Stable Radicals During Photodecarbonylations of Trityl-alkyl Ketones Enable Solid State Reactions through Primary and Secondary Radical Centers

Gregory Kuzmanich\textsuperscript{a}, Arunkumar Natarajan\textsuperscript{a,c} Yanhui Shi\textsuperscript{b}, Brian O. Patrick\textsuperscript{b}, John R. Scheffer\textsuperscript{b,*} and Miguel A. Garcia-Garibay\textsuperscript{a,*}

\textsuperscript{a}Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095-1559, USA. Tel: 1 (310) 825 3159  E-mail: mgg@chem.ucla.edu
\textsuperscript{b}Chemistry Department, University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, Canada V6T 1Z1
\textsuperscript{c}Current address, GE Global Research, Niskayuna, NY 12309-1027, USA.

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General Methods: All chemicals were purchased from Sigma-Aldrich Co. Inc. and used without further purification. Anhydrous THF was acquired via distillation from sodium. Silica used for purification was Silica-P flash silica gel (40-62 Å), purchased from SiliCycle Inc. 1H and 13C NMR was acquired on a Bruker Advance AV300, AV400, or DRX500. IR spectra were obtained with a Perkin-Elmer Spectrum instrument equipped with a universal attenuated total reflectance (ATR) accessory. Mass spectra was acquired on an Applied Biosystems Voyager DE-STR-MALDI-TOF. Gas Chromatography data was acquired on a Hewlett-Packard 5890 Series II Gas Chromatography equipped with an HP3396 Series II integrator and HP-5 capillary column of dimension 25 m × 0.2 mm with a film thickness of 0.11 mm. UV-vis spectra were taken on an Ocean Optics USB2000.

Scheme S1. Synthesis of Trityl ketones 1b – f.

1,1,1-triphenyl-2-pentanol (S2b).

Yield 78%; 1H NMR (300 MHz, CDCl3) δ 7.57 (m, 6H), 7.31 (m, 9H), 4.46 (m, 1H), 2.43 (br. s, 1H), 1.54 (m, 2H), 0.93 (t, J = 7.5 Hz, 3H); 13C NMR (75 MHz, CDCl3) δ 147.6, 129.6, 127.6, 126.6, 82.9, 60.8, 39.5, 20.2, 13.7; FTIR (solid, HATR, cm⁻¹): 3054, 2966, 1597, 1493, 1444, 1122, 757, 728, 704; MS (EI): calcd. 316; found 316 (M⁺).

1,1,1-triphenyl-3-methyl-2-butanol (S2c).

Yield 31%; 1H NMR (300 MHz, CDCl3) δ 7.59 (m, 6H), 7.25 (m, 9H), 4.21 (dd, J = 3 Hz, 1H), 2.24 (br. s, 1H), 1.96 (m, 1H), 1.01 (d, J = 7.0, 3H), 0.90 (t, J = 7.0 Hz, 3H); 13C NMR (75 MHz, CDCl3) δ 147.7, 129.7, 128.0, 126.0, 83.2, 59.6, 33.7, 20.7, 17.6; FTIR (solid, HATR, cm⁻¹): 3552, 2961, 2955, 2934, 1594, 1493, 1449, 1444, 1122, 757, 728, 704; MS (EI): calcd. 316; found 244 (triphenylmethyl), 316 (M⁺).

1,1,1-triphenyl-3,3-dimethyl-2-butanol (S2d).

Yield 61%; 1H NMR (300 MHz, CDCl3) δ 7.57 (m, 6H), 7.25 (m, 9H), 5.42(s, 1H), 2.02 (br. s, 1H), 0.69 (s, 9H); 13C NMR (75 MHz, CDCl3) δ 148.3, 141.6, 131.1, 129.5, 128.5, 127.8, 126.7, 126.6, 80.5, 61.6, 43.3; FTIR (solid, HATR, cm⁻¹): 3556, 3060, 2983, 2970, 2934, 1596, 1583, 1494, 1477, 1446, 1398, 1366, 856, 744, 728, 705; MS (EI): calcd. 330; found 243 (triphenylmethyl), 330 (M⁺).
1,1,1,3-tetraphenyl-2-propanol (S2e).
Yield 66%; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.25-7.55 (m, 20H), 5.51 (d, $J$ = 9.6 Hz, 1H), 3.13 (d, $J$ = 9.6, 2H), 1.75 (br. s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 140.3, 130.1, 129.7, 129.3, 128.6, 128.1, 126.5, 126.4, 75.7, 62.6, 40.7; FTIR (solid, HATR, cm$^{-1}$): 3564, 3551, 3056, 2932, 1599, 1494, 1447, 766, 745, 705; MS (EI): calcd. 364; found 243 (triphenylmethyl), 364 (M$^+$).

1,1,1,3-tetraphenyl-3-methyl-2-propanol (S2f).
Yield 56%; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.25-7.55 (m, 20H), 5.78 (d, $J$ = 7.5 Hz, 1H), 3.15 (dd, $J$ = 7.5 and 7.3 Hz, 1H), 2.69 (br. s, 1H), 0.31 (d, $J$ = 7.3 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 140.7, 131.1, 129.6, 129.1, 128.9, 128.1, 126.6, 126.1, 76.1, 63.7, 41.6, 16.7.

General Synthesis of 1b – f.
Following a modified procedure by Seebach,$^1$ to a 100 mL round bottom flask, alcohol S2b – f (1 eq) was added to 30 mL of acetone at 0 °C. To this solution, CrO$_3$ (1.25 eq) dissolved in 2 mL of H$_2$O and 0.5 mL H$_2$SO$_4$ was added over 20 minutes. When the reaction was complete, as monitored by TLC, the solution was filtered through cotton washed with brine and dried over magnesium sulfate. The resulting crystalline solid was further recrystallized from ethanol. All characterization agreed well with reported literature values.

Characterization of 1b – f.

1,1,1-triphenyl-2-pentanone (1b).$^1$
Yield 98%; m.p. 115-116 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.29 (m, 6H), 7.28 (m, 9H), 2.35 (t, $J$ = 7.5 Hz, 2H), 1.38 (m, 2H), 0.70 (t, $J$ = 7.4 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 208.5, 142.4, 130.4, 128.0, 126.7, 73.2, 43.7, 19.2, 13.8; FTIR (solid, HATR, cm$^{-1}$): 3054, 2964, 1711, 1598, 1495, 1445, 1122, 1086, 1059, 1036, 758, 727; MS (EI): calcd. 314; found 243 (triphenylmethyl), 314 (M$^+$); UV-Vis (hexane), $\lambda_{\text{Max}}$ = 300.1 nm, $\varepsilon$ = 336.6 cm$^{-1}$M$^{-1}$.

1,1,1-triphenyl-3-methyl-2-pentanone (1c).$^1$
Yield 98%; m.p. 79-80 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.41 (m, 6H), 7.33 (m, 6H), 7.24 (m, 3H), 3.08 (m, 1H), 0.80 (d, $J$ = 7.0 Hz, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 213.6, 142.5, 130.7, 128.3, 126.9, 74.5, 38.6, 22.1; FTIR (solid, HATR, cm$^{-1}$): 3060, 2974, 1703, 1596, 1493, 1466, 1447, 1442, 1380, 1088, 1052, 1037, 756, 745, 704; MS (EI): calcd. 314; found 243 (triphenylmethyl), 314 (M$^+$); UV-Vis (hexane), $\lambda_{\text{Max}}$ = 305.1 nm, $\varepsilon$ = 404.3 cm$^{-1}$M$^{-1}$.

1,1,1-triphenyl-3,3-dimethyl-2-butane (1d).$^1$
Yield 95%; m.p. 94-95 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.31 (m, 12H), 7.22 (m, 3H), 1.02 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 213.5, 142.3, 131.3, 127.8, 126.7, 74.2, 47.3, 31.1; FTIR (solid, HATR, cm$^{-1}$): 3061, 2982, 2969, 2934, 1687, 1596, 1583, 1494, 1476, 1462, 1446, 3938, 1367, 1087, 1052, 856, 752, 728, 705. MS (EI): calcd. 328; found 243 (triphenylmethyl), 328 (M$^+$); UV-Vis (hexane), $\lambda_{\text{Max}}$ = 309.9 nm, $\varepsilon$ = 967 cm$^{-1}$M$^{-1}$.

1,1,1,3-tetraphenyl-2-propanone (1e).$^2$
Yield 40%; m.p. 115-116 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.32-7.18 (m, 18H), 6.96 (dd, 2H), 3.66 (s, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 205.6, 142.0, 135.3, 130.8, 129.6, 128.4, 128.2, 127.1, 126.7, 73.6, 47.6; FTIR (solid, HATR, cm$^{-1}$): 3067, 3024, 2934, 1712, 1602, 1494, 1449, 1303, 1094, 1033, 1003, 764, 751, 743, 704, 617; MS (EI): calcd. 362; found 243 (triphenylmethyl), 362 (M$^+$); UV-Vis (hexane), $\lambda_{\text{Max}}$ = 305.1 nm, $\varepsilon$ = 330.6 cm$^{-1}$M$^{-1}$.

1,1,1,3-tetraphenyl-3-methyl-2-propanone (1f).
Yield 66%; m.p. 109-110 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.51 (m, 6H), 7.36 (m, 14H), 4.32 (d, $J$ = 6.5 Hz, 1H), 1.32 (d, $J$ = 6.5 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 209.7, 142.7, 131.9, 130.8, 128.2, 128.1, 127.5, 126.8, 126.4, 74.6, 50.4, 24.3; FTIR (solid, HATR, cm$^{-1}$): 3055, 3015, 2924, 2865, 1701, 1597, 1491, 1448, 1370, 1104, 1062, 1043, 1002, 867, 764, 669; HRMS (MALDI-TOF): calcd. 376.1827 (M$^+$), 399.1725 (M + Na$^+$); found 372.9716 (triphenylmethyl + Na$^+$), 399.0543 (M + Na$^+$); UV-Vis (hexane), $\lambda_{\text{Max}}$ = 307.0 nm, $\varepsilon$ = 637.9 cm$^{-1}$M$^{-1}$.
Figure S1. $^1$H NMR spectra of 1b in CDCl$_3$.

Figure S2. $^{13}$C NMR spectra of 1b in CDCl$_3$. 
Figure S3. $^1$H NMR spectra of 1c in CDCl$_3$.

Figure S4. $^{13}$C NMR spectra of 1c in CDCl$_3$. 
Figure S5. $^1$H NMR spectra of 1d in CDCl$_3$.

Figure S6. $^{13}$C NMR spectra of 1d in CDCl$_3$. 
Figure S7. $^1$H NMR spectra of 1e in CDCl$_3$.

Figure S8. $^{13}$C NMR spectra of 1e in CDCl$_3$. 
Figure S9. $^1$H NMR spectra of 1f in CDCl$_3$.

Figure S10. $^{13}$C NMR spectra of 1f in CDCl$_3$. 
Photolysis in Benzene.
Compounds 1a - f were dissolved in benzene (0.1 M) and degassed for 15 minutes with Argon. Samples were then irradiated at 312 nm using a Rayonet photochemical reactor (BLE-8T312). Aliquots were removed every 10 minutes and reaction progress was monitored by gas chromatography. Because the reactions produced numerous products in minor yields, the exact identification of the products was not attempted.

Photolysis of Bulk Crystalline Samples.
Powdered samples (ca. 5 mg) of crystalline material were acquired by crushing large single crystals with two pyrex plates, such that the powder remained on the plates. Plates were then irradiated at room temperature, without a Pyrex filter, at 254 nm (Hanovia 400W mercury-vapor lamp) or 312 nm (in a Rayonet photochemical reactor using 312 nm lamps [BLE-8T312]). Aliquots were removed hourly and reaction progress was monitored by gas chromatography. Moderate quantities of crystals (ca. 30 mgs) were irradiated for extended periods of time and subjected to column chromatography (20:1 hexane:diethyl ether) to isolate the major product.
Characterization of photolyzed products.

Scheme S2.

1,1,1-triphenylbutane (2b).
Yield 100%; m.p. 58-60 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.24 (m, 6H), 7.23 (m, 6H), 7.15 (m, 3H), 2.52 (t, \(J=8.0\) Hz, 2H), 1.05 (m, 2H), 0.90 (t, \(J=7.3\), 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 147.9, 129.4, 127.9, 125.9, 56.9, 43.0, 19.3, 14.9; MS (EI): calcd. 286; found 243 (triphenylmethyl), 286 (M\(^+\)).

1,1,1-triphenyl-i-butane (2c).
Yield 100%; m.p. 92-94 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.37 (m, 6H), 7.27 (m, 6H), 7.14 (m, 3H), 3.59 (m, 1H), 0.83 (d, \(J=6.6\) Hz, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 141.8, 129.7, 128.5, 125.7, 61.7, 30.7, 19.3; MS (EI): calcd. 286; found 243 (triphenylmethyl), 286 (M\(^+\)).

1,1,1,2-tetraphenylethane (2e).
Yield 100%; m.p. 106-108 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.0-7.48 (m, 18H), 6.99 (m, 2H), 3.96 (s, 2H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 146.8, 138.7, 131.3, 130.0, 127.8, 127.5, 126.2, 126.1, 58.7, 46.5; MS (EI): calcd. 334; found 243 (triphenylmethyl), 334 (M\(^+\)).

1,1,1,3-tetraphenyl-3-methyl-2-propane (2f).
Yield 100%; m.p. 119-121 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.34-7.42 (m, 6H), 7.11-7.42 (m, 9H), 6.97-7.09 (m, 3H), 6.65-6.72 (m, 2H), 4.79 (q, \(J=7.5\) Hz, 1H), 1.33 (d, \(J=7.5\) Hz, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 145.4, 143.0, 131.2, 130.8, 127.2, 126.9, 126.1, 125.7, 63.1, 43.6, 19.3. FTIR (solid, HATR, cm\(^{-1}\)): 3059.5, 2992.1, 1595.6, 1490.5, 1445.8, 1193.2, 1087.6, 772.2, 738.7. MS (MALDI-TOF): calcd. 348; found 243 (triphenylmethyl), 371 (M + Na\(^+\)).
Synthesis of Nanocrystalline Suspensions. Samples to be used for actinometry experiments were prepared by injecting a solution of I in acetone (ca. 10 µL of a ca. 1M) into 3 mL of vortexing water (millipore). The resulting suspension (ca. $1 \times 10^{-3}$ M) was sonicated three times at room temperature for 4 min, allowing for 2 min rest between runs.

Quantum Yield Determination for Nanocrystalline Suspension. Relative quantum yield determinations were performed with dicumyl ketone ($\phi = 0.18$) as an internal standard in a Rayonet photochemical reactor using 312 nm lamps (BLE-8T312). Quantum yields were determined with equimolar, optically dense suspensions. Two independent suspensions of actinometer and substrate were independently synthesized. The samples were then combined immediately prior to irradiation in a 50 mL quartz Erlenmeyer flask and irradiated for 10 min. Every 2 minutes, an aliquot was removed (approximately one-twentieth of the suspension). The aliquots were subjected to gas chromatography to determine the extent of reaction.
References


