The Reversible Cycloaddition of Isomünchnones to C_{60}

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Summary: The Rh(II)-catalyzed reaction of diazo imides with buckminsterfullerene C_{60} gives rise to dipolar cycloadducts which readily undergo thermal cycloreversion.

Among the large number of functionalization reactions of buckminsterfullerene C_{60}, the cycloadditions stand out as the cleanest and most useful.[1,2] The products of [2 + 2],[3] [2 + 3],[4] [2 + 4],[5,6] and higher electron count reactions[7] have been reported. In our group we have been studying and using the 1,3-dipolar addition of diazoalkanes. Another family of dipoles which has the versatility of high degree of functionalization is that of the mesoionic heterocycles.[8,9] Of the known members of this class of 1,3-dipoles, the structure, physical properties, and reactions of sydnones, münchnones, and isomünchnones have drawn the closest scrutiny.

Cycloaddition of mesoionic compounds with multiple π-bonds has been employed for the preparation of numerous functionalized monocyclic and ring-annulated heterocycles.[10] For example, facile preparation of a highly functionalized five-membered heterocycle is accomplished by cycloaddition of the dipole to an acetylenic dipolarophile followed by thermal elimination of a small molecular fragment such as carbon dioxide, carbonyl sulfide, or isocyanate. Such eliminations are not as easily achieved when the dipolarophile is olefinic, as is the case with C_{60}. Moreover, dipolar cycloadditions of the mesoionic heterocycles to olefins have not been reported to be reversible.

In this paper we report that several isomünchnone precursors react readily with buckminsterfullerene C_{60} under very mild conditions. In addition, we have made the unprecedented observation that the cycloaddition is reversible in solution, even at 25 °C, and that the isomünchnone dipole is released without decomposition.

Ylide formation as a result of carbene interaction with the unshared electron pair of heteroatoms has been extensively studied.[11] The Rh(II)-catalyzed reaction of diazo imides has been utilized by several groups[12–15] to generate the anhydro-4-hydroxy-1,3-oxazolium hydroxide (isomünchnone) ring system. As shown in Scheme 1, the reaction of four diazo imide isomünchnone precursors with C_{60} was carried out in the presence of a rhodium catalyst (pfb = perfluorobutyrate). The reactions were carried out without special precautions,[10] other than the requirement of a solvent (ODCB = *o*-dichlorobenzene) which was compatible with both C_{60} and the other components. The cycloadducts were obtained in 24–52% isolated yield.

Even though the indoline derivative **3** is racemic and C_{60} is essentially spherically symmetric (I_h), remarkably, the cycloadduct is produced as a 2.1:1 mixture of diastereomers (HPLC, Regis Trident-Tri-DNP "Buckyclutcher I" column, 10% ethyl acetate in toluene, 1 mL/min, UV/320 nm). The implication is that one of the transition states is energetically more favored. Since examination of molecular models does not reveal any large, qualitative differences in steric requirements of either one of the diastereomeric transition state structures, as is the case with, e.g., *N*-phenylmaleimide (*exo* vs *endo* carbonyls), there must exist a subtle electronic interplay (charge-transfer) between the weakly electron-donating indoline of one of the isomünchnone enantiomers and the electron acceptor C_{60}.[16]

Hydrolysis of the ester function in adducts **5** and **8** could have led to potentially biologically active C_{60} derivatives whose activity could be more easily assertained due to their solubility in physiologic fluids. Interestingly, attempts to produce the carboxylic acids by electrophilic catalysis (trifluoroacetic acid, rt, 48 h and BF_3·etherate, rt, 12 h; the reactions proceed cleanly at higher temperature, see supplemetary material) afforded *only C_{60} as the sole characterizable product*. Since acid hydrolysis was not effected and since, in another work, we discovered that *t*-Bu ester derivatives of methanofullerenes and fulleroids are easily thermolyzed to the corresponding carboxylic acids,[17] we attempted a pyrolytic "hydrolysis" of **8**. When a solution of **8** was heated to reflux in toluene, *the only characterizable product was C_{60}*. As was previously encountered with some Diels–Alder adducts of C_{60},[2,18] these isomünchnone adducts

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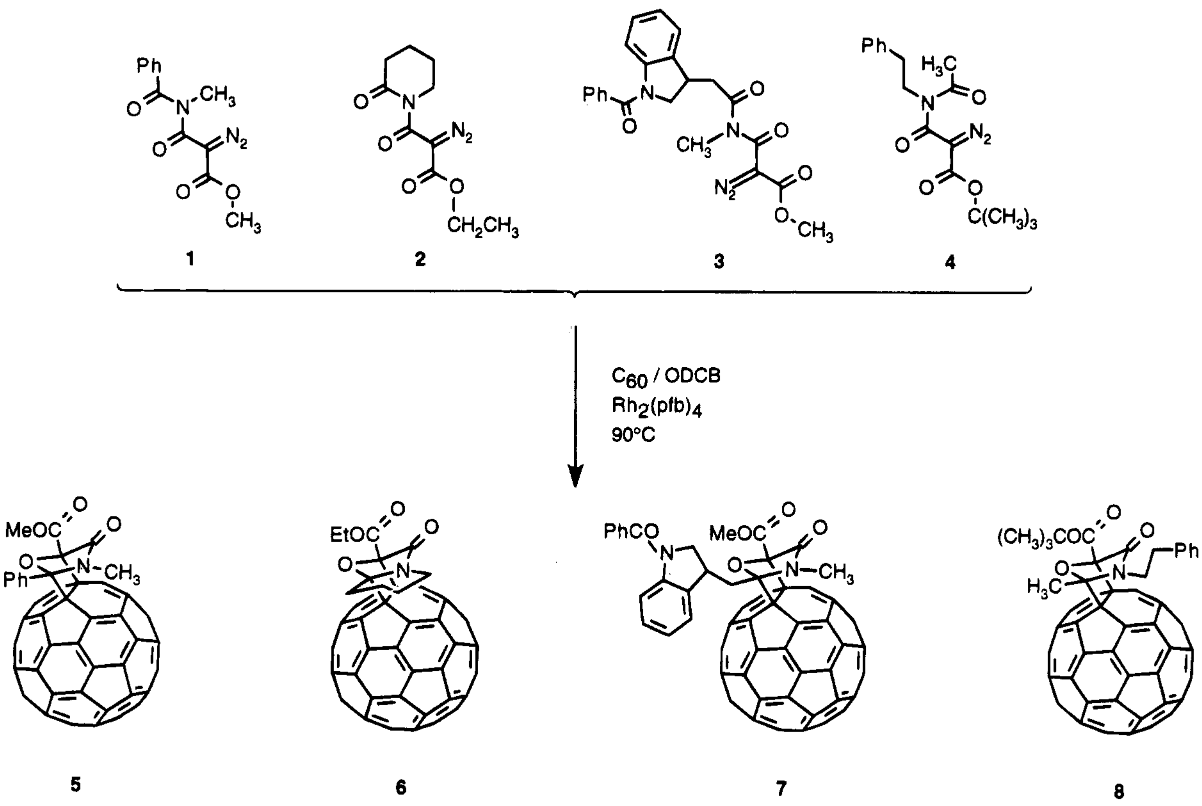
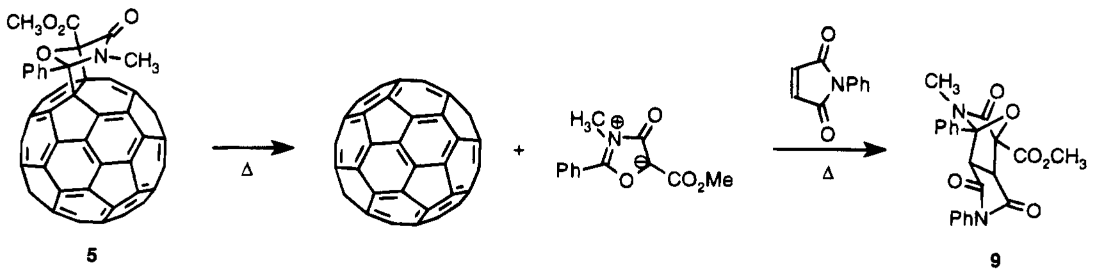
Scheme 1



Scheme 2



undergo ready thermal cycloreversion.[19] To determine if the isomünchnone dipole remained intact in the process, we heated adduct **5** in toluene in the presence of *N*-phenylmaleimide. Besides C_{60}, the reaction mixture contained the known adduct **9**, isolated in 94% yield (Scheme 2).

It is clear that C_{60} is more electrocyclofugal than *N*-phenylmaleimide which does not show signs of reversal at 110 °C. It is also obvious that C_{60} can act as a repository of isomünchnones and could be used as an isomünchnone reagent, especially in cases where the addend has $Rh_2(pfb)_4$-sensitive functional groups.

Electrochemical properties determined using cyclic voltammetry show that all the adducts undergo three well-defined, single-electron, nearly reversible waves.[20] In addition there is a fourth, irreversible reduction wave for each adduct, which appears to consist of more than one part. A study using Osteryoung square wave voltammetry (OSWV)[21] demonstrated that this fourth reduction does indeed consist of at least two, and possibly three, separate processes. The half cell potentials (defined as $E_1 = 0.5(E_{p,c} + E_{p,a})$), for the reduction of the adducts **5–8**, relative to Fc/Fc^+, are given in Table 1. The corresponding values for C_{60} are included for comparison.

Table 1. Half-Cell Potentials (mV)

compd	E_1	E_2	E_3	E_4[22]
5	−1064	−1459	−1939	−2447[23]
6	−1075	−1470	−1955	−2455[23]
8	−1095	−1500	−1995	−2551[23]
C_{60}	−1056	−1451	−1906	−2384

The reductions of **5–8** occur at potentials only slightly negative to that of C_{60}. The small magnitude of this shift is somewhat surprising, especially considering the magnitude of the shifts reported earlier for the [6,6]metha-

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(25) Further studies employing stronger electron-accepting and -donating carboxy derivatives are underway.

nofullerenes.[24] It is especially interesting to note that there is a relationship between the reduction potential E_1 and the donor ability of the alkyl group attached to the ester moiety; i.e., *t*-Bu > Et > Me. This would tend to suggest that there is an interaction between the HOMO of the ester group and the LUMO, which is primarily of C_{60} character.[25]

In conclusion, the 1,3-dipolar cycloaddition of several isomünchnone dipoles with buckminsterfullerene C_{60} gives rise to [3 + 2] cycloadducts which, on thermolysis, regenerate the mesoionic heterocycle in excellent yield. Further studies in this area are in progress and will be reported at a later date.

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Supplementary Material Available: Experimental details for the preparation of all cycloadducts as well as spectroscopic data for all new compounds (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.