stirring the mixture at 0 °C for 0.5 h, and workup (aqueous NH_4Cl) afforded a single diastereoisomer (7) (NMR, GC). Flash chromatography and crystallization (pentane) gave pure (*S*,*S*,*S*)-cyclopropylcarbinol 7[5] in 91% yield (mp 79–80 °C). Swern oxidation[6] of carbinol 7 and regioselective cyclopropane hydrogenolysis of the resulting, known ketone[4c,11] with lithium in rigorously anhydrous NH_3/Et_2O at −78 °C provided, after bulb-to-bulb distillation, pure (*R*)-muscone[12] (**8**, 82% yield).

In summary, we have synthesized pure (*R*)-muscone **8** from the commercial precursors propargyl alcohol and bromododecane in 48% overall yield, which compares very favorable with previous syntheses of **8**.[4,13] This work represents, to our knowledge, the first asymmetrically catalyzed macrocyclization;[14] moreover, it highlights the synthetic potential of the novel (1-alkenyl)ethylzinc reagents **2** and demonstrates the suitability of cyclic (*E*)-allyl alcohols for efficient chirality transfer.

Acknowledgment. Financial support of this work by the Swiss National Science Foundation, Sandoz Pharma Ltd., Basel, and Givaudan-Roure AG, Dübendorf, is gratefully acknowledged. We thank Firmenich SA, Geneva for kindly providing a sample of (*R*,*S*)-muscone.

Supplementary Material Available: Preparations and analysis data, including mp, IR, ^1H NMR, ^{13}C NMR, MS, and [α] values (4 pages). Ordering information is given on any current masthead page.

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[11] The use of rigorously dried liquid ammonia was essential to prevent the reported[4c] concomitant reduction of the carbonyl group.

[12] Identified by comparison (GC, IR, ^1H NMR, ^{13}C NMR, MS) with racemic muscone. $[\alpha]_D = -12.7°$ (c = 0.9, MeOH, 18 °C); lit.[4g] $[\alpha]_D = -12.5°$ (c = 5.0, MeOH, 18 °C).

[13] Using the same protocol but employing 1 mol % of (−)-DAIB as a macrocyclization "catalyst" gave unnatural (*S*)-muscone.

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[3 + 2] and [4 + 2] Cycloadditions of C_{60}

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Table I. Cyclic Voltammetry of C_{60}, **2**, **3**, **5**, and $C_{61}Ph_2$ Fulleroid[a]

	peak position (mV)			
compd	E1	E2	E3	E4
C_{60}	−238	−838	−1418	−1921
2	−406	−979	−1585	−2042
3	−362	−930	−1578	−2002
5	−366	−930	−1536	−1992
Ph_2C_{61}	−346	−924	−1476	−1953

[a] Conditions: Pt working and counter electrodes; scan rate, 1000 mV/s; Ag/AgCl/3 M NaCl, reference electrode; ferrocene internal reference (+620 mV); 0.1 M $TBABF_4$ in THF in a drybox.

The unique structure and properties of C_{60} (buckminsterfullerene)[1–5] have resulted in an outburst of scientific investigation. During a systematic study of the reactivity of C_{60} with substituted diazomethanes,[6] we obtained experimental evidence of the dipolarophilic character and hence of the high reactivity of C_{60} in cycloadditions.[5]

In this communication we report the behavior of C_{60} toward trimethylenemethane (TMM, [3 + 2] cycloaddition) and isobenzofuran ([4 + 2] cycloaddition).[7]

There are at least two types of TMM intermediates which could be employed, "nonpolar" (diradicaloid) and "polar" (dipolar). A nonpolar TMM would be one generated from a 7-alkylidene-2,3-diazabicycloheptene,[8–10] whereas a polar TMM would be generated by thermolysis of methylenecyclopropanes.[11] The former and the latter have provided simple access to five-membered ring compounds, e.g., cyclopentanes[8,11] and tetrahydrofurans.[10,12] The TMM precursor which gave the best results in terms of isolation and characterization,[13] in the present work, was the methylenecyclopropanone ketal **1**,[11,12] which was heated overnight in 1,2-dichlorobenzene at 70 °C in the presence of equimolar C_{60}. Purification through column chromatography

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[6] The process was named fullerene inflation, with formation of "fulleroids C_{61}–C_{66}.

[7] In a preliminary work we observed that excess cyclopentadiene and excess anthracene react with C_{60}, giving products of multiple addition (Wudl, F.; Hirsch, A.; Khemani, K. C.; Suzuki, T.; Allemand, P.-M.; Koch, A.; Eckert, H.; Srdanov, G.; Webb, H. In ref 4, p 161).

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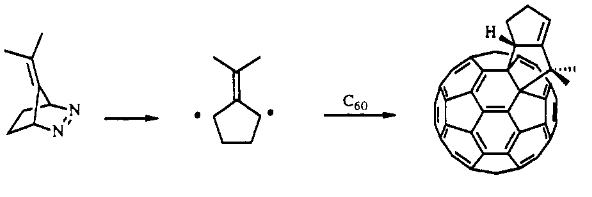
[13] We have also examined the diradical addition of 2-isopropylidenecyclopentane-1,3-diyl[8–10] (A) to C_{60}. The diazene precursor of A was heated with a slight excess of C_{60} in refluxing toluene under argon atmosphere to give unreacted C_{60} and a monoadduct whose structure was determined as B on the basis of ^1H NMR spectroscopy [(500 MHz, $CS_2/CDCl_3$, δ) 5.99 (dd, $J = 2.0$, 1 H, bridgehead), 5.20 (m, 1 H, vinyl), 3.04–2.90 (m, 2 H), 2.80–2.71 (m, 1 H), 2.70–2.63 (m, 1 H), 2.12 (s, 3 H, CH_3), 2.00 (s, 3 H, CH_3)]. Unfortunately, we were unable to chromatographically separate C_{60} and this adduct because of their similar polarities. Any dimer expected to be produced by the combination of triplet diradicals was not detected by TLC (Berson, J. A.; Bushby, R. J.; McBride, J. M.; Tremelling, M. *J. Am. Chem. Soc.* **1971**, *93*, 1544). An excess of the reagent A led to multiple additions, and up to six substituents were observed by FAB mass spectrometry (m/z 1368, 1260, 1152, 1044, 936, and 720 amu).



A

B

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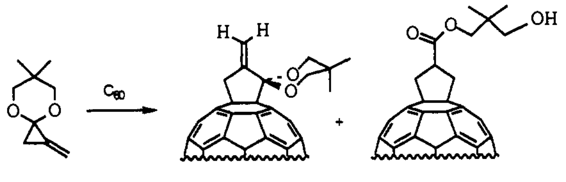
(silica gel, mixtures of hexanes and toluene) allowed the isolation of two products, **2** and **3** in 34 and 27% yield, respectively, along with 35% unreacted C_{60} (eq 1).

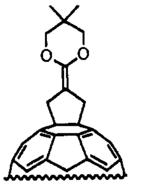


(1)

1 **2** **3**

The structure of the interesting α-methylene cyclopentanone ketal **2** is reminiscent of the addition mode of **1** to C=O.[12] The ^1H NMR spectrum shows a singlet at 4.18 ppm for the CH_2 protons in the five-membered ring, thus accounting for an attack on the 6–6 (symmetrical) junction on the ball.[14] The two vinyl protons resonate at 6.0 and 5.9 ppm as broad singlets whereas the axial and equatorial protons in the dioxane ring appear as an AB quartet (J = 11 Hz) and the methyls give two different singlets.

The ester **3** is probably the product of the silica gel catalyzed hydrolysis of the ketene acetal **4**. The latter is the expected product in the reaction of TMM with electron-deficient olefins.[11]

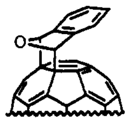


4

The UV–vis spectra of **2** and **3** are virtually superimposable, showing the absorptions typical for fullerene-containing materials at 209, 256, and 308 nm. The cyclic voltammograms of **2** and **3** exhibit the four reversible reduction waves observable in all fulleroids C_{61}.[5] A cathodic shift of ca. 60–150 mV and of ca. 20–100 mV relative to Ph_2C_{61} can be seen in the cases of **2** and **3**, respectively, probably due to saturation of a double bond and partial loss of conjugation (see Table I).

Since the dienes used in the previous study of [4 + 2] cycloadditions were relatively unreactive and hence required conditions which led to inseparable mixtures of products and isomers characterizable only by FABS,[7] we decided to attempt reactions with a "hot" diene. Treatment of C_{60} with isobenzofuran (generated in situ from 1,4-dihydro-1,4-epoxy-3-phenylisoquinoline[15]) in refluxing benzene gave the mono adduct **5** in 46% yield. This adduct is stable in the solid state and easy to isolate by chromatography. It is also stable in solution, showing no tendency to undergo cycloreversion.[16] The ^1H NMR spectrum supports C_s symmetry, indicating that the isobenzofuran adds to the junction of two hexagons. A ^{13}C NMR spectrum shows 29 peaks between 153.8 and 121.5 ppm as well as two peaks at 88.9 and 76.0 ppm. The C_s structure of **5** requires 34 peaks in the sp^2 region.[17]

The adduct **5** has the three characteristic absorptions of fullerene derivatives in the UV region (217, 255, and 310 nm). The spectrum is almost identical to those of **2** and **3**, as one would expect from the chromophore's similarity in the three compounds. The cyclic voltammogram is also very similar to that of **3** (see Table I).



5

In conclusion, we have shown that, according to its proposed electrophilic reactivity, C_{60} can be a good 2π-component cycloaddition partner. The [3 + 2] cycloadducts are stabilized by virtue of the irreversible addition mode provided by the TMMs. This new way of functionalization gives fullerene-containing compounds which exhibit electronic properties similar to those of fulleroids, notwithstanding the loss of conjugation due to saturation of one double bond.

Acknowledgment. We thank the National Science Foundation for support through Grants DMR-88-20933, DMR-91-11097, and CHE-89-08323.

Supplementary Material Available: Experimental details and full characterization of compounds **2**, **3**, and **5** and UV–vis spectra of compounds **2** and **3** (1st figure) and **5** (2nd figure) (4 pages). Ordering information is given on any current masthead page.

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(14) For a dramatic effect of five- and six-membered rings in fulleroids on chemical shifts, see: Suzuki, T.; Li, Q.; Khemani, K.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 7301.

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(16) Room temperature ^1H NMR in $CDCl_3/CS_2$ showed slow disappearance of the adduct's resonances. The initial conclusion was that a retro Diels–Alder decomposition process was occurring at an unusually low temperature. However, control experiments [attempts to trap IBF with *N*-methylmaleimide (NMM) both at room temperature and at toluene reflux, treatment with trifluoroacetic acid (TFA)] revealed that the cycloadduct *is robust and stable even to 12-h exposure to warm TFA*. The initial, incorrect conclusion was due to (a later) observation of slow crystallization of the cycloadduct during the recording of the NMR spectrum, leading to the diminution of signal intensity.

(17) The remaining five quaternary carbon resonances are probably too weak to be detected with our equipment.

Intramolecular Alkene Trapping of Pyran-4-one-Derived Zwitterions: A Novel Synthesis of Diquinanes and Hydrindans[1]

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Diquinane and hydrindan skeletons are widely distributed in nature and form key portions of many biologically important natural products.[2] The development of efficient approaches to the synthesis of such structures is of continuing importance. The photochemistry of pyran-4-ones[3] has yielded several intriguing mechanistic and synthetic insights. The observation of solvent adduct formation upon photolysis in hydroxylic media[4] provided evidence for a transient bicyclic oxyallyl zwitterion intermediate and suggested a novel cyclopentannulation strategy relying on pyran-4-one precursors.[5] We report here a powerful new method for the direct construction of diquinane and hydrindan skeletons via intramolecular zwitterion capture with olefinic nucleophiles.[6] This reaction entails the concomitant formation of two strategic

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[†] All inquiries regarding crystallographic data should be directed to this author.

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