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> SHORT COMMUNICATIONS

Thermolysis of 3-(1-Adamantyl)-2-hydroxy-5-methylbenzyl-(trimethyl)ammonium Iodide

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In the absence of nucleophiles and dienophiles o-quinomethanes undergo fast oligomerization with formation of a complex mixture of products as a result of hetero-Diels–Alder reaction with opposite electronic requirements. In some cases, the corresponding trimerization product can be isolated as the major one. Here, initial o-quinomethanes were generated *in situ* by oxidation of o-alkylphenols with Ag₂O or K₃[Fe(CN)₆] [1], from unstable o-halomethylphenols [2], difficultly accessible enediynes [3] and 4-alkynylcyclobutenones [4], as well as by flash vacuum pyrolysis of salicyl alcohols, o-methoxymethylphenols [5], and 4H-1,3,2-benzodioxaborinines [6].

We have found that heating of sterically hindered 3-(1-adamantyl)-2-hydroxy-5-methylbenzyl(trimethyl)-ammonium iodide (I) in boiling dimethylformamide leads to the formation of formal trimerization product of the corresponding*o*-quinomethane**A**via tandem [4+2]-cycloaddition.

The ¹H NMR spectrum of trimer **II** contained a set of singlets in the region δ 6.66–6.96 ppm from aromatic protons and signals from protons in the adamantane fragments at δ 1.56–2.30 ppm. The vinylic proton resonated as a singlet at δ 6.16 ppm, and methylene protons in the C_{arom}–C**H**₂–CH fragment gave doublets of doublets at δ 2.93 and 3.23 ppm. In the IR spectrum



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of II, absorption band corresponding to the conjugated carbonyl group was observed at 1697 cm^{-1} . The base peak in the mass spectrum of II belonged to adamantyl cation.

Initial iodide I was synthesized by aminomethylation of 2-(1-adamantyl)-4-methylphenol in ethanol, followed by quaternization with methyl iodide [7].

3-(1-Adamantyl)-2-hydroxy-5-methylbenzyl(trimethyl)ammonium iodide (I). 2-(1-Adamantyl)-4methylphenol, 5 g (0.021 mol), was dissolved in 30 ml of ethanol, 3.5 g (0.026 mol) of 33% aqueous dimethylamine and 2.6 g (0.026 mol) of 30% aqueous formaldehyde were added, and the mixture was kept for 2 days at room temperature and then for 2 h at -20° C. The colorless precipitate was filtered off, washed with ice-cold methanol, and dried in air. A mixture of the Mannich base thus obtained and 20 ml of methyl iodide was heated for 12 h under reflux with stirring. The mixture was cooled, and the colorless precipitate was filtered off and washed with ice-cold diethyl ether. Yield 5.5 g (60%), mp 217–219°C. IR spectrum, v, cm⁻¹: 3387, 3190 (OH); 2901, 2847 (CH, Ad); 1609 (C=C); 1462, 1269, 1211, 1180, 1011, 872, 756. ¹H NMR spectrum (DMSO- d_6), δ , ppm: 1.70 s (6H, Ad), 2.01 s (3H, Ad), 2.05 s (6H, Ad), 2.22 s (3H, CH₃), 2.95 s (9H, NMe₃), 4.49 s (2H, CH₂), 7.00 s (1H, H_{arom}), 7.08 s (1H, H_{arom}), 8.59 s (1H, OH). Found, %: C 56.98; H 7.29. C₂₁H₃₂INO. Calculated, %: C 57.08; H 7.25.

8,3',5'-Tris(1-adamantyl)-6,4a',7'-trimethyl-9',9a'-dihydro-4a'*H***-spiro[chroman-2,1'-xanthen]-2'-one (II). A solution of 2 g (4.5 mmol) of quaternary salt I in 20 ml of DMF was heated for 2 h under reflux. The mixture was cooled to 0°C, and the precipitate was filtered off, washed with methanol, and recrystallized from DMF. Yield 0.98 g (85%), colorless crystals, mp 302–304°C. IR spectrum, v, cm⁻¹: 2905, 2847 (CH, Ad), 1697 (C=O), 1601 (C=C), 1466, 1454, 1342, 1315, 1250, 1231, 1215, 1180, 1161, 1107, 1065, 1045, 984, 945. ¹H NMR spectrum (CDCl₃), \delta, ppm: 1.56– 1.64 m (9H, Ad, 4a'-CH₃), 1.75–1.85 m (15H, Ad), 1.88–1.97 m (6H, Ad), 2.07–2.19 m (12H, Ad), 2.21– 2.30 m (12H, Ad, CH₃), 2.44–2.73 m (5H, CH₂CH₂,** CH), 2.93 d.d and 3.24 d.d (1H each, 9'-H), 6.16 s (1H, =CH), 6.66 s (1H, H_{arom}), 6.72 s (1H, H_{arom}), 6.89 s (1H, H_{arom}), 6.96 s (1H, H_{arom}). Mass spectrum, m/z $(I_{rel}, \%)$: 762 (3) $[M]^+$, 747 (1) $[M - Me]^+$, 627 (2) $[M - C_{10}H_{15}]^+$, 508 (15) $[C_{36}H_{44}O_2]^+$, 507 (14) $[C_{36}H_{43}O_2]^+$, 506 (11) $[C_{36}H_{42}O_2]^+$, 494 (7), 493 (4), 373 (3) $[C_{26}H_{29}O_2]^+$, 256 (12), 255 (24), 254 (7) $[C_{18}H_{22}O]^+$, 253 (11), 242 (5), 199 (6), 185 (5), 159 (5), 135 (100) $[C_{10}H_{15}]^+$, 107 (7), 93 (12), 79 (11), 67 (6). Found, %: C 85.08; H 8.68. $C_{54}H_{66}O_3$. Calculated, %: C 84.99; H 8.72.

The IR spectra were measured in KBr on a Shimadzu FTIR-8400S spectrometer. The ¹H NMR spectra were recorded on a Bruker AM-400 spectrometer at 400 MHz using tetramethylsilane as internal reference. The mass spectrum (electron impact, 70 eV) was obtained on a Finnigan Trace DSQ instrument. The elemental compositions were determined on a EuroVector EA-3000 automatic CHNS analyzer.

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