Pergamon

Tetrahedron Letters, Vol. 38, No. 24, pp. 4323-4326, 1997

0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)00891-5

# [2+2] Photocycloadditions of cis/*trans*-4-Propenylanisole to $C_{60}$. A Step-Wise Mechanism.

**Georgios Vassilikogiannakis and Michael Orfanopoulos***
Department of Chemistry, University of Crete, Iraklion, 71409, Greece.

***Abstract:*** *The photocycloaddition of cis- and trans-1-(p-methoxyphenyl)-1-propene to $C_{60}$ gives only the trans [2+2] adducts. Irradiation of the isolated adduct gives a mixture of cis- and trans-1-(p-methoxyphenyl)-1-propene and $C_{60}$ cycloreversion products. These results exclude a concerted addition and are consonant with a two step mechanism.* © 1997 Elsevier Science Ltd.

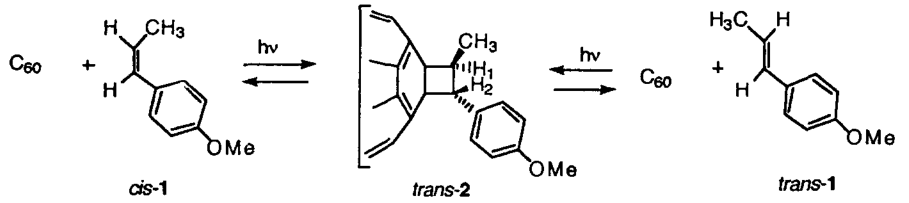
Fullerene $C_{60}$ is an electrophile and undergoes a large variety of chemical reactions. The preparation of synthetically useful monoadducts of $C_{60}$, continues to be the prime effort in the area of fullerene chemistry.[1] Many [4+2][2,3] and [3+2][4-6] cycloadditions have been reported and their monoadducts have been well characterized. However the [2+2] cycloadditions are less common and only a few examples with electron rich unsaturated molecules have been reported.[7,8] Furthermore, [2+2] photocycloaddition of electron poor alkenes (cycloenones) to $C_{60}$ have been also reported recently, however in this case the reaction proceeds through the excited state of the enone[9]. Although most of the efforts have been focused mainly on [2+2] product isolation and characterization,[7-9] little is known about the mechanism of this reaction.[8c,9a]

We report here the stereochemistry of the products formed in the photocycloadditions of $C_{60}$ with *cis* and *trans*-4-propenylanisole (*cis*-**1** and *trans*-**1**). These results may shed more light on the mechanism of the [2+2] cycloadditions.

A mixture of $C_{60}$ and 200-fold excess of *trans*-**1**[10] or *cis*-**1**[10] (in separate experiments) in deoxygenated toluene, when heated for 10 hrs at reflux, without light, gave no products. However, both *cis*-**1** and *trans*-**1** with $C_{60}$, upon 30 minutes irradiation at $\lambda$>500 nm (with a Xenon lamp Variac Eimac Cermax 300W) at ambient temperature, gave a 40% of the corresponding [2+2] adduct -monitored by HPLC- based on the recovered $C_{60}$. This is the first example of a stable [2+2] monoadduct derived from a moderate electron rich alkene with $C_{60}$. It is interesting to note that only electron rich alkynes and alkenes such as ynamines and tetraalkoxyethylene react in a [2+2] mode with $C_{60}$, while several other electron rich alkynes, including ethyl ethynyl ether, bis(ethylthio)ethyne and the alkene tetrakis(morpholino)ethylene, did not react with $C_{60}$ either thermally or photochemically.[8c]

The [2+2] adduct which is stable at room temperature, was purified by flash column chromatography (toluene/hexane: 2/1) and characterized by $^1H$ NMR (Figure 1) and FAB MS. The expected M+1 ion at 869 was not found, instead ions at 720 and 148 were detected, corresponding to cycloreversion fragments $C_{60}$ and 4-propenylanisole. It is likely that fullerene adducts fragment under MS conditions.

Both photocycloadditions of *trans*-**1** and *cis*-**1** with $C_{60}$, gave identical cycloadducts. Analysis of the $^1H$ NMR spectrum shows that only one stereoisomer is formed with *trans* stereochemistry in the $C_{60}$-fused cyclobutyl ring.



Only one doublet at 4.98 ppm due to the resonance of $H_2$ hydrogen next to the phenyl ring, only one methoxy peak at 3.62 ppm and only one methyl doublet at 2.00 ppm appear in the $^1H$ NMR spectrum (Figure 1). If a mixture of stereoadducts had been formed, there should have been expected more hydrogen resonances. Furthermore, the coupling constant between $H_1$ and $H_2$ protons (Figure 1) is 8.8 Hz, consistent with a *trans* configuration.[12] These results indicate that from *cis*-**1** or *trans*-**1**, the most thermodynamically stable *trans* -**2** stereoadduct was formed exclusively.

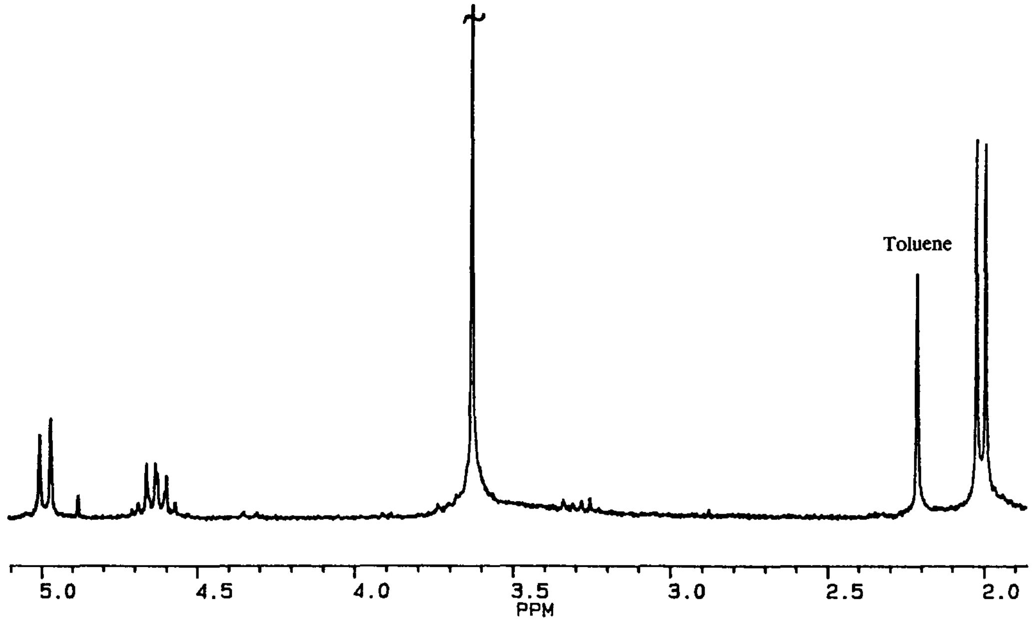
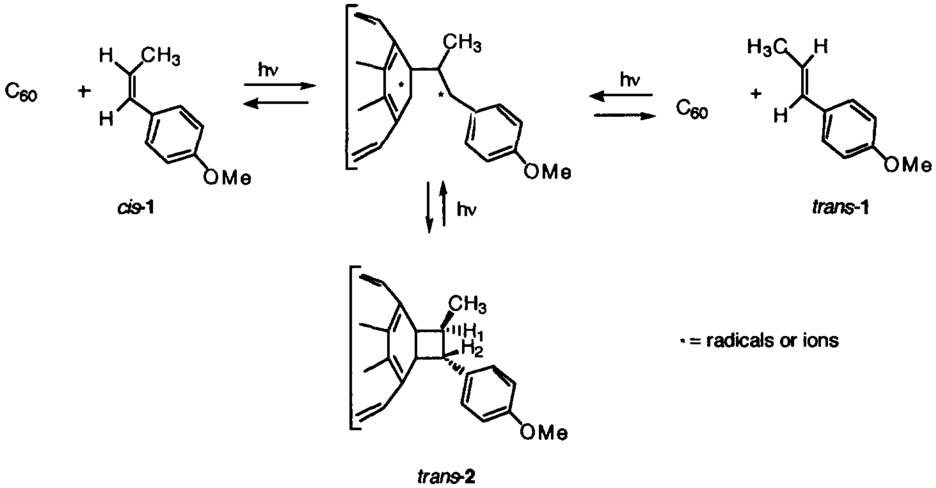


**Figure 1.** $^1H$ NMR spectrum of [2+2] adduct *trans*-**2**, from $C_{60}$ and *cis*-**1** or *trans*-**1**

A possible mechanism that could account for the formation of only one [2+2] stereoadduct, *trans*-**2**, regardless to the stereochemistry (*cis* or *trans*) of the initial arylalkene, includes the formation of a common dipolar or diradical intermediate between the triplet excited state[13] of $C_{60}$ and the arylalkene. Subsequent fast rotation of the aryl moiety around the former double bond, leads exclusively to the most thermodynamicaly stable *trans* [2+2] adduct (scheme 1). Gas chromatography analysis of the unreacted *trans*-**1** arylalkene showed variable amounts of *cis*-**1** depending on the irradiation time. Furthermore, irradiation of the isolated *trans*-**2** adduct, gave 90% *trans*-**1**, 10% *cis*-**1** and $C_{60}$ cycloreversion products. These results eliminate a concerted mechanism because in that case the photocycloreversion reaction is expected to give the *trans*-**1** as the only product. These results are consonant with a dipolar or a diradical intermediate. Similarly, cycloreversion products from $C_{60}$ and tetraalkoxyethylene adducts were also observed recently by Foote and coworkers. They proposed that cycloreversion undergoes through the triplet excited state of the adduct, because rubrene and oxygen efficiently inhibit photocycloreversion. However these results do not exclude an electron transfer or charge transfer mechanism with loss of stereochemical integrity of the initial alkenes in the first step. An electron transfer or charge transfer mechanism has been also reported recently for the [2+2] photocycloaddition of electron rich ynamines with $C_{60}$.

**Scheme 1**



We conclude that the photochemical [2+2] cycloaddition of *cis*-**1** and *trans*-**1** to $C_{60}$ is stereospecific for the most thermodynamically stable cycloadduct and occurs by the involvement of a common dipolar or diradical intermediate.

## Acknowledgements

This work was supported by the Greek General Secretariat of Research and Technology (ΥΠΕΡ grant No 408 1994) and NATO (Grant No. 931419). The financial support of M & S Hourdakis SA. is also acknowledged.

**References and notes.**

1. Hirsch, A. *Synthesis* **1995**, 895-913.
2. a) Kräutler, B.; Puchberger, M. *Helv. Chim. Acta* **1993**, 76, 1626. b) Rubin, Y.; Khan, S.; Freedberg, D. I.; Yeretzian, C. *J. Am. Chem. Soc.* **1993**, 115, 344. c) Khan, S. I.; Oliver, A. M.; Paddon-Row, M. N.; Rubin, Y. *J. Am. Chem. Soc.* **1993**, 115, 4919.
3. a) Gügel, A.; Kraus, A.; Spikermann, J.; Belik, P.; Müllen, K. *Angew. Chem. Int. Ed. Engl.* **1994**, 33, 559. b) Zhang, X.; Foote, C. S. *J. Org. Chem.* **1994**, 59, 5235.
4. a) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, Ö. *Science* **1991**, 254, 1186. b) Prato, M ; Suzuki, T.; Wudl, F.; Lucchini, V.; Maggini, M. *J. Am. Chem. Soc.* **1993**, 115, 7876. c) Isaacs, L.; Diederich, F. *Helv. Chem. Acta* **1993**, 76, 2454. d) Diederich, F.; Isaacs, L.; Philp, D. *J. Chem. Soc., Perkin. Trans. 1* **1994**, 391.
5. a) Isaacs, L.; Wehrsig, A.; Diederich, F. *Helv. Chim. Acta* **1993**, 76, 1231. b) Prato, M.; Li, Q.; Wudl, F.; Lucchini, V. *J. Am. Chem. Soc.* **1993**, 115, 1148. c) Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, 115, 9798.
6. a) Vasella, A.; Uhlmann, P.; Waldraff, C. A.; Diederich, F.; Thilgen, C. *Angew. Chem. Int. Ed. Engl.* **1992**, 31, 1388. b) Anderson, H. L.; Faust, R.; Rubin, Y.; Diederich, F. *Angew. Chem. Int. Ed. Engl.* **1994**, 33, 1366.
7. Hoke II, S. H.; Molstad, J.; Dilattato, D.; Jay, M. J.; Carlson, D.; Kahr, B.; Cooks, R. G. *J. Org. Chem.* **1992**, 57, 5069.
8. a) Zhang, X.; Romero, A.; Foote, C. S. *J. Am. Chem. Soc.* **1993**, 115, 11024. b) Zhang, X.; Romero, A.; Foote, C. S. *J. Am. Chem. Soc.* **1995**, 117, 4271. c) Zhang, X.; Fan, A.; Foote, C. S. *J. Org. Chem.* **1996**, 61, 5456.
9. a) Wilson, S. R.; Kaprinidis, N.; Wu, Y.; Schuster, D. I. *J. Am. Chem. Soc.* **1993**, 115, 8495. b) Wilson, S. R.; Wu, Y.; Kaprinidis, N.; Schuster, D. I. *J. Org. Chem.* **1993**, 58, 6548.
10. *trans*-1-(p-Methoxyphenyl)-1-propene (anethol) is commercially available. *cis*-(p-Methoxyphenyl)-1-propene was prepared by the following method: p-methoxyphenylacetylene was prepared in good yield from p-methoxybenzaldehyde by known method.[11] The lithium salt of p-methoxyphenylacetylene was prepared by the addition of n-Buli to p-methoxyphenyl acetylene. Addition of $CH_3I$ to the above salt gave the 1-(p-methoxyphenyl)-1-propyne in good yield. Subsequent hydrogenation of 1-(p-methoxyphenyl)-1-propyne with Lindlar catalyst gave the *cis*-(p-methoxyphenyl)-1-propene in greater than 95% geometrical purity. $^1H$ NMR, ($CDCl_3$), $\delta$ 1.89 (dd, $J_1$=7.2 Hz, $J_2$=1.7 Hz, 3H), 3.81 (s, 3H), 5.71 (dq, $J_1$=7.2Hz, $J_2$=11.5 Hz, 1H), 6.38 (J=11.5 Hz, 1H), 7.06 (AA' MM,' $J_1$=11.4 Hz, $J_2$=3.2 Hz, $J_3$=2.7 Hz, 4H).
11. Matsumoto, M.; Kuroda K. *Tetrahedron Lett.* **1980**, 21, 4021.
12. The benzylic hydrogen in the cycloadduct derived from p-methoxyphenyl ethylene and $C_{60}$ showed two coupling constants, the *trans* $J_{trans}$=8.3 Hz and the *cis* $J_{cis}$=10.4 Hz. (unpublished results).
13. Previous results have demonstrated that the triplet excited state of $C_{60}$ has a reduction pontential near 0.98 eV (36 Kcal/mol) VS SCE, and is formed with a quantum yield of nearly unity: Arbogast, J. W.; Darmanyan, A. O.; Foote, C. S.; Rubin, Y.; Diedrich, F. N.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L.; *J. Phys. Chem.* **1991**, 95, 11.

(*Received in UK* 22 *April* 1997; *accepted* 2 *May* 1997)