side chains of molecule (II) was carried out in three stages, the first of which involved obtaining aldehydes (X), (XI). Our earlier attempts to

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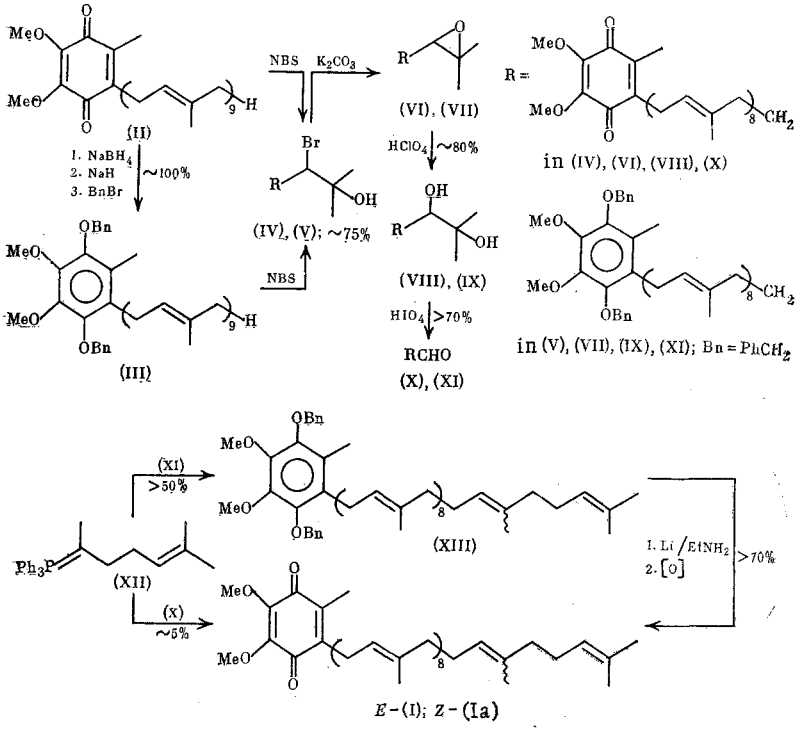
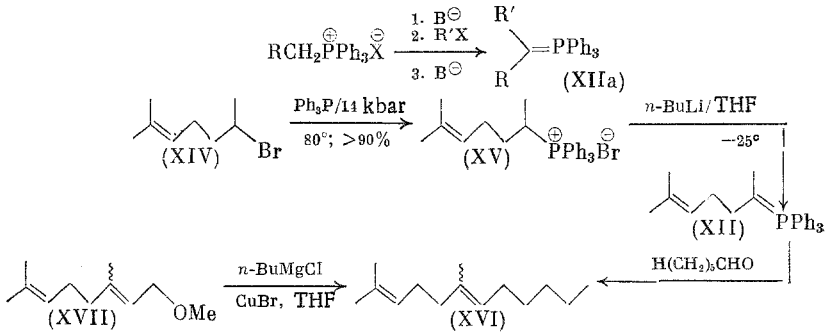
synthesize aldehyde (X) directly from quinone (II) by ozonolysis or conversion to epoxide (VI) by means of peracids were not successful [4]. We therefore used a standard reaction sequence for linear isoprenoids, with an initial selective functionalization of the terminal isoprenoid group of quinone (II) or diether (III) by means of N-bromosuccinimide (NBS) [5], leading to bromohydrins (IV), (V).



The use of aqueous 90% THF (instead of 75%) as solvent increased the yield of (IV) by 25%, compared to that described in [6]. Under the same conditions, diether (III) afforded bromohydrin (V) in a yield of 75% at 48% conversion. The purity of (V) and the selectivity of the terminal C=C bond attack were determined by comparing the integral intensities of isolated signals at δ 1.673 (3H, $CH_3C^{3'}$), 1.310, and 1.325 ppm (6H, $CH_3C^{3S'}$) in the PMR spectra (200 MHz).

The cyclization of bromohydrins (IV), (V) by means of K_2CO_3 in ether–MeOH afforded epoxides (VI), (VII) quantitatively. When the reaction was carried out in MeOH–hexane, epoxide (VI) was obtained in a yield of 74% [6]. The acid-catalyzed hydrolysis of oxides (VI), (VII) afforded glycols (VIII), (IX). Periodate cleavage of the glycols afforded aldehydes (X) and (XI) in an overall yield of 36 and 45%, respectively, with respect to the initial quinone (II). The structures of compounds (IV), (VI), and (X), described in [6], and of the newly obtained quinone (VIII) and ethers (V), (VII), (IX), and (XI) were confirmed by means of PMR based on the known characteristics of ubiquinone-7 derivatives [3].

The next stage of the scheme entailed the synthesis of phosphorane (XII), which is needed for the Wittig condensation of aldehydes (X), (XI) to produce olefins (I), (XIII). Phosphoranes of series (XIIa), including (XII), are routinely obtained in three stages from appropriate primary halogenide derivatives without isolation of the intermediate type (XV) phosphonium salts [7]. When obtained directly from methylheptenyl bromide (XIV) under standard conditions, the corresponding salt (XV) is formed in a yield of ~3%, as shown for the reaction of PPh_3 with asymmetric secondary halogenides. Since this interaction proceeds via a Menshutkin-type bimolecular reaction mechanism, we may expect that it would be facilitated by high pressure. Indeed, bromide (XIV) reacts with PPh_3 at 14 kbar and 80°C (5 h) to give an almost quantitative yield of salt (XV) [8]. This method was used by us earlier to synthesize onium salts of group V elements [9] and, recently, has been employed independently in [10] for obtaining several phosphonium derivatives.



The structure of salt (XV) was confirmed spectrally. In particular, the signal at 1.44 ppm in its PMR spectrum (250 MHz) consists of four lines that characterize the CH_3 group of the CH_3CHP fragment; this pattern is caused by the interaction of the CH_3 group with the neighboring P nucleus ($J_{H,P}$ = 20 Hz) and the methine proton ($J_{H,H}$ = 7.2 Hz). Moreover, in a model experiment, phosphorane (XII), readily generated from salt (XV), was smoothly converted to a mixture (E/Z ≈ 5:1) of known [11] hydrocarbons (XVI), synthesized independently from methyl ethers (XVII) according to Norman. The content of the Z-Δ^6-isomer (XVI) was determined from the ratio in the PMR spectrum of the integral intensities of the signals at δ 1.585 and 1.598 ppm (trans-CH_3 of the E,Z-isomers and CH_3C^6 of the E-isomer) and at 1.674 ppm (CH_3C^2 of the E,Z-isomers and CH_3C^6 of the Z-isomer); this was confirmed by comparing the signal intensities at δ 15.4 (CH_3C^6 of the E-isomer) and 23.5 ppm (CH_3C^6 of the Z-isomer), as well as at 39.2 (C^5 of the E-isomer) and 31.4 ppm (C^5 of the Z-isomer) in the ^{13}C NMR spectrum of hydrocarbons (XVI) (cf. [12]).

By working with preparative quantities of salt (XV), we were readily able to condense phosphorane (XII) with aldehyde (XI) and diether (XIII). Reductive removal of the benzyl protective group with Li in $EtNH_2$ afforded (after air oxidation of the intermediate hydroquinone) the desired ubiquinone-10 (I) in a yield of >35% with respect to aldehyde (XI). Under the same conditions, the reaction of (X) with (XII) affords quinone (I) in a yield of ~5%, suggesting the preferential participation of the quinone fragment of molecule (X) in the Wittig reaction. However, this is at variance with the known facts [13] about the high chemoselectivity of the aldehyde group in this reaction.

Analysis of quinone (I) samples by ^1H and ^{13}C NMR shows that they contain the Z-Δ^{34}-isomer (Ia). As in the ^{13}C NMR spectrum of the E,Z-isomers (XVI), the spectrum of quinone (I) contains methyl and methylene group signals associated with the C=C bond which are characteristic of the Z-isomer [13] — at δ 23.3 ($\underline{C}H_3C^{35'}$) and 32.0 ppm ($C^{36'}$). The content of the Z-Δ^{34}-isomer (Ia) was determined from the ratio in the PMR spectrum of the integral intensities of the signals at 1.652 (trans-CH_3 of the E,Z-isomers and $CH_3C^{35'}$ of the Z-isomer) and 1.720 ppm ($CH_3C^{3'}$ of the E,Z-isomers).

Experimental

IR spectra were recorded on a film* on a UR-20 instrument. UV spectra of alcoholic solutions were recorded on a Specord UV-VIS spectrometer. NMR spectra for $CDCl_3$* solutions relative to TMS were recorded on Bruker WP-80 (20.1 MHz); Tesla BS-497 (100 MHz); and Bruker WP-200.54, WM-250, and WM-360 spectrometers. R_f values are given for a fixed SiO_2 (Silufol) layer in the solvent system hexane—ether, 1:1*. GLC analysis was carried out on a LKhM-8MD instrument (2 m × 3 mm column with 15% Carbowax 20M on Chromaton N-AW-DMCS).

1,4-Dibenzyloxy-2,3-dimethoxy-5-methyl-6-(3',7',11',15',19',23',27',31',35'-nonamethylhexatriaconta-2'E,6'E,10'E,14'E,18'E,22'E,26'E,30'E,34'-(nonaenyl)-benzene (III). A 0.35-g (9.21-mmole) portion of $NaBH_4$ was added to a mixed (Ar) solution containing 6.1 g (7.67 mmoles) of compound (II) in 40 ml EtOH—ether (1:1). The reaction mixture was kept for 30 min at 25°C and then evaporated in a vacuum. The residue was dissolved in 50 ml DMF and treated with 1.2 g (50 mmoles) NaH and 3.5 ml (29.5 mmoles) BnBr. The reaction mixture was kept for 3 h at 25°C, dissolved in H_2O, and extracted with hexane. The extract was washed with H_2O and dried over $MgSO_4$. The residue (9.2 g), after removal of solvents in a vacuum, was chromatographed on 100 g SiO_2. Gradient elution from hexane

*Unless specified otherwise.

to ether (up to 5% of the latter) afforded 7.43 g (99%) of product (III) as a colorless oil; R_f 0.80 (hexane–ether, 1:2). UV spectrum (λ_{max}, nm): 210 (ε 10,400), 278 (ε 700). PMR spectrum (δ, ppm): 1.508 s and 1.528 br. s (24H, $CH_3C{=}C$), 1.610 br. s (6H, $CH_3C^{3'}$ and $CH_3C^{35'}$), 2.0 m (32H, $CH_2C{=}C$), 2.048 s (3H, CH_3C_5), 3.268 br. d (2H, J = 6.0 Hz, $HC^{1'}$), 3.869 s and 3.878 s (6H, CH_3O), 4.884 br. s (4H, CH_2O), 4.93 br. t (1H, $HC^{2'}$), 5.1 m (8H, HC=C), 7.4 m (10H, C_6H_5). Found, %: C 83.34, H 10.04. $C_{68}H_{96}O_6$. Calculated, %: C 83.38, H 10.08.

Bromohydrin (IV). A 1.07-g (6 mmole) portion of NBS was added to a mixed solution (0°) containing 3.97 g (5 mmoles) of compound (II) in 15 ml THF–H_2O (9:1). The reaction mixture was kept for 1 h at 25°C, diluted with ether, washed with H_2O, and dried with Na_2SO_4. The residue (5.4 g), after removal of solvents in a vacuum, was chromatographed on 100 g SiO_2. Gradient elution from hexane to ether (up to 20% of the latter) afforded 2.06 g of compound (II) and 1.6 g (75%) of product (IV) as a colorless oil; R_f 0.25. The PMR spectrum was identical to the one described in [6].

1,4-Dibenzyloxy-2,3-dimethoxy-5-methyl-6-(34'-bromo-35'-hydroxy-3',7',11',15',19',23',27',31',35'-nonamethylhexatriaconta-2'E,6'E,10'E,14'E,18'E,22'E,26'E,30'E-octaenyl)-benzene (V). In a similar manner, 7.5 g (7.7 mmoles) of compound (III) and 1.64 g (9.2 mmoles) of NBS in 100 ml THF–H_2O (9:1) after 3 h at 0-25°C afforded a product, which was chromatographed on 180 g SiO_2. Gradient elution from hexane to ether (up to 15% of the latter) afforded 3.11 g of compound (III) and 3.7 g (75%) of product (V), a colorless oil with a R_f of 0.25 (ether–hexane, 1:2). PMR spectrum (δ, ppm): 1.310 s and 1.325 s (6H, $CH_3C^{35'}$), 1.563 s and 1.582 br. s (21H, $CH_3C{=}C$), 1.673 s (3H, $CH_3C^{3'}$), 1.8 m (2H, $HC^{33'}$), 2.0 m (30H, $CH_2C{=}C$), 2.101 s (3H, CH_3C^5), 3.322 d (2H, J = 7.0 Hz, $HC^{1'}$), 3.924 s and 3.933 s (6H, CH_3O), 3.945 m (1H, HCBr), 4.938 s (4H, CH_2O), 4.986 br. t (1H, $HC^{2'}$), 5.1 m (7H, HC=C), 7.4 m (10H, C_6H_5).

Epoxide (VI). A suspension of 1.6 g (1.8 mmoles) of compound (IV) and 0.2 g (2 mmoles) of K_2CO_3 in 40 ml MeOH–ether (3:1) was mixed for 40 min at 25°C, diluted with ether, washed with water, neutralized with 1 N HCl, and dried with Na_2SO_4. The residue (2 g), after removal of solvents in a vacuum, was chromatographed on 40 g SiO_2. Gradient elution from hexane to ether (up to 10% of the latter) afforded 1.32 g (90%) of product (VI), an orange oil with a R_f of 0.60. IR spectrum (ν, cm^{-1}): 1675, 2850, 2870, 2960, 3000, 3020, 3030. The PMR spectrum was identical to that described in [6].

1,4-Dibenzyloxy-2,3-dimethoxy-5-methyl-6-(34',35'-epoxy-3',7',11',15',19',23',27',31',35'-nonamethylhexatriaconta-2'E,6'E,10'E,14'E,18'E,22'E,26'E,30'E-octaenyl)benzene (VII). In a manner similar to that described for compound (VI), 3.8 g (3.54 mmoles) of compound (V) and 0.5 g (5 mmoles) of K_2CO_3 in 120 ml MeOH–ether (2:1), after reacting for 2 h at 25°C, afforded 2.1 g of a product which was chromatographed of 40 g SiO_2. Gradient elution from hexane to ether (up to 10% of the latter) afforded 3.29 g (93%) of product (VII), a colorless oil with a R_f of 0.65 (hexane–ether, 2:1). IR spectrum (CCl_4, ν, cm^{-1}): 1260, 1290, 1350, 1380, 1430, 1460, 1500, 1670, 2850, 2930, 2960, 3030. UV spectrum (λ_{max}, nm): 210 (ε 71,250), 280 (ε 630). PMR spectrum (δ, ppm): 1.260 s and 1.300 s (6H, $CH_3C^{35'}$), 1.573 br. s, 1.595 br. s and 1.64 br. s (21H, $CH_3C{=}C$), 1.686 s (3H, $CH_3C^{3'}$), 2.0 m (32H, $CH_2C{=}C$), 2.150 s (3H, CH_3C^5), 2.710 t (1H, J = 7.0 Hz, $HC^{1'}$), 3.933 s (6H, CH_3O), 4.953 s (4H, CH_2O), 5.1 m (8H, HC=C), 7.4 m (10H, C_6H_5). Found, %: C 81.94, H 9.94. $C_{68}H_{96}O_5$. Calculated, %: C 82.21, H 9.74.

2,3-Dimethoxy-5-methyl-6-(34',35'-dihydroxy-3',7',11',15',19',23',27',31',35'-nonamethylhexatriaconta-2'E,6'E,10'E,14'E,18'E,22'E,26'E,30'E-octaenyl)benzoquinone-1,4 (VIII). A solution of 2.5 g (3.08 mmoles) of compound (VI) and 0.5 ml of 37% $HClO_4$ in 36 ml THF–H_2O (5:1) was kept for 30 min at 25°C, diluted with ether, washed with water, neutralized with $NaHCO_3$, and dried with Na_2SO_4. The residue (2.8 g), after removal of solvents in a vacuum, was chromatographed on 30 g SiO_2. Gradient elution from hexane to ether (up to 20% of the latter) afforded 1.0 g (75%) of product (VIII), an orange oil with a R_f of 0.15. IR spectrum (ν, cm^{-1}): 1110, 1160, 1270, 1380, 1450, 1610, 1660, 2860, 2925, 2970, 3530. PMR spectrum (δ, ppm): 1.09 s and 1.13 s (6H, $CH_3C^{35'}$), 1.58 br. s (21H, $CH_3C{=}C$), 1.73 s (3H, $CH_3C^{3'}$), 2.0 m (35H, $CH_3C{=}C$ and CH_3C^5), 3.11 d (2H, J = 7.0 Hz, $HC^{1'}$), 3.9 m (1H, $HC^{34'}$), 3.91 s (6H, CH_3O), 4.89 br. t (1H, $HC^{2'}$), 5.1 m (7H, HC=C).

1,4-Dibenzyloxy-2,3-dimethoxy-5-methyl-6-(34',35'-dihydroxy-3',7',11',15',19',23',27',31',35'-nonamethylhexatriaconta-2'E,6'E,10'E,14'E,18'E,22'E,26'E,30'E-octaenyl)benzene (IX). In a similar manner, 1.3 g (1.31 mmoles) of compound (VII) and 0.2 ml of 37% $HClO_4$ in 5 ml THF–H_2O (4:1), after reacting for 2 h at 25°C, afforded 1.6 g of a product which was chromatographed on 30 g SiO_2. Gradient elution from hexane to ether (up to 15% of the latter) afforded 0.22 g of compound (VII) and 0.97 g (88%) of product (IX), a colorless oil with a R_f of 0.20 (ether–hexane, 1:2). IR spectrum (ν, cm^{-1}): 1110, 1380, 1430, 1455, 2870, 2930, 2980. PMR spectrum (δ, ppm): 1.127 s and 1.168 s (6H, $CH_3C^{35'}$), 1.571 s (3H, $CH_3C^{7'}$), 1.590 s (18 H, $CH_3C{=}C$), 1.680 s (3H, $CH_3C^{3'}$), 2.0 m (32H, $CH_2C{=}C$), 2.110 s (3H, CH_3C^5), 3.3 m (3H, $HC^{1'}$ and $HC^{34'}$), 3.926 s and 3.934 s (6H, CH_3O), 4.940 br. s (4H, CH_2O), 4.990 br. t (1H, $HC^{2'}$), 5.1 m (7H, HC=C), 7.4 m (10H, C_6H_5). Found, %: C 81.41, H 10.12. $C_{68}H_{98}O_6$. Calculated, %: C 80.74, H 9.76.

Aldehyde (X). A solution containing 2.1 g (2.54 mmoles) of compound (VIII), 1.0 g (4.67 mmoles) $NaIO_4$, and 0.2 ml concentrated H_2SO_4 in 50 ml THF–H_2O (4:1) was kept for 30 min at 25°C; it was then diluted with ether, neutralized with $NaHCO_3$, washed with water, and dried with Na_2SO_4. The residue (2 g), after removal of solvents in a vacuum, was chromatographed on 40 g SiO_2. Gradient elution from hexane to ether (up to 15% of the latter) afforded 1.4 g (72%) of product (X), orange crystals with a mp of 41-43°C (hexane) and a R_f of 0.45. IR spectrum (KBr, ν, cm^{-1}): 1655, 1725, 2730, 2850. UV spectrum (λ_{max}, nm): 278 (ε 14,600). The PMR spectrum was identical to that described in [6]. Found, %: C 79.35, H 10.12. $C_{51}H_{76}O_5$. Calculated, %: C 79.64, H 9.96.

1,4-Dibenzyloxy-2,3-dimethoxy-5-methyl-6-(33'-formyl-3',7',11',15',19',23',27',31'-octamethyltritriaconta-2'E,6'E,10'E,14'E,18'E,22'E,26'E,30'E-octaenyl)-benzene (XI). In a manner similar to that described for compound (X), 4.4 g (4.35 mmoles) of compound (IX), 1.12 g (5.23 mmoles) of $NaIO_4$, and 0.5 ml of concentrated H_2SO_4 in 100 ml THF–H_2O (4:1), after reacting for 30 min at 25°C, afforded 4.6 g of a product which was chromatographed on 120 g SiO_2. Gradient elution from hexane to ether (up to 10% of the latter) afforded 3.06 g (74%) of product (XI), a colorless oil with a R_f of 0.55 (ether–hexane, 1:2). PMR spectrum (δ, ppm): 1.496 s, 1.517 br. s, and 1.524 s (21H, $CH_3C{=}C$), 1.608 s (3H, $CH_3C^{3'}$), 2.0 m (28H, $CH_2C{=}C$), 2.030 s (3H, CH_3C^5), 2.219 m (2H, J = 7.5 Hz, $HC^{32'}$) 2.396 tr. d (2H, J = 7.5 Hz, J = 1.5 Hz, $HC^{33'}$) 3.261 br.d (2H, J = 6.0 Hz, $HC^{1'}$), 3.860 s and 3.870 s (6H, CH_3O), 4.877 s and 4.884 s (4H, CH_2O), 4.933 br. t (1H, $HC^{2'}$), 5.1 m (7H, HC=C), 7.4 m (10H, C_6H_5), 8.553 t (1H, J = 1.5 Hz, CHO). Found, %: C 81.79, H 9.51. $C_{65}H_{90}O_5$. Calculated, %: C 82.05, H 9.53.

2-Methyl(hept-2-en-6-yl)triphenylphosphonium Bromide (XV). A solution consisting of 6.5 g (24.81 mmoles) PPh_3 and 5.0 g (26.18 mmoles) of bromide (XIV) [14] was kept for 6 h at 80°C and 14 kbar and then for 16 h at 25°C and 3 kbar. The reaction mixture was washed with ether until no more organic material was extracted. The residue (5.1 g, 91%) represented salt (XV), an amorphous powder with a mp of 146-154°C. IR spectrum (KBr, ν, cm^{-1}): 695, 720, 1440, 1585. PMR spectrum (CD_3OD, δ, ppm): 1.44 double d (3H, $J_{H,P}$ = 20.0, $J_{H,H}$ = 7.2 Hz, CH_3CP), 1.62 br. d (3H, $J_{H,H}$ = 1.1 Hz, cis-CH_3), 1.71 br. d (3H, $J_{H,H}$ = 7.2 Hz, CH_3CP), 1.62 br. d (3H, $J_{H,H}$ = 1.1 Hz, cis-CH_3), 1.71 br. d (3H, $J_{H,H}$ = 1.1 Hz, trans-CH_3), 1.95 m (2H, CH_3CP), 2.34 q (2H, J = 6.7 Hz, $CH_2C{=}C$, 4.1 m (1H, HCP), 5.18 br. t (1H, $J_{H,H}$ = 6.7 Hz, HC=C), 7.75-8.00 m (15H, C_6H_5). Found, %: P 6.40. $C_{26}H_{30}BrP$. Calculated, %: P 6.83.

1,4-Dibenzyloxy-2,3-dimethoxy-5-methyl-6-(3',7',11',15',19',23',27',31',35',39'-decamethyltetraconta-2'E,6'E,10'E,14'E,18'E,22'E,26'E,30'E,34'E/Z,38'-decaenyl)benzene (XIII). A mixed (Ar) suspension of 2.28 g (5.03 mmoles) of compound (XV) in 30 ml THF at –25°C was treated for 5 min with 10.9 ml of 0.46 M n-BuLi in hexane (5.01 mmoles) and then for another 5 min (at –45°C) with 0.95 g (1 mmole) of compound (XI) in 5 ml THF. After 30 min the mixture was heated to 0°C, diluted with hexane, and neutralized with 1 N HCl; it was then washed with water and dried with $MgSO_4$. The residue (4.2 g), after removal of solvents in a vacuum, was chromatographed on 80 g SiO_2. Gradient elution from hexane to ether (up to 10% of the latter) afforded 0.15 g of compound (XI) and 0.45 g (51%) of product (XIII), a colorless oil with a R_f of 0.80 (ether–hexane, 1:2). PMR spectrum (δ, ppm): 1.57 br. s (27H, $CH_3C{=}C$), 1.64 br. s (6H, $CH_3C^{3'}$ and $HC^{36'}$), 2.0 m (39H, CH_3C^5 and $CH_2C{=}C$), 3.25 br. d (2H, J = 6.0 Hz, $HC^{1'}$), 3.86 s (6H', CH_3O), 4.91 s (4H, CH_2O), 5.1 m (10H, HC=C), 7.4 m (10H, C_6H_5). Found, %: C 82.16, H 9.81. $C_{73}H_{104}O_4$. Calculated, %: C 82.03, H 9.55.

Ubiquinone-10 (I) and 34'Z-Ubiquinone-10 (Ia). A 1.32 g (2.91 mmole) portion of compound (XV) was added at −30°C to a mixed (Ar) $(i\text{-Pr})_2NLi$ solution prepared during 15 min at 0°C from 0.3 g (3 mmoles) of $(i\text{-Pr})_2NH$ in 20 ml THF and 4.7 ml of 0.6 M n-BuLi in hexane (2.82 mmoles); the mixture was allowed to stand for 15 min at 0°C. After 5 min at −60°C, 0.77 g (1 mmole) of compound (X) in 3 ml THF was added, with mixing, to the phosphorane (XII) solution prepared in this manner. The mixture was kept for 30 min at −20°C, then diluted with ether, neutralized with 1 N HCl, washed with water, and dried with Na_2SO_4. The residue (3.2 g), after removal of solvents in a vacuum, was chromatographed on 60 g SiO_2. Gradient elution from hexane to ether (up to 10% of the latter) afforded 50 mg of compound (X) and 50 mg (6%) of mixture (I, Ia), orange crystals with a mp of 45-48°C (hexane) and a R_f of 0.75. PMR spectrum (δ, ppm): 1.581 br. s (26H, $CH_3C{=}C$), 1.652 br. s (4H, $HC^{40'}$ for [I, Ia] and $CH_3C^{35'}$ for [Ia]), 1.720 br. s (3H, $CH_3C^{3'}$), 2.0 m (36H, $CH_2C{=}C$), 1.982 s (3H, CH_3CH^5), 3.118 br. d (2H, J = 7.0 Hz, $HC^{1'}$), 3.923 s and 3.936 s (6H, CH_3O), 4.857 br. t (1H, J = 7.0 Hz, HC^2), 5.0 m (9H, $HC{=}C$). ^{13}C NMR spectrum (δ, ppm): 11.8 (1C, $\underline{C}H_3C^5$), 16.0 (7.7C, $\underline{C}H_3C{=}C$), 16.3 (1C, $CH_3C^{3'}$), 17.6 (1C, $CH_3C^{39'}$), 23.3 (0.3C, $CH_3C^{35'}$ [Ia]), 25.3 and 25.6 (2C, $C^{1'}$ and $C^{40'}$), 26.8 (8.7C, $\underline{C}H_2CCH_3{=}C$), 29.7 (0.3C, $C^{33'}$ for [Ia]), 32.0 (0.3C, $C^{36'}$ for [Ia]), 39.7 (8.7C, $CH_2\underline{C}CH_3{=}C$), 118.3 (1C, $C^{2'}$), 123.1 (1C, $C^{6'}$), 123.5 (7.7C, $H\underline{C}{=}C$), 124.3 (0.3C, $C^{34'}$ for [Ia]), 129.9 (1C, $C^{39'}$), 133.5 (1C, $C^{7'}$), 133.8 (6.7C, $\underline{C}CH_3$ C), 134.2 (0.3C, $C^{35'}$ for [Ia]), 136.5 (1C, $C^{3'}$), 137.7 (1C, C^6), 140.7 (1C, C^5), 143.4 and 143.5 (2C, C^2 and C^3), 182.0 (1C, C^4), 182.8 (1C, C^1).

A solution containing 0.44 g (0.42 mmoles) of compound (XIII) in 2 ml THF was added to a mixed (Ar) solution of 50 mg (7.25 mg-atom) Li in 15 ml $EtNH_2$. The reaction mixture was decomposed for 5 min with 1 ml isoprene, 2 ml MeOH, and 1 g NH_4Cl; it was then diluted with ether and vigorously mixed in air for 40 min at 25°C. Subsequent routine processing afforded a product which was chromatographed on 20 g SiO_2. Gradient elution from hexane to ether (up to 10% of the latter) afforded 0.1 g of compound (XIII) and 0.2 g (70%) of mixture (I, Ia); mp 45-48°C (hexane).

Hydrocarbon (XVI). A 0.15 g (1.5 mmole) portion of hexanal was added at −25°C to a mixed (Ar) solution of phosphorane (XII), prepared as described above from 0.46 g (1 mmole) of compound (XV) in 30 ml THF and an equivalent amount of n-BuLi in hexane. The mixture was kept for 2 h at −25°C; it was then diluted with ether, neutralized with 1 N HCl, washed with water, and dried with $MgSO_4$. The residue (0.6 g), after removal of solvents in a vacuum, was dissolved in 30 ml hexane, purified by filtration through SiO_2, concentrated and distilled in a vacuum. A 0.11-g yield (57%) of product (XVI) was obtained as an isomeric mixture (E/Z ≈ 5:1, GLC); bp 84°C (2 mm) (cf. [11], in which the bp is 86-90°C at 15 mm). PMR spectrum (δ, ppm): 0.890 t (3H, J = 6.5 Hz, CH_3), 1.3 m (6H, CH_2), 1.585 and 1.598 s (5.4H, E,Z-isomer HC^1 and E-isomer CH_3C^6), 1.674 s (3.6H, E,Z-isomer CH_3C^2 and Z-isomer CH_3C^6), 2.0 m (6H, $CH_2C{=}C$), 5.1 m (2H, $HC{=}C$). ^{13}C NMR spectrum (δ, ppm): 13.5 (1C, C^{12}), 15.4 (0.8C, E-isomer $\underline{C}H_3C^6$), 17.1 (1C, $\underline{C}H_3C^2$), 22.1 (1C, C^{11}), 23.5 (0.2C, Z-isomer CH_3C^6), 25.0 (1C, C'), 26.2 (0.8C, Z-isomer C^4), 26.3 (0.2C, E-isomer C^4), 27.4 (1C, C^8), 29.0 and 31.0 (2C, C^8 and C^9), 31.4 (0.2C, Z-isomer C^5), 39.2 (0.8C, E-isomer C^5), 124.6 (1C, C^3), 125.0 (0.8C, E-isomer C^7), 125.7 (0.2C, Z-isomer C^7), 131.2 (0.8C, E-isomer C^2), 131.3 (0.2C, Z-isomer C^2), 134.7 (0.8C, E-isomer C^6), 134.8 (0.2C, Z-isomer C^6).

A solution was prepared at −35°C from 1.0 g (5.94 mmoles) of an isomeric mixture (E/Z ≈ 3:1) of ethers (XVII) [15] and 40 mg (0.32 mmole) CuBr in 10 ml THF. After 30 min, 8.5 ml of 1.1 M n-BuMgCl in ether was added to the mixed (Ar) solution. The mixture was kept for 30 min at −35°C, for 2 h at −10°C, and for 14 h at 25°C. Subsequent routine processing afforded 1.1 g (95%) of product (XVI) as an isomeric mixture (E/Z ≈ 4:1) identical (GLC, NMR) to that described above.

Conclusions

1. Five- and seven-stage methods were developed for converting ubiquinone-9 and the dibenzyl ether of the corresponding hydroquinone to ubiquinone-10 by use of the Wittig reaction at the key stage; the overall yield was 2 and 17%, respectively.

2. The use of a pressure of 10-14 kbar was proposed for the direct synthesis of 2-methyl(hept-2-en-6-yl)triphenylphosphonium bromide.

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GRAFT POLYMERIZATION OF CARBOHYDRATES ON THE SURFACE OF A MACROPOROUS SILICA

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The surfaces of macroporous silicas, aluminum earths and siloxane rubbers sorb and (or) denaturate many biological materials (proteins, nucleic acids, viruses). To suppress these reactions, the inorganic surface has to be modified by organic coatings. In producing various biocompatible materials (specific or related sorbents, materials with low hemosorbability, etc.), the surface of inorganic materials is modified by polysaccharide coatings [1-4]. This is achieved by adsorption of polysaccharides from solutions, followed by crosslinking of the coating formed (without chemical interaction of the organic phase with the inorganic surface) [5], or by chemical grafting of polysaccharides on the surface of the inorganic material, preliminarily modified by the corresponding organoalkoxysilane [6].

In the present work, a method is proposed for producing carbohydrate coatings covalently bonded to the inorganic surface by copolymerization of the carbohydrate monomer with epoxy groups of a modified silica. The activated surface of the macroporous glass (MPG) 1150 Å, 50 m^2/g, was treated with γ-glycidoxypropyltriethoxysilane (I)

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