Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Electronic Supplementary Information

The gas phase Smiles rearrangement of anions $PhO(CH_2)_nO^-$ (n = 2-4). A joint theoretical and experimental approach.

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Tables S1-S5 contain data concerning the geometries [B3LYP/6-31++G(d,p) level of theory] and single point energies [calculated at CCSD(T)/6-31++G(d,p)] of all minima and transition states shown in the appropriate Figures in the text. Relative energies with zero-point corrections are recorded in kJ mol^{-1} units in all tables.

Table S1 The Smiles and S_Ni Reaction Pathways of the Singlet $PhO(CH_2)_2O^-$ Anion. Energies and Selected Geometries of Anion Minima and Transition States. **Level of theory used – CCSD(T)/6-31++G(d,p)//B3LYP/6-31++G(d,p). Relative energies in kJ mol^{-1} with respect to 1 (0 kJ mol^{-1})**

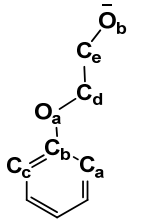
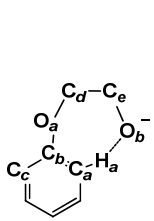
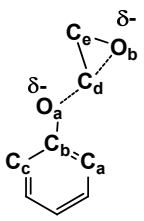
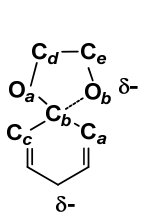
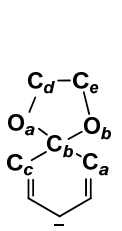
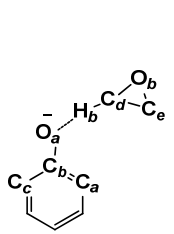
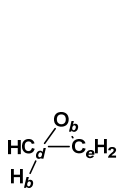
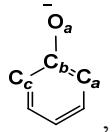
	 **1**	 **2**	 **TS 1/4**	 **TS 2/3**	 **3**	 **4**	 **P_1**
State	^1A	^1A	^1A	^1A	^1A	^1A	^1A
Symmetry	C_1	C_1	C_1	C_1	C_1	C_1	C_1
Energy (Hartree)	-459.31722	-459.32230	-459.29483	-459.30401	-459.30467	-459.32170	-153.32851
Energy Relative to 1 (kJ mol^{-1})	0	-13	59	35	33	-12	23 **[P_1+PhO$^-$]**
Gibbs Free Energy (Hartree, 298 K)	-459.35221	-459.35640	-459.33166	-459.33693	-459.33899	-459.36327	-153.35260
Gibbs Free Energy Relative to 1 (kJ mol^{-1})	0	-11	54	40	35	-29	-24 **[P_1+PhO$^-$]**
Dipole Moment (Debye)	15.57	8.62	7.26	3.19	4.13	3.31	2.49
Bond Length (Å)							
C_aC_b	1.410	1.402	1.431	1.448	1.458	1.442	—
C_bO_a	1.342	1.357	1.303	1.476	1.537	1.276	—
O_aC_d	1.467	1.460	2.006	1.408	1.402	—	—
C_dC_e	1.548	1.552	1.463	1.532	1.528	1.465	1.467
C_eO_b	1.344	1.338	1.390	1.390	1.402	1.432	1.431
H_aO_b	—	1.917	—	—	—	—	—
C_dO_b	2.374	2.464	1.907	1.665	1.547	—	—
O_aH_b	—	—	2.333	—	—	2.059	—
H_bC_d	1.098	1.097	1.080	1.096	1.098	1.089	1.087
Bond Angle (°)							
$C_aC_bO_a$	124.8	123.5	124.3	111.6	109.8	123.0	—
$C_bO_aC_d$	120.1	120.3	121.9	111.1	110.4	—	—
$O_aC_dC_e$	111.7	117.4	109.5	103.6	103.2	—	—
$C_dC_eO_b$	110.2	116.8	83.8	103.9	103.3	60.1	59.2
$C_bO_bC_e$	—	—	—	109.1	110.5	—	—
$O_aH_bC_d$	—	—	59.1	—	—	154.5	—

Table S1 Continued.

Dihedral Angle (^{o})							
$O_aC_bC_aC_c$	-180.0	-178.6	-180.0	-132.0	-126.6	179.9	—
$C_dO_aC_bC_a$	0.0	-27.0	1.0	-139.0	-131.9	—	—
$C_eC_dO_aC_b$	180.0	84.1	179.2	39.2	32.2	—	—
$O_bC_eC_dO_a$	-180.0	-76.7	-180.0	-37.0	-37.6	—	—
$H_bO_aC_bC_a$	—	—	-23.6	—	—	-23.3	—
$C_dH_bO_aC_b$	—	—	130.1	—	—	-131.9	—
$C_eC_dH_bO_a$	122.1	125.5	114.0	114.9	114.7	95.4	—



, **State** ^{1}A**, Symmetry** C_1**, Dipole Moment** 5.31 Debye**, Energy** -305.97980 Hartree**, Gibbs Free Energy (298 K)** -306.00871 Hartree, **C_aC_b** 1.447 Å, **C_bO_a** 1.270 Å, **$C_aC_bO_a$** 123.1^o, **$O_aC_bC_aC_c$** 180.0^o.

Table S2 The Smiles and S_Ni Reaction Pathways of the Singlet $PhO(CH_2)_4O^-$ Anion. Energies and Selected Geometries of Anion Minima and Transition States. **Level of theory used – CCSD(T)/6-31++G(d,p)//B3LYP/6-31++G(d,p). Relative energies in kJ mol^{-1} with respect to 5 (0 kJ mol^{-1})**

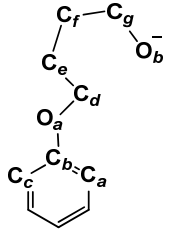
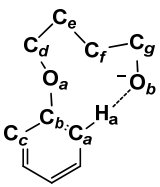
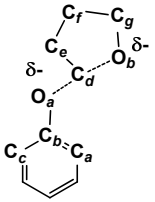
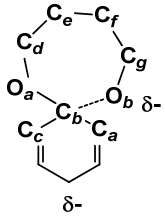
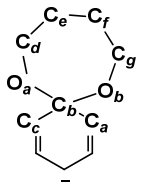
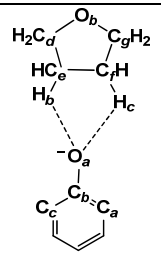
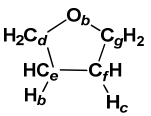
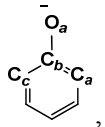
							
	5	**6**	**TS 5/8**	**TS 6/7**	**7**	**8**	**P_2**
State	^1A	^1A	^1A	^1A	^1A	^1A	^1A
Symmetry	C_1	C_1	C_1	C_1	C_1	C_1	C_1
Energy (Hartree)	-537.66536	-537.66156	-537.64546	-537.64096	-537.64338	-537.70094	-231.70556
Energy Relative to 5 (kJ mol^{-1})	0	10	52	68	62	-93	-53 **[P_2+PhO$^-$]**
Gibbs Free Energy (Hartree, 298 K)	-537.70428	-537.69898	-537.68427	-537.67626	-537.67974	-537.74741	-231.73399
Gibbs Free Energy Relative to 5 (kJ mol^{-1})	0	14	53	74	64	-113	-101 **[P_2+ PhO$^-$]**
Dipole Moment (Debye)	12.19	9.09	5.32	4.73	6.06	3.34	2.16
Bond Length (Å)							
C_aC_b	1.408	1.399	1.425	1.451	1.469	1.444	—
C_bO_a	1.349	1.382	1.314	1.435	1.503	1.282	—
O_aC_d	1.462	1.442	1.876	1.417	1.412		—
C_dC_e	1.520	1.529	1.511	1.535	1.540	1.529	1.533
C_eC_f	1.540	1.536	1.537	1.534	1.534	1.547	1.536
C_fC_g	1.562	1.565	1.541	1.562	1.560	1.551	1.531
C_gO_b	1.346	1.351	1.368	1.392	1.412	1.436	1.435
H_aO_b	—	1.852	—	—	—	—	—
C_bO_b	—	—	—	1.728	1.525	—	—
O_aH_b	—	—	—	—	—	2.526	—
O_aH_c	—	—	—	—	—	2.408	—
H_bC_e	1.101	1.101	1.095	1.102	1.098	1.092	1.094
H_cC_f	1.106	1.104	1.103	1.102	1.100	1.093	1.096
Bond Angle (^{o})							
$C_aC_bO_a$	124.6	121.0	124.6	118.8	115.3	122.8	—

Table S2 Continued.

$C_bO_aC_d$	118.6	117.1	120.4	119.1	117.9	—	—
$O_aC_dC_e$	107.9	117.0	95.5	115.3	114.4	—	—
$C_dC_eC_f$	112.5	116.9	111.2	113.6	112.3	102.0	101.9
$C_eC_fC_g$	113.8	113.8	106.4	111.2	111.7	104.0	101.6
$C_fC_gO_b$	114.6	113.3	108.3	112.7	113.0	107.1	106.1
$C_bO_bC_g$	—	—	—	115.5	116.7	—	—
$O_aH_bC_e$	—	—	—	—	—	115.7	—
$H_bO_aC_b$	—	—	—	—	—	150.4	—
$O_aH_cC_f$	—	—	—	—	—	128.3	—
$H_cO_aC_b$	—	—	—	—	—	139.8	—
Dihedral Angle (^{o})							
$O_aC_bC_aC_c$	180.0	176.3	179.7	-131.5	-122.6	179.9	—
$C_dO_aC_bC_a$	-2.6	85.9	5.9	-42.0	-49.4	94.7	—
$C_eC_dO_aC_b$	177.4	-74.4	174.3	-61.6	-63.5	155.3	—
$C_fC_eC_dO_a$	176.5	-67.1	154.7	-41.2	-34.7	77.1	—
$C_gC_fC_eC_d$	64.6	80.9	47.0	59.7	61.6	19.6	36.4
$O_bC_gC_fC_e$	-60.2	51.3	-44.9	22.3	14.1	3.5	-32.1
$H_bO_aC_bC_a$	—	—	-81.1	—	—	-159.8	—
$H_bC_eC_dO_b$	—	—	-148.9	—	—	-155.2	-153.8
$H_cO_aC_bC_a$	—	—	—	—	—	-51.2	—
$H_cC_fC_gO_b$	178.1	176.1	-167.2	146.9	137.5	119.8	87.9



, **See the structure Table S1.**

Table S3 The Smiles and S_Ni Reaction Pathways of the Singlet $PhO(CH_2)_3O^-$ Anion. Energies and Selected Geometries of Anion Minima and Transition States. **Level of theory used – CCSD(T)/6-31++G(d,p)//B3LYP/6-31++G(d,p). Relative energies in kJ mol^{-1} with respect to 9 (0 kJ mol^{-1})**

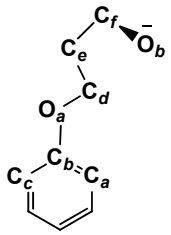
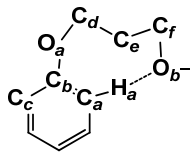
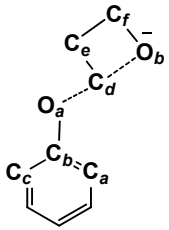
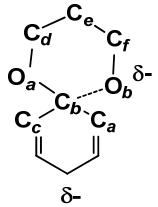
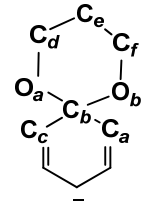
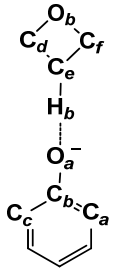
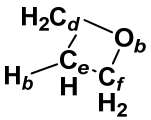
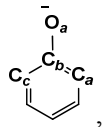
							
	9	**10**	**TS 9/12**	**TS 10/11**	**11**	**12**	**P_3**
State	^1A	^1A	^1A	^1A	^1A	^1A	^1A
Symmetry	C_1	C_1	C_1	C_1	C_1	C_1	C_1
Energy (Hartree)	-498.49110	-498.49580	-498.46333	-498.47090	-498.47421	-498.49704	-192.50282
Energy Relative to 9 (kJ mol^{-1})	0	-12	73	53	44	-16	22 **[P_3+ PhO$^-$]**
Gibbs Free Energy (Hartree, 298 K)	-498.52808	-498.53156	-498.50172	-498.50471	-498.50837	-498.54109	-192.52969
Gibbs Free Energy Relative to 9 (kJ mol^{-1})	0	-9	69	61	52	-34	-27 **[P_3+ PhO$^-$]**
Dipole Moment (Debye)	14.85	8.68	6.43	3.91	5.61	3.34	2.45
Bond Length (Å)							
C_aC_b	1.408	1.405	1.427	1.447	1.474	1.442	—
C_bO_a	1.348	1.360	1.309	1.432	1.514	1.276	—
O_aC_d	1.460	1.454	1.916	1.420	1.411	—	—
C_dC_e	1.511	1.529	1.520	1.526	1.530	1.540	1.543
C_eC_f	1.572	1.567	1.531	1.537	1.530	1.540	1.542
C_fO_b	1.339	1.343	1.394	1.385	1.411	1.457	1.450
H_aO_b	—	2.069	—	—	—	—	—
C_bO_b	—	—	—	1.783	1.515	—	—
O_aH_b	—	—	—	—	—	2.071	—
H_bC_e	1.099	1.095	1.097	1.096	1.096	1.094	1.090
Bond Angle (°)							
$C_aC_bO_a$	124.8	124.4	124.6	117.7	113.3	122.9	—
$C_bO_aC_d$	119.0	118.5	120.6	117.4	115.5	—	—
$O_aC_dC_e$	110.3	114.8	95.4	112.5	111.1	—	—
$C_dC_eC_f$	108.9	110.1	95.6	108.8	108.1	84.6	84.8

Table S3 Continued.

$C_eC_fO_b$	113.8	112.7	100.2	110.9	111.1	92.0	91.8
$C_bO_bC_f$	—	—	—	113.2	115.4	—	—
$O_aH_bC_e$	—	—	—	—	—	173.5	—
$H_bO_aC_b$	—	—	—	—	—	140.1	—
Dihedral Angle (^{o})							
$O_aC_bC_aC_c$	-179.8	-179.8	-179.8	-133.3	-121.9	-179.9	—
$C_dO_aC_bC_a$	1.4	2.9	-5.4	-58.4	-63.8	—	—
$C_eC_dO_aC_b$	-178.7	-78.1	-177.4	-65.2	-60.2	—	—
$C_fC_eC_dO_a$	177.2	141.6	-165.3	54.4	52.8	—	—
$O_bC_fC_eC_d$	-53.6	-58.0	-22.6	-55.0	-52.8	-5.9	0.2
$H_bO_aC_bC_a$	—	—	—	—	—	90.0	—
$H_bC_eC_dO_a$	58.6	24.0	78.2	-64.7	-66.0	—	—



, **See the structure Table S1.**

Table S4 The Elimination Reaction Pathways of the Singlet $PhO(CH_2)_3O^-$ Anion. Energies and Selected Geometries of Anion Minima and Transition States. **Level of theory used – CCSD(T)/6-31++G(d,p)//B3LYP/6-31++G(d,p). Relative energies in kJ mol^{-1} with respect to 9 (0 kJ mol^{-1})**

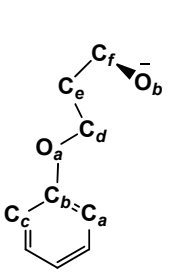
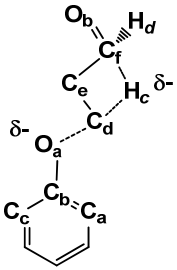
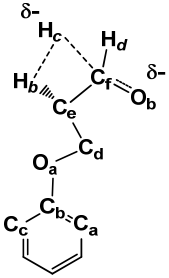
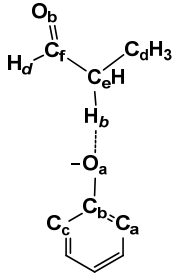
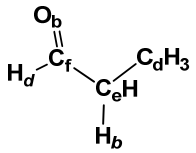
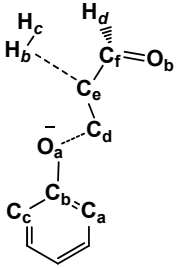
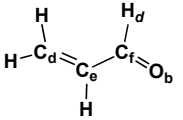
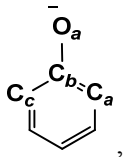
							
	9	**TS 9/13**	**TS 9/14**	**13**	**P_4**	**14**	**P_5**
State	^{1}A	^{1}A	^{1}A	^{1}A	^{1}A	^{1}A	^{1}A
Symmetry	C_1	C_1	C_1	C_1	C_1	C_1	C_1
Energy (Hartree)	-498.49110	-498.43070	-498.43613	-498.54503	-192.54482	-498.48908	-191.34790
Energy Relative to 1 (kJ mol^{-1})	0	159	144	-142	-88 **[P_4+ PhO$^-$]**	5	22 **[P_5+ H_2 +PhO$^-$]**
Gibbs Free Energy (Hartree, 298 K)	-498.52808	-498.46970	-498.47532	-498.58938	-192.57251	-498.53024	-191.37420
Gibbs Free Energy Relative to 1 (kJ mol^{-1})	0	153	139	-161	-140 **[P_4+ PhO$^-$]**	-6	-56 **[P_5+ H_2+ PhO$^-$]**
Dipole Moment (Debye)	14.85	8.89	21.73	4.28	3.48	11.20	
Bond Length (Å)							
C_aC_b		1.430	1.405	1.443	–	1.413	–
C_bO_a		1.304	1.355	1.284	–	1.340	–
O_aC_d		2.053	1.442	–	–	1.525	–
C_dC_e		1.492	1.515	1.540	1.539	1.462	1.340
C_eC_f		1.549	1.505	1.494	1.510	1.399	1.474
C_fO_b		1.279	1.225	1.223	1.214	1.265	1.218
H_dC_f		1.118	1.105	1.114	1.114	1.122	1.112
H_cC_f	**See Structure 9 in**	1.335	3.167	–	–	–	–
H_cC_d	**Table S3**	1.640	–	1.095	–	–	–
H_bC_e		1.093	1.106	1.112	1.100	2.805	–
H_bO_a		–	–	2.012	–	–	–
H_cH_b		–	2.158	–	–	0.751	–
Bond Angle (^{o})							
$C_aC_bO_a$		124.2	124.8	122.7	–	125.3	–
$C_bO_aC_d$		120.4	119.0	–	–	119.3	–

Table S4 Continued.

$O_aC_dC_e$		98.6	108.2	–	–	112.0	–
$C_dC_eC_f$		92.5	113.2	112.1	112.0	122.2	121.0
$C_eC_fO_b$		121.9	124.8	126.2	125.0	129.2	124.2
$H_cC_fC_e$		90.8	73.0	–	–	–	–
$H_cC_dC_e$		82.1	–	110.8	–	–	–
$H_dC_fC_e$		109.9	113.6	114.5	115.1	113.4	115.2
$H_bC_eC_d$		113.4	114.3	106.5	109.2	89.5	–
Dihedral Angle (°)	**See Structure 9 in Table S3**						
$O_aC_bC_aC_c$		179.7	180.0	-179.6	–	179.9	–
$C_dO_aC_bC_a$		18.7	0.6	88.6	–	5.2	–
$C_eC_dO_aC_b$		165.0	179.7	141.5	–	178.1	–
$C_fC_eC_dO_a$		-179.3	168.3	-116.9	–	102.4	–
$O_bC_fC_eC_d$		-117.4	-13.2	-128.6	-127.0	1.4	-180.0
$H_bC_eC_dO_a$		-59.5	-71.4	0.4	–	-92.4	–
$H_cC_fC_eO_b$		118.2	132.8	–	–	–	–
$H_dC_fC_eO_b$		-147.6	165.7	-179.5	179.9	178.3	-180.0

H_2, **State** $^1\Sigma_g$, **Symmetry** $D_{\infty v}$, **Dipole Moment** 0.00 Debye**, Energy** -1.15514 Hartree**, Gibbs Free Energy (298 K)** -1.16663 Hartree, **H-H** 0.743 Å.



, **See the structure in Supplementary Table 1.**

Table S5 The Decomposition Reaction Pathways of the Singlet $PhO(CH_2)_3O^-$ Anion. Energies and Selected Geometries of Anion Minima and Transition States. **Level of theory used – CCSD(T)/6-31++G(d,p)//B3LYP/6-31++G(d,p). Relative energies in kJ mol^{-1} with respect to 9 (0 kJ mol^{-1})**

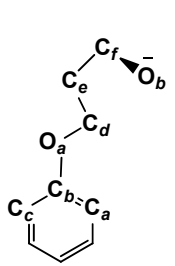
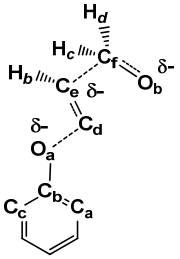
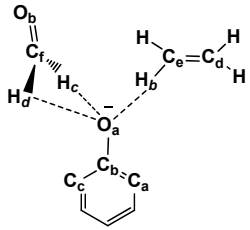
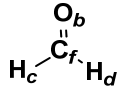
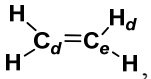
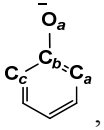
				
	9	**TS 9/15**	**15**	**P_6**
State	^1A	^1A	^1A	$^1A_1$
Symmetry	C_1	C_1	C_1	C_{2V}
Energy (Hartree)	-498.49110	-498.45918	-498.50627	-114.18954
Energy Relative to 1 (kJ mol^{-1})	0	84	-40	29**[P_6+P_7+PhO^-]**
Gibbs Free Energy (Hartree, 298 K)	-498.52808	-498.49905	-498.55486	-114.21121
Gibbs Free Energy Relative to 1 (kJ mol^{-1})	0	76	-70	-65**[P_6+P_7+PhO^-]**
Dipole Moment (Debye)	14.85	7.08	2.83	2.98
Bond Length (Å)				
C_aC_b		1.426	1.440	–
C_bO_a		1.314	1.288	–
O_aC_d		1.879	–	–
C_dC_e		1.401	1.337	–
C_eC_f		2.185	–	–
C_fO_b		1.251	1.222	1.210
H_dC_f		1.251	1.102	–
H_cC_f	**See Structure 9 in**	1.110	1.102	1.108
H_cC_d	**Table S3**	–	–	–
H_bC_e		1.091	1.092	–
H_bO_a		–	2.147	–
H_cO_a		–	2.504	–
H_dO_a		–	2.509	–
Bond Angle (^{o})				
$C_aC_bO_a$		124.5	122.52586	–

Table S5 Continued

$C_bO_aC_d$		119.9	–	–
$O_aC_dC_e$		112.9	–	–
$C_dC_eC_f$		103.0	–	–
$C_eC_fO_b$		113.8	–	–
$H_cC_fC_e$		93.5	–	–
$H_cC_fO_b$		120.6	–	121.9
$H_dC_fC_e$		86.0	–	–
$O_aC_fO_b$		–	126.4	–
$H_bO_aC_b$		–	143.6	–
$H_cO_aC_b$		–	92.0	–
$H_dO_aC_b$		–	91.6	–
Dihedral Angle (°)	**See Structure 9 in Table S3**			
$O_aC_bC_aC_c$		179.6	-179.0	–
$C_dO_aC_bC_a$		19.2	–	–
$C_eC_dO_aC_b$		164.9	–	–
$C_fC_eC_dO_a$		174.9	–	–
$O_bC_fC_eC_d$		-72.7	–	–
$H_bC_eC_dO_a$		-73.2	–	–
$H_cC_fC_eO_b$		53.3	–	–
$H_dC_fC_eO_b$		165.5	–	–
$H_dC_fO_bH_c$		150.2	–	180.0
$H_bO_aC_bC_a$		–	-108.3	
$O_bC_fO_aC_b$		–	179.5	
$C_dC_eH_bO_a$		–	-176.6	



, [P_7] **State** ^1A_g**, Symmetry** C_i**, Dipole Moment** 0.00 Debye**, Energy** -78.31058 Hartree**, Gibbs Free Energy (298 K)** -78.33277 Hartree, C_dC_e 1.334 Å, H_dC_e 1.087 Å, $H_dC_eC_d$ 121.7°.



, **See the Structure in Table S1.**