Pergamon

Tetrahedron Letters 40 (1999) 5087–5090

TETRAHEDRON
LETTERS

Cycloaddition reactions of carbonyl ylides to [60] fullerene: Synthesis of novel C_{60} derivatives[#]

Vijay Nair,*[a] D. Sethumadhavan,[a] K. C. Sheela,[a] and Guenter K. Eigendorf.[b]

a. Organic Chemistry Division, Regional Research Laboratory, (CSIR), Trivandrum-695 019, INDIA
b. Department of Chemistry, The University of British Columbia, Vancouver, V6T 1Z1, CANADA

Received 16 March 1999; accepted 13 May 1999

***Abstract*:**

1,3-Dipolar cycloaddition reactions of carbonyl ylides with [60] fullerene afforded novel cycloadducts.

Key words: Cycloaddition; [60] fullerene; carbonyl ylides.

Ever since the discovery of fullerenes by Kroto, Smalley and Curl [1] there has been enormous interest in the synthesis of their derivatives suitable for physicochemical and biological investigations. Although a number of protocols have been devised, to date, cycloadditions [2] are among the most important methods for the derivatization of [60] fullerene. A number of 1,3-dipoles [3] ranging from diazomethane to thiocarbonyl ylides have been shown to participate in cycloaddition to [60] fullerene with varying efficiency. In all such reactions C_{60} serves as a dipolarophile leading to heterocyclic compounds. Carbonyl ylides have been shown to be versatile dipoles by Padwa and others [4]. In the context of our recent interest in the cycloaddition of carbonyl ylides to electrophilic systems [5], we were intrigued by the possibility of dipolar cycloaddition of carbonyl ylides to C_{60}, leading to novel

---

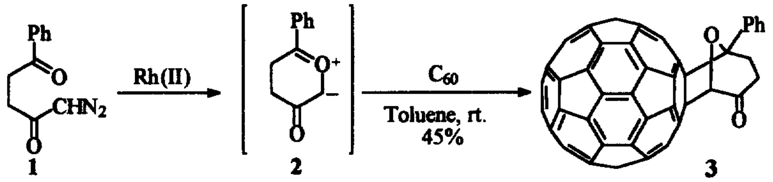
*To whom correspondence should be addressed. E-mail: gvn@csrrltrd.ren.nic.in , Fax: 91-471-491712

[#] This paper is dedicated with best personal regards to Professor Dr. Armin de Meijere on the occasion of his 60th birthday.

PII: S0040-4039(99)00988-0

derivatives of the latter and therefore some work was undertaken in this area. Except for an isolated report [6] on the addition of TCNE oxide serving as a carbonyl ylide, there has been no work in this area. The reactivity of six membered carbonyl ylides towards C_{60} was of special interest and the preliminary results of our studies showing the formation of novel [3+2] adducts from carbonyl ylides and C_{60} are presented here.

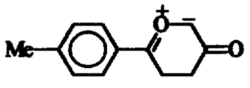
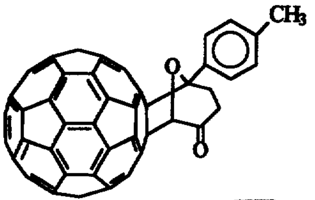
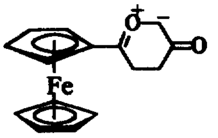
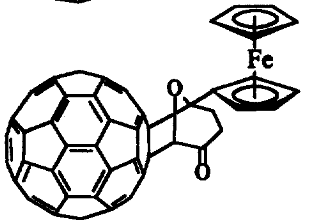
Our studies were initiated with Rh(II) catalyzed transformation of 1-diazo-5-phenyl-2,5-pentanedione **1** to the ylide **2** and the cycloaddition of the latter to C_{60}. This reaction proceeded smoothly to afford the product **3** in 45 % isolated yield (86 % based on recovered C_{60}) as shown in Scheme1.



Scheme 1

The product was purified [7] by silica gel column chromatography and characterized by spectral analysis [8]. The IR spectrum of **3** showed carbonyl absorption at 1732 cm^{-1} and in its ^1H NMR spectrum, the bridgehead proton resonated at δ 6.03 as a singlet. In the ^{13}C NMR spectrum of the same, the characteristic *sp*^{3} carbons at the 6,6 junction on the [60] fullerene resonated at δ 75.27 and 79.43. The two bridgehead carbons resonated at δ 92.26 and 92.15. The signal at δ 92.15 is due to the bridgehead methine carbon. These assignments were confirmed by DEPT studies. In the DEPT-135 spectrum of **3**, peaks at δ 92.26, 79.43 and 75.27 disappeared. The mass spectrum showing a molecular ion peak at 894 and the HRMS supported the assigned structure. The experiments were repeated with two other carbonyl ylides and in these cases also the reaction proceeded smoothly to afford the products. The results are summarized in Table1.

Table1. Cycloaddition of carbonyl ylides with [60]- fullerene.

Carbonyl Ylides	Adducts	Yields(%) a (b)
		48 (87)
		40 (85)

a. Isolated yield, b. Based on recovered C_{60}

All reported new compounds were characterized by IR, ^{1}H NMR, ^{13}C NMR, DEPT-135 and high resolution mass spectra.

In conclusion, it has been found that carbonyl ylides undergo facile cycloaddition to [60]-fullerene, leading to novel C_{60} adducts. Further studies aimed at unraveling the chemistry of the adducts are currently being pursued.

ACKNOWLEDGEMENTS

The authors thank Dr. P. Shanmugam and Ms. Soumini Mathew for the NMR spectra. DSM and KCS thank the CSIR, New Delhi for research fellowships. Thanks are also due to Professors M .V. George, G. Mehta, and E. Nakamura for the C_{60} used in our experiments. Useful discussion with Mr. V. Biju is acknowledged.

REFERENCES

[1] Kroto HW, Heath JR, O'Brien SC, Curl RF, Smalley RE. *Nature*. 1985; *318*: 162.

[2] Hirsh A. *The Chemistry of the Fullerenes*. Georg Thieme Verlag, Stuttgart: 1994; 79.

[3] (a) Suzuki T, Li QC, Khemani KC, Wudl F. *J. Am. Chem. Soc.* 1992; 114: 7300. (b) Pellicciari R., Annibali D, Costantino G, Marinozzi M, Natalini B *Synlett.* 1997; 1198. (c) Prato M, Li QC, Wudl F, Lucchini V. *J. Am. Chem. Soc.* 1993; *115*: 1148. (d).Maggini M, Prato M *Acc. Chem. Res.* 1998; *31*: 519. (e) Meier MS, Poplawska M *J. Org. Chem.* 1993; *58*: 4524. (f) Ovcharenko AA, Chertkov VA., Karchava AV, Yurovskaya MA. *Tetrahedron Lett.* 1997; *38*: 6933. (g) Muthu S.,

Maruthamuthu P, Ragunathan R, Rao PV, Mathews C K. *Tetrahedron Lett.* **1994**; *35*: 1763. (h) Ohno M, Yashiro A, Eguchi S. *Synlett.* **1996**; 815. (i) Gonzalez R, Knight B, Wudl F, Padwa A. *J. Org. Chem.* **1994**; 59: 7949. (j) Ohno M, Ishida H. *Tetrahedron Lett.* **1999**;*40*: 1543.

[4] Padwa A, Weingarten M D. *Chem. Rev.* **1996**; *96*: 223.

[5] Nair V, Sheela KC, Radhakrishnan KV, Rath NP. *Tetrahedron Lett.* **1998**; *39*; 5627.

[6] Jagerovic N, Elguero J, Aubagnac JL. *J. Chem. Soc., Perkin Trans.1.* **1996**; 499.

[7] Typical Experimental Procedure: C_{60} (36 mg, 0.05 mmol) was dissolved in 35 ml of dry toluene by sonication. 1-Diazo-5-phenyl-2,5-pentanedione in 10 ml toluene (10 mg,.0.05 mmol) was taken in a pressure equalizing funnel. A catalytic amount of $Rh_2(OAc)_4$ was added to the C_{60} solution and the diazo compound was added slowly over a period of 150 minutes with constant stirring under an argon atmosphere. After the addition the reaction mixture was further stirred for one hour. The solvent was removed under reduced pressure and the contents were charged on a silica gel (100-200 mesh) column and eluted with toluene: hexane (1:4) mixture. The unreacted C_{60} was eluted first and then eluting with toluene: hexane (1:1) afforded the product (brown solid, 20.1 mg). The product was dissolved in the minimum amount (3 ml) of dry chloroform and dry methanol was added dropwise to it. The precipitated product was purified further by washing three time with dry methanol.

[8] Spectral data for illustrative example 3. UV-Vis ($CHCl_3$) λ_{max} (nm) 256, 314, 430. FT-IR [KBr (cm^{1})] 3058, 2959, 2859, 1732, 1434, 1215, 1062, 1029, 883, 751, 691, 525. ^{1}H NMR [300 MHz, $CDCl_3$-CS_2 (1:1)] δ 3.10-3.22 (m, 2H), 3.61-3.87 (m, 2H), 6.03 (s, 1H), 7.25-7.92 (m, 5H). ^{13}C NMR [75MHz, $CDCl_3$-CS_2 (1:1)] δ 33.62, 36.52, 75.27, 79.43, 92.15, 92.26, 125.52, 128.27, 128.66, 134.44, 135.68, 137.61, 139.05, 140.08, 140.25, 140.35, 141.40, 141.58, 141.67, 141.87, 141.90, 142, 142.02, 142.18, 142.26, 142.30, 142.61, 142.72, 142.87, 143.03, 143.15, 144.06, 144.24, 144.38, 144.49, 145, 145.17, 145.25, 145.43, 145.51, 145.61, 145.71, 145.81, 145.92, 146.05, 146.13, 146.30, 146.41, 146.57, 147.08, 147.18, 149.19, 151.11, 153.26, 153.71, 202.23. Due to accidental overlapping the remaining thirteen peaks could not be seen. DEPT-135 [75MHz, $CDCl_3$-CS_2 (1:1)] δ 33.62, 36.52, Negative. δ 92.2, 125.6, 128.4, 128.82, Positive..

EI MS (*m/z*) 894. 06765 (M$^+$), 720 (C_{60}).