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Leaving Group Effect on Photochemistry of *ortho*-Alkylphenacyl Carboxylate

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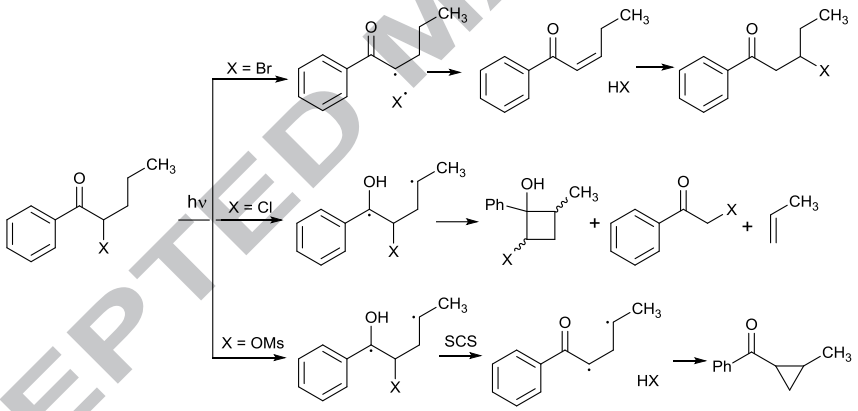
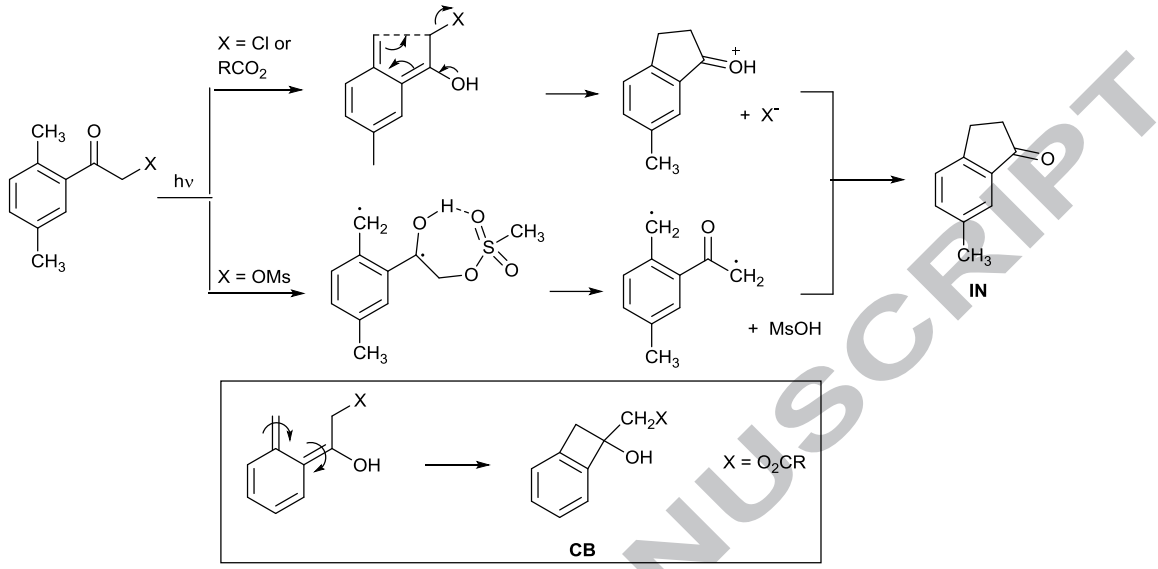
Leaving groups often play a significant role in determining reaction routes and/or product selectivity in organic photochemistry.[1] For example, in photochemistry of valerophenone, the reaction follows totally different pathways depending on substituents at alpha position to the carbonyl of the ketone as shown in Scheme 1. If the ketone has a bromine substituent, the C-Br bond cleavage reaction becomes the predominant reaction pathway. As for chlorine substitution, instead of bromine, the reaction follows the Norrish/Yang reaction route.[2] In the case of a non-halogen leaving group, sulphonate, another completely different reaction, spin center shift (SCS), occurs.[3]



Scheme 1. Photochemistry of α-substituted valerophenones.

Among many photochemical reactions involving leaving groups, photoremovable protecting groups (PPG) or photocages have been an hot research topic in organic photochemistry, which has recently been reviewed several times.[4] *o*-Alkylphenacyl PPG is one of them, which has been extensively studied mainly by Klan and coworkers.[5] This system also shows a very versatile mechanistic scenario dependent upon leaving groups. In this *o*-alkylphenacyl PPG system, the leaving group departs with the formation of indanone. Two different reaction mechanisms for the indanone formation depending on leaving groups have been proposed as shown in Scheme 2. For chlorine or carboxylate, the indanone is suggested to be formed by the cyclization of an *o*-xylylenol intermediate, while for the mesylate leaving group, HX elimination concurrent with spin center shift is proposed.

Wessig suggested the intramolecular hydrogen bonded transition state for the elimination process as shown in Scheme 2.[6]



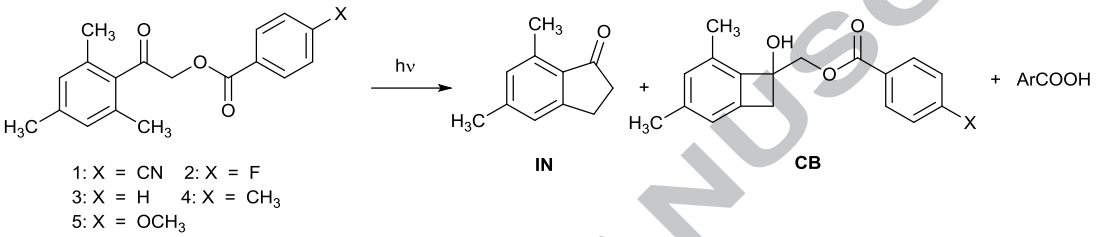
Scheme 2. Photochemistry of α-substituted o-alkylphenacyl photoremovable protecting groups.

Our research group has also studied photochemical behaviors of *o*-alkylphenacyl PPG and reported that photolysis of *o*-alkylphenacyl carboxylates gave not only the indanone (IN) but also the benzocyclobutenol (CB).[7] The CB product was formed *via* conrotatory type of thermal electrocyclic reaction of the *o*-xylylenol intermediate shown in Scheme 2. The IN to CB ratio was dependent on various reaction parameters; solvents, temperature, size of *o*-alkyl group, reaction time, etc. When the leaving group was Cl, Br, or mesylate, which are better leaving groups than carboxylates, CB product was never detected. These results suggested that the IN to CB ratio is strongly dependent upon leaving group properties. As continuing with our efforts to understand the relationship between structure and photoreactivity,[8] we decided to investigate the effect of leaving group on photochemistry of *o*-alkylphenacyl PPG more closely by using *para* substituted benzoate leaving groups. 2,4,6-Trimethylphenacyl benzoates were chosen as backbone skeletons instead of *o*-methylphenacyl benzoates, because the tri-methyl system gave much higher yields of CB products than the mono-methyl system, therefore we could compare the IN to CB ratios with each other more easily. It was our hope that this study could resolve the mechanistic ambiguity of this reaction as shown in Scheme 2. In fact, several new insights on the reaction mechanism were made through this study, which will be described below.

2,4,6-trimethylphenacyl benzoates **1-5** were prepared by simple substitution reaction of 2,4,6-

trimethylphenacyl bromide with corresponding benzoic acids. Each compound was dissolved in 0.75 mL of benzene-d_6 to make ca. 0.01 M solution, which was degassed and sealed. Photolysis of the ketone was done using Pyrex filtered light of a 450 W Hanovia medium pressure mercury arc lamp. All the ketones gave the indanone (IN) and the benzocyclobutenol (CB), together with the corresponding benzoic acid upon photolysis, and the ratios of IN to CB are given in Table 1.[9]

Table 1. Indanone to benzocyclobutenol ratios obtained from photolysis of **1-5.** [a]



1: X = CN 2: X = F
3: X = H 4: X = CH_3
5: X = OCH_3

Compound	X	IN/CB ratio[b]	pKa of benzoic acid[c]	Hammett σ_p[d]	Hammett σ_p^+[e]
1	CN	7.3	3.55	0.66	0.67
2	F	4.2	4.14	0.062	-0.25
3	H	1.7	4.20	0	0
4	CH_3	2.4	4.37	-0.17	-0.26
5	OCH_3	2.2	4.50	-0.27	-0.65

[a] Photolysis was done at 21 ± 1℃ in benzene-d_6. [b] The ratio was taken from integration of ^{1}H NMR spectra. [c] J. J. Christensen, R. M. Izatt, L. D. Hanse, *J. Am. Chem. Soc.* **1967**, *89*, 213. [d] D. H. McDaniel, H. C. Brown, *J. Org. Chem.* **1958**, *24*, 420. [e] C. G. Swain, E. C. Lupton, Jr., *J. Am. Chem. Soc.* **1968**, *90*, 4328.

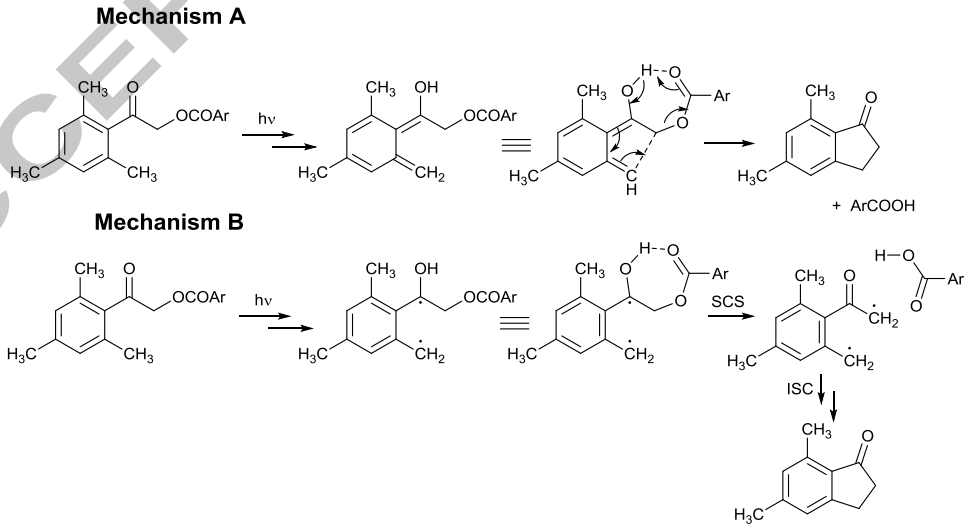
As noted in our previous report[7], the IN to CB ratios increased as photolysis proceeded due to autocatalytic effect of the departing acid. Thus, in order to minimize interference of other factors, we took the IN/CB ratios at the lowest conversion that we could measure by ^{1}H NMR spectroscopy.[10]

Our data revealed a few intriguing features. All the substituted benzoates gave higher IN/CB ratios than the unsubstituted one, **3**. In addition, the benzoates with electron withdrawing groups (EWG) (**1**, **2**) gave higher IN/CB ratios than the ones with electron donating groups (EDG) (**4**, **5**). Our results do not seem to show any correlation with Hammett substituent parameters as shown in the table.

Since only the IN forming process involves the departure of benzoic acid moiety, electronic effects

of *para*-substituents would be reflected mainly in the rate of IN forming route rather than that of CB forming route. Leaving group power (or nucleofugality) can be evaluated by many different ways, but one of the most popular and easiest way, is to correlate it by the acidity of conjugate acid of the leaving group.[11] If any reaction involves a rate determining departure of the leaving group, the reaction would be favored by any factors increasing the acidity of conjugate acid of the leaving group. Our results do not match with this trend, because the EDG containing benzoates show higher IN/CB ratios than the unsubstituted one.

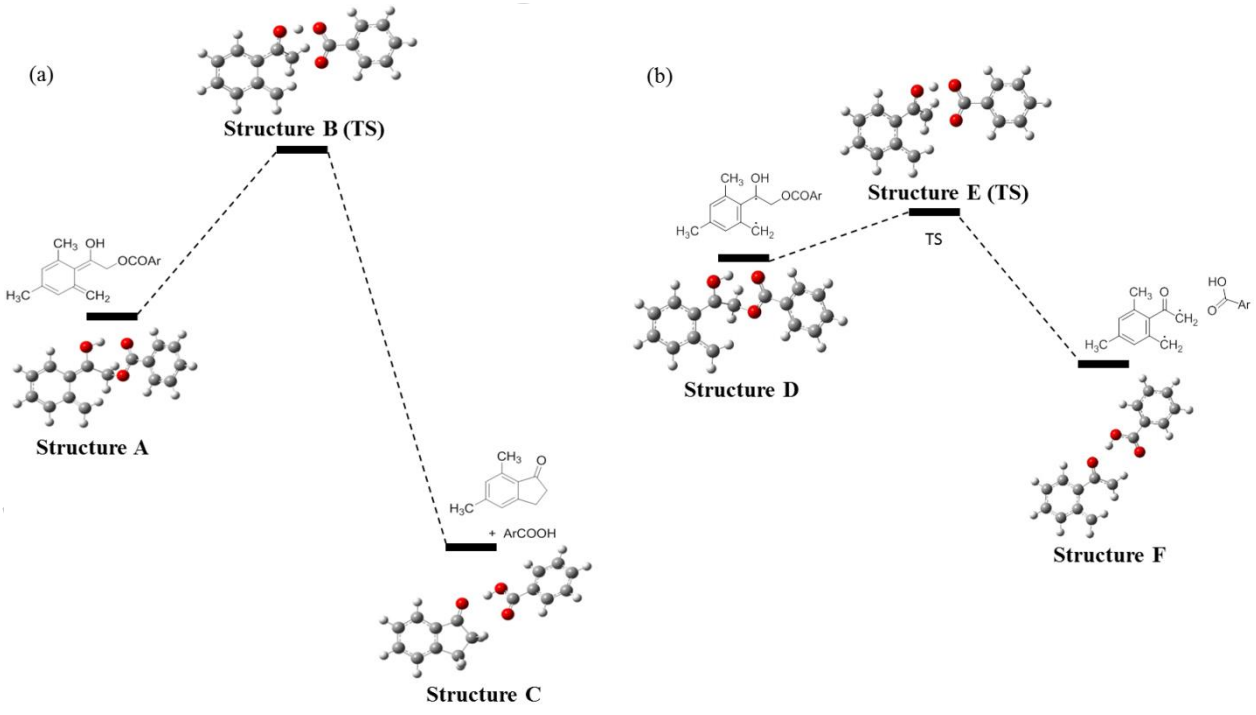
The fact that both EDG and EWG containing benzoates gave higher IN/CB ratios than the unsubstituted one implies that the IN forming process does not depend entirely on the pKa of the leaving benzoic acid. Another factor to be considered would be the basicity of the carbonyl oxygen of the benzoate leaving group, which will be increased as the electron donor ability of the substituent increases. Protonation of the carbonyl oxygen by any proton sources would eventually facilitate the leaving group's departure. Thus, a combination of two opposite electronic effects of substituents may be involved in the leaving group departure. One of a few mechanistic scenarios to meet this dual effect would be that the IN forming process goes through an intramolecular hydrogen bonded transition state from *E*-xylylenol intermediate as shown in mechanism A of Scheme 3. The other possible mechanism is mechanism B of the same Scheme, in which a biradical intermediate is involved instead of the *E*-xylylenol.



Scheme 3. Two possible mechanisms of indanone formation from photolysis of **1-5.**

Mechanism B resembles the one proposed for IN formation from a mesylate precursor by Wessig.[6]

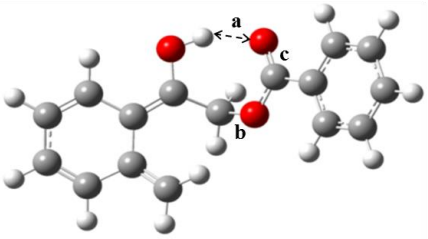
In both mechanisms A and B, the C-O bond connecting the carboxyl leaving group will be loosened and the hydrogen bonded O-H will be shortened as the reaction proceeds, which eventually will lead to the departure of the leaving group. Considering standard electron flow, the C-O bond cleavage can get more help from the electron withdrawing substituents, while the O-H bond formation will obtain assistance from the electron donating groups, even though the effect may be much less in mechanism B as compared to mechanism A. In order to obtain a clue to its mechanism, we have carried out a quantum chemical calculation using Gaussian 09 programs.[12] Energy minimized structures were searched for reactants, products, and transition states (TS) of IN forming reactions for both mechanism A and B.(Scheme 4) The optimization and frequency calculations were conducted at the B3LYP/6-31G(d) level using density functional (DFT) method. The intrinsic reaction coordinate (IRC) approach was performed to verify that the calculated TS, intermediates, and products were on the potential energy surface. For simplicity, 2-methylphenacyl carboxylates were used for calculation instead of 2,4,6-trimethylphenacyl carboxylates. The biradical intermediate of mechanism B is a triplet state. Its singlet state is identical to the xylylenol intermediate of mechanism A.[13] Table 2 and 3 show the summary of calculations.



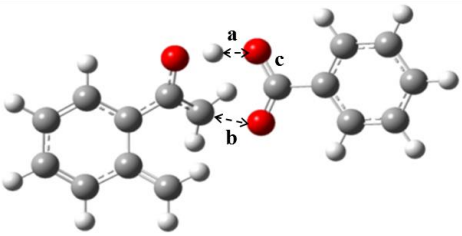
Scheme 4. Two different energy paths for quantum chemical calculations showing each stationary structure: (a) mechanism A, (b) mechnism B.

Table 2. Energy minimized structures of stationary points shown in Scheme 4 and some important

structural parameters

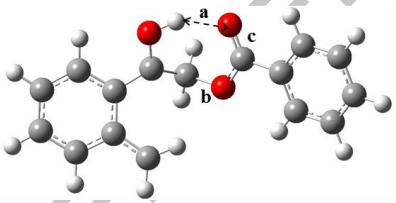


Structure A

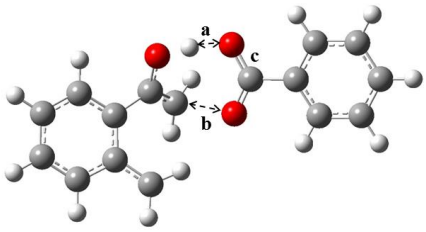


Structure B (TS)

	a, C=O—H-O (Å)			b, C-O (Å)			c, C=O (Å)		
Compound	Structure A	Structure B (TS)	**Δ**	Structure A	Structure B (TS)	**Δ**	Structure A	Structure B (TS)	**Δ**
1	1.86	1.42	-0.44	1.47	2.51	1.04	1.23	1.28	0.05
2	1.84	1.34	-0.50	1.47	2.46	0.99	1.23	1.28	0.05
3	1.84	1.31	-0.53	1.47	2.42	0.95	1.23	1.28	0.05
4	1.83	1.27	-0.56	1.47	2.38	0.91	1.23	1.29	0.06
5	1.83	1.20	-0.63	1.47	2.26	0.79	1.23	1.29	0.06



Structure D



Structure E (TS)

	a, C=O—H-O (Å)			b, C-O (Å)			c, C=O (Å)		
Compound	Structure D	structure E (TS)	**Δ**	Structure D	Structure E (TS)	**Δ**	Structure D	Structure E(TS)	**Δ**
1	1.83	1.39	-0.44	1.49	2.22	0.73	1.23	1.27	0.05
2	1.81	1.37	-0.44	1.49	2.19	0.70	1.23	1.27	0.04
3	1.81	1.37	-0.44	1.49	2.18	0.69	1.23	1.27	0.04
4	1.81	1.37	-0.44	1.49	2.17	0.68	1.23	1.27	0.04
5	1.80	1.36	-0.44	1.48	2.16	0.66	1.23	1.27	0.04

Table 3. Activation barriers for mechanism A and B calculated using DFT method (B3LYP/6-31G(d) level) of Gaussian 09 programs .

Compound	Mechanism A	Mechanism B
	$\Delta G^{\ddagger}$ (kcal/mol K)	$\Delta G^{\ddagger}$ (kcal/mol K)
1	19.73	3.41
2	21.18	4.55
3	22.07	4.78
4	21.51	5.11
5	21.69	5.32

The result of our calculation shows that activation barriers of the departure of the benzoic acid from xylylenol intermediates of ketones **1**-**5** correlate with our experimental CB/IN ratios remarkably well as shown in Figure 1, while the barriers from biradical intermediates do not show such correlation at all. The correlation between product ratios and computational results seem to support mechanism A of Scheme 3 for the indanone formation from photolysis of *o*-alkylphenacyl carboxylates. The calculation predicted not only that all the substituted benzoates gave lower barriers than the unsubstituted one, but also that *p*-methoxy substituted ketone, **5**, gave lower barrier than *p*-methyl substituted one, **4**, which all agreed well with experimental results shown by their CB/IN ratios. It also predicted the lowest barrier of *p*-cyano ketone, **1**, of all the ketones studied, which coincided with the lowest CB/IN ratio of all for **1**.

It is worthwhile to note that structural parameters shown on Table 2 show different trends from mechanism A and B, especially in changes of bond length of hydrogen bonded O-H. The O-H bond becomes more shorter in electron donating substituents than in electron withdrawing ones as the reaction goes towards TS of mechanism A, while the bond is essentially unchanged towards TS of mechanism B no matter what the substituent is. In contrast, C-O bond cleavage shows similar trends for both mechanism A and B, where the C-O bond is more cleaved in electron withdrawing substituents than in electron releasing ones towards TS. The result can be explained that effects of basicity of carbonyl oxygen are almost neglected in mechanism B, whereas the effects certainly become a determining factor to reaction barrier for mechanism A.

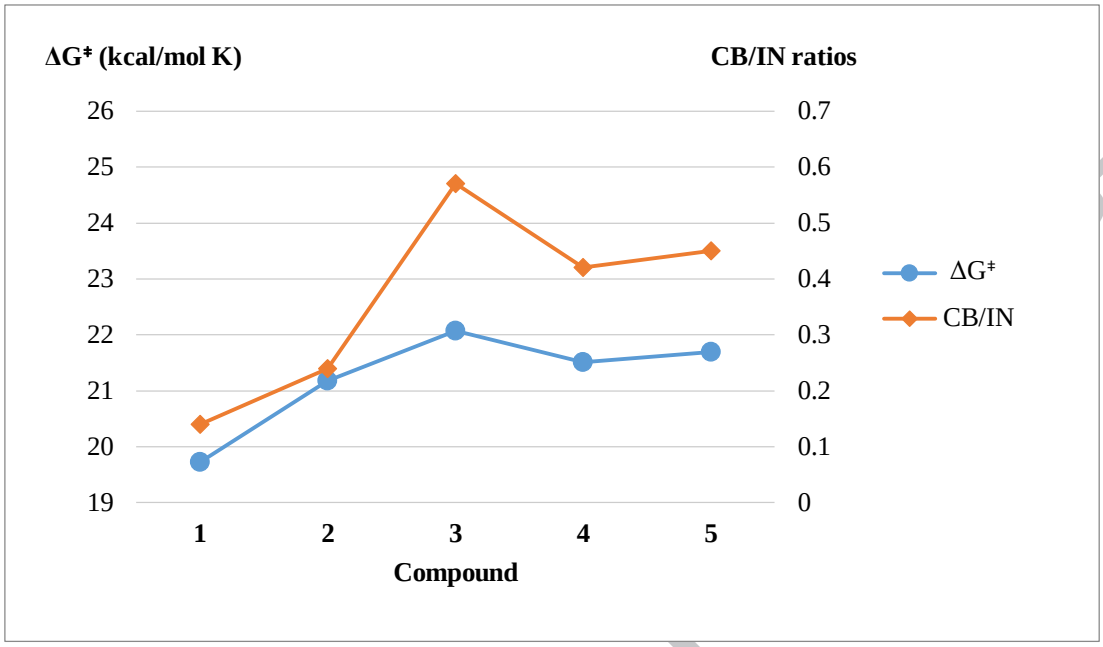


Figure 1. Comparison of calculated reaction barriers of mechanism A (ΔG‡ in kcal/molK) and experimental CB/IN ratios in photolysis of ketones **1**-**5**

As noted above, reaction mechanism of the indanone formation of o-alkylphenacyl PPG has been studied for a long time, but there still have been debates over which of the xylylenol and the biradical intermediate is responsible for the indanone formation. Our experimental and computational results support that the xylylenol is the direct precursor for the indanone product, at least for carboxylate leaving groups. We are planning to investigate other leaving groups such as sulphonates using a similar approach under the reaction condition where the CB product can be formed as well as the IN product such as at low temperature.

In summary, from our research on photochemical reaction mechanism of *p*-substituted *o*-alkylphenacyl benzoates, we have discovered a very interesting substituent effect in which both electron donating and electron withdrawing groups accelerate the departure of the *p*-substituted benzoate leaving groups. Quantum chemical calculation on the reaction paths revealed that the photochemical reaction forming the indanone product resulted from the xylylenol intermediate rather than the biradical intermediate. The electron donating substituents increased the basicity of the carbonyl oxygen of the carboxylate leaving group which helped the proton transfer and eventually promoted the departure of the leaving group *via* an intramolecular hydrogen bonded transition state. The electron withdrawing substituents also helped in the departure of the carboxylate leaving groups

in a more classical sense, whereby the more acidic the benzoic acids are, the better the leaving groups. Our results added an evidence supporting the intermediacy of xylylenol on the way to indanone formation from *o*-alkylphenacyl PPG, which has been debated.

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[9] Spectroscopic properties of **1**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.23 (d, 2H, J = 8.4 Hz), 7.80 (d, 2H, J = 8.4 Hz), 6.91 (s, 2H), 5.20 (s, 2H), 2.34 (s, 6H), 2.33 (s, 3H), ^{13}C NMR ($CDCl_3$, 50 MHz) δ 202.2, 164.5, 139.8, 134.8, 134.0, 133.3, 132.4, 130.5, 128.8, 118.0, 116.9, 70.1, 21.2, 19.1 ppm, IR (CCl_4) 2230 (CN), 1725, 1715 (CO) cm^{-1}, HRMS ($C_{19}H_{18}NO_3$, M+H) calcd. 308.1287, found 308.1294.
Spectroscopic properties of **IN:** ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.10 (s, 1H), 6.94 (s, 1H), 3.06 (t, 2H, J = 5.6 Hz), 2.68 (t, 2H, J = 5.6Hz), 2.61 (s, 3H), 2.40 (s, 3H), ^{13}C NMR ($CDCl_3$, 50 MHz) δ 207.5, 156.6, 145.1, 138.6, 132.4, 130.4, 124.5, 37.0, 25.3, 21.9, 18.3 ppm, IR (CCl_4) 1698 (CO) cm^{-1}, EI MS ($C_{11}H_{12}O$) 160 (M^+)
Spectroscopic properties of **CB-1:** ^{1}H NMR ($CDCl_3$, 200MHz) δ 8.15 (d, 2H, J = 8.4 Hz), 7.74 (d, 2H, J = 8,4 Hz), 6.87 (s, 2H), 4.68 (s, 2H), 3.30 (AB quartet, 2H, J = 14.2 Hz), 2.80 (broad s, 1H, OH), 2.32 (s, 3H), 2.26 (s, 3H), ^{13}C NMR ($CDCl_3$, 50 MHz) δ 165.1, 141.9, 140.8, 140.2, 133.8, 132.5, 132.2, 130.2, 129.6, 121.6, 117.9, 116.5, 78.5, 70.1, 43.8, 22.0, 17.1 ppm, IR (CCl_4) 3446 (OH), 2233 (CN), 1727 (CO) cm^{-1}, HRMS ($C_{19}H_{18}NO_3$, M+H) calcd. 308.1287, found 308.1292.
Spectroscopic properties of **2:** ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.18-8. 10 (m, 2H), 7.20-7.11 (m, 2H), 6.90 (s, 2H), 5.17 (s, 2H), 2.34 (s, 6H), 2.32 (s, 3H), ^{13}C NMR ($CDCl_3$, 50 MHz) δ 202.8, 166.1 (d, $^{1}J_{CF}$ = 253 Hz), 165.1, 139.6, 135.1, 134.0, 132.6 ($^{3}J_{CF}$ = 9.5 Hz), 128.7, 125.7, 115.7 (d, $^{2}J_{CF}$ = 22

Hz), 69.7, 21.2, 19.1 ppm, IR (CCl_4) 1729, 1720 (CO) cm^{-1}, HRMS ($C_{18}H_{18}FO_3$, M+H) calcd. 301.1240, found 301.1244.

Spectroscopic properties of **CB-2:** ^1H NMR ($CDCl_3$, 200 MHz) δ 8.18-8.10 (m, 2H), 7.14 (t, 2H, J = 8.4 Hz), 6.86 (s, 2H), 4.66 (s, 2H), 3.30 (AB quartet, 2H, J = 14.2 Hz), 3.20 (broad s, 1H, OH), 2.34 (s, 3H), 2.28 (s, 3H), ^{13}C NMR ($CDCl_3$, 50 MHz) δ 165.9, 165.8 (d, $^1J_{CF}$ = 253 Hz), 142.2, 140.9, 140.0, 132.5, 132.2 ($^3J_{CF}$ = 9.5 Hz), 129.5, 126.1, 121.5, 115.5 (d, $^2J_{CF}$ = 22 Hz), 78.6, 69.7, 43.6, 22.0, 17.1 ppm, IR (CCl_4) 3455 (OH), 1728 (CO) cm^{-1}, HRMS ($C_{18}H_{18}FO_3$, M+H) calcd. 301.1240, found 301.1243.

Spectroscopic properties of **3:** ^1H NMR ($CDCl_3$, 200 MHz) δ 8.12 (d, 2H, J = 8.2 Hz), 7.72-7.45 (m, 3H), 6.90 (s, 2H), 5.18 (s, 2H), 2.35 (s, 6H), 2.31 (s, 3H), ^{13}C NMR ($CDCl_3$, 50 MHz) δ 203,0, 166.1, 139.6, 135.2, 134.1, 133.5, 13.0, 129.4, 128.6, 69.7, 21.2, 19.2 ppm IR (CCl_4) 1722, 1703 (CO) cm^{-1}, HRMS ($C_{18}H_{19}O_3$, M+H) calcd. 283.1334, found 283.1329.

Spectroscopic properties of **CB-3:** ^1H NMR ($CDCl_3$, 200 MHz) δ 8.11 (d, 2H, J = 8.2 Hz), 7.68-7.43 (m, 3H), 6.87 (s, 2H), 4.69 (AB quartet, 2H, J = 11.8 Hz), 3.34 (AB quartet, 2H, J = 14.2 Hz), 3.10 (broad s, 1H, OH), 2.36 (s, 3H), ^{13}C NMR ($CDCl_3$, 50 MHz) δ 167.0, 142.3, 141.1, 140.1, 133.3, 132.7, 129.9, 129.6, 128.5, 121.6, 114.6, 78.8, 69.9, 43.8, 22.8, 17.3 ppm. IR (CCl_4) 3463 (OH), 1726 (CO) cm^{-1}, HRMS ($C_{18}H_{19}O_3$, M+H) calcd. 283.1334, found 283.1337.

Specgtroscopic properties of **4:** ^1H NMR ($CDCl_3$, 200 MHz) δ 8.01 (d, 2H, J = 8.2 Hz), 7.28 (d, 2H, J = 8.2 Hz), 6.90 (s, 2H), 5.16 (s, 2H), 2.45 (s, 3H), 2.35 (s, 6H), 2.31 (s, 3H), ^{13}C NMR ($CDCl_3$, 50 MHz) δ 203.2, 166.1, 144.2, 139.5, 135.3, 134.1, 130.1, 129.3, 128.7, 126.7, 69.5, 21.8, 21.2, 19.2 ppm IR (CCl_4) 1720, 1699 (CO) cm^{-1}, HRMS ($C_{19}H_{21}O_3$, M+H) calcd. 297.1491, found 297.1495.

Spectroscopic properties of **CB-4:** ^1H NMR ($CDCl_3$, 200 MHz) δ 8.03 (d, 2H, J = 8.4 Hz), 7.21 (d, 2H, J = 8.4 Hz), 6.89 (s, 1H), 4.63 (AB quartet, 2H, J = 11.5 Hz), 3.30 (AB quartet, 2H, J = 14.4 Hz), 2.32 (s, 3H), 2.27 (s, 3H), 2.13 (s, 3H), ^{13}C NMR ($CDCl_3$, 50 MHz) δ 166.5, 142.5, 141.0, 140.8, 132.5, 1131.7, 129.3, 124.2, 122.4, 121.6, 113.6, 78.8, 69.8, 43.7, 22.0, 21.3, 17.0 ppm IR (CCl_4) 3450 (OH), 1727 (CO) cm^{-1}, HRMS ($C_{19}H_{21}O_3$, M+H) calcd. 297.1491, found 297.1498.

Spectroscopic properties of **5:** ^1H NMR ($CDCl_3$, 200 MHz) δ 8.07 (d, 2H, J = 8.4 Hz), 6.99 (s, 2H), 6.91 (d, 2H, J = 8.2 Hz), 5.15 (s, 2H), 3.90 (s, 3H), 2.34 (s, 6H), 2.31 (s, 3H), ^{13}C NMR ($CDCl_3$, 50 MHz) δ 203.3, 165.7, 163.8, 139.5, 135.3, 134.0, 132.1, 128.7, 121.8, 113.8, 69.5, 55.6, 21.2, 9.1 ppm, IR (CCl_4) 1725, 1701 (CO) cm^{-1}, HRMS ($C_{19}H_{21}O_4$, M+H) calcd. 313.1440, found 313.1435.

Spectroscopic properties of **CB-5:** ^1H NMR ($CDCl_3$, 200 MHz) δ 8.05 (d, 2H, J = 8.4 Hz), 6.95 (d, 2H, J = 8.4 Hz), 6.85 (broad s, 1H, OH), 4.65 (AB quartet, 2H, J = 11.6 Hz), 3.89 (s, 3H), 3.31 (AB quartet, 2H, J = 14.4 Hz), 2.34 (s, 3H), 2.29 (s, 3H), ^{13}C NMR ($CDCl_3$, 50 MHz) δ 166.9, 163.7, 142.5, 141.1, 140.0, 132.7, 131.9, 129.6, 122.4, 121.6, 113.8, 78.9, 69.8, 55.5, 43.7, 22.1, 17.3 ppm. IR (CCl_4) 3445 (OH), 1726 (CO) cm^{-1}, HRMS ($C_{19}H_{21}O_4$, M+H) calcd. 313.1440, found 313.1446.

[10] The CB products were formed at the lowest amount of all the photoproducts, so we tried to limit the conversion using the NMR peaks of the CB, where their integration numbers were not too small. See ^1H NMR spectra given in the supporting information.

[11] J. Bartl, S. Steenken, H. Mayr, R. A. McClelland, *J. Am. Chem. Soc.*, **1990**, *112*, 6918–6928.

[12] Gaussian 09 suite of programs M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. H. Petersson, M. C. Nakatsuji, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W.

Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Parkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09*, revision A.02; Gaussian Inc.: Wallingford, CT, **2009**.

[13] Any attempts to get energy minimized structure of the singlet biradical intermediate always resulted in the xylylenol structure.

Graphical Abstract

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Leaving Group Effect on Photochemistry of *ortho*-Alkylphenacyl Carboxylate

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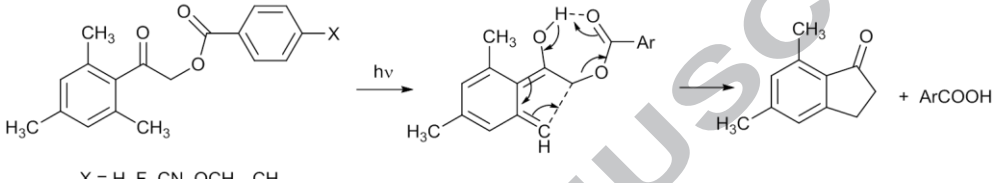

Highlights

· Leaving group effects on photochemistry of *o*-alkylphenacyl PPG
· Unique way to evaluate substituent effect on a reaction involving carboxylate leaving group
· Re-evaluation of reaction mechanism of photochemistry of *o*-alkylphenacyl PPG