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Abstract: The synthesis of pentaoxa[5]peristylanes, a novel oxa-cage system, has been accomplished via ozonolysis of 7-anti-2,3-bis-endo-triacylbicyclo[2.2.1]-5-heptenes and via a direct chemical transformation of the tetraacetal tetraoxa-cages 5a-c and 6a-c. © 1997 Elsevier Science Ltd.

The synthesis of peristylanes, such as [5]peristylene and [4]peristylene, has been accomplished and attempts to roof [5]peristylene has been made. On the other hand, the synthesis of heterocyclic analogs of peristylanes has received much less attention. Recently, we conceived that some heterocyclic cage systems might be viewed as novel classes of cage-backboned coronands (crown ethers) and might exhibit interesting cation-binding properties. We also visualized that the "creation" of oxa-cage compounds from carbocyclic cages might be achieved by replacing the skeletal carbon atoms with oxygen atoms at the proper positions and by extending the skeletal backbone. Thus, we have accomplished the synthesis of tetraacetal tetraoxa-cages, tetraacetal pentaoxa-cages, diacetal trioxa-cages, and triacetal trioxa-cages.

We report in this communication the synthesis of pentaoxa[5]peristylanes, a novel oxa-cage system, via ozonolysis of 2,3-bis-endo-7-anti-triacyclonorbornenes. We also wish to demonstrate for the first time the direct transformation of tetraacetal tetraoxa-cages to pentaoxa[5]-peristylanes.

Diels-Alder reaction of compound 1 with cis-enediones 2a-f in dichloromethane at 0 °C for 72 h gave the anti-endo adducts 3a-f in 70-75% yields. Treatment of 3a-f with Cu(BF₄)₂ or methanesulfonic acid in dichloromethane at 25 °C gave the hydrolysis products 4a-f in 75-80% yields (Scheme 1). Compounds 4g-i were prepared from (Z)-γ-oxo-α,β-unsaturated thioesters.
at -78 °C followed by reduction with dimethyl sulfide gave the tetraacetal tetraoxa-cages 5a-c (30-34%) and 6a-c (34-38%) and the pentaacetal pentaoxa-cages 7a-c (18-22%), the pentaoxa[5]-peristylenes. Ozonolysis of 4d-f under the same reaction conditions gave the pentaacetal pentaoxa-cages 7d-f in 75-80% yields. The by-products 5d-f and 6d-f were too small amount to be isolated. Ozonolysis of 4g-i under the same reaction conditions gave the tetraacetal tetraoxa-cages 8a-c in 85-90% yields. No detectable amount of the pentaoxa[5]peristylenes 9a-c or the tetraacetal tetraoxa-cages 10a-c or 11a-c was obtained. The thioester group may exhibit much less reactive than the acyl groups for the cyclization reaction.

Scheme 1

![Scheme 1 diagram](image-url)
Compounds 7a-f are white solid. The IR spectra of 7a-f lacked carbonyl absorptions and showed strong absorptions near 1050 cm⁻¹ for the ether C-O bonds. The ¹H NMR spectrum of 7a revealed one doublet at δ 5.91 for the acetal proton on C-5 and one doublet at δ 5.85 for the two acetal protons on C-3 and C-7. The absorption at δ 2.09 (a singlet) for the methyl ketone protons of 4a shifted to δ 1.50 for the angular methyl protons of 7a. The ¹³C NMR spectrum of 7a lacked any carbonyl absorption and displayed one peak at δ 113.33 for the acetal carbon C-5, one peak at δ 112.46 for the acetal carbons C-3 and C-7, one singlet at δ 120.30 for the quaternary carbons, and one peak at δ 26.94 for the angular methyl carbons. The IR spectra and ¹H and ¹³C NMR spectra of 7b-f revealed that these compounds possess the same skeleton as 7a.

Treatment of the tetraacetal tetraoxa-cages 5a-c with catalytic amount of TiCl₄ in dichloromethane at 25 °C for 4 h gave the pentaoxa[5]peristylanes 7a-c in 70-75% yields and the hydride rearrangement products 12a-c in 20-15% yields (Scheme 2). Reaction of 6a-c under the same reaction conditions gave 7a-c in 85-90% yields. The amount of 12a-c was too small to be isolated.

Scheme 2

Thus, we have accomplished for the first time the synthesis of pentaoxa[5]peristylanes, a novel and interesting oxa-cage system.

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References and Notes

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(11) Selected spectral data for 7. 7a: white solid; mp 214-215 °C; 1H NMR (300 MHz,
CDCl3) δ 5.91 (d, J = 5.4 Hz, 1H), 5.85 (d, J = 5.1 Hz, 2H), 3.70-3.65 (m, 3H), 3.39-3.35
(m, 2H), 1.50 (s, 6H); 13C NMR (75 MHz, CDCl3) δ 120.30 (2C), 113.33 (CH), 112.46
(2CH), 62.72 (2CH), 58.91 (2CH), 58.53 (CH), 26.94 (2CH3); MS m/z (rel int.) 238 (M+, 12),
208 (100). 7e: white solid; mp 178-179 °C; 1H NMR (300 MHz, CDCl3) δ 5.90 (d, J =
6.0 Hz, 2H), 5.86 (d, J = 5.1 Hz, 2H), 3.68-3.62 (m, 4H), 3.38-3.34 (m, 1H), 1.76-1.70
(m, 2H), 1.40-1.26 (m, 4H), 0.92 (t, J = 6.9 Hz, 3H); 13C NMR (75 MHz, CDCl3) δ
123.59 (C), 113.51 (2CH), 112.81 (2CH), 59.96 (CH), 58.76 (2CH), 58.27 (2CH),
39.30(CH2), 26.04(CH2), 22.66 (CH2), 13.98 (CH3); MS m/z (rel int.) 266 (M+, 14), 209
(100).

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