Supporting Information

Dynamic path bifurcation in the Beckmann reaction: Support from kinetic analyses

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Sigma values used in the present study

Table S1. σ° and $\Delta\bar{\sigma}_{R+}$ values used in the present study.

X	σ°	$\Delta\bar{\sigma}_{R}^{+}$
p-MeO	-0.100	-0.700
m,*p*-Me_2	-0.193	0.000
p-Me	-0.124	-0.187
m-Me	-0.069	0.000
H	0.000	0.000
p-Cl	0.281	-0.166
m-Cl	0.373	0.000
p-CF_3	0.540	0.000
p-CN	0.670	0.000
p-NO_2	0.780	0.000

Free energy difference between the two product states calculated at MP2/6-31G*

Table S2. Free energy differences between the rearrangement product and the fragmentation products for **4**-H and **6**-H calculated at MP2/6-31G*

	$PhCR_2N{=}C^{+}CH_3$[a]	$PhCR_2^{+}$[a]	CH_3CN[a]	$\delta\Delta G$[b]
4-H (R = H)	-402.003514	-269.653980	-132.316370	20.81
6-H (R = Me)	-480.295233	-347.964585	-132.316370	8.95

[a] In hartree. [b] Free energy of the fragmentation products relative to the rearrangement product in kcal/mol.

MP2/6-31G* optimized Cartesian coordinates and free energies of compounds studied

6-H, −480.295233

N	1.704239	−0.036075	−0.058206
C	2.500760	−0.849174	−0.310556
C	3.481229	−1.876301	−0.627483
C	0.675526	0.988919	0.232524
C	−0.660089	0.282575	0.062304
C	−0.915242	−0.879823	0.806405
C	−2.143619	−1.528729	0.699214
C	−3.132418	−1.018693	−0.146394
C	−2.883425	0.138590	−0.884467
C	−1.649679	0.787153	−0.789504
C	0.906819	1.446388	1.674925
H	4.101776	−1.537890	−1.461096
H	2.959645	−2.795439	−0.906774
H	4.109694	−2.059766	0.247578
H	−0.160731	−1.285716	1.478918
H	−2.331282	−2.428037	1.279618
H	−4.092836	−1.520265	−0.226271
H	−3.648845	0.540689	−1.542539
H	−1.483486	1.685449	−1.375214
H	1.891476	1.908845	1.788202
H	0.806485	0.618181	2.378620
H	0.138346	2.187690	1.907875
C	0.945940	2.124702	−0.752631
H	0.824104	1.798104	−1.787395
H	0.242960	2.935355	−0.549623
H	1.958206	2.511684	−0.610476

$PhC(CH_3)_2^+$, −347.964585

C	−1.574851	0.000031	0.000042
C	−0.164805	0.000042	0.000025
C	0.562779	1.228833	0.051220
C	1.946557	1.218298	0.070419
C	2.639053	−0.000029	−0.000007
C	1.946491	−1.218322	−0.070406
C	0.562714	−1.228783	−0.051172
C	−2.381987	−1.243913	0.108887
H	0.041108	2.177216	0.118498
H	2.496564	2.152653	0.130040
H	3.726621	−0.000058	−0.000019
H	2.496447	−2.152706	−0.130028
H	0.040975	−2.177136	−0.118403
H	−2.686318	−1.539715	−0.906834
H	−3.306461	−1.037526	0.656210
H	−1.865997	−2.079471	0.576710
C	−2.382107	1.243893	−0.108836
H	−2.686762	1.539497	0.906844
H	−1.866155	2.079596	−0.576429
H	−3.306418	1.037429	−0.656415