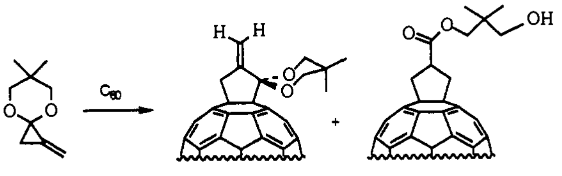
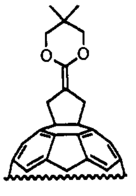
(silica gel, mixtures of hexanes and toluene) allowed the isolation of two products, **2** and **3** in 34 and 27% yield, respectively, along with 35% unreacted C$_{60}$ (eq 1).



1 2 3 (1)

The structure of the interesting α-methylene cyclopentanone ketal **2** is reminiscent of the addition mode of **1** to C=O.[12] The ^{1}H 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]

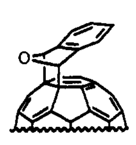


4

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$_2$C$_{61}$ 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 ^{1}H 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.

(15) Whitney, S. E.; Winters, M.; Rickborn, B. *J. Org. Chem.* **1990**, *55*, 929.

(16) Room temperature ^{1}H 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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Received November 19, 1992

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.

(1) (a) Reported in preliminary form: West, F. G.; Fisher, P. V.; Willoughby, D. W. *Abstracts of Papers*, 201st National Meeting of the American Chemical Society, Atlanta, GA, April 1991; American Chemical Society: Washington, DC, 1991; ORGN 338.

(2) (a) For a recent review of the synthesis of di- and polyquinanes, see: Fu, X.; Cook, J. M. *Aldrichimica Acta* **1992**, *25*, 43. (b) Paquette, L. A. *Polyquinane Chemistry, Synthesis and Reactions*; Springer-Verlag: Heidelberg, 1987. For recent approaches to the hydrindan skeleton, see: (c) Fernândez, B.; Pêrez, J. A. M.; Granja, J. R.; Castedo, L. Mouriño, A. *J. Org. Chem.* **1992**, *57*, 3173 and references therein. (d) Satoh, S.; Sodeoka, M.; Sasai, H.; Shibasaki, M. *Ibid.* **1991**, *56*, 2278 and references therein.

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(4) (a) Barltrop, J. A.; Day, A. C.; Samuel, C. J. *J. Am. Chem. Soc.* **1979**, *101*, 7521. (b) Pavlik, J. W.; Pauliukonis, L. T. *Tetrahedron Lett.* **1976**, 1939. (c) Keil, E. B.; Pavlik, M. W. *J. Heterocycl. Chem.* **1976**, *13*, 1149.

(5) West, F. G.; Fisher, P. V.; Willoughby, C. A. *J. Org. Chem.* **1990**, *55*, 5936.

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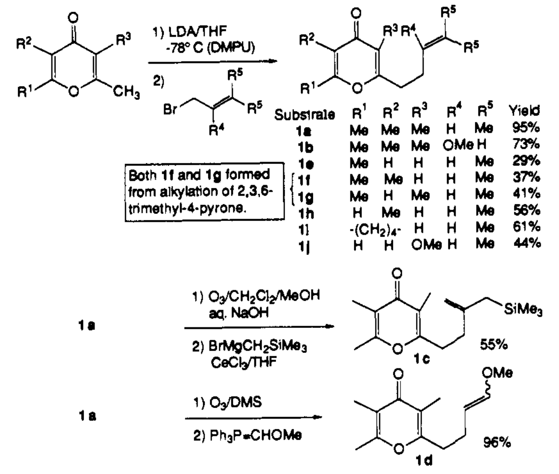
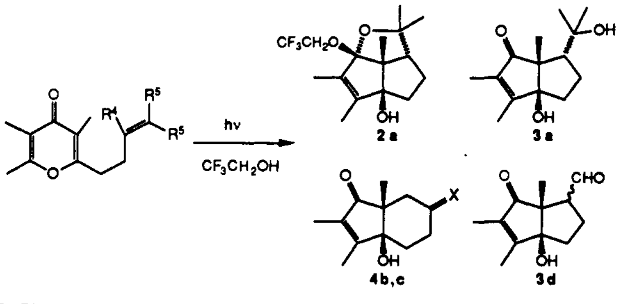
Scheme I



Substrate	R^1	R^2	R^3	R^4	R^5	Yield
1a	Me	Me	Me	H	Me	95%
1b	Me	Me	Me	OMe	H	73%
1e	Me	H	H	H	Me	29%
1f	Me	Me	H	H	Me	37%
1g	Me	H	Me	H	Me	41%
1h	H	Me	H	H	Me	56%
1i	$-(CH_2)_4-$		H	H	Me	61%
1j	H	H	OMe	H	Me	44%

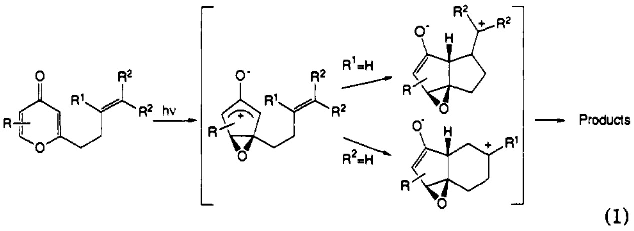
Table I. Effect of Alkene on 4-Pyrone Photolyses[a]



Entry	Substrate	R^4	R^5	Products (Yield, %)[b]
1	1a	H	Me	2a (49),[c] 3a (20)[c]
2	1b	OMe	H	4b, X = O (61)[d]
3	1c	CH_2SiMe_3	H	4c, X = CH_2 (69)
4	1d	H	H, OMe	3d (76)[d]

[a] See Table II for standard photolysis procedure. [b] Isolated yields after chromatography. Satisfactory IR, ^1H and ^{13}C NMR, and combustion analysis or HRMS data were obtained for all substrates and products. [c] Yields of 2a and 3a reflect partial hydrolysis of 2a during chromatography. [d] Without acid workup, products are the mixed methyl trifluoroethyl acetals. 3d was isolated as a 2:1 mixture of aldehyde epimers.

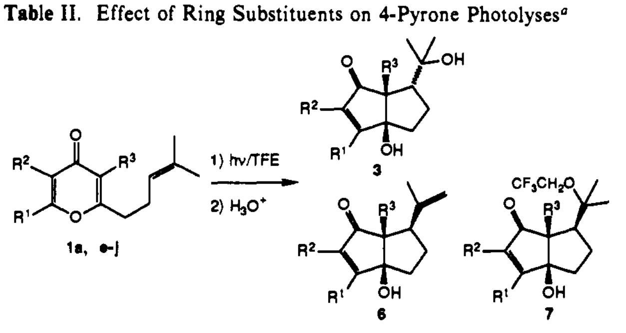
carbon–carbon bonds and two carbocyclic rings from simple heterocycle precursors (eq 1).



(1)

The substrates for the key photoreaction could be efficiently prepared in 1–3 steps. Attachment of pendant alkenes to the 4-pyrone nucleus was straightforward via the facile γ-deprotonation at position 2 (Scheme I).[5,7] Allylation of the resulting anion, followed in some cases by side-chain modification,[8,9] gave substrates 1a–j in moderate to excellent yield.

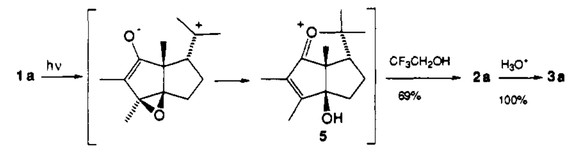
Table II. Effect of Ring Substituents on 4-Pyrone Photolyses[a]



Entry	Substrate	R^1	R^2	R^3	Products (Yield, %)[b]
1	1a	Me	Me	Me	3a (69)
2	1e	Me	H	H	
3	1f	Me	Me	H	3f (22), 6f (18), 7f (9)
4	1g	Me	H	Me	
5	1h	H	Me	H	3h (17), 6h (5), 7h (5)
6	1i	$-(CH_2)_4-$		H	3i (14), 6i (22), 7i (5)
7	1j	H	H	OMe	3j (75)

[a] Standard conditions: substrate was dissolved in trifluoroethanol in a quartz vessel at a concentration of 3 mM. After degassing, the reaction mixture was photolyzed (Hanovia 450-W medium-pressure Hg lamp) until starting material was consumed. Crude products were stirred with dilute HCl in aqueous THF to hydrolyze mixed ketals. [b] Isolated yields after chromatography. Satisfactory IR, ^1H and ^{13}C NMR, and combustion analysis or HRMS data were obtained for all substrates and products.

With 1a–j in hand, we sought to examine the effect of both ring and alkene substitution on the reaction outcome. Table I lists the results from photolysis of 1a–d, in which the ring substituents were held constant and the olefin trap was varied. Prenylated substrate 1a (entry 1) gave a mixture of mixed ketal 2a and its hydrolysis product 3a in good overall yield. Ketal 2a presumably arose from solvent capture of oxocarbenium ion 5 (eq 2) and could be quantitatively converted to 3a by workup with dilute acid. Single crystal X-ray diffraction analysis of 3a confirmed the relative stereochemistry of the three chiral centers. *The synthetic potential of this transformation is apparent given the one-step conversion of achiral 4-pyrone 1a into diquinane 3a with concomitant formation of two carbocyclic rings and three contiguous stereocenters.*



(2)

Ring closure in a 6-endo sense to give a bicyclo[4.3.0]nonenone skeleton was then examined. Enol ether 1b and allyl silane 1c (entries 2 and 3) were found to undergo efficient closure in the desired fashion to give the hydrindenones 4b and 4c. As expected, isomeric enol ether 1d gave diquinane aldehydes 3d, also in very good yield.

The effect of ring substituents was then probed via a series of 4-pyrones bearing identical olefin traps (Table II). In comparison to the original example (entry 1), results ranged from comparable yields of diquinane products to complete recovery of starting material. For the polymethylated series, we have observed an apparent requirement for the presence of a non-hydrogen substituent at position 5 ($R^2 \neq H$); those substrates which were unsubstituted at that position (entries 2 and 4) were recovered unchanged despite extended photolysis.[10] Surprisingly, ring-

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(8) (a) Conversion of olefin to methyl ester: Marshall, J. A.; Garofalo, A. W.; Sedrani, R. C. *Synlett.* **1992**, 643. (b) Conversion of ester to allyl silane: Bunnelle, W. H.; Narayanan, B. A. *Org. Synth.* **1990**, *69*, 89.

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(10) In contrast, the efficiency of photolysis of 4-pyrones bearing pendant alcoholic nucleophiles displays little dependence on ring substituents.[5] We are currently attempting to determine the origin of this surprising difference between hydroxylic and olefinic nucleophiles.

oxygenated substrate **1j** (entry 7) led to diquinane **3j** in good yield despite the hydrogen at position 5.

Substitution at position **3** was also significant. Those cases in which $R^3 \neq H$ (entries 1 and 7) showed complete diastereoselectivity for α-disposition of the side chain, corresponding to a compact transition state with the olefin tucked underneath the zwitterion to avoid unfavorable steric interactions with R^3. Those cases with $R^3 = H$ (entries 3, 5, and 6) gave roughly equal amounts of products derived from compact and extended transition states. Cyclization products with β-disposed tertiary carbocations are geometrically precluded from mixed ketal formation and suffer either elimination or solvent capture.[11]

In summary, we have found that photochemically generated oxyallyl zwitterions bearing pendant olefinic groups undergo efficient cyclization to yield fused bicyclic products. Complete selectivity for either 5-exo closure to give diquinanes or 6-endo closure to give hydrindans is possible by varying alkene substitution, and high diastereoselectivity is also possible. The substantial complexity of the products relative to the 4-pyrone precursors renders this a powerful method for the rapid construction of functionalized carbocyclic skeletons. Further applications of this new class of reactions will be reported in due course.

Acknowledgment. We thank the National Institutes of Health (GM44720-01) for generous support of this work, the American Cancer Society for a Junior Faculty Research Award (F.G.W.), and the University of Utah for a Graduate Research Fellowship (P.V.F.). Mass spectrometry facilities were funded by NSF (CHE-9902690) and the University of Utah Institutional Funds Committee.

Supplementary Material Available: Representative experimental procedures for the preparation and photolysis of **1a–d**, and an ORTEP drawing and tables of positional parameters, bond angles, and bond distances for **3a** (11 pages). Ordering information is given on any current masthead page.

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[11] In several cases, we have observed slow consumption of **6** and **7** due to secondary photochemistry. The somewhat higher overall yields seen in entries 1 and 7 may be attributed to their clean formation of mixed ketal **2**, which is not photolabile.

Synthesis of Mixed Copper–Indium Chalcogenolates. Single-Source Precursors for the Photovoltaic Materials $CuInQ_2$ (Q = S, Se)

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Currently, *thin film* solar cells of $CuInSe_2$ are the most radiation tolerant and among the most efficient solar cells at 12%.[1] $CuInS_2$ is also a promising photovoltaic thin film material with achieved solar cell efficiency of 7%.[2] $CuInSe_2$ has been prepared by a number of physical techniques:[3] (1) flash evaporation and evaporation of $CuInSe_2$ powder; this leads to copper deficient material unless the source temperature is approximately above 1300 °C; often adding an additional Se evaporation source to help control reevaporation of Se from the substrate is necessary; (2) evaporation from the binary compounds, for example, Cu_2Se, In_2Se_3; (3) three-source coevaporation from the elements; (4) RF and ion beam sputtering of polycrystalline $CuInSe_2$; (5) molecular beam epitaxy; and (6) spray pyrolysis.[3] All these techniques involve high temperatures. Electrochemical deposition from solutions has also been employed, but stoichiometric control of the product is difficult due to the different rates of Cu, In, and Se deposition.[3] The films obtained can have high defect density and nonstoichiometry, both detrimental to device performance. It is clear that a reliable, low-temperature method for producing high-quality $CuInSe_2$ is highly desirable. By controlling the synthesis of $CuInSe_2$ at the molecular level via proper precursor compounds, we should be able to achieve milder synthetic conditions for $CuInSe_2$. Ideally, such precursors should have the correct Cu/In stoichiometry built in (i.e., Cu:In ratio 1:1) and should decompose in simple steps to the desired product. Although many excellent single-source precursors exist for binary solid-state compounds, such as GaAs,[4] CdSe,[5a] ZnSe,[5b] MnTe,[5c] TiB_2,[6] In_2Se_3,[7] GaN,[8] FeB,[9] etc.,[10] reports on single-source precursors

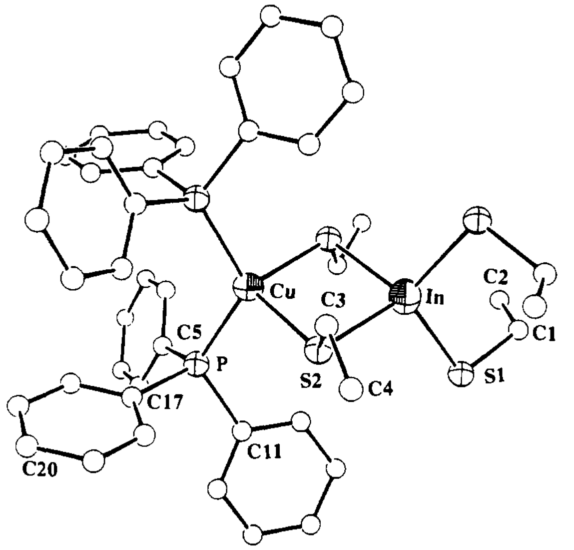

Figure 1. ORTEP drawing of $(Ph_3P)_2CuIn(SEt)_4$. The molecule is sitting on a 2-fold crystallographic axis. Selected bond distances (Å) and angles (deg): Cu–P1 2.278(2), Cu–μ–S2 2.418(2), S2–C3 1.816(7), In–S1 2.419(3); P–Cu–P 120.7(1), S2–Cu–S2 96.3(1), Cu–S2–In 85.58(8), S1–In–S1 112.7(1). The structure of $(Ph_3P)_2CuIn(SeEt)_4$ is essentially the same, the difference being in the conformation of the ethyl groups and the lack of a 2-fold rotation axis. Selected average bond distances (Å) and angles (deg): Cu–P 2.275(3), Cu–^{br}Se 2.526(2), In–^{br}Se 2.611(2); In–^{t}Se 2.557(2); P1–Cu–P2 114.9(1), ^{br}Se–Cu–^{br}Se 101.78(7), Cu–^{br}Se–In 80.42(6), ^{t}Se–In–^{t}Se 117.48(6). ^{br}Se and ^{t}Se denote bridging and terminal Se atoms.

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