Reaction of C_{60} with Benzocyclobutenol: Expeditious Route to Fullerene Adducts

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Received May 19, 1994®

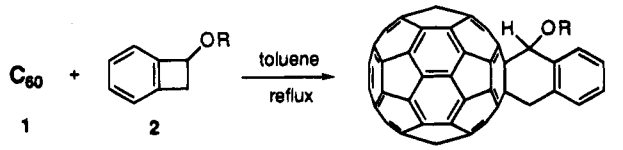
Reaction of C_{60} with benzocyclobutenol (**2a**) and its methoxy ether (**2b**) in refluxing toluene gave 1,9-dihydrofullerene cycloadducts **3a** and **3b** in 59% and 50% yields, respectively. The alcohol was converted to pyranyl ether (**4**), acrylate (**5**), *p*-vinylbenzoate (**6**) and acid succinate esters (**7**) in good yields under very mild conditions. The adducts exist as two interconverting boat conformers. Acrylate **5** and *p*-vinylbenzoate **6** should be useful for polymerization studies. Acid **7** shows enhanced solubility in polar solvents.

Introduction

Since the discovery and isolation of buckminsterfullerene (C_{60})[1,2], this fascinating molecule continues to attract great interest.[3–5] The literature on its chemical reactivity and transformations is growing rapidly.[6,7] Fullerene adducts with interesting structural and physical properties have been prepared.[8–14] A few water-soluble compounds with potential biological activity have recently been reported.[15–19] Amphiphilic fullerene derivatives, which can be transported in biological systems and can potentially bind to membranes, are particularly desirable for biological testing.

Among the derivatization methods available, cycloadditions have been particularly successful. Müllen et al. reported that *o*-quinodimethane, generated by 1,4-elimination of Br_2 from 1,2-bis(bromomethyl)benzene, reacted with C_{60} to give a stable monoadduct.[20] We thought that benzocyclobutenol should be an ideal reagent, since its ring opening ($[\sigma_2 + \pi_2]$, conrotatory) to generate hydroxy-*o*-quinodimethane can be smoothly achieved in refluxing toluene[21] (an excellent solvent for C_{60}), but also because the hydroxyl group in the resulting adduct would be particularly useful for further functionalization. We now report that C_{60}-benzocyclobutenol adducts are readily prepared in high yields and provide expeditious access to fullerene derivatives with a wide variety of substitution. Dynamic behavior of two C_{60}-adducts is also investigated.

Scheme 1



3a: R = H (59%)
3b: R = Me (50%)

Results

Benzocyclobutenol (**2a**) was prepared from 2-bromostyrene oxide.[22] Refluxing a mixture of C_{60} and a slight excess of **2a** in deoxygenated toluene afforded 61-hydroxy-1,9-(methano[1,2]benzenomethano)fullerene[60] (**3a**) in 59% yield, along with 6% of a diadduct and traces of more polar (by HPLC and TLC) material and unreacted C_{60} (Scheme 1). C_{60}, **3a**, and diadduct were easily separated by flash column chromatography. HR-FAB MS of **3a** showed it to have the molecular formula $C_{68}H_8O$. FT-IR shows distinctive bands corresponding to the dihydrofullerene core,[23,24] and the UV–vis spectrum of **3a** is similar to that of most dihydrofullerenes.[19,25–29] ^1H and ^{13}C NMR spectra of the adduct

® Abstract published in *Advance ACS Abstracts,* August 1, 1994.

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Table 1. Chemical Shifts (δ, ppm) of the C_{60}-Fused Cyclohexene Ring Protons[a]

	3a-A	3a-E	3b-A	3b-E	5-A	5-E	6-A	6-E	7-A	7-E
H_a	5.62	4.51	5.44	4.46	5.40	4.54	5.52	4.57	5.34	4.51
H_b	4.37	4.82	4.29	4.79	4.42	4.95	4.49	4.99	4.38	4.87
H_c	6.37	6.51	5.79	5.92	7.46	7.69	7.68–7.58[b]	7.87	7.41	7.66–7.55[b]

[a] ARX 400 or ARX 500-MHz spectrometer. [b] H_c signal overlaps with phenyl protons.

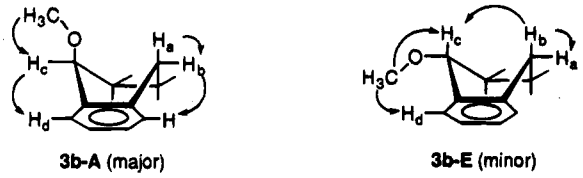
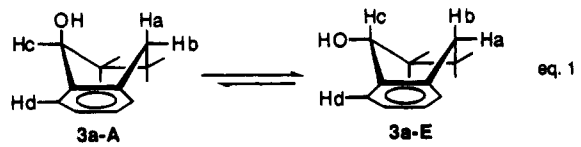


Figure 1. Observed positive NOEs of compound **3b**.

are consistent with the assigned structure. The molecular formula of the diadduct was shown to be $C_{76}H_{16}O_2$ by FAB MS, but the ^1H NMR indicates it to be a mixture of isomers which could not be further purified or assigned.

^1H NMR of **3a** showed two sets of signals, apparently resulting from isomers, in a ratio of 1:1.4. The ^{13}C NMR spectrum showed a total of 94 resolved resonances, of which 8 are in the aliphatic region between 80.5 and 43.5 ppm. Two possibilities are conceivable: (a) 6,6- and 6,5-ring junction isomers are formed from addition of the *o*-quinodimethane[30] or (b) two "frozen" 6,6-addition benzocyclohexene conformers exist at room temperature. Variable-temperature NMR studies support only the latter possibility: on warming, the signals corresponding to hydroxy and methine protons began to coalesce at 80 °C and sharpened to one set above 140 °C in $Cl_2CDCDCl_2$, with the number of resonances corresponding to pseudoplanar **3a**. The original shape and ratio of the two sets of signals were restored on cooling to room temperature. This behavior is characteristic of slow boat–boat inversion, previously observed in fullerene Diels–Alder adducts (eq 1).[31,32]



To assist in assigning structures to the two conformers, the methoxy-substituted cycloadduct **3b** was prepared in 50% yield from 1-methoxybenzocyclobutene (**2b**)[21] and C_{60}, using a similar procedure. Spectral properties (see Experimental Section) were very similar to those of **3a**. The ^1H NMR spectrum of **3b** also showed two sets of signals in a ratio of 2.5:1. NOE measurements allow configurational assignment (Figure 1). By comparison with the chemical shifts (Table 1), the *less* stable isomer **3b-E** has a pseudoequatorial hydroxy group, which is the *more* stable conformer of **3a**.

We next investigated conversion of the hydroxyl group to other derivatives. Tetrahydropyranyl ether **4** was prepared by treatment of **3a** with 3,4-dihydro-2*H*-pyran (45 equiv) and PTSA (0.8 equiv) in CH_2Cl_2 in good yield, suggesting that steric hindrance of the vicinal C_{60} cage does not prevent acetal formation. Esterification of **3a** with acrylic acid, *p*-vinylbenzoic acid, and succinic anhydride under very mild conditions furnished esters **5**, **6**, and **7**, respectively, in reasonable yields (Table 2). Acid **7** is soluble in DMSO and sparingly soluble in neutral water (ca. 1.0×10^{-5} M). The solution showed broad UV/vis absorption around 300 nm probably due to aggregation in water. This derivative offers a prospect for biological probes based on the dihydrofullerene nucleus which, like the fullerenes themselves,[33–39] has rich redox[10,40,41] and photochemistry.[42] Compounds **5** and **6** are potentially useful for polymerization studies.

Table 2. Synthesis of Fullerene Derivatives 4–7 from Adduct 3a[a]

entry	reagent (equiv)	time	product	% yield[b]
1	(45) PTSA (0.8)	1.5 h	4 (1:1)	86
2	(3) DCC (3), DMAP (0.3)	27 h	5	31
3	(3) DCC (3), DMAP (1)	28 h	6	50
4	(8) DMAP (8), pyridine (10)	24h	7	78

[a] All of the reactions were carried out in dry deoxygenated CH_2Cl_2 at room temperature. [b] Isolated yields. DCC = dicyclohexylcarbodiimide, DMAP = 4-(dimethylamino)pyridine, PTSA = *p*-toluenesulfonic acid.

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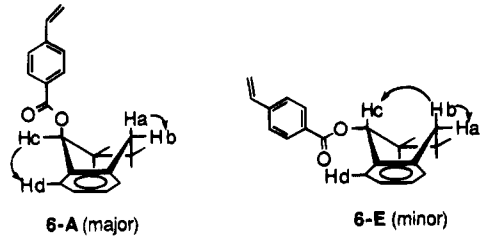


Figure 2. Observed positive NOEs of compound **6**.

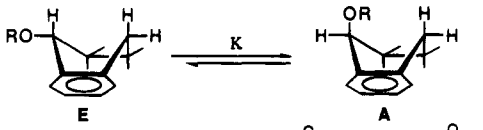
The structures of **4**–**7** were substantiated by spectroscopic methods. HR-FAB MS gave expected molecular ions. UV–vis spectra are almost identical to those of **3a** and **3b**. FT-IR spectra of **5**–**7** show characteristic carbonyl and C–O stretches, besides the fullerene bands. The strong electron-withdrawing properties of the fullerene core shift the carbonyl stretch to slightly higher frequencies (1735, 1725 cm^{-1} for unsaturated ester **5** and **6**, and 1749 cm^{-1} for acid succinate ester **7**) relative to the normal ester C=O. The ^1H NMR spectrum indicates that all resonances derive from a mixture of two "frozen" boat conformers at room temperature. NOE measurements of vinylbenzoate **6** shown in Figure 2 and comparison of chemical shifts (Table 1) with **5** and **7** allowed assignment of structures to the isomers.

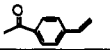
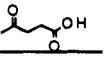
Discussion

Like all other Diels–Alder reactions of C_{60},[9,31,40,43] and all other additions, cycloaddition of the ring-opened benzocyclobutenol and its methyl ether to C_{60} take place at the 6,6-ring junction to give 1,9-dihydrofullerenes. The structures of the adducts are confirmed by ^1H, ^{13}C NMR, FT-IR, and HR-FAB MS data. The cycloadducts **3a** and **3b** are thermally stable up to 180 °C, and no traces of decomposition or cycloreversion could be detected by ^1H NMR or HPLC, in contrast to fullerene Diels–Alder adducts derived from anthracene, furan, and cyclopentadiene.[5] This is apparently due to the fact that extra stabilization was gained during the formation of the cycloadducts from aromatization of the *o*-xylylene residue.

The coalescence temperature method allows an estimate of $\Delta G^{\ddagger}$ for the boat–boat inversion of 17.6 ± 0.3 kcal/mol for **3a** and 19.3 ± 0.3 kcal/mol for **3b**, respectively. The barrier is substantially higher than that in tetrahydronaphthalene[44] and cyclohexene.[45] The high barrier to inversion of **3a** and **3b** can be attributed to severe torsional and angular constraints imparted by the rigidity of the C_{60} backbone (similar to that (14.6 ± 0.1 kcal/mol) observed by Rubin in 63,66-dimethyl-64,65-diphenyl-1,9-(methano[1,2]benzenomethano)fullerene-[60][31]) and the consequent need to have all six atoms in the cyclohexene ring nearly planar in the transition state. The peri-interactions between the α-substituent with the *o*-phenyl proton (observed in many tetrahydronaphthalene compounds[44]) and/or the C_{60} surface also contribute to the barrier and qualitatively account for the ratio of pseudoequatorial (**E**) to pseudoaxial (**A**) isomers in the derivatives (Table 3). All but the α-OH-substituted adduct tend to have α-OR pseudoaxial to avoid these interactions. The smaller size of the OH group or its ability to H-bond to the fullerene surface may cause this group to be an exception in prefering the pseudoequatorial conformation.

Table 3. Equilibrium Constants and Free Energy Differences of Pseudoequatorial (E) and Pseudoaxial (A) Conformers at Room Temperature



R	H	CH_3			
K (A/E)[a]	0.723	2.54	1.30	1.31	1.24
$\Delta G°$ cal/mol[b]	-188	540	152	157	125

[a] *K* values were measured by 400-MHz ^1H NMR at 20 °C. [b] $\Delta G° = -RT \ln K$, $T = 293$ K.

Conclusions

Cycloaddition of C_{60} with benzocyclobutenol constitutes a versatile prototype for further functionalization of fullerene derivatives with defined structural units. The products obtained exist as two interconverting boat conformers at room temperature and show interesting dynamic behavior because of the rigidity of the C_{60} backbone and the peri-interactions of the α-substituent.

Experimental Section

General. ^1H and ^{13}C NMR spectra were recorded on a Bruker ARX-400 or ARX-500 instrument equipped with a temperature control unit, and chemical shifts are in ppm (δ) relative to TMS in CS_2–$CDCl_3$. IR spectra were recorded as a KBr pellet on a Nicolet FT-205 spectrophotometer. UV–vis spectra were recorded on a Varian CARY 2300 spectrophotometer in optima CH_2Cl_2. FAB mass spectra were obtained on a VG-ZAB-SE mass spectrometer using *m*-nitrobenzyl alcohol as a matrix. CH_2Cl_2 and toluene were distilled from CaH_2 and sodium benzophenone ketyl, respectively.

Preparation of 61-Hydroxy-1,9-(methano[1,2]benzenomethano)fullerene[60] (3a). A 100-mL three-neck flask with a magnetic stirrer and condenser was oven-dried. C_{60} (147 mg, 0.2 mmol) benzocyclobutenol (42 mg, 0.35 mmol), and 70 mL of toluene were added, and the mixture was refluxed with stirring. The reaction progress was monitored by HPLC (Hypersil, 340 nm detection, 1.0 mL/min, toluene/acetonitrile = 1/1) or TLC and stopped after 3 h. Toluene was evaporated under vaccum, and the residue was chromatographed (silica gel). Elution with hexane–toluene and then toluene–ethyl acetate (gradient) afforded unreacted C_{60}, monocycloadduct **3a** (100 mg, 59%), and diadduct (10 mg, 6%). FAB-MS of **3a**: 841 (M + 1, 80), 720 (100). HR-FAB: obsd 840.0570, calcd for $C_{68}H_8O$ 840.0573. FT-IR cm^{-1}: 1508 (w), 1458 (w), 1429 (w), 1188 (m), 1057 (w), 1036 (w), 748 (m), 698 (m), 669 (m), 577 (w), 553 (w), 527 (s). UV–vis (CH_2Cl_2) λ_{max}: 700, 430, 310, 264. ^{13}C NMR (125 MHz, $CS_2/CDCl_3$) showed a total of 94 signals, of which 86 are between 157.49 and 123.33 ppm. The remaining eight signals are located at 80.48, 73.86, 71.64, 70.73, 65.72, 63.91, 43.65, and 43.47 ppm (see supplementary material). ^1H NMR (500 MHz, $CS_2/CDCl_3$) indicates the sample is a mixture of **3a-A** and **3a-E** in a ratio of 0.723. **3a-A** δ: 7.75 (d, 1 H, J = 7.30 Hz), 7.72–7.59 (m, 3 H), 6.37 (d, 1 H, J = 1.95 Hz, H_c), 5.62 (d, 1 H, J = 13.65 Hz, H_a), 4.37 (d, 1 H, J = 13.65 Hz, H_b), 3.14 (d, 1 H, J = 2.20 Hz, OH). **3a-E** δ: 7.95 (d, 1 H, J = 7.90 Hz, H_d), 7.72–7.59 (m, 3 H), 6.51 (d, 1 H, J = 6.85 Hz, H_c), 4.82 (d, 1 H, J = 13.95 Hz, H_b), 4.51 (d, 1 H, J = 13.95 Hz, H_a), 3.27 (d, 1 H, J = 6.85 Hz, OH).

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61-Methoxy-1,9-(methano[1,2]benzenomethano)-fullerene[60] (3b) was prepared in 50% yield in a procedure similar to that for **3a**. FAB-MS: 855 (M + H, 55), 823 (M − 32, 30), 720 (100). HR-FAB: obsd 854.0692, calcd for $C_{69}H_{10}O$ 854.0732. FT-IR cm^{-1}; 1620 (w), 1458 (m), 1430 (m), 1188 (m), 1121 (w), 1089 (s), 753 (m), 702 (w), 573 (m), 527 (s). UV−vis (CH_2Cl_2) λ_{max}: 704, 430, 324, 260. ^1H NMR (400 MHz, CS_2/$CDCl_3$) indicates the sample is a mixture of **3b-A** and **3b-E** in a ratio of 2.54. **3b-A** δ: 7.72−7.54 (m, 4 H, aromatic protons), 5.79 (s, 1 H, H_c), 5.44 (d, 1 H, J = 13.51 Hz, H_a), 4.29 (d, 1 H, J = 13.59, H_b), 3.65 (s, 3 H, OCH_3). **3b-E** δ: 7.87 (d, 1 H, J = 7.52 Hz, H_d), 7.72−7.54 (m, 3 H, aromatic protons), 5.92 (s, 1 H, H_c), 4.79 (d, 1 H, J = 14.05 Hz, H_b), 4.46 (d, 1 H, J = 14.12 Hz, H_a), 4.06 (s, 3 H, OCH_3).

Preparation of 61-Pyranyl-1,9-(methano[1,2]bezeno-methano)fullerene[60] (4). Compound **3a** (27 mg, 0.032 mmol), 3,4-dihydro-2*H*-pyran (0.13 mL, 1.44 mmol), and PTSA (5.0 mg, 0.026 mmol) were dissolved in 25 mL of dry CH_2Cl_2, and the mixture was stirred for 1.5 h. The reaction was stopped by adding 25 mL of phosphate buffer solution, and the organic layer was separated and dried (Na_2SO_4). Flash column chromatography (SiO_2, hexane:ethyl acetate = 10:1) gave diastereomers of **4** (25 mg, 85%) in a 1:1 ratio. FAB-MS: 925 (M + H, 30), 823 (M − 101, 80), 720 (100). HR-FAB: obsd 924.1150, calcd for $C_{73}H_{16}O_2$ 924.1150. FT-IR cm^{-1}: 2942 (m), 2865 (w), 1458 (w), 1116 (m), 1036 (m), 1020 (m), 972 (m), 750 (w), 575 (w), 554 (w), 526 (s). UV−vis (CH_2Cl_2) λ_{max}: 704, 434, 310, 258. ^1H NMR: see supplementary material.

Preparation of 61-(Acryloxy)-1,9-(methano[1,2]benzeno-methano)fullerene[60] (5). Compound **3a** (20 mg, 0.024 mmol), DCC (15 mg, 0.073 mmol), DMAP (0.7 mg, 0.006 mmol), and acrylic acid (5.2 μL, 0.073 mmol) were mixed in 20 mL of dry CH_2Cl_2, and the mixture was stirred for 27 h at room temperature. Phosphate buffer (15 mL) was added to quench the reaction. The organic layer was separated and dried (Na_2SO_4). Flash column chromatography (SiO_2, hexane:toluene = 2:1) of the condensed crude product gave 7 mg (31%) of **5**. FAB-MS: 894 (M^+, 30), 822 (M − 72, 35), 720 (100). HR-FAB: obsd 894.0680, calcd for $C_{71}H_{10}O_2$ 894.0681. FT-IR cm^{-1}: 1734 (s), 1401 (m), 1252 (m), 1167 (s), 1061 (m), 1034 (m), 979 (m), 749 (m), 699 (m), 575 (w), 527 (s). UV−vis (CH_2Cl_2) λ_{max}: 702, 432, 312, 260. ^1H NMR indicates the sample is a mixture of **5-A** and **5-E** in a ratio of 1.30. **5-A** δ: 7.87 (d, 1 H, J = 7.62 Hz, aromatic proton), 7.67−7.58 (m, 3 H, aromatic protons), 7.46 (s, 1 H, H_c), 6.67 (dd, 1 H, J = 17.30, 1.40 Hz), 6.43 (dd, 1 H, J = 17.30, 10.30 Hz), 6.04 (dd, 1 H, J = 10.3, 1.40 Hz), 5.40 (d, 1 H, J = 13.90 Hz, H_a), 4.42 (d, 1 H, J = 13.90 Hz, H_b). **5-E** δ: 7.67−7.58 (m, 4 H, aromatic protons), 7.69 (s, 1 H, H_c), 6.63 (dd, 1 H, J = 16.50, 1.36 Hz), 6.40 (dd, 1 H, J = 16.50, 8.90 Hz, H_d), 6.01 (dd, 1 H, J = 8.90, 1.36 Hz), 4.95 (d, 1 H, J = 14.07 Hz, H_b), 4.54 (d, 1 H, J = 14.07 Hz, H_a).

61-(*p*-Benzoyloxy)-1,9-(methanol[1,2]benzenomethano)-fullerene[60] (6) was prepared in 50% yield by a procedure similar to that for **5** using **3a** (24 mg, 0.028 mmol), *p*-vinylbenzoic acid (13 mg, 0.084 mmol), DCC (18.3 mg, 0.084 mmol), and DMAP (2.8 mg, 0.028 mmol). FAB-MS: 972 (M + 2, 35), 720 (100). HR-FAB: obsd 970.1044, calcd for $C_{77}H_{14}O_2$ 970.0994. FT-IR cm^{-1}: 1725 (s), 1613 (w), 1460 (w), 1430 (w), 1262 (s), 1177 (m), 1094 (s), 1075 (m), 1015 (w), 857 (m), 766 (w), 700 (w), 575 (m), 554 (w), 527 (s). UV−vis (CH_2Cl_2) λ_{max}: 702, 432, 306, 262. ^1H NMR (400 MHz, CS_2/$CDCl_3$) indicates the sample is a mixture of **6-A** and **6-E** in a ratio of 1.31. **6-A** δ: 8.24 (d, 2 H, J = 8.36 Hz), 7.96 (d, 1 H, J = 8.30 Hz), 7.68−7.58 (m, 4 H, H_c + aromatic protons), 7.54 (d, 2 H, J = 8.32 Hz), 6.80 (dd, 1 H, J = 17.52, 10.87 Hz), 5.92 (d, 1 H, J = 17.52 Hz), 5.52 (d, 1 H, J = 13.84 Hz, H_a), 5.43 (d, 1 H, J = 10.87 Hz), 4.49 (d, 1 H, J = 13.90 Hz, H_b). **6-E** δ: 8.14 (d, 2 H, J = 8.39 Hz), 7.87 (s, 1 H, H_c), 7.68−7.58 (m, 4 H, aromatic protons), 7.46 (d, 2 H, J = 8.35 Hz), 6.75 (dd, 1 H, J = 17.49, 10.87 Hz), 5.87 (d, 1 H, J = 17.49 Hz), 5.40 (d, 1 H, J = 10.87 Hz), 4.99 (d, 1 H, J = 14.09 Hz, H_b), 4.57 (d, 1 H, J = 14.16 Hz, H_a).

Preparation of Acid Succinate Ester of 61-Hydroxy-1,9-(methano[1,2]benzenomethano(fullerene)[60] (7). Compound **3a** (30 mg, 0.036 mmol), succinic anhydride (29 mg, 0.288 mmol), DMAP (35 mg, 0.288 mmol), and pyridine (30 μL, 0.36 mmol) were mixed in 25 mL of dry CH_2Cl_2, and the mixture was stirred at room temperature for 24 h. The solvent was evaporated in vacuo. Toluene (5 mL) and 4 N HCl/EtOAc were added to dissolve the solid residue, and the solution was stirred at room temperature for 30 min. The mixture was extracted with a mixture of toluene and ethyl acetate and dried with Na_2SO_4. The solvent was evaporated in vacuo, and the remaining solid was redissolved by a small amount of toluene. Pure **7** (26 mg, 77%) was precipitated by adding petroleum ether. FAB-MS: 941 (M + 1, 16), 720 (100). HR-FAB: obsd 940.0739, calcd for $C_{72}H_{12}O_4$ 940.0736. FT-IR cm^{-1}; 3450 (w), 2940 (w), 2920 (w), 1749 (s), 1711 (s), 1429 (w), 1156 (m), 748 (w), 577 (w), 527 (s). UV−vis (CH_2Cl_2) λ_{max}: 700, 430, 309, 260. ^1H NMR (400 MHz, CS_2/$CDCl_3$) indicates the sample was a mixture of **7-A** and **7-E** in a ratio of 1.24. **7-A** δ: 7.82 (d, 1 H, J = 7.27 Hz, aromatic proton), 7.66−7.55 (m, 3 H, aromatic protons), 7.41 (s, 1 H, H_c), 5.34 (d, 1 H, J = 13.94 Hz, H_a), 4.38 (d, 1 H, J = 13.94 Hz, H_b), 2.96−2.77 (m, 4 H, -CH_2CH_2-). **7-E** δ: 7.66−7.55 (m, 5 H, H_c + aromatic protons), 4.87 (d, 1 H, J = 14.12 Hz, H_b), 4.51 (d, 1 H, J = 14.12 Hz, H_a), 2.96−2.77 (m, 4 H, -CH_2CH_2-).

Acknowledgment. This work was supported by NIH Grant GM20080.

Supplementary Material Available: ^1H NMR spectra of compounds **3**−**7** and ^{13}C NMR spectrum of **3a** (7 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.