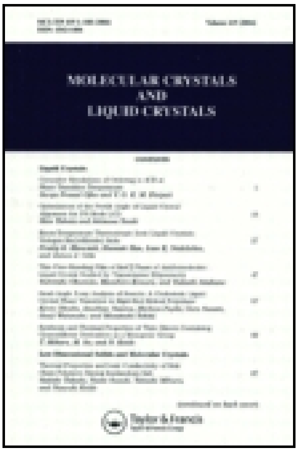
This article was downloaded by: [University of Haifa Library]
On: 13 August 2012, At: 20:47
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Photoreactions of 1,3-Dipolar Cycloadducts of Mesoionic Compounds with Buckminsterfullerene

Yasuhiko Kawamura [a] , Kazuyuki Akaishi [a] , Masaki Nishiuchi [a] & Masao Tsukayama [a]

[a] Faculty of Engineering, The University of Tokushima, Minamijosanjima-cho, Tokushima, 770-8506, Japan

Version of record first published: 18 Oct 2010

To cite this article: Yasuhiko Kawamura, Kazuyuki Akaishi, Masaki Nishiuchi & Masao Tsukayama (2002): Photoreactions of 1,3-Dipolar Cycloadducts of Mesoionic Compounds with Buckminsterfullerene, Molecular Crystals and Liquid Crystals, 376:1, 219-224

To link to this article: http://dx.doi.org/10.1080/10587250210790

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Mol. Cryst. Liq. Cryst., Vol. 376, pp. 219-224
Copyright © 2002 Taylor & Francis
1058-725X/02 $12.00 + .00

Downloaded by [University of Haifa Library] at 20:47 13 August 2012

Photoreactions of 1,3-Dipolar Cycloadducts of Mesoionic Compounds with Buckminsterfullerene

YASUHIKO KAWAMURA*, KAZUYUKI AKAISHI, MASAKI NISHIUCHI and MASAO TSUKAYAMA

Faculty of Engineering, The University of Tokushima,
Minamijosanjima-cho, Tokushima 770-8506, Japan

Cycloaddition reactions of buckminsterfullerene (C_{60}) with mesoionic compounds gave the 1 to 1 cycloadducts reacted at the 6-6 double bond of C_{60} as a sole product. A thermal reaction of the adducts proceeded in a reversed fashion and another dienophile trapped the liberated mesoionic compounds. Thermogravimetric analyses of the adducts reveal that extrusion of small fragment occurs at controlled temperature. UV-VIS spectra of the adducts altered with isosbestic points upon irradiation of them. Preparative photoreaction gave only a black compound insoluble in major organic solvents.

Keywords Mesoionic compound; fullerene; 1,3-dipolar cycloaddition; extrusion; thermogravimetry; photoreaction

INTRODUCTION

Derivatization of fullerenes continues to attract much attention, since its

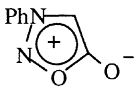
Downloaded by [University of Haifa Library] at 20:47 13 August 2012

unique spherical structure with delocalized π-electron system is expected to create new functional properties by a synergistic action between fullerenes and the exohedral moieties incorporated. Apparently, cycloaddition is one of the most common strategies to this end. We report here our recent effort on 1,3-dipolar cycloaddition reactions of C_{60} with mesoionic compounds.

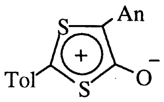
Mesoionic compounds known as a "masked 1,3-dipole" are recognized to be a versatile reagent for the synthesis of heterocyclic compounds by a sequence of a 1,3-dipolar cycloaddition-extrusion reaction [1]. Thus, we anticipated obtaining intriguing information on fullerene functionalization. Two papers have been reported so far in relation to our work: One describes Rh-catalyzed reactions of ketodiazo compounds with C_{60} [2] and another refers to the reactions of C_{60} with mesoionic compounds which lead to an intramolecular hydrogen migration after initial CO_2 extrusion from the cycloadduct [3].

RESULTS AND DISCUSSION

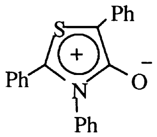
Candidates for the reactions are sydnone (**1**, -9.33 eV), a mesoionic dithiolone (**2**, -8.30 eV) [4], and a thiazolone (**3**, -7.81 eV) and their HOMO energies (shown in the parentheses) increase by the order



1



2



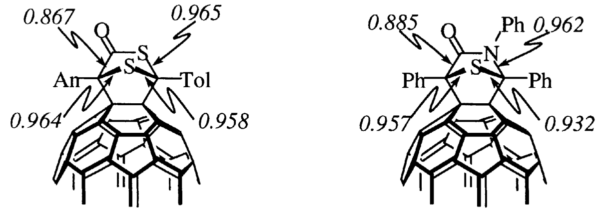
3

[An =*p*-Anisyl; Tol =*p*-Tolyl]

Downloaded by [University of Haifa Library] at 20:47 13 August 2012

estimated by PM3 semiempirical molecular orbital calculations [5].

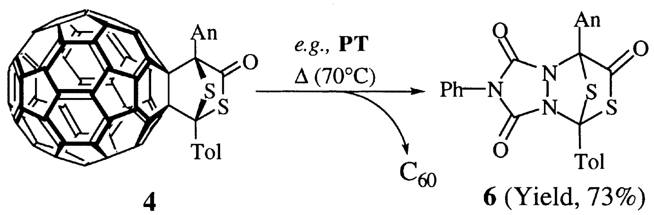
Actually, no reaction took place in **1**, but mesoionic compounds **2** and **3** reacted with C_{60} at 80 °C and at room temperature, respectively. Black or dark brown crystals were separated by column chromatography and analyzed by spectroscopic means [4]. More than fifty signals of the sp^2 carbons and four sp^3 carbons appeared in the ^{13}C NMR spectra suggest that compounds **4** (Yield, 57%) and **5** (Yield 41%) are one-to-one adducts of C_{60} with **2** and **3**. The feature appeared in the UV-VIS spectra suggests that compounds **2** and **3** cycloadd across the 6-6 double bond of C_{60}.



4 **5**

FIGURE 1 The values show the respective bond orders obtained by PM3-MO calculations.

It is found that the adducts **4** and **5** react with other dienophiles to give the cycloadducts [*e.g.* **6**, obtained by the reaction of **4** with *N*-phenyltriazolinedione (**PT**)] which consisted with mesoionic compounds and dienophiles [6]. That is, the cycloadducts can act as a repository of a mesoionic compound. The cycloaddition-retrocycloaddition-



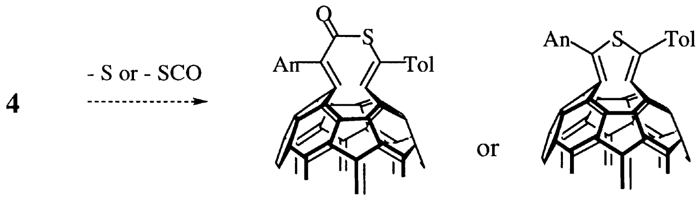
4

6 (Yield, 73%)

Downloaded by [University of Haifa Library] at 20:47 13 August 2012

cycloaddition (CRC) procedure provides unique route for preparations of heterocyclic compounds.

Extrusion reactions are investigated. The reactions of stable, small molecules from the adducts may open further transformation routes to intriguingly modified C_{60}, *e.g.*, compounds **7** and **8**. The PM3-MO calculations [5] of **4** and **5** show the feasible nature of the extrusion mode of them (FIGURE 1).



7 **8**

First of all, pyrolytic process was analyzed by thermogravimetry. A thermochemical profile of **2** and the C_{60}-adduct **4** showed two peaks of weight loss of each. An initial one of **2** (150-230 °C) and **4** (140-250 °C) seems to be due to the elimination of a fragment SCO. The final decomposition products of **4** were C_{60} and polymeric materials determined by IR and ^{13}C NMR spectra. Comparing both profiles (decomposition peak temperature: 277 °C for **2** and 307 °C for **4**), cycloaddition brings about a beneficial effect on the stability of a mesoionic compound **2**. A similar observation was made in **3** and the cycloadduct **5** (decomposition peak temperature: 281 °C for **3** and 300 °C for **5**). As a result, it is possible to eliminate only SCO from the cycloadduct **4** by controlling the heating temperature. Moreover, the fact gives another proof to utility of the cycloadduct as a repository of unstable mesoionic compounds described in the foregoing page.

Photoirradiation is also a useful technique for giving rise to the extrusion reaction. The photoreaction of the cycloadduct **4** was followed by UV-VIS spectra in cyclohexane. Before irradiation with light of the wavelength longer than 280 nm from a Xenon lamp, three major absorption maxima similar to C_{60} was observed. Depending on the time for irradiation, the peaks altered with apparent two isosbestic points. The absorbance of peaks at 320-nm and especially, 270-nm regions decreased. We consider that the hypsochromic change of the absorption at 270 nm is due probably to perturbation of the orthogonal interaction of orbitals of fullerene π-bonds and newly formed double bonds. This turns out to be that a secofullerothiophene **7** or **8** may be formed. Preparative photoreaction of the adduct **4** gave insoluble black material which showed no presence of monomeric C_{60}. It may be a putative fullerene polymer. The property and structure of the product is scrutinizing at present.

Downloaded by [University of Haifa Library] at 20:47 13 August 2012

Acknowledgements
We thank Professors H. Kato of Shinshu University and T. Horie of this university for their encouragement and helpful discussions. We acknowledge also the Center for Cooperative Research of this university for the use of the NMR facilities.

References

[1] K. T. Pots, *1,3-Dipolar Cycloaddition Chemistry*, ed. by A. Padwa (Wiley, New York, 1984), Vol.2, pp. 1-82.

[2] R. Gonzâlez, B. W. Knight, and F. Wudl, *J. Org. Chem.,* **59**, 7949-7951 (1994).

[3] S.-H. Wu, W.-Q. Sun, D.-W. Zhang, L.-H. Shu, H.-M. Wu, J.-F. Xu, and X.-F. Lao, *J. Chem. Soc., Perkin 1*, **1998**, 1733-1738.

[4] All new compounds were characterized by elemental and spectroscopic analyses, and the selected data are shown: Compound **2**: violet needles from EtOAc-hexane; mp 175-177 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (3H, s), 3.84 (3H, s), 6.94 (2H, d, *J* = 9.1 Hz), 7.25 (2H, d, *J* = 8.3 Hz), 7.53 (2H, d, *J* = 8.3 Hz), 7.78 (2H, d,

Downloaded by [University of Haifa Library] at 20:47 13 August 2012

J = 9.1 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 21.56, 55.36, 114.37, 115.32, 124.41, 124.98, 127.45, 129.66, 130.30, 141.68, 151.96, 158.76, 181.05, MS (EI, 20 eV) *m/z* 314 (M$^+$, 35%), 135 (100%); IR (KBr) ν 1590 cm^{-1}. Adduct **4**: black prisms; mp >300 °C; ^{1}H NMR (400 MHz, CS$_2$/CDCl$_3$ = 9/1) δ 2.39 (3H, s), 3.76 (3H, s), 6.84 (2H, d, *J* = 8.8 Hz), 7.23 (2H, d, *J* = 8.3 Hz), 7.64 (2H, d, *J* = 8.3 Hz), 7.76 (2H, d, *J* = 8.8 Hz); ^{13}C NMR (100 MHz, CS$_2$/CDCl$_3$ = 9/1) δ 21.32 (Me), 54.54 (MeO), 79.68, 80.07, 84.09, 85.61 (4 sp^3's), 113.51, 122.44, 128.24, 129.33, 129.94, 131.82, 136.47, 137.20, 138.42, 138.57, 138.77, 138.88, 138.95, 139.50, 140.85, 141.20, 141.31, 141.42, 141.48, 141.59, 141.64, 141.77, 141.88, 142.06, 142.19, 142.28, 142.50, 142.57, 142.77, 143.95, 144.20, 144.48, 144.64, 144.68, 144.95, 145.01, 145.04, 145.12, 145.17, 145.24, 145.48, 145.65, 145.68, 145.87, 146.07, 146.25, 146.30, 146.67, 147.04, 147.11, 150.35, 150.84, 150.97, 153.05, 159.71, 198.37 (C=O); IR (KBr) ν 1710 cm^{-1}; UV (toluene) λ_{max} (ε) 432.5 nm (700); FAB-MS (for **4**-*S*-O, prepared by the MCPBA oxidation, matrix: Thiol 2 + NBA) m/z 1051 (M$^+$). Adduct **5**: dark brown prisms; mp >300 °C; ^{1}H NMR (400 MHz, CS$_2$/CDCl$_3$ = 9/1) δ 7.13-7.42 (11H, m), 7.45 (2H, d, *J* = 7.3 Hz), 7.13-7.42 (11H, m), 7.64 (2H, d, *J* = 8.3 Hz), 7.76 (2H, d, *J* = 8.8 Hz); ^{13}C NMR (100 MHz, CS$_2$/CDCl$_3$ = 9/1) δ 76.22, 80.17, 86.76, 89.85 (4 sp^3's), 127.70, 128.00, 128.64, 128.93, 129.42, 129.81, 130.28, 130.43, 130.78, 136.13, 137.25, 137.40, 138.18, 138.93, 139.01, 139.06, 141.20, 141.24, 141.47, 141.57, 141.75, 141.97, 142.06, 142.11, 142.22, 142.43, 142.59, 142.63, 142.83, 143.94, 144.09, 144.18, 144.44, 144.73, 144.95, 145.10, 145.13, 145.17, 145.28, 145.37, 145.55, 145.74, 145.79, 145.86, 145.90, 146.17, 146.25, 146.32, 146.39, 146.63, 146.69, 147.00, 147.05, 150.14, 150.91, 151.17, 152.92, 172.20 (C=O); IR (KBr) ν 1720 cm^{-1}; UV (toluene) λ_{max} (ε) 433 nm (780).

[5] Calculations were carried out using the MOPAC 94 program contained in the CAChe groupserver program (Release 3.8) available from Fujitsu, Co. or Conflex, Co.

[6] Dienophiles tested were maleic anhydride and *N*-phenylmaleimide, in addition to **PT**. They reacted with **5** to give the corresponding cycloadducts. But compound **4** reacted only with **PT**, although reactions of **2** and **3** with all dienophiles proceeded well. The cycloadducts were obtained in >70% yield after flash chromatography and recrystallization in all cases.