July, 1987] © 1987 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 60, 2429—2433 (1987)

Synthesis of (*E*,*E*)- and (*Z*,*Z*)-1,5-Cycloalkadienes by Means of the Electrochemical Cyclization of Allylic 1,ω-Dibromides

Masao Tokuda,* Kuniaki Satoh, and Hiroshi Suginome*
Division of Organic Synthesis, Department of Chemical Process Engineering,
Faculty of Engineering, Hokkaido University, Sapporo 060

(Received January 21, 1987)

Electrolysis of (*E*,*E*)-1,*n*-dibromo-2,(*n*-2)-alkadienes (n=12, 14) in tetrahydrofuran gave the corresponding twelve or fourteen-membered (*E*,*E*)-1,5-cycloalkadienes, albeit in low yields, together with (*E*)-4-vinylcycloalkenes and isomeric alkadienes. Similar electrolysis of (*Z*,*Z*)-1,*n*-dibromo-2,(*n*-2)-alkadienes (n=10, 12, 14) gave the corresponding ten, twelve, or fourteen-membered (*Z*,*Z*)-1,5-cycloalkadienes in 11 to 13% yields, with the accompanying formation of (*Z*)-4-vinylcycloalkenes and isomeric alkadienes.

Electroreductive cyclization of 1,3-dihalides has been reported to be useful for the preparation of substituted[1–5] and strained cyclopropanes.[1] Cyclobutane derivatives[1,4] have also been prepared by the electrochemical reduction of 1,4-dihalides. However, higher cycloalkanes have not been prepared by the electrolysis of simple aliphatic dihalides. We ourselves have previously reported that the three to seven-membered cycloalkanes are obtained by the electrochemical reductive cyclization of 1,ω-dibromides with alkoxycarbonyl groups at their terminal carbons.[6] A similar cyclization of 1,5-dibromopentanes with an electron-withdrawing group at their one termini was also reported recently.[7] As one of the extensions of our study of the electroreductive cyclization of 1,ω-dibromides we studied the preparation of even higher cycloalkanes by means of the electrochemical cyclization of (*E*,*E*)- or (*Z*,*Z*)-1,*n*-dibromo-2,(*n*-2)-alkadienes. We now report that ten, twelve, and fourteen-membered (*E*,*E*)- or (*Z*,*Z*)-1,5-cycloalkadienes can be prepared by the electrolysis of the corresponding (*E*,*E*)- or (*Z*,*Z*)-allylic dibromides, albeit in low yields.

A transition metal-catalyzed cyclization of allylic dibromides has been reported to lead generally to more stable (*E*,*E*)-1,5-cycloalkadiene rather than to (*Z*,*Z*)-dienes, regardless of the geometry of the double bonds of the starting allylic dibromides.[8,9] For the preparation of (*Z*,*Z*)-1,5-cycloalkadienes only a few methods have been reported, however, (*Z*,*Z*)-1,5-Cyclotetradecadiene was prepared by partial hydrogenation of 1,5-cyclotetradecadiynes with a Lindler catalyst.[10] (*Z*,*Z*)-1,5-Cyclododecadiene was formed, as one of several isomers, either in the photochemical isomerization of its (E,E)-isomer[11] or in the hydrogenation of 1,5,9-cyclododecatriene.[12] (*Z*,*Z*)-1,5-Cyclodecadiene was similarly formed either in the photochemical isomerization of its (E,Z)-isomer[13] or in the partial hydrogenation of cyclodecatrienes.[14] Of these (*Z*,*Z*)-1,5-cycloalkadienes, (*Z*,*Z*)-1,5-cyclododecadiene has not been isolated in a pure form and the stereochemistries of (*Z*,*Z*)-1,5-cyclotetradecadiene and (*Z*,*Z*)-1,5-cyclododecadiene have not been established in an unambiguous manner.

Results and Discussion

The starting (*E*,*E*)-allylic dibromides **1**, **5**, and **10** were readily prepared by reduction of the corresponding 2,(*n*-2)-alkadiyn-1,*n*-diols with lithium aluminum hydride, followed by bromination.[8,9] On the other hand, the (*Z*,*Z*)-allylic dibromides **11**, **15**, and **19** were prepared by partial hydrogenation of the corresponding alkadiyne diols with a Lindler catalyst.[8,9]

Electrochemical reduction of (*E*,*E*)- and (*Z*,*Z*)-allylic dibromides was carried out at a constant current in tetrahydrofuran (THF) containing 0.1 M[†] tetrabutylammonium perchlorate (n-Bu_4NClO_4) as a supporting electrolyte. Each allylic dibromide was gradually added to the cathodic solution with a microfeeder. The electricity passed was 2.2 Faradays per mole of the dibromide. The electrochemical reduction of (*E*,*E*)-1,14-dibromo-2,12-tetradecadiene (**1**) afforded three major products **2** (8%), **3** (5%), and **4** (19%) which could be separated by preparative GLC (Scheme 1). High resolution mass spectrometry indicated that **2** and **3** were isomeric and had the molecular formula $C_{14}H_{24}$. The ^{1}H NMR spectrum of **2** exhibited overlapped multiplets due to the four olefinic protons of the two unconjugated vinyl groups at δ 5.28. The geometry of the double bonds of **2** was deduced from the IR spectrum. (E)-Double bonds of the medium-sized cycloalkenes give rise to a medium to a strong band at 965—980 cm^{-1} while (Z)-double bonds at 700—710 cm^{-1}.[15,16] (E)-Double bonds of several 1,5-cycloalkadienes give a characteristic band at 960—970 cm^{-1} while (Z)-double bonds at 695—710 cm^{-1}.[8,9,16,17] A strong band at 980 cm^{-1} in the IR spectrum of cycloalkadiene **2** indicated that the configurations of the two double bonds are (E).

The ^{1}H NMR spectrum of **3** showed characteristic signals due to a vinyl group and its IR spectrum showed a characteristic band due to an (E) double bond at 970—980 cm^{-1}. On the basis of these results an (*E*)-4-vinylcyclododecene structure was assigned to **3**. The alkadiene **4** isolated was a mixture of two

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[†] 1 M=1 mol dm $^{-3}$.

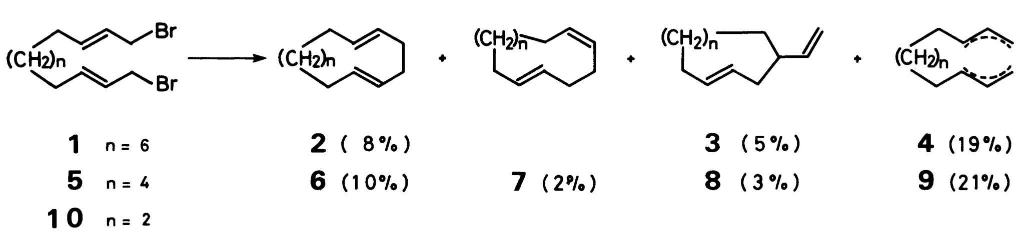
isomers and the structure of the major isomer was determined to be (*E,E*)-2,12-tetradecadiene (**4a**) as described in the experimental section.

Similar electrolysis of (*E,E*)-1,12-dibromo-2,10-dodecadiene (**5**) gave (*E,E*)-1,5-cyclododecadiene (**6**) (10%), (*E*)-4-vinylcyclodecene (**8**) (3%), (*E,Z*)-1,5-cyclododecadiene (**7**) (2%), and a mixture of isomeric dodecadienes (**9**) (21%) (Scheme 1). The structures of these products [including the geometries of their double bonds] were determined by MS, IR, and ^{1}H NMR spectra; the details are described in the experimental section. The structure of **7** was confirmed additionally by a direct comparison with an authentic specimen prepared by the selective reduction of (*E,E,Z*)-1,5,9-cyclododecatriene with hydrazine.[16]

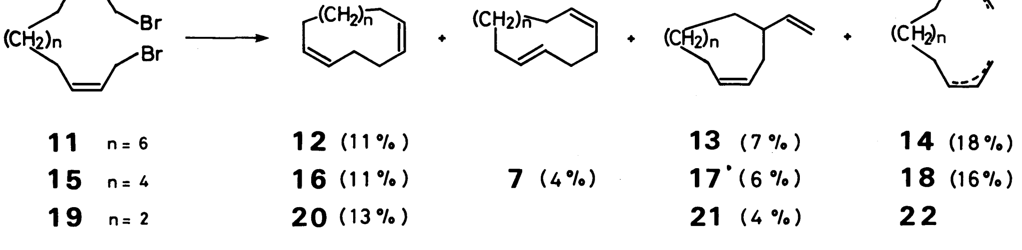
Electrochemical reduction of (*E,E*)-1,10-dibromo-2,8-decadiene (**10**), however, gave a complex mixture of products that contained a large amount of isomeric decadienes.

We then turned our attention to the electrolysis of (*Z,Z*)-allylic bromides **11**, **15**, and **19**. Electrochemical reductions of (*Z,Z*)-1,14-dibromo-2,12-tetradecadiene (**11**), (*Z,Z*)-1,12-dibromo-2,10-dodecadiene (**15**), and (*Z,Z*)-1,10-dibromo-2,8-decadiene (**19**) afforded (*Z,Z*)-1,5-cycloalkadienes (**12**, **16**, and **20**) in 11—13% yields and (*Z*)-4-vinylcycloalkenes (**13**, **17**, and **21**) in 4—7% yields as outlined in Scheme 2. The structures of the above products [including their geometries] were deduced by MS, IR, and ^{1}H NMR spectroscopy. Thus, cycloalkadienes **12**, **16**, and **20** showed bands 715, 720, and 700 cm^{-1} respectively in their IR spectra, indicating (Z,Z)-geometries of their isolated double bonds. The ^{1}H NMR of **16** exhibited a double triplet at δ 5.26 and a multiplet at δ 5.60 that were due to the olefinic protons as well as two multiplets at δ 2.10 and δ 1.35. Irradiation at δ 2.10 collapsed the former two olefinic signals to two doublets each with J=10.7 Hz. Since the coupling constants of the olefinic protons of seven to ten-membered (*Z*)-cycloalkenes are in the range of 10.3—10.8 Hz,[18] we assigned Z-configurations to the geometry of the double bonds of **16**. Similar decoupling studies on the ^{1}H NMR spectra of **12** and **20** by 400 MHz NMR spectrometer indicated that the coupling constants of the four olefinic protons of **12** were 10.7 Hz in each case while those of two pairs of olefinic protons of **20** were 10.7 and 11.2 Hz. On the basis of these results, (Z)-configuration is assigned to all the double bonds of **12** and **20**. The IR showed that 4-vinylcycloalkenes **13**, **17**, and **21** have bands at 690—705 cm^{-1}; (Z)-configuration is therefore also assigned to their double bonds. The coupling constant of the olefinic protons of the internal double bond of **13** was found to be 10.0 Hz; this was consistent with its (Z)-geometry. In addition to these cyclic olefins, electrolysis of **15** gave (*E,Z*)-cyclic diene **7** in a 4% yield. It was identical with **7** obtained by the electrolysis of **5**. Electrolysis of **11** and **15** also gave a mixture of the isomeric alkadienes **14** and **18** in 18% and 16% yields. The major isomers of **14** and **18**, separated by preparative GLC, were shown to be (*Z,Z*)-2,12-tetradecadiene (**14c**) and (*Z,Z*)-2,10-dodecadiene (**18c**), respectively.

Cyclic voltammetry of the starting dibromides and the electrode potential during the electrolysis indicated that such an electrolysis as the one we have described involves a two-electron reduction of the carbon–bromine bond. Cyclic voltammetry has shown that the reduction peaks of **5**, **15**, and crotyl bromide in an *N,N*-dimethylformamide (DMF) solution are −2.00, −2.00, and −1.81 V vs. Ag/AgI and the reduction peak of crotyl bromide in a THF solution is −1.65 V vs. Ag/AgI. Although the present elec-



Scheme 1.



Scheme 2.

trochemical reduction was carried out at a constant current in a THF solution, the working electrode in the electrolysis of **15** was kept at the potential ranging from −1.6 V to −1.8 V, which nearly corresponded to the reduction potential of **15**. These results suggest that the electroreductive cyclization described above proceeds via an intramolecular nucleophilic attack at a bromine-bearing allylic carbon atom by the allylic carbanion which is generated by a two-electron reduction of the carbon–bromine bond.19) In agreement with this mechanism the geometry of at least one of the double bonds in each of the starting dibromide was retained in all the cycloalkadienes obtained.

During such cyclizations as these, a partial interconversion between (E) and (Z) geometries may take place,20) as the formation of (*E,Z*)-cycloalkadiene **7** from (*E,E*)-dibromide **5** and (*Z,Z*)-dibromide **15** indicates. Vinylcycloalkenes **3**, **8**, **13**, **17**, and **21** are likely to be formed via either an intramolecular nucleophilic attack on the bromine-carrying carbon atom by an allylic carbanion centered on the C-3 or by an intramolecular attack on the C-3 carbon by an allylic carbanion centered on the terminal carbon with allylic rearrangement.

Experimental

Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl and distilled before use. The IR spectra were obtained with a Hitachi Model 285 spectrometer. The ^{1}H NMR spectra in $CDCl_3$ were measured with a JEOL FX 100 (100 MHz) and a JEOL FX 400 (400 MHz) (Faculty of Science of this University), using tetramethylsilane as an internal reference. Mass spectra were obtained with a JEOL JMS-D300 mass spectrometer (Faculty of Agriculture). Quantitative GLC analyses were carried out with a Hitachi 063 instrument by the internal standard method.

Preparation of Allylic Dibromides. (*E,E*)-Allylic dibromides **1**, **5**, and **10** were prepared according to an established procedure.8,9) Since purification of these dibromides by distillation or column chromatography led to decomposition, the prepared dibromides were therefore immediately subjected to electrolysis without further purification. The spectral data of the (*E,E*)-allylic dibromides are recorded below.

(*E,E*)-1,14-Dibromo-2,12-tetradacadiene (1): n^{20} 1.5089; IR (neat) 3030, 1660, 965 cm^{-1}; ^{1}H NMR ($CDCl_3$)9) δ=1.28 (bs, 12H), 2.02 (m, 4H), 3.94 (d, 4H, *J*=5.9 Hz), 5.71 (m, 4H); MS *m/z* (rel intensity) 273 (M^+ −Br, 1.0), 271 (M^+ −Br, 1.3), 109 (75), 97 (41), 95 (100), 83 (69), 81 (63), 69 (47), 67 (73), 55 (92).

(*E,E*)-1,12-Dibromo-2,10-dodecadiene (5): n^{20} 1.5237; IR (neat) 3030, 1660, 963 cm^{-1}; ^{1}H NMR ($CDCl_3$)9) δ=1.32 (m, 8H), 2,06 (m, 4H), 3.95 (d, 4H, *J*=5.9 Hz), 5.72 (m, 4H); MS *m/z* (rel intensity) 326 (0.23), 324 (0.40), 322 (0.22), 163 (29), 109 (29), 95 (84), 81 (100), 69 (36), 67 (90), 55 (70). Found: m/z 323.9932. Calcd for $C_{12}H_{20}Br_2$: M, 323.9913.

(*E,E*)-1,10-Dibromo-2.8-decadiene (10): n^{20} 1.5291; IR (neat) 3030, 1660, 965 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.39 (m, 4H), 2.04 (m, 4H), 3.94 (d, 4H), 5.72 (m, 4H). MS *m/z* (rel intensity) 296 (0.17), 135 (56), 93 (40), 81 (79), 79 (38), 67 (100), 53 (48). Found: *m/z* 295.9621. Calcd for $C_{10}H_{16}Br_2$: M, 295.9599.

(*Z,Z*)-Allylic dibromides **11**, **15**, and **19** were prepared by bromination of (*Z,Z*)-alkadiene diols; these were obtained by hydrogenation of the corresponding 2, (*n*-2)-alkadiyn-1, *n*-diols by a Lindler catalyst.8,9) The dibromides were subjected to electrolysis without any further purification.

(*Z,Z*)-1,14-Dibromo-2,12-tetradacadiene (11): n^{20} 1.5199; IR (neat) 3030, 1645, 720—750 (br) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.31 (bs, 12H), 2.13 (m, 4H), 4.00 (d, 4H), 5.66 (m, 4H); MS *m/z* (rel intensity) 273 (M^+ −Br, 0.9), 271 (M^+ −Br, 1.2), 109 (65), 97 (32), 95 (100), 83 (58), 81 (71), 69 (44), 67 (85).

(*Z,Z*)-1,12-Dibromo-2,10-dodecadiene (15): n^{20} 1.5310; IR (neat) 3030, 1645, 720—750 (br) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.33 (bs, 8H), 2.11 (m, 4H), 3.88 (d, 4H), 5.61 (m, 4H); MS *m/z* (rel intensity) 326 (0.20), 324 (0.38), 322 (0.21), 163 (26), 109 (32), 95 (80), 81 (100), 69 (41), 67 (91), 55 (70), 54 (35), 53 (41). Found: *m/z* 323.9890. Calcd for $C_{12}H_{20}Br_2$: M, 323.9913.

(*Z,Z*)-1,10-Dibromo-2,8-decadiene (19): n^{20} 1.5381; IR (neat) 3030, 1645, 720—750 (br) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.44 (m, 4H), 2.12 (m, 4H), 3.98 (d, 4H), 5.65 (m, 4H); MS *m/z* (rel intensity) 298 (0.15), 296 (0.29), 294 (0.17), 135 (54), 93 (34), 81 (63), 79 (30), 67 (100), 53 (40). Found: *m/z* 295.9576. Calcd for $C_{10}H_{16}Br_2$: M, 295.9599.

General Procedure for Electrolysis. For most of the electrolyses, we used a normal undivided cell (2.8 cm dia.) equipped with a magnetic stirrer, a reflux condenser, and a serun cap for the introduction of nitrogen gas. Electrolysis was carried out under a nitrogen atmosphere at a constant current (20 mA cm^{-2}) using two platinum electrodes (2×2 cm^2). Allylic dibromide (0.6—1.0 mmol) dissolved in 1 ml of THF was added to a 20 ml of THF solution containing 0.1 M Bu_4NClO_4 over a period of 3—4 h with a micro-feeder. The electricity passed was 2.2 Faradays per mole of the dibromide. After electrolysis, most of THF had been evaporated and the residue was dissolved in diethyl ether. The ethereal solution was washed with water and dried over magnesium sulfate. A column chromatography (silica gel; hexane) of the reaction mixture gave a mixture of cycloalkadienes and alkadienes which was subjected to a preparative GLC (Carbowax 20M 15%, 150—170 °C) to give pure products. Yields of the products were determined by GLC using an internal standard method and were based on the starting allylic dibromides employed. An amount of the unreacted allylic dibromides was not determined because of their instability in the GLC column.

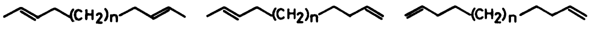
Spectral data of the products obtained by electrolysis are recorded below.

(*E,E*)-1,5-Cyclotetradecadiene (2):9) IR (neat) 3070, 980 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.29 (bs, 12H), 1.96 and 2.11 (bs and m, total 8H), 5.28 (m, 4H); MS *m/z* (rel intensity) 192 (M^+, 7), 95 (57), 82 (54), 81 (100), 80 (95), 68 (62), 67 (97), 55 (50), 54 (99). Found: *m/z* 192.1859. Calcd for $C_{14}H_{24}$: M, 192.1876. An attempt to determine the coupling constant between olefinic protons of **2** by decoupling technique was unsuccessful.

(*E*)-4-Vinylcyclododecene (3): IR (neat) 990, 978, 915 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.30 (s, 14H), 2.07 (m, 5H), 4.9—5.1 (m, 2H), 5.41 (m, 2H), 5.6—6.0 (m, 1H); MS *m/z* (rel intensity)

192 (M^+, 2), 95 (22), 82 (49), 81 (92), 80 (77), 68 (72), 67 (95), 55 (65), 54 (100). Found: *m/z* 192.1905. Calcd for $C_{14}H_{24}$: M, 192.1878.

A Mixture of Isomeric Tetradecadiene (4): IR (neat) 3020, 1640, 965, 910 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.27 (bs, CH_2), 1.64 (d, CH_3), 1.97 (bs, =$CHCH_2$–), 4.8—5.1 (m, =CH_2), 5.41 (m, –CH=CH–), 5.5—6.1 (m, –CH=CH_2); MS *m/z* (rel intensity) 194 (M^+, 4), 96 (26), 95 (25), 82 (39), 81 (37),69 (32), 68 (100), 67 (31), 55 (96). Found: *m/z* 194.2045. Calcd for $C_{14}H_{26}$: M, 194.2035. Tetradecadiene **4** was proved to be a 74:26 mixture of (*E*,*E*)-2, 12-tetradecadiene (**4a**) and (*E*)-1,12-tetradecadiene (**4b**).



n=6 **4a** **4b**
n=4 **9a** **9b** **9c**

(*E*,*E*)-1,5-Cyclododecadiene (6):[9] IR (neat) 3025, 973, 927 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.19 (m, 4H), 1.42 (bs, 4H), 2.03 and 2.12 (m and bs, total 8H), 5.10 (m, 4H); MS *m/z* (rel intensity) 164 (M^+, 4), 121 (65), 81 (81), 67 (100), 54 (99). Found: *m/z* 164.1569. Calcd for $C_{12}H_{20}$: M, 164.1564.

(*E*,*Z*)-1,5-Cyclododecadiene (7): IR (neat) 3030, 977, 970, 703 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.26 and 1.56 (m and bs, total 8H), 2.09 (m, 8H), 5.0—5.8 (m, 4H); MS *m/z* (rel intensity) 164 (M^+, 2), 121 (45), 81 (61), 80 (41), 68 (41), 67 (100), 54 (63). Found: *m/z* 164.1558. Cacld for $C_{12}H_{20}$: M, 164.1564. Various spectra of **7** were identical with those of (*E*,*Z*)-1,5-cyclododecadiene which was prepared by means of a selective reduction of (*E*,*E*,*Z*)-1,5,9-cyclododecatriene with hydrazine. Reduction of the triene (77 mmol scale) was carried out according to an established procedure[16] but in order to obtain a best yield of **7**, the reduction was discontinued after a shorter reaction time (20 min.). GLC analysis showed that the reaction mixture consisted of **7** (50%), a starting cyclododecatriene (30%), and (*Z*)-cyclododecene (20%). These three products were separated by a preparative GLC (Carbowax 20M 15% on Uniport B).

(*E*)-4-Vinylcyclodecene (8): IR (neat) 3030, 970, 913 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.38 and 1.57 (m and m, 10H), 2.12 and 2.25 (m and m, 5H), 4.8—5.2 (m, 2H), 5.48 (m, 2H), 5.6—6.1 (m, 1H); MS *m/z* (rel intensity) 164 (M^+, 3), 121 (66), 93 (26), 81 (94), 80 (46), 68 (30), 67 (100), 54 (59). Found: *m/z* 164.1560. Calcd for $C_{12}H_{20}$: M, 164.1562.

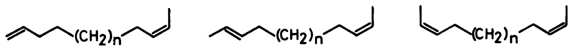
A Mixture of Isomeric Dodecadienes (9): IR (neat) 3020, 1640, 967, 910 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.30 (bs, CH_2), 1.64 (d, =$CHCH_3$), 1.97 (bs, =$CHCH_2$–), 4.8—5.2 (m, =CH_2), 5.44 (m, –CH=CH–), 5.5—6.1 (m, –CH=CH_2); MS *m/z* (rel intensity) 166 (M^+, 2), 95 (31), 82 (50), 81 (51), 69 (44), 68 (100), 67 (67), 55 (88), 54 (40). Found: *m/z* 166.1736. Calcd for $C_{12}H_{22}$: M, 166.1721. GLC analysis and ^{1}H NMR spectrum of the mixture showed that it consisted of **9a** (90%), **9b** (8%), and **9c** (2%).

(*Z*,*Z*)-1,5-Cyclotetradecadiene (12): IR (neat) 3003, 1650, 945, 715 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.32 (m, 12H), 2.05 (m, 8H), 5.43 (m, 4H, J=7.3 Hz, J=10.7 Hz); MS *m/z* (rel intensity) 192 (M^+, 10), 135 (35), 121 (31), 95 (67), 87 (100), 67 (96), 59 (70), 54 (71). Found: *m/z* 192.1883. Calcd for $C_{14}H_{24}$: M, 192.1878. Irradiation of the multiplet due to the allylic protons at δ 2.05 using a 400 MHz machine caused the multiplet of the olefinic protons at δ 5.43 to collapse into two doublets (each J=10.7 Hz).

(*Z*)-4-Vinylcyclododecene (13): IR (neat) 3060, 1650, 985, 945, 905, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.34 and 1.57 (bs and s, 14H), 1.8—2.5 (m, 5H), 4.9—5.2 (m, 2H), 5.35 (m, 2H), 5.7—6.2 (m, 1H); MS *m/z* (rel intensity) 192 (M^+, 2), 135 (25), 121 (29), 95 (67), 81 (100), 67 (92), 54 (75). Found: *m/z* 192.1879. Calcd for $C_{14}H_{24}$: M, 192.1878. Irradiation of the multiplet due to the allylic protons at δ 2.2 caused the multiplet of the olefinic protons at δ 5.35 to collapse into two doublets (each J=10.0 Hz).

(*Z*)-1,12-Tetradecadiene (14a): IR (neat) 3030, 985, 910, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.28 (s, 14H), 1.60 (d, 3H), 2.00 (m, 4H), 4.8—5.1 (m, 2H), 5.39 (m, 2H), 5.7—6.04 (m, 1H); MS *m/z* (rel intensity) 194 (M^+, 3), 96 (33), 95 (28), 82 (47), 81 (42), 68 (100), 55 (70). Found: *m/z* 194.2069. Calcd for $C_{14}H_{26}$: M, 194.2035. Tetradecadienes **14a** and **14c** were obtained in a ratio of 17:83.

(*Z*,*Z*)-2,12-Tetradecadiene (14c): IR (neat) 3003, 1655, (w), 965, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.28 (s, 12H), 1.60 (d, 6H), 2.03 (m, 4H), 5.39 (m, 4H); MS *m/z* (rel intensity) 194 (M^+, 2), 96 (34), 82 (65), 81 (45), 68 (100), 55 (63). Found: *m/z* 194.2051. Calcd for $C_{14}H_{26}$: M, 194.2035.



n=6 **14a** **14c**
n=4 **18a** **18b** **18c**

(*Z*,*Z*)-1,5-Cyclododecadiene (16): IR (neat) 3005, 855, 805, 720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.32 and 1.42 (bs and m, total 8H), 2.10 (m, 8H), 5.27 (m, 2H, J=10.7 Hz, J=8.2 Hz), 5.57 (m, 2H, J=10.7 Hz, J=8.2 Hz); MS *m/z* (rel intensity) 164 (M^+, 3), 81 (60), 67 (100), 54 (66). Found: *m/z* 164.1564. Calcd for $C_{12}H_{20}$: M, 164.1564. Irradiation of the multiplet due to the allylic protons at δ 2.10 caused the multiplets at δ 5.27 and δ 5.57 to collapse into the doublets (each J=10.7 Hz).

(*Z*)-4-Vinylcyclodecene (17): IR (neat) 3060, 1635, 990, 968, 915, 705 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.43 and 1.56 (m and s, total 10H), 2.11 and 2.25 (m and m, 5H), 4.8—5.2 (m, 2H), 5.44 (m, 2H), 5.7—6.2 (m, 1H); MS *m/z* (rel intensity) 164 (M^+, 3), 81 (86), 67 (100), 54 (88). Found: *m/z* 164.1563. Calcd for $C_{12}H_{20}$: M, 164.1563.

A Mixture of Isomeric Dodecadiene (18): IR (neat) 3020, 1650, 968, 910, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.32 (bs, 8.2H), 1.59 (d, 5.3H), 2.02 (m, 4.0H), 5.41 (m, 4.1H). GLC analysis of the mixture showed the presence of three isomers in a ratio of 14:36:50. Each of these isomers of nearly 80% purity was separated by a preparative GLC (Ucon oil 150 15% on Uniport HB 7000; 120 °C). The first peak was identified to be (*Z*)-1,10-dodecadiene (**18a**): IR (neat) 3030, 990, 910, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.30 (m, 10H), 1.59 (d, 3H), 1.93—2.05 (m, 4H), 4.9—6.0 (m, 5H); MS *m/z* (rel intensity) 166 (M^+, 4), 81 (40), 68 (100), 55 (56). Found: *m/z* 166.1713. Calcd for $C_{12}H_{22}$: M, 166.1719. The second peak was identified to be (*E*,*Z*)-2,10-dodecadiene (**18b**): ^{1}H NMR ($CDCl_3$) δ=1.31 (m, 8H), 1.60 (d, 6H), 1.93—2.05 (m, 4H), 5.42 (m, 4H), MS *m/z* (rel intensity) 166 (M^+, 4), 81 (43), 68 (100), 55 (78). Found: *m/z* 166.1731. Calcd for $C_{12}H_{22}$: M, 166.1721. The third peak was identified to be (*Z*,*Z*)-2,10-dodecadiene (**18c**): IR (neat) 3030, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.32 (m, 8H), 1.60 (d, 6H, J=5.0 Hz), 1.93—2.05 (m, 4H), 5.42 (m, 4H); MS *m/z* (rel intensity) 166 (M^+, 4), 81

(34), 68 (100), 55 (65). Found: m/z 166.1727. Calcd for $C_{12}H_{22}$: M, 166.1721.

(Z,Z)-1,5-Cyclodecadiene (20): IR (neat) 3005, 1650, 945, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$; 400 MHz) δ=1.50 (m, 4H), 2.16 (m, 4H), 2.35 (m, 4H), 5.33 (m, 4H, J=11.2 Hz), 5.45 (dt, 4H, J=10.7 Hz, J=8.3 Hz); MS m/z (rel intensity) 136 (M^+, 38), 107 (34), 95 (64), 94(56), 93 (62), 81 (27), 80 (54), 79 (82), 67 (100), 54 (61). Found: m/z 136.1270. Calcd for $C_{10}H_{16}$: M, 136.1253. Irradiation of the multiplet due to the allylic protons at δ 2.35 caused the multiplet at δ 5.33 to collapse into a doublet (J=11.2 Hz). While irradiation of the multiplet at δ 2.16 caused the multiplet at δ 5.45 to collapse into a doublet (J=10.7 Hz).

(Z)-4-Vinylcyclooctene (21): IR (neat) 3060, 1660, 990, 910, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.56 (m, 6H), 2.17 (m, 5H), 4.8—5.2 (m, 2H), 5.40 (m, 1H), 5.6—6.1 (m, 2H); MS m/z (rel intensity) 136 (M^+, 17), 121 (35), 107 (32), 95 (49), 94 (44), 93 (43), 82 (40), 81 (37), 80 (45), 79 (71), 67 (100), 54 (63). Found: m/z 136.1236. Calcd for $C_{10}H_{16}$: M, 136.1249.

Cyclic Voltammetry. Cyclic voltammetry was carried out with a Nichia potentiostat HP-E_{500H} in combination with a Nichia linear potential scanner. The sweep rate was 0.2 V s^{-1} and a platinum disc (1 mm dia.) was used as a working electrode. Reduction peaks of **5**, **15**, and crotyl bromide in DMF containing 0.1M n-Bu_4NClO_4 were observed at −2.00, −2.00, and −1.81 V vs. Ag/AgI. Another reduction peak was observed at −1.32 V only in the case of **15**. The reduction peak of crotyl bromide shifted to −1.65 V when a cyclic voltammetry was carried out in THF containing 0.1M n-Bu_4NClO_4.

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