

Supplementary data

Investigation of porphyrin-forming reactions. Part 4. Examination of the reaction course in syntheses of porphyrins *via* dipyrromethanecarbinols

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Peak Assignments for Dipyrrromethane-Monocarbinol Self-Condensation and the Dipyrrromethane-Dicarbinol + Dipyrrromethane Condensation. The molecular weights for oligomers possessing all of the possible combinations of phenyl and *p*-tolyl substituents are compiled in Tables S1 and S2. Masses due to oligomers that can be formed by direct condensation of starting material(s) or intermediate oligomers (expected oligomers) are circled. Masses due to oligomers that can only be formed via acidolytic cleavage of an oligomer are enclosed in a box. All other oligomers can only be formed via scrambling.

Table S1. Assignment of peaks to expected (circled), acidolysis (box), or scrambled oligomers for the self-condensation of dipyrrromethane-monocarbinol 1.

Series	n	all phenyl	phenyl and <i>p</i> -tolyl mixed oligomers										all <i>p</i> -tolyl
			1	2	3	4	5	6	7	8	9	10	
(PA)n	1	155											169
	2	308	322										336
	3	461	475	489									503
	4	614	628	642	656								670
	5	767	781	795	809	823							837
	6	920	934	948	962	976	990						1004
	7	1073	1087	1101	1115	1129	1143	1157					1171
	8	1226	1240	1254	1268	1282	1296	1310	1324				1338
	9	1379	1393	1407	1421	1435	1449	1463	1477	1491			1505
	10	1532	1546	1560	1574	1588	1602	1616	1630	1644	1658		1672
A(PA)n	1	245	259										273
	2	398	412	426									440
	3	551	565	579	593								607
	4	704	718	732	746	760							774
	5	857	871	885	899	913	927						941
	6	1010	1024	1038	1052	1066	1080	1094					1108
	7	1163	1177	1191	1205	1219	1233	1247	1261				1275
	8	1316	1330	1344	1358	1372	1386	1400	1414	1428			1442
	9	1469	1483	1497	1511	1525	1539	1553	1567	1581	1595		1609
	10	1622	1636	1650	1664	1678	1692	1706	1720	1734	1748	1762	1776
(PA)nP	1	220											234
	2	373	387										401
	3	526	540	554									568
	4	679	693	707	721								735
	5	832	846	860	874	888							902
	6	985	999	1013	1027	1041	1055						1069
	7	1138	1152	1166	1180	1194	1208	1222					1236
	8	1291	1305	1319	1333	1347	1361	1375	1389				1403
	9	1444	1458	1472	1486	1500	1514	1528	1542	1556			1570
	10	1597	1611	1625	1639	1653	1667	1681	1695	1709	1723		1737
P(PA)nP	1	285											299
	2	438	452										466
	3	591	605	619									633
	4	744	758	772	786								800
	5	897	911	925	939	953							967

Table S2. Assignment of peaks to expected (circled), acidolysis (box), or scrambled oligomers for the condensation of dipyrromethane-dicarbinol **2** and 5-phenyldipyrromethane (PDPM).

Series	n	all phenyl	phenyl and <i>p</i> -tolyl mixed oligomers										all <i>p</i> -tolyl
			1	2	3	4	5	6	7	8	9	10	
(PA)n	1	155											169
	2	308	322										336
	3	461	475	489									503
	4	614	628	642	656								670
	5	767	781	795	809	823							837
	6	920	934	948	962	976	990						1004
	7	1073	1087	1101	1115	1129	1143	1157					1171
	8	1226	1240	1254	1268	1282	1296	1310	1324				1338
	9	1379	1393	1407	1421	1435	1449	1463	1477	1491			1505
	10	1532	1546	1560	1574	1588	1602	1616	1630	1644	1658		1672
A(PA)n	1	245	259										273
	2	398	412	426									440
	3	551	565	579	593								607
	4	704	718	732	746	760							774
	5	857	871	885	899	913	927						941
	6	1010	1024	1038	1052	1066	1080	1094					1108
	7	1163	1177	1191	1205	1219	1233	1247	1261				1275
	8	1316	1330	1344	1358	1372	1386	1400	1414	1428			1442
	9	1469	1483	1497	1511	1525	1539	1553	1567	1581	1595		1609
	10	1622	1636	1650	1664	1678	1692	1706	1720	1734	1748	1762	1776
(PA)nP	1	220											234
	2	373	387										401
	3	526	540	554									568
	4	679	693	707	721								735
	5	832	846	860	874	888							902
	6	985	999	1013	1027	1041	1055						1069
	7	1138	1152	1166	1180	1194	1208	1222					1236
	8	1291	1305	1319	1333	1347	1361	1375	1389				1403
	9	1444	1458	1472	1486	1500	1514	1528	1542	1556			1570
	10	1597	1611	1625	1639	1653	1667	1681	1695	1709	1723		1737
P(PA)nP	1	285											299
	2	438	452										466
	3	591	605	619									633
	4	744	758	772	786								800
	5	897	911	925	939	953							967

LD-MS Spectra from PDPM + *p*-Tolualdehyde Condensations. Condensations of PDPM + *p*-tolualdehyde (5 mM each) were performed under TFA catalysis (20 mM) or BF₃-etherate (1.0 mM) catalysis in CH₂Cl₂ at room temperature. The results of these reactions were compared with those from reactions involving dipyrromethane-carbinols under identical conditions. Figure S1 shows LD-MS spectra from selected timepoints.

Figure S1. LD-MS spectra from selected timepoints from the condensation of PDPM + *p*-tolualdehyde (5 mM each) under different acid catalysis conditions. (a) 20 mM TFA. (b) 1.0 mM BF₃-etherate. The peak with *m/z* corresponding to the desired porphyrin is marked with an asterisk.

