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First Direct Detection of 2,3-Dimethyl-2,3-diphenylcyclopropanone

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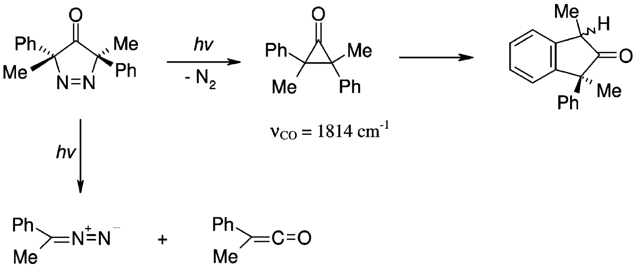
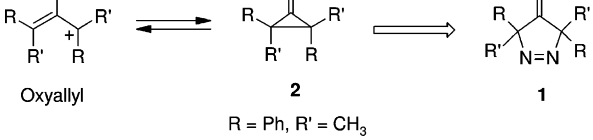


3,5-Dihydro-3,5-dialkyl-3,5-diaryl-4*H*-pyrazol-4-ones stimulate interest as potential precursors for 2,3-diarylcyclopropanones. Photoreactions of *trans*-3,5-dihydro-3,5-dimethyl-3,5-diphenyl-4*H*-pyrazol-4-one were studied by continuous-wave (CW) and pulsed laser UV photolysis revealing an intermediate that undergoes rearrangement to form *cis*- and *trans*-1,3-dimethyl-1-phenyl-2-indanones with the yield of ca. 60%. Steady-state photolysis (254 and 350 nm excitation) in different solvents produced an intermediate cyclohexadiene as evidenced by UV/vis, IR, and ^{1}H NMR spectra. In contrast, the nanosecond laser pulsed photolysis at 355 nm produced 2,3-dimethyl-2,3-diphenylcyclopropanone along with two products of retro-1,3-dipolar addition phenylmethylketene and 1-phenyldiazoethane. These can be observed by time-resolved IR (TRIR) spectroscopy as characteristic absorption bands at 1814, 2101, and 2038 cm^{-1}, respectively. Similar retro-1,3-dipolar addition showed 1-phenyldiazoethane formed following flash photolysis of 1-pyrazoline (*trans*-4,5-dihydro-3,5-dimethyl-3,5-diphenyl-3*H*-pyrazol-4-ol). The formation of the corresponding cyclopropanone as well the products of retro-1,3-dipolar addition during photoreaction of starting pyrazol-4-one is directly confirmed by the nanosecond TRIR spectroscopy for the first time. On the basis of the CW and pulsed laser UV photolysis, a dynamic equilibrium between cyclopropanone and intermediate 2,4-diphenyl-3-pentanone-2,4-diyl (dimethyldiphenyloxyallyl) was proposed.

Introduction

Cyclopropanones are key intermediates in a number of organic reactions.[1] One unique feature of cyclopropanones is that they exist in equilibrium with oxyallyls (Scheme 1).[2] Oxyallyls have been proposed as transient species in classical organic reactions such as the Favorskii rearrangement,[1] [3+2] as well as in [4+3] cycloadditions,[3] Nazarov cyclization,[4] photochemical rearrangement of cyclohexadienones,[5] and also the biosynthesis of prostaglandins.[6] Though various dialkyl- and tetralkylcyclopropanones have been isolated and characterized spectroscopically,[7] there is no spectroscopic evidence for the existence of diarylcyclopropanones including diphenylcyclopropanone.[8] 3,5-Dialkyl-3,5-diaryl-3,5-dihydro-4*H*-pyrazol-4-ones[9] (**1**, R = Ar, R′ = alkyl) are potential photochemical precursors for 2,3-dialkyl-2,3-diarylcyclopropanones (**2**, R = Ar, R′ = alkyl), because photodecomposition of a similar derivative, 3,5-dihydro-3,3,5,5-tetramethyl-4*H*-pyrazol-4-one (**1**,

SCHEME 1



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[‡] Contribution No. 608 from the Center for Photochemical Sciences.

(1) (a) Chenier, P. J. *Chem. Educ.* **1978**, *55*, 286. (b) Lee, E.; Yoon, C. H. *J. Chem. Soc., Chem. Commun.* **1994**, 479.

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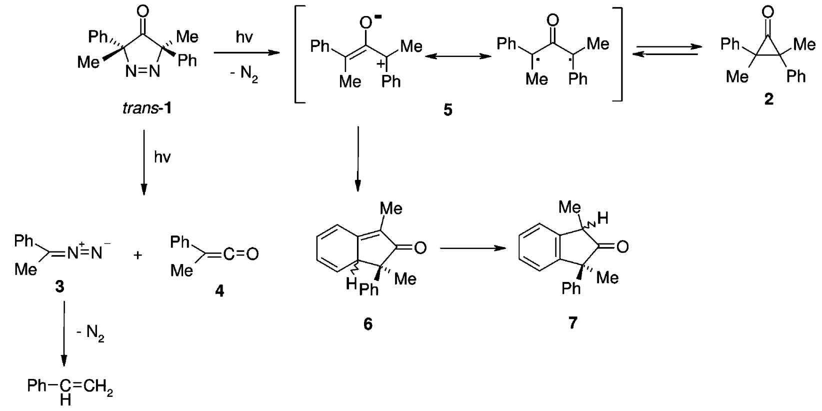
SCHEME 2



R = R′ = CH_3), is a well-established route to 2,2,3,3-tetramethylcyclopropanone (**2**, R = R′ = CH_3)[10] (Scheme 1).

Recently we have optimized a five-step stereoselective synthesis of the trans isomer of **1** (R = Ph, R′ = CH_3) and developed the synthesis of two new derivatives of **1** (R = Ph, R′ = alkyl).[9a] In this paper, we report the first observation of 2,3-dimethyl-2,3-diphenylcyclopropanone (**2**) photochemically generated from *trans*-**1** by 10-ns laser pulses at 355 nm. Another pathway of photodecomposition of *trans*-**1** is found to be a retro-1,3-dipolar addition.

Results and Discussion

We propose the mechanism in Scheme 2. Evidence substantiating the proposed mechanism follows. In general, we expect our photoreaction to be a reverse of that presented in Scheme 1.

Steady-State Photolysis of *trans*-1. CW photodecomposition of *trans*-**1** at 350 nm in acetonitrile and carbon tetrachloride produced a mixture of *cis*- and *trans*-1,3-dimethyl-1-phenyl-2-indanones (**7**) (Scheme 2) in ca. 60% along with minor products of retro-1,3-dipolar addition (ca. 10% yield). The same photochemical products were observed during the CW irradiation of *trans*-**1** at 254 nm in acetonitrile or CW irradiation at 350 nm in benzene and methanol. One of the products of retro-1,3-dipolar addition is phenylmethylketene (**4**) found during the CW photolysis. This was trapped with methanol producing the methyl ester of 2-phenylpropanoic acid. Another product of retro-1,3-dipolar addition, styrene, was observed in the GC/MS during the CW irradiation of *trans*-**1** at 350 nm in argon-saturated benzene. The retention times and mass spectra of **4** and styrene were compared to those of authentic samples.

^{1}H NMR, IR, and UV spectroscopies were used to follow the course of the steady-state photolysis of *trans*-**1** in order to observe cyclopropanone **2**.

^{1}H NMR Spectroscopy during Steady-State Photolysis of *trans*-1. CW irradiation of a 0.05 M solution of *trans*-**1** in argon-saturated acetonitrile-d_3 at 350 nm for a time that resulted in 20% consumption of the initial material produced a mixture of two diastereoisomers **7** as seen in the ^{1}H NMR spectrum. However, 254 nm irradiation of *trans*-**1** (to 20% conversion) in argon-saturated acetonitrile-d_3 for 10 min revealed, along with the signals from **7,** additional peaks due to an intermediate (Figure 1). The change in the NMR spectrum was accompanied by a color change of the solution from colorless to bright yellow. The ^{1}H NMR signals of this intermediate disappeared after several minutes in the dark at 25 °C with a concomitant growth of signals corresponding to **7**, along with a change in the color of the solution to light-yellow. The intermediate was assigned the structure of the cyclohexadiene **6** based on the characteristic ^{1}H NMR signals of the cyclohexadiene ring and integration: 1.45 (s, 3H), 1.78 (d, 3H), 4.17 (broad s, 1H), 6.20 (m, 1H), 6.29 (dd, 1H), 6.40 (dd, 1H), 6.80 (dd, 1H), 7.26 (m, 2H),

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(2) (a) Green, F. D.; Sclove, D. B.; Pazos, J. F.; Camp, R. L. *J. Am. Chem. Soc.* **1970**, *92*, 7488. (b) Sorensen, T. S.; Sun, F. *Can. J. Chem.* **1997**, *75*, 1030. (c) Ichimura, A. S.; Lahti, P. M.; Martlin, A. R. *J. Am. Chem. Soc.* **1990**, *112*, 2868. (d) Hirano, T.; Kumagai, T.; Miyashi, T.; Akiyama, K.; Ikegami, Y. *J. Org. Chem.* **1991**, *56*, 1907. (e) Rauk, A.; Sorensen, T. S.; Sun, F. *J. Am. Chem. Soc.* **1995**, *117*, 4506. (f) Hrovat, D. A.; Rauk, A.; Sorensen, T. S.; Powell, H. K.; Borden, W. T. *J. Am. Chem. Soc.* **1996**, *118*, 4159. (g) Sorensen, T. S.; Sun, F. *J. Chem. Soc., Prekin. Trans. 2* **1998**, 1053. (h) Bhargava, S.; Hou, J.; Parvez, M.; Sorensen, T. S. *J. Am. Chem. Soc.* **2005**, *127*, 3704. (i) Sorensen, T. S.; Sun, F. *J. Am. Chem. Soc.* **1995**, *17*, 5592. (j) Berson, J. A.; Cordes, M. H. *J. Am. Chem. Soc.* **1996**, *118*, 6241.

(3) (a) Turro, N. J.; Edelson, S. S.; Williams, J. R.; Darling, T. R.; Hammond, W. B. *J. Am. Chem. Soc.* **1969**, *91*, 2283. (b) Takaya, H.; Makino, S.; Hayakawa, Y.; Noyori, R. *J. Am. Chem. Soc.* **1978**, *100*, 1765. (c) Takaya, H.; Hayakawa, Y.; Makino, S.; Noyori, R. *J. Am. Chem. Soc.* **1978**, *100*, 1778. (d) Hayakawa, Y.; Yokoyama, K.; Noyori, R. *J. Am. Chem. Soc.* **1978**, *100*, 1791. (e) Hayakawa, Y.; Baba, Y.; Makino, S.; Noyori, R. *J. Am. Chem. Soc.* **1978**, *100*, 1786. (f) Lee, K.; Cha, J. K. *Org. Lett.* **1999**, *1*, 523. (g) Harmata, M.; Sharma, U. *Org. Lett.* **2000**, *2*, 2703. (h) Lee, J. C.; Jin, S. J.; Cha, J. K. *J. Org. Chem.* **1998**, *63*, 2804. (i) Lee, J.; Oh, J.; Jin, S. J.; Choi, J. R.; Atwood, J.; Cha, J. K. *J. Org. Chem.* **1994**, *59*, 6955.

(4) (a) Harding, K. E.; Clement, K. S.; Tseng, C. Y. *J. Org. Chem.* **1990**, *55*, 4403. (b) Miesch, M.; Miesh-Gross, L.; Frank-Neumann, M. *Tetrahedron* **1997**, *53*, 2103. (c) Cheng, K. F.; Cheung, M. K. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1213. (d) Liang, G.; Trauner, D. *J. Am. Chem. Soc.* **2004**, *126*, 9544.

(5) (a) Patel, D. J.; Schuster, D. I. *J. Am. Chem. Soc.* **1968**, *90*, 5137. (b) Schuster, D. I.; Patel, D. J. *J. Am. Chem. Soc.* **1968**, *90*, 5145.

(6) (a) Lopez, C. S.; Faza, O. N.; York, D. M.; de Lera, A. R. *J. Org. Chem.* **2004**, *69*, 3635. (b) Corey, E. J.; Matsuda, S. P. T.; Nagata, R.; Cleaver, M. B. *Tetrahedron Lett.* **1988**, *29*, 2555. (c) Koljak, R.; Boutaud, O.; Shieh, B. H.; Samuel, N.; Brash, A. R. *Science* **1997**, *277*, 1994. (d) Hess, B. A.; Smentek, L.; Brash, A. R.; Cha, J. K. *J. Am. Chem. Soc.* **1999**, *121*, 5603. (e) Baertschi, S. W.; Brash, A. R.; Harris, T. M. *J. Am. Chem. Soc.* **1989**, *111,* 5003.

(7) Turro, N. J. *Acc. Chem. Res.* **1969**, *2*, 25.

(8) (a) Fort, A. W. *J. Am. Chem. Soc.* **1962**, *84,* 4979. (b) Noyori, R.; Hayakawa, Y.; Takaya, H.; Murai, S.; Kobayashi, R.; Sonoda, N. *J. Am. Chem. Soc.* **1978**, *100*, 1759. (c) Hayakawa, Y.; Yokoyama, K.; Noyori, R. *J. Am. Chem.* **1978**, *100*, 1799.

(9) (a) Moiseev, A. G.; Neckers, D. C. *Synthesis* **2005**, *17*, 2901. (b) Pirkle, W. H.; Hoover, D. J. *J. Org. Chem.* **1980**, *45*, 3407.

(10) (a) Adam, W.; Fuss, A.; Mazenod, F. P.; Quast, H. *J. Am. Chem. Soc.* **1981**, *103*, 998. (b) Sander, W.; Wrobel, R.; Komnick, P.; Rademacher, P.; Muchall, H. M.; Quast, H. *Eur. J. Org. Chem.* **2000**, *1*, 91.

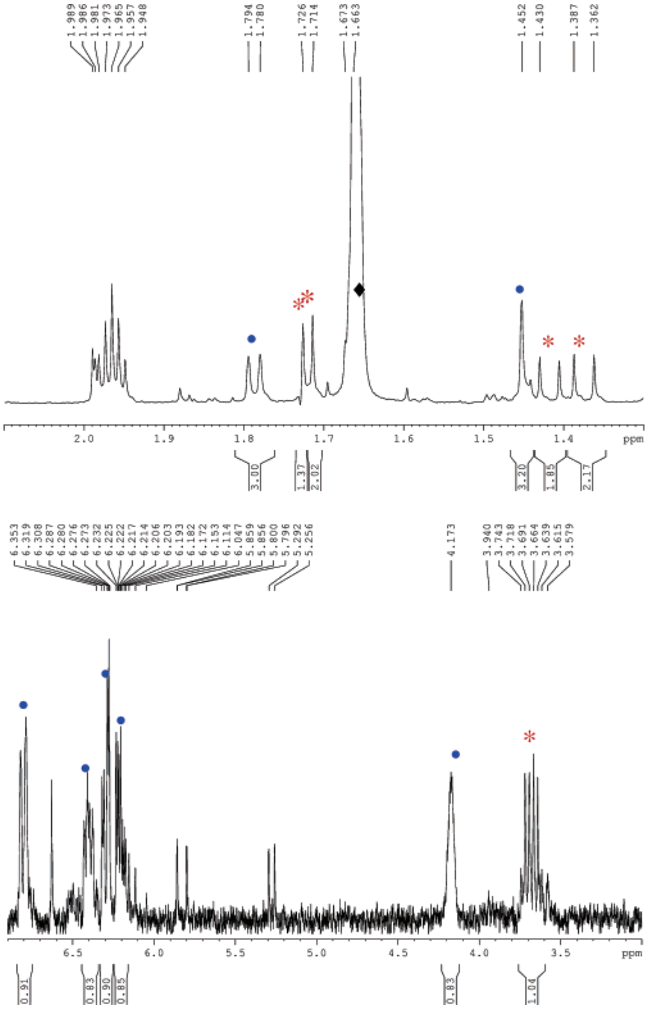


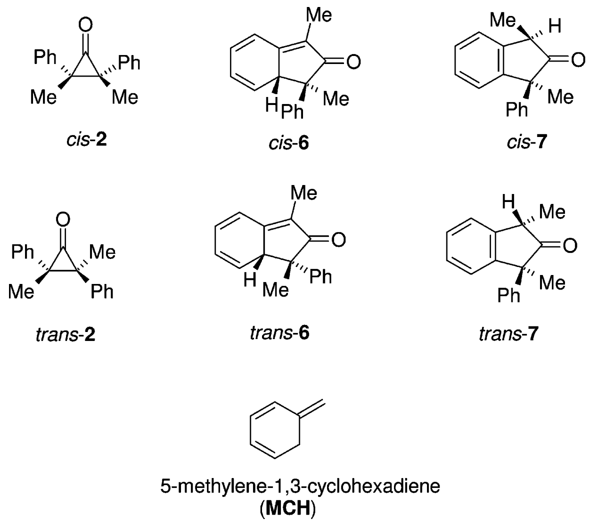
FIGURE 1. ^{1}H NMR spectra of *trans*-**1** in the argon-saturated acetonitrile-d_3 at 300 MHz after 254 nm irradiation for 10 min at 25 °C: cyclohexadiene **6** (●), *cis*- and *trans*-**7** (∗), and starting *trans*-**1** (◆).

7.35 ppm (m, 3H). These data indicate that **6** is a precursor of **7**. Signals in Figure 1 have been assigned as follows: the doublet centered at 1.362−1.387 ppm and the singlet centered at 1.726 ppm correspond to CH_3 groups of *cis*-**7.** The doublet centered at 1.405−1.430 ppm and the singlet centered at 1.714 ppm correspond to CH_3 groups of *trans*-**7**. The singlet centered at 1.663 ppm corresponds to a CH_3 group of starting *trans*-**1**.

It should be noted that the top and bottom spectra in Figure 1 are parts of the same ^{1}H NMR spectrum. However, we magnified the 3−6.9 ppm region to obtain a better view of the cyclohexadiene pattern. The intensity of signals in the bottom panel is lower, because each signal corresponds to a single hydrogen, while in the top spectrum each signal corresponds to three hydrogens of methyl groups. [We also performed 600 MHz ^{1}H NMR experiments to record a better spectrum of cyclohexadiene **6**. The signals between 4.0 and 6.9 ppm appeared to be much less noisier than the ones recorded at 300 MHz (see the Supporting Information).]

IR Spectroscopy during Steady-State Photolysis of *trans*-1. Due to the characteristics of our nanosecond TRIR spectrometer, carbonyl vibrations with higher IR oscillator strength (IR intensity) were used for identification as most reliable.

CHART 1



Starting *trans*-**1** has a distinct carbonyl absorption peak at 1764 cm^{-1}. Cyclopropanones can be easily identified by their characteristic carbonyl absorptions in the 1813−1843 cm^{-1} region.[7] To assist with assignments, Gaussian 98 quantum chemical calculations[11] at the B3LYP/6-31G(d) level of theory were used to calculate carbonyl vibrational frequencies of **2**. Chart 1 shows intermediates and photochemical products observed during the photodecomposition of *trans*-**1**. Cyclopropanone **2** can exist as both the cis and trans isomer and, according to the calculations, *cis*-**2** (1841 cm^{-1} [this value, as all other calculated frequencies in this paper, was obtained and reported in the text by scaling the frequency resulting from the quantum chemical calculations by the factor of 0.96; we used the same scaling factor for all calculated frequencies in this paper]) and *trans*-**2** (1843 cm^{-1}) have very similar carbonyl vibrational frequencies.

CW irradiation of *trans*-**1** at 350 nm in carbon tetrachloride or acetonitrile leads to formation of three distinct absorption peaks at 2103, 1755, and 1691 cm^{-1} (Figure 2) accompanied by a decrease of carbonyl absorption of *trans*-**1** at 1764 cm^{-1}. However, no carbonyl absorption for product **2** expected in accordance with the proposed mechanism (Scheme 2) was found in the spectra. The strong absorption at 2103 cm^{-1} can be readily assigned to ketene **4**, based on the comparison with the IR spectrum of an authentic sample (2099 cm^{-1}).

The band at 1755 cm^{-1}, which overlaps with carbonyl absorption of *trans*-**1** at 1764 cm^{-1}, corresponds to the carbonyl absorption of **7**. Isolated *trans*-**7** (Chart 1) showed carbonyl absorption at 1749 cm^{-1}. In addition, quantum chemical calculations[11] predict 1765 cm^{-1} for carbonyl absorption of *trans*-**7** in good agreement with the observed value of 1755 cm^{-1}.

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(11) Gaussian 98 program was used for the calculations: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, J. V.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A 11.3; Gaussian, Inc.: Pittsburg, PA, 2002.

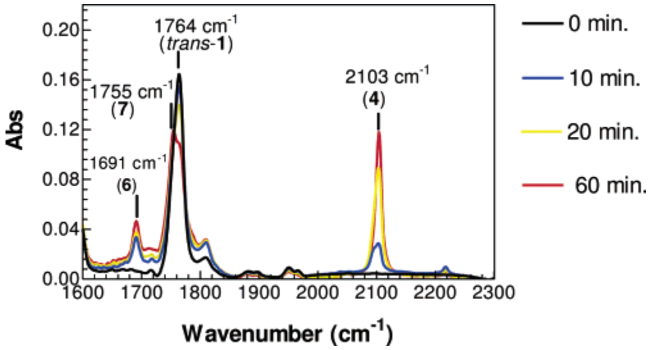

FIGURE 2. Time evolution of infrared spectra of *trans*-**1** in carbon tetrachloride acquired after 350 nm CW irradiation (0−60 min) at 25 °C.

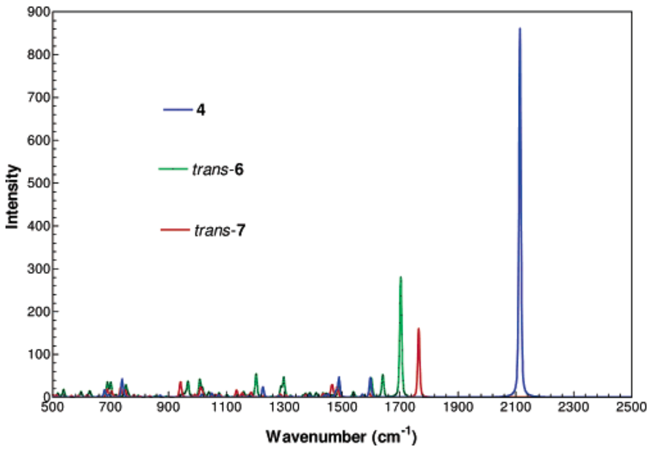

FIGURE 3. IR spectra of **4**, *trans*-**6**, and *trans*-**7** calculated with the Gaussian 98 package[11] at the B3LYP/6-31G(d) level of theory and scaled by 0.96.

Cyclohexadiene **6**, observed in the ^{1}H NMR spectra (Figure 1), is a precursor of **7**. The quantum chemical calculations[11] predict strong carbonyl absorption for *trans*-**6** at 1703 cm^{-1}, which is expected to appear in the IR spectra (Figure 2). The s-*trans* and s-*cis* conformations of α,β-unsaturated ketones may have different carbonyl vibrational frequencies. For example, benzalacetone in carbon disulfide at 25 °C shows carbonyl absorption at 1699 cm^{-1} for s-*cis* and 1674 cm^{-1} for s-*trans* conformation.[12] Since cyclohexadiene **6** has an *s-cis* configuration, its carbonyl absorption is expected to lie close to 1699 cm^{-1}, similar to the s-*cis* conformation of benzalacetone. This experimental evidence and the quantum chemical calculations compel the assignment of the 1691 cm^{-1} peak to the carbonyl absorption of **6**.

The quantum chemical calculations[11] were also carried out to compare IR band intensities in compounds **4**, **6**, and **7**. The results show that the ketene absorption of **4** (2115 cm^{-1}) has much higher intensity than the carbonyl absorptions of *trans*-**6** (1703 cm^{-1}) and *trans*-**7** (1765 cm^{-1}) (Figure 3). This explains the high intensity of the ketene band of **4** in Figure 2 compared to the carbonyl intensities of **6** and **7** even though **6** and **7** are produced in much higher yield (ca. 60%) than **4** (ca. 10%).

UV/Vis Spectroscopy during Steady-State Photolysis of *trans*-1. CW irradiation at 350 nm of a 0.002 M solution of *trans*-**1** in argon-saturated carbon tetrachloride or acetonitrile leads to the formation of an intermediate having a broad absorption in the 300−400 nm region and a much higher extinction coefficient than the starting *trans*-**1** (Figure 4). This 300−400 nm band cannot be attributed to the absorption of formed products such as indanones **7** because *trans*-**7** following isolation has no absorption at wavelengths above 350 nm (Figure 5). The band cannot be attributed to fragmentation products either since they are formed in low yield and have different absorption characteristics. This broad absorption can, however, be assigned to highly conjugated **6** as observed by ^{1}H NMR and IR spectroscopies. A related derivative of 1,3-cyclohexadiene **6**, 5-methylene-1,3-cyclohexadiene[13] (**MCH**, Chart 1), has a similar UV/vis absorption spectrum. The extinction coefficient of **6** is expected to be higher than that of **MCH** ($\epsilon = 520^{13}$ at 350 nm in benzene) due to the extended conjugation of the **MCH** moiety with the carbonyl group in enone **6**.

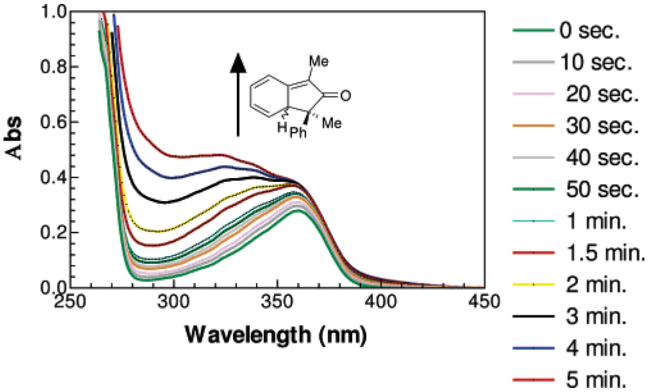

FIGURE 4. Time evolution of UV/vis absorption spectra of *trans*-**1** in argon-saturated carbon tetrachloride acquired after CW irradiation at 350 nm (0−5 min) at 25 °C.

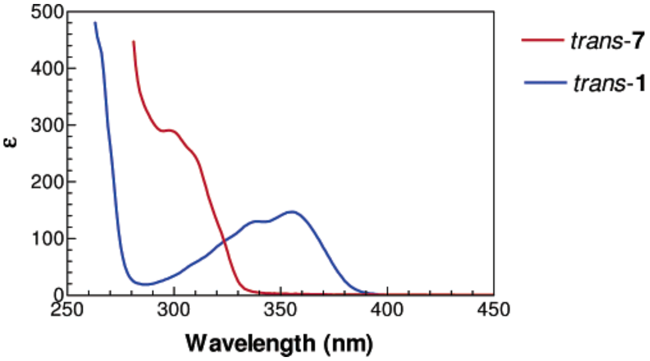

FIGURE 5. UV/vis absorption spectra of *trans*-**1** and *trans*-**7** in carbon tetrachloride at 25 °C.

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[12] Silverstein, R. M.; Webster, F. X. *Spectrometric Identification of Organic Compounds*; Wiley: New York, 1998.

[13] (a) Graham, W. D.; Green, J. G.; Pryor, W. A. *J. Org. Chem.* **1979**, *44*, 907. (b) Gajewski, J. J.; Gortva, A. M. *J. Org. Chem.* **1989**, *54*, 373.

[14] McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* **1987**, *109*, 683.

[15] (a) Buchwalter, S. L.; Closs, G. L. *J. Org. Chem.* **1975**, *40*, 2549. (b) Schneider, M. P.; Bippi, H. *J. Am. Chem. Soc.* **1980**, *102*, 7363. (c) Adam, W.; Gillaspey, W. D.; Peters, E. M.; Peters, K.; Rosenthal, R. J.; Schnering, H. G. *J. Org. Chem.* **1985**, *50*, 580. (d) Adam, W.; Doerr, M.; Peters, E. M.; Peters, K.; Schnering, H. G. *J. Am. Chem. Soc.* **1985**, *50*, 587. (e) Adam, W.; Oppenlander, T.; Zang, T. G. *J. Org. Chem.* **1985**, *50*, 3303. (f) Begley, M. J.; Dean, F. M.; Houghton, L. E.; Johnson, R. S.; Park, K. B. *J. Chem. Soc., Chem. Commun.* **1978**, 461.

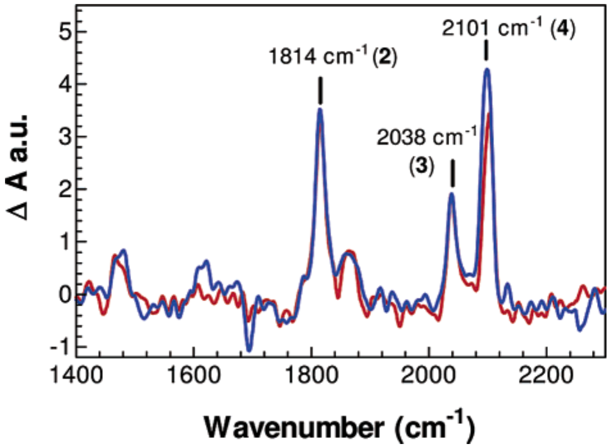


FIGURE 6. TRIR difference spectra recorded 2 μs after 355 nm pulsed laser excitation of argon-saturated (blue) and oxygen-saturated (red) 0.06 M solutions of *trans*-**1** in carbon tetrachloride at 25 °C.

On the basis of the structures of the photochemical products and ^{1}H NMR, IR, and UV/vis data obtained during the steady-state photolysis of *trans*-**1**, two photodecomposition pathways are proposed. The first is the expulsion of nitrogen to form 2,4-diphenyl-3-pentanone-2,4-diyl (**5**), Scheme 2. Oxyallyl **5** could be of diradical or zwitterionic nature. Since calculations show the zwitterionic character of oxyallyls[16] predominates upon α-substitution, oxyallyl **5** should have zwitterionic nature. Electrocyclic conrotatory ring closure of zwitterionic oxyallyl **5** (Nazarov-type intermediate[4]) results in cyclohexadiene **6** followed by the aromatization to *cis*- and *trans*-indanones **7**. A second pathway of photodecomposition of *trans*-**1** is a retro-1,3-dipolar addition affording 1-phenyldiazoethane (**3**) and **4**. Photochemically labile **3** easily decomposes with nitrogen expulsion to give styrene. Previously Chapman and McMahon[14] showed that photodecomposition of matrix-isolated **3** leads to phenylmethylcarbene that rearranges to styrene.

Similar retro-1,3-dipolar addition was proposed as a photoreaction for the related 1-pyrazolines.[15] For example, the photodecomposition of 3,5-diphenyl-1-pyrazoline led mainly to 1,2-diphenylcyclopropane (70%) along with minor retro-1,3-dipolar addition (10%).[15a] It was assumed that retro-1,3-dipolar addition leads to alkene and a labile diazo compound followed by decomposition of the latter. However, the formation of diazo compounds has not been confirmed following the photodecomposition of 1-pyrazolines.

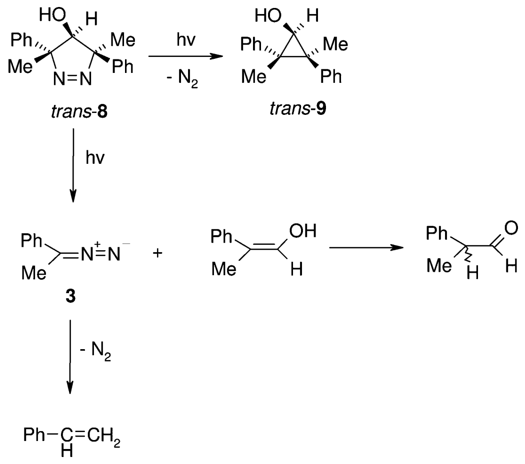
The observation of cyclohexadiene **6** during the steady-state photolysis of *trans*-**1** gives credence to the existence of oxyallyl **5**, which can close to cyclopropanone **2**. The absence of **2** during the steady-state photolysis of *trans*-**1** indicates that **2** is a transient species and therefore should be amenable to observation by transient techniques. TRIR[17] and time-resolved UV/vis (TR UV)[18] spectroscopies were used to determine the structure and to measure lifetimes of short-lived intermediates in solution. Absorption peaks in TRIR spectra are more pronounced and preferred for structure characterization compared to featureless and broad absorption bands in transient UV/vis spectra. Therefore, nanosecond TRIR spectroscopy was the technique of choice for observing cyclopropanone **2** by its characteristic carbonyl absorption in the IR spectrum.

TABLE 1. Experimental and Calculated Carbonyl Frequencies of Photochemical Products

species no.	label	obsd freq (cm^{-1})	calcd freq^a (cm^{-1})
	trans-**2**		1843 (238)
1		1814	
	cis-**2**		1841(238)
2	*trans*-**6**	1691	1703 (250)
3	*trans*-**7**	1755	1765 (162)

^{a} Gaussian 98 results at the B3LYP/6-31G(d) level of theory and scaled by 0.96.[11] The IR intensities are given in parentheses.

SCHEME 3



Nanosecond TRIR Studies of *trans*-1. The TRIR spectrum of *trans*-**1** in argon-saturated carbon tetrachloride was obtained with a 30-ns time resolution (Figure 6). Three positive transients at 1814, 2038, and 2101 cm^{-1} were observed.

The transients formed within 30 ns after the 355 nm laser pulse remained unchanged throughout the experimental time window of ca. 10 μs (see the kinetic traces in the Supporting Information for details). The position of the absorption peak at 1814 cm^{-1} is in good agreement with calculated carbonyl vibrational frequencies of cis and trans isomers of **2** (Table 1, row 1) and with reported IR absorption of cyclopropanones.[7] Therefore, the 1814 cm^{-1} band was assigned to the carbonyl absorption of **2**. No decrease in IR intensity or lifetime of **2** was observed in the presence of oxygen, implying that **2** is not reactive toward oxygen. The absence of carbonyl absorption bands of steady-state products, cyclohexadiene **6** (1691 cm^{-1}) and indanones **7** (1755 cm^{-1}), in the TRIR spectra (Figure 6) suggests that cyclopropanone **2** forms cyclohexadiene **6** on a longer time scale.

The transient absorption peak at 2101 cm^{-1} (Figure 6) looks similar to the strong peak at 2103 cm^{-1} in Figure 2. Accordingly, the 2101 cm^{-1} transient was assigned to the ketene **4**. As mentioned, the presence of styrene during the steady-state photolysis of *trans*-**1** and the literature data on photoreactions for other 1-pyrazolines[15] suggest the presence of labile diazo compound **3** in the reaction. The diazo group of matrix-isolated **3**[14] has characteristic strong absorption at 2050 cm^{-1}, which is

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[16] (a) *Magnetic Properties of Organic Materials*; Lahti, P. M., Ed.; Marcel Dekker, Inc.: New York, 1999. (b) Hrovat, D. A.; Murko, M. A.; Lahti, P. M.; Borden, W. T. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1037. (c) Hess, B. A. *J. Am. Chem. Soc.* **2002**, *124*, 920.

[17] (a) Toscano, J. P. *Adv. Photochem.* **2001**, *26*, 41. (b) George, M. W.; Kato, C.; Hamaguchi, H. *Chem. Lett.* **1993**, 873. (c) Neville, A. G.; Brown, C. E.; Rayner, D. M.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *113*, 1869. (d) Showalter, B. M.; Bentz, T. C.; Ryzhkov, L. R.; Hadad, C. M.; Toscano, J. P. *J. Phys. Org. Chem.* **2000**, *13*, 309.

[18] (a) Johnston, L. J. *Chem. Rev.* **1993**, *93*, 251. (b) Johnston, L. J.; Scaiano, J. C. *Chem. Rev.* **1989**, *89*, 521.

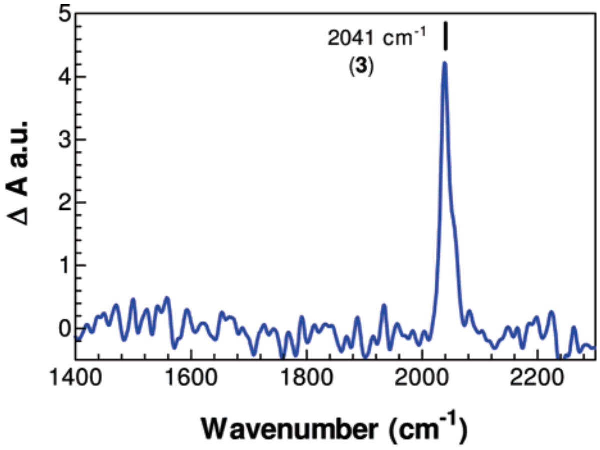

FIGURE 7. TRIR difference spectra recorded 2 μs after 355 nm pulsed laser excitation of an argon-saturated 0.06 M solution of *trans*-**8** in carbon tetrachloride at 25 °C.

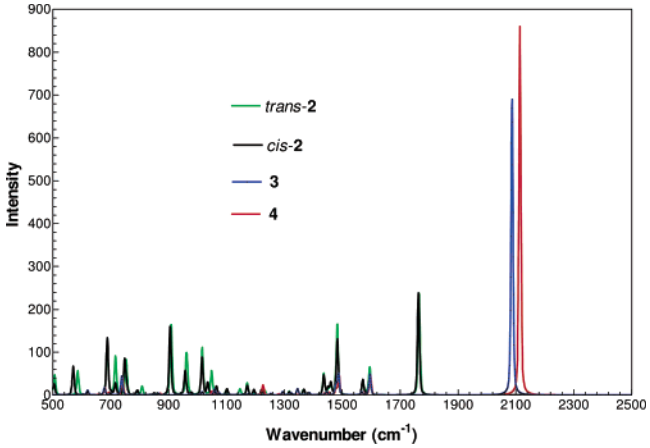

FIGURE 8. IR spectra of *cis*- and *trans*-**2**, **3**, and **4** calculated with the Gaussian 98 package[11] at the B3LYP/6-31G(d) level of theory and scaled by 0.96.

similar to the transient observed at 2038 cm^{-1} in Figure 6; therefore, this absorption was tentatively assigned to **3**.

One of the goals of the current study was to confirm the assignment of the 2038 cm^{-1} transient in the TRIR spectra of *trans*-**1**. *trans*-4,5-Dihydro-3,5-dimethyl-3,5-diphenyl-3*H*-pyrazol-4-ol (*trans*-**8**) has a structure similar to that of *trans*-**1** and, therefore, should also generate products of retro-1,3-dipolar addition upon photodecomposition. The steady-state photolysis of *trans*-**8** at 350 nm in different solvents mainly gave a product of nitrogen expulsion: *trans*-2,3-dimethyl-2,3-diphenylcyclopropanol (*trans*-**9**, ca. 80%) along with ca. 10% of products of retro-1,3-dipolar addition (styrene and 2-phenylpropionaldehyde) (Scheme 3).

The expected retro-1,3-dipolar addition of *trans*-**8** in argon-saturated carbon tetrachloride was observed and persisted within the experimental time window. The immediate formation of a transient absorption at 2041 cm^{-1} was found in the TRIR spectrum of *trans*-**8** (Figure 7) and this transient did not change within ca. 10 μs, similar to that of *trans*-**1**. Thus, the absorptions at 2038 (*trans*-**1**) and 2041 cm^{-1} (*trans*-**8**) in the TRIR spectra were assigned to the same transient species, namely diazo compound **3**.

TABLE 2. Calculated Free Energy Differences and Equilibrium Constants for Ring Opening of Cyclopropanone 2 and Cyclohexadiene 6

entry	reaction	ΔG (kcal/mol)	K_{eq}
1	*cis*-**2** → oxyallyl **5**	5.3	1.3×10^{-4}
2	*trans*-**2** → oxyallyl **5**	7.2	5.2×10^{-6}
3	*cis*-**6** → oxyallyl **5**	17.0	3.1×10^{-13}
4	*trans*-**6** → oxyallyl **5**	17.7	1.0×10^{-13}

Parallel to the calculations done for compounds **4**, **6**, and **7**, the IR spectra of *cis*- and *trans*-**2**, **3**, and **4** were simulated at the B3LYP/6-31G(d) level of theory (Figure 8). The results show that the ketene absorption in **4** and diazo absorption in **3** have much higher IR intensities relative to the carbonyl peak of cyclopropanone **2**. This explains the strong signals from **3** and **4** (Figure 6) compared to the carbonyl absorption of **2**, even though **3** and **4** are produced in lower yield than **2** (ca. 10% according to the steady-state photolysis data).

Labile diazo compounds have not been observed or isolated during the steady-state photolysis of 1-pyrazolines.[15] The reason for this is that they easily decompose forming carbenes with subsequent rearrangement to alkenes following the absorption of an additional photon.[14,15] Whether the photoreaction of 3,5-diphenyl-1-pyrazoline is a direct decomposition or retro-1,3-dipolar addition remains unclear.[15a,b] The direct decomposition should form styrene, phenylcarbene, and nitrogen in one step while the retro-1,3-dipolar addition should produce phenyldiazomethane and styrene followed by the decomposition of the diazo compound. Decisive evidence in favor of the retro-1,3-dipolar addition would be the presence of the diazo compound among the photodecomposition products. Previously,[15a] irradiation of 3,5-diphenyl-1-pyrazoline at 5.5 K revealed phenylcarbene. Apparently, the photodecomposition rate of the diazo compounds is too high to observe them under the steady-state conditions. In contrast, we observed characteristic IR peaks of diazo compound **3** in the time-resolved spectra during the nanosecond laser photolysis of *trans*-**1** and *trans*-**8** (Figures 6 and 7). Therefore, the evidence collected suggests that the photodecomposition of 1-pyrazolines proceeds by retro-1,3-dipolar addition.

Calculations by the UDFT Method at the UB3LYP/6-31G(d) Level of Theory. To rationalize the interrelation between oxyallyl **5** and cyclopropanone **2** and thermodynamical reasons for rearrangement of cyclopropanone **2** to cyclohexadiene **6**, spin-unrestricted quantum chemical calculations (UDFT) were performed to estimate free energy differences and equilibrium constants. The results are summarized in Table 2.

There are several reports of the free energy difference between cyclopropanone and the corresponding oxyallyl for several stable cyclopropanones.[2] The free energy difference between *cis*-2,3-(di-*tert*-butyl)cyclopropanone and the corresponding oxyallyl is 11.3 kcal/mol and that for *trans*-2,3-(di-*tert*-butyl)cyclopropanone is 28 kcal/mol.[2i] Berson and Cordes found that the free energy difference between spiro(bicycle[2.2.1]heptane-2,1-cyclopropane)-2-one and corresponding oxyallyl is 16−19 kcal/mol.[2j] We found that the calculated free energy difference between oxyallyl **5** and cyclopropanone **2** (5.3−7.2 kcal/mol) is two times less than that for the reported cyclopropanones. Therefore, cyclopropanone **2** should be more likely to be in equilibrium with oxyallyl **5** than the cyclopropanones reported. The calculated equilibrium constant (0.052−1.3 × 10^{-4}) shows that the equilibrium between **2** and **5** should be shifted toward cyclopropanone **2**. Therefore, cyclopropanone **2** should be present in higher concentration, while a lower concentration of oxyallyl **5** should be seen. Indeed, we observed only cyclopropanone **2** in the TRIR spectra (Figure 6) and no signal corresponding to oxyallyl **5** was found. [The absence of the carbonyl band of oxyallyl **5** in the TRIR spetra can also be explained by two additional reasons: (a) The UDFT calculations predict a low IR intensity (ca. 150) for the 1536 cm^{-1} band. As a result, the corresponding transient signal will be weak and masked by the baseline noise in the TRIR spectra (Figure 6). (b) The formation time of cyclopropanone **2** within the time resolution of our TRIR setup (30 ns) suggests that the time scale of interconversion between **5** and **2** is less than 30 ns. Therefore, oxyallyl **5** is too short-lived to be observed in the TRIR spectra.]

Because it is in dynamic equilibrium with cyclopropanone **2** oxyallyl **5** also forms cyclohexadiene **6**. The comparison of calculated free energy difference and equilibrium constant for oxyallyl **5**-cyclohexadiene **6** equilibrium (Table 2, entries 3 and 4) with free energy difference and equilibrium constant for oxyallyl **5**-cyclopropanone **2** equilibrium (Table 2, entries 1 and 2) indicates that cyclohexadiene **6** should be much more stable than cyclopropanone **2** and the overall equilibrium should be shifted toward cyclohexadiene **6**. Another driving force toward the formation of cyclohexadiene **6** is aromatization to form indanone **7**, which is an irreversible process. The calculations agree with our experimental observations. Fast ring closure of oxyallyl **5** leads to cyclopropanone **2** observed in TRIR spectra on a shorter time scale, while on a longer time scale oxyallyl **5** forms cyclohexadiene **6**.

Conclusion

We have found distinct differences in the products of the UV photolysis of *trans*-**1** depending on the regime of irradiation (steady state vs pulsed). From the analysis of ^{1}H NMR, IR, and UV/vis spectra, the steady-state photolysis of *trans*-**1** at 254 and 350 nm produces intermediate cyclohexadiene **6** (Scheme 2). The cyclohexadiene undergoes rearrangement to form *cis*- and *trans*-1,3-dimethyl-1-phenyl-2-indanones **7** with a yield of ca. 60%. On the other hand, the pulsed laser UV photolysis of *trans*-**1** at 355 nm results in a characteristic carbonyl absorption peak attributed to 2,3-dimethyl-2,3-diphenylcyclopropanone **2** at 1814 cm^{-1} in the TRIR spectra. Cyclopropanone **2** was observed for the first time in our time-resolved experiments. The other two products, 1-phenyldiazoethane **3** and phenylmethylketene **4**, were detected by their characteristic IR bands in the TRIR spectra as characteristic absorption bands at 2101 and 2038 cm^{-1}, respectively. Similarly, the formation of 1-phenyldiazoethane was observed after the pulsed laser photolysis of another 1-pyrazoline (*trans*-4,5-dihydro-3,5-dimethyl-3,5-diphenyl-3*H*-pyrazol-4-ol, *trans*-**8**).

We propose that the irradiation of *trans*-**1** leads to zwitterionic oxyallyl **5** by nitrogen expulsion. The intermediate cyclopropanone **2** exists in a dynamic equilibrium with **5**, and the latter closes to cyclohexadiene **6** on a longer time scale. Aromatization of **6** produces indanones **7**. Another decomposition pathway of *trans*-**1** is retro-1,3-dipolar addition that yields the diazo compound **3** and ketene **4**. Accordingly, our TRIR experiments conclusively prove, for the first time, that retro-1,3-dipolar addition is indeed an actual fragmentation pathway of 1-pyrazolines (*trans*-**1** and *trans*-**8**).

Experimental Section

trans-**1** and *trans*-**8** were synthesized according to literature procedures.[9a] Phenylmethylketene (**4**) was synthesized according to the method described by Dehmlow.[19]

The detailed description of our time-resolved FTIR (TRIR) setup is available elsewhere.[20] Briefly, the third harmonic of a YAG:Nd^{3+} laser (354.7 nm, 10 ns, 1.5−5 mJ per pulse, 10 Hz repetition rate) was used as an excitation source in all experiments. The sample solutions were pumped through a 1 mm thick CaF$_2$ flow cell with a flow rate up to 150 mL per minute. All spectra were recorded in the 1500−2800 cm^{-1} spectral window with 8 cm^{-1} resolution every 20 ns. The raw data were processed and visualized with custom written LabView based software.

Isolation of *cis*- and *trans*-7. Starting *trans*-**1** (0.128 g, 0.76 mmol) was dissolved in acetonitrile (50 mL) in a 125 mL Erlenmeyer flask. The flask was fitted with a rubber septum, argon inlet, and magnetic stir bar. The solution of *trans*-**1** was purged with argon for 15 min and irradiated in a photochemical reactor at 350 nm for 12 h. After irradiation was complete, the solution became bright yellow. Solvent was removed under reduced pressure to afford crude product (0.100 g) as light-yellow oil. Column chromatography on silica gel with hexanes−ethyl acetate (98:2) as eluant afforded *cis*- and *trans*-**7** (0.061 g, 57%) as a light-yellow oil.

***trans*-7:** ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.34−7.41 (m, 3H), 7.28−7.34 (m, 2H), 7.20−7.28 (m, 1H), 7.13−7.20 (m, 3H), 3.57 (q, J = 7.2 Hz, 1H), 1.73 (s, 3H), 1.43 (d, J = 7.2 Hz, 3H); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 14.2, 24.2, 45.1, 57.8, 123.9, 125.0, 127.0, 127.3, 128.0, 128.1, 128.6, 141.6, 142.3, 144.9, 220.0; MS, *m/z* (I) 236 (44) (M^{+}), 221 (68), 208 (7), 193 (77), 178 (100), 165 (33), 152 (13), 128 (14), 103 (41), 89 (23), 77 (32), 63 (14), 51 (19); IR (neat) 3063, 2968, 2926, 2869, 1749, 1597, 1447, 1373, 1290, 1151, 1075, 1026, 964, 909, 731, 697 cm^{-1}; HRMS (EI) *m/z* calcd for C$_{17}$H$_{16}$O 236.1201, found 236.1204.

***cis*-7:** ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.34−7.41 (m, 3H), 7.28−7.34 (m, 2H), 7.20−7.28 (m, 1H), 7.13−7.20 (m, 3H), 3.59 (q, J = 7.8 Hz, 1H), 1.74 (s, 3H), 1.36 (d, J = 7.8 Hz, 3H); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 17.6, 24.9, 46.4, 57.9, 124.2, 125.2, 126.6, 126.7, 126.9, 128.0, 128.5, 141.8, 143.0, 145.8, 220.0.

A total of 15 rather than the expected 17 signals in the ^{13}C NMR spectrum of indanone *trans*-**7** were observed. The reason for that is an overlap of two signals of ortho-carbons of the aromatic ring (at the C1 carbon of the indanone ring) at 126.7 ppm as well as two signals of meta-carbons at 128.7 ppm (see the Supporting Information).

We believe that this apparent mismatch is a common phenomenon for 1-phenyl-2-indanone aromatic systems (see, for example, the previously reported ^{13}C NMR spectrum of 1-phenyl-1,3,3-trimethyl-2-indanone[21]).

Steady-State Photolysis of *trans*-8. A 0.05 M solution of *trans*-**1** in deuterated solvent (C$_6$D$_6$, CD$_3$CN, or CD$_3$OD) was placed in a NMR tube and the tube was capped with a rubber septum. The solution was purged with argon for 15 min. Then the appropriate volume of toluene (0.05 M) was added. The solution was photolyzed for 30 min in a photochemical reactor at 350 nm monitoring by 300 MHz ^{1}H NMR spectroscopy in 2 min intervals (conversion 40%). According to ^{1}H NMR spectra *trans*-**9** was formed with ~77% yield. The solvent was evaporated under reduced pressure to afford *trans*-**9** as a light-yellow oil (~0.010 g).

***trans*-9:** ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 7.43−7.49 (m, 2H), 7.38−7.42 (m, 2H), 7.32−7.37 (m, 4H), 7.23−7.30 (m, 2H), 3.74 (d, J

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[19] (a) Dehmlow, E. V.; Slopianka, M. *Liebigs. Ann. Chem.* **1979**, 572−593. (b) Baigrie, L. M.; Seiklay, H. R.; Tidwell, T. T. *J. Am. Chem. Soc.* **1985**, *107*, 5391.

[20] Fedorov, A. V.; Danilov, E. O.; Merzlikine, A. G.; Rodgers, M. A. J.; Neckers, D. C. *J. Phys. Chem. A* **2003**, *107*, 3208.

[21] Korth, H. G.; Sustmann, R.; Lommes, P.; Paul, T.; Ernst, A.; de Groot, H.; Hughes, L.; Ingold, K. U. *J. Am. Chem. Soc.* **1994**, *116*, 2767.

= 3.0 Hz, 1H), 1,36 (d, $J = 3.0$ Hz, 1H), 1.27 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 20.3, 26.7, 33.4, 35.6, 63.2, 126.4, 128.7, 128.8, 129.2, 129.4, 131.0, 141.6, 144.6; MS, *m*/*z* (I) 238 (17) (M^+), 220 (7), 205 (9), 178 (10), 145 (8), 129 (24), 117 (18), 105 (100), 91 (65), 77 (38), 65 (8), 51 (14); HRMS (EI) *m*/*z* calcd for $C_{17}H_{18}O$ 238.1358, found 238.1359.

Formation of 2-phenylpropionaldehyde (fragmentation product, ca. 10%) was observed in the ^{1}H NMR spectrum of irradiated solution. The ^{1}H NMR spectrum of 2-phenylpropionaldehyde was identified by comparison of its ^{1}H NMR spectrum to the previously reported spectrum.[22] Formation of styrene was confirmed by GC/MS with use of an authentic sample.

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Supporting Information Available: Kinetic traces, calculated IR spectra of photochemical products and intermediates, ^{1}H and ^{13}C NMR spectra of photochemical products. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Blankespoor, R. L.; Smart, R. P.; Batts, E. D.; Kiste, A. A.; Lew, R. E.; Van der Vliet, M. E. *J. Org. Chem.* **1995**, *60*, 6852.