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Cycloadditions to [60]Fullerene Using Microwave Irradiation : A Convenient and Expeditious Procedure.

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Abstract : Several Diels-Alder and 1,3-dipolar cycloadditions to C_{60} were performed, under microwave irradiation, in a modified domestic microwave oven and a focused microwave reactor. Reactions proceed within minutes to afford the respective cycloadducts in similar or increased yields related to the described methods by conventional heating. This methodology simplifies the procedure and overcomes the drawbacks resulting from the long reaction times required under classical heating conditions.

INTRODUCTION

Although the first compact microwave ovens were available in the 1950s, only recently has this technique been applied in the chemical laboratory for a wide variety of purposes such as digestion and extraction of analytical samples,[1] soil decontamination,[2] vitrification of radioactive waste,[3] polymer technology,[4] ceramics[5] or inorganic synthesis[6]. In 1986, Gedye[7] and Giguere[8] demonstrated that many organic reactions can be conducted rapidly under microwave irradiation; since then, more than 250 papers in this field have appeared, including several recent reviews.[9] Microwave assisted organic synthesis has several advantages over conventional technology: remarkable decreases in the times necessary to carry out reactions (up to 3 orders of magnitude), improved isolated yields of products (when thermal decomposition is associated with the conventionally heated reactions) and, sometimes, effects on chemo[10]-, regio[11]- and stereoselectivity[12] are also achieved.

Since Krätschmer and Huffmann discovered a procedure for preparing bulk quantities of C_{60}[13], the chemistry and derivatization of fullerene continues to attract attention for accessing to derivatives with interesting physical properties and biological activities.[14] Among the suitable procedures for functionalising C_{60}, cycloadditions provide a powerful tool because C_{60} behaves as an electron-deficient olefin with a relatively low lying LUMO. In this context Diels-Alder and 1,3-dipolar cycloadditions have been performed[14b,c] and the conditions for the cycloadduct formation strongly depend on the energy gap between the controlling orbitals; so, frequently necessitating of several hours -or days- under reflux in high boiling point solvents.

RESULTS

Diels-Alder[15] and 1,3-dipolar[16] cycloadditions are easily performed under microwave irradiation. Consequently, it results of interest to investigate the potential of microwave irradiation in the preparation of fullerene derivatives when this type of reactions are involved; in this regard, we have recently described the first application of microwave irradiation to the preparation of a functionalized C_{60}[17]. In this work, we explore the application of microwave irradiation to several other cycloaddition reactions in order to determinate the scope of this technique in the preparation of fullerene derivatives[18].

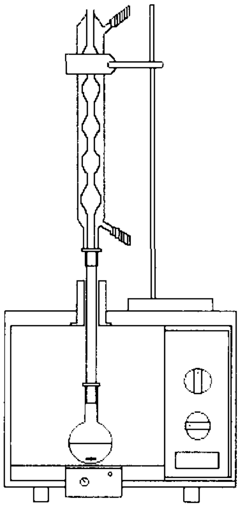


Fig. 1. Modified microwave oven.

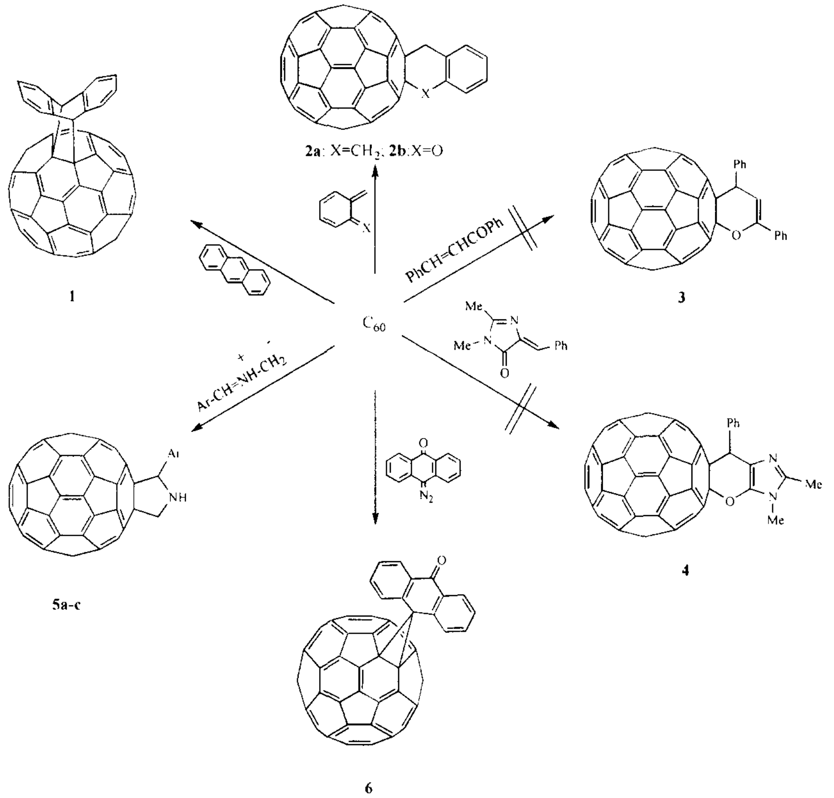
We have used a modified domestic microwave oven (the oven was perforated on the top to accomodate a reflux condenser and a -10 cm- pipe was used to avoid the microwave leakage ; the turnable dish was replaced by a magnetic stirrer as shown in Figure 1 and a focused microwave reactor (Maxidigest MX350). Although better results have been described [19] using the focused microwave reactor, in this kind of reactions we did not find any dependence of the yield with respect to the system employed.

With this aim in view, and in order to compare with conventional heating, we have chosen several well known Diels-Alder reactions of C_{60}: with anthracene,[20] *o*-quinodimethane[17] (generated *in situ* from sultine) and *o*-quinone methide[21] (formed *in situ* from *o*-hydroxybenzyl alcohol) ; we have also tried the hetero-Diels-Alder reaction with chalcone and 4-benzyliden-1,2-dimethyl-2-imidazolin-5-one; among the 1,3-dipolar cycloadditions we choose arylazomethine ylides[22] (prepared *in situ* from the corresponding aldehyde and glycine), and diazoanthrone as reactants. [23] Results are collected in Table 1.

The facile reaction of C_{60} with anthracene, extensively studied,[20] has been reported to form, under thermal conditions, multiply-substituted cycloadducts which undergo cycloreversion to the starting materials. Irradiation for 15 min. of C_{60} and 10 equiv. of anthracene in toluene as solvent using the modified microwave oven (method A) at 800 W produced cycloadduct **1** in 35% yield; this result improves the yields obtained by conventional heating (13%[20a], reflux, toluene, three days; 25%[20b], reflux, benzene, 12 h.) and shows how this methodology not only reduces, as expected, the reaction times to minutes, but yields can also be improved; this fact is probably due, to overcoming the reversion of the cycloaddition in the shorter period of time needed for the irradiated reaction.

Reaction with *o*-quinodimethane, formed from sultine, by method A for 20 min. at 800 W, affords cycloadduct **2a** in higher yield (39%) in comparison with thermal conditions (30% after 18 h., refluxing).[17] Longer reaction times result in lower yields due to the formation of polyadducts.

The reaction of C_{60} with *o*-quinone methide, prepared from o-hydroxybenzyl alcohol, was performed by method A (see experimental), at 800 W, yielding **2b** in only 4 min. within 27% yield. Although Eguchi *et al.*[21] described the reaction with a slightly better yield (31%) by thermolysis in sealed vessel, the microwave approach to this adduct offers the simplicity of the procedure, thus avoiding the risk of high pressured conditions.



Encouraged by these results, we tried the reaction with chalcone, where the resulting cycloadduct (**3**) can not be stabilised by aromatization. Frontier Orbital calculations (see below) indicates that the energy gap between the controlling orbitals is not higher than that observed for the reaction with *o*-quinone methide. Nevertheless, adduct **3** was not formed under any thermal or microwave conditions. In the case of the reaction with 4-benzyliden-1,2-dimethyl-2-imidazolin-5-one[24] **10**, the cycloaddition adduct (**4**), should be stabilised by aromatization of the imidazol ring, thus avoiding cycloreversion of this allowed reaction, according to the energy gap between the HOMO of diene and LUMO of C_{60} (see Table 2). However, reaction does not work, probably due to the steric hindrance between the fullerene surface and the phenyl group of the heterodiene system. Another contributing factor to the lack of reactivity observed for this heterodiene could be the larger distance between the extremes in the heterodiene moiety ($R_{1,4}$= 3.08 Å) than in the case of *o*-quinone methide ($R_{1,4}$= 2.84 Å); this distance, $R_{1,4}$, has been related to the reactivity of some outer-ring dienes.[25]

Table 1. Comparative Results in Cycloadditions to C_{60} using Microwave and Classical Procedures.

Final	Microwave irradiation				Conventional heating		
Product	Solvent	Method, Power (W)	Time (min)	Yield (%)[a]	Solvent/T (°C)	Time (h)	Yield (%)[a]
1	Toluene	A, 800	15	35(40)	Benzene/reflux	12	25(n.r.)[b, 20b]
2a	Benzene	A, 800	20	39(44)[17]	Benzene/reflux	18	30(47)[17]
2b	ODCB[c]	A, 800	4	27(38)	ODCB/180 (sealed glass cylinder)	0.5	31(50)[21]
2b	ODCB	A, 400	8	21(49)		-	-
3	Toluene	A, 800	45	0	Toluene	48	0
3	ODCB	B, 90	60	0	-	-	-
4	ODCB	B, 60	120	0	Toluene	48	0
5a	ODCB	B, 60	120	37(62)	Toluene/reflux	"several"	35(n.r.)[b, 22d]
5b	ODCB	B, 60	60	30(62)	-	-	-
5c	ODCB	B, 70	70	15(43)	-	-	-
6	ODCB	A, 800	60	25(38)	ODCB/60-70	overnight	47 (65)[23]

[a] Figure in brackets indicates yield based on reacted C_{60}; [b] n.r.: no reported ; [c] ODCB = *o*-dichlorobenzene.

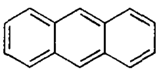
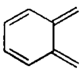
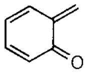
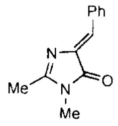
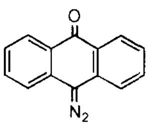
A general method for the functionalization of C_{60} is the 1,3-dipolar cycloaddition of azomethine ylides, firstly described by Prato[22a], leading to fulleropyrrolidines. We have prepared several fulleropyrrolidines **5a-c**, under microwave irradiation and observed that this method irradiation competes again favourably and thus, derivative **5a** was prepared in 37% using a focused microwave reactor (method B); fulleropyrrolidines **5b** and **5c**, non previously reported, were also prepared in 30% and 15% yield, respectively.

Formation of derivative **4** from diazoanthrone was the only case in which microwave irradiation could not compete with classical heating; under microwaves, compound **4** was obtained in lower yield (25%) than that previously described[23] (47%). Because under conventional heating reaction is carried out at 60-70° in ODCB, we think that the absence of temperature control in our reactor is the cause of this decreasing of yield and shows the importance of this control.

It is remarkable that in the microwave irradiation conditions indicated in Table 1, no bisadducts formation were found; nevertheless, no general conditions can be designed for all reactions. The search of ideal conditions (irradiation time and power) to obtain the optimum yield with the desired selectivity, depends on the nature of reactants, specially on their polarities. A higher polar substance absorbs microwave irradiation more efficiently and generally requires a shorter reaction time.

In principle, a reduction of reaction times and the improvement of yields are not the only benefits of microwaves in fullerene chemistry. With a kinetic model based on Arrhenius law, and in relation with kinetical parameters (preexponential factor and activation energy) Stuerga[10] foresee that "induced selectivity" or "inversion" of selectivity can be achieved with the benefits of a very high heating rate ; the model was demonstrated in the sulfonation of naphthalene under microwaves : the isomeric ratio depends on the microwave power, related with the heating rate, foreseeing interesting potentialities in term of reactivity associated with control of very fast heating rate -inaccessible by conventional heating- and particularly interesting as a way to kinetic control. Since then other cases of selectivity have been described[26]. The possibility of controlling the

Table 2. Distance between the extremes in the butadiene moiety ($R_{1,4}$) and calculated HOMO and LUMO levels of C_{60} and dienes and 1,3-dipoles **7-12.** (PM3)

	Compound	$R_{1\text{-}4}$ (Å)	E (eV)	ΔE^a
	C_{60}		LUMO :-2.888 HOMO -9.484	
7		2.808	LUMO :-0.970 HOMO -8.248	5.360
8a		2.872	LUMO :-0.730 HOMO -8.394	5.506
8b		2.843	LUMO :-1.142 HOMO :-9.331	6.443
9	Ph-CH=CH-CO-Ph		LUMO :-0.847 HOMO -9.377	6.489
10		3.084	LUMO : -1.061 HOMO :-8.759	5.871
11a	$Ph\text{-}CH{=}\overset{+}{N}H\text{-}\overset{-}{C}H_2$		LUMO :-0.132 HOMO :-7.599	4.711
11b	$MeO\text{-}C_6H_4\text{-}CH{=}\overset{+}{N}H\text{-}\overset{-}{C}H_2$		LUMO :-0.083 HOMO :-7.454	4.566
11c	$O_2N\text{-}C_6H_4\text{-}CH{=}\overset{+}{N}H\text{-}\overset{-}{C}H_2$		LUMO :-1.187 HOMO :-8.297	5.409
12			LUMO :-1.027 HOMO :-8.514	5.626

[a] ΔE= HOMO (diene) - LUMO (C_{60})

formation of [5,6]-open isomers (kinetic product) or [6,6]-closed adduct (thermodynamically more stable) in the formation of some kind of fullerene derivatives is an interesting matter to be studied.

In order to explain the reactivity of C_{60} with the dienes and 1,3-dipoles used in this work and, particularly with chalcone **9** and imidazolone **10**, we calculated the HOMO and LUMO energy levels for the reactants employed and the results obtained are summarised in Table 2. Calculations were performed with the program Hyperchem[27] using the semiempirical method PM3[28]. In all cases, the reactivity of dienes and 1,3-dipoles towards C_{60} is determined by the stabilisation afforded by interaction of the HOMO (diene) or HOMO (1,3-dipole) and the LUMO (C_{60}) as shown in Table 2. With anthracene and *o*-quinodimethane the energy gap is smaller (see Table 1) and, consequently, the reaction conditions are easy. *o*-Quinone methide shows a higher energy gap and requires a higher boiling point solvent ; from these results can be deduced that chalcone -with a similar energy gap- should be able to react with C_{60} ; the lack of reactivity observed indicates that the retro-Diels-Alder could be operative or, on the other hand, the larger 1,4-distance in this diene could be responsible for the lack of reactivity of imidazolone **10**, where the final product should be stabilised by aromatization.

Taking into account the electron-acceptor character of [60]fullerene, there is a great interest in the electrochemical behaviour of [60]fullerene derivatives bearing an organic addend.[29] The redox potentials of the prepared compounds have been studied by cyclic voltammetry (CV) at room temperature and the data are collected in Table 3, together to the C_{60} as reference compound. It is worth mentioning that although the CV data of some adducts (**1**,[20c] **2a**,[17] **6**[23]) had been previously reported, we have determined the reduction potentials values of the studied compounds under the same experimental conditions for comparison purposes.

Most of cycloadducts exhibit four one-electron quasireversible reduction waves in a similar way to that observed for the parent [60]fullerene. The first reduction potentials are cathodically shifted, related to [60]fullerene, thus indicating that saturation of a double bond on the [60]fullerene cage results in a slight decreasing of the accepting properties. This finding is in agreement with that previously observed for other dihydrofullerenes, and it has been explained by the raising of the LUMO energy of the adducts.[30]

Table 3. Reduction potentials of C_{60} and compounds **1-6.**

Compound	E^1_{red}	E^2_{red}	E^3_{red}	E^4_{red}
C_{60}	-0.60	-1.00	-1.52	-2.04
1	-0.64	-1.06	-1.62	-2.08
2a	-0.71	-1.14	-1.69	-
2b	-0.62	-1.08	-1.48	-1.73
5a	-0.66	-1.09	-1.63	-1.85
5b	-0.66	-1.07	-1.65	-2.06
5c	-0.62	-1.04	-1.51	-2.10
6	-0.62	-0.97	-1.13	-1.58

[a] All potentials in V *vs.*SCE; Toluene:MeCN (5:1); 0.1 mol dm^{-3} Bu_4NClO_4 ; scan rate : 0.2 V s^{-1}.

Compounds **5b** and **5c** showed additional reduction waves at -1.45 V for **5b** and -1.18 V, -1.67 V for **5c**, which were assigned to the reduction waves of the organic substituent on the C_{60} framework. The electrochemistry of cycloadduct **6** has been previously explained.[23]

It is interesting to note that compounds bearing an electronegative oxygen atom (**2b**), an electrowithdrawing group (**5b**) or that showing a "periconjugative" effect[23] (**6**) show a E^1_{red} value very close to that of [60]fullerene. This observation suggests that an electronic interaction could take place between the organic addend and the C_{60} core.[30]

CONCLUSIONS

In this work we show that the general features of *microwave chemistry* (faster and cleaner reactions) can be successfully applied to the preparation of fullerene derivatives by cycloaddition reactions, affording cycloadducts generally in higher yields than under conventional heating. The redox potentials of the prepared compounds were determined by cyclic voltammetry measurements in solution. The values obtained follow the trend observed for other dihydrofullerenes, leading to slightly poorer electron-acceptors than the parent C_{60}. More work on other type of reactions involving C_{60} and the influence of irradiation power on the nature of the resulting products will be the target of further studies.

EXPERIMENTAL

C_{60} was purchased from TechnoCarbo (>99.95). ^1H NMR and ^{13}C NMR spectra were obtained with a Varian Gemini 200 and Varian Unity 300 spectrometers. Chemical shifts are given in parts per million (δ) relative to tetramethylsilane. IR spectra were recorded on a Nicolet Magna IR-550 spectrometer and UV/vis spectra on a UV-Beckman DU-70 spectrophotometer. FAB mass spectra were obtained on a VG-AutospecEBE mass spectrometer using *m*-nitrobenzylalcohol as a matrix. Microwave irradiations were performed into a modified LYNX domestic oven or a Maxidigest MX 350 (Prolabo) microwave reactor with a single focused system. Reactions were monitored by thin layer chromatography using 0.2 mm. Merck silica gel F_{254} plates. Column chromatography was performed employing SDS (70-230 mesh) silica gel. Reaction yields were not optimised and refer to pure, isolated products. Cyclic voltammograms were taken on a Versastat PAR EG & G.

General procedures for cycloadittions.

Method A : A solution of C_{60} and the adequate reactive in dry solvent under argon atmosphere, was irradiated in a modified domestic microwave oven with a suitable power for an appropriate time. After cooling to room temperature and evaporation of the solvent in vacuo, the residue was chromatographed on a silica gel column. Further purification was accomplished by washing the obtained solid three times with methanol, centrifuged and then dried under reduced pressure.

Method B : A solution of C_{60} and the adequate reactive in dry solvent was placed in a Pyrex tube. Then the tube was introduced into a Maxidigest MX 350 Prolabo microwave reactor fitted with adjustable power within the range 0-300 W and a waveguide (monomode T_{01}) and irradiated under argon (power and time are indicated in each case) ; then the procedure is similar to that described in method A.

Reaction of C_{60} with anthracene.

A solution of C_{60} (30 mg, 0.042 mmol) and anthracene (74 mg, 0.416 mmol) in dry toluene (40 mL) under argon was irradiated (method A) at 800 W for 15 min. Chromatography (hexane-toluene) afforded 4 mg of unreacted C_{60} and 13 mg (35%), (40% based on reacted C_{60}) of **1** identified by ^{1}H NMR and UV-vis spectra

Reaction of C_{60} with 4,5-benzo-3,6-dihydro-1,2-oxathiin-2-oxide (sultine).

A solution of C_{60} (30 mg, 0.0420 mmol) and 4,5-benzo-3,6-dihydro-1,2-oxathiin-2-oxide (14 mg, 0.084 mmol) in dry toluene (35 mL) was irradiated (method A) at 800 W for 20 min. Chromatography (hexane-toluene) afforded 3 mg of unreacted C_{60} and 13 mg (39%), (44% based on reacted C_{60}) of **2a** identified by FAB MS (m/z 824), ^{1}H NMR and UV-vis. Higher reaction times (45 min) diminished yield of **2a** (30%) as well as a lower molar relation of sultine (23% for 1.1 equiv. of sultine, reaction time: 20 min at 800 W).

Reaction of C_{60} with 2-hydroxybenzyl alcohol.

A solution of C_{60} (37 mg, 0.051 mmol) with 2-hydroxybenzyl alcohol (124 mg, 1.00 mmol) in dry *o*-dichlorobenzene (ODCB) (25 mL) was irradiated (method A) at 800 W for 4 min. Chromatography (hexane-toluene) afforded 21 mg of unreacted C_{60} and 9 mg (27%), (38% based on reacted C_{60}) of **2b** identified by FTIR, ^{1}H NMR and UV-vis. When the reaction was performed at 400 W for 10 min in the same solvent, yield decreased to 21% (49% based on reacted C_{60}) and traces of dicycloaddition products were formed.

Reaction of C_{60} with chalcone.

A solution of C_{60} (30 mg, 0.042 mmol), chalcone (22 mg, 0.104 mmol) in dry toluene (40 mL) was irradiated (method A) at 800 W for 45 min. No formation of adduct **3** was detected and C_{60} was recovered unchanged. Same result was obtained after irradiation (method B) in dry ODCB during 60 min at 90 W or refluxing under classical heating in toluene for 48 h.

Reaction of C_{60} with 4-benzyliden-1,2-dimethyl-2-imidazolin-5-one.

A solution of C_{60} (30 mg, 0.042 mmol) and 4-benzyliden-1,2-dimethyl-2-imidazolin-5-one **(10)** (42 mg, 0.210 mmol) in dry ODCB (30 mL) was irradiated (method B) at 60 W for 20 min. No formation of adduct **4** was detected and C_{60} was recovered unchanged. Same result was obtained after irradiation (method B) during 90 min at 105 W or refluxing under conventional heating in toluene for 48 h.

Reaction of C_{60} with benzaldehyde and glycine.

A solution of C_{60} (40 mg, 0.055 mmol), benzaldehyde (20 mg, 0.187 mmol) and glycine (10 mg, 0.133 mmol) in dry ODCB (30 mL) was irradiated (method B) at 90 W for 30 min. Chromatography (hexane-toluene 1:4) afforded 24 mg of unreacted C_{60} and 13 mg (26%), (73 % based on reacted C_{60}) of fulleropyrrolidine **5a.** FTIR ν/cm^{-1} (KBr): 2934, 2855, 1466, 1394, 1104, 696, 532. ^{1}H-RMN (300 MHz, $CDCl_3$, δ ppm): 4.89 (d, 1H, J = 10.7 Hz), 5.11 (d, 1H, J = 10.7 Hz), 5.81 (s, 1H), 7.36-7.45 (m, 3H), 7.79-7.81 (m, 2H) ; UV-vis ($CHCl_3$) λ_{max} (nm): 272, 310, 324, 404, 430 ; FAB MS m/z 839 (M^+), 720 (C_{60}). When the solution was irradiated (method B) with 60 W during 110 min, afforded 16 mg of unreacted C_{60} and 17.5 mg (37%), (62 % based on reacted C_{60}) of **5a.**

Reaction of C_{60} with *p*-methoxybenzaldehyde and glycine.

A solution of C_{60} (50 mg, 0.070 mmol), *p*-methoxybenzaldehyde (20 mg, 0.187 mmol) and glycine (11 mg, 0.147 mmol) in dry ODCB (30 mL) was irradiated (method B) at 60 W for 60 min. Chromatography (toluene-$CHCl_3$ 1:1) afforded 26 mg of unreacted C_{60} and 18 mg (30%), (62 % based on reacted C_{60}) of **5b**. FTIR ν/cm^{-1} (KBr): 2927, 2855, 1440, 1387, 1249, 1098, 1032, 834, 532. ^{1}H-RMN (300 MHz, $CDCl_3$, δ ppm): 3.82 (s, 3H), 4.87 (d, 1H, J = 10.6 Hz), 5.09 (d, 1H, J = 10.6 Hz), 5.76 (s, 1H), 6.97 (d, 2H, J = 8.6 Hz), 7.71 (d, 2H, J = 8.6 Hz). UV-vis ($CHCl_3$) λ_{max} (nm): 257, 328, 430. MS m/z 869 (M^+), 720 (C_{60})

Reaction of C_{60} with *p*-nitrobenzaldehyde and glycine.

A solution of C_{60} (50 mg, 0.070 mmol), *p*-methoxybenzaldehyde (26 mg, 0.172 mmol) and glycine (11 mg, 0.147 mmol) in dry ODCB (30 mL) was irradiated (method B) at 60 W for 70 min. Chromatography (toluene-$CHCl_3$) afforded unreacted C_{60} and 9 mg (15%), (43 % based on reacted C_{60}) of **5c.** FTIR ν/cm^{-1} (KBr): 2940, 2854, 1525, 1466, 1249, 1183, 1031, 841, 762, 538. ^{1}H-RMN (300 MHz, $CDCl_3$, δ ppm): 4.91 (d, 1H, J = 10.4 Hz), 5.14 (d, 1H, J = 10.4 Hz), 5.90 (s, 1H), 8.05 (d, 2H, J = 8.4 Hz), 8.30 (d, 2H, J = 8.4 Hz) UV-vis ($CHCl_3$) λ_{max} (nm): 256, 313, 431. MS m/z 884 (M^+), 720 (C_{60})

Reaction of C_{60} with 10-diazoanthrone.

A solution of C_{60} (50 mg, 0.070 mmol) and 10-diazoanthrone (24 mg, 0.109 mmol) in dry ODCB (40 mL) was irradiated (method A) at 800 W for 40 min. Chromatography (hexane-toluene 1 :1) afforded 3 mg of unreacted C_{60} and 13 mg (39%), (44% based on reacted C_{60}) of **6** identified by FAB MS, ^{1}H NMR and FTIR.

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