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Dynamic Path Bifurcation in the Beckmann Reaction: Support from Kinetic Analyses

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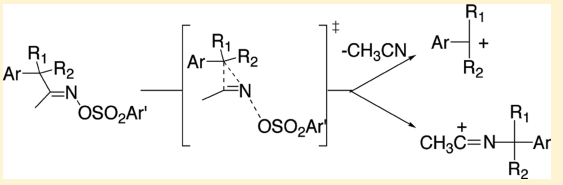
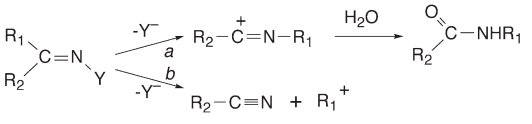
Supporting Information

ABSTRACT: The reactions of oximes to amides, known as the Beckmann rearrangement, may undergo fragmentation to form carbocations + nitriles when the migrating groups have reasonable stability as cations. The reactions of oxime sulfonates of 1-substituted-phenyl-2-propanone derivatives (**7**-X) and related substrates (**8**-X, **9a**-X) in aqueous CH_3CN gave both rearrangement products (amides) and fragmentation products (alcohols), the ratio of which depends on the system; the reactions of **7**-X gave amides predominantly, whereas **9a**-X yielded alcohols as the major product. The log*k*−log*k* plots between the systems gave excellent linear correlations with slopes of near unity. The results support the occurrence of path bifurcation after the rate-determining TS of the Beckmann rearrangement/fragmentation reaction, which has previously been proposed on the basis of molecular dynamics simulations. It was concluded that path-bifurcation phenomenon could be more common than thought and that a reactivity-selectivity argument based on the traditional TS theory may not always be applicable even to a well-known textbook organic reaction.



INTRODUCTION

The Beckmann rearrangement is a classical textbook reaction, in which oximes under acidic conditions or oximes with an appropriate leaving group (Y) under solvolytic conditions give amide via intramolecular rearrangement (path *a* in eq 1). The Beckmann rearrangement proceeds via a concerted mechanism with a higher reactivity for a more electron-donating R_1 group.[1,2] Oximes have also been known to give fragmentation products when the R_1 group is stabilized as a cation by an adjacent group, such as O,[3] S,[4] N,[5] Si,[6] and CH═CHR.[7] Grob and co-workers have shown that the rearrangement of an oxime tosylate (Y = OTs, eq 1) in 80% ethanol gave the mixture of the amide and nitrile products and that the product ratio varied depending on R_1 and R_2.[8] For a series of R_1, the ratio (%) of fragmentation was reported to be 0 (*i*-Pr), 10 (*t*-Bu), and 80 ($CHPh_2$). On the other hand, the overall reactivity varied with the R_1 group in the order (relative reactivity), Me (1) < $CHPh_2$ (40) < Et (60) < Ph (100) < *i*-Pr (810) < *t*-Bu (870). The ratio of fragmentation to amide formation was not related to the overall reactivity, but increases with the stability of R_1^+.



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It has increasingly been recognized by means of molecular dynamics (MD) simulation studies that dynamics effect plays a crucial role in controlling the mechanism of mechanistically borderline reactions.[9] Following a pioneer study by Carpenter in 1985,[10] dynamics effect has been claimed to appear in different ways, such as nonstatistical barrier recrossing,[11] nonstatistical product distribution,[12] shallow minimum skip on the intrinsic reaction coordinate (IRC),[13] non-IRC path,[14] and path bifurcation.[15−18] All these results suggested that the mechanism of these reactions could not be defined by the reaction paths on the potential energy surface (PES) and by the traditional transition state (TS) theory.

Recent molecular orbital (MO) and MD study indicated that the Beckmann rearrangement/fragmentation reactions of 1-substituted-phenyl-2-propanone oximes in the gas phase proceeded through a single TS, and that the introduction of an electron-donating substituent into the phenyl ring changed the mechanism from rearrangement to fragmentation. The trajectory calculations suggested that both rearrangement/fragmentation products were formed through path bifurcation on the way from the TS to the product states and that the product ratio varied as a function of substituent.[17] Thus, the rate-determining TS did not contain enough information to define the product ratio and therefore to define the entire reaction mechanism.[17,18] Under these circumstances, it is important to know whether the bifurcation mechanism operates in solution reaction as well.

In the present study, we have carried out kinetics as well as product-analysis experiment on the reactions of a series of sulfonate esters of ketoximes in aqueous CH_3CN to address two important mechanistic issues; (1) whether experimental results agree with the bifurcation mechanism that was previously proposed on the basis of the simulation study,[17] and (2) what is

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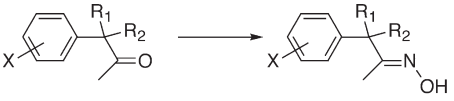
the factor which controls the overall reactivity and the relative importance of rearrangement and fragmentation routes in the borderline reaction systems. The results have supported the occurrence of path bifurcation for this classical reaction.

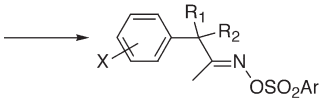
RESULTS AND DISCUSSION

Substituted ketones (**1**-X) were synthesized from corresponding benzaldehydes by nitroaldol with $EtNO_2$,[19] and Fe reduction.[20] Ketones, **2**-X and **3**-X, were prepared from **1**-X by methylation (MeI/NaOH). Oximation with NH_2OH, followed by esterification by Tipson's method[21] gave esters, (7-X−**9a**-X, eq 2). We used 2-naphthalenesulfonate esters for **7**-X and most **8**-X, but 4-methoxybenzenesulfonates were used for **8a**-*p*-MeO and **9a**-X, since the 2-naphthalenesulfonates were difficult to purify for **8**-*p*-MeO and **9**-X.



1-X : $R_1 = R_2 = H$
2-X : $R_1 = H$, $R_2 = Me$
3-X : $R_1 = R_2 = Me$

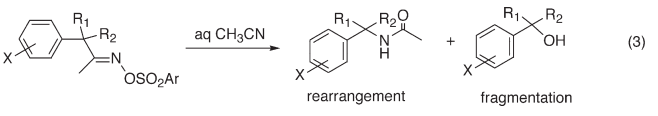
4-X : $R_1 = R_2 = H$
5-X : $R_1 = H$, $R_2 = Me$
6-X : $R_1 = R_2 = Me$



(2)

7-X : $R_1 = R_2 = H$; Ar = 2-Naph
8-X : $R_1 = H$, $R_2 = Me$; Ar = 2-Naph
8a-X : $R_1 = H$, $R_2 = Me$; Ar = *p*-$MeOC_6H_4$
9a-X : $R_1 = R_2 = Me$; Ar = *p*-$MeOC_6H_4$

The three reaction systems were chosen in the hope that they all would give either or both rearrangement (R) and fragmentation (F) products and that the product ratios would vary with systems (eq 3), thus allowing us to examine the correlation between the overall reactivity and the product selectivity. The reactions of **7**-X−**9a**-X were carried out in aqueous CH_3CN at 25 °C in the presence of 1.1 equiv of *N*,*N*-dimethylaniline. We chose aqueous CH_3CN as the solvent system, where the product composition was simple with only amide (rearrangement) and alcohol (fragmentation) as each type of the product and the reaction rates were conveniently measured by a spectroscopic method. Pseudo first-order rate constants are summarized in Table 1. Rate constants are averages of multiple runs with reproducibility of ±3%. The rate of **8**-*p*-MeO could not be measured directly, since this compound could not be purified by recrystallization. Instead, the rate constant for **8**-*p*-MeO was calculated from the log*k*−log*k* plot between **8**-X (X = H and *p*-Cl) and **8a**-X (X = H (1.35×10^{-3} s^{-1}), *p*-Cl (4.57×10^{-4} s^{-1}) and *p*-MeO (1.19×10^{-2} s^{-1})).



(3)

The product compositions for these reactions were determined by NMR, and the results are listed in Table 2. It is seen that the product ratio is different for the three systems. Acetamides are the major product for **7**-X, whereas 2-phenyl-2-propanols are the major product for **9a**-X. For **8**-X, the relative yield of alcohol (F%) spans in a wide range from 0 to 95%. In all cases, there is a general trend that a more fragmentation product is formed with a more electron-donating substituent.

The substituent effect on the reactivity was analyzed by means of an extended Hammett equation (the Yukawa-Tsuno equation, eq 4), in which *r* is a parameter to measure the relative importance of resonance effect over inductive effect and $r = 1.0$ for $\sigma_{app} = \sigma^+$ by definition and $r = 0.27$ for $\sigma_{app} = \sigma$.[22] Figure 1 shows the Yukawa-Tsuno plot for the reactions of 7-X in 80% CH_3CN at 25 °C. The values of σ° and $\Delta\bar{\sigma}_R^+$ are listed in the Supporting Information. The observed excellent linear correlation with $r = 0.52$ indicates that the reaction mechanism is basically the same for all 7-X's. The medium sized ρ and *r* values suggest that the migrating benzyl group bears a significant amount of positive charge on the benzylic carbon, consistent

Table 1. Pseudo First-Order Rate Constants for the Reactions of 7-X−9a-X in Aqueous CH_3CN at 25 °C

	k/s^{-1}		
X	7-X[a]	8-X[b]	**9a**-X[b,c]
p-MeO	9.79×10^{-3}	4.27×10^{-2} [d]	1.48×10^{-2}
m,*p*-Me_2	3.24×10^{-3}	1.80×10^{-2}	
p-Me	2.41×10^{-3}	1.14×10^{-2}	4.09×10^{-3}
m-Me	1.04×10^{-3}	5.01×10^{-3}	
H	8.15×10^{-4}	4.07×10^{-3}	1.46×10^{-3}
p-Cl	2.82×10^{-4}	1.54×10^{-3}	
m-Cl	1.01×10^{-4}	5.52×10^{-4}	2.22×10^{-4}
p-CF_3	4.52×10^{-5}	2.46×10^{-4}	
p-CN	2.63×10^{-5}	1.35×10^{-4}	
p-NO_2	1.33×10^{-5}	7.63×10^{-5}	3.50×10^{-5}

[a] In 80% (v/v) CH_3CN. [b] In 90% (v/v) CH_3CN [c] Rate constants for *p*-methoxybenzensulfonates of **6**. [d] Calculated from the rate constant for **8a**-*p*-MeO and the relative reactivity of the two leaving groups. See text in detail.

Table 2. Product Distributions for the Reactions of 7-X−9a-X in Aqueous CH_3CN at 25 °C

	7-X[a]			8-X[b]			**9a**-X[b]		
X	R[c]	F[d]	F%[e]	R[c]	F[d]	F%[e]	R[c]	F[d]	F%[e]
p-MeO	77.6	27.7	26.3	4.9	90.9	94.9	0.0	100.0[f]	100.0
m,*p*-Me_2	86.6	9.0	9.4	40.3	57.8	58.9			
p-Me	90.4	7.4	7.6	46.5	50.2	51.9	0.0	100.0[f]	100.0
m-Me	100.0[f]	0.0	0.0	74.5	24.2	24.4			
H	100.0[f]	0.0	0.0	77.3	20.9	21.3	5.6	95.7	94.5
p-Cl	100.0[f]	0.0	0.0	76.7	19.7	20.4			
m-Cl	100.0[f]	0.0	0.0	95.3	5.9	5.8	41.8	61.1	59.4
p-CF_3	100.0[f]	0.0	0.0	94.7	1.5	1.6			
p-CN	100.0[f]	0.0	0.0	100.0[f]	0.0	0.0			
p-NO_2	100.0[f]	0.0	0.0	100.0[f]	0.0	0.0	76.6	21.8	22.2

[a] In 80% (v/v) CH_3CN. [b] In 90% (v/v) CH_3CN. [c] Yield of rearrangement product (%). [d] Yield of fragmentation product (%). [e] Relative yield of fragmentation product (F/(R + F)). [f] Single product was obtained.

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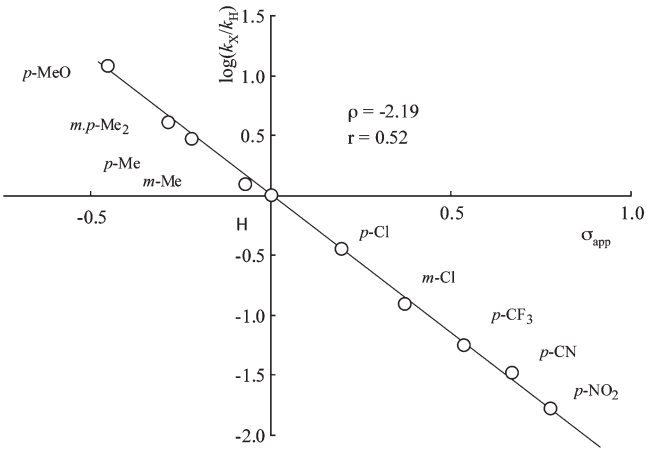


Figure 1. Yukawa-Tsuno plot for the reaction of 7-X in 80% (v/v) CH_3CN at 25 °C.

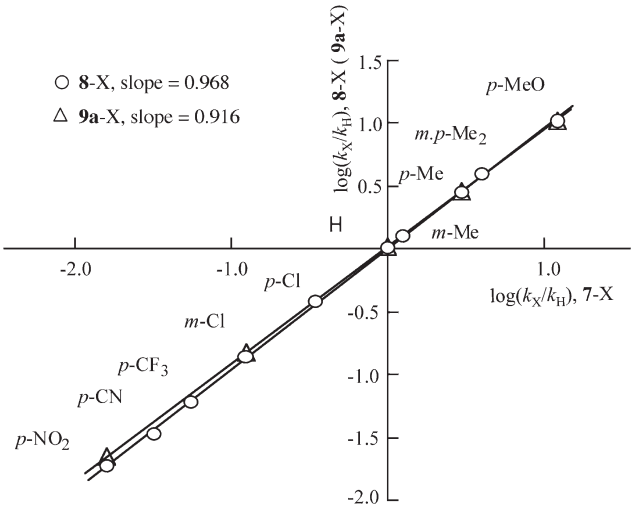


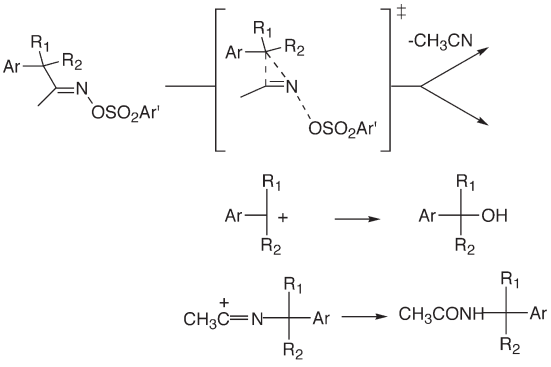
Figure 2. Log*k*−log*k* plot between the reactions of **8**-X and **9a**-X in 90% (v/v) CH_3CN vs 7-X in 80% (v/v) CH_3CN at 25 °C.

with previous observations.[1] The Yukawa-Tsuno analyses of the substituent effects for **8**-X and **9a**-X gave similar results with ρ and r values of −2.15 and 0.56, and −2.00 and 0.59, respectively. The linear free energy (log*k*−log*k*) plots between the three systems are more straightforward as shown in Figure 2. The observed excellent linear correlations with slopes of near unity clearly indicate that the substituent effects for all three systems are the same despite the fact that the product ratios are very different.

$$\log(k/k_0) = \rho\{\sigma^\circ + r(\sigma^+ - \sigma^\circ)\} = \rho\{\sigma^\circ + r\Delta\bar{\sigma}_R{}^+\} = \rho\sigma_{app} \quad (4)$$

Path Bifurcation. Previous MO calculations showed that the acid-catalyzed reactions of **4**-X in the gas phase proceeded through TSs, whose structures had features characteristic to the rearrangement reactions.[17] The analyses of activation energies indicated that the substituent effects gave an excellent linear Hammett correlation, despite the fact that the intrinsic reaction coordinate (IRC) from each respective TS led to different products depending on the substituent; **4**-X with an electron-donating X gave the fragmentation product, whereas **4**-X with an electron-withdrawing X yielded the rearrangement product. Ab initio dynamics simulations gave trajectories, which followed the IRC path for X = *p*-NH_2 and *p*-MeO giving fragmentation products, and almost so for X = *p*-NO_2 giving the rearrangement products. However, in borderline cases where X was less electron-donating than *p*-MeO or less electron-withdrawing than *p*-NO_2, the trajectories did not follow the minimum energy path on the PES, but gave both rearrangement and fragmentation products directly from the single TS through path bifurcation after the TS.[17]

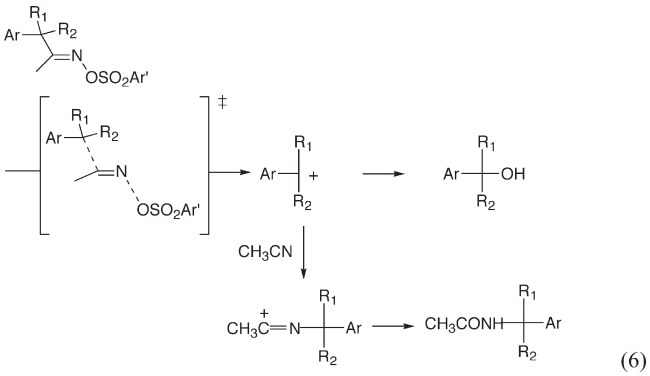
The present experimental observations agree with these computational results and the observed mismatch between relative reactivity and product selectivity is best rationalized as arising from path bifurcation occurring on the way from the rate-determining TS to the product states (eq 5). An excellent linear correlation was observed between 7-X−**9a**-X despite the fact that the product varied depending on the system and the substituent. Interestingly **9a**-X, which gave mostly fragmentation products showed the same substituent effects as 7-X, for which rearrangement products are the major product. These results demonstrate that the stability of the TS, or the reactivity, has no relevance to the identity of the product. The product ratio could be determined by dynamics effect and is likely to be controlled by the relative stability of the two cationic intermediates (carbocation and nitrilium ion), as indicated by the previous calculations.[17] A substrate with a more electron-donating substituent yields more fragmentation product because the barrier that separates the two product regions on the PES is located closer to the less stable product region, in accordance with the Leffler−Hammond postulate[23] and the Thornton rule.[24] As a result, more trajectories lead to a more stable product region. It should be noted that the resultant product selectivity is in line with the prediction based on the traditional electronic theory.



(5)

Alternative Interpretations. There are three alternatives that do not invoke unfamiliar bifurcation for the fundamental organic reaction: (1) concurrent and competitive pathways for rearrangement and fragmentation as in eq 1, (2) a mechanism with the fragmentation intermediate ($ArCR_1R_2{}^+$) as a common precursor for both rearrangement and fragmentation products (eq 6),

and (3) a mechanism with the rearrangement intermediate as a common precursor for the both products (eq 7).



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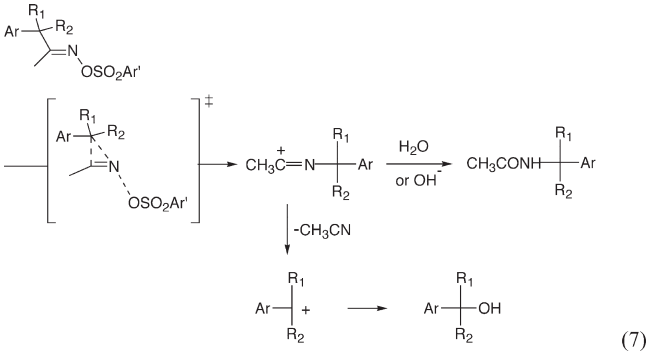

(7)

The first alternative is unlikely, since it requires that the two pathways have the same substituent effect although the two initial intermediates are very different. It is also inconsistent with the previous computational results that there is only one TS leading to either the fragmentation or the rearrangement product for the reactions of **4**-X.

The second mechanism with the fragmentation intermediate as a common precursor requires the fragmentation step being rate-determining (eq 6). Since the intermediate cation is much more stable for **9a**-H ($PhCMe_2^+$) than for **8a**-H ($PhCHMe^+$), the rate constant should be much larger for **9a**-H than for **8a**-H, which is not consistent with the observations: $k = 1.35 \times 10^{-3}$ s^{-1} for **8a**-H and 1.46×10^{-3} s^{-1} for **9a**-H. Similarly, the α-Me rate-acceleration effect for **8**-X/**7**-X is ca. 5, which is much smaller than that ($\sim 10^3$–10^5) known for carbocation-formation reactions in aqueous solvent.[25] To further examine the second possibility, the reaction of **8**-*p*-Me was carried out in 90% aqueous CD_3CN and deuterium content of the product *p*-$MeC_6H_4CHCH_3NHCOCH_3$ was determined. If the benzylic cation is the common intermediate for the rearrangement and the fragmentation product, the amide product for the reaction in CD_3CN solvent should contain deuterium in the acetyl methyl group. It was found that the F% for the reaction in aqueous CD_3CN was 53.3%, which was similar to 51.9% in aqueous CH_3CN. The NMR analysis of the product revealed that the H-content in the acetyl CH_3 group of the amide was 99.1 ± 1.3%. The result eliminates a possible involvement of *p*-$MeC_6H_4CHCH_3$ cation as a precursor of the rearrangement product.

In the third interpretation, the reaction goes through a TS to give the rearrangement intermediate, which may afford CH_3CN + benzylic cation upon N−C bond cleavage in addition to the amide formation (eq 7). Although it is difficult to completely eliminate the possibility, this mechanism is unlikely since it requires that the N−C bond cleavage in the cationic intermediate is competitive with the attack of solvent water on the cation. The former step is endergonic in the gas phase (20.8 and 9.0 kcal/mol for $PhCH_2N{=}C^+CH_3$[18] and $PhC(CH_3)_2N{=}C^+CH_3$, respectively, in free energy at MP2/6-31G*), whereas the latter step is likely to be exergonic and in know to be fast in aqueous solvent.[26] The mechanism also requires that the observed fully exclusive formation of the fragmentation products for **9a**-*p*-Me and **9a**-*p*-MeO have occurred via the rearrangement intermediates, which is very unlikely. In order to further examine the possibility, the reactions of four substrates (**8**-H, **8**-*p*-Me, **9a**-*m*-Cl, and **9a**-*p*-Me) were carried out in 90% aqueous CH_3CN in the presence of $NMe_4^+OH^-$. Under the reaction conditions, F% would be suppressed if the fragmentation product were formed via the rearrangement intermediate, since OH^- is known to be much better nucleophile than H_2O in the reaction with nitrilium ions,[26] and therefore OH^- should effectively trap the intermediate to give the rearrangement product. The results of the reactions are summarized in Table 3. The reaction of **8**-*p*-Me showed an only slight decrease in F% by the addition of 1.1 equiv of OH^- and F% stayed unchanged with a higher concentration of OH^-, which suggests that a small portion of the fragmentation product may have arisen from the rearrangement intermediate. The reaction of **9a**-*m*-Cl also gave a decrease in F% with an increase of the concentration of OH^-, and the F% value stayed constant at 2 equiv of OH^-. Thus, roughly 15% out of total 60% fragmentation product was judged to have arisen through the rearrangement intermediate. Similarly, 20% of the fragmentation product was assigned to have formed through the rearrangement intermediate for **9a**-*p*-Me. Thus, the major part of the fragmentation product is considered to be formed via a reaction route that does not involve the rearrangement intermediate. In summary, the results of the product analyses and the substituent effect on reactivities are best rationalized by the mechanism that involves path bifurcation after the rate-determining TS.

Table 3. Product Distributions for the Reactions of Selected Substrates with Added $NMe_4^+OH^-$ [a]

	$NMe_4^+OH^-$ [b]	R[c]	F[d]	F%[e]
8-H	0.00	81.7	19.3	19.1
	1.30	82.2	19.9	19.5
	2.60	81.0	19.8	19.6
8-*p*-Me	0.00	50.2	46.5	48.1
	1.10	54.4	42.9	44.1
	2.76	55.4	44.8	44.7
9a-*m*-Cl	0.00	40.1	59.5	59.8
	0.29	45.6	58.7	56.3
	0.51	48.8	54.1	52.6
	1.20	53.8	45.9	46.0
	2.00	56.8	45.2	44.4
	4.00	53.9	43.8	44.8
9a-*p*-Me	0.00	0.0	99.4	100.0
	2.00	20.5	81.2	80.7
	4.00	20.5	80.4	80.9

[a] In 90% (v/v) CH_3CN at 25 °C with the reactant concentration of 2.4 mmol/L. [b] Molar ratio of $NMe_4^+OH^-$ added relative to the reactant. [c] Yield of rearrangement product (%). [d] Yield of fragmentation product (%). [e] Relative yield of fragmentation product (F/(R + F)).

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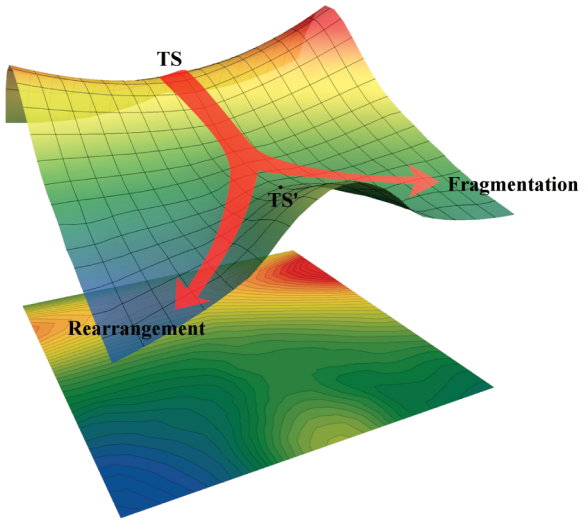

Figure 3. Schematic 3D energy surface and the mode of bifurcation for the Beckmann reaction.

CONCLUDING REMARKS

The previous computational study has predicted that the reactions of **4**-X proceed via a single TS for each substituted compound, but gave both rearrangement and fragmentation products from the single TS through path bifurcation after the TS.[17] Extensive kinetic and product analysis results presented here for the reactions of **7**-X−**9a**-X are consistent with the occurrence of bifurcation after the TS for the Beckmann reactions. In Figure 3 is shown a schematic presentation of 3D energy surface, in which the main TS is located on the center of the top edge and the two product regions are separated by the second TS (TS′). Reacting molecule coming down from the main TS lead to either of the two product regions, and the ratio of the two products depends on the location of TS'. The present result that more fragmentation product was obtained for **9**-X than **7**-X and with a more electron-donating substituent is explained by the shift of TS′ in a manner consistent with the Leffler-Hammond principle[23] and the Thornton rule.[24] It is thus concluded that TSs may not always have information about what product they would give and that a conventional reactivity-selectivity argument and mechanistic assignment based on the TS theory may not always be applicable even to well-known organic reactions.

EXPERIMENTAL SECTION

Materials. Acetonitrile was distilled over CaH_2. Substituted phenylpropanones (**1**-X) were synthesized from corresponding benzaldehydes by nitroaldol with $EtNO_2$,[19] and Fe reduction.[20] 2-Phenylbutanones (**2**-X) and 2-methyl-2-phenylbutanones (**3**-X) were prepared from **1**-X by methylation (MeI/NaOH). Oximation with NH_2OH, followed by esterification by Tipson's method[21] gave esters, (**7**-X−**9a**-X).

1-Phenyl-2-propanone oxime (4-H). To 1-phenyl-2-propanone (**1**-H) (12.2 g, 91.1 mmol) were added aqueous NaOH (20 mL, 154 mmol) and aqueous $NH_2OH\cdot HCl$ (30 mL, 205 mmol), and then ethanol to obtain a clear solution. The solution was refluxed for 1 h, mixed with water, extracted with ether, and the ether layer was dried over $MgSO_4$. Evaporation of the solvent gave oily material, which solidified on cooling. Recrystallization from hexane **4**-H (2.4 g, 16.1 mmol, 18%). Mp 87−88 °C. ^{1}H NMR (CDCl3, 400 MHz): δ 8.31 (bs, 1H), 7.33−7.21 (m, 5H), 3.50 (s, 2H), 1.82 (s, 3H).

1-*p*-Methoxyphenyl-2-propanone Oxime (4-*p*-MeO). The procedure is the same as for **4**-H. Yield: 64%. Mp 73−75 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.56 (bs, 1H), 7.13 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 3.79 (s, 3H), 3.43 (s, 2H), 1.81 (s, 3H).

1-*m*,*p*-Dimethylphenyl-2-propanone Oxime (4-*m*,*p*-Me$_2$). The procedure is the same as for **4**-H. Yield: 67%. Mp 60−61 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.81 (bs, 1H), 7.07 (d, J = 8.0 Hz, 1H), 6.98 (s, 1H), 6.95 (d, J = 8.0 Hz, 1H), 3.42 (s, 2H), 2.240 (s, 3H), 2.236 (s, 3H), 1.81 (s, 3H).

1-*p*-Methylphenyl-2-propanone Oxime (4-*p*-Me). The procedure is the same as for **4**-H. Yield: 53%. Mp 79−81 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.77 (bs, 1H), 7.11 (s, 4H), 3.45 (s, 2H), 2.32 (s, 3H), 1.81 (s, 3H).

1-*m*-Methylphenyl-2-propanone Oxime (4-*m*-Me). The procedure is the same as for **4**-H. The crude product was purified by column chromatography (Hexane/AcOEt = 4:1). Yield: 82%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.59 (bs, 1H), 7.25−7.01 (m, 4H), 3.47 (s, 2H), 2.32 (s, 3H), 1.82 (s, 3H).

1-*p*-Chlorophenyl-2-propanone Oxime (4-*p*-Cl). The procedure is the same as for **4**-H. Yield: 44%. Mp 91−92 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.13 (bs, 1H), 7.28 (d, J = 8.2 Hz, 2H), 7.15 (d, J = 8.2 Hz, 2H), 3.46 (s, 2H), 1.80 (s, 3H).

1-*m*-Chlorophenyl-2-propanone Oxime (4-*m*-Cl). The procedure is the same as for **4**-H. The crude product was purified by column chromatography (Hexane/AcOEt = 4:1). Yield: 93%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.60 (bs, 1H), 7.23−7.21 (m, 3H), 7.12 (s, 1H), 3.48 (s, 2H), 1.83 (s, 3H).

1-*p*-Trifluoromethyl-2-propanone Oxime (4-*p*-CF$_3$). The procedure is the same as for **4**-H. Yield: 38%. Mp 83−85 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.18 (bs, 1H), 7.57 (d, J = 7.8 Hz, 2H), 7.34 (d, J = 7.8 Hz, 2H), 3.56 (s, 2H), 1.83 (s, 3H).

1-*p*-Cyano-2-propanone Oxime (4-*p*-CN). The procedure is the same as for **4**-H. Yield: 9%. Mp 70−72 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.59 (bs, 1H), 7.61 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 3.56 (s, 2H), 1.83 (s, 3H).

1-*p*-nitro-2-propanone oxime (4-*p*-NO$_2$). The procedure is the same as for **4**-H. Yield: 48%. Mp 143−144 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.19 (d, J = 8.4 Hz, 2H), 7.64 (bs, 1H), 7.39 (d, J = 8.4 Hz, 2H), 3.60 (s, 2H), 1.83 (s, 3H).

3-*p*-Methoxyphenyl-2-butanone Oxime (5-*p*-MeO). The procedure is the same as for **4**-H. Recrystallized from ethanol. Yield: 35%. Mp 121 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.36 (bs, 1H), 7.16 (d, J = 7.6 Hz, 2H), 6.86 (d, J = 7.6 Hz, 2H), 3.79 (s, 3H), 3.61 (q, J = 7.0 Hz, 1H), 1.73 (s, 3H), 1.42 (d, J = 7.0 Hz, 3H).

3-*m*,*p*-Dimethylphenyl-2-butanone Oxime (5-*m*,*p*-Me$_2$). The procedure is the same as for **4**-H. Yield: 49%. Mp 78−80 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.69 (bs, 1H), 7.08 (d, J = 7.6 Hz, 1H), 7.00 (s, 1H), 6.97 (d, J = 7.6 Hz, 1H), 3.58 (q, J = 7.2 Hz, 1H), 2.25 (s, 3H), 2.24 (s, 3H), 1.74 (s, 3H), 1.42 (d, J = 7.2 Hz, 3H).

3-*p*-Methylphenyl-2-butanone Oxime (5-*p*-Me). The procedure is the same as for **4**-H. Yield: 37%. Mp 73−75 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.52 (bs, 1H), 7.13 (s, 4H), 3.62 (q, J = 7.0 Hz, 1H), 2.32 (s, 3H), 1.74 (s, 3H), 1.43 (d, J = 7.0 Hz, 3H).

3-*m*-Methylphenyl-2-butanone Oxime (5-*m*-Me). The procedure is the same as for **4**-H. Yield: 82%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.63 (bs, 1H), 7.23−7.04 (m, 4H), 3.62 (q, J = 7.0 Hz, 1H), 2.33 (s, 3H), 1.75 (s, 3H), 1.44 (d, J = 7.0 Hz, 3H).

3-Phenyl-2-butanone Oxime (5-H). The procedure is the same as for **4**-H. Yield: 27%. Mp 57 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.36 (bs, 1H), 7.34−7.22 (m, 5H), 3.65 (q, J = 7.2 Hz, 1H), 1.74 (s, 3H), 1.45 (d, J = 7.2 Hz, 3H).

3-*p*-Chlorophenyl-2-butanone Oxime (5-*p*-Cl). The procedure is the same as for **4**-H. Recrystallized from ethanol. Yield: 44%. Mp 91−92 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.33 (bs, 1H), 7.29 (d, J = 8.5

Hz, 2H), 7.18 (d, J = 8.5 Hz, 2H), 3.64 (q, J = 7.2 Hz, 1H), 1.73 (s, 3H), 1.43 (d, J = 7.2 Hz, 3H).

3-*m*-Chlorophenyl-2-butanone Oxime (5-*m*-Cl). The procedure is the same as for **4**-H. The crude product was purified by column chromatography (Hexane/AcOEt = 4:1). Yield: 84%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.71 (bs, 1H), 7.25−7.13 (m, 4H), 3.65 (q, J = 7.3 Hz, 1H), 1.76 (s, 3H), 1.44 (d, J = 7.3 Hz, 3H).

3-*p*-Trifluoromethylphenyl-2-butanone Oxime (5-*p*-CF_3). The procedure is the same as for **4**-H. Yield: 10%. Mp 59−60 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.24 (bs, 1H), 7.58 (d, J = 7.8 Hz, 2H), 7.37 (d, J = 7.8 Hz, 2H), 3.73 (q, J = 7.2 Hz, 1H), 1.75 (s, 3H), 1.47 (d, J = 7.2 Hz, 3H).

3-*p*-Cyanophenyl-2-butanone Oxime (5-*p*-CN). The procedure is the same as for **4**-H. Yield: 26%. Mp 84−86 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.38 (bs, 1H), 7.63 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 3.71 (q, J = 7.2 Hz, 1H), 1.74 (s, 3H), 1.46 (d, J = 7.2 Hz, 3H).

3-*p*-Nitrophenyl-2-butanone Oxime (5-*p*-NO_2). The procedure is the same as for **4**-H. Yield: 60%. Mp 108−110 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.19 (d, J = 8.8 Hz, 2H), 8.09 (bs, 1H), 7.42 (d, J = 8.8 Hz, 2H), 3.76 (q, J = 7.2 Hz, 1H), 1.75 (s, 3H), 1.49 (d, J = 7.2 Hz, 3H).

3-Methyl-3-*p*-methoxyphenyl-2-butanone Oxime (6-*p*-MeO). The procedure is the same as for **4**-H. Yield: 55%. Mp 165−166 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.77 (bs, 1H), 7.20 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H), 1.64 (s, 3H), 1.47 (s, 6H).

3-Methyl-3-*p*-methylphenyl-2-butanone Oxime (6-*p*-Me). The procedure is the same as for **4**-H. Yield: 34%. Mp 89−91 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.70 (bs, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 2.33 (s, 3H), 1.65 (s, 3H), 1.48 (s, 6H).

3-Methyl-3-phenyl-2-butanone Oxime (6-H). The procedure is the same as for **4**-H. Yield: 28%. Mp 104−106 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.46 (bs, 1H), 7.35−7.21 (m, 5H), 1.65 (s, 3H), 1.50 (s, 6H).

3-Methyl-3-*m*-chlorophenyl-2-butanone oxime (6-*m*-Cl). The procedure is the same as for **4**-H. Yield: 25%. Mp 107−109 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.03 (bs, 1H), 7.28−7.16 (m, 4H), 1.66 (s, 3H), 1.49 (s, 6H).

3-Methyl-3-*p*-nitrophenyl-2-butanone Oxime (6-*p*-NO_2). The procedure is the same as for **4**-H. Recrystallized from ether-hexane. Yield: 46%. Mp 157−159 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.19 (d, J = 8.8 Hz, 2H), 7.65 (bs, 1H), 7.46 (d, J = 8.8 Hz, 2H), 1.65(s, 3H), 1.53 (s, 6H).

1-Phenyl-2-propanone Oxime 2-Naphthalenesulfonate (7-H). To an ice-cooled dry pyridine solution (20 mL) of 1-phenyl-2-propanone oxime (**4**-H) (1.63 g, 10.0 mmol) was added 2-naphthalenesulfonyl chloride (2.51 g, 11.1 mmol), which requires 1 h. The solution was allowed to react for additional 1 h at the same temperature, and was poured onto ice−water (200 mL). The resulted precipitates were collected by suction and recrystallized from ether-hexane. Yield: 59%. Mp 57 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.60 (s, 1H), 8.02−7.92 (m, 4H), 7.72−7.63 (m, 2H), 7.19−6.92 (m, 5H), 3.45 (s, 2H), 1.86 (s, 3H).

1-*p*-Methoxyphenyl-2-propanone Oxime 2-Naphthalenesulfonate (7-*p*-MeO). The procedure is the same as for 7-H. Yield: 20%. Mp 127−128 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.37 (s, 1H), 7.89−7.85 (m, 4H), 7.59−7.52 (m, 2H), 7.18 (d, J = 8.0 Hz, 2H), 6.80 (d, J = 8.0 Hz, 2H), 4.40 (s, 2H), 3.73 (s, 3H), 2.33 (s, 3H).

1-*m*,*p*-Dimethylphenyl-2-propanone Oxime 2-Naphthalenesulfonate (7-*m*,*p*-Me_2). The procedure is the same as for 7-H. Yield: 34%. Mp 81−82 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.61 (s, 1H), 8.03−7.93 (m, 4H), 7.72−7.63 (m, 2H), 6.87 (d, J = 8.0 Hz, 1H), 6.70−6.67 (m, 2H), 3.38 (s, 2H), 2.16 (s, 3H), 2.04 (s, 3H), 1.85 (s, 3H).

1-*p*-Methylphenyl-2-propanone Oxime 2-Naphthalenesulfonate (7-*p*-Me). The procedure is the same as for 7-H. Yield: 59%. Mp 73−75 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.59 (s, 1H), 8.02−7.92 (m, 4H), 7.72−7.63 (m, 2H), 6.91 (d, J = 7.1 Hz, 2H), 6.82 (d, J = 7.1 Hz, 2H), 3.40 (s, 2H), 2.25 (s, 3H), 1.85 (s, 3H).

1-*m*-Methylphenyl-2-propanone Oxime 2-Naphthalenesulfonate (7-*m*-Me). The procedure is the same as for 7-H. Yield: 49%. Mp 69−70 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.60 (s, 1H), 8.03−7.93 (m, 4H), 7.71−7.62 (m, 2H), 7.02−6.73 (m, 4H), 3.41 (s, 2H), 2.13 (s, 3H), 1.86 (s, 3H).

1-*p*-Chlorophenyl-2-propanone Oxime 2-Naphthalenesulfonate (7-*p*-Cl). The procedure is the same as for 7-H. Yield: 43%. Mp 138−141 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.56 (s, 1H), 8.01−7.89 (m, 4H), 7.73−7.64 (m, 2H), 7.06 (d, J = 8.1 Hz, 2H), 6.86 (d, J = 8.1 Hz, 2H), 3.42 (s, 2H), 1.86 (s, 3H).

1-*m*-Chlorophenyl-2-propanone Oxime 2-Naphthalenesulfonate (7-*m*-Cl). The procedure is the same as for 7-H. Yield: 43%. Mp 69−71 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.59 (s, 1H), 8.00−7.93 (m, 4H), 7.70−7.65 (m, 2H), 7.17−6.82 (m, 4H), 3.44 (s, 2H), 1.88 (s, 3H).

1-*p*-Trifluoromethylphenyl-2-propanone Oxime 2-Naphthalenesulfonate (7-*p*-CF_3). The procedure is the same as for 7-H. Yield: 47%. Mp 111−112 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.57 (s, 1H), 8.01−7.88 (m, 4H), 7.72−7.66 (m, 2H), 7.33 (d, J = 7.6 Hz, 2H), 7.04 (d, J = 7.6 Hz, 2H), 3.52 (s, 2H), 1.89 (s, 3H).

1-*p*-Cyanophenyl-2-propanone Oxime 2-Naphthalenesulfonate (7-*p*-CN). The procedure is the same as for 7-H. Yield: 51%. Mp 100 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.54 (s, 1H), 8.01−7.87 (m, 4H), 7.76−7.66 (m, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 3.52 (s, 2H), 1.90 (s, 3H).

1-*p*-Nitrophenyl-2-propanone Oxime 2-Naphthalenesulfonate (7-*p*-NO_2). The procedure is the same as for 7-H. Yield: 28%. Mp 112−113 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.54 (s, 1H), 7.99−7.87 (m, 6H), 7.76−7.65 (m, 2H), 7.09 (d, J = 8.7 Hz, 2H), 3.57 (s, 2H), 1.92 (s, 3H).

3-*p*-Methoxyphenyl-2-butanone Oxime *p*-Methxybenzenesulfonate (8a-*p*-MeO). The procedure is the same as for 7-H. *p*-Methoxybenzenesulfonyl chloride was used in place of 2-naphthalenesulfonyl chloride. Yield: 24%. Mp 45−46 °C (dec.). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.94 (d, J = 8.45 Hz, 2H), 7.02 (d, J = 8.7 Hz, 2H), 6.96 (d, J = 8.45 Hz, 2H), 6.79 (d, J = 8.7 Hz, 2H), 3.91 (s, 3H), 3.78 (s, 3H), 3.61 (q, J = 7.0 Hz, 1H), 1.73 (s, 3H), 1.36 (d, J = 7.0 Hz, 3H).

3-*m*,*p*-Dimethylphenyl-2-butanone Oxime 2-Naphthalenesulfonate (8-*m*,*p*-Me_2). The procedure is the same as for 7-H. Yield: 17%. Mp 45−46 °C (dec.). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.62 (s, 1H), 8.03−7.95 (m, 4H), 7.70−7.63 (m, 2H), 6.86 (d, J = 8.0 Hz, 1H), 6.69−6.67 (m, 2H), 3.56 (q, J = 8.0 Hz, 1H), 2.15 (s, 3H), 2.01 (s, 3H), 1.75 (s, 3H), 1.33 (d, J = 8.0 Hz, 3H).

3-*p*-Methylphenyl-2-butanone Oxime 2-Naphthalenesulfonate (8-*p*-Me). The procedure is the same as for 7-H. Yield: 44%. Mp 50 °C (dec.) ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.61 (s, 1H), 8.02−7.95 (m, 4H), 7.71−7.62 (m, 2H), 6.89 (d, J = 7.8 Hz, 2H), 6.82 (d, J = 7.8 Hz, 2H), 3.58 (q, J = 6.9 Hz, 1H), 2.24 (s, 3H), 1.74 (s, 3H), 1.33 (d, J = 6.9 Hz, 3H).

3-*p*-Methylphenyl-2-butanone Oxime *p*-Methxybenzenesulfonate (8a-*p*-Me). The procedure is the same as for **8a**-*p*-MeO. Yield: 42%. Mp 53−54 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (d, J = 8.8, 2H), 7.06 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.0 Hz, 2H), 3.91 (s, 3H), 3.62 (q, J = 7.2 Hz, 1H), 2.31 (s, 3H), 1.73 (s, 3H), 1.36 (d, J = 7.2 Hz, 3H).

3-*m*-Methylphenyl-2-butanone Oxime 2-Naphthalenesulfonate (8-*m*-Me). The procedure is the same as for 7-H. Yield: 49%. Mp 46−47 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.62 (s, 1H), 8.03−7.95 (m, 4H), 7.72−7.63 (m, 2H), 7.01−6.97 (m, 2H), 6.74−6.73 (m, 2H), 3.59 (q, J = 8.0 Hz, 2H), 2.13 (s, 3H), 1.75 (s, 3H), 1.34 (d, J = 8.0 Hz, 3H).

3-Phenyl-2-butanone Oxime 2-Naphthalenesulfonate (8-H). The procedure is the same as for **7**-H. Yield: 59%. Mp 57 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.62 (s, 1H), 8.03−7.95 (m, 4H), 7.73−7.63 (m, 2H), 7.17−6.92 (m, 5H), 3.63 (q, J = 7.0 Hz, 1H), 1.75 (s, 3H), 1.36 (d, J = 7.0 Hz, 3H).

3-Phenyl-2-butanone Oxime *p*-Methxybenzenesulfonate (8a-H). The procedure is the same as for **8a**-*p*-MeO. Yield: 12%. Mp 60−62 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (d, J = 7.1 Hz, 2H), 7.28−7.23 (m, 2H), 7.05−7.01(m, 4H), 3.91 (s, 3H), 3.66 (q, J = 7.3 Hz, 1H), 1.74(s, 3H), 1.39 (d, J = 7.3 Hz, 3H).

3-*p*-Chlorophenyl-2-butanone Oxime 2-Naphthalenesulfonate (8-*p*-Cl). The procedure is the same as for **7**-H. Yield: 32%. Mp 68−69 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.59 (s, 1H), 8.02−7.93 (m, 4H), 7.74−7.64 (m, 2H), 7.05 (d, J = 8.2 Hz, 2H), 6.86 (d, J = 8.2 Hz, 2H), 3.60 (q, J = 7.0 Hz, 1H), 1.75 (s, 3H), 1.34 (d, J = 7.0 Hz, 3H).

3-*p*-Chlorophenyl-2-butanone Oxime *p*-Methxybenzenesulfonate (8a-*p*-Cl). The procedure is the same as for **8a**-*p*-MeO. Yield: 40%. Mp 74−75 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.92 (d, J = 7.05 Hz, 2H), 7.23 (d, J = 6.6 Hz, 2H), 7.01 (d, J = 7.05 Hz, 2H), 6.98 (d, J = 6.6 Hz, 2H), 3.92 (s, 3H), 3.63 (q, J = 7.05 Hz, 1H), 1.75 (s, 3H), 1.37 (d, J = 7.05 Hz, 3H).

3-*m*-Chlorophenyl-2-butanone Oxime 2-Naphthalenesulfonate (8-*m*-Cl). The procedure is the same as for **7**-H. Yield: 46%. Mp 73−75 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.60 (s, 1H), 8.02−7.94 (m, 4H), 7.72−7.62 (m, 2H), 7.13 (d, J = 7.8 Hz, 1H), 7.01 (t, J = 7.8 Hz, 1H), 6.96 (s, 1H), 6.81 (d, J = 7.8 Hz, 1H), 3.60 (q, J = 7.0 Hz, 1H), 1.77 (s, 3H), 1.34 (d, J = 7.0 Hz, 3H).

3-*p*-Trifluoromethylphenyl-2-butanone Oxime 2-Naphthalenesulfonate (8-*p*-CF_3). The procedure is the same as for **7**-H. Yield: 41%. Mp 93−94 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.60 (s, 1H), 8.01−7.93 (m, 4H), 7.73−7.64 (m, 2H), 7.31 (d, J = 8.2 Hz, 2H), 7.04 (d, J = 8.2 Hz, 2H), 3.69 (q, J = 7.2 Hz, 1H), 1.77 (s, 3H), 1.3 (d, J = 7.2 Hz, 3H).

3-*p*-Cyanophenyl-2-butanone Oxime 2-Naphthalenesulfonate (8-*p*-CN). The procedure is the same as for **7**-H. Yield: 23%. Mp 79−80 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.58 (s, 1H), 8.02−7.91 (m, 4H), 7.76−7.66 (m, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 3.68 (q, J = 8.0 Hz, 1H), 1.78 (s, 3H), 1.38 (d, J = 8.0 Hz, 3H).

3-*p*-Nitrophenyl-2-butanone Oxime 2-Naphthalenesulfonate (8-*p*-NO_2). The procedure is the same as for **7**-H. Yield: 25%. Mp 82 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.58 (s, 1H), 8.01−7.97 (m, 3H), 7.94−7.91 (m, 3H), 7.77−7.66 (m, 2H), 7.09 (d, J = 8.7 Hz, 2H), 3.74 (q, J = 7.1 Hz, 1H), 1.80 (s, 3H), 1.41 (d, J = 7.1 Hz, 3H).

3-Methyl-3-*p*-methoxyphenyl-2-butanone Oxime *p*-Methxybenzenesulfonate (9a-*p*-MeO). The procedure is the same as for **8a**-*p*-MeO. Yield: 44%. Mp 41−43 °C (dec.). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97 (d, J = 9.2 Hz, 2H), 7.03 (d, J = 9.2 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 6.78 (d, J = 8.8 Hz, 2H), 3.92 (s, 3H), 3.78 (s, 3H), 1.64 (s, 3H), 1.40 (s, 6H).

3-Methyl-3-*p*-methylphenyl-2-butanone Oxime *p*-Methxybenzenesulfonate (9a-*p*-Me). The procedure is the same as for **8a**-*p*-MeO. Yield: 20%. Mp 45−46 °C (dec.). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97 (d, J = 9.2, 2H), 7.06 (d, J = 8.24 Hz, 2H), 7.03 (d, J = 9.2 Hz, 2H), 6.93 (d, J = 8.24 Hz, 2H), 3.92 (s, 3H), 2.30 (s, 3H), 1.65 (s, 3H), 1.41 (s, 6H).

3-Methyl-3-phenyl-2-butanone Oxime *p*-Methxybenzenesulfonate (9a-H). The procedure is the same as for **8a**-*p*-MeO. Yield: 26%. Mp 47−48 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97 (d, J = 8.8 Hz, 2H), 7.28−7.18 (m, 3H), 7.06−7.01 (m, 4H), 3.91 (s, 3H), 1.65 (s, 3H), 1.43 (s, 6H).

3-Methyl-3-*m*-chlorophenyl-2-butanone Oxime 2-Naphthalenesulfonate (9-*m*-Cl). The procedure is the same as for **7**-H. Yield: 23%. Mp 58−60 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.62 (s, 1H), 8.03−7.96 (m, 4H), 7.73−7.63 (m, 2H), 7.13 (d, J = 8.0 Hz, 1H), 7.00 (t, J = 8.0 Hz, 1H), 6.98 (s, 1H), 6.79 (d, J = 8.0 Hz, 1H), 1.68 (s, 3H), 1.39 (s, 6H).

3-Methyl-3-*m*-chlorophenyl-2-butanone Oxime *p*-Methxybenzenesulfonate (9a-*m*-Cl). The procedure is the same as for **8a**-*p*-MeO. Yield: 6%. Mp 66−67 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96 (d, J = 8.8 Hz, 2H), 7.20−7.18 (m, 2H), 7.05−6.92 (m, 4H), 3.91 (s, 3H), 1.67 (s, 3H), 1.42 (s, 6H).

3-Methyl-3-*p*-nitrophenyl-2-butanone Oxime 2-Naphthalenesulfonate (9-*p*-NO_2). The procedure is the same as for **7**-H. Yield: 46%. Mp 70−72 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.61 (s, 1H), 8.04−7.91 (m, 6H), 7.77−7.66 (m, 2H), 7.09 (d, J = 8.0 Hz, 2H), 1.70 (s, 3H), 1.45 (s, 6H).

3-Methyl-3-*p*-nitrophenyl-2-butanone Oxime *p*-Methxybenzenesulfonate (9a-*p*-NO_2). The procedure is the same as for **8a**-*p*-MeO. Yield: 38%. Mp 83−84 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.12 (d, J = 9.2, 2H), 7.95 (d, J = 8.8 Hz, 2H), 7.24 (d, J = 9.2 Hz, 2H), 7.04 (d, J = 8.8 Hz, 2H), 3.93 (s, 3H), 1.69 (s, 3H), 1.48 (s, 6H).

***N*-*p*-Methoxybenzylacetamide.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.19 (d, J = 8.2 Hz, 2H), 6.85 (d, J = 8.2 Hz, 2H), 6.07 (bs, 1H), 4.32 (d, J = 5.5 Hz, 2H), 3.78 (s, 3H), 1.98 (s, 3H). Mp 97 °C.

***N*-*m*,*p*-Dimethylbenzylacetamide.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.10 (d, J = 7.6 Hz, 1H), 7.06 (s, 1H), 7.02 (d, J = 7.6 Hz, 1H), 5.63 (bs, 1H), 4.36 (d, J = 5.6 Hz, 2H), 2.25 (s, 3H), 2.25 (s, 3H), 2.01 (s, 3H). Mp 87−88 °C.

***N*-*p*-Methylbenzylacetamide.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.17 (d, J = 8.2 Hz, 2H), 7.14 (d, J = 8.2 Hz, 2H), 5.82 (bs, 1H), 4.37 (d, J = 6.0 Hz, 2H), 2.33 (s, 3H), 2.00 (s, 3H). Mp 112−113 °C.

***N*-*m*-Methylbenzylacetamide.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.21−7.03 (m, 4H), 6.50 (bs, 1H), 4.32 (d, J = 5.5 Hz, 2H), 2.31 (s, 3H), 1.96 (s, 3H).

***N*-*p*-Benzylacetamide.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35−7.26 (m, 5H), 6.05 (bs, 1H), 4.40 (d, J = 6.0 Hz, 2H), 1.99 (s, 3H). Mp 56−57 °C.

***N*-*p*-Chlorobenzylacetamide.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.29 (d, J = 8.2 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 5.91 (bs, 1H), 4.39 (d, J = 5.5 Hz, 2H), 2.02 (s, 3H). Mp 107−108 °C.

***N*-*m*-Chlorobenzylacetamide.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32 (s, 1H), 7.21−7.18 (m, 3H), 7.09−7.07 (m, 1H), 4.27 (d, J = 6.0 Hz, 2H), 1.92 (s, 3H).

***N*-*p*-Trifluoromethylbenzylacetamide.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.57 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 6.03 (bs, 1H), 4.48 (d, J = 6.0 Hz, 2H), 2.04 (s, 3H). Mp 103−104 °C.

***N*-*p*-Cyanobenzylacetamide.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.63 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 5.85 (bs, 1H), 4.50 (d, J = 6.0 Hz, 2H), 2.07 (s, 3H). Mp 145−147 °C.

***N*-*p*-Nitrobenzylacetamide.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.19 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 5.96 (bs, 1H), 4.55 (d, J = 6.0 Hz, 2H), 2.08 (s, 3H). Mp 128−130 °C.

***N*-*p*-Methoxyphenylethylacetamide.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.24 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 5.78 (bs, 1H), 5.08 (quin, J = 6.9 Hz, 1H), 3.79 (s, 3H), 1.96 (s, 3H), 1.46 (d, J = 6.9 Hz, 3H). Mp 68−69 °C.

***N*-*m*,*p*-Dimethylphenylethylacetamide.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.12−7.04 (m, 3H), 5.62 (bs, 1H), 5.07 (quin, J = 6.8 Hz, 1H), 2.26 (s, 3H), 2.24 (s, 3H), 1.97 (s, 3H), 1.47 (d, J = 6.8 Hz, 3H). Mp 89−91 °C.

***N*-*p*-Methylphenylethylacetamide.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.20 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 5.97 (bs, 1H), 5.08 (quin, J = 6.9 Hz, 1H), 2.32 (s, 3H), 1.95 (s, 3H), 1.46 (d, J = 6.9 Hz, 3H). Mp 73−75 °C.

***N*-*m*-Methylphenylethylacetamide.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.23−7.05 (m, 4H), 6.23 (bs, 1H), 5.09−5.02 (m, 1H), 2.33 (s, 3H), 1.94 (s, 3H), 1.43 (d, J = 7.3 Hz, 3H).

***N*-Phenylethylacetamide.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35−7.23 (m, 5H), 6.09 (bs, 1H), 5.10 (quin, J = 69 Hz, 1H), 1.95 (s, 3H), 1.47 (d, J = 6.9 Hz, 3H). Mp 76 °C.

***N*-*p*-Chlorophenylethylacetamide.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.28 (d, J = 8.5 Hz, 2H), 7.23 (d, J = 8.5 Hz, 2H), 6.10 (bs, 1H), 5.06 (quin, J = 6.9 Hz, 1H), 1.96 (s, 3H), 1.44 (d, J = 6.9 Hz, 3H). Mp 98−99 °C.

***N*-*m*-Chlorophenylethylacetamide.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.23−7.14 (m, 4H), 5.01 (quin, J = 6.9 Hz,1H), 1.92 (s, 3H), 1.39 (d, J = 6.9 Hz, 3H).

***N*-*p*-Trifluoromethylphenylethylacetamide.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.58 (d, J = 8.2 Hz, 2H), 7.42 (d, J = 8.2 Hz, 2H), 6.01 (bs, 1H), 5.17−5.10 (m, 1H), 1.99 (s, 3H), 1.48 (d, J = 7.3 Hz, 3H). Mp 105−106 °C.

***N*-*p*-Cyanophenylethylacetamide.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.63 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 5.68 (bs, 1H), 5.14 (m, 1H), 2.02 (s, 3H), 1.49 (d, J = 7.2 Hz, 3H). Mp 156−158 °C.

***N*-*p*-Nitrophenylethylacetamide.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.19 (d, J = 8.8 Hz, 2H), 7.48 (d, J = 8.8 Hz, 2H), 5.74 (bs, 1H), 5.18 (quin, J = 6.9 Hz, 1H), 2.03 (s, 3H), 1.51 (d, J = 6.8 Hz, 3H). Mp 119−121 °C.

***N*-2-*p*-Methylphenyl-2-propylacetamide.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.28 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 5.69 (bs, 1H), 2.32 (s, 3H), 1.96 (s, 3H), 1.69 (s, 6H). Mp 140−141 °C.

***N*-2-Phenyl-2-propylacetamide.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40−7.21 (m, 5H), 5.74 (bs, 1H), 1.97 (s, 3H), 1.70 (s, 6H). Mp 95−96 °C.

***N*-2-*m*-Chlorophenyl-2-propylacetamide.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34−7.18 (m, 4H), 5.73 (bs, 1H), 1.98 (s, 3H), 1.66 (s, 6H). Mp 112−113 °C.

***N*-2-*p*-Nitrophenyl-2-propylacetamide.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.18 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 8.8 Hz, 2H), 5.82 (bs, 1H), 2.00 (s, 3H), 1.69 (s, 6H). Mp 122−124 °C.

***p*-Methoxybenzyl Alcohol.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.29 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 4.61 (s, 2H), 3.81 (s, 3H).

***m*,*p*-Dimethylbenzyl Alcohol.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.15−7.09 (m, 3H), 4.63 (s, 2H), 2.07 (s, 3H), 2.06 (s, 3H).

***p*-Methylbenzyl Alcohol.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.26 (d, J = 7.6 Hz, 2H), 7.17 (d, J = 7.6 Hz, 2H), 4.64 (s, 2H), 2.35 (s, 3H).

***p*-Methoxyphenylethyl Alcohol.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.25 (d, J = 8.0 Hz, 2H), 6.85 (d, J = 8.0 Hz, 2H), 4.76 (q, J = 6.4 Hz, 1H), 3.74 (s, 3H), 2.64 (bs, 1H), 1.41 (d, J = 6.4 Hz, 3H).

***m*,*p*-Dimethylphenylethyl Alcohol.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.15−7.09 (m, 3H), 4.84 (q, J = 6.4 Hz, 1H), 2.27 (s, 3H), 2.25 (s, 3H), 1.48 (d, J = 6.4 Hz, 3H).

***p*-Methylphenylethyl Alcohol.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.24 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 4.82 (q, J = 6.4 Hz, 1H), 2.33 (s, 3H), 2.15 (bs, 1H), 1.45 (d, J = 6.4 Hz, 3H).

***m*-Methylphenylethyl Alcohol.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.22−7.05 (m, 4H), 4.78 (q, J = 6.4 Hz, 1H), 2.33 (s, 3H), 1.43 (d, J = 6.4 Hz, 3H).

***p*-Chlorophenylethyl Alcohol.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.28 (d, J = 8.7 Hz, 2H), 7.24 (d, J = 8.7 Hz, 2H), 4.80 (q, J = 6.3 Hz, 1H), 2.58 (bs, 1H), 1.41 (d, J = 6.3 Hz, 3H).

***m*-Chlorophenylethyl Alcohol.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36 (s, 1H), 7.29−7.21 (m, 3H), 4.89−4.83 (m, 1H), 1.47 (d, J = 6.4 Hz, 3H).

***p*-Trifluoromethylphenylethyl Alcohol.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.65 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 4.97 (q, J = 6.4 Hz, 1H), 1.50 (d, J = 6.4 Hz, 3H).

2-*p*-Methoxyphenyl-2-propyl Alcohol. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.41 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H), 1.75 (bs, 1H), 1.57 (s, 6H).

2-*p*-Methylphenyl-2-propyl Alcohol. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 2.34 (s, 3H), 1.75 (bs, 1H), 1.57 (s, 6H).

2-Phenyl-2-propyl Alcohol. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.51−7.26 (m, 5H), 1.75 (bs, 1H), 1.59 (s, 6H).

2-*m*-Chlorophenyl-2-propyl Alcohol. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.50 (s, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.27 (t, J = 8.0 Hz, 1H), 7.22 (d, J = 8.0 Hz, 1H), 1.75 (bs, 1H), 1.57 (s, 6H).

Kinetics. The rates of the reactions were studied photometrically at 25.0 ± 0.1 °C with the substrate concentration of 2.0 mmol/L in the presence of 1.1 equiv of *N*,*N*-dimethylaniline in aqueous CH_3CN (80% (v/v) for **7**-X and 90% (v/v) for **8**-X, **8a**-X and **9a**-X). The decay of absorbance of the esters at 327 nm for **7**-X and **8**-X and the decay of absorbance of *N*,*N*-dimethylaniline at 300 nm for **8a**-X and **9a**-X were followed. Excellent first-order rate plots (R^2 > 0.9997) were obtained with reproducibility within 3%.

Product Analysis. The authentic samples of the reaction products were either isolated from the reaction mixture or synthesized separately. Product distributions were measured by running the reaction with the substrate concentration of 2.4 mmol/L for 10 half-lives and analyzing the reaction mixture by means of NMR by using dibenzyl ether as an internal standard.

■ ASSOCIATED CONTENT

Supporting Information. Hammett σ values and free energies and geometrical coordinates of the species discussed in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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