SUPPORTING INFORMATION

An Ultrafast Carbene-Carbene Isomerization

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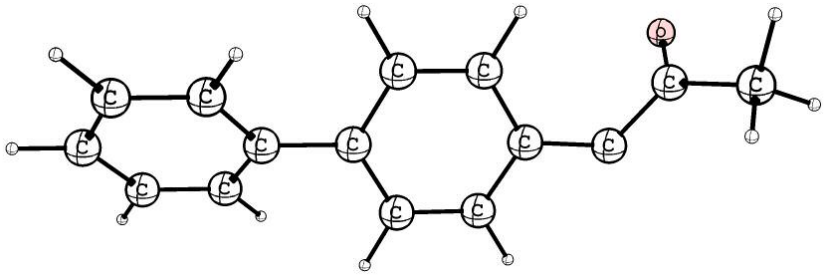
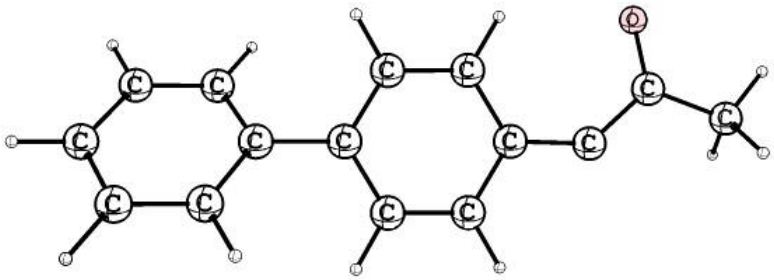


E = -654.116365003 Hartree

λ / nm	*f*	λ / nm	*f*
1012.15	0.0069	247.65	0.0269
454.83	0.0555	246.39	0.0545
347.91	0.5041	245.51	0.0082
331.18	0.0041	241.66	0.0182
328.46	0.0124	237.54	0.0028
318.16	0.0297	235.31	0.0069
315.18	0.0533	230.58	0.0148
284.56	0.0009	228.00	0.0067
269.80	0.0284	225.84	0.0136
255.54	0.1899	224.27	0.0022

Cartesian Coordinates			
C	0.031530	-0.865774	0.361099
C	-0.837080	0.181870	-0.022862
C	-0.273804	1.415263	-0.410346
C	1.099156	1.599222	-0.400960
C	1.983291	0.545969	-0.047636
C	1.403115	-0.697271	0.334708
C	3.380195	0.779609	-0.112968
C	4.396456	-0.164333	0.142075
O	4.630925	-0.394215	1.345755
C	5.262766	-0.699443	-0.979525
C	-2.304718	-0.011572	-0.011951
C	-3.169157	1.043436	0.331674
C	-4.550015	0.860119	0.343252
C	-5.097200	-0.378913	0.003841
C	-4.252036	-1.434994	-0.342738
C	-2.870656	-1.255132	-0.346383
H	-0.389812	-1.807953	0.698366
H	-0.925385	2.222338	-0.730590
H	1.537698	2.550143	-0.686995
H	2.061033	-1.501250	0.650756
H	6.238230	-0.199525	-0.961491
H	4.809247	-0.539413	-1.964264
H	5.432205	-1.769577	-0.819426
H	-2.754093	2.003853	0.622858
H	-5.199440	1.684623	0.624189
H	-6.174318	-0.520734	0.010237
H	-4.669254	-2.400190	-0.616318
H	-2.224572	-2.076929	-0.641044

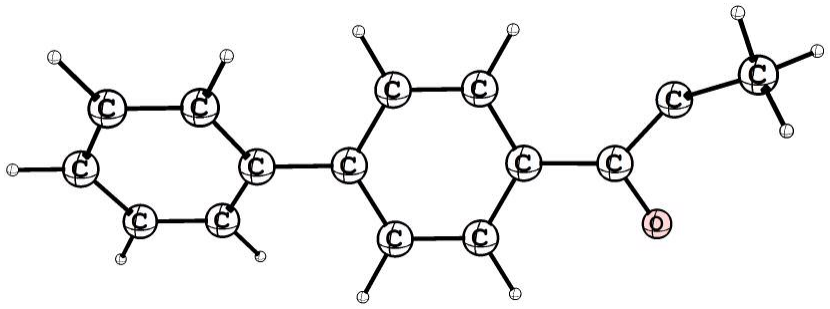
Table S2. TD-B3LYP/6-311G+(d,p)//B3LYP/6-31G(d) calculations of triplet $BpCCOCH_3$ and its Cartesian coordinates



E = -654.118450251 Hartree

λ / nm	*f*	λ / nm	*f*	Cartesian Coordinates			
				C	-0.046830	-0.957150	-0.224242
588.50	0.0001	309.48	0.0001	C	-0.886852	0.146601	0.038099
				C	-0.274046	1.383970	0.330043
				C	1.102551	1.515382	0.359780
476.72	0.0407	298.85	0.2653	C	1.952667	0.405382	0.094720
				C	1.331975	-0.845505	-0.200953
				C	3.348223	0.569110	0.130242
422.98	0.0025	295.21	0.0054	C	4.505881	-0.262306	-0.070889
				O	4.364472	-1.460414	-0.355716
				C	5.874352	0.369777	0.074499
393.07	0.0326	287.60	0.0044	C	-2.360396	0.012144	0.007431
				C	-3.174088	1.066762	-0.445455
				C	-4.561284	0.940371	-0.475252
374.04	0.0011	286.59	0.0003	C	-5.169280	-0.242745	-0.050662
				C	-4.376055	-1.298617	0.402780
				C	-2.988663	-1.173440	0.430457
364.97	0.0006	275.55	0.0639	H	-0.492240	-1.914246	-0.480478
				H	-0.894932	2.243639	0.564558
				H	1.553963	2.474042	0.597701
358.97	0.4700	266.80	0.0000	H	1.967674	-1.696262	-0.414882
				H	6.646337	-0.383172	-0.100695
				H	5.996143	0.795226	1.077992
342.06	0.0276	263.91	0.0038	H	5.994610	1.192468	-0.640833
				H	-2.712436	1.981742	-0.805537
				H	-5.168285	1.765167	-0.839054
318.60	0.0000	261.91	0.0007	H	-6.251126	-0.341047	-0.073049
				H	-4.839030	-2.220632	0.744236
317.95	0.0069	260.03	0.0001	H	-2.385387	-1.992015	0.812184

Table S3. TD-B3LYP/6-311G+(d,p)//B3LYP/6-31G(d) calculations of singlet $BpCOCCH_3$ and its Cartesian coordinates



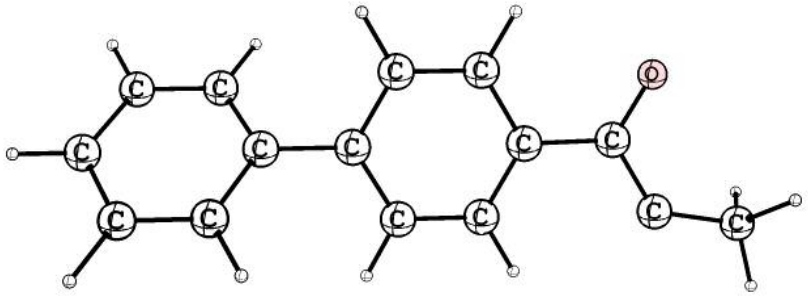
E = -654.103969977 Hartree

λ / nm	*f*	λ / nm	*f*
595.48	0.0008	260.20	0.0221
368.83	0.0919	250.17	0.0134
334.25	0.0837	249.78	0.0101
291.59	0.4980	240.67	0.0342
284.99	0.0233	233.55	0.0048
277.67	0.0119	231.76	0.0090
276.43	0.0212	227.13	0.0880
275.00	0.0105	226.38	0.0637
268.17	0.0068	219.75	0.0041
261.39	0.0033	216.89	0.0091

Cartesian Coordinates

C	0.023506	-1.004176	-0.505389
C	0.804904	0.071075	-0.041391
C	0.144343	1.241748	0.376449
C	-1.241300	1.337356	0.332681
C	-2.006531	0.256515	-0.124268
C	-1.362661	-0.914987	-0.545350
C	-3.469739	0.358706	-0.123982
C	-4.464754	-0.533688	-0.501276
C	-5.373809	-1.215996	0.433068
C	2.285053	-0.027213	0.002212
C	3.091715	1.081916	-0.305322
C	4.481812	0.988542	-0.265557
C	5.096086	-0.215409	0.084181
C	4.307908	-1.325545	0.393167
C	2.917875	-1.232531	0.351751
H	0.513795	-1.903427	-0.866251
H	0.726646	2.073688	0.761444
H	-1.751172	2.238071	0.661357
H	-1.952016	-1.743403	-0.931589
H	-6.375116	-1.382881	0.021446
H	-5.443763	-0.738272	1.421174
H	-4.928368	-2.217679	0.579374
H	2.625025	2.016041	-0.604974
H	5.086111	1.856244	-0.516419
H	6.179760	-0.287876	0.115608
H	4.775784	-2.265068	0.675032
H	2.314263	-2.095213	0.619691
O	-4.147175	1.406489	0.087282

Table S4. TD-B3LYP/6-311G+(d,p)//B3LYP/6-31G(d) calculations of triplet $BpCOCCH_3$ and its Cartesian coordinates



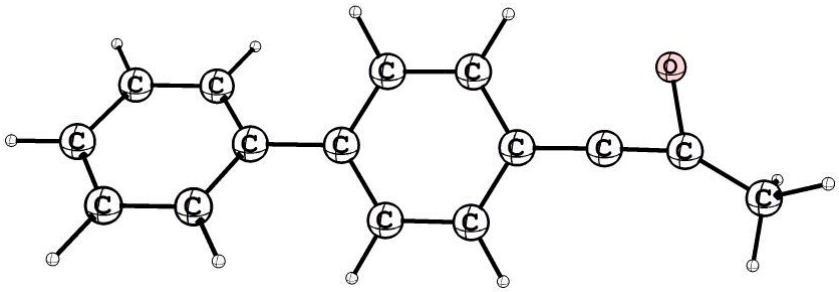
E = -654.110171166 Hartree

λ / nm	*f*	λ / nm	*f*
586.73	0.0001	315.97	0.0001
493.34	0.0648	293.52	0.0619
388.13	0.0148	292.91	0.0401
386.90	0.0082	289.97	0.0053
382.97	0.0357	285.17	0.0021
378.29	0.0558	281.45	0.0032
347.83	0.0004	274.76	0.0011
333.43	0.0044	273.74	0.0000
321.02	0.0021	268.48	0.3111
320.57	0.0774	268.13	0.0043

Cartesian Coordinates

C	0.039120	-1.078427	0.259093
C	0.831699	0.050863	-0.014503
C	0.177656	1.262964	-0.306445
C	-1.208998	1.343862	-0.323648
C	-1.989984	0.212296	-0.049813
C	-1.349179	-0.999709	0.241219
C	-3.472056	0.326545	-0.075759
C	-4.287675	-0.819292	0.201137
C	-5.749288	-0.969494	0.243590
C	2.313176	-0.032346	0.004660
C	3.089243	1.031468	0.496402
C	4.480749	0.953983	0.515292
C	5.128007	-0.188673	0.041400
C	4.370814	-1.253326	-0.450876
C	2.979239	-1.176157	-0.468361
H	0.518834	-2.018846	0.514372
H	0.768137	2.142167	-0.547771
H	-1.711453	2.277288	-0.557196
H	-1.946600	-1.880308	0.463339
H	-6.042365	-2.015104	0.391281
H	-6.207612	-0.609448	-0.689651
H	-6.181993	-0.376243	1.063662
H	2.595368	1.914628	0.891803
H	5.060058	1.785187	0.908575
H	6.212846	-0.248799	0.055309
H	4.864639	-2.143874	-0.830689
H	2.401240	-1.999464	-0.878719
O	-4.055781	1.398184	-0.333080

Table S5. TD-B3LYP/6-311G+(d,p)//B3LYP/6-31G(d) calculations of oxirene OX and its Cartesian coordinates



E = -654.102814669 Hartree

λ / nm	*f*	λ / nm	*f*
374.97	0.6307	242.25	0.0004
368.51	0.0039	238.68	0.0009
319.78	0.0234	228.88	0.0170
294.55	0.0040	225.87	0.0090
282.35	0.0009	222.92	0.0031
279.32	0.0157	219.99	0.0059
265.85	0.2232	219.27	0.0265
258.31	0.0000	218.43	0.0019
255.96	0.0065	212.86	0.0083
245.77	0.0474	212.53	0.0337

Cartesian Coordinates

O	4.402068	-1.249907	-0.318858
C	3.348109	0.028618	0.007060
C	4.641314	0.054709	0.012935
C	1.939982	0.032894	0.009077
C	5.915153	0.773190	0.195947
C	1.213414	1.205985	0.320995
C	-0.173030	1.191583	0.316243
C	-0.899967	0.025730	0.006754
C	-0.166573	-1.134424	-0.300779
C	1.221440	-1.142277	-0.303115
C	-2.382181	0.022992	0.005928
C	-3.104737	-1.101498	0.443164
C	-4.498441	-1.104952	0.441161
C	-5.204996	0.017159	0.004094
C	-4.502650	1.142197	-0.432117
C	-3.108915	1.144468	-0.432137
H	5.742481	1.820011	0.457907
H	6.502197	0.292961	0.988395
H	6.505872	0.722640	-0.726883
H	1.745113	2.118352	0.575154
H	-0.708196	2.097694	0.585709
H	-0.696143	-2.043738	-0.570621
H	1.773383	-2.041711	-0.552449
H	-2.567358	-1.970043	0.813588
H	-5.033756	-1.983660	0.791542
H	-6.291601	0.014840	0.003325
H	-5.041224	2.018517	-0.783552
H	-2.574845	2.015160	-0.802508

Table S6. B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) calculations of relative energies (kcal·mol^{-1}) for ^{1}BpCCOMe, ^{1}BpCOCMe and the corresponding oxirene OX in the gas phase.[a]

	^{1}BpCCOMe	OX	^{1}BpCOCMe
$H_{(0\ K)}$	0	8.10	7.44
$H_{(298\ K)}$	0	8.27	7.39
$G_{(298\ K)}$	0	8.16	7.89

a. The zero point energy (ZPE) for the gas phase calculations is corrected by a factor of 0.9806.

Table S7. B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) calculations of relative energies (kcal·mol^{-1}) for syn and anti conformers for $BpCN_2COMe$, $BpCOCN_2Me$ in the gas phase.[a]

	$BpCN_2COMe$		$BpCOCN_2Me$	
	syn	anti	syn	anti
$H_{(0\ K)}$	0.97	0	1.56	0
$H_{(298\ K)}$	0.97	0	1.56	0
$G_{(298\ K)}$	1.15	0	1.89	0
Percentage	12.5%	87.5%	3.9%	96.1%

a. The zero point energy (ZPE) for the gas phase calculations is corrected by a factor of 0.9806.

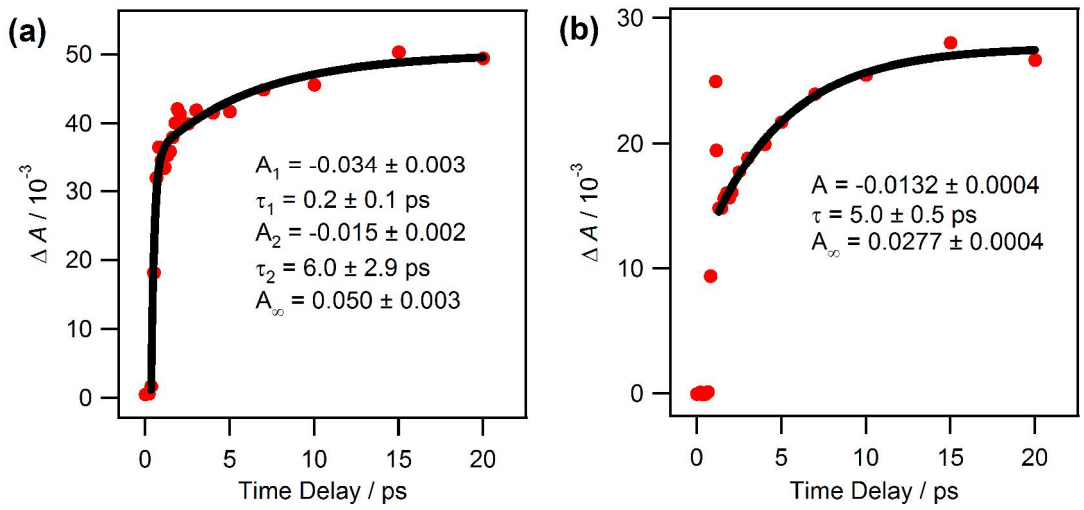
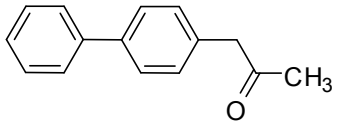


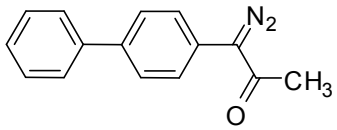
Figure S1. Kinetic traces of (a) $BpCN_2COMe$ and (b) $BpCOCN_2Me$ produced by ultrafast LFP (308 nm) in methanol and probed at 400 nm.

Material and Synthesis

All materials and solvents were purchased from Aldrich. The solvents for ultrafast studies were spectrophotometric grade from Aldrich and used as received.

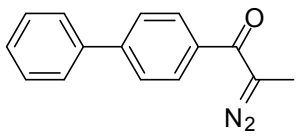


***p*-Biphenylacetone.** A 50 mL of flask is charged with 2.12 g of biphenylacetic acid (10.0 mmol), 3.6 mL of thionyl chloride (50 mmol) and 20 mL of dichloromethane. The solution is refluxed overnight and the solvent and excess thionyl chloride is removed under vacuum to afford biphenylacetic chloride. Biphenylacetic chloride is dissolved in 20 mL of dichloromethane and 1.07 g of *N*,*O*-dimethylhydroxylamine hydrochloride (11.0 mmol). The solution is cooled in an ice bath and 4.5 mL of DBU is added dropwise. The reaction is monitored by GC-MS. The reaction mixture is washed by saturated ammonium chloride (10 mL × 2), then water (10 mL) and dried with sodium sulfate. The solvent is removed under vacuum to afford $BpCH_2CON(OCH_3)CH_3$, where Bp = biphenylyl. $BpCH_2CON(OCH_3)CH_3$ is dissolved in 30 mL of anhydrous THF and 5 mL of 3 M CH_3MgCl solution is added dropwise at 0 °C over 1 hr. The reaction mixture is stirred for 4 hr and monitored by GC-MS. Upon completion of the reaction, it is quenched by saturated ammonium chloride solution and washed by brine. The solvent is removed under vacuum. The crude material is purified by column chromatography with a mixture of pentane and ether (10 : 1). White solid is afforded (1.26 g, yield 60%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56–7.59 (m, 4H), 7.42–7.45 (m, 2H), 7.33–7.36 (m, 1H), 7.27–7.29 (m, 2H), 3.74 (s, 2H), 2.20 (s, 3H).



$BpCN_2COCH_3$. *p*-Biphenylacetone (0.210 g, 1.0 mmol) and tosyl azide (0.197 g, 1.0 mmol) is dissolved in 10 mL of dichloromethane. DBU (0.3 mL, 2.0 mmol) is added to the solution dropwise at 0 °C and stirred overnight. The reaction mixture is quenched by saturated ammonium chloride solution,

washed by brine and dried by sodium sulfate. The solvent is removed under vacuum. The crude material is purified by column chromatography with a mixture of pentane and dichloromethane (1 : 1). Orange crystal is afforded (0.14 g, yield 60%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64–7.66 (m, 2H), 7.57–7.61 (m, 4H), 7.43–7.47 (m, 2H), 7.34–7.38 (m, 1H), 2.41 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.2, 139.8, 128.9, 127.7, 127.5, 126.9, 124.3, 27.0.



BpCOCN$_2$Me. A 100 mL of three-neck round-bottom flask, wrapped with aluminum foil and argon inlet, is charged with *N*-nitroso-*N*-ethyl urea (0.86 g, 7.34 mmol) and 40 mL of diethyl ether. The solution is kept at 0°C and purged with argon for 20 min. Then, 10 mL of 40% aqueous KOH solution was added and stirred at 0°C for 30 min. The organic layer was separated from the water layer to afford a diethyl solution of diazoethane. *Caution! Diazoethane is toxic and explosive. Ambient light should be avoided to prevent explosion of diazoethane. Due to the low boiling point of diethyl ether, it can dilute the concentration of diazo-ethane in the air to avoid explosion. Thus, diethyl ether CANNOT be replaced by THF*. Sodium hydroxide (2 g) was added to the diazoethane diethyl ether solution and stirred at 0°C for 5 min. Diethyl ether (10 mL) and 0.18 g of *p*-phenylbenzoyl chloride (0.85 mmol) were added and stirred at 0°C overnight. The organic layer was washed with pentane and dried. The solvent was removed under vacuum. The crude material was recrystalized from pentane to afford bright yellow solid (0.10 g, 50% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64–7.68 (m, 4H), 7.60–7.62 (m, 2H), 7.45–7.48 (m, 2H), 7.38–7.41 (m, 1H), 2.18 (s, 3H).

Details of Calculations

DFT and TD-DFT calculations were performed using the Gaussian 03 suite of programs at The Ohio Supercomputer Center. Geometries were optimized at the B3LYP/6-31G(d) level of theory with single-point energies obtained at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level of theory. Vibrational frequency analyses at the B3LYP/6-31G(d) level were utilized to verify that stationary points obtained corresponded to energy minima. The zero point energy (ZPE) was corrected with a factor of 0.9806. The electronic spectra were computed using Time-Dependent Density Functional Theory with Gaussian 03 at the B3LYP/6-311+G(d,p) level and using the B3LYP/6-31G(d) geometry; for these calculations, 20 allowed electronic transitions were calculated.

Complete Reference for Gaussian 03:

Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.