Supporting Material to Accompany "Ketene-Forming Eliminations from Aryl phenylacetates Promoted by $R_2NH/R_2NH_2^+$ in MeCN(aq). Mechanistic Borderline between E2 and E1cb

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Table S1. Observed rate constants for eliminations from 4-NO_2-$C_6H_4CH_2CO_2C_6H_3$-2-Cl-4-NO_2 (**1c**) [a] promoted by $R_2NH/R_2NH_2^+$ in 70 mol % MeCN (aq) [b,c] at 25.0 °C.

	$10k_{obs}$, s^{-1} [d,e] when R_2NH is			
10^3[base], M	Bz(i-Pr)NH	i-Bu_2NH	i-Pr_2NH	2,6-DMP [f]
0.840	0.165	0.350	0.239	0.454
1.00	0.207	0.427	0.305	0.538
2.00	0.369	0.831	0.612	1.13
4.00	0.669	1.56	1.23	2.31
6.00	1.01	2.34	1.88	3.29
8.00	1.32	2.78	2.50	4.13

[a] [Substrate] = (2.0–4.0) × 10^{-5} M. [b] $[R_2NH]/[R_2NH_2^+]$ = 1.0. [c] μ = 0.10 M ($Bu_4N^+Br^-$). [d] Average of three or more kinetic runs. [e] Estimated uncertainty, ± 5 %. [f] cis-2,6-Dimethylpiperidine.

Table S2. Observed rate constants for eliminations from 4-NO_2-$C_6H_4CH_2CO_2C_6H_3$-2-X-4-NO_2 (**1d-e**) [a] promoted by $R_2NH/R_2NH_2^+$ in 70 mol % MeCN (aq) [b-d] at 25.0 °C.

	10^2k_{obs}, s^{-1} [e,f] when R_2NH is			
X	Bz(i-Pr)NH	i-Bu_2NH	i-Pr_2NH	2,6-DMP [g]
CF_3 (**1d**)	0.165	0.350	0.239	0.454
NO_2 (**1e**)	0.207	0.427	0.305	0.538

[a] [Substrate] = (2.0–4.0) × 10^{-5} M. [b] $[R_2NH]/[R_2NH_2^+]$ = 1.0. [c] [Base] = 8.00 × 10^{-4} M. [d] μ = 0.10 M ($Bu_4N^+Br^-$). [e] Average of three or more kinetic runs. [f] Estimated uncertainty, ± 5 %. [g] cis-2,6-Dimethylpiperidine.

Table S3. Observed rate constants for eliminations from 2,4-$(NO_2)_2$-$C_6H_3CH_2CO_2C_6H_4$-4-NO_2 (**2a**) [a] promoted by $R_2NH/R_2NH_2^+$ in 70 mol % MeCN (aq) [b,c] at 25.0 °C.

	10^2k_{obs}, s^{-1} [d,e] when R_2NH is		
10^3[base], M	Bz(i-Pr)NH	i-Bu_2NH	2,6-DMP [f]
0.600	2.00	4.17	4.09
0.800	2.29	4.87	5.02
1.00	2.46	5.88	6.78
1.40	2.75	7.11	9.82
1.80	3.03	8.11	12.6
2.00	3.10	8.77	14.2
3.00	3.47	10.1	20.0
4.00	3.62	10.9	24.7
6.00	3.83	14.7	29.6
8.00	3.98	18.3	36.0
10.0	3.96	19.3	41.2
20.0	4.20	19.1	49.8

See footnotes in Table S1.

Table S4. Observed rate constants for eliminations from 4-NO_2-$C_6H_4CH_2CO_2C_6H_3$-4-NO_2 (**1a**) [a] promoted by $R_2NH/R_2NH_2^+$ in 70 mol % MeCN (aq) [b,c] at 25.0 °C.

	10^2k_{obs}, s^{-1} [d,e] when R_2NH is		
10^3[base], M	Bz(i-Pr)NH	i-Bu_2NH	2,6-DMP [f]
0.960	0.778	1.83	3.00
1.20	0.878	2.16	3.53
2.40	1.21	3.43	7.13
4.80	1.56	4.74	12.7
7.20	1.80	5.88	17.3
9.60	1.92	6.62	21.4
12.0	2.03	6.82	24.0
24.0	2.39	8.84	36.1
36.0	2.62	10.6	43.8
48.0	2.83	10.7	48.8
60.0	3.06	11.3	53.5

See footnotes in Table S1.

Table S5. Observed rate constants for eliminations from 4-NO_2-$C_6H_4CH_2CO_2C_6H_3$-4-NO_2 (**1a**) [a] promoted by Bz(i-Pr)NH/Bz(i-Pr)NH_2^+ in 70 mol % MeCN (aq) [b] at 25.0 °C.

10^3[base] [c], M	10^2k_{obs}, s^{-1} [d,e]	10^3[base] [f], M	10^2k_{obs}, s^{-1} [d,e]
0.480	0.392	0.960	0.938
0.600	0.432	1.20	1.06
1.20	0.625	2.40	1.66
2.40	0.785	4.80	2.37
3.60	0.897	7.20	2.80
4.80	0.967	9.60	3.08
6.00	1.02	12.0	3.33
12.0	1.18	24.0	4.08
18.0	1.32	36.0	4.65
24.0	1.40	48.0	4.99
30.0	1.49	60.0	5.07

[a] [Substrate] = (2.0–4.0) × 10^{-5} M. [b] μ = 0.10 M ($Bu_4N^+Br^-$). [c] [R_2NH]/[$R_2NH_2^+$] = 0.5. [d] Average of three or more kinetic runs. [e] Estimated uncertainty, ± 5 %. [f] [R_2NH]/[$R_2NH_2^+$] = 2.0.

Table S6. Observed rate constants for eliminations from 4-NO_2-$C_6H_4CH_2CO_2C_6H_3$-2-MeO-4-NO_2 (**1b**) [a] promoted by R_2NH/$R_2NH_2^+$ in 70 mol % MeCN (aq) [b,c] at 25.0 °C.

	10^2k_{obs}, s^{-1} [d,e] when R_2NH is		
10^3[base], M	Bz(i-Pr)NH	i-Bu_2NH	2,6-DMP [f]
0.960	0.490	1.28	2.07
1.20	0.570	1.50	2.61
2.40	0.765	2.25	5.04
4.80	0.950	3.18	8.67
7.20	1.07	3.72	11.8
9.60	1.16	4.11	14.0
12.0	1.23	4.43	15.6
24.0	1.46	5.37	22.3
36.0	1.60	5.97	29.0
48.0	1.77	6.57	30.3
60.0	1.92	6.97	31.8

See footnotes in Table S1.

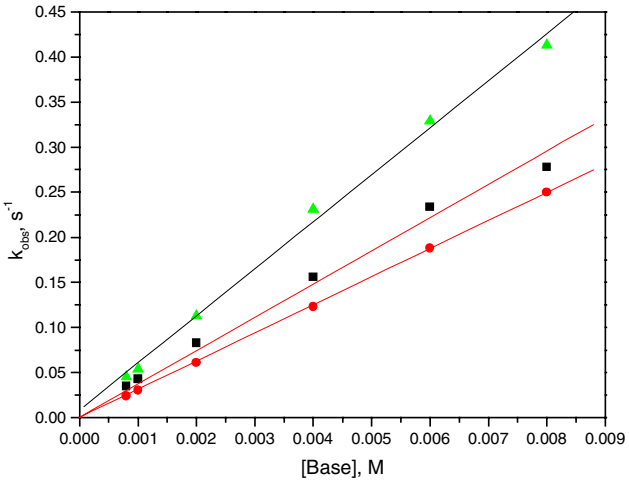

Figure S1. Plots of k_{obs} vs base concentration for eliminations from **1c** promoted by $R_2NH/R_2NH_2^+$ in 70 mol % MeCN(aq) at 25 °C, $[R_2NH]/[R_2NH_2^+]$ = 1.0, μ = 0.10 M ($Bu_4N^+Br^-$). [R_2NH = i-Bu_2NH (▲), i-Pr_2NH (■), 2,6-DMP(●)].

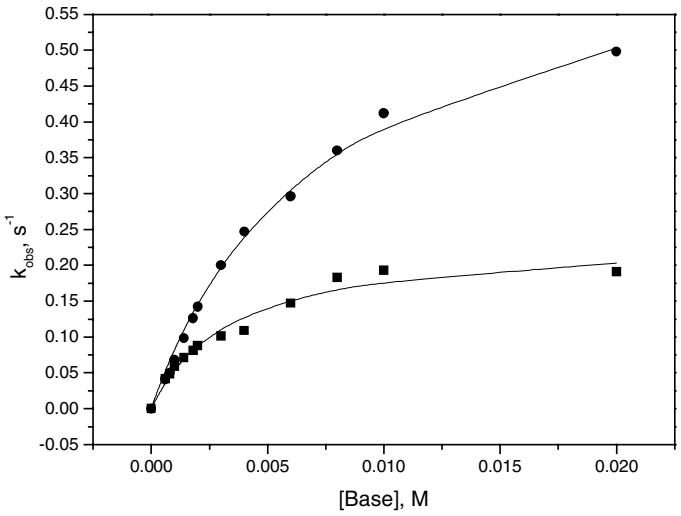

Figure S2. Dependence of k_{obs} vs base concentration for elimination from **2a** promoted by 2,6-DMP/2,6-$DMPH^+$ (●) and i-Bu_2NH/i-$Bu_2NH_2^+$ (■) in 70 mol % MeCN(aq) at 25 °C, $[R_2NH]/[R_2NH_2^+]$ = 1.0, μ = 0.10 M ($Bu_4N^+Br^-$).

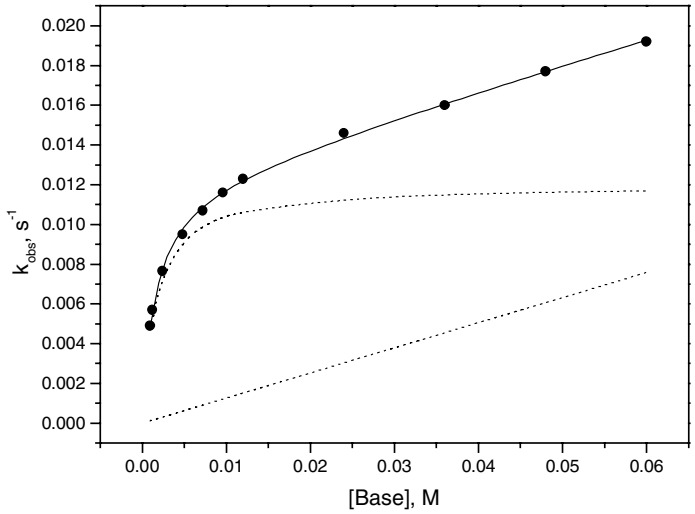

Figure S3. Dependence of k_{obs} vs base concentration for elimination from **1a** promoted by Bz(i-Pr)NH/Bz(i-Pr)NH_2^+ in 70 mol % MeCN(aq) at 25 °C, [Bz(i-Pr)NH]/[Bz(i-Pr)NH_2^+] = 1.0, μ = 0.10 M ($Bu_4N^+Br^-$).

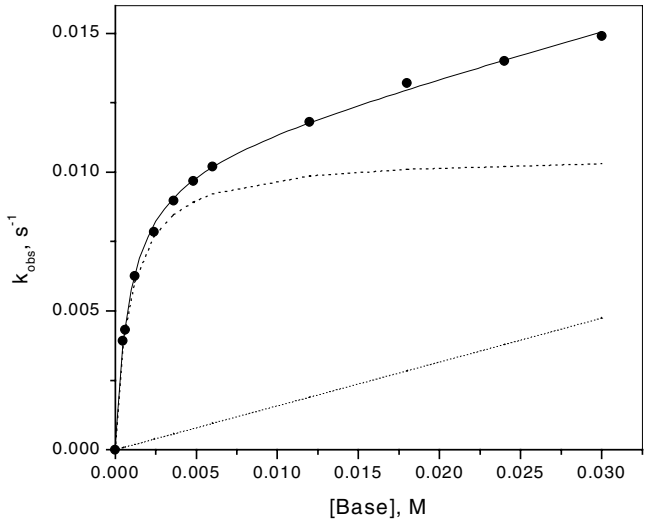

Figure S4. Dependence of k_{obs} vs base concentration for elimination from **1a** promoted by Bz(i-Pr)NH/Bz(i-Pr)NH_2^+ in 70 mol % MeCN(aq) at 25 °C, [Bz(i-Pr)NH]/[Bz(i-Pr)NH_2^+] = 0.5, μ = 0.10 M ($Bu_4N^+Br^-$)

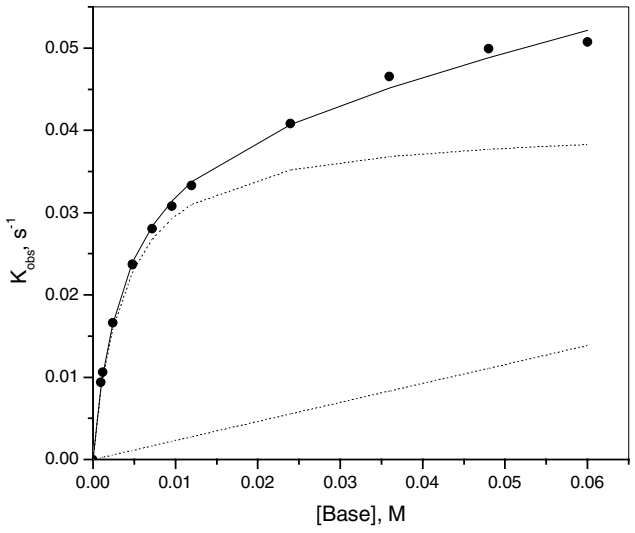

Figure S5. Dependence of k_{obs} vs base concentration for elimination from **1a** promoted by Bz(i-Pr)NH/Bz(i-Pr)NH_2^+ in 70 mol % MeCN(aq) at 25 °C, [Bz(i-Pr)NH]/[Bz(i-Pr)NH_2^+] = 2.0, μ = 0.10 M ($Bu_4N^+Br^-$).

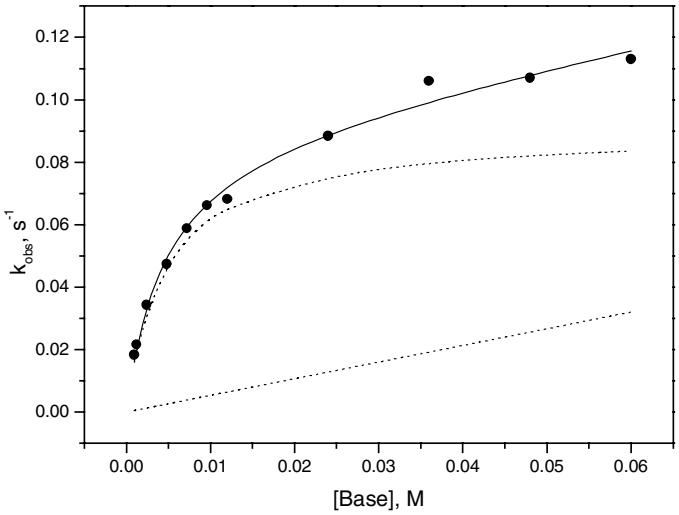

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Figure S6. Dependence of k_{obs} base concentration for the elimination **1a** promoted by by i-Bu_2NH/ i-$Bu_2NH_2^+$ in 70 mol % MeCN(aq) at 25 °C, [i-Bu_2NH]/[i-$Bu_2NH_2^+$] = 1.0, μ = 0.10 M ($Bu_4N^+Br^-$).

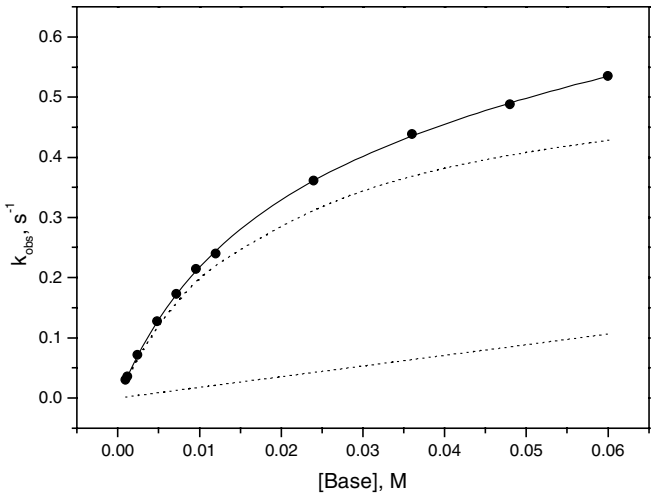

Figure S7. Dependence of k_{obs} vs base concentration for elimination from **1a** promoted by 2,6-DMP/2,6-DMPH$^+$ in 70 mol % MeCN(aq) at 25 °C, [2,6-DMP]/[2,6-DMPH$^+$] = 1.0, μ = 0.10 M ($Bu_4N^+Br^-$).

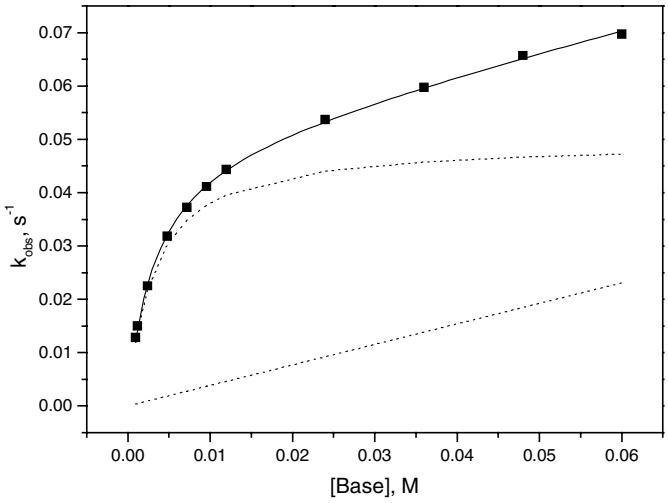

Figure S8. Dependence of k_{obs} vs base concentration for the elimination from **1b** promoted by i-Bu_2NH/ i-$Bu_2NH_2^+$ in 70mol % MeCN(aq) at 25 °C, [i-Bu_2NH]/[i-$Bu_2NH_2^+$] = 1.0, μ = 0.10 M ($Bu_4N^+Br^-$).

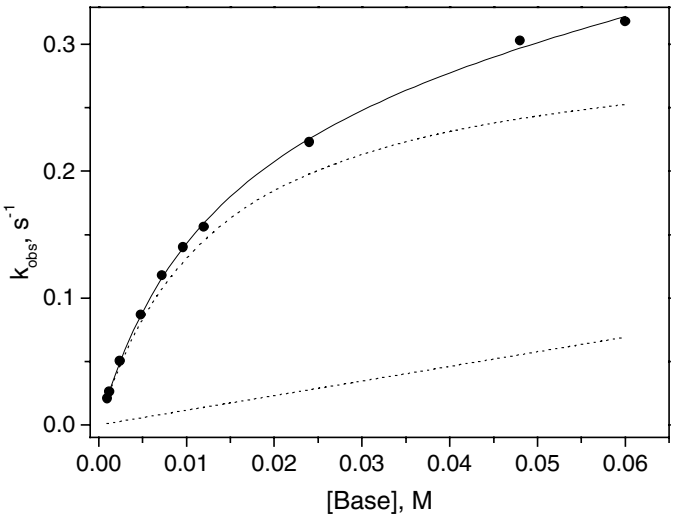

Figure S9. Dependence of k_{obs} vs base concentration for the elimination from **1b** promoted by 2,6-DMP/2,6-DMPH$^+$ in 70mol % MeCN(aq) at 25 °C, [2,6-DMP]/[2,6-DMPH$^+$] = 1.0, μ = 0.10 M ($Bu_4N^+Br^-$).