The photochemistry of *trans*-1,4,4,4-tetraphenylbut-2-en-1-one: A highly efficient aryl migration (type B) enone photorearrangement

John R. Scheffer and Kodumuru Vishnumurthy

Abstract: Photolysis of *trans*-1,4,4,4-tetraphenylbut-2-en-1-one (**3**) in acetonitrile or benzene leads to *trans–cis* isomerization (**7**) along with rearrangement to *trans*-1-benzoyl-2,2,3-triphenylcyclopropane (**8**). Formation of the latter product represents a new example of the aryl migration (type B) enone photorearrangement reaction first reported by Zimmerman and co-workers for 4,4-diphenylcyclohex-2-en-1-one (**1**). The quantum yield in the case of enone **3** (0.4) is approximately 10 times greater than that for 4,4,-diphenylcyclohex-2-en-1-one, a result that is ascribed to steric acceleration of phenyl migration from the triphenylmethyl group plus greater resonance stabilization of the intermediate biradical.

Key words: photochemistry, mechanism, rearrangement, aryl migration, enone, di-π-methane.

Résumé : La photolyse de la *trans*-1,4,4,4-tétraphénylbut-2-én-1-one (**3**) dans l'acétonitrile ou le benzène conduit à une isomérisation *trans–cis* (**7**) ainsi qu'à un réarrangement en *trans*-1-benzoyl-2,3,3-triphénylcyclopropane (**8**). La formation de ce dernier produit représente un nouvel exemple de réaction de photoréarrangement d'énone avec migration d'aryle (type B) qui avait été observé pour la première fois par Zimmerman et ses collaborateurs pour la 4,4-diphénylcyclohex-2-én-1-one (**1**). Le rendement quantique dans le cas de l'énone **3** (0,4) est approximativement dix fois plus grand que celui observé avec la 4,4-diphénylcyclohex-2-én-1-one; on attribue cette différence à l'accélération stérique associée à la migration du phényle à partir du groupe triphénylméthyle ainsi qu'à la plus grande stabilisation par résonance du biradical intermédiaire.

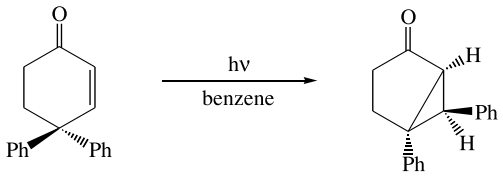
Mots clés : photochimie, mécanisme, réarrangement, migration d'un groupe aryle, énone, di-π-méthane.

[Traduit par la Rédaction]

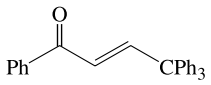
Introduction

Many of the principles of organic photochemistry with which we are familiar today rest on early studies of the light-induced behavior of enones and dienones (1). As an example, consider the case of 4,4-diphenylcyclohex-2-en-1-one (**1**) (eq. [1]), whose photochemistry was first reported by Zimmerman and Wilson (2) in 1964 and subsequently investigated in more detail by Zimmerman and Hancock (3) in 1968. In these studies, irradiation of ketone **1** in solution was shown to afford *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**2**) in rather low quantum efficiency ($\Phi = 0.043$) but excellent chemical yield; trace amounts of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one and 3,4-diphenylcyclohex-2-en-1-one were also formed. Formally a di-π-methane process involving the enone double bond and a double bond on one of the phenyl groups, the formation of photoproduct **2** takes place in the triplet state via a 1,2-phenyl shift accompanied by cyclopropane ring closure. Subsequent studies by the Zimmerman group used the aryl migration cyclohexenone photorearrangement reaction to investigate the relative excited-state migratory aptitudes of aryl groups bearing electron-donating and electron-withdrawing substituents (4).

[1]



1 **2**



3

In seeking variations of the aryl migration enone photorearrangement for the purpose of investigating asymmetric induction in organic photochemical reactions, we chose *trans*-1,4,4,4-tetraphenylbut-2-en-1-one (**3**, eq. [1]) as a potential target molecule. This choice is attractive from several points of view. For one, we anticipated that modification of the benzoyl group to accept ionic chiral auxiliaries (5) would be relatively easy. A second, unrelated motivation was that preparation of analogs of enone **3** in which the

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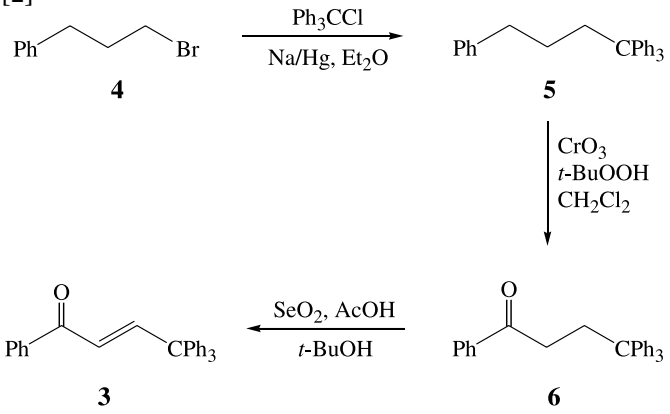
three terminal aryl groups are, for example, phenyl, *p*-methoxyphenyl, and *p*-cyanophenyl, offers the possibility of investigating the relative excited-state migratory aptitude of three aryl groups simultaneously, rather than only two at a time as in the case of cyclic enones. In the present article we outline the synthesis of the parent compound (**3**) and describe its basic photochemical behavior in solution.

Results

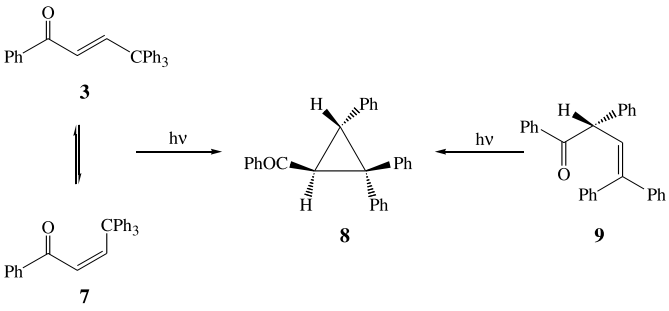
The synthesis of enone **3** was accomplished in straightforward fashion through the known intermediates **5** and **6** (6) (eq. [2]). The final step, selenium dioxide oxidation of ketone **6**, proceeded in 94% overall yield to afford the target enone **3** as a colorless crystalline solid, mp 133–136°C. The assignment of *trans* stereochemistry to enone **3** followed from its proton NMR spectrum, which showed the vinyl hydrogens as doublets at 8.00 and 6.67 ppm with a 15.6 Hz coupling constant between them. By way of contrast, the *cis* isomer of enone **3** (i.e., compound **7**, eq. [3]), which could be isolated in small amounts when **3** was irradiated for relatively short periods of time (vide infra), exhibited an NMR spectrum in which the vinyl doublets appeared at 6.79 and 6.32 ppm with a mutual coupling constant of 12 Hz.

The photochemistry of enone **3** was examined in both benzene and acetontrile solution and the progress of the reaction monitored by gas chromatography. This showed the formation of two photoproducts, subsequently shown to be *cis*-enone **7** and *trans*-1-benzoyl-2,2,3-triphenylcyclopropane (**8**) (eq. [3]). Photolysis was stopped when GC analysis indicated the complete disappearance of enone **3**, at which point the **7**:**8** ratio was approximately 1:3; chromatography of this reaction mixture allowed small amounts of *cis*-enone **7** to be isolated and characterized. Continuing the photolysis until no further enone **7** could be detected by GC analysis (ca. 2 h) and subsequent silica gel column chromatograpy allowed cyclopropyl ketone **8** to be isolated in 96% yield. The structure and *trans* stereochemistry of photoproduct **8** were assigned on the basis of a comparison of its mp and spectroscopic properties with those reported in the literature for the same compound prepared via the oxadi-π-methane photorearrangement of β,γ-unsaturated ketone **9** (eq. [3]) (7). The quantum yield for formation of photoproduct **8** from enone **3** in benzene, extrapolated to 0% conversion, was found to be 0.4 (valerophenone actinometry). Although sensitization–quenching studies were not carried out, given the high efficiency with which phenyl ketones form triplets it seems virtually certain that the photorearrangement of enone **3** is triplet-mediated.

[2]



[3]

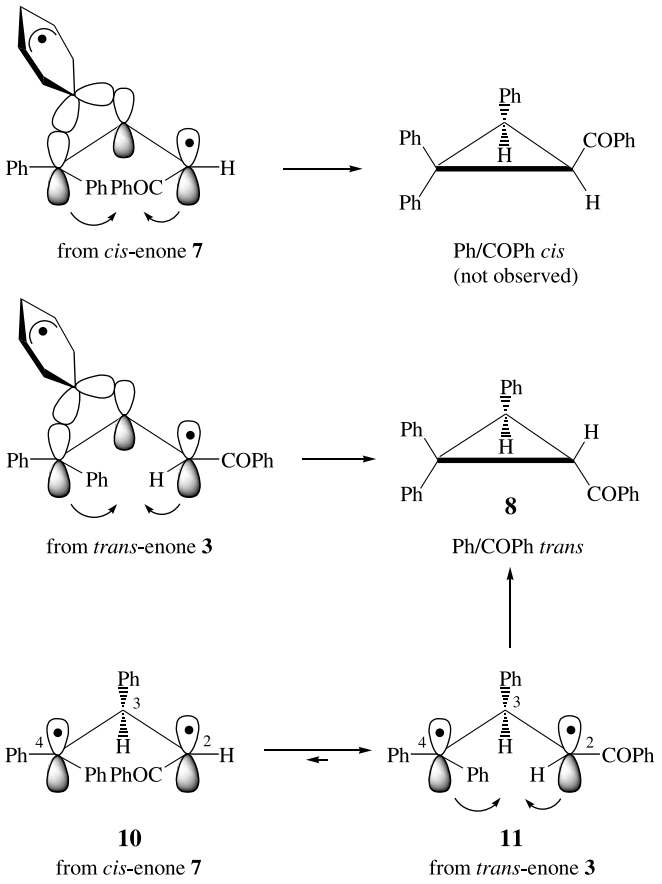


Discussion

While cyclopropyl ketone **8** has the gross structure expected of a straightforward 1,2-phenyl migration photorearrangement of enone **3**, its stereochemistry differs from that of the major product **2** formed in the photolysis of 4,4-diphenylcyclohex-2-en-1-one. In the latter case, the migrating phenyl group ends up *cis* to the carbonyl group, whereas in ketone **8** there is a *trans* relationship between these two moieties. Both results are consistent with the concerted mechanism proposed by Zimmerman and Hancock (3) in which phenyl migration is synchronous with cyclopropane ring formation. As depicted in eq. [4], this mechanism predicts that *cis*-enones (e.g., **1** and **7**) will form products in which the migrating group (Ar) and the C=O group are *cis* to one another (e.g., **2**), and that *trans*-enones (e.g., **3**) will lead to products having a *trans*-Ar – C=O relationship (e.g., **8**). There is a problem with this picture, however, in that independent photolysis of *cis*-enone **7** did not form the expected *cis*-Ar – C=O diastereomer; only photoproduct **8** was observed. This indicates that either the concerted photorearrangement of *cis*-enone **7** is slower than its isomerization to *trans*-enone **3** (no **3** could be detected, however), or that both enones rearrange by a non-concerted mechanism through a common, conformationally equilibrated intermediate such as **11** (eq. [4]) in which ring closure with clockwise rotation about the C-2—C-3 bond is favored, leading to photoproduct **8**.[2] Zimmerman and Hancock (3) also concluded that a non-concerted mechanism is capable of rationalizing the stereochemical course of the photorearrangement of cyclohexenone **1**. At the moment, therefore, a definitive choice between the concerted and non-

[2] Biradical **11** is expected to be more stable than its conformer **10** in which the benzoyl group interferes with a phenyl group on C-4. Clockwise rotation around C-2—C-3 during ring closure of biradical **11** is favored over counterclockwise rotation, since the latter pathway leads to increased nonbonded interactions between the benzoyl group and the phenyl group on C-3.

[4]



concerted pathway cannot be made, although it could be argued that the triplet nature of the photorearrangement favors the latter.

A final point of discussion concerns the 10-fold higher quantum yield for the photorearrangement of acyclic enone **3** compared with that of cyclic enone **1**. Although quantum yields are not always a reflection of rates of reaction, it is tempting to equate the higher quantum yield for the photorearrangement of enone **3** with relief of steric crowding in the triphenylmethyl group as well as greater resonance stabilization of the intermediate biradical **10**.

Work is continuing in our laboratory on developing methods for carrying out the aryl migration enone photorearrangement enantioselectively as well as synthesizing triarylmethane analogs of enone **3** for use in excited-state migratory aptitude studies.

Experimental

Instrumentation and general procedures

Commercial spectral grade solvents were used for photochemical experiments unless otherwise noted. Infrared spectra were recorded on a Perkin-Elmer 1710 Fourier transform spectrometer. Solid samples were ground in KBr (1–5%) and liquid samples were run neat as thin films. Melting points were determined on a Fisher-Johns hot stage apparatus and are uncorrected. ^{1}H NMR spectra were recorded in deuterated solvents as noted on a Varian AV-300 (300 MHz) instrument. ^{13}C NMR spectra were run on the same instrument at 75 MHz under broadband ^{1}H decoupling. Low- and high-resolution mass spectra were obtained from a Kratos MS 50 instrument using electron impact (EI) ionization at 70 eV or the chemical ionization (CI) method; intensities of the ions are given in parentheses. Ultraviolet spectra were recorded on a PerkinElmer Lambda-4B spectrophotometer in the solvent indicated. Gas chromatographic analyses were performed on a Hewlett-Packard HP 5890 instrument.

1,1,1,4-Tetraphenylbutane (5)

The known compound **5** (6) was synthesized by a modified procedure of Brook and Pierce (6) (8). Mercury (36.5 g, 182 mmol) was placed in a 100 mL two-necked round-bottomed flask equipped with a magnetic stirrer and a reflux condenser and the system thoroughly flushed with anhydrous nitrogen. Sodium (0.365 g, 15.9 mmol) was carefully added in several small pieces to the mercury under nitrogen with cooling by means of a water bath. A solution of 2.0 g (7.2 mmol) of triphenylmethyl chloride (Aldrich) in 50 mL of anhydrous ether was then added to the sodium amalgam under nitrogen with stirring, whereupon a blood red color developed over a period of approximately 1 h. Stirring was continued for an additional 2 h after which 1.78 g (8.9 mmol) of 3-phenyl-1-bromopropane (**4**) (Aldrich) was added. The red color disappeared immediately and the resulting solution was stirred at room temperature for 4 h. The reaction mixture was worked up by hydrolysis with 20 mL of distilled water followed by extraction with diethyl ether. The ether layers were combined, dried over anhydrous sodium sulphate, and concentrated in vacuo to afford a non-crystalline residue that was subjected to silica gel column chromatography using 2% ethyl acetate in petroleum ether as the eluting solvent. This afforded 1.70 g (53%) of compound **5** as a colorless solid. Recrystallization from ether:petroleum ether (2:1) gave colorless needles, mp 94 to 95°C (lit. (6) mp 92 to 93.5°C).

1,4,4,4-Tetraphenylbutan-1-one (6)

The known compound **6** (6) was prepared using an oxidation procedure of Muzart (9). To a solution of 0.89 g (2.5 mmol) of compound **5** in 4.2 mL of dichloromethane was added 0.074 g (0.74 mmol) of chromium trioxide (Aldrich) and 6.6 mL of a 70% aqueous solution of *tert*-butylperoxide (Aldrich) and the resulting mixture stirred for 36 h at room temperature. The biphasic reaction mixture was worked up by addition of 8 mL of saturated aqueous sodium thiosulphate solution until no longer oxidizing to starch-iodide paper and then extracted with dichloromethane (2 × 15 mL). The combined organic layers were washed with water and brine and then dried over anhydrous magnesium sulphate. Removal of the solvent in vacuo followed by radial chromatography over silica gel (2% ethyl acetate in petroleum ether) afforded 0.7 g (75%) of ketone **6** as a colorless solid. Recrystallization from ethyl acetate gave small prisms, mp 141–143°C (lit. (6) mp 139 to 140.5°C).

trans-*1,4,4,4-Tetraphenylbut-2-en-1-one (3)*

Following an oxidation procedure of Bernstein and Littell (10), a solution of 1.0 g (2.7 mmol) of ketone **6** and 1.2 g (10.8 mmol) of selenium dioxide (Aldrich) in 125 mL of *tert*-butanol and 5.6 mL of glacial acetic acid was refluxed

with stirring for 48 h. The reaction mixture was diluted with 25 mL of ethyl acetate, filtered, and the filtrate washed with water, 10% aqueous sodium hydroxide, water again, brine, and then dried over anhydrous sodium sulphate. Removal of the solvent in vacuo followed by GC analysis of the residue revealed the presence of both ketone **3** and ketone **6** in a 2:1 ratio. This mixture was subjected to a second oxidation identical to the first but on half the scale until GC analysis indicated the complete disappearance of starting material **6**. Workup as before afforded a crude reaction mixture that was subjected to radial chromatography over silica gel (5% ethyl acetate in petroleum ether) to afford 0.94 g (94%) of solid enone **3**. Recrystallization from ethyl acetate:hexane (3:1) gave colorless needles, mp 133–136°C. IR (KBr) (cm^{-1}): 3054, 1667, 1610, 1490, 1445, 1326, 1304, 1291, 1223, 1179, 1033, 1004, 757, 702, 590. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.0 (d, 1H, *J* = 15.6 Hz, vinyl), 7.79–7.76 (m, 2H), 7.51–7.46 (m, 1H), 7.4–7.35 (m, 2H), 7.30–7.19 (m, 9H), 7.09–7.06 (m, 6H), 6.67 (d, 1H, *J* = 15.6 Hz, vinyl). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 190.7, 154.4, 144.4, 137.9, 132.8, 130.1, 129.1, 128.6, 128.1, 126.9, 126.6, 125.5, 61.3. LR-MS (EI) *m*/*z*: 374 (M^+), 269, 191, 165, 105, 91, 77, 51. HR-MS (EI) *m*/*z* calcd. for $C_{28}H_{22}O$: 374.1671; found: 374.1672. Anal. calcd. for $C_{28}H_{22}O$: C 89.80, H 5.93; found: C 89.81, H 5.95.

Photolysis of enone 3

Enone **3** (0.1 g, 0.27 mmol) was dissolved in 30 mL of acetonitrile and the solution purged with nitrogen for 30 min. The solution was then irradiated for 2 h through Pyrex using the output of a Hanovia 450 W medium pressure mercury lamp. GC analysis of an aliquot revealed the complete consumption of starting material and the formation of a single photoproduct. Removal of the solvent in vacuo followed by radial chromatography over silica gel (2% ethyl acetate in petroleum ether) afforded 0.096 g (96%) of photoproduct **8** as a colorless solid. Recrystallization from a mixture of diethyl ether and petroleum ether afforded small prisms, mp 126–128°C (lit. (7) mp 125–127°C). The methine hydrogens of compound **8** exhibited a mutual 6 Hz coupling in the ^{1}H NMR, thus confirming their *trans* relationship (11). When 0.02 g of enone **3** in 15 mL of benzene was irradiated through Pyrex for 1 h, GC analysis indicated the presence of a mixture of *trans*-enone **3**, its *cis* isomer **7**, and cyclopropyl ketone **8** in a 3:10:20 ratio. Photolysis was continued for an additional 15 min until GC analysis showed the complete consumption of starting material **3**. Subsequent removal of solvent in vacuo followed by radial chromatography as before afforded 0.012 g of photoproduct **8** and 0.004 g of *cis*-enone **7**, mp 136–139°C (from ethyl acetate). IR (KBr): 3058, 2974, 1672, 1597, 1581, 1494, 1447, 1226, 1175, 1036, 991, 901, 842, 738, 702. ^{1}H NMR (C_6D_6, 300 MHz) δ: 7.59–7.56 (m, 2H), 7.32–7.29 (m, 6H), 7.12–6.91 (m, 12H), 6.79 (d, 1H, *J* = 12 Hz, vinyl), 6.32 (d, 1H, *J* = 12 Hz, vinyl). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 192.4, 147.4, 145.5, 136.7, 132.7, 130.4, 129.6, 128.6, 128.4, 128.1, 128.0, 127.7, 126.4, 61.7. LR-MS (EI) *m*/*z*: 374 (M^+), 269, 191, 165, 105, 91, 77, 51. HR-MS (EI) *m*/*z* calcd. for $C_{28}H_{22}O$: 374.1671; found: 374.1669. Anal. calcd. for $C_{28}H_{22}O$: C 89.80, H 5.93; found: C 89.78, H 5.97.

Quantum yield determination

The quantum yield for formation of cyclopropyl ketone **8** in benzene was determined using valerophenone actinometry (Φ = 0.33) (12) according to the standard protocol used in our group (13). *n*-Tetradecane and *n*-nonadecane were used as internal standards for the solutions of actinometer and ketone **8**, respectively. Quantum yields were determined at varying conversions and plotted against conversion; the reported quantum yield of 0.4 represents the value extrapolated to 0% conversion.

Acknowledgement

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