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Cyclic and Linear Oligomerization Reaction of 3,4,5-Trimethoxybenzyl Alcohol with a Bentonite-Clay*

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Abstract.- The catalytic induction and structures of cyclic and linear oligomers from 3,4,5-trimethoxybenzyl alcohol with a bentonite clay as catalyst are discussed.

The use of montmorillonite type-clay as a catalyst to induce organic reactions is of particular interest because these reactions proceed with high selectivity and good yields under mild conditions.[1] This kind of catalyst has been found to show versatile Lewis-Brönsted properties in inducing aromatic substitutions involving benzylic carbocation species formed by heterolytic scission, that produce electrophilic substitution, linear oligomerization or polymerization of benzyl halides and benzyl alcohol.[2,3]

On the other hand, it is well known that methoxy substitution of benzyl alcohols such as veratryl alcohol (3,4-dimethoxybenzyl alcohol), provides exclusively cyclooligomerization, forming rings from three to six benzylic units upon different acidic conditions.[4]

In this heterogeneous catalyzed reaction, 3,4,5-trimethoxybenzyl alcohol **1** was dissolved in carbon disulfide and refluxed with a bentonite clay suspension, providing, after the usual work-up 1,2,3,6,7,8,11,12,13-nonamethoxy-10,15-dihydro-5 *H*-tribenzo (a, d, g) cyclononene **2**, bis [3,4,5 trimethoxybenzyl] ether **3**, [2' (3'', 4'', 5'', trimethoxybenzyl) (3', 4', 5', trimethoxybenzyl) ether **4**, and 2' [2'', (3''', 4''', 5''' -trimethoxybenzyl) 3'', 4'', 5'', -trimethoxybenzyl] 3, 4, 5 -trimethoxybenzyl ether **5**, as pure compounds with yields of 12, 40, 20, and 7 % respectively. Their ^{1}H and ^{13}CNMR and other spectroscopic data that confirm the proposed structures are given in reference.[5]

Based on the structures of these products, we can infer that they should be formed through a different pathway than the one suggested by Collet and others for acidic reactions.[4] The aromatic cyclooligomerization of the methoxybenzyl alcohols is preferred when the reaction is performed with diluted acids. This was clearly established since the 3,4,5-trimethoxybenzyl alcohol **1**, afforded the C_3 trimer when it was treated with 10 % sulfuric acid.[6]

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* This paper is dedicated to the memory of Carmen S. de Salmón.

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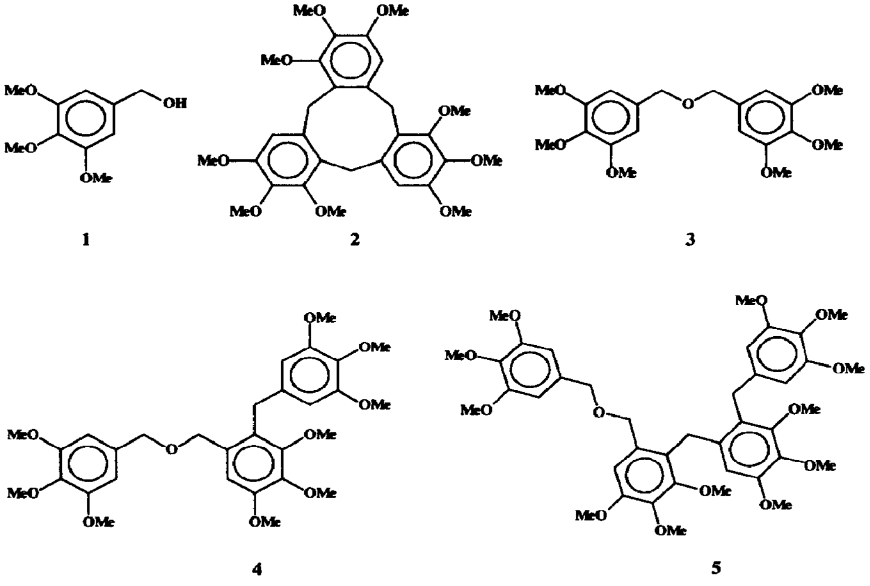
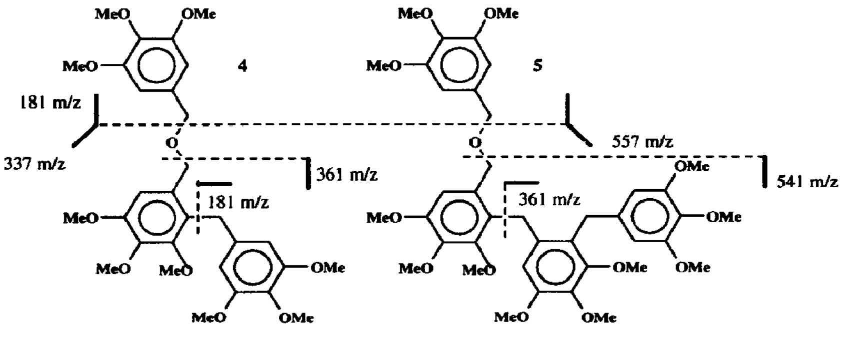


Scheme 1

The formation of the ether **3** should be considered as a typical example of an acid-catalyzed reaction of a primary alcohol to afford ethers, while the presence of **4** and **5** in the reaction mixture, might be explained by a subsequent electrophilic aromatic substitution reaction between the ether **2** and the respective benzyl cation formed from the alcohol **1**. In addition to the ^{1}H and ^{13}C NMR analysis of compounds **4** and **5**, Their linear structures were clearly established by the comparative mass spectral fragmentation pattern of both compounds. Both yield the same radical-cation fragments of 181 and 377 m/z that support the proposed structures as represented in scheme 2.



Scheme 2

The cyclotriveratrylene (CTV) analog **2** must be the condensation product of three molecules of the 3,4,5 trimethoxybenzylic cation. This reaction should proceed stepwise *via* the mono, di, and trimeric cation species followed by a closure step to form the compound C3 **2**. This mechanism has been pointed out by some authors to explain the formation of CTV from the veratryl cation.[4] One of the most interesting properties of CTV and its congeners is their stable crown conformation, established by X-ray crystallography[7] and by ^{1}H NMR spectra that show the characteristic AB system of the methylene bridges.[4] The same conformation is preferred in **2**, since its ^{1}H NMR spectrum displays the two doublet signals of the AB system at δ 4.42 and 4.03 (J=13.7 Hz), as reported by Bosh in 1976.[6]

It is concluded that the catalytic reaction proceeds through carbocation formation, as was previously suggested for the polymerization of unsubstituted benzyl alcohol.[3] The main difference in both pathways is the ether **3** which is further substituted yielding mainly linear oligomers.

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5. A carbon disulfide solution (5 ml) of 3,4,5-trimethoxybenzyl alcohol (0.5g) was refluxed in presence of bentonite-clay (0.1 g) during 7h. The reaction was monitored by TLC. The suspension was allowed to stand at room temperature, filtered over celite to remove the bentonite, and the filtrate concentrated under reduced pressure. The residue was chromatographed on Si gel using hexane with increasing proportions of ethyl acetate. 1,2,3,6,7,8,11,12,13-nonamethoxy-10,15-dihydro-5*H*-tribenzo-[a,d,g]-cyclononene **2** was isolated as white crystals (0.035g, mp 200-202°C, lit mp 201-202[6]), ^{1}H NMR ($CDCl_3$, 300 MHz), 7.23 (s, 3H), 4.42 (d, 1H; J=13.7), 4.03 (d, 1H; J=13.7), 3.97 (s, 9H), 3.79 (s, 9H), 3.77 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) 151.49 (s), 140.36 (s), 136.19 (s), 125.49 (s), 110.26 (d), 110.02 (s), 60.60 (q), 60.50 (q), 55.72 (q), 29.91 (t); MS (70eV) 540 (M^{+}, 35), 509 (45), 478 (15), 360 (100), 329 (75), 298 (10), 181 (71). Bis(3,4,5-trimethoxybenzyl) ether **3** was obtained as white solid (0.210g, mp 74-75°C), ^{1}H NMR ($CDCl_3$, 300 MHz), 6.60 (s, 4H), 4.50 (s, 4H), 3.86 (s, 6H), 3.84 (s, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz), 153.24 (s), 137.41 (s), 133.75 (s), 104.70 (d), 72.24 (t), 60.75 (q), 56.01 (q); MS (70eV), 378 (M^{+}, 10), 181 (100), 167 (30), 151 (43). [2´(3",4",5"-trimethoxybenzyl) (3´,4´,5´-trimethoxybenzyl) 3,4,5-trimethoxybenzyl] ether **4**, was isolated as a white powder (0.098g, mp 90-93°C), ^{1}H NMR ($CDCl_3$, 300 MHz), 6.78 (s, 1H), 6.76 (s, 2H), 6.54 (s, 2H), 4.45 (s, 2H), 4.41 (s, 2H), 3.94 (s, 2H), 3.85 (s, 6H), 3.81 (s, 3H), 3.79 (s, 6H), 3.76 (s, 3H),

3.70 (s, 9H); ^{13}C NMR (CDCl$_3$, 75 MHz), 153.21 (s), 152.92 (s), 152.36 (s), 151.87 (s), 141.89 (s), 137.03 (s), 136.99 (s), 135.92 (s), 133.74 (s), 132.02 (s), 125.09 (s), 108.50 (d), 105.11 (d), 104.64 (d), 72.72 (t), 70.15 (t), 60.89 (q), 60.76 (q), 60.63 (q), 55.96 (q), 55.91 (q), 31.44 (t); MS (70eV), 558 (M$^+$, 20), 377 (13), 361 (20), 329 (100), 298 (36); 2' [2'', (3''', 4''', 5''' -trimethoxybenzyl) 3'', 4'', 5'', -trimethoxybenzyl] 3, 4, 5 - trimethoxybenzyl ether **5**, was isolated as a gum ^{1}H NMR (CDCl$_3$, 300 MHz), 6.79 (s, 1H), 6.50 (s, 2H), 6.42 (s, 2H), 6.30 (s, 1H), 4.80 (s, 2H), 4.24 (s, 2H), 4.09 (s, 2H), 3.96 (s, 2H), 3.88-3.54 (m, 36H); ^{13}C NMR (CDCl$_3$, 75 MHz), 154.62 (s), 153.50 (s), 152.97 (s), 152.86 (s), 152.52 (s), 152.42 (s), 152.18 (s), 137.43 (s), 137.31 (s), 135.83 (s), 134.29 (s), 132.99 (s), 132.54 (s), 125.52 (s), 124.59 (s), 109.08 (d), 108.64 (d), 105.79 (d), 105.11 (d), 72.94 (t), 70.39 (t), 61.22 (q), 56.48 (q), 32.20 (t), 28.72 (t); MS (70eV), 738 (M$^+$, 2), 557 (5), 441 (10), 509 (22), 377 (10), 361 (15), 329 (45), 209 (38), 181 (100).

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