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Photodecarbonylation of Ketodiacids as Ammonium Salts: Efficient Formation of C−C Bonds Between Adjacent Quaternary Centers in the Crystalline State

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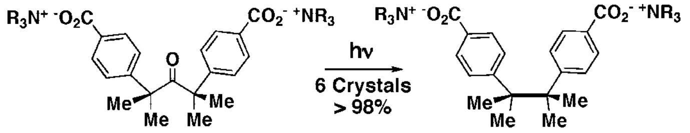

Here we report the crystallization and solid photochemistry of six quaternary ammonium salts of 2,4-di-*p*-carboxyphenyl-2,4-dimethyl pentanone. While salt formation resulted in solids with different melting temperatures and crystallinities, photochemical excitation in the solid state resulted in the chemoselective formation of a single product arising from the homolytic loss of CO followed by combination of the intermediate radical pair. Photochemical experiments in solution led to the product mixtures formed by combination and disproportionation of the corresponding free radical intermediates. The crystallinity of all salts was documented by DSC, ^{13}C CP-MAS NMR, and XRPD.

Introduction

Along with the formation of cocrystals,[1] salt formation is one of the most practical and efficient methods for improving the chemical and physical properties of many active pharmaceutical ingredients (APIs) without changing the structure of the drug candidate.[2,3] Salts can enhance bioavailability by improving aqueous solubility[4,5] and lengthen shelf stability by increasing resistance to thermal degradation.[6] Along with these advantages, the recent advances in pharmaceutical development, such as high-throughput crystallization,[7] have made salt formulations of APIs commonplace. Enhanced physical properties such as high melting temperatures and a robust crystal lattice can also provide an advantage for organic photochemical reactions carried out in the solid state.[8] Similar to reactions in zeolites, organic reactions in the solid state are influenced by their confined space and therefore may lead to cleaner reactions.[9] An example of a chemical reaction that is much more efficient in crystals than in solution or in amorphous solids is the photoinduced decarbonylation of substituted dialkyl ketones.[10,11]

The solid-state photodecarbonylation of ketones is particularly valuable because it offers a general and effective strategy for the formation of all-carbon adjacent quaternary centers,[10−12] which remains a formidable task in organic synthesis.[13,14] The transformation relies on (1) the use of known strategies for the synthesis of ketones with substituents at the two α-positions

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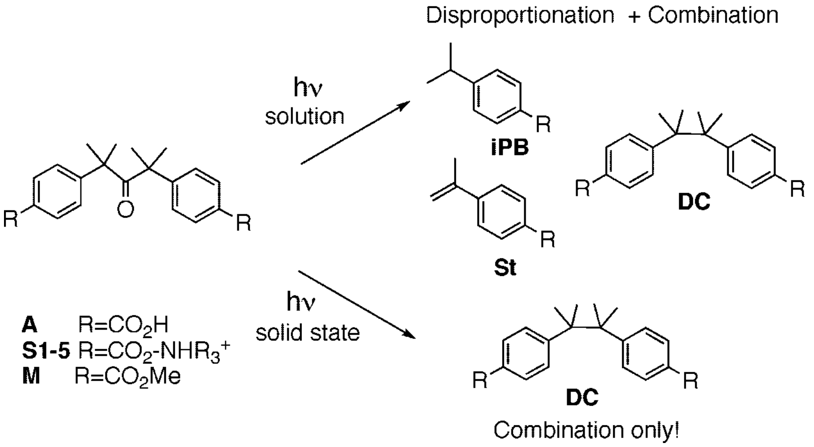
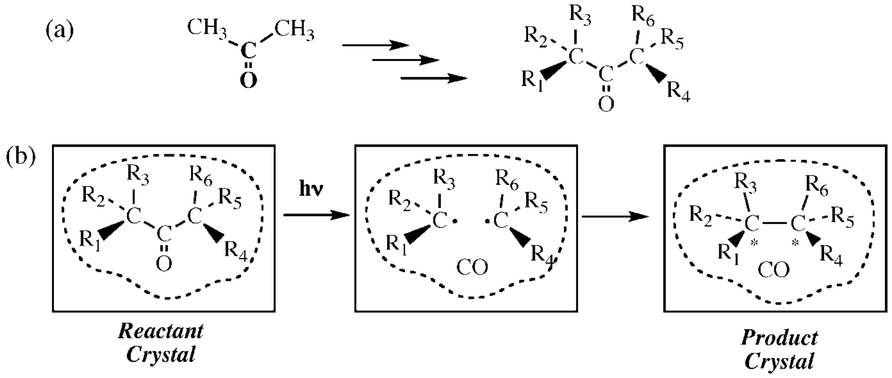


FIGURE 1. Photodecarbonylation of *para*-substituted dicumyl ketones **1** yielding disproportionation and combination products in solution (top) and only the combination product in the solid state (bottom).

SCHEME 1



(Scheme 1a), (2) the intrinsic reactivity of substituted ketones to sequential cleavage of the two α-bonds in their singlet and triplet excited states,[15,16] (3) the configurational stability of the radical intermediates in the crystal lattice (Scheme 2b),[17] (4) the formation of the desired σ bond between the two radical centers, and (5) the potential of scaling up the reaction by taking advantage of nanocrystalline suspensions.[18]

Although the reaction has been used recently as a green chemistry method for the synthesis of natural products,[19,20] it is limited to ketones with a relatively high melting point. The purpose of this study was to determine whether salt formation is a viable strategy to expand the generality of the reaction to compounds with low melting temperatures that have suitable acidity or basicity. Since ionic crystals have higher melting points and are less likely to melt during the photochemical transformation, they should help ensure that the reaction occurs in the solid state. With that in mind, we decided to explore a set of quaternary ammonium ion derivatives of 2,4-di-*p*-carboxyphenyl-2,4-dimethyl pentanone **A** (R = $-CO_2^-NHR_3^+$, Figure 1). We selected a di-*p*-dicarboxylic acid derivative of dicumyl ketone (R = H) as a simple model system because dicumyl ketones are known to react with high efficiency in solution and in the solid state.[21]

Here we report the formation, characterization, and photochemical reactivity of five quaternary ammonium salts, **S1**−**S5** prepared with five different amines. The amines selected for the study include structures with size and symmetry that are likely to form crystalline salts.[22] On the basis of their expected basicity, we decided to include aliphatic amines that are primary and secondary, such a tetradecyl amine **1**, diisopropyl amine **2**, piperidine **3**, and (±)-1-naphthylethylamine **4** (Figure 2). Knowing that the pK_a of the diacid is ca. 4.2,[23] one may expect full proton transfer from the diacid to all of those amines. The pK_a values of the corresponding ammonium salts are 10.64 for **1**, 11.05 for **2**, 11.22 for **3**,[24] and ca. 9.3 for **4** (estimated from the corresponding benzylic analog). Samples of 4-*N*,*N*-dimethylaminopyridine (DMAP) **5** were included as an example of potential proton transfer to the pyridine nitrogen, which is known to form a pyridinium ion with a pK_a = 9.2.[25]

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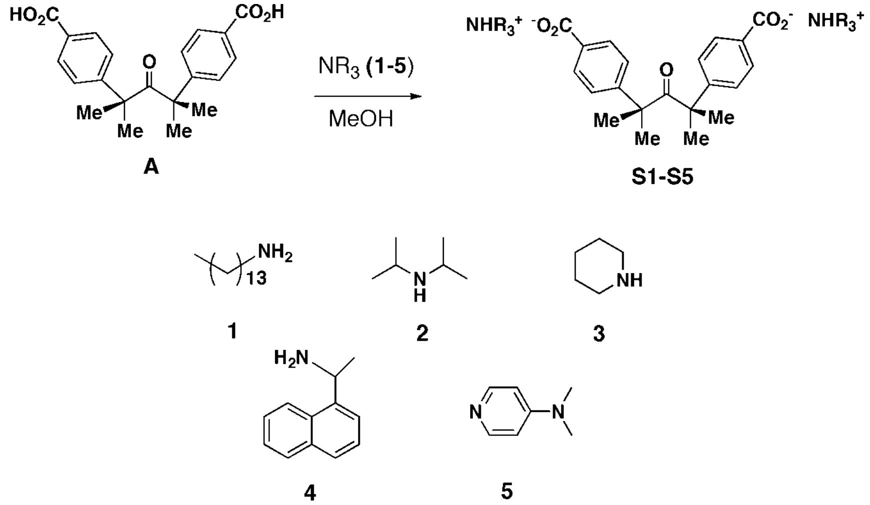

FIGURE 2. Formation of salts **S1**−**S5** in methanol using amines **1**−**5**.

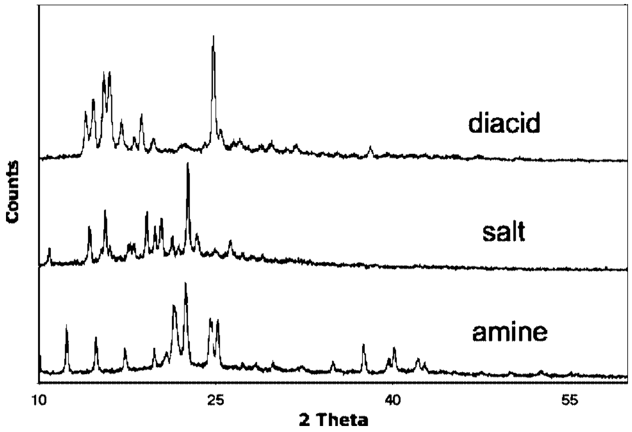

FIGURE 3. XRPD of tetradecylamine **1**, salt **S1**, and bis-benzoic acid **A**.

Results and Discussion

Formation and Characterization of Quaternary Ammonium Salts. We expected amines to modify and improve the physicochemical properties of photoreactive carboxylic acids as a result of the simplicity of salt formation and removal and the possibility of recycling the amine for subsequent reactions. Each salt was prepared as illustrated in Figure 3 by dissolving 2 equiv of amines **1**−**5** and 1 equiv of bis-benzoic acid **A** in methanol.

The resulting solids were characterized by FT-IR, ^{1}H NMR, and ^{13}C NMR by cross polarization and magic angle spinning (CP-MAS) after evaporation of the solvent. Integration of the ^{1}H NMR was used to verify that the bis-benzoate and the ammonium ion were indeed in a 1:2 ratio. The simplest and most useful characterization method was FT-IR. The characteristic carboxylic acid carbonyl absorption at 1685 cm^{-1} is replaced by two new peaks that occur at 1600−1500 and 1450−1380 cm^{-1}, respectively. The protonated amine presents the broad absorption band characteristic of the ammonium ion around 3000 cm^{-1}. Analysis by ^{13}C CPMAS NMR showed that the carboxylic acid carbonyl appears at 168 ppm and that it shifts downfield to 172 ppm once the salt has formed.

X-ray powder diffraction was used also to distinguish between the salt and its components. Figure 3 shows the powder pattern for the bis(tetradecylammonium) salt **S1** and the corresponding tetradecylamine **1** and bis-benzoic acid **A**. As is apparent in the figure, all three solids have peaks at different positions in the powder pattern. The powder pattern of the salt contains new peaks, which do not appear in either the amine or the bis-benzoic acid. The appearance of new peaks confirms that the salt is indeed a new compound, while the lack of signals from the components indicates the purity of the resulting solid phase.

TABLE 1. Melting Point and CPMAS ^{13}C NMR Data for Salts S1−S5

salt	melting point (°C)	DSC T_m (°C)	^{13}C CPMAS line width of COO$^-$ (Hz)	^{13}C CPMAS line Ar−C peaks
S1	185	184 (s)	49	sharp
S2	275−290	282−293 (vb)	230	very broad
S3	220−240[a]	*b*	85	sharp
S4	204, 228	207, 243 (2 s)	230	broad, overlapping
S5	297	303 (s)	78	sharp

[a] S3 decomposes upon melting. [b] No observable endothermic process.

TABLE 2. Product Distribution after 1 h of Photolysis[a]

	solid state products			solution (MeOH) products		
	disp	comb	sm	disp	comb	sm
A	0	33	67	81	12	7
M	0	42	58	65	16	18
S1	0	51	49	62	15	23
S2	0	14	86	13	21	67
S3	0	10	90	19	21	60
S4	0	15	85	23	9	68
S5	0	11	89	20	11	69

[a] Product distribution analyzed by gas chromatography of the methyl esters generated by reaction with TMS−diazomethane. Experiments were carried out in triplicate. disp = disproportionation, comb = combination, sm = starting material.

To establish the crystallinity of the various salts, we determined their melting points by visual observation and by differential scanning calorimetry (DSC). The results of these determinations along with the ^{13}C CPMAS NMR measured line width of the carboxylate carbonyl and the appearance of the aromatic signals are collected in Table 1. A relatively good match was obtained between visual onset of melting and DSC, with **S4** clearly showing two transitions that suggest the formation of the two diastereomeric salts with 1-napthylethyamine. The decomposition of **S3** was observed upon melting, which was consistent with the lack of an observable

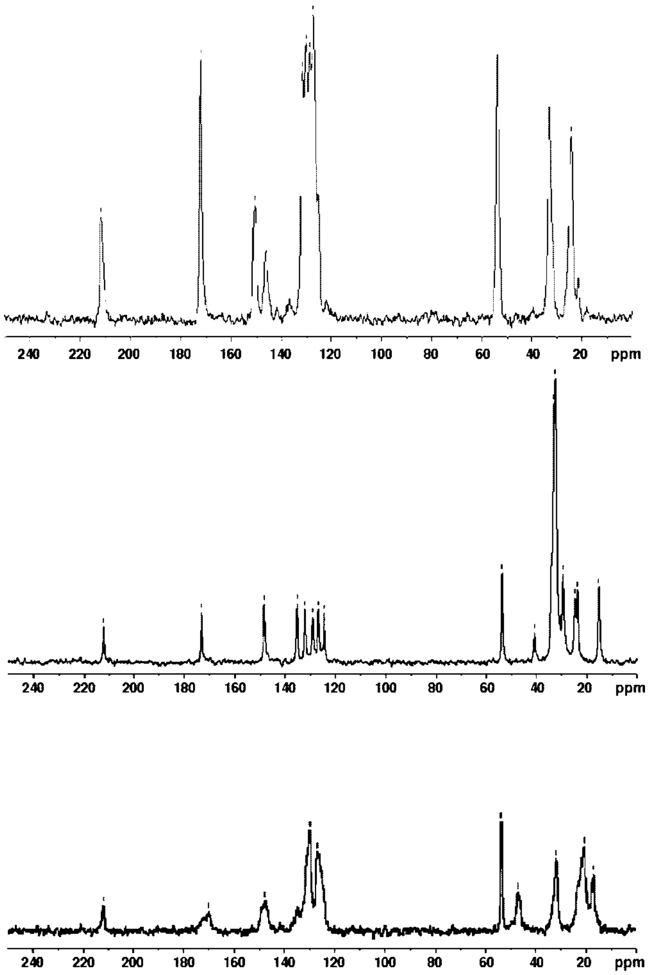

FIGURE 4. ^{13}C CPMAS NMR of bis-benzoic acid **A** (top), tetradecyl ammonium salt **S1** (middle), and diispropyl ammonium salt **S2** (bottom). The parameters used to acquire the spectra on the 300 MHz NMR were delay time = 10 s, contact time = 10 ms, and ns = 256. Samples were spun at the magic angle at a frequency of 10 KHz, and there are no observable spinning side bands in the spectra.

endothermic process in the DSC trace. A correlation was observed between the sharpness of the melting transitions and the line widths of the ^{13}C CPMAS NMR spectra, suggesting sample heterogeneity as a result of formation of crystal mixtures or disordered crystal phases.

Clearly distinguishable in all of the ^{13}C CPMAS NMR spectra were the signals of the ketone and carboxylate carbonyl in the region of 210 and 170 ppm, respectively (e.g., Figure 4).[26] The dispersion and resolution of the aromatic signals constitutes a potential fingerprint for each of the salts. Signals corresponding to quaternary carbons appeared in the vicinity of 53 ppm, and the signals corresponding to the methyl groups (at ca. 33 and 24 ppm in the diacid) tend to overlap with signals of the quaternary ammonium component. As indicated before, a comparison of the ^{13}C CPMAS NMR of bis-benzoic acid **A** and salts **S1** and **S2** in Figure 4 shows that the peaks of the aromatic carbons of the bis-benzoate **A** and **S1** are significantly sharper that those of **S2**, suggesting that the structure of the latter may be more heterogeneous than those of the other two. Similarly, the ^{13}C CPMAS NMR of **S4** had broad peaks that resulted in strong overlap among the aromatic carbons. Interestingly, the ^{13}C CPMAS NMR of salt **S3** showed no peaks corresponding to the amine at room temperature, despite the fact that the **A**:**S3** = 2:1 stoichiometry could be confirmed in solution by ^{1}H NMR. This observation may be caused by ring flipping in a time scale corresponding to signal coalescence, which would make the piperidine carbon peaks broaden and disappear in the baseline. To test this theory, the ^{13}C CPMAS NMR was repeated at −100 °C to slow the ring flipping. In support of this interpretation, the low temperature spectrum revealed the presence of the piperidine carbons with a new peak at 43.0 ppm for the carbons α to the nitrogen and an increase in the peak intensity at 22.5 ppm, which accounts for the presence of the other three methylenes.

Photochemical Experiments. The results of photolysis carried out for 1 h are listed in Table 1 as percentage yields of combination and disproportionation products and are a qualitative measure of the relative quantum yields for the different salts in solution and in the solid state. It should be pointed out that all solid and solution samples reacted to completion when enough time was allowed, which was usually 5 or 6 h. The most remarkable aspect of the photolysis experiments is the fact that all solid-state photolyses provided the combination product exclusively regardless of the ammonium (pyridinium) ion, its pK_a, or the crystallinity of the corresponding salt. Whereas the extent of reaction of the free diacid and diester are significantly smaller in crystals than in MeOH solution, the extent of reaction for salts **S1**−**S5** is comparable in the two media. The most reactive of the five ionic crystals after 1 h was the one formed with hexadecyl amine (**S1**, 51% convesion), and the least reactive was the one formed with piperidine (**S4**, 10% conversion).

The chemoselectivity of the reaction in solution in terms of the relative yields of combination and disproportionation products varied as a function of starting material. While irradiation of the diacid, methyl diester, **S1**, and **S4** preferentially gave the disproportionation products, **S2** and **S5** favored radical combination and **S3** gave essentially the same amount of the two products. While no obvious trend arises from the small set of structures analyzed, we speculate that differences in selectivity as a function of the counterion are probably due to the effects of ion pairing on the rates of the radical reactions.

Conclusions

With this study we have been able to establish that the use of quaternary ammonium salts is a viable experimental strategy to modify the physical properties of ketones bearing carboxylic acid substituents without adversely affecting their solid-state photodecarbonylation reaction. The solid-state reaction is tolerant of several counterions, yielding exclusively the desired radical−radical combination product, while reactions in solution yielded mixtures of disproportionation and combination products. A simple strategy to make highly congested C−C bonds in a solvent-free transformation, the simple recovery of the amine by deprotonation of the ammonium ion and the potential use of sunlight (UV-A and UV-B) make the reaction very appealing from a green chemistry perspective. The results of this study also suggest that salt formation will be a valuable strategy to carry out solid-state photochemical reactions with substrates that are liquid at ambient temperature.

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(26) While the resonance at 210 ppm for the ketone seems uncharacteristically downfield, such chemical shift has precedence in literature See, for example: Auksi, H.; Gosbee, J. A.; Langford, G. E.; MacLachlan, F. N. *Org. Magn. Reson.* **1980**, *14*, 153–154.

Experimental Section

Solution and solid-state photolysis experiments were conducted for each salt. For solution experiments, each salt (5 mg) was dissolved in 5 mL of deoxygenated 50% methanol/50% water. For the solid state, the salts were sandwiched between two pyrex slides and placed in the photolysis chamber approximately 6 cm away from the lamp. After 1 h of exposure to the output of a medium pressure Hg Hannovia lamp, the reaction mixtures were acidified with 1 M HCl and the organic photoproducts and starting material extracted with ethyl acetate. The resulting mixture was dissolved in dry methanol and treated with an excess of 1.0 M Trimethylsilyldiazomethane in ether to produce the methyl esters, which were then analyzed by GC and ^{1}H NMR for conversion. The methyl ester analogue of bis-benzoic acid **A** was also photolyzed as a control.

Synthesis of 2,4-Di-*p*-carboxyphenyl-2,4-dimethyl-3-pentanone A. Periodic acid (360 mg, 1.6 mmol, 5.2 mmol) was dissolved in acetonitrile (50 mL) by vigorous stirring.[27] Then CrO_3 (12 mg, 0.119 mmol, 50 mol%) was dissolved into solution. 2,4-Di-*p*-tolyl-2,4-dimethyl-1,3-pentanone (prepared from a known literature synthesis)[13] (90 mg, 0.306 mmol, 1 equiv) was then added, and the reaction mixture was allowed to stir for 2 h. The solvent was removed in vacuo, and the reaction residue was then washed with water. The product was extracted with ethyl acetate, and the organic layer was washed with brine and dried with MgSO4. The product was obtained in quantitative yield as a white powder after evaporation of the solvent. Mp 305 °C. ^{1}H NMR (500 MHz, MeOD) δ 1.36 (12H, s), 7.33 (4H, d, $J = 8.5$ Hz), 7.94 (4H, d, $J = 8.5$ Hz) (acid protons were not observed in this solvent). ^{13}C NMR (125 MHz, MeOD) δ 26.8, 125.4, 125.6, 128.9, 129.3, 149.1, 168.2, 212.0. HATR-IR (cm^{-1}) 2975.92 (broad), 1680.74, 1608.42. HR-EIMS *m/z* calcd for $C_{21}H_{22}O_5Na$ [M + Na] 377.1359, found 377.1352.

Salts.

Tetradecan-1-aminium 4,4′-(2,4-Bis(carboxyphenyl)-2,4-dimethyl-3-pentanone) (S1, Tetradecyl Salt). Mp 185 °C. ^{1}H NMR (500 MHz, CD_3OD) δ 1.23 (12H, s), 1.27 (48H, broad s), 1.60 (6H, s), 2.84 (8H, t, $J = 7.5$ Hz), 7.23 (4H, d, $J = 8.5$ Hz), 7.87 (4H, d, $J = 8.5$ Hz). ^{13}C NMR (125 MHz, CD_3OD) δ 12.88, 22.19, 25.94, 26.84, 27.23, 28.70, 28.93, 28.97, 29.11, 29.21, 29.25, 31.53, 39.26, 52.7, 124.73, 129.01, 135.74, 146.50, 173.56, 212.52. HATR-IR (cm^{-1}): 2920, 2850, 2168, 1685, 1627, 1607, 1582, 1509, 1468, 1384.

Diisopropylammonium 4,4′(2,4-Bis(carboxyphenyl)-2,4-dimethyl-3-pentanone) (S2, DIPA Salt). Mp 275−290 °C. ^{1}H NMR (500 MHz, CD_3OD) δ 1.30 (12H, s), 1.34 (24H, d, $J = 6.5$ Hz), 3.51 (4H, m), 7.29 (4H, d, $J = 8.5$ Hz), 7.93 (4H, d, $J = 8.5$ Hz). ^{13}C NMR (125 MHz, CD_3OD) δ 17.8, 26.8, 26.9, 52.8, 125.1, 129.2, 147.6, 171.3, 212.4. HATR-IR (cm^{-1}): 3379, 2977, 2869, 2747, 2513, 1683, 1607, 1587, 1542, 1501, 1463, 1380, 1234.

Piperidinium 4,4,′-(2,4-Bis(carboxyphenyl)-2,4-dimethyl-3-pentanone) (S3, Piperidinium Salt). Mp 220−240 °C. ^{1}H NMR (500 MHz, CD_3OD) δ 1.29 (12H, s), 1.67 (4H, broad), 1.74 (8H, broad s), 3.06 (8H, broad s), 7.23 (4H, d, $J = 8.3$ Hz), 7.86 (4H, d, $J = 8.3$ Hz). ^{13}C NMR (125 MHz, CD_3OD) δ 21.8, 22.6, 26.8, 26.9, 44.3, 52.7, 124.7, 128.9, 129.0, 135.8, 146.4, 212.6. HATR-IR (cm^{-1}): 3430, 2948, 2859, 2741, 2537, 2457, 1681, 1623, 1605, 1583, 1534, 1455, 1379.

(*R*)-1-(Naphthalene-1-yl)ethanaminium 4,4′-(2,4-Bis(carboxyphenyl)-2,4-dimethyl-3-pentanone) (S4, (*R*)-Dinapthyethyl Salt). Mp 204 °C, 228 °C ^{1}H NMR (500 MHz, CD_3OD) δ 1.23 (12H, s), 1.68 (6H, d, $J = 6.5$ Hz), 5.27 (2H, q, $J = 6.5$ Hz, 7 Hz), 7.23 (4H, d, $J = 8.5$ Hz), 7.58 (10H, dt), 7.88 (2H, m), 7.93 (2H, d, $J = 8.5$ Hz), 8.11 (4H, d, $J = 8.5$ Hz). ^{13}C NMR (125 MHz, CD_3OD) δ 19.4, 20.6, 26.8, 26.9, 45.9, 52.6, 52.7, 121.7, 121.8, 124.7, 124.8, 125.0, 125.3, 125.6, 126.4, 128.4, 128.5, 128.6, 128.9, 129.0, 130.0, 133.9, 135.6, 136.5, 146.4, 173.4, 212.6. HATR-IR (cm^{-1}): 2971, 2927, 2168, 1684, 1607, 1582, 1515, 1467, 1383, 794.

4-(Dimethylamino)pyridinium 4,4′-(2,4-Bis(carboxyphenyl)-2,4-dimethyl-3-pentanone) (S5, DMAP Salt). Mp 297 °C. ^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ 1.20 (12H, s), 2.910 (12H, s), 6.55 (4H, dd, $J = 6.5$ Hz), 7.24 (4H, d, $J = 8.5$ Hz), 7.81 (4H, d, $J = 8$ Hz), 8.06 (4H, d, $J = 6.5$ Hz). ^{13}C NMR (125 MHz, CD_3OD) 26.8, 26.9, 38.3, 52.8, 106.6, 124.9, 125.3, 128.5, 129.0, 129.1, 134.1, 141.2, 147.1, 156.8, 172.2, 212.5. HATR-IR (cm^{-1}) 2923, 2517 (broad), 1684, 1646, 1604, 1560, 1460, 1385, 1212.

2,4-Di-*p*-carboxyphenyl-2,4-dimethyl-3-pentanone Methyl Ester (M). Mp 179 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.30 (12H, s), 3.92 (6H, s), 7.24 (4H, d), 7.92 (4H, d, $J = 8$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.6, 52.0, 53.3, 125.7, 128.4, 129.6, 149.2, 166.7, 211.9 HATR-IR (cm^{-1}) 2924, 1719, 1681, 1609, 1441, 1271. HR-EIMS *m/z* calcd for $C_{23}H_{26}O_5Na$ [M + Na] 405.1672, found 405.1686.

Photoproducts.

DC Benzoic Acid, 4,4^1-(1,1,2,2-tetramethyl-1,2-ethanediyl)-bis-, Dimethyl Ester.[28] Mp 195 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34 (12H, s), 3.91 (6H, s), 7.08 (4H, d, $J = 8$ Hz), 7.83 (4H, d, $J = 8$ Hz). ^{13}C NMR (125 MHz, C_6D_6) δ 25.7, 43.6, 51.1, 124.5, 128.5, 129.5, 133.2, 166.4. HR-EIMS *m/z* calcd for $C_{22}H_{26}O_4Na$ [M + Na] 377.1723, found 377.1732.

St Benzoic Acid, 4-(1-Methylethenyl)-, Methyl Ester.[29] ^{1}H NMR (500 MHz, C_6D_6) δ 1.96 (3H, s), 3.49 (6H, s), 4.95 (1H, s), 5.26 (1H, s), 6.87 (2H, d, $J = 8$ Hz), 6.97 (4H, d, $J = 8$ Hz). ^{13}C NMR (125 MHz, C_6D_6) δ 23.2, 51.1, 114.1, 128.5, 129.8, 133.4, 140.1, 151.4, 166.4.

iPB Ethyl, 1-[4-(Methoxycarbonyl)phenyl]-1-methyl.[30] ^{1}H NMR (500 MHz, C_6D_6) δ 1.12 (6H, d) 2.52−2.58 (1H, m), 3.50 (3H, s), 7.62 (2H, d, $J = 7$ Hz), 8.12 (2H, d, $J = 7$ Hz). ^{13}C NMR (125 MHz, C_6D_6) δ 24.6, 33.9, 51.1, 125.4, 126.3, 153.7, 166.4.

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Supporting Information Available: Spectroscopic data for all salts and experimental procedures for the photochemical experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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