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Oxidation with Potassium Permanganate of *p-tert*-Butylcalix[4]Arene Derivatives Containing Olefinic Substituents at the Lower Rim

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Abstract—In oxidation with potassium permanganate of *p-tert*-butylcalix[4]arene derivatives containing olefinic substituents at the lower rim, with the formation of the corresponding carbonyl compounds, calixarene acts as both the substrate and the catalyst.

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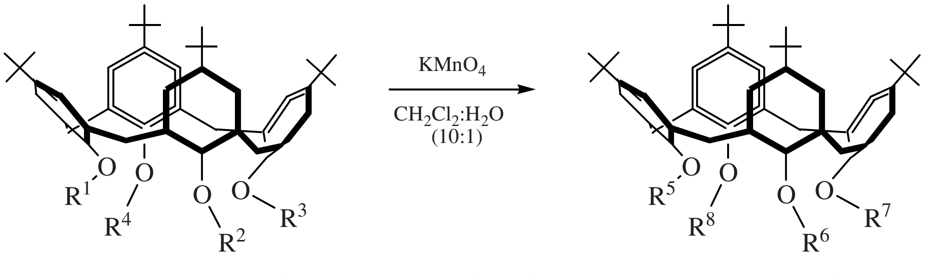
Nomura et al. [1] showed that *p-tert*-butylcalix[6]arene bearing six trioxydecyl groups at the lower rim can be used as effective catalyst of oxidation of alkenes, alkynes, and alcohols with potassium permanganate. The oxidation of unsaturated compounds containing a terminal multiple bond and of primary alcohols with excess $KMnO_4$ in the CH_2Cl_2–H_2O system (10 : 1) yields the corresponding carboxylic acids, whereas the oxidation with $KMnO_4$ of secondary alcohols and alkenes containing the double bond at a secondary carbon atom yields the corresponding ketones. Oxidation of multiple bonds and alcoholic groups in the presence of calixarenes is no less efficient than that performed under similar conditions in the presence of crown ethers (in the given case, 18-crown-6).

It seemed interesting to examine the possibility of oxidation with potassium permanganate of O-substituted derivatives of *p-tert*-butylcalix[4]arene containing olefinic fragments as substituents. In this case, the calixarenes should act as both the substrates and the catalysts. As starting compounds we chose tetrakis(2-propenyloxy)- (**I**) [2], bis(*p*-methylbenzyloxy)bis(2-propenyloxy)- (**II**) [3], bis(*m*-methylbenzyloxy)bis(2-propenyloxy)- (**III**) [3], and bis- and tetrakis(2-methyl-2-propenyloxy)-p-*tert*-butylcalix[4]arenes (**IV** and **V**, respectively) [2], whose molecules occur in the cone conformation.

Oxidation of **I–V** was performed with $KMnO_4$ in CH_2Cl_2–H_2O (10 : 1) at 15 and 40°C. In both cases, the reaction products were carbonyl-containing derivatives of *p-tert*-butylcalix[4]arene. Oxidation of **I–III** gives the corresponding tetrakis(carboxymethoxy) (**VI**) [4], bis(*p*-methylbenzyloxy)bis(carboxymethoxy) (**VII**), and bis(*m*-methylbenzyloxy)bis(carboxymethoxy) (**VIII**)



I: $R^1 = R^2 = R^3 = R^4 = CH_2–CH{=}CH_2$; **II**: $R^1 = R^3 = p$-$CH_3–C_6H_4$, $R^2 = R^4 = CH_2–CH{=}CH_2$; **III**: $R^1 = R^3 = m$-$CH_3–C_6H_4$, $R^2 = R^4 = CH_2–CH{=}CH_2$; **IV**: $R^1 = R^3 = CH_2(CH_3)C{=}CH_2$, $R^2 = R^4 = H$; **V**: $R^1 = R^2 = R^3 = R^4 = CH_2(CH_3)C{=}CH_2$; **VI**: $R^5 = R^6 = R^7 = R^8 = CH_2–COOH$; **VII**: $R^5 = R^7 = p$-$CH_3–C_6H_4$, $R^6 = R^8 = CH_2–COOH$; **VIII**: $R^5 = R^7 = m$-$CH_3–C_6H_4$, $R^6 = R^8 = CH_2–COOH$; **IX**: $R^5 = R^7 = CH_2C(O)CH_3$, $R^6 = R^8 = H$; **X**: $R^5 = R^6 = R^7 = R^8 = CH_2C(O)CH_3$.

derivatives of *p*-*tert*-butylcalix[4]arene in yields exceeding 90%/. Oxidation of calixarenes **IV** and **V** gives bis (methylcarbonylmethoxy) (**IX**) and tetrakis(methylcarbonylmethoxy) (**X**) derivatives of *p*-*tert*-butylcalix[4] arene in 85–90% yields.

The IR spectra of **VI–VIII** contain absorption bands of the carbonyl group at 1730–1750 cm^{-1} and the ν_{O-H} bands at 3250 and 3600 cm^{-1}. The IR spectra of calixarenes **IX** and **X** contain absorption bands of the carbonyl group at 1710–1715 cm^{-1}. In the ^{1}H NMR spectra of tetrasubstituted derivatives **I, V, VI**, and **X**, there are a singlet from *tert*-butyl protons (36H), a pair of doublets from protons of the methylene bridges, and a singlet from aromatic protons of the macroring (8H); this spectral pattern of tetrasubstituted calixarenes is typical of compounds whose molecules occur in the cone conformation. The ^{1}H NMR spectra of disubstituted calixarenes **IV** and **IX** (two signals from *tert*-butyl protons with 1 : 1 ratio of integral intensities, two singlets from aromatic protons with the same intensity ratio, and a pair of doublets from methylene protons of the macroring) suggest that the molecules of these compounds also occur in the cone conformation. The spectra of calixarenes **II** and **VII** contain three singlets from *tert*-butyl protons (2 : 1 : 1), three singlets from protons of the aromatic rings (2 : 1 : 1), and two pairs of doublets with a relatively small difference in the chemical shifts ($\Delta\delta < 0.5$ ppm) from methylene protons. In the spectra of **III** and **VIII**, *tert*-butyl protons give four singlets, and aromatic protons give two singlets and a pair of doublets. The ^{1}H NMR spectrum of **III** contains a pair of doublets and two multiplets with small $\Delta\delta$ from methylene protons of the macrocyclic moiety; in the spectrum of calixarene **VIII**, each proton of the methylene bridges gives a separate signal, with $\Delta\delta < 0.3$ ppm. Increased number of nonequivalent protons of the methylene components of the calixarene ring and decreased $\Delta\delta$ for the signals of these protons, as follows from [5–7], suggests certain flattening of the cone conformation in **III** or its distortion in **II, VII**, and **VIII**.

Such modification of *p*-*tert*-butylcalix[4]arene derivatives allows their solubility to be considerably increased. For example, the carbonyl derivatives prepared are fairly well soluble in alcohols. Compounds containing a keto group can also be prepared by direct alkylation of *p*-*tert*-butylcalixarene, and calixarenes containing acid fragments can be prepared by hydrolysis of the corresponding esters, but these methods are insufficiently selective with respect to the degree of substitution of the starting calixarene and conformation of the alkylation products, and the yields of the carboxymethoxy derivatives prepared by hydrolysis are lower than in the reactions considered above.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Varian VXR-300 device (300 MHz) from ~10% solutions in $CDCl_3$, internal reference TMS. The FAB mass spectra were taken on a VG 70-70EQ mass spectrometer using a beam of Xe atoms with an energy of 8 keV. The IR spectra were measured on a Specord IR-75 spectrophotometer in $CHCl_3$ solutions.

Oxidation of calix[4]arenes containing olefinic fragments. A suspension of 0.2 mol of appropriate calixarene and 1.6 mmol (for **I** and **V**) or 0.8 mmol (for **II–IV**) of $KMnO_4$ in CH_2Cl_2–H_2O (15–1.5 ml) was stirred for 3–3.5 h at 15°C (or for 1.5 h at 40°C). Excess $KMnO_4$ was removed by adding a solution of $NaHSO_3$ (1 g in 20 ml of water). The resulting mixture was washed with 5–10 ml of dilute HCl and a $NaHSO_3$ solution. The organic phase was separated, the aqueous phase was extracted with CH_2Cl_2 (3 × 10 ml), and the combined organic extracts were washed with a sodium carbonate solution and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was recrystallized from aqueous alcohol.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis(*p*-methylbenzyloxy)-26,28-bis(carboxymethoxy)calix[4]arene VII. Yield 92%, mp 105–107°C. IR spectrum, ν, cm^{-1}: 3250, 3600 (OH), 1730 (C=O). ^{1}H NMR spectrum, δ, ppm: 0.99 s [18H, $(CH_3)_3C$], 1.18 s [9H, $(CH_3)_3C$], 1.23 s [9H, $(CH_3)_3C$], 2.25 s (3H, CH_3), 2.31 s (3H, CH_3), 2.96 d (2H, $ArCH_2Ar$, *J* 13.8 Hz), 3.34 d (2H, $ArCH_2Ar$, *J* 13.8 Hz), 4.35 d (2H, $ArCH_2Ar$, *J* 13.8 Hz), 4.56 d (2H, $ArCH_2Ar$, *J* 13.0 Hz), 5.14 s (4H, CH_2O), 6.38 s (2H, CH_2O), 6.44 s (2H, CH_2O), 7.07 s (4H, ArH), 7.09 s (2H, ArH), 7.12 s (2H, ArH), 7.2–7.44 m (8H, Bzl), 9.5 s (2H, OH). FAB-MS: *m*/*z* 973 $(M + 1)^+$.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis(*m*-methylbenzyloxy)-26,28-bis(carboxymethoxy)calix[4]arene VIII. Yield 95%, mp 92–93°C. IR spectrum, ν, cm^{-1}: 3200, 3600 (OH), 1730 (C=O). ^{1}H NMR spectrum, δ, ppm: 0.83 s [9H, $(CH_3)_3C$], 0.85 s [9H, $(CH_3)_3C$], 1.27 s [9H, $(CH_3)_3C$], 1.31 s [9H, $(CH_3)_3C$], 2.31 s (3H, CH_3), 2.33 s (3H, CH_3), 3.06 d (1H, $ArCH_2Ar$, *J* 13.8 Hz), 3.15 d (1H, $ArCH_2Ar$), 4.34 d (1H, $ArCH_2Ar$), 4.4 d

(1H, $ArCH_2Ar$), 4.47 d (1H, $ArCH_2Ar$), 4.58 d (1H, $ArCH_2Ar$), 4.72 d (1H, $ArCH_2Ar$), 4.75 d (1H, $ArCH_2Ar$), 5.15 s (4H, CH_2O), 6.46 s (2H, CH_2O), 6.51 s (2H, CH_2O), 7.1 d (2H, ArH), 7.14 s (2H, ArH), 7.18 d (2H, ArH), 7.21 s (2H, ArH), 7.2–7.44 m (8H, Bzl), 9.6 s (2H, OH). FAB-MS: *m*/*z* 973 $(M + 1)^+$.

5,11,17,23-Tetra-*tert*-butyl-25,27-bis(methylcarbonylmethoxy)-26,28-dihydroxycalix[4]arene IX. Yield 90%, mp 235–237°C. IR spectrum, ν, cm^{-1}: 1710 (C=O). ^1H NMR spectrum, δ, ppm: 1.02 s [18H, $(CH_3)_3C$], 1.27 s [18H, $(CH_3)_3C$], 2.19 s (6H, CH_3), 2.39 d (4H, $ArCH_2Ar$, *J* 14 Hz), 4.42 d (4H, $ArCH_2Ar$), 4.54 s (4H, CH_2O), 6.94 s (4H, ArH), 7.1 s (4H, ArH), 8.1 s (2H, OH). FAB-MS: *m*/*z* 761 $(M + 1)^+$.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis(methylcarbonylmethoxy)calix[4]arene X. Yield 85%, mp 187–189°C. IR spectrum, ν, cm^{-1}: 1715 (C=O). ^1H NMR spectrum, δ, ppm: 1.2 s [36H, $(CH_3)_3C$], 2.24 s (12H, CH_3), 3.35 d (4H, $ArCH_2Ar$, *J* 12.6 Hz), 4.25 d (4H, $ArCH_2Ar$), 4.6 s (8H, CH_2O), 6.86 s (8H, ArH). FAB-MS: *m*/*z* 873 $(M + 1)^+$.

REFERENCES

1. Nomura, E., Taniguchi, H., and Otsuji, Y., *Bull. Chem. Soc. Jpn.*, 1994, vol. 67, p. 309.
2. Alekseeva, E.A., Mazepa, A.V., and Gren', A.I., *Zh. Obshch. Khim.*, 2002, vol. 72, no. 1, p. 164.
3. Alekseeva, E.A., Mazepa, A.V., and Gren', A.I., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 11, p. 1887.
4. Arnaud-Neu, F., Barrett, G., Cremin, S., Deasy, M., Ferguson, G., Harris, S.J., Lough, A.I., Guerra, Z., McKervey, M.A., Schwing-Weill, M.J., and Schwinte, P., *J. Chem. Soc., Perkin Trans. 2*, 1992, no. 4, p. 1119.
5. Iwamoto, K., Araki, K., and Shinkai, S., *Tetrahedron,* 1991, vol. 47, no. 28, p. 4325.
6. Gutsche, C.D., Dhawam, B., Levine, J.A., No, K.H., and Bauer, L.J., *Tetrahedron*, 1983, vol. 39, no. 3, p. 409.
7. Pitarch, M., Browne, J.K., and McKervey, M.A., *Tetrahedron*, 1997, vol. 53, no. 30, p. 10 505.