

# Diversity with Light: Photoreaction Pathways and Products of Butyrophenone

Heiko Hoffmann<sup>1,\*</sup>, Michael W. Tausch<sup>2</sup>

<sup>1</sup>Faculty of Natural Sciences and Technology, Provdavis Hochschule, Industriepark Höchst, Gebäude B835, 65926, Frankfurt am Main, Germany

<sup>2</sup>Faculty of Mathematics and Natural Sciences, Bergische Universität Wuppertal, Gebäude V.11.027, Gaußstraße 20, 42119 Wuppertal, Germany

\*Corresponding author: [heiko.hoffmann@provadis-hochschule.de](mailto:heiko.hoffmann@provadis-hochschule.de)

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**Abstract** Photochemistry is an important topic which is relevant regarding the usage of solar light as clean energy source. By employing photoreactions, a broad variety of molecular transformations can be conducted which is different from classical thermal chemistry. Ketones provide advantages and thus can be used as model compounds to develop central aspects and principles of photochemistry for teaching purposes. A photochemical experiment for university teaching, dealing with the basic reaction modes of ketones with  $\gamma$ -C-H-bonds, can be introduced and adjusted to the learners capability and pre-knowledge. Different basic characteristics of photochemistry and radical reactions as well as advanced topics and working techniques can be accessed in a hands-on-way using the model reaction. Depending on the equipment and the time frame available, the experiment can be conducted on preparative or on micro scale.

**Keywords:** ketones, photochemistry, H-atom transfer, radical reactions, hands-on laboratory learning

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## 1. Introduction

### 1.1. Relevance of Photochemistry

Photochemistry is a current facet of chemistry and has experienced a renaissance in the recent years [1] against the background of renewable and clean energy sources and of sustainable syntheses and processes using solar light [2,3]. Its inclusion into university study courses [4,5,6,7] and school teaching [8,9,10] is important because of its relevance in nature, everyday life, industry and education [4,9,10,11] as well as because of its interdisciplinarity [4,11]. The Sustainable Development Goals of the United Nations also imply and emphasize its very recent relevance. Photoreactions, however, are based on concepts which are partly different from those of the so-called thermal "dark reactions" [11].

In general, different reaction types can be conducted photochemically, namely by irradiation [4,11,12]:

- Isomerizations resp. rearrangements (including electrocyclizations and sigmatropic reactions) leading to changings of the constitution or the configuration of the molecules
- Dissoziations (homolysis, heterolysis or cycloreversions) resp. fragmentations and cleavages of chemical species

- Addition resp. covalent bond formation between reaction partners (radical recombinations, radical additions to unsaturated systems and cycloadditions), e.g. starting of radical polymerizations
- Oxidations and reductions

In the course of these reaction types, also strained cyclic compounds can be generated, e.g. by additions and isomerizations.

### 1.2. Ketones - Photoactive Compounds

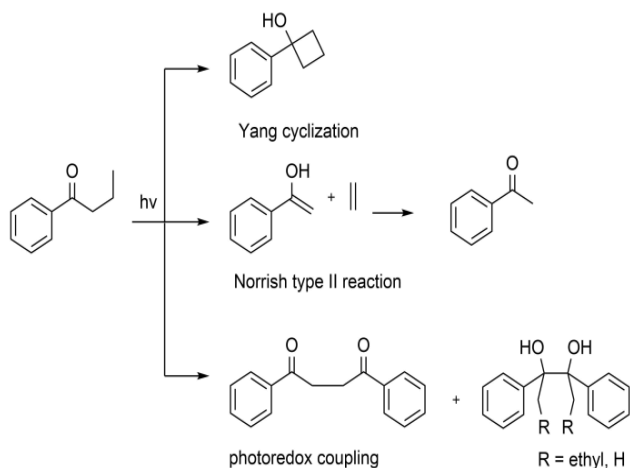
Ketones are a fundamental class of compounds in organic chemistry. Simple ketones are also known to pupils from everyday life (e.g. acetone as solvent and nail polish remover). The photoreaction modes of the substance class are well studied and include most of the typical photoreactions of organic molecules [2,12,13], amongst them (i) the photoreduction of benzophenone and other ketones in the presence of H-atom donors, (ii) the photoenolization of *ortho*-methyl phenylketones, (iii) the  $\alpha$ -cleavage (Norrish type I reaction) and decarbonylation, (iv) the Norrish type II reaction and Yang cyclization of ketones with  $\gamma$ -C-H-bonds, (v) the Paternó-Buechi reaction (oxetane formation) between an excited ketone and an alkene, and (vi) the photosensitization of other species by excited ketones via energy transfer resp. triplet transfer. Due to the  $n\pi^*$ -transition, simple aromatic keto compounds absorb already in the UVA range [4] and do

readily undergo photochemistry. For both reasons, they are suitable as model substances for developing the topic of photochemistry in laboratory teaching in university settings [13].

### 1.3. A New Pathway of the Photoconversion of Butyrophenone

Butyrophenone has been chosen as model compound for teaching purposes (experimental and theoretical) [11,12,13,14]. We have discovered, scientifically investigated and published another reaction pathway which occurs in connection and in competition with the Norrish type II reaction [15,16] (Scheme 1, bottom) and will show in this article how it can be utilized didactically in teaching in university laboratory education.

We propose an laboratory experiment which allows to retrace typical characteristics of ketone photochemistry in a hands-on-, low-cost- and most important up-to-date-way. It allows to be adjusted to (i) the learners pre-knowledge and abilities, to (ii) the equipment and budget available, and (iii) to the time frame possible.



Scheme 1. Photoreactions of butyrophenone [16]

## 2. Model Reactions and Didactical Simplification

After photochemical excitation via light absorption and Inter System Crossing (ISC), butyrophenone deactivates mainly via intra- and intermolecular H-atom-transfer (HAT) [16], shown in Scheme 2.

Via the Norrish type II reaction, a 1,4-biradical is formed by intramolecular HAT, which afterwards undergoes fragmentation to main products ethene and acetophenone enol [12,17-24]. Acetophenone enol tautomerizes uncatalyzed on the seconds to minutes-scale to acetophenone [12,25,26]. As a by-product, 1-phenylcyclobutanol is formed via Yang cyclization of the 1,4-biradical [12,17,27,28].

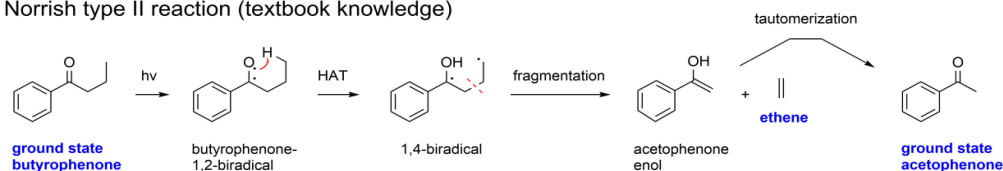
Our investigations show that in competition to intramolecular HAT, products generated by intermolecular

HAT arise via the photoredox coupling [15,16]. Excited keto forms attack the O-H-bond of the intermediate acetophenone enol [15,16,17], forming phenacyl and ketyl radicals [29]. These then react by phenacyl radical addition [30,31] to acetophenone enol, followed by H-atom loss via HAT or via ketyl radical transfer to ground state ketones [32], and by radical recombination to give 1,2-dibenzoylthane [31,33] and pinacols [2,12,18,29,34].

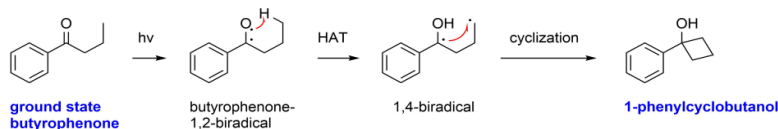
On the university level, the topic could and should be taught as outlined, e.g. in organic chemistry or photochemistry courses and laboratory teaching settings. It provides the opportunity to develop and deepen the following concepts strongly interlinked with each other [15]:

- Basic radical reactions modes (Scheme 2): In essence, most of the reaction steps considered are simply radical follow-up chemistry of photochemically generated radicals. The topic therefore offers the opportunity to address several important radical reactions of organic molecules [12,35]: (i) Radical substitution (e.g. radical HAT), (ii) radical addition to double bonds, and (iii) radical recombination. The reverse reactions are in each case (i) back-HAT, (ii) fragmentation (analogy to the McLafferty fragmentation in mass spectrometry), and (iii) homolytic cleavage (also a fragmentation).
  - Synthetic accessibility of tensed systems via photoreactions, exemplified by 1-phenylcyclobutanol
  - The principle of capturing an intermediate species can be strengthened (acetophenone enol scavenged by excited ketones or by phenacyl radicals)
  - Keto-enol-tautomerism: A portion of the acetophenone enol is captured before its tautomerization, giving rise to the intermolecular products. Enols may have lifetimes on the minute scale. The Norrish type II reaction is a standard method for the generation of acetophenone enol [24,36,37].
  - A core characteristic of photochemistry becomes succinctly clear: There is typically a competitive situation [7] between several deactivation pathways. The fastest path leads to the main event or product. [4,12]
  - The principle behind the intramolecular deactivation pathways can be deepened (Scheme 3): By observing the energetics of the intermediates and products, the fundamental principle becomes clear that nature strives for the energetic minimum. Depending on the pre-knowledge of the learners, reasons regarding molecular structure can be discussed.
- In general, the teacher should decide (adapted to the respective learning group) which of the concepts is a learning objective. For teaching the photophysical deactivation processes occurring after excitation (if desired in both cases), a proposal can be used that has already been made available to the community [38].

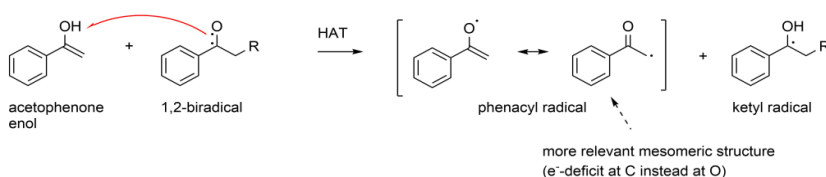
## Norrish type II reaction (textbook knowledge)



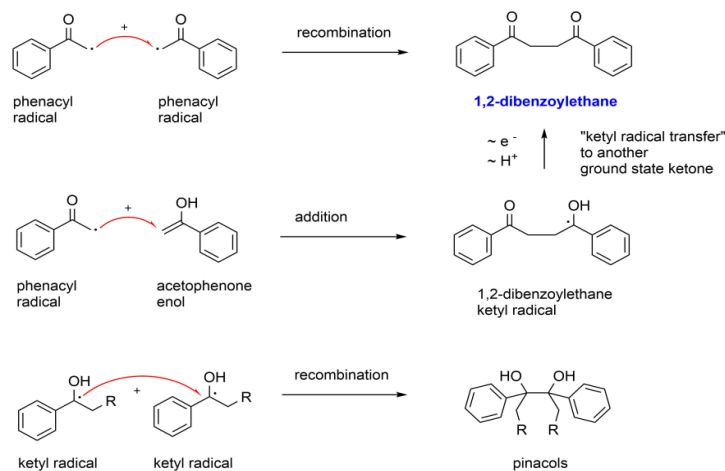
## Yang cyclization (textbook knowledge)



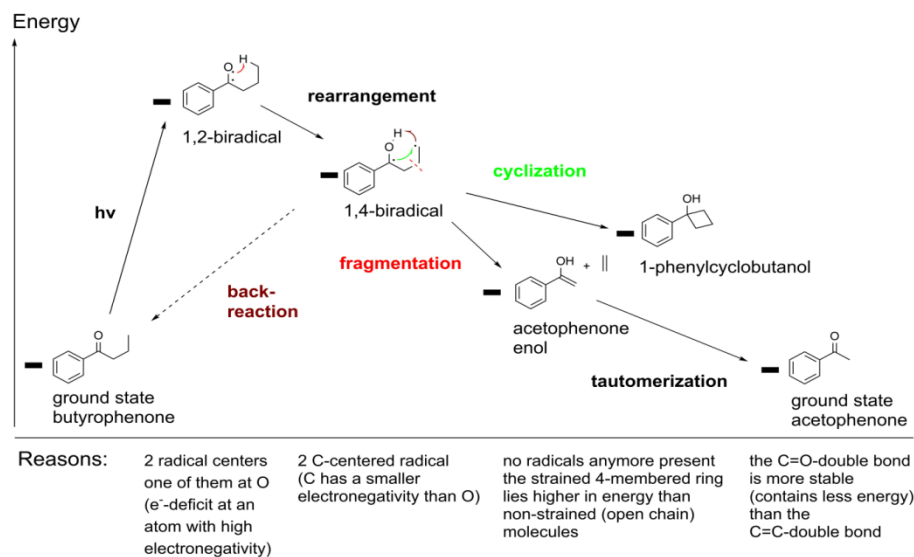
## intermolecular H-atom-transfer (new pathway)



## product formation by recombination or addition to double bonds



Scheme 2. The main mechanistic photochemistry of butyrophenone presented in a suitable degree of detail for university teaching [15]



Scheme 3. Energy considerations of the intramolecular deactivation after excitation [15]

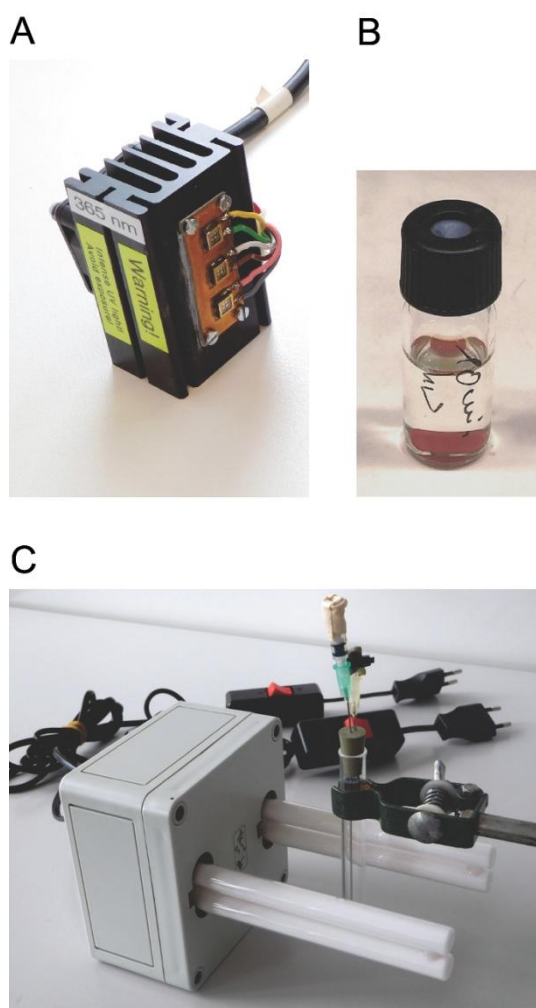
### 3. Experimental Setups and Observations

#### 3.1. Variant as Microscale Experiment

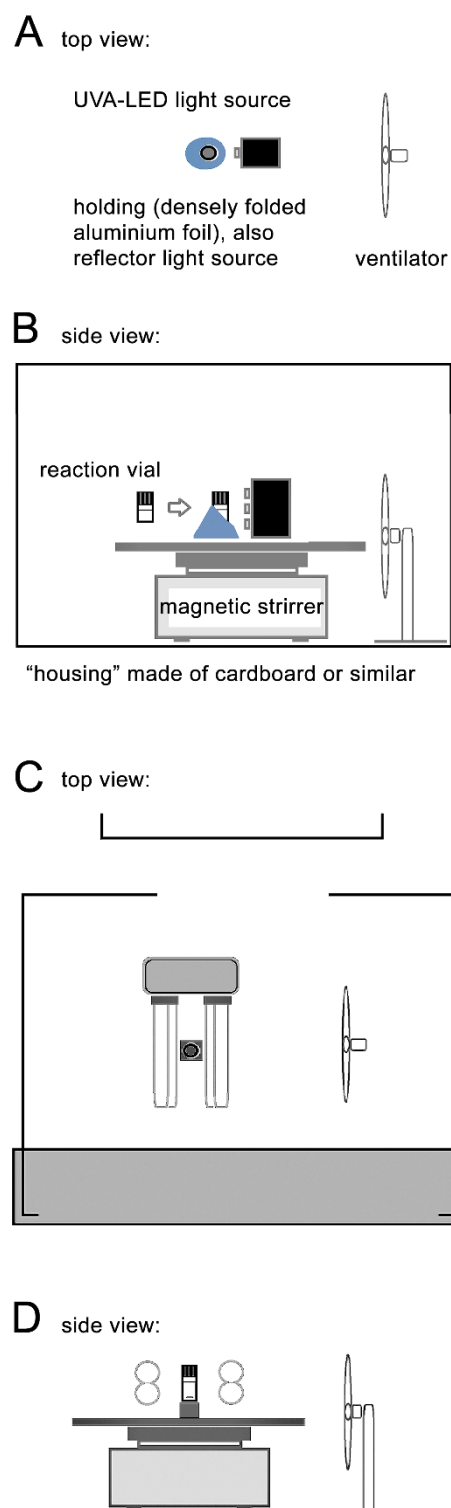
The experiment [15] can be conducted on micro scale. Advantages are the low costs and the most safe conditions (1 mL reaction volumes). As an option, the whole experiment can be conducted as experimental demonstration by the teacher, in parallel to the ongoing lecture.

By analyzing and comparing thin layer chromatography (TLC) product bands obtained by irradiation of a butyrophenone and a acetophenone solution, the photochemical reactions of butyrophenone can be retraced.

*Experiment:* The students irradiate 1 mL-HPLC borosilicate vials, containing the butyrophenone or the acetophenone solution respectively (0.05 M in acetonitrile each) and a small magnetic stirrer bar under ventilator cooling, with UVA-LED-, UVA bulb- or UVB bulb light sources using published low-cost equipment for photochemical reactions [39] or LED-solutions commercially available for teaching purposes [40] (Figure 1). An exemplary setup is schematically shown in Figure 2.



**Figure 1.** Light sources and reaction vessels for the irradiation on microscale: A: UVA-LED lamp [40]. B: 1 mL borosilicate HPLC vial with septum used as reaction volume, equipped with a small magnetic stirrer bar. C: UVB-bulb lamps [39] and quartz test tube, sealed with a rubber stopper



**Figure 2.** Schematic representation of irradiating the reaction volumes on microscale

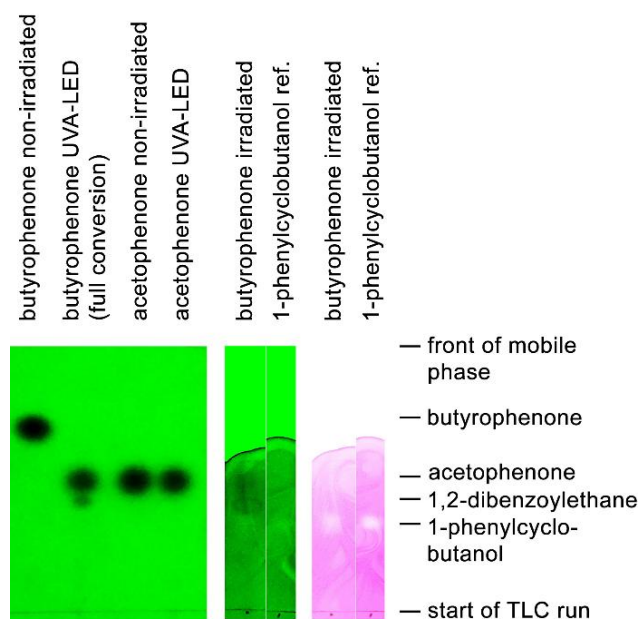
Prior to irradiation, the reaction vials are shortly flushed with inert gas (nitrogen or argon) by employing needles piercing the septum [39]. For pressure compensation, one syringe piercing the septum can be kept during irradiation. The shielding of the experimentalists from the UV-light can easily be realized using the published approach [39]. Depending on the light sources used (Table 1), different irradiation times can be compared. Several vials can be irradiated in parallel or for different lengths one after the other.



**Table 1. Materials and time for the microscale experiment**

light source	irradiation time to high conversion
1 UVA-LED, vial or test tube positioned in aluminium foil stand, approx. 1 cm distance	approx. 30-60 min
2 UVB bulbs, vial or test tube positioned in between, approx. 2 cm distance each	approx. 60-90 min
compounds	costs approx.
butyrophenone (25 mL)	15 €
acetophenone (25 g)	15 €
1,2-dibenzoylthane (1 g)	40 €
acetonitrile > 99,5% (500 mL)	25 €
cyclohexane 99% (1 L)	20 €
ethyl acetate 99% (1 L)	20 €
ethanol (1 L, denat. with MEK)	20 €
iodine monobromide (50 g)	30 €
potassium permanganate (500g)	60 €

**Results and Observation:** After irradiation of butyrophenone, the resulting product mixture can be made visible by fluorescent TLC (e.g. Silica Gel 60 F<sub>254</sub>, Merck, 80%) (Figure 3). Due to the phenyl carbonyl chromophore in butyrophenone, acetophenone and 1,2-dibenzoylthane, the compounds are visible under 254 nm TLC-lamp wavelength.



**Figure 3.** TLC-observations and results of the microscale experiment (Mobile phase 80% cyclohexane and 20% ethyl acetate). All solutions were 0.05 M before irradiation or are non-irradiated references. A very small crumb of 1-phenylcyclobutanol has been dissolved in 1 mL acetonitrile. 1  $\mu$ L of the solutions were spotted on each lane. Regarding the stained TLC plates, only parts of the photographs are shown. The photographs have been adjusted regarding their size, and the contrast has been processed.

By comparing the irradiated butyrophenone with the irradiated acetophenone lanes, the products formed from butyrophenone can be observed. The main spot has the same  $R_f$  value as acetophenone (assignment of acetophenone). The spot below acetophenone can be attributed to 1,2-dibenzoylthane, also by employing a purchased reference (cf. Figure 6 below) or by giving the information to the students.

1-Phenylcyclobutanol can be observed by staining the plate (after photographing) with a diluted potassium permanganate solution in ethanol (Stock solution (based on [41]):  $\text{KMnO}_4$  (5 g),  $\text{K}_2\text{CO}_3$  (33.3 g), NaOH solution (5%, 8.3 mL), 500 mL of bidistilled water. This stock solution was diluted by a factor of 5 with bidistilled water for staining the butyrophenone-photoproduct mixture.). Alcohols can be oxidized by  $\text{KMnO}_4$  [41,42], whereby  $\text{KMnO}_4$  is reduced and the spot on the TLC plate loses the purple color. Since the 1-phenylcyclobutanol reference is expensive and difficult to purchase, the proof is shown as an example obtained with a purchased reference for comparison (Figure 3).

The acetophenone solution is treated equally, but no visible product bands are observed. This finding can be used to raise the question of the formation mechanism of 1,2-dibenzoylthane (“investigative learning”). If the  $\alpha$ -C-H-bond would be the donor for an H-atom-transfer (radical H-atom-abstraction), the formation of 1,2-dibenzoylthane also from acetophenone should be found, which is not the case (and which has been shown in mechanistic investigations [16]).

**Minimal hazards, precautions and disposal of waste:** During photochemical experiments, the uninterrupted wearing of UV-intransparent protective goggles is mandatory. The following personal protective equipment is recommended and is assumed to be given in the following: Protective goggles, lab coat, closed footwear and splash protection gloves. The dangers posed by the UV radiation used and the possibility of peroxide formation and the safe control of these have been already discussed in detail [38,39]; what is said there applies analogously, but an eventual peroxide formation is uncritical and harmless, since only smallest quantities can be formed in the microscale experiment of only 1 mL. The shielding of the experimentalists from the UV-radiation can easily be done by positioning the setup within an enclosure made of cardboard. The setup can be cooled during irradiation using a small ventilator. An open part at the backside of the cardboard housing ensures air exchange and cooling (Figure 2C).

All following dangers and hazards are uncritical and inherently safe due to a smallest volume scale.

- Properties of the organic solvents (highly flammable, toxicity and harmfulness to health).
- Breakage of a reaction vial.
- Ketones used diluted (0.05 M): Butyrophenone (contradiction in the literature: Classified as “harmless” [43,44] or attributed with H317, H318 in older sources), acetophenone (H302, H319 [43]), 1,2-dibenzoylthane (“harmless” [45]). Not all the subcomponents formed in smallest traces [16] are fully toxicologically characterised, so splash guard gloves are advised.

Potassium permanganate is a well known oxidant (H272, H302, H314, H410). Inert gas cylinders should be connected outside the building if possible, otherwise they should be secured against falling over. Care must be taken not to eject much choking gas unnoticed. The usage of small gas cylinders [39] is proposed.

The waste should not be disposed with the normal sewage water but should be collected according to the institutions chemical waste disposal process.

### 3.2. Variant as Preparative Experiment

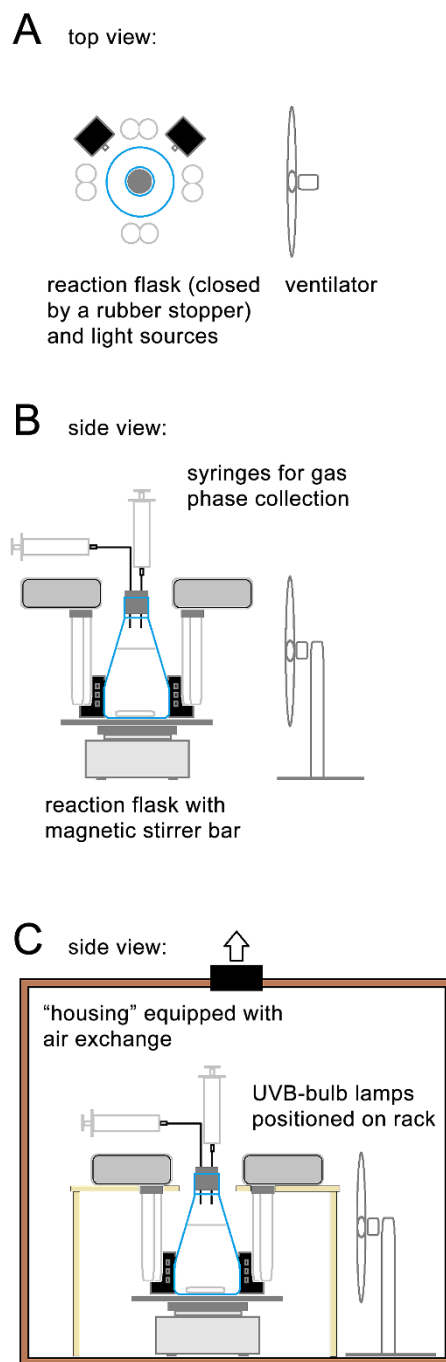
By using the preparative experiment, e.g. in hands-on laboratory organic chemistry courses in universities, in addition to the aspects outlined in the explanation of the microscale experiment, the students can:

- Isolate and characterize 1,2-dibenzoylthane (and optionally acetophenone) via NMR, MS, IR methods if available for teaching purposes in the institution. 1,2-Dibenzoylthane characterization data are given in the Supporting Information. Acetophenone characterization data are available on the internet [46]. The spectra of both compounds can be compared (similar NMR- and IR-spectra). If a mono-crystal of 1,2-dibenzoylthane is obtained, also X-ray characterization can be considered (Supporting Information). Note: The isolation of the small amounts of 1-phenylcyclobutanol and of pinacols is difficult and not suitable for teaching purposes.
- Collect the formed ethene resp. gas phase. The alkene presence can be verified by adding a iodine monobromide solution (brown color). The color disappears after shaking the solution in the collected gas phase (halogen addition to the double bond). As a further development of the classical alken detection by means of elemental bromine, the use of iodine monobromide is far less dangerous.
- Learn and practice typical working techniques of preparative photochemistry (oxygen exclusion, irradiation in enclosure).

**Experiment:** Butyrophenone (0.05 M, 2.25 mL in 300 mL acetonitrile) is filled in a borosilicate 300 mL single-neck Erlenmeyer flask (equipped with a magnetic stirrer bar) and closed with a rubber stopper pierced with two syringe needles (a long needle for the inlet and a short one for the outlet). By flushing with protective gas (Ar or N<sub>2</sub>, cf. low-cost equipment [39]) for 3 min while stirring, previously dissolved gases are replaced by protective gas. The inert gas flow rate is selected in such a way that a strong “bubble” occurs, but not so strong as to cause solution to leak outwards. After that, both cannulas are quickly closed with two 50 mL syringes, which will serve as low-cost piston samplers to collect the ethene. The closed reaction volume is positioned between the light sources in an enclosure (subject to air exchange), cooled by a small ventilator (Figure 4), and irradiated for 4 hours (Table 2) under stirring with 4 UVB tube lamps and 2 UVA-LED lamps (distance approx. 1 cm to the flask each). If ethene shall not be collected by the students, the irradiation can be paused and samples can be taken using a syringe.

**Table 2. Irradiation times for the preparative experiment**

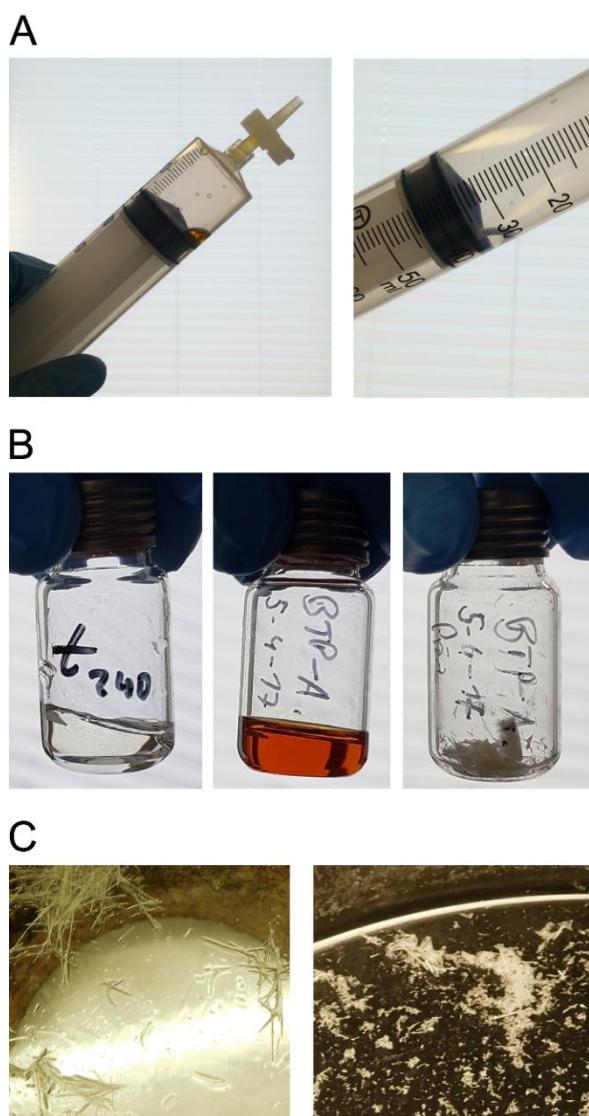
light source	irradiation time to full conversion
2 UVA-LED and 4 UVB-bulb light sources, quartz or borosilicate Erlenmeyer flask positioned in the middle of the lamps, approx. 1 cm distance	approx. 4 h



**Figure 4.** Schematic representation of irradiating the reaction volume on preparative scale

**Ethene detection:** During irradiation, the pistons of the syringes have been pushed outwards by the successive development of gas. The gas phase is mixed and homogenised by careful one-time flushing it back and forth from one syringe to the other (in the still closed reaction volume). One syringe is completely emptied so that the other syringe is filled. The filled syringe is quickly closed with a luer lock tap (or otherwise). By quick opening, injecting several drops (0.5 mL) of iodine monobromide water (specification: 40 mg IBr in 10 mL bidist. H<sub>2</sub>O, solid sediment under the saturated solution), closing again and shaking the closed syringe vigorously, the iodine monobromide water is rapidly decolored by the

ethene contained in the gas phase (Figure 5A). This is due to the interhalogen adding to the C-C-double bond [47,48,49,50]. Shaking the iodine monobromide solution in an air-filled reference syringe does not cause discoloration.



**Figure 5.** Observations during the preparative experiment. A: Left: Closed syringe containing the collected gas phase and several drops of iodine monobromide water. Right: After shaking, the drops are colorless. B: Left: Sample of the reaction mixture taken after irradiation for 4 h. Middle: Product mixture obtained after separation of the solvent under reduced pressure (liquid phase, main component acetophenone with strong acetophenone scent). Right: 1,2-Dibenzoyl ethane crystals obtained after leaving the liquid product mixture over night and after removal of the liquid supernatant. C: 1,2-Dibenzoyl ethane crystals formed in a crystalizing dish before (left) and after rinsing (right) with cooled ethanol.

**Solvent removal:** Variant 1: Using a rotary evaporator, the solvent is separated in a 500 mL single-neck flask under reduced pressure (60 °C, successively up to 130 mbar). Approximately 1,5 mL of a yellowish and viscous-liquid residue strongly smelling of acetophenone is obtained. The residue is transferred into a small, sealed screw cap glass and allowed to stand for a day or

longer (Figure 5B, middle). It becomes darker and crystal formation is observed, consisting of 1,2-dibenzoyl ethane (as “second main component” besides acetophenone). After separating the supernatant (pipette), the crystals are clearly visible but slightly yellowish (Figure 5B, right). A small part of both the crystals and the supernatant can be dissolved in acetonitrile and subjected to TLC analysis. Optionally, acetophenone (boiling point 202 °C [43]) can be purified by distillation of the supernatant.

**Variant 2:** If a rotary evaporator is not available, the following preparative procedure is appropriate: The liquid components of reaction mixture are allowed to evaporate in a large crystallization dish for several days in a fume hood. Afterwards, the residue is completely dissolved twice (each in approximately 20 mL of ethyl acetate) and the ethyl acetate is evaporated again to remove acetophenone rests. As soon as the acetophenone odor no longer appears, it has been approximately separated. The residue is dissolved a third time in 20 mL of ethyl acetate and the crystallization dish is positioned as plain as possible. After the crystallization of 1,2-dibenzoyl ethane occurred, the dish with the still moist content (Figure 5C, left) is placed inclined standing and the supernatant is removed with the pipette. It contains most of the by-products. The crystals are quickly washed with a little cold ethanol (pipette!). Whitish to colorless 1,2-dibenzoyl ethane crystals are obtained (Figure 5C, right) that are purer than those obtained using variant 1, since both acetophenone and other components were removed more thoroughly before crystallization occurred. The TLC examination is similar to that of variant 1, except that no supernatant sample is available because the acetophenone has been evaporated.

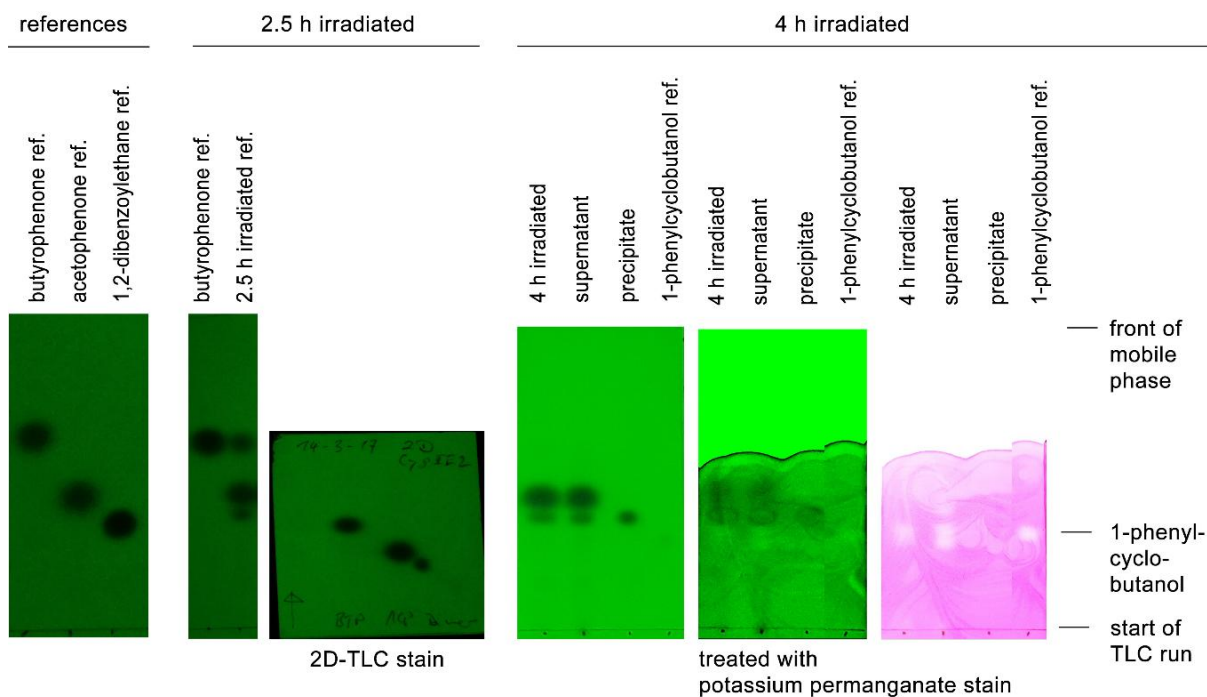
The obtained crystals can be characterized depending on the available resources: By spectroscopic methods (NMR, MS, IR, UV-VIS, and X-ray diffractometry), melting point determination (literature values: 142-144 °C [51], 144-148 °C [52], 145-149 °C [45] and 145-150 °C [11]) or staining (derivatization) on TLC plates with 2,4-dinitrophenylhydrazine solution in ethanol (keto group specific reagent, not shown) [42,45]. The crystals can optionally be further purified by (flash) chromatography until colorless crystals are obtained. Alternatively, they can be recrystallized multiple times from ethyl acetate.

**Results and Observation:** The product mixture can be made visible by fluorescent TLC (e.g. Silica Gel 60 F<sub>254</sub>, Merck, 80% cyclohexane and 20% ethyl acetate as mobile phase, Figure 6), similar to the microscale experiment (Figure 3). In addition, the obtained crystals and the supernatant can be observed separately resp. distinguished. As an option, e.g. if a sample of the reaction mixture has been taken prior to full conversion, a two-dimensional TLC run (2 subsequent runs) can be conducted.

**Time required:** The preparative experiment requires about 4 hours for the complete butyrophenone turnover; one laboratory day should be planned including assembly, sampling, solvent separation, crystallization and clean-up.

If the solvent is removed without a rotary evaporator overnight, the experiment should be run in parallel with other experiments during the laboratory week.





**Figure 6.** TLC analysis of the preparative butyrophenone conversion and photoproducts formed. (Parameters: Mobile phase 80% cyclohexane and 20% ethyl acetate). All solutions were 0.05 M before irradiation or are non-irradiated reference. A very small crumb of 1-phenylcyclobutanol and 1,2-dibenzoyl ethane has been dissolved in 1 mL acetonitrile each. 1  $\mu$ L of the solutions were spotted on each lane. Regarding the stained TLC plates, only parts of the photographs are shown. The photographs have been adjusted regarding their size, and the contrast has been processed.

*Risk Assessment of the preparative experiment, hazards and precautions:* All aspects mentioned in section 3.1 apply accordingly. Conducting a preparative experiment, the following aspects have to be taken into account. One main hazard is the properties of the organic solvents (highly flammable, possibility of creating an explosive atmosphere, toxicity and harmfulness to health). The irradiation must be done in a housing with high air exchange at room temperature, or similar (cf. Figure 4). In the case of breakage of the flask, the solution can be spilled into a small tray in which the setup is positioned. Solvent evaporation must be done in a fume hood. In the case of rotary evaporator usage, the operating instructions apply. The main hazards are solvent vapours (inhalative) and the possibility of implosion (especially when applying or removing the negative pressure). The rotary evaporator should therefore not be operated openly, but either in a closed enclosure (with sufficient air exchange) or in the fume hood with the front gate closed. Butyrophenone is used diluted in acetonitrile (0.05 M). Not all the subcomponents formed in very small quantities of a few milligrams [16] are fully toxicologically characterised, so caution is advised when handling (splash guard gloves). The main components are laboratory-standard. The weighing and preparation of the iodine monobromide water can be done by the teacher with protective glasses and gloves. Iodine monobromide is corrosive (eyes, skin) and has specific target organ toxicity (single exposure) category 3 [43]. However, it is safer to handle than the very volatile and acutely toxic elemental bromine [43], which is why the teaching experiment was developed using iodine monobromide. Finally, when working with syringe needles, there is a risk of prickling oneself or prick oneself with contaminated needles; syringe disposal containers should therefore be used and recapping is forbidden.

## 4. Conclusion

Butyrophenone as model system is suitable for the development of advanced concepts through research-based learning [53,54,55,56] in universities. The basic reaction modes of ketones with  $\gamma$ -C-H-bonds can be introduced and deepened. The system-immanent HAT donor acetophenone enol creates a competitive situation of intra- and intermolecular reaction possibilities. It is, beside the Norrish type II and Yang cyclization name reactions, a suitable example for dealing with the topics of H-atom transfer, photoreduction resp. pinacolization, side reactions, secondary photochemistry, involvement of intermediates in photoreactions and stabilization of the excited system by different deactivation pathways.

Advantages of this model reaction are the inactivity, air and oxygen stability and the relative harmlessness of the components of the butyrophenone system.

Several experimental working techniques can be learned: Exclusion of oxygen (for preventing energy transfer to oxygen molecules and subsequent side reactions), irradiation of photochemical setups, detection of gaseous olefins by decoloration of iodine monobromide water, isolation of a compound by crystallization, and staining of thin-film chromatography plates with  $\text{KMnO}_4$ .

As an option, the model reaction can also be used as microscale experiment in high schools with high-performance learning groups preparing for the A-levels.

## Conflict of Interest

The authors declare no conflict of interest.



## List of Abbreviations

HAT H-atom-transfer  
 ISC inter system crossing  
 MEK methyl ethyl ketone  
 TLC thin layer chromatography

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## Supporting Information

### Analytics

**NMR-spectra** were recorded on Bruker DRX 500 (500 MHz), Avance III (300 MHz) or Avance II (300 MHz) spectrometers in the solvents indicated. Chemical shifts ( $\delta$ ) are reported in ppm relative to TMS. Coupling constants ( $J$ ) are given in Hz.  $^{13}\text{C}$  spectra were recorded in  $\{^1\text{H}\}$ -decoupled manner. Signals were assigned using  $^1\text{H}$ ,  $^{13}\text{C}$ , HSQC, DEPT, HMBC, COSY and NOESY experiments.

**Mass spectra** were measured using the following devices: MS-EI: MAT 95 (Finnigan), MS-APCI and MS-ESI: Impact II (Bruker Daltonik)

**IR spectra** were recorded on Nexus FT-IR (Thermo Nicolet) or Spectrum-Two-FTIR-ATR (PerkinElmer) at ambient temperature. Wavenumbers ( $\tilde{\nu}$ ) are given in  $\text{cm}^{-1}$ .

**Crystal structure determination** was conducted using an AXS Mach3 (Bruker) device. Microscopy for single crystal identification was done using a VHX digital microscope (Keyence), equipped with a VH-Z100R-lens.

### Materials

Unless otherwise noted, materials obtained from commercial suppliers were used as received without further purification.

acetonitrile ( $\geq 99.9\%$ , $\text{H}_2\text{O} \leq 0.02\%$ , LiChrosolv®, quality for chromatography)	Merck
acetophenone ( $\geq 98\%$ , food grade)	Sigma-Aldrich
argon (99.999%, $\text{H}_2\text{O} < 2$ ppm-mol, $\text{O}_2 < 2$ ppm-mol)	AlphaGaz, Air Liquide
butyrophenone ( $\geq 98.0\%$ , for synthesis)	Merck
cyclohexane (99.5%, for analysis)	Bernd Kraft
1,2-dibenzoylthane ( $>98\%$ )	TCI and Alfa-Aesar
ethanol (99%, Rectapur, denaturated with methyl ethyl ketone, benzoat, 2-prop.)	VWR Chemicals
ethyl acetate (99.9%, Rectapur)	VWR Chemicals
1-phenylcyclobutanol (no purity indicated)	Enamin
TLC-plates (Silica-gel 60 F <sub>254</sub> )	Merck
water (bidist.)	Apparatur of Provalid School
water (Millipore quality - unless stated otherwise the usage of this water is implied.)	Milli-Q-Gerät

### Characterization Data of 1,2-dibenzoylthane

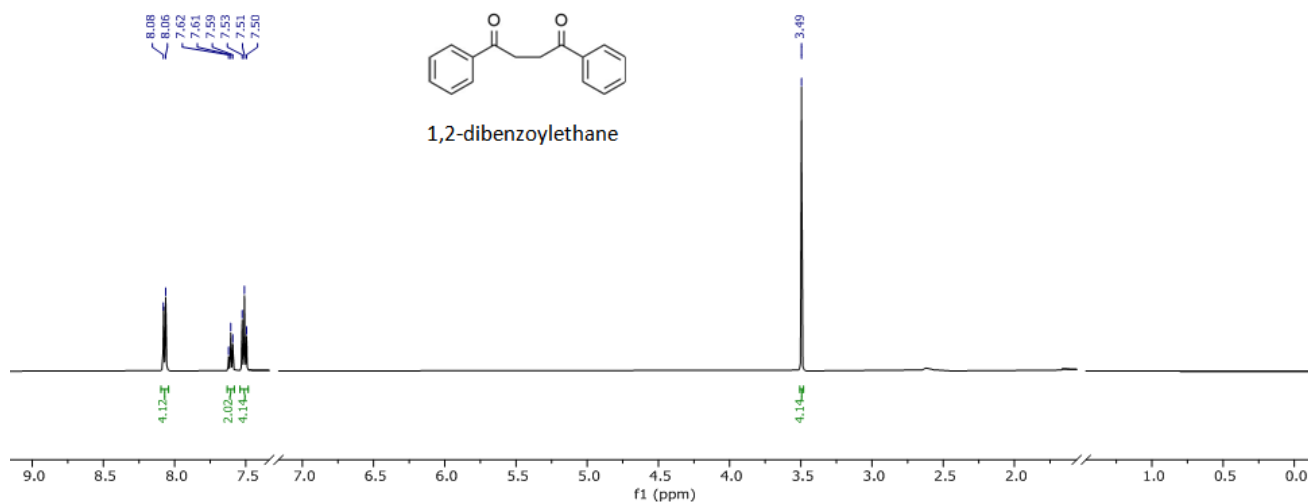
The  $^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR, and IR signals of 1,2-dibenzoylthane obtained have been compared with literature data [57]. Abbreviations used: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br. = broad signal, overl. = overlapping signals, w. = weak signal. NMR spectra or corresponding images were created and processed by using MestReNova ("Mnova", version 12.0.4-22023, Mestrelab Research S. L.) and have been partially reprocessed for better clarity.

Table S1. NMR data for 1,2-dibenzoylthane summarized in tabular form based on Kwan and Huang [58]

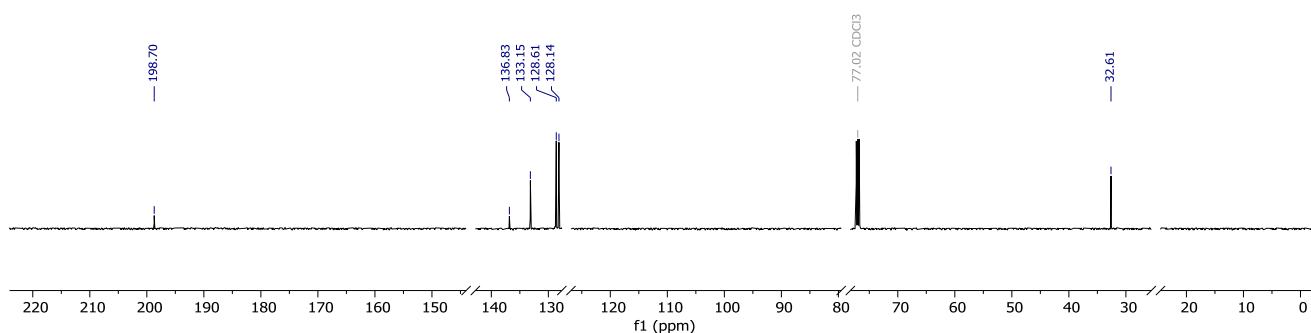
NMR data for 1,2-dibenzoylthane ( $\text{CDCl}_3$ )							
ID	$\delta$ [ppm]		# of Hs	Type	Multiplet Structure		Connectivity Correlations HMBC [ppm]
	$^1\text{H}$	$^{13}\text{C}$ (from HSQC)			Type	Couplings	
1	8.07	128.16	4	CH (Ar, ortho)	d	with phenyl-Hs	128.16, 133.17, 198.68
2	7.60	133.03	2	CH (Ar, para)	t	with phenyl-Hs	128.16, 136.48 (weak)
3	7.51	128.60	4	CH (Ar, meta)	t	with phenyl-Hs	128.72, 136.84, 198.62 (weak)
4	3.49	32.61	4	$\text{CH}_2$	s	-	32.63, 136.88 (weak), 198.70

Quarternary carbon atoms (according to HMBC spectrum): 136.84, 198.69

$\text{CH}_2$ -pairs: 4



**Figure S1.**  $^1\text{H-NMR}$  for 1,2-dibenzoyl ethane (relevant parts), taken from [59]



**Figure S2.**  $^{13}\text{C-NMR}$  for 1,2-dibenzoyl ethane (relevant parts), taken from [59]

MS (ESI+):  $m/z$  calcd for  $\text{C}_{16}\text{H}_{15}\text{O}_2$  [ $M+\text{H}$ ] $^+$ : 239.10720, found: 239.11.

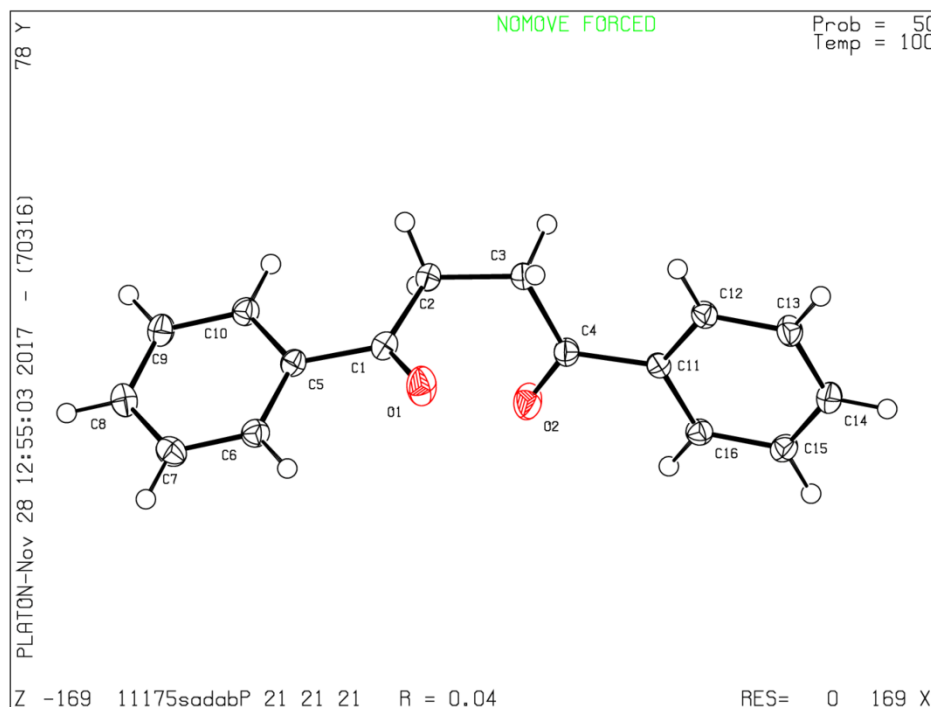
MS (ESI+):  $m/z$  calcd for  $\text{C}_{16}\text{H}_{14}\text{NaO}_2$  [ $M+\text{Na}$ ] $^+$ : 261.08915, found: 261.09.

MS (ESI+):  $m/z$  calcd for  $\text{C}_{32}\text{H}_{28}\text{NaO}_4$  [ $2M+\text{Na}$ ] $^+$ : 499.18853, found: 499.19.

MS (APCI+):  $m/z$  calcd for  $\text{C}_{16}\text{H}_{15}\text{O}_2$  [ $M+\text{H}$ ] $^+$ : 239.10720, found: 239.11.

IR (ATR)  $\text{cm}^{-1}$  (relevant parts): 3490 (overlay), 1676 (Carbonyl), 1593 (Ar-C=C), 736, 693.

Crystal structure of 1,2-dibenzoyl ethane (taken from [59]):



**Figure S3.** Crystal structure of 1,2-dibenzoyl ethane

**Table S2. Bonding lengths [Å] and bonding angles [°] of the 1,2-dibenzoylthane mono-crystal**

O(1)-C(1)	1.2187(19)	O(2)-C(4)	1.2183(19)
C(1)-C(2)	1.514(2)	C(1)-C(5)	1.499(2)
C(2)-C(3)	1.522(2)	C(3)-C(4)	1.517(2)
C(4)-C(11)	1.501(2)	C(5)-C(6)	1.403(2)
C(5)-C(10)	1.400(2)	C(6)-C(7)	1.390(2)
C(7)-C(8)	1.390(2)	C(8)-C(9)	1.389(2)
C(9)-C(10)	1.395(2)	C(11)-C(12)	1.395(2)
C(11)-C(16)	1.401(2)	C(12)-C(13)	1.397(2)
C(13)-C(14)	1.393(2)	C(14)-C(15)	1.394(2)
C(15)-C(16)	1.388(2)		
O(1)-C(1)-C(2)	121.37(14)	O(1)-C(1)-C(5)	120.38(14)
C(5)-C(1)-C(2)	118.25(13)	C(1)-C(2)-C(3)	112.88(13)
C(4)-C(3)-C(2)	112.38(13)	O(2)-C(4)-C(3)	120.97(14)
O(2)-C(4)-C(11)	120.14(14)	C(11)-C(4)-C(3)	118.88(13)
C(6)-C(5)-C(1)	118.44(13)	C(10)-C(5)-C(1)	122.24(13)
C(10)-C(5)-C(6)	119.32(13)	C(7)-C(6)-C(5)	120.07(14)
C(8)-C(7)-C(6)	120.34(15)	C(9)-C(8)-C(7)	120.05(15)
C(8)-C(9)-C(10)	120.10(14)	C(9)-C(10)-C(5)	120.12(14)
C(12)-C(11)-C(4)	122.30(13)	C(12)-C(11)-C(16)	119.41(13)
C(16)-C(11)-C(4)	118.28(13)	C(11)-C(12)-C(13)	120.27(14)
C(14)-C(13)-C(12)	119.89(14)	C(13)-C(14)-C(15)	120.03(14)
C(16)-C(15)-C(14)	120.08(14)	C(15)-C(16)-C(11)	120.31(14)

**Table S3. Crystal structure data of the 1,2-dibenzoylthane mono-crystal**

Identification code	11175	
Empirical formula	C <sub>16</sub> H <sub>14</sub> O <sub>2</sub>	
Color	colorless	
Formula weight	238.27 g mol <sup>-1</sup>	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	ORTHORHOMBIC	
Space group	<b>P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, (no. 19)</b>	
Unit cell dimensions	a = 8.2477(10) Å b = 10.5063(18) Å c = 14.0268(19) Å	α = 90° β = 90° γ = 90°
Volume	1215.5(3) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.302 Mg · m <sup>-3</sup>	
Absorption coefficient	0.085 mm <sup>-1</sup>	
F(000)	504 e	
Crystal size	0.3 x 0.13 x 0.07 mm <sup>3</sup>	
θ range for data collection	2.865 to 33.197°	
Index ranges	-12 ≤ h ≤ 12, -16 ≤ k ≤ 16, -21 ≤ l ≤ 21	
Reflections collected	21747	
Independent reflections	4640 [R <sub>int</sub> = 0.0392]	
Reflections with I > 2σ(I)	3812	
Completeness to θ = 25.242°	99.7%	
Absorption correction	Gaussian	
Max. and min. transmission	0.99 and 0.98	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	4640 / 0 / 163	
Goodness-of-fit on F <sup>2</sup>	1.042	
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0426	wR <sup>2</sup> = 0.0994
R indices (all data)	R <sub>1</sub> = 0.0592	wR <sup>2</sup> = 0.1094
Absolute structure parameter	<b>0.2(4)</b>	
Largest diff. peak and hole	0.3 and -0.2 e · Å <sup>-3</sup>	

