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Iodine/DMSO Promoted Oxidation of Benzylic C_{sp}^{3}–H Bonds to Diketones – a Mechanistic Investigation

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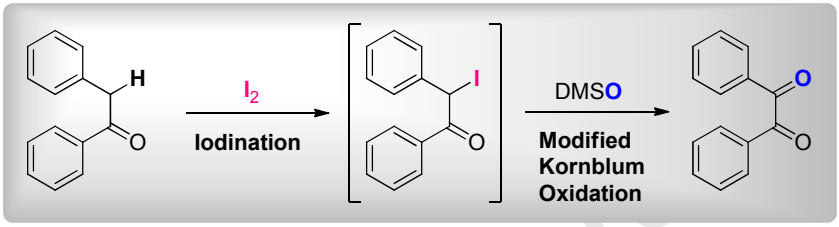

Iodine/DMSO Promoted Oxidation of Benzylic C_{sp}^3–H Bonds to Diketones – a Mechanistic Investigation

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Abstract

This article describes a mechanistic investigation into the I_2/DMSO mediated benzylic C_{sp}^3–H oxidation of an α-methylene ketone. The electron paramagnetic resonance (EPR) spectrum centred at g = 2.0011 supports the involvement of iodine and benzylic radicals, as the α-iodinated compound 2-iodo-1, 2-diphenylethanone was isolated as a key reactive intermediate. The oxidation reaction relies, primarily, on DMSO as a source of oxygen in benzil, proven by the reaction of benzyl phenyl ketone with diphenyl sulfoxide (DPSO).

1. Introduction

Conceptually, the direct transformation of C_{sp}^3–H bonds into carbon–carbon (C–C) and carbon–heteroatom (C–X, X=N, O, S) bonds offers new methodologies to prepare synthetically valuable molecules, as these approaches reduce pre-functionalization of starting materials while improving atom/step economy.[1] The chemically inert nature of C_{sp}^3–H bonds, however, due to: poor acidity, a high bond dissociation energy (BDE), thermodynamic

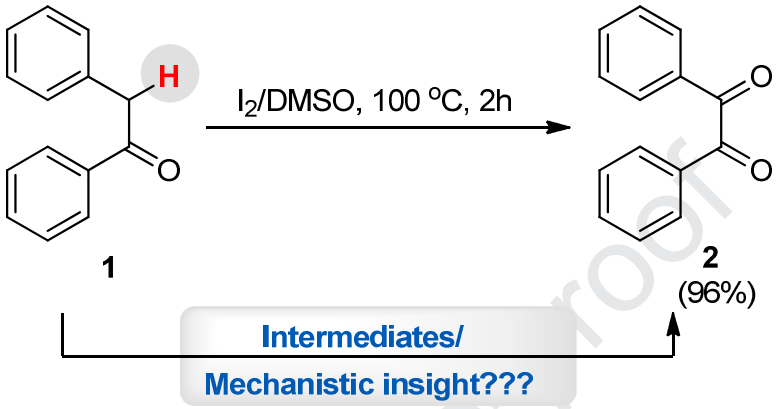
stability and an unreactive molecular orbital profile, hinder the achievement of a complete regio-selectivity without requiring multiple synthetic steps.[2] Despite selectivity issues in recent decades, direct C_{sp}^3–H functionalization methods have developed substantially.[3] This, however, often necessitates the use of expensive transition metal catalysts, toxic reagents, high energy throughput and harsh reaction conditions which result in functional group incompatibility and limited substrate scope.[4]

Accordingly, C_{sp}^3–H functionalization reactions, inspired by a rational design of experimental conditions, leading to significant improvement in both selectivity and applicability, present an ongoing challenge to researchers engaged in modern synthetic organic chemistry.[5] In context the highly appealing, direct and selective, oxidation of benzylic C_{sp}^3–H bonds is currently an active area of research, owing to its relevant approach to synthetically useful arylcarbonyl compounds such as α-diketones which often serve as important precursors for heterocyclic syntheses, with various attractive methodologies documented in literature.[6]

In particular, molecular iodine (I_2) is now the most frequently used catalyst for many organic transformations and, is widely recognized as a replacement for environmentally unfriendly reagents, owing to its low toxicity, operational simplicity, high stability and various other user-friendly characteristics.[7] Moreover, dimethyl sulfoxide (DMSO) is an inexpensive and environmentally friendly dipolar aprotic solvent, oxidant and oxygen source in many organic syntheses.[8] Collectively, the I_2/DMSO combination is currently a distinct and complimentary alternative to unsustainable oxidation methodologies, since it has realized numerous organic transformations.[9]

Accordingly, we have recently reported an I_2/DMSO oxidation of the benzylic C_{sp}^3–H bonds of benzyl phenyl ketone **1** to afford the corresponding α-diketone **2** in an isolated yield of 96% (Scheme 1).[10] While we were satisfied with the excellent yield, our mechanistic

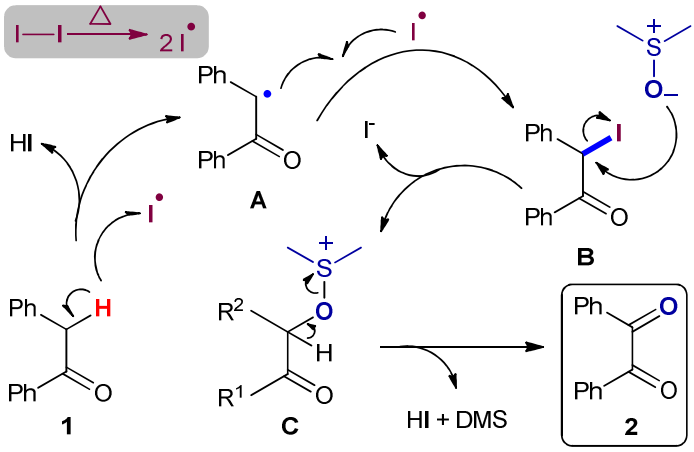
insight into the reaction pathway was minimal. Thus, a significant point of interest, in the current study, was to provide definitive, mechanistic proof for the oxidation of the α-methylene ketone to the α-diketone using the I_2/DMSO system.



Scheme 1: I_2/DMSO oxidation of benzyl phenyl ketone **1** to benzil **2**.

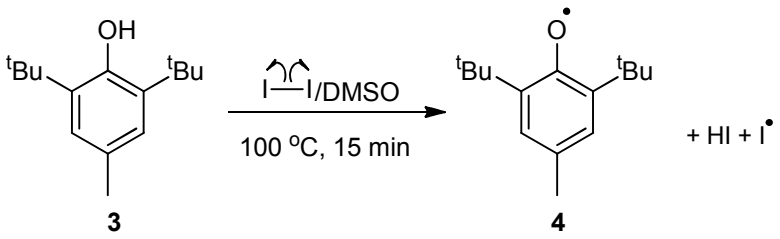
2. Results and Discussion

Our theoretically proposed mechanism was anticipated to proceed *via* initial iodination by molecular iodine (I_2), followed by a modified Kornblum oxidation in the presence of dimethyl sulfoxide (DMSO) as presented in Scheme 2. Consequently, a series of experimental reactions and spectroscopic techniques were undertaken to rationalize each step in the proposed reaction pathway for the formation of the α-diketone, benzil **2**.



Scheme 2: Plausible mechanism for the I_2/DMSO oxidation of benzyl phenyl ketone **1**.

Based on literary studies, the homolytic cleavage of molecular iodine is known to occur under thermal conditions so as to afford iodine radicals.[11] Our mechanistic studies, therefore, commenced by exploring the formation of iodine radicals in our reaction, under thermal conditions, using Electron Paramagnetic Resonance (EPR) spectroscopy. Generally, free radicals are extremely unstable and a highly reactive species with a half-life of the order 10^{-9} s[12] hence butylated hydroxytoluene (BHT) was used as an anti-oxidant to detect the formation of iodine radicals in our reaction. BHT is a diamagnetic molecule and, accordingly, no EPR signal was observed in the absence of iodine in our experiments. Subsequently, molecular iodine and BHT were reacted in DMSO and the mixture heated to 100°C (Scheme 3).



Scheme 3: Formation of oxygen radical from the reaction of I_2 and BHT in DMSO.

Following transfer into a flat quartz tube, an EPR signal, consistent with the presence of an organic radical, was observed (Figure 1). The spectrum is characterized by four intense lines centered at g = 2.0011 which arises, as BHT quenches iodine radicals through *H*-atom transfer and generates a stable BHT radical species. The unpaired electron which is located on the sterically hindered oxygen atom, and protected by the tertiary butyl groups, is stabilized by the π-system of the benzene ring. The coupling of the electron to the three equivalent protons of the 4-methyl group gives rise to the recorded four-line EPR spectrum.[13] The EPR spectrum and the *g*-value for the BHT radical, obtained under our reaction conditions, are comparable with the experimental data provided in literature.[14, 15] This result therefore correlates with the formation of a phenoxy radical (g = 2.0010-2.0091, $RPhO^{\cdot}$),[16] which subsequently implies the presence of iodine radicals in our reaction.

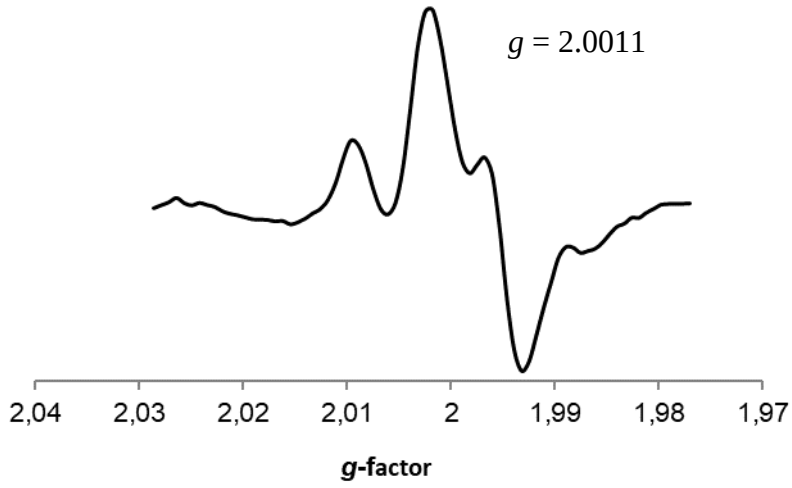


Figure 1: EPR spectrum of a heated I_2/BHT sample in DMSO.

Since the iodine radical was detected using EPR spectroscopy, this indicates that the oxidation reaction is initiated by the thermal homolytic cleavage of molecular iodine supporting a radical mediated mechanism. The presence of iodine radicals in the reaction infers the formation of a benzylic radical on benzyl phenyl ketone **1**. Consequently, an iodine radical assisted proton abstraction from the α-methylene position of **1** was proposed to generate benzylic radical **A**. As a result, we aimed to trap the benzylic radical using the spin trap (2, 2, 6, 6-tetramethylpiperidin-1-yl)oxyl (TEMPO) and, under the standard reaction conditions, benzyl phenyl ketone, iodine and the radical inhibitor TEMPO were added to DMSO and heated to 100 °C for 2 h, affording the capture product **5** in 46% yield (Scheme 4).

Scheme 4: Reaction of benzyl phenyl ketone 1 with TEMPO to afford 1,2-diphenyl-2-((2, 2, 6, 6-tetramethylpiperidin-1-yl)oxy)ethanone **5**.

The singlet at 5.92 ppm[17] in the NMR spectrum corresponds to the α-proton (C–H) of 1, 2-diphenyl-2-((2, 2, 6, 6-tetramethylpiperidin-1-yl)oxy)ethanone **5** (Figure 2), indicating the formation of the C–O bond between the benzylic radical of intermediate **A** and the oxygen radical of TEMPO.

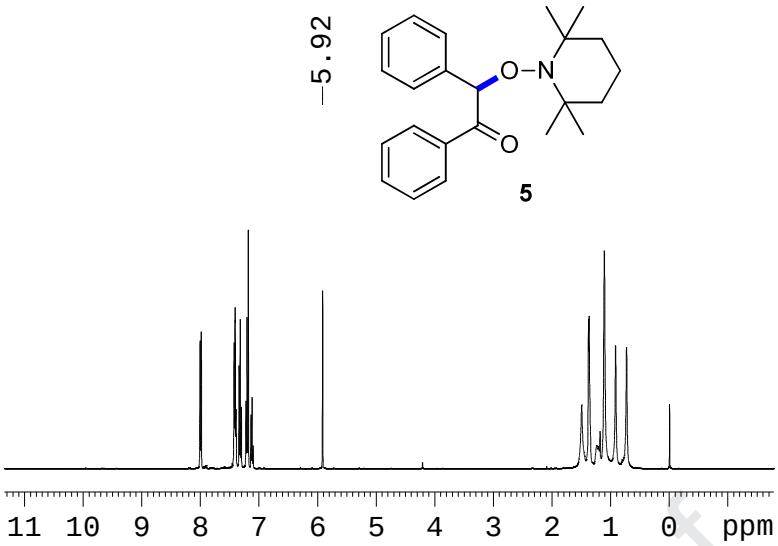
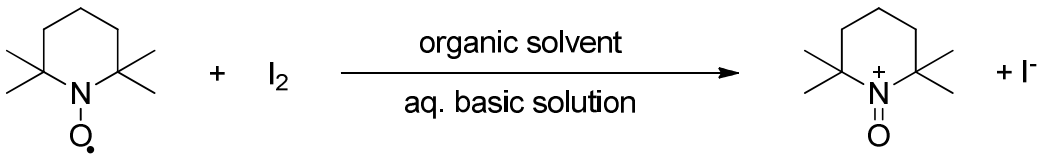


Figure 2: NMR spectrum of 1,2-diphenyl-2-((2, 2, 6, 6-tetramethylpiperidin-1-yl)oxy)ethanone **5**.

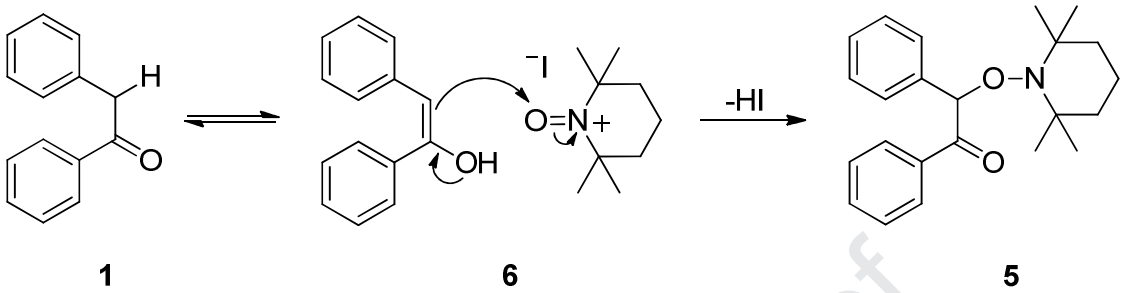
While the TEMPO trapped reaction in Scheme 4 theoretically supports the formation of **A**, in which the radical is located on the α-position of **1**, this experiment does not necessarily lead to this conclusion. It has been reported that in the presence of a halogen co-catalyst,[18] TEMPO is readily oxidized to the corresponding *N*-oxoammonium cation as shown in Scheme 5.



Scheme 5: Iodine catalyzed *N*-oxoammonium cation generation.

Additionally, it is known that *N*-oxoammonium cations, upon heating, react with enolizable ketones to generate the α-TEMPO ketone **5** (Scheme 6). This is the *same* end product as though the α-benzylic radical **A** was hypothetically trapped by TEMPO itself. It was, however, noted that the conversion to the *N*-oxoammonium salt is significantly

influenced by the pH of the applied reaction media and the addition of an aqueous solution of base is necessary to achieve the required conversion.[19]



Scheme 6: *N*-oxoammonium catalyzed oxidation of enolizable **6**.

Thus, in order to support the involvement of iodine and benzylic radicals in our reaction, supplementary studies were undertaken to rule out the formation of the *N*-oxoammonium salt. This was achieved by monitoring the TEMPO radical using EPR spectroscopy. Initially, molecular iodine and TEMPO were reacted in DMSO under the optimized reaction conditions to afford the EPR spectrum, displayed in Figure 3. An intense triplet signature is ascribed to the stable free radical of TEMPO,[20] indicating that TEMPO was not oxidized by molecular iodine upon heating within the elapsed time of the experiment.

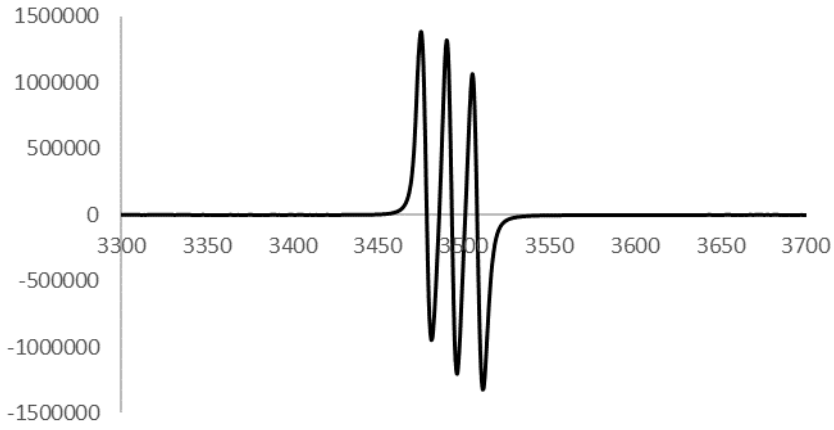


Figure 3: EPR spectrum for the reaction of iodine and TEMPO in DMSO.

The reaction was repeated with the addition of an aqueous solution of sodium bicarbonate ($NaHCO_3$), followed by heating for 2 hours and analyzed using EPR spectroscopy. This resulted in the disappearance of the characteristic TEMPO signal, indicating the formation of the *N*-oxoammonium cation (Figure 4). Consequently, these experiments support the proposed reaction mechanism presented in Scheme 2 in which the reaction proceeds *via* a radical pathway and indicates that the capture product **5** originates from the formation of **A,** rather than by reaction of the enolizable ketone and *N*-oxoammonium salt.

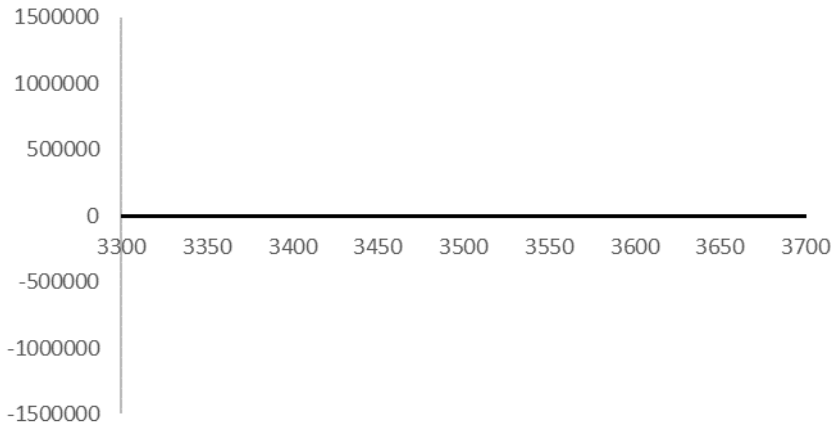
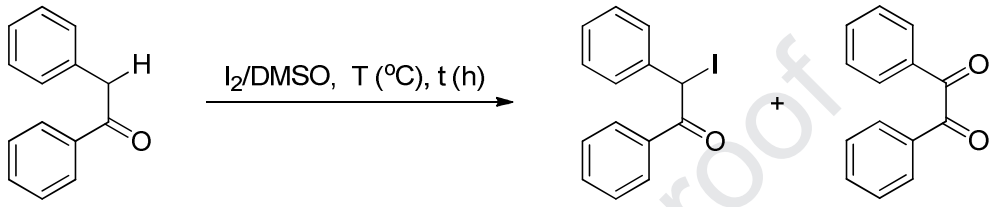


Figure 4: EPR spectrum for the reaction of iodine and TEMPO with aqueous $NaHCO_3$.

Next, owing to the involvement of iodine and benzylic radicals in our reaction, an α-iodinated species **B** was predicted to be the reactive intermediate in the oxidation of **1** to afford benzil **2**. As a result, we sought to isolate the α-iodinated intermediate from the reaction by varying time and temperature (Table 1), since the optimized reaction conditions afford complete oxidation of benzyl phenyl ketone **1** to benzil **2** (Table 1, entry 1). Despite numerous attempts of varying reaction conditions, we did not achieve any success in isolating

the target α-iodinated intermediate. On the contrary, the reaction proceeded to deliver the α-diketone **2** or unreacted benzyl phenyl ketone **1** (Table 1, entry 2). We attempted to further decrease the reaction temperature so as to decrease the rate of oxidation, however, only quantitative yields of benzyl phenyl ketone **1** was obtained (Table 1, entries 3-4).

Table 1: Varying reaction conditions for isolation of the α-iodinated intermediate.[a]



1 **B** **2**

Entry	Time (h)	Temp (°C)	Yield (%)		
			1	**B**	**2**
1[b]	2	100	n. d.	n. d.	96
2	24	25	90	n. d.	10
3	24	0	100	n. d.	n. d.
4	24	– 78	100	n. d.	n. d.

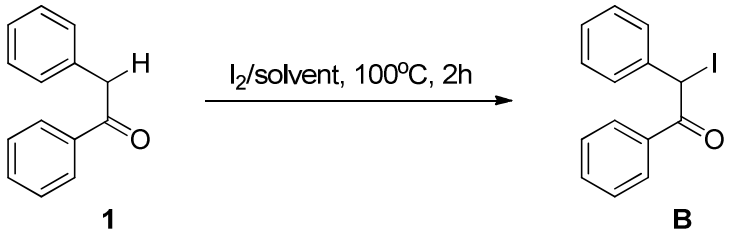
[a] Determined by ^{1}H NMR. [b] Isolated yield.

As a result, the failure to isolate the α-iodinated reactive intermediate from the reaction is reasoned by solvation effects, as well as the instability and reactivity of the C–I bond in dipolar aprotic solvents:[21] (i) Carbon–iodine (C–I) bonds are easily cleaved thermally, or photo-chemically, due to the lower bond dissociation energy (BDE), 56.5 kcal mol^{-1}, as compared to other carbon–halogen bonds. (ii) Molecular iodine is least dependent upon hydrogen bond stabilization with dipolar aprotic solvents. Its nucleophilicity thus decreases, allowing for immediate attack by DMSO on the α–carbon of **B**. (iii) The sulfoxide

moiety of DMSO has an electronic charge, residing on both the oxygen and sulfur atoms, which increases its nucleophilicity for interaction with an electrophile such as **B**. (iv) The corresponding iodide ion (I^-) distributes, more effectively, the negative charge that it has obtained, making it a highly reactive leaving group in nucleophilic displacements. Benzylic iodates are therefore difficult to observe and isolate, if formed *in situ*, in the presence of a strong nucleophilic solvent such as DMSO.

As a result, the utility of alternate reaction conditions were explored and literary studies disclosed that benzylic iodates have successfully been synthesized and isolated *via* oxidation in weak, nucleophilic protic solvents, in good to excellent yields.[22] Using this approach, the oxidation was performed in a series of weak nucleophilic solvents (Table 2), rather than DMSO, under the optimized reaction conditions to provide the α-iodinated intermediate, 2-iodo-1, 2-diphenylethanone **B**. Initially, benzyl phenyl ketone **1** was heated to 100°C in tetrahydrofuran (THF) or dichloroethane (DCE) for 2 hours, however, the reaction failed to produce the α-iodinated intermediate **B** (Table 1, entries 1-2). We, subsequently, changed the solvent to acetonitrile (CH_3CN) and *iso*-propanol (*i*-PrOH), however, only a minor amount of iodo-intermediate was detected (Table 1, entries 3-4). However, when benzyl phenyl ketone **1** and iodine were reacted in ethanol, under the optimized reaction conditions, the target α-iodinated intermediate **B** was isolated in a yield of 26% (Table 2, entry 5).

Table 2: Oxidation of benzyl phenyl ketone **1** in weak nucleophilic solvents.[a]



1 **B**

Entry	Solvent	Yield (%)	
		1	**B**
1	Tetrahydrofuran (THF)	100	n. d.
2	Dichloroethane (DCE)	100	n. d.
3	Acetonitrile (CH_3CN)	91	9
4	*Iso*-propanol (*i*-PrOH)	90	10
5[b]	**Ethanol (EtOH)**	**74**	**26**

[a] Determined by ^{1}H-NMR. [b] Isolated yield.

Analysis of the NMR spectra, provided in Figure 5, shows the singlet at 6.65 ppm[23] corresponding to the α-proton of **B**, identifying the iodo-ketone as a key intermediate in the oxidation process, thus further supporting the mechanism proposed in Scheme 2.

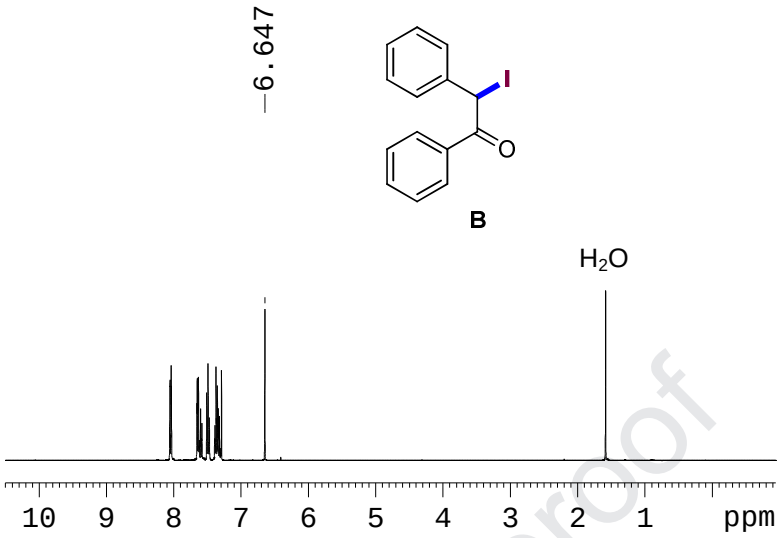
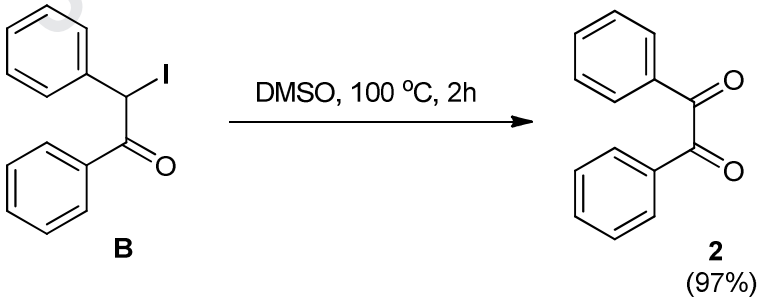


Figure 5: NMR spectrum of α-iodinated intermediate 2-iodo-1, 2-diphenylethanone **B**.

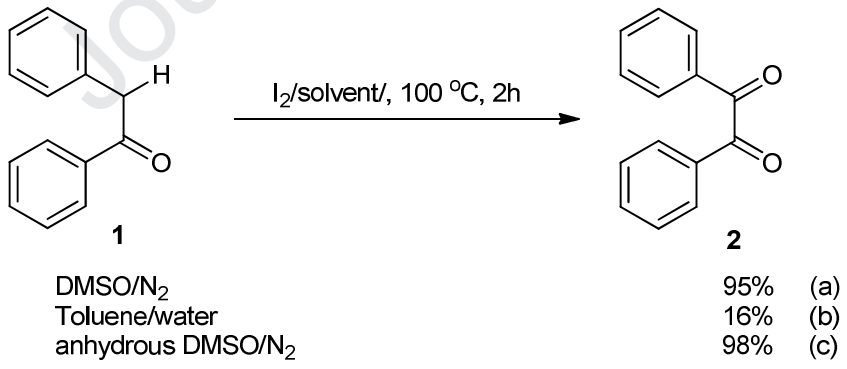
A supplementary study was performed in which the α-iodinated intermediate was heated in DMSO, under the optimized reaction conditions, to afford benzil in 97% yield thus adding further credence that **B** is the key intermediate in our reaction (Scheme 7).



Scheme 7: Oxidation of α-iodinated intermediate **B** to afford benzil **2**.

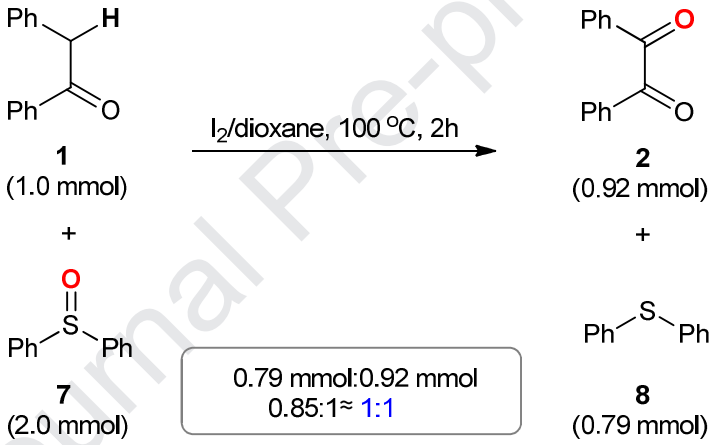
This result supports the effect of solvent (solvation) on the reaction pathway in terms of the nucleophilicity of the oxidant (solvent) and isolation of the highly reactive intermediate, **B**, in the I_2/DMSO oxidation of the α-methylene group of benzyl phenyl ketone.

Having completed the isolation of the reactive intermediate 2-iodo-1, 2-diphenylethanone from the reaction, we turned our attention to determining the source of oxygen in the reaction. Accordingly, there are three potential oxygen sources in the reaction system: molecular oxygen in the air, a trace amount of water in the solvent DMSO and DMSO itself. The reaction proceeded well under a nitrogen atmosphere, affording **2** in 95% yield and indicating that oxygen from the air does not participate in the reaction (Scheme 8, a). When the reaction was performed in a 1:1 toluene/water biphasic media, the oxidation product **2** was isolated in 16% yield, indicating that water plays a minor role in the oxidation reaction to afford **2** (Scheme 8, b). Finally, the reaction of benzyl phenyl ketone **1** in anhydrous DMSO, under a nitrogen atmosphere, afforded the diketone in 98% yield (Scheme 8, c).



Scheme 8: Control experiments determining oxygen source in benzil **2**.

This result suggests that the major source of oxygen in the diketone originates from DMSO and, in order to support this result, we aimed to isolate the reductive product of the sulfoxide moiety. The reductive product of DMSO is dimethyl sulfide (DMS) which is difficult to isolate and spectroscopically analyze; hence we turned our attention to the use of diphenyl sulfoxide (DPSO)[24] as the source of oxygen, since its reductive product, diphenyl sulfide (DPS), can be isolated and analyzed using NMR spectroscopy. Thus, the reaction of benzyl phenyl ketone and diphenyl sulfoxide (DPSO) in dioxane afforded benzil **2** and DPS **8** in 92% and 79% yield, respectively, with a mole ratio of approximately 1:1 (Scheme 9).



Scheme 9: Oxidation of benzyl phenyl ketone with DPSO under the optimized reaction conditions.

This indicates that one molecule of DMSO reacts with one molecule of benzyl phenyl ketone and the second oxygen atom in benzil originates from the sulfoxide. Accordingly, the oxidation of **1** is not solely a DMSO catalyzed reaction, since the catalytic water still exists but relies, primarily, on DMSO to react with the α-iodinated intermediate to afford the diketone benzil **2**.

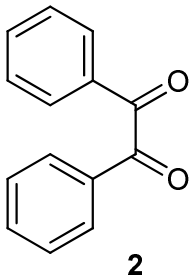
3. Conclusions

In conclusion, this research provides insight into the mechanism of the benzylic C_{sp}^3–H oxidation of an α-methylene ketone using an I_2/DMSO system. The proposed reaction mechanism was proven to proceed through: iodine and benzylic radicals, an α-iodinated intermediate, 2-iodo-1, 2-diphenylethanone, and oxidation *via* DMSO (the major source of oxygen in benzil). Each key intermediate and reaction step was proven using isolation and spectroscopic techniques: EPR spectroscopy, NMR analysis, the judicious choice of radical spin traps and experimental conditions to support our proposed oxidation reaction. This study, therefore, provides much needed insight into the benzylic C_{sp}^3–H oxidation of an α-methylene bond to afford synthetically useful α-diketones.

4. Experimental Details

All reagents were purchased without further purification. All ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Advance III spectrometer operating at 400 MHz. Chemical shifts (δ) were reported in ppm using the Dimethyl Sulfoxide-d6 (DMSO-d6) residual peak (δ 2.50) or Chloroform ($CDCl_3$) residual peak (δ 7.26) for ^{1}H NMR. Chemical shifts of ^{13}C NMR were reported, relative to DMSO-d6 (δ 39.51) or $CDCl_3$ (δ 77.0). The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants, J, were reported in Hertz unit (Hz). High-resolution/Low-resolution electron-spray ionization (ESI) mass spectra were recorded on a time-of-flight (TOF) micromass spectrometer. Infra-Red (IR) spectra were recorded on Carey 630 FTIR. Absorption maxima are expressed in wavenumbers (cm^{-1}). Melting points were determined using Kofler hot-stage melting apparatus. EPR measurements were conducted using a Bruker EMX Ultra X spectrometer.

4.1 General procedure for α-methylene oxidation with I_2/DMSO to afford benzil (2). Benzyl phenyl ketone (1.0 mmol, 0.196 g)) and iodine (0.5 mmol, 0.126 g) were mixed in a round bottomed flask with 1 mL DMSO and heated to 100 °C for 2h. After cooling, a $Na_2S_2O_3$/water solution was added to the reaction mixture, extracted with dichloromethane and dried over anhydrous $MgSO_4$. Removal of the solvent, under vacuum, afforded the crude product which was purified by column chromatography using 5:1 hexane:ethyl acetate.



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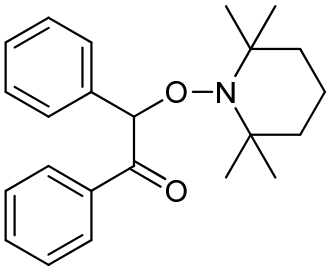
Benzil **2** (0.202 g, 96%) was obtained as a yellow solid: Mp 94-96 °C; υ_{maz} (neat, cm^{-1}): 3064, 1655, 1590, 1449, 1208. ^{1}H NMR (400 MHz, $CDCl_3$): 7.95-7.93 (m, 4H), 7.83-7.78 (m, 2H), 7.66-7.62 (m, 4H). ^{13}C NMR (400 MHz, $CDCl_3$): 129.5, 129.5, 132.2, 135.5, 194.8. GC-MS (*m/z*): 210.0 (10), 105.0 (100).[25]

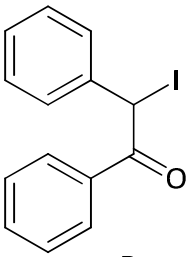
4.2 General procedure for synthesis of 1, 2-diphenyl-2-((2, 2, 6, 6-tetramethylpiperidin-1-yl)oxy)ethanone (5). Benzyl phenyl ketone (1.0 mmol, 0.196 g), TEMPO (1.0 mmol, 0.156 g) and iodine (0.5 mmol, 0.126 g) were mixed in a round bottomed flask with 1 mL DMSO and heated to 100 °C for 2h. After cooling, a $Na_2S_2O_3$/water solution was added to the reaction mixture, extracted with dichloromethane, and dried over anhydrous $MgSO_4$. Removal of the solvent under vacuum, afforded the crude product which was purified by column chromatography using 9:1 hexane:ethyl acetate.



5

1, 2-Diphenyl-2-((2, 2, 6, 6-tetramethylpiperidin-1-yl)oxy)ethanone **5** (0.163 g, 46%) was obtained as a white solid: Mp 229-231 °C; υ_{maz} (neat, cm^{-1}): 3068, 2922, 2852, 1667, 1596, 1446, 1262, 1042; ^{1}H NMR (400 MHz, $CDCl_3$): 8.01-7.99 (m, 2H), 7.43-7.39 (m, 3H), 7.34-7.30 (m, 2H), 7.22-7.18 (m, 2H), 7.14-7.10 (m, 1H), 5.92 (s, 1H), 1.38-1.37 (m, 6H), 1.24-1.11 (m, 6H), 0.92 (m, 3H), 0.73 (m, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): 198.3, 137.8, 135.3, 132.9, 129.3, 128.3, 127.5, 127.2, 93.5, 60.0, 59.8, 40.3, 33.6, 33.3, 20.3, 20.2, 17.0; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{30}NO_2$ 352.2276; found 352.2277.[17]

4.3 General procedure for synthesis of α-iodinated Intermediate 2-Iodo-1, 2-diphenylethanone (B). Benzyl phenyl ketone (1.0 mmol, 0.196 g) and iodine (0.5 mmol, 0.126 g) were mixed in a round bottomed flask with 1 mL ethanol and heated to 100 °C for 2h. After cooling, the solvent was removed under vacuum, affording the crude product which was purified by column chromatography using 9:1 hexane:ethyl acetate.

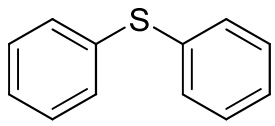


B

2-Iodo-1, 2-diphenylethanone **B** (0.085 g, 26%) was obtained as a yellow solid: Mp 92-93 °C; υ_{maz} (neat, cm^{-1}): 3056, 1670, 1210, 746; ^{1}H NMR (400 MHz, $CDCl_3$): 8.06-8.04 (m, 2H), 7.66-7.58 (m, 3H), 7.51-7.47 (m, 2H), 7.39-7.30 (m, 3H), 6.65 (s, 1H); ^{13}C NMR (400 MHz, $CDCl_3$): 27.8, 128.7, 128.8, 128.9, 129.0, 129.5, 133.6, 133.7, 137.4,

192.3; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{11}IONa^+$ 344.9752; found 344.9745.[23]

4.4 General procedure for α-methylene oxidation by diphenyl sulfoxide (DPSO) to afford diphenyl sulfide (DPS) (8). Benzyl phenyl ketone (1.0 mmol, 0.196 g), diphenyl sulfoxide (2.0 mmol, 0.404 g) and iodine (0.5 mmol, 0.126 g) were mixed in a round bottomed flask with 1 mL dioxane and heated to 100 °C for 2h. After cooling, a $Na_2S_2O_3$/water solution was added to the reaction mixture, extracted with dichloromethane and dried over anhydrous $MgSO_4$. Removal of the solvent, under vacuum, afforded the crude product which was purified by column chromatography using 9:1 hexane:ethyl acetate to afford benzil **2** (0.194 g, 92%) as a yellow solid and diphenyl sulfide **7**.



8

Diphenyl sulfide **8** (0.147 g, 79%) was obtained as a clear liquid: Mp 60-62 °C; υ_{maz} (neat, cm^{-1}): 3056, 1578, 1474, 1438, 1023; ^1H NMR (400 MHz, DMSO-d6): 7.2-7.41 (m, 10H); ^{13}C NMR (400 MHz, DMSO-d6): 127.4, 129.5, 130.7, 134.8; HRMS (ESI-TOF) *m/z*: $[M]^+$ Calcd for $C_{12}H_{10}S$ 186.0503; found 186.0507.[26]

5. Acknowledgements

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UNIVERSITY OF KWAZULU-NATAL
INYUVESI YAKWAZULU-NATALI

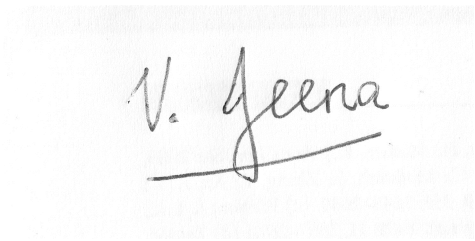
09 September 2019

Subject: Highlights for **Iodine/DMSO Promoted Oxidation of Benzylic Csp^3–H Bonds to Diketones – a Mechanistic Investigation**

Dear Sir/Madam

- A mechanistic investigation into a benzylic C-H oxidation to diketones, using an Iodine/DMSO system, is reported.
- A cocktail of techniques such as NMR, EPR, radical traps and a surrogate nucleophile was used.
- Key intermediates were detected spectroscopically or isolated to confirm the proposed mechanism.

Kind Regards



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