New Concepts for Regio- and
Stereoselective Bis- and
Triscyclopropanations of C₆₀

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ABSTRACT: The synthesis of isomerically multiple adducts of C₆₀ with a defined three-dimensional structure is still one of the most challenging tasks of exohedral fullerene chemistry. The inherent regioselectivity of successive additions of addends such as malonates to the fullerene's [6,6]-double bonds is only moderate. In most cases difficult-to-isolate mixtures of regioisomers are obtained. The regioselectivity can be significantly improved if multifunctional addends able to undergo two or more additions are allowed to react with C₆₀. Preorganization and minimization of strain energy within the addend skeleton reduce the number of sterically allowed addition patterns. Improved concepts for highly regio- and stereoselective bis- and triscyclopropanations of C₆₀ are described. Two examples of the bisadditions with complete regioselectivity leading to *trans*-2- and *cis*-2 are presented. Here, the two malonate binding sites are linked by rigid tetraphenylporphyrin and calix-[4]-arene spacers. Selective trisadditions were achieved with the easy-to-synthesize and easy-to-modify tripodal addends **5–7**, where the malonates are held together by a focal aryl moiety. Another very elegant approach for bis- and trisadditions involves cyclo-[*n*]-alkylmalonates. Selection between addition patterns with and without rotational axes is possible by choosing the right combinations of the flexible alkyl chains connecting the malonates. If alkyl chains of identical lengths are used bis- and trisadducts such as **19–21** and **25** with rotational symmetry are formed with high regioselectivity. These addition patterns are avoided if cyclo-[*n*]-malonates containing alkyl chains of different lengths are employed. In this case adducts such as **26** and **27** with C_s-symmetry are formed. The use of the chiral cyclo-[3]-malonate **28** allows for the regio- and stereoselective synthesis of the enantiomerically pure *e,e,e*-trisadducts **29** and **30** containing an inherently chiral addition pattern with C₃-symmetry. © 2005 The Japan Chemical Journal Forum and Wiley Periodicals, Inc. Chem Rec 5: 196–208; 2005; Published online in Wiley InterScience (www.interscience.wiley.com) DOI 10.1002/tcr.20047

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Introduction

Fullerenes are multifunctional molecules with outstanding electronic, topologic, and photophysical properties.¹ Usually, the most reactive sites in a fullerene are the bonds common to two hexagons ([6,6]-bonds). They are shorter than the [5,6]-bonds fusing a hexagon and a pentagon, exhibit more

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Fig. 1. VB-structure of C_{60} with lengths of the [6,6]-double bonds and [5,6]-single bonds.

pronounced double-bond character and, as a consequence, are susceptible to a broad variety of addition reactions such as cycloadditions.¹ The major driving force for such addition reactions is the release of strain energy stored in the bent 'sp²'-framework of the fullerene core. The most prominent fullerene is C_{60} because it is the most abundant in the raw material obtained from the usual production methods and it has the highest symmetry (I_h) (Fig. 1). C_{60} contains 30 identical [6,6]-double bonds, which guarantees that in the case of addition to one double bond (monoaddition) adducts are formed which are isomerically pure. The easiness of synthesis and characterization of monoadducts was the reason that the first period of exohedral fullerene chemistry was mainly devoted to the devel-

opment of various types of monoaddition reactions. However, the polyfunctionality of C_{60} asks for the systematic investigation of multiple additions to the [6,6]-double bonds. The most challenging aspect in this regard is to gain control over the regio- and stereoselectivity of subsequent additions. The defined spatial arrangement of functional addends in an oligoadduct of C_{60} is the key for the design of compounds with interesting materials, biological, and supramolecular properties. Moreover, the degree and pattern of a multiple addition allows for fine tuning of the electronic and topologic fullerene properties.

Whereas nowadays C_{60} can be made in ton quantities and is comparatively inexpensive² the application of tailor-made oligoadducts could still be hampered by high production prices if no efficient methods for their regioselective synthesis are available. A frequently applied method for the functionalization of C_{60} is nucleophilic cyclopropanation with malonates.^{1,3} Mild reaction conditions, good yields, straightforward purification, and compatibility with many functional moieties that are part of the malonate addend make this reaction very attractive. Next to the easy availability of monoadducts, hexakisadducts with an aesthetically pleasing and highly symmetrical T_h -addition pattern can be easily obtained in a one-pot reaction starting from C_{60} using a methodology that we developed several years ago.⁴ Here, advantage is taken of the fact that (i) a T_h -symmetrical hexakisaddition pattern is thermodynamically significantly favoured and that (ii) C_{60} is allowed to react *in situ* with an excess of a reversibly binding addend (9,10-dimethylantracene) preferably occupying octahedral sites and being replaceable by irreversible binding malonate addends. In this way we have synthesized dozens of hexakisadducts of C_{60}

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Fig. 2. a) Positional relationships of [6,6]-bonds with respect to the first addend in a monoadduct of C₆₀ (the position of the first addend is marked with an arrow; b) preferred bisadducts formed by the subsequent addition of a diethyl malonate- and a nitrene addend; c) relative yields of isolated regioisomeric bisadducts of C₆₁(COOEt)₂(NCOOEt).

containing one or various types of functional addends in octahedral binding sites. Many of these spherical adducts exhibit remarkable properties. We have reviewed this subject recently.⁵ However, a much more difficult situation is experienced if the regioselective synthesis of lower oligoadducts such as bis- and tris-adducts is investigated.

In fact, the second addition of diethyl malonate to a monoadduct of C₆₀ leads to a mixture of seven out of eight possible regioisomers involving the addition patterns *trans*-(1-4), *e*, *cis*-3 and *cis*-2 (Fig. 2).⁶ In the case of subsequent additions of malonate and nitrene addends, nine regioisomers are formed (Fig. 2).⁷ In the latter case attack of the two topologically different equatorial position (*e'* and *e''*) give rise to different adducts and, furthermore, the *cis*-1-addition, which is sterically forbidden in the case of twofold malonate additions, is possible and even preferred. The common feature of this and other studies of bisadditions of segregated addends to C₆₀ is that the inherent regioselectivity governed mainly by kinetic control is not high enough to target the efficient synthesis and isolation of a specific bisadduct.⁸ Although the second attack of a malonate reaction favours *e*- and *trans*-3- and if possible

cis-1 addition patterns, the product mixture has to be purified by a tedious chromatographic separation.^{6,7} The regioselectivity of further additions to bisadducts is higher, however, the separation of isomerically pure reaction products remains difficult.^{9,10}

Concepts for Regioselective Bisadditions Using Tethered Open Chain Malonates

The search for alternatives to this stepwise procedure, with its attendant problems outlined above, has been a challenge ever since the development of fullerene chemistry began. One way to achieve a high degree of control of the regiochemistry of additions to fullerenes is the use of tethered addend systems, for example, malonates which are connected by a more or less rigid spacer. This concept of regioselective bisfunctionalization of C₆₀ was introduced by Diederich and coworkers.^{1,11,12,13} It proved to be a major breakthrough and provides relatively easy access to otherwise strongly disfavoured addition patterns, such as *trans*-1. Similar results were obtained subsequently

Scheme 1. Regioselective formation of doubly bridged C₆₀-tetraphenylporphyrin dyads involving a *trans*-2-addition pattern.

using other types of tether-controlled addition reactions.^{14,15,16,17} The complex regiochemistry of C₇₀ can also be controlled.^{18,19} The selectivity of the known tether methods can be very high and may lead to quite unusual addition patterns.²⁰ Also, the diastereoselective formation of bisadducts with an inherently chiral addition pattern has been achieved by using bismalonates involving a chiral tether-like Tröger's base.²¹

To illustrate this concept of tether controlled bisfunctionalization, two examples investigated in our laboratories will now be presented. In an effort to design fullerene-based donor–acceptor dyads that are suitable to undergo photoinduced electron transfer we synthesized the bismalonate **1** containing a tetraphenylporphyrin moiety as rigid tether either as free base or as Zn and Co complex. The twofold cyclopropanation of C₆₀ with **1** leads with complete regioselectivity to the bisadduct **2** (Scheme 1), which involves a chiral *trans*-2 addition pattern.^{22,23,24,25,26,27} The structure was unambiguously assigned using a combination of spectroscopy and computational investigations and more recently by single crystal X-ray analysis.²⁸ The two chromophores of the very rigid architecture are held together in close proximity. The interplanar distance between the fullerene and the porphyrin is as small as 2.71 Å. This is considerably shorter than the interplanar distance in graphite (3.35 Å). Upon irradiation the system undergoes a photoinduced electron transfer in which one electron is transferred from the porphyrin to the fullerene moiety serving as the electron acceptor. Significantly, the back electron transfer takes place in the Marcus-inverted region, which is reflected, for example, by the longer lifetime of the charge-separated state in apolar solvents compared to more polar solvents (e.g.

619 ps in toluene vs. 38 ps in benzonitrile). This behavior is due to the very rigid structure of the dyad, in particular of the fullerene unit, causing very low reorganization energies. Fullerene-based dyads and oligoads such as **2** are currently a subject of intensive investigation with respect to the development of model systems for the photosynthetic reaction center and of solar cells.¹ A similar dyad involving a *trans*-1 addition pattern using a structurally modified tetraphenylporphyrin was synthesized by Diederich and coworkers.²⁹ If tetraphenylporphyrin isomers of **1** are allowed to react with C₆₀, where the same malonate groups are attached to adjacent instead of opposing phenyl rings, the regioselectivity changes and dyads involving an *e* addition pattern are formed as the only regioisomers.²⁶

Biscyclopropanation of C₆₀ with the calix[4]arene malonate **3** afforded conjugate **4** also in complete regioselectivity exhibiting a *cis*-2 addition pattern (Scheme 2).³⁰ The space-filling model of this nano object resembles that of the FIFA world cup whose dimensions of course are many orders of magnitude larger (Fig. 3). This molecule was synthesized in our laboratory a few days before the final game of the soccer championship in 1998. We dedicated this contribution to the winning team, France.³⁰

Regioselective Formation of Trisadducts Using Tripodal Tethers

Next to bismalonates involving rigid tethers, tripodal malonates have been used targeting the regioselective access to

Scheme 2. Synthesis of the fullerene-calix[4]arene conjugate **4** involving a *cis*-2-addition pattern.

Fig. 3. Shape relationship of the football world cup (left) and the fullerene-calix[4]arene conjugate **4** as a PM3-calculated space-filling model (right)

trisadducts of C_{60} . As the first example a cyclotrimeratylene-based trisalonate was employed.³¹ The corresponding tris-cyclopropanation of C_{60} afforded roughly a 1:1 mixture of *trans*-3,*trans*-3,*trans*-3 and *e,e,e*-trisadducts. The overall yield was about 20%. Although the synthesis of the tether system is not too difficult, it does require a multistep sequence.

More recently we prepared the very simple tripodal malonates **5–7**.³²

Cyclopropanation of C_{60} with **5–7** leads to the regioselectively preferred formation of the *e,e,e*-trisadducts **8–10** (Scheme 3). The best result was obtained with the malonate **7**. In this case the *e,e,e* adduct **10** was formed with a very pronounced regioselectivity (100%) and can easily be isolated in 35% yield. A topologically interesting aspect associated with the trisadducts **8–10** is the preorientation of the two different sides of each malonate addend. Whereas the arms connected to the focal aryl unit are oriented towards the pole region, the freely pending side chains are oriented equatorially. Conceptually, subsequent orthogonal deprotection of the two

Scheme 3. Tether-directed remote functionalization of C_{60} with the tripodal trismalonates **5–7** and subsequent selective deprotection of the polar (**11**) and equatorial (**12**, **13**) addend zones.

different side chains allows addressing of topologically well-defined and distinct addend zones, which could be used for further functionalization. The selective deprotection of the terminal hydroxyl groups located in the polar addend zone was achieved by the treatment of **8** with BBr_3 to afford the triol **11** (Scheme 3). On the other hand the treatment of **9** and **10** with formic acid lead to the deprotection of the *t*-butyl ester groups within the equatorial zone to give the trisacids **12** and **13** (Scheme 3).

Highly Regioselective Functionalization Using Cyclo[*n*]malonates

Although the results obtained from the addition of open-chain malonates involving rigid tethers are very encouraging there are still some drawbacks, especially where the formation of bisadducts is concerned. For example, the synthesis of bis-malonates containing the required rigid tether is not always straightforward and in many cases the regioselectivity is not

complete so that elaborate separation protocols are still necessary. Furthermore, one-step synthesis to tetra- and higher adducts using open-chain tethers is still unknown. A highly satisfactory concept for a tether-controlled multiple functionalization of C_{60} should fulfil the following requirements: (a) easy synthesis of the malonate addends from cheap starting materials; (b) easy adaptation to a wide diversity of steric requirements; (c) possibility to attach external functionalities; (d) high yield and regioselectivity for the direct addition to C_{60} .

These requirements are met to a large extent by an extension of the tether remote functionalization concept that we developed recently.³³ The idea was to completely abandon the concept of rigid spacers and substitute for them with the most flexible and simplest system at hand, which is an alkyl chain. Of course, almost all regioselectivity would be lost, if these systems were open chained. To compensate for this we incorporated the malonates into a macrocyclic ring. This way, the regioselectivity is not based on steric preorganization, but on the avoidance of unequal strain in the alkyl chains. The corresponding macrocycles that we developed for this approach are cyclo-[n]-alkylmalonates. The number in brackets represents the number of repetition units. Examples are the cyclo-[2]-octylmalonate **14** and the cyclo-[3]-octylmalonate **15** which are easily accessible by the condensation of the corresponding diol with malonyl dichloride and subsequent separation by flash chromatography.

Also larger macrocycles with four to seven repetition units are formed, however, in much lower yield. The synthesis of macrocycles with other chain lengths is also straightforward and, what is very important for the concept, also macrocycles containing alkyl chains of different lengths such as cyclo-[2]-butyloctylmalonate (**16**) and cyclo-[2]-octyl-tetradecylmalonate (**17**) can easily be prepared by a statistic reaction of a 1:1 mixture of the corresponding diols and malonyl dichloride.

In principle one can distinguish different groups of bis- and trisadducts, those containing rotational axes (Fig. 4) and those without rotational axes (Fig. 5). In the case of bisadducts the latter ones have a mirror plane. In bis- and trisadducts having a rotational axis, topologically identical connections between two adjacent binding sites can be found. This is not the case for adducts lacking this symmetry element, which has important consequences for the selection of cyclo-[n]-malonates to be attached to C_{60} . Due to the desired even distribution of strain energy within the alkyl bridges cyclo-[n]-malonates containing only one type of alkyl bridge will selectively form adducts involving rotational axes (Fig. 4). On the other hand cyclo-[n]-malonates with alkyl bridges of different length will preferably lead to the formation of adducts without rotational axes. In the case of bisadducts such molecules have a C_s -symmetry (Fig. 5).

We will now present the successful proof of concept.³³ Reaction of C_{60} with cyclo-[2]-dodecylmalonate (**18**) leads in complete regioselectivity and 56% isolated yield to the *trans*-3 adduct **19** (Scheme 4). Indeed, this adduct contains a twofold rotational axis and exhibits C_2 -symmetry. Similarly, the triscyclopropanation of C_{60} with cyclo-[3]-octylmalonate **15** leads in excellent regioselectivity (94%) to the C_3 -symmetrical trisadduct **20**. As a minor byproduct, the olive green adduct **21** involving a *trans*-4,*trans*-4,*trans*-4-addition pattern was formed (Scheme 5). This was the first example of a trisadduct having this C_3 , symmetrical addition pattern. Both **20** and **21** contain C_3 axes and as a consequence three topographically identical connections between the adjacent binding sites are possible allowing for an even distribution of strain energy in the alkyl bridges.

Trisadduct **20** is a precursor of the trismalonic acid **22** which has generated a lot of interest because of its remarkable activity as neuroprotective antioxidant.³⁴ This water-soluble fullerene derivative can easily be generated by hydrolysis of **20**. Also the very selective formation of the chiral C_3 -symmetrical hexakisadducts is possible using **20** as starting material. This is demonstrated for example with the synthesis of the amphiphile **23** which shows interesting pH-switchable aggregation properties in water.³⁵ Switching from one to another addition pattern involving rotational axes is possible when the length of the alkyl bridges is changed. For example, allowing cyclo-[3]-tetradecylmalonate (**24**) instead of **15** to react with C_{60} leads to formation of the D_3 -symmetrical adduct **25** where the binding sites on the C_{60} sphere are further remote.³³

Now we move to the reactions of cyclo-[2]-malonates with two different alkyl bridges. As expected the biscyclopropanation of C_{60} with **16** and **17** leads in complete regioselectivity to the C_s -symmetrical adducts **26** and **27** involving a *cis*-2 and *e*-addition pattern (Scheme 6). In this case no topologically identical connections between the two binding sites can be found and as a consequence cyclo-[2]-malonates with two dif-

Fig. 4. Possible bis- and trisadducts of C_{60} containing rotational axes. All distances between adjacent addend positions are identical. The yellow bonds denote the positions of the malonate addends.

Fig. 5. Bisaddition patterns of C_{60} with C_s -symmetry. The two possible distances between adjacent positions are different. The yellow bonds denote the positions of the malonate addends.

ferent alkyl bridges are selected. Only this guarantees the most strain-free preorganization of the addends.

Trisadducts such as **20** and **22** exhibit C_3 -symmetry and therefore are inherently chiral. Of course, it is highly desirable to achieve access to enantiomerically pure isomers. A few years ago we were able to isolate and characterize enantiom-

erically pure trisadducts with an *e,e,e*-addition pattern and also a couple of further chiral bisadducts and trisadducts of C_{60} .^{10,36} This was accomplished by subsequent additions of chiral bisoxazolines which exhibit the same reactivity towards the cyclopropanation of C_{60} as malonates. Since now the two stereoisomers of an adduct with an inherently chiral

Scheme 4. Synthesis of the trans-3 bisadduct 19.

Scheme 5. Synthesis of the *e,e,e*-(20) and *trans-4,trans-4,trans-4*-(21) trisadducts.

Scheme 6. Synthesis of the *cis*-2 and *e*-bisadducts **26** and **27**.

addition pattern represent a pair of diastereomers, isolation is possible by chromatography on an achiral stationary phases. We were able to investigate the chiroptical properties of a variety of enantiomerically pure bis- and trisadducts. Most importantly we succeeded in determining the absolute configuration by comparison of the calculated and experimental CD-spectra.^{10,36} More recently, we were able to achieve the regio- and stereoselective synthesis of trisalonates with a C_3 -symmetrical *e,e,e*-addition pattern using chiral cyclo-[3]-malonates.³⁷ For this purpose we synthesized the enantiomerically pure trisalonate **28** in 4 steps starting from 3,4-*O*-isopropylidene-D-mannitol. Cyclopropanation of C_{60} with **28** afforded the C_3 -symmetrical *e,e,e*-adducts **29** and **30** in 21% and 74 % relative yield, respectively (Scheme 7).³⁸ This corresponds to a *de* value of 53%. The isolation of **29** and **30** was possible by chromatography on silica gel. Next to **29** and **30** the *trans*-4,*trans*-4,*trans*-4-adduct **31** exhibiting an achiral C_{3v} -symmetrical addition pattern was formed as a minor byproduct in 5% relative yield. The absolute configuration of **29** and **30** could be determined by the comparison of their CD-spectra with those of the related bisoxazoline adducts characterized previously.¹⁰

Conclusions and Outlook

We have presented efficient concepts for regio- and stereoselective bis- and trisadditions of malonates to C_{60} . Either open-chain bipodal and tripodal malonates or cyclo-[*n*]-malonates can be used as precursor addends. Most of the malonate addends presented here are easily accessible from inexpensive starting mate-

Scheme 7. Synthesis of the *trans-4,trans-4,trans-4* (**31**) and the enantiomerically pure *e,e,e*-(**29**), (**30**) trisadducts.

rials. This is a very important prerequisite for possible applications of such stereochemically defined multiple adducts. We have demonstrated that some of the bis- and trisadducts, such as the dyad **2** and the *e,e,e*-trismalonate **22** are interesting *per se* because of their remarkable photophysical or biological properties. However, and maybe even more importantly, they can serve as very useful building blocks for further chemical transformations. This is shown, for example, with the synthesis of the hexak-

isadduct **23** involving an octahedral addition pattern. Compound **23** shows remarkable pH-switchable aggregation properties in water. Fine tuning of the molecular and supramolecular properties of follow-up adducts such as **23** is possible because its stepwise formation process allows for the introduction of topologically distinct addend zones whose chemical nature can be varied over a wide range. The possibilities for structural and functional variations are very broad.

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