SYNTHESIS OF 3E-TETRADECENOL, 3E,9E-TETRADECADIENOL, AND THEIR ACETATES STARTING FROM ACETYLCYCLOPROPANE

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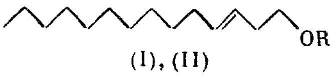
Stereospecific synthesis of the linear E-olefins mentioned in the title was realized by a general scheme that was worked out earlier by the authors and which includes as key steps homologization of the corresponding aliphatic pentakisnoraldehydes by means of trimethylsilyloxyvinylcyclopropane and $ZnBr_2$-initiated rearrangement of the intermediate cyclopropylcarbinols under the influence of Me_3SiBr.

The methodology for the regio- and stereocontrolled E-C_5-homologization of aliphatic aldehydes with acetylcyclopropane that we have worked out recently disclosed a simple way to linear E-homoallyl halides and thus to a large group of transoidal components of acetogenin pheromones of many species of insects [1-3]. In this article we discuss applications of this strategy to the synthesis of four mono- and diene C_{14}-alcohols and acetates (I)-(IV). According to chromato-mass spectroscopic data such compounds (or their stereoisomers) are part of the multicomponent formula of the sex pheromone of female reddish-brown click beetle, Melanotus fusciceps, a harmful pest of many agricultural crops that lives in the soil [4].



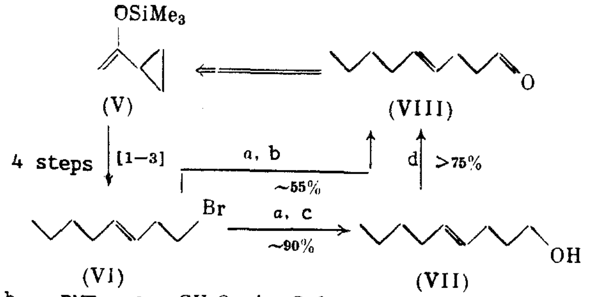
(I), (II)

(III), (IV)

R = H(I), (III); Ac(II), (IV).

In accordance with the accepted route, the synthesis of target compounds (I)-(IV) has been carried out starting from silyloxyvinylcyclopropane (V) and celapronaldehyde or its known, but rather difficultly obtainable (cf. [4]) 4E-dehydro derivative (VIII). From them were then prepared by C_1-homologization, via two independent routes, C_8-homoallyl bromide (VI), which has been prepared by us earlier [1-3] from the same silyl ether (V) and propionaldehyde (Scheme 1). Thereby, direct formulation with DMF of the easily prepared Grignard reagent of (VI) to aldehyde (VIII) proved to be somewhat less effective than its two-step synthesis from the mentioned reagent and formaldehyde, comprising oxidation of the known [4, 5] intermediate bishomoallyl alcohol (VII).

Scheme 1



a — Mg/THF; b — DMF; c — CH_2O; d — $CrO_3/Py \cdot HCl/CH_2Cl_2$.

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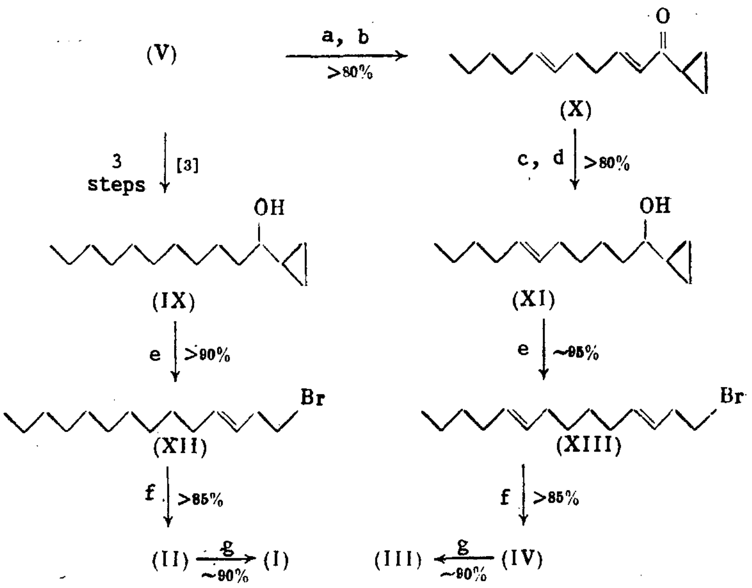
The subsequent stage in the construction of desired olefins (I)-(IV) comes down to rearrangement of the corresponding key cyclopropyl carbinols (IX) and (XI) (Scheme 2). Thereby (IX) was prepared by us earlier from celapronaldehyde and the mentioned C_5-block synthon (V) [3]. In much the same way $ZnCl_2$-catalyzed low-temperature condensation of the latter with γ,δ-unsaturated aldehyde (VIII) and then treatment of the intermediate β-ketosilyl ether (without further purification of it) in refluxing benzene in the presence of TsOH yields desired cyclopryopyldienone (X) in high overall yield. Two-step chemoselective reductive conversion of the Δ^2-1-keto fragment of molecule (X) was carried out by hydrogenation of the initially conjugated C=C bond under influence of Cu(I) hydride, generated in situ from CuBr [6], and further borohydride reduction of the crude intermediate ketone to alcohol (XI).

Scheme 2



a — (VIII)Cat: $ZnCl_2/CH_2Cl_2$, —20°; b - Cat: TsOH/refl. PhH;
c — $CuBr—NaAlH_2(OCH_2CH_2OMe)_2$/THF — PhMe, —20°;
d — $NaBH_4$/MeOH; e — Me_3SiBr-Cat: $ZnBr_2/CH_2Cl_2$, —10°;
f — AcOK-Cat: DB18C6/refl. MeCN; g — $NaOH/MeOH_{aq}$.

$ZnBr_2$-initiated cyclopropylcarbinyl rearrangement of alcohols (IX) and (XI) under influence of Me_3SiBr (cf. [1-3]) leads in practically quantitative yields to the corresponding monoene (XII) and diene (XIII) E-homoallyl bromides with a stereochemical purity of ≥97% (GLC and PMR data). Finally, acetolysis of bromides (XII) and XIII) under influence of AcOK catalyzed by dibenzo-18-crown-6 (DB18C6) gives in yields of >85% acetates (II) and (IV), which are easily saponified to corresponding alcohols (I) and (II), the first of which was prepared earlier from acetylenic precursors [7].

The structures of compounds (II)-(IV) and (X)-(XIII) discussed above and not described before were reliably confirmed by data of spectral and elemental analyses.

The attractant activity of synthesized compounds (I)-(IV) with regard to the reddish-brown click beetle is now being investigated.

EXPERIMENTAL

IR spectra were taken from CH_3Cl solutions on a UR-20 spectrometer, PMR spectra from $CDCl_3$ solutions on a Bruker WM-250 spectrometer, and mass spectra on a Varian MAT CH-6 spectrometer at an ionization voltage of 70 eV. GLC was carried out on an LKhM-80 chromatograph (column 3 m × 3 mm with 15% Carbowax 20M on Chromation N-AW-HMDS).

4E-Nonenol (VII). Through a suspension of a Grignard reagent stirred under an Ar atmosphere at −40°C and prepared from 0.8 g (4.2 mmoles) of (VI) [1-3] and 0.11 g (4.6 mmoles) of Mg in 8 ml of ether is passed for 30 min formaldehyde, prepared by pyrolysis of 0.4 g (13.3 mmoles) of paraform. The mixture is warmed up to ~25°C over 0.5 h, treated with a saturated NH_4Cl solution, and extracted with ether. The extract is washed with a saturated aqueous NaCl solution, dried over $MgSO_4$, and evaporated under vacuum. The residue (0.7 g) is chromatographed over 30 g of SiO_2. Gradient elution from hexane to ether (till 20% of the latter) yielded 0.54 g (90%) of (VII) [4, 5] as a colorless liquid, bp 74°C (2 mm), n_D^{20} 1.4472. PMR spectrum (δ, ppm, J, Hz): 0.89 t (3H, CH_3, J = 7), 1.2-1.4 m (4H, HC^7, HC^8), 1.63 quintet (2H, HC^2, J = 7), 1.9-2.1 m (4H, HC^3, HC^6), 3.66 t (2H, HC^1, J = 7), 5.43 m (2H, HC^4, HC^5).

4E-Nonenal (VIII). To a suspension of a Grignard reagent stirred under an Ar atmosphere at −30°C and freshly prepared from 1.67 g (8.7 mmoles) of (VI) and 0.22 g (9.2 mmoles) of Mg in 10 ml of ether is added over 10 min a solution of 1.4 g (19.2 mmoles) of DMF in 3 ml of ether. The reaction mixture is heated to ~25°C over 1 h and after 1.5 h it is treated as described in the preceding experiment. Yield ~1 g of material, which is chromatographed over 50 g of SiO_2. Gradient elution with hexane to 5% ether in hexane yielded 0.66 g (54%) of (VIII) [4] as a colorless liquid, bp 81°C (17 mm), n_D^{20} 1.4382. PMR spectrum (δ, ppm, J, Hz): 0.90 t (3H, CH_3, J = 7), 1.2-1.4 m (4H, HC^7, HC^8), 1.99 br. q (2H, HC^6, J = 7), 2.33 br. q (2H, HC^3, J = 7), 2.49 br. t (2H, HC^2, J = 7), 5.42 m (2H, HC^4, HC^5), 9.77 t (1H, HC^1, J = 1.8).

To a stirred suspension of 1.8 g (4.8 mmoles) pyridine chlorochromate [8] in 7 ml of CH_2Cl_2 is added in one portion a solution of 0.45 g (3.17 mmoles) of (VII) in 2 ml of CH_2Cl_2. After 1.5 h the mixture is diluted with ether, filtered through a layer (~5 cm) of SiO_2, the filtrate is evaporated, and the residue is distilled under vacuum. Yield 0.34 g (76%) of (VIII), identical (GLC, PMR) with the sample of this compound as described above.

1-Cyclopropyl-2E,6E-undecadienone-1 (X). To a suspension, stirred at −20°C under an Ar atmosphere, of 0.47 g (3.36 mmoles) of (VIII) and 90 mg (0.67 mmoles) of $ZnCl_2$ in 7 ml of CH_2Cl_2 is added over 5 min a solution of 0.65 g (4.2 mmoles) of (V) [9] in 2 ml of CH_2Cl_2, the mixture is stirred at −20°C for 2 h (checked with GLC), treated at 0°C with a saturated aqueous $NaHCO_3$ solution, and extracted with ether. The extract is washed with a saturated aqueous NaCl solution, dried over $MgSO_4$, and evaporated under vacuum. A solution of the residue (~1.2 g) in 30 ml of benzene containing 0.05 g of $TsOH{\cdot}H_2O$ is refluxed on a Dean-Stark separator until the separation of water stops (1.5 h, checked with GLC), then extracted with saturated aqueous solutions of $NaHCO_3$ and NaCl, dried over $MgSO_4$, and evaporated under vacuum. The residue is distilled. Yield 0.56 g (81%) of (X) as a colorless oil, bp 82°C (0.03 mm), n_D^{20} 1.4848. IR spectrum (ν, cm^{-1}): 905, 970, 1030, 1060, 1090, 1105, 1200, 1230, 1390, 1415, 1440, 1465, 1625, 1660, 1680, 2860, 2930, 2960. UV spectrum (EtOH, λ_{max}, nm): 226 (ε 17,500), 278 (ε 1030). PMR spectrum (δ, ppm, J, Hz): 0.8-1.1 m (7H, CH_3, CH_2 of cyclopropane), 1.2-1.4 m (4H, HC^9, HC^{10}), 2.00 br. q (2H, HC^8), 2.1-2.4 m (5H, CH of cyclopropane, HC^4. HC^5), 5.43 m (2H, HC^6, HC^7), 6.22 d (1H, HC^2, J = 16), 6.90 d.t (1H, HC^3, J = 16 and 7). Mass spectrum, m/z (I, %): M+ 206(1), 188(2), 168(2), 137(2), 136(2), 135(18), 128(5), 121(5), 111(8), 110(100), 95(42), 81(10), 79(10), 69(36), 55(92), 41(58). Found, %: C 81.52, H 10.93. $C_{14}H_{22}O$. Calculated, %: C 81.50, H 10.75.

1-Cyclopropyl-6E-undecenol-1 (XI). To a suspension of 0.4 g (1.94 mmoles) of (X) and 2.79 g (19.4 mmoles) of CuBr in 20 ml of THF that is stirred at −70°C under an Ar atmosphere is added over 5 min 5.7 ml of a 3.4 M $NaAlH_2(OCH_2OMe)_2$ solution (19.4 mmoles) in PhMe. The mixture is warmed up to −20°C over 30 min, stirred at that temperature for 1 h (checked with GLC), treated at 0°C with a saturated aqueous NH_4Cl solution, and extracted with ether. The extract is washed with a saturated aqueous NaCl solution, dried over $MgSO_4$, and evaporated under vacuum. To a solution of the residue (~0.5 g) in 20 ml of MeOH is added 0.3 g (7.8 mmoles) of $NaBH_4$, the mixture is stirred at ~25°C for 20 min (checked with TLC), diluted with water, and extracted with a 1:1 mixture of ether and hexane. The extract is washed with a saturated aqueous NaCl solution, dried over $MgSO_4$, evaporated under vacuum, and the residue (~0.5 g) is chromatographed over 20 g of SiO_2. Gradient elution with hexane to ether (until 10% of the latter) yielded 0.33 g (81%) of (XI) as a colorless oil, bp 90°C (0.05 mm), n_D^{22} 1.4645. IR spectrum (ν, cm^{-1}): 825, 920, 970, 1020, 1050, 1070, 1210, 1240, 1380, 1410, 1435, 1465, 2860, 2930, 2960, 3005. PMR spectrum (δ, ppm, J, Hz): 0.2-0.6 m (4H, CH_2 of cyclopropane), 0.8-1.0 m (1H, CH), 0.89 t (3H, CH_3, J = 7), 1.2-1.7 m (10H, CH_2), 1.9-2.1 m (4H, HC^5, HC^8), 2.87 m (1H, HC^1), 540 m (2H, HC^6, HC^7). Mass spectrum, m/z (I, %): M^+ 210(1), 192(1), 177(1), 167(1), 164(2), 163(3), 135(37), 121(38), 97(29), 95(37), 93(30), 81(59), 71(81), 67(70), 55(75), 43(100), 41(87). Found, %: C 79.95, H 12.48. $C_{14}H_{26}O$. Calculated, %: C 79.94, H 12.46.

1-Bromo-3E-tetradecene (XII). To a suspension of 0.26 g (1.2 mmoles) of (IX) [3] and 60 mg (0.27 mmole) of $ZnBr_2$ in 8 ml of CH_2Cl_2 stirred under an Ar atmosphere at −10°C is added over 10 min a solution of 0.41 g (2.7 mmoles) of Me_3SiBr in 3 ml of CH_2Cl_2, the mixture is stirred at −10°C for 1.5 h (checked with GLC and TLC), then treated at 0°C with a saturated aqueous $NaHCO_3$ solution, and extracted with ether. The extract is washed with a saturated aqueous NaCl solution, dried over $MgSO_4$, evaporated under vacuum, and the residue is distilled. Yield 0.31 g (92%) of (XII) as a colorless oil, bp 90°C (0.04 mm), n_D^{23} 1.4688. IR spectrum (ν, cm^{-1}): 565, 640, 910, 1060, 1110, 1265, 1380, 1465, 2860, 2930, 2970, 3010. PME spectrum (δ, ppm, J, Hz): 0.90 t (3H, CH_3, J = 7), 1.2-1.4 m (16H, CH_2), 2.01 q (2H, HC^5, J = 7), 2.57 q (2H, HC^2, J = 7), 3.38 t (2H, HC^1, J = 7), 5.39 dt (1H, HC^3, J = 15 and 7), 5.55 d.t (1H, HC^4, J = 15 and 7). Mass spectrum, m/z (I, %): M^+ 276(4) and 274(4), 150(25), 148(26), 111(12), 109(8), 97(37), 83(46), 81(28), 70(35), 69(74), 67(52), 57(58), 55(85), 43(86), 41(100). Found, %: C 60.76, H 9.69, Br 28.91. $C_{14}H_{27}Br$. Calculated, %: C 61.09, H 9.89, Br 29.03.

1-Bromo-3E,9E-tetradecadiene (XIII). In much the same way, from 0.53 g (2.5 mmoles) of (XI), 0.12 g (0.54 mmole) of $ZnBr_2$, and 0.85 g (5.5 mmoles) of Me_3SiBr in 22 ml of CH_2Cl_2 was obtained 0.65 g (94%) of (XIII) as a colorless oil, bp 87°C (0.05 mm) n_D^{24} 1.4812. IR spectrum (ν, cm^{-1}): 570, 640, 970, 1270, 1380, 1435, 1460, 1620, 2860, 2930, 2960. PMR spectrum (δ, ppm, J, Hz): 0.89 t (3H, CH_3, J = 7), 1.2-1.4 m (8H, CH_2), 1.9-2.1 m (6H, HC^5, HC^8, HC^{11}), 2.55 q (2H, HC^2, J = 7), 3.38 t (2H, HC^1, J = 7), 5.30-5.45 m (3H, HC^3, HC^9, HC^{10}), 5.55 d.t (1H, HC^4, J = 15 and 7). Mass spectrum, m/z (I, %): M^+ 274(3) and 272(3), 204(4), 203(4), 202(6), 162(9), 160(9), 138(23), 110(10), 109(16), 96(30), 95(47), 82(51), 81(100), 67(98), 55(86), 54(47), 41(84). Found, %: C 61.64, H 9.29, Br 29.21. $C_{14}H_{25}Br$. Calculated, %: C 61.54, H 9.22, Br 29.24.

3E-Tetradecenyl Acetate (II). A mixture of 1.91 g (6.9 mmoles) of (XII), 3.38 g (34.5 mmoles) of AcOK, 50 mg (0.1 mmole) of DB18C6, and 60 ml of MeCN is refluxed for 5 h, filtered, the filtrate is diluted with water, and extracted with ether. The extract is washed with a saturated NaCl solution, dried over $MgSO_4$, evaporated under vacuum, and the residue (1.6 g) is chromatographed over 40 g of SiO_2. Elution with a 95:5 hexane–ether mixture yielded 1.53 g (87%) of (II) as a colorless oil, bp 91°C (0.03 mm), n_D^{21} 1.4448. IR spectrum (ν, cm^{-1}): 975, 1040, 1250, 1370, 1390, 1470, 1735, 2860, 2935, 2960. PMR spectrum (δ, ppm, J, Hz): 0.89 t (3H, CH_3, J = 7), 1.2-1.4 m (16H, CH_2), 1.99 br.q (2H, HC^5, J = 7), 2.06 s (3H, CH_3CO), 2.32 br. q (2H, HC^2, J = 7), 4.07 t (2H, HC^1, J = 7), 5.37 d.t (1H, HC^3, J = 15 and 7), 5.52 d.t (1H, HC^4, J = 15 and 7). Mass spectrum, m/z (I, %): 194(32), 110(35), 109(30), 97(29), 96(86), 95(48), 83(44), 82(93), 81(74), 68(100), 67(90), 60(48), 55(73), 54(90), 45(69). Found %: C 75.73, H 11.86. $C_{16}H_{30}O_2$. Calculated, %: C 75.54, H 11.89.

3E,9E-Tetradecadienyl Acetate (IV). In much the same way from 0.49 g (1.8 mmoles) of (XIII), 0.88 g (9.0 mmoles) of AcOK and 10 mg of DB18C6, and 20 ml of MeCN was obtained 0.39 g (86%) of (IV) as a colorless oil, bp 88°C (0.02 mm), n_D^{20} 1.4529. IR spectrum (ν, cm^{-1}): 970, 1035, 1215, 1250, 1370, 1390, 1435, 1460, 1735, 2860, 2930, 2960. PMR spectrum (δ, ppm, J, Hz): 0.89 t (3H, CH_3, J = 7), 1.2-1.4 m (8H, CH_2), 1.9-2.1 m (6H, HC^5, HC^8, HC^{11}), 2.06 s (3H, CH_3CO), 2.31 br. q (2H, HC^2, J = 7), 4.08 t (2H, HC^1, J = 7), 5.3-5.4 m (3H, HC^3, HC^9, HC^{10}), 5.51 d.t (1H, HC^4, J = 15 and 7). Mass spectrum m/z (I, %): 192(9), 138(9), 135(21), 121(22), 95(24), 82(25), 81(36), 80(35), 67(68), 55(53), 54(24), 43(100), 41(47). Found, %: C 76.34, H 11.36. $C_{16}H_{28}O_2$. Calculated, %: C 76.14, H 11.18.

3E-Tetradecenol (I). To a solution of 0.9 g (3.5 mmoles) of (II) in 5 ml of MeOH is added in one portion, a solution of 0.43 g (10.6 mmoles) of NaOH in 1 ml of water. After 5 min the mixture is evaporated under vacuum, the residue is diluted with water, and extracted with ether. The extract is washed with a saturated NaCl solution, dried over $MgSO_4$, evaporated under vacuum, and the residue is distilled. Yield 0.66 g (88%) of (I) [7] as a colorless oil, bp 97°C (0.03 mm), n_D^{22} 1.4565. IR spectrum (ν, cm^{-1}): 970, 995, 1385, 1415, 2860, 2930, 3010, 3620. PMR spectrum (δ, ppm, J, Hz): 0.89 t (3H, CH_3, J = 7), 1.2-1.4 m (16H, CH_2), 2.02 br. q (2H, HC^5, J = 7), 2.28 br. q (2H, HC^2, J = 7), 3.63 t (2H, HC^1, J = 7), 5.38 d.t (1H, HC^3, J = 15 and 7), 5.57 d.t (1H, HC^4, J = 15 and 7). Mass spectrum, m/z (I, %): M^+ 212(1), 194(7), 132(8), 109(20), 97(28), 96(45), 95(34), 83(48), 87(70), 81(57), 71(29), 69(63), 68(87), 67(60), 57(59), 56(34), 55(100), 54(34), 43(74), 41(74). Found, %: C 79.43, H 13.45. $C_{14}H_{28}O$. Calculated, %: C 79.18, H 13.29.

3E,9E-Tetradecadienol (III). In much the same way from 0.23 g (0.9 mmole) of (IV) and 0.11 g (2.7 mmoles) of NaOH in 3 ml of MeOH and 0.5 ml of water was obtained 0.17 g (90%) of (III) as a colorless oil, bp 84°C (0.03 mm), n_D^{23} 1.4651. IR spectrum (ν, cm^{-1}): 860, 870, 915, 975, 1050, 1185, 1240, 1340, 1385, 1440, 1465, 1670, 2860, 2940, 3020, 3450, 3630. PMR spectrum (δ, ppm, J, Hz): 0.90 t (3H, CH_3, J = 7), 1.2-1.4 m (8H, CH_2), 1.9-2.1 m (6H, HC^5,

HC^8, HC^{11}), 2.28 q (2H, HC^2, J = 7), 3.64 t (2H, HC^1, J = 7), 5.3-5.5 m (3H, HC^3, HC^9, HC^{10}), 5.56 d.t (1H, HC^4, J = 15 and 7). Mass spectrum, m/z (I, %): M^+ 210(3), 192(3), 121(14), 109(16), 107(14), 96(27), 95(37), 93(26), 82(41), 81(60), 80(33), 79(40), 69(33), 68(44), 67(81), 55(100), 54(48), 43(29), 41(86). Found, %: C 79.97, H 12.56. $C_{14}H_{26}O$. Calculated, %: C 79.94, H 12.46.

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ELECTROCHEMICAL CLEAVAGE OF THE DOUBLE BOND OF 1-ALKENYLARENES

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571.3:547.538.1

A study has been made of the electrochemical cleavage of the double bond of propenylbenzene (Ia) and p-propenylanisole (Ib), which takes place upon anodic oxidation of (Ia, b) in alcoholic solutions of sodium trifluoroacetate and other electrolytes and which leads to conversion of (Ia, b) to benzaldehyde dialkylacetals. Conditions are found that provide for highly selective (>80%) conversion of (Ib) and p-propenyltoluene to p-methyl- and p-methoxybenzaldehyde dimethylacetals.

1-Alkenylarenes (ALARs) (anethole, isosafrole, etc.) are used as starting materials for the production of important benzaldehydes (oubepine, piperonal, and others) by means of oxidative cleavage of the double bond of the ALAR under the effect of bichromates and other oxidizers [1]. The basic shortcoming of this process is the formation of a large amount of hazardous wastes.

We established earlier that cleavage of the double bond of ALARs, for example, styrene, trans-stilbene, propenylbenzene, p-propenyltoluene, and p-propenylanisole can be accomplished electrochemically in an alcoholic medium [2].

$$\mathrm{Ar{-}CH{=}CH{-}R} \xrightarrow[\text{C-anode}, \ 4-8F, \ 55^{\circ}]{CH_3OH/CF_3COONa} \mathrm{ArCH(OCH_3)_2} + \mathrm{RCH(OCH_3)_2}$$

The basic condition for successful realization of this process is a low concentration of the ALAR (less than 0.45 mole/liter). At high ALAR concentrations the conversion of ALARs to acetals is suppressed by well-known electrochemical processes of intermolecular oxidative dimerization and cyclodimerization [3-9].

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