Regioselectivity and Stereospecificity in a Contrastereoelectronically Controlled Pinacol Rearrangement of Alkoxycyclobutane Derivatives. A Novel Route to Vicinally Substituted Cyclopentanones

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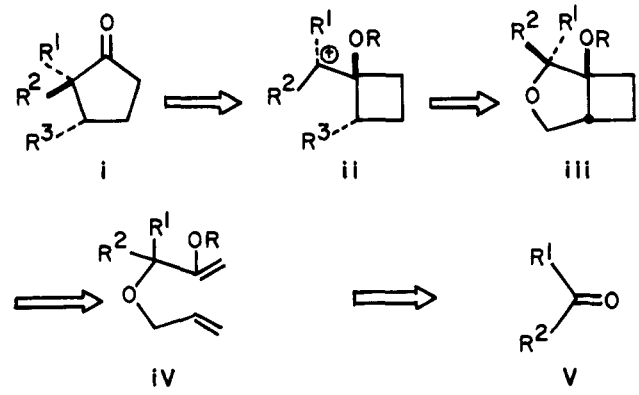
A four-step sequence for the synthesis of vicinally substituted cyclopentanones **5** and **9** has been developed starting from the acyclic ketones **1**. The key step involves a stereospecific pinacol-type rearrangement of the cyclobutane ring embodied in oxabicyclo[3.2.0]heptanes **4** and **8** involving exclusive migration of the stereoelectronically disfavored cyclobutane bond. The oxabicyclo[3.2.0]-heptanes have been obtained by copper(I) triflate (CuOTf) catalyzed intramolecular photocycloaddition of the dienes **3** prepared from the ketones **1** on reaction with (ethoxyvinyl)lithium followed by allylation of the carbinols **2**. The regioselectivity observed in bond migration has been attributed to be the result of the stabilization of the cation **15** by the neighboring hydroxyl group that is generated during the rearrangement.

Vicinally substituted cyclopentanes constitute a major group of cyclopentanoid natural products.[1] Moreover, they serve as precursors[2] in the synthesis of polycyclic natural products having fused cyclopentane rings. Thus, construction of vicinally substituted cyclopentanes is considered to be of fundamental importance for entry into the cyclopentanoid family. Many of the synthetic methodologies[3] that have been developed to annealate a 5-membered ring onto preexisting ring systems are not applicable for constructing 1,2-substituted cyclopentanes. Considerable efforts have thus been spent for their construction leading to many elegant strategies.[4] We considered the possibility of developing a fundamentally new technique for the construction of substituted cyclopentanones. The essential feature of this protocol relies on the facile rearrangement[5] of cyclobutane derivatives which are, in general, available conveniently and stereoselectively through [2 + 2] photocycloaddition.

Scheme 1



We were primarily concerned with the synthesis of the cyclopentanone derivatives **i**, especially those with R^1 = Me as a large number of natural products contain a quaternary Me. We envisioned that pinacol-type rearrangement[6] of the cyclobutylcarbinyl cation **ii** (Scheme 1) would provide the cyclopentanone derivative **i** by migration of the central cyclobutane bond. The cation **ii**, in turn, may be generated by acid treatment of the oxabicyclo[3.2.0]heptane **iii** which would be available

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1995.

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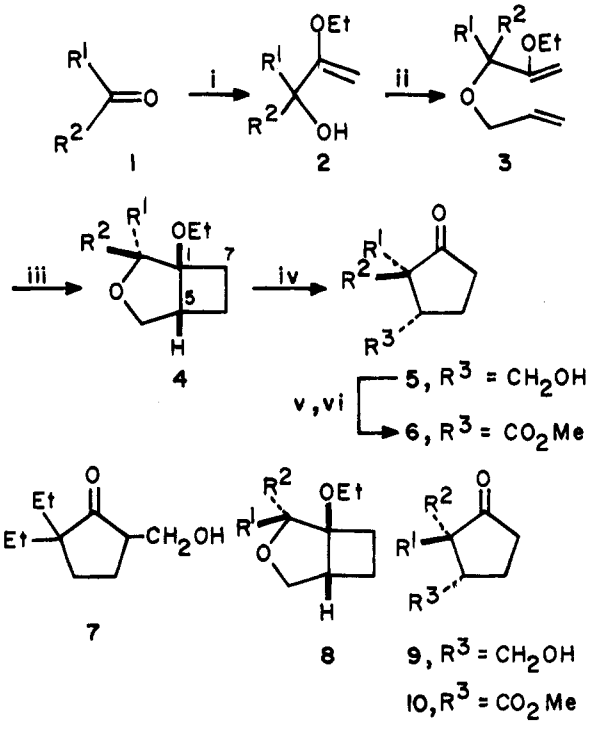
Scheme 2



a: $R^1 = R^2 = Et$; b: $R^1 = R^2 = Me$; c: $R^1 = Me, R^2 = Et$; d: $R^1 = Me, R^2 = CH_2CH_2Ph$; e: $R^1 = Me, R^2 = CH_2Ph$; f: $R^1 = Me$, R^2 = 4-methyl cyclohexyl; g: $R^1 = Me$, R^2 = 1,4-dimethyl cyclohexyl; h: $R^1 = Me$, R^2 = p-tolyl; i: $R^1 = H$, $R^2 = CMe_2$

Reagents: i, t-BuLi, ethyl vinyl ether, THF, -70°C. ii, NaH, THF, HMPA, allyl bromide, reflux. iii, hν, Et_2O, CuOTf. iv, TfOH, CH_2Cl_2, -78°C to r.t. v, Jones reagent, acetone, 0°C. vi, CH_2N_2, Et_2O.

from intramolecular cycloaddition of the diene **iv** derivable from the ketone **v**. Thus, a proper choice of the starting ketone would allow synthesis of the cyclopentanones **i** with the desired substituents. We, herein, describe the results of our investigation[7] according to the plan delineated in Scheme 1 offering a convenient route to the synthesis of 2,3-substituted cyclopentanones.

Results and Discussion

To illustrate the reaction sequence involved in the synthesis of cyclopentanones, diethyl ketone (**1a**) was chosen as a model. Reaction of diethyl ketone (**1a**) with (ethoxyvinyl)lithium prepared according to the literature procedure,[8] afforded the carbinol **2a** in 70% yield (Scheme 2). The sensitive carbinol **2a** was immediately transformed to the diene **3a** in excellent yield by coupling of its sodium salt with allyl bromide. After successfully preparing the diene **3a**, recourse to the work of Mackor and Salomon was made for its cycloaddition. Mackor[9] has demonstrated that diallyl ether when irradiated in presence of CuOTf as catalyst, undergoes smooth cycloaddition to form oxabicyclo[3.2.0]heptane. The synthetic potential of this photocycloaddition reaction was subsequently explored by Salomon,[10] and later it was employed by Rosini[11] for a synthesis of grandisol. Intrigued by these investigations, we prepared an ether solution of the diene **3a** and irradiated in presence of CuOTf as catalyst. Gratifyingly, the cycloadduct **4a** was obtained in 76% yield. The structure of the photoadduct as oxabicyclo[3.2.0]heptane was established through its ^1H and ^{13}C NMR spectral analysis. The characteristic feature in the ^{13}C NMR spectrum is the presence of two downfield quaternary carbons at δ 91.1 and 86.3 attributable to the absorption due to the carbons attached to oxygen i.e. C_2 and C_1. The two methylenes at δ 69.8 and 60.4 indicate the presence of the tetrahydrofuran and OCH_2CH_3 units, respectively. The deshielding of the only methine carbon (δ 42.1) over the reported chemical shift (26.5) for C_3 of tetrahydrofuran is quite expected as it is β to an alkoxy group.

After firmly establishing the structure, the cyclobutane derivative **4a** was subjected to rearrangement. Only trifluoromethanesulfonic acid (TfOH) was found to be effective for this rearrangement. The single compound (by ^1H and ^{13}C NMR and GC) obtained after rearrangement of **4a**, displayed IR absorptions at 1735 (s) and 3400 (br) cm^{-1}, indicating it to be a hydroxycyclopentanone derivative. The ^{13}C NMR spectrum of the rearrangement product showed a carbonyl absorption at δ 222.3, deshielded from the usually observed cyclopentanone carbonyl absorption at δ 213.8, indicating it as an α-geminally substituted cyclopentanone derivative. A triplet at δ 62.7 indicated the presence of a CH_2OH unit. Differentiation between the two regioisomeric hydroxycyclopentanones **5a** and **7** which might arise by migration of the 1,5- and 1,7-bonds respectively was based on comparison of the observed chemical shift (δ 44.8) of the methine carbon to which the CH_2OH unit was attached with those (δ 42 for **5a** and 56 for **7**) theoretically expected. This clearly establishes that during rearrangement of the cyclobutane derivative **4a**, the 1,5-bond i.e. the central bond migrates exclusively to produce the hydroxycyclopentanone **5a**. This structural assignment is further corroborated by the appearance of the base peak at *m/z* 111 in the mass spectra of the hydroxycyclopentanone **5a** and the keto ester **6a** resulting from the fragmentation as delineated in Scheme 3. Subsequent loss of a hydrogen radical from the base peak accounts for the peak at *m/z* 110. Finally by following the above methodology acetone **1b** was converted[12] to a hydroxycyclopentanone derivative which was found identical to the known[13] cyclopentanone derivative **5b**. This transformation demonstrates that during rearrangement of the oxabicyclo[3.2.0]heptanes **4**, the 1,5-bond migrated exclusively. Also, the present four-step synthesis of **5b** in contrast to its earlier 11-step synthesis demonstrates the efficiency of the present synthetic protocol.

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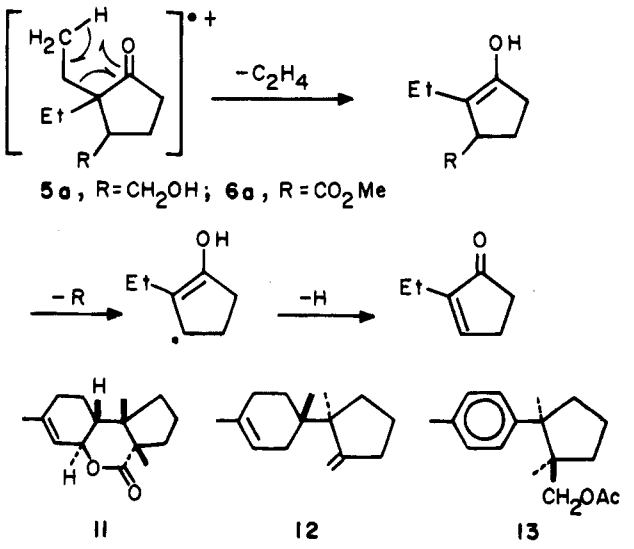
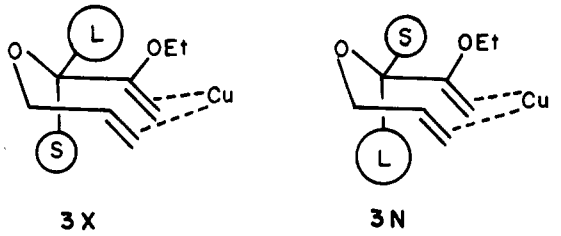
Scheme 3



Application of this four-step sequence on unsymmetrical ketones **1** may result in a mixture of the photoadducts **4** and **8** and hence a mixture of the corresponding cyclopentanones **5** and **9**. On the basis of the earlier observations,[10] it is expected that the Cu(I)–diene complex **3X** with the more bulkier substituent L



occupying an exo position is less sterically crowded than **3N** with an endo bulky group and the photoadduct having the more bulkier group L syn to the OEt group should predominate. Thus, photocycloaddition can be made stereoselective by increasing the difference in size of the groups R^1 and R^2 in **1**. To determine the influence of size on the stereoselectivity during cycloaddition and to construct vicinally substituted cyclopentanones with quaternary Me, the methyl ketones **1c–h** were chosen. The dienes **3c–h**, prepared according to the sequence already described, were irradiated in the presence of CuOTf as catalyst and the resulting photoadducts were treated with TfOH. The results are summarized in Table 1. The table reveals that in going from the ketone **1c** to **1d** to **1e** (entries 3–5), there is an increase in the ratio[14] of the photoadducts **4** and **8** from 3.8:1 to 5:1 to 19:1, with gradual increase in the size of the group relative to Me. The stereochemical assignment to the photoadducts is based on their transformation to the corresponding cyclopentanone derivatives **5** and **9** in almost the same ratio at which the photoadducts were formed. The sterochemical assignment to **5** and **9** are based on analysis of ^1H and ^{13}C NMR spectra. In the ^1H NMR spectra of the mixture, the methyl protons of the major isomers **5c–e** are shielded by 0.18–0.27 ppm relative to the analogous protons in the minor isomers **9c–e**. This shielding is comparable[15] to the shielding by 0.20 ppm of the methyl protons observed previously in an analogous compound where Me is syn to the vicinal substituent relative to the one with anti Me. Additionally, in the ^{13}C NMR spectrum of the mixture of cyclopentanones **5d** and **9d**, the shielding of the methyl carbon (δ 17 ppm) of the major isomer over that (δ 21 ppm) of the minor isomer, attributable to be the result of steric interaction[16] of syn substituents, is a clear indication of syn orientation of Me and CH_2OH in the major cyclopentanone derivative. To gain additional support for this stereochemical assignment, the mixture of the hydroxycyclopentanones in each case was transformed to the keto esters **6c–e** and **10c–e**. In ^1H NMR of the mixture of the keto esters, the methyl protons of the major isomers **6c–e** are shielded by 0.22–0.29 ppm over the minor isomers **10c–e**. This shielding is possible only when the methyl protons lie in the shielding cone[15] of the ester–carbonyl group requiring a syn orientation of the Me and the CO_2-Me groups. Thus, the major diastereoisomeric cyclopentanone derivatives were assigned the structures **5c–e**. Rearrangement of the pure major photoadduct **4e** isolated by careful chromatography of the mixture of photoadducts **4e** and **8e**, afforded the cyclopentanone derivative **5e**. This cyclopentanone derivative is identical to the major component in the mixture of the cyclopentatones obtained from rearrangement of the mixture of the photoadducts **4e** and **8e**. This stereospecificity in the rearrangement of cyclobutane derivatives led to the stereochemical assignment to the major and minor photoadducts as **4c–e** and **8c–e**, respectively. Similarly, the ketones **1f** and **1g** (entries 6 and 7) having a bulkier cyclohexane derivative as one of the substituents gave only the photoadducts **4f** and **4g** and the cyclopentanones **5f** and **5g**, respectively. Such an easy access to the cyclopentanone derivatives **5f** and **5g**, the novel carbocyclic skeleta present in the sesquiterpenes cuprenolide **11**[17] and trichodiene **12**,[18] respectively, certainly demonstrates the synthetic potential of this route.

A direct entry to tochuinyl acetate (**13**)[19] would be possible if *p*-methylacetophenone **1h** could be transformed to the cyclopentanone derivative **5h**. However, irradiation of the diene **3h** (entry 8) produced an intractable mixture of products from which no **5h** could be isolated. To extend further the scope of this protocol, an aldehyde **1i** was chosen. Irradiation of the diene **3i** (entry 9), prepared from isobutyraldehyde, gave in excellent yield a single photoadduct to which structure **4i** was assigned on the basis of the above results. Attempted rearrangement of **4i** failed to produce any cyclopentanone derivative **5i** as indicated by the absence of carbonyl absorption in IR. About 50% of the photoadduct was recovered unchanged. Thus, through this sequence only acyclic ketones (and not aldehyde) can be converted to vicinally substituted cyclopentanones.

The regioselectivity observed in the pinacol rearrangement of the 1-ethoxy-3-oxabicyclo[3.2.0]heptane derivatives **4** and **8** involving exclusive migration of the central cyclobutane bond is interesting in the light of the stereoelectronic requirement. The stereoelectronic re-

(14) The ratios of diastereioisomeric pairs in the mixture were determined from integration of the quaternary methyl protons in ^1H NMR of the mixture.

(15) Lee, G. M.; Parvez, M.; Weinreb, S. M. *Tetrahedron* **1988**, *44*, 4671.

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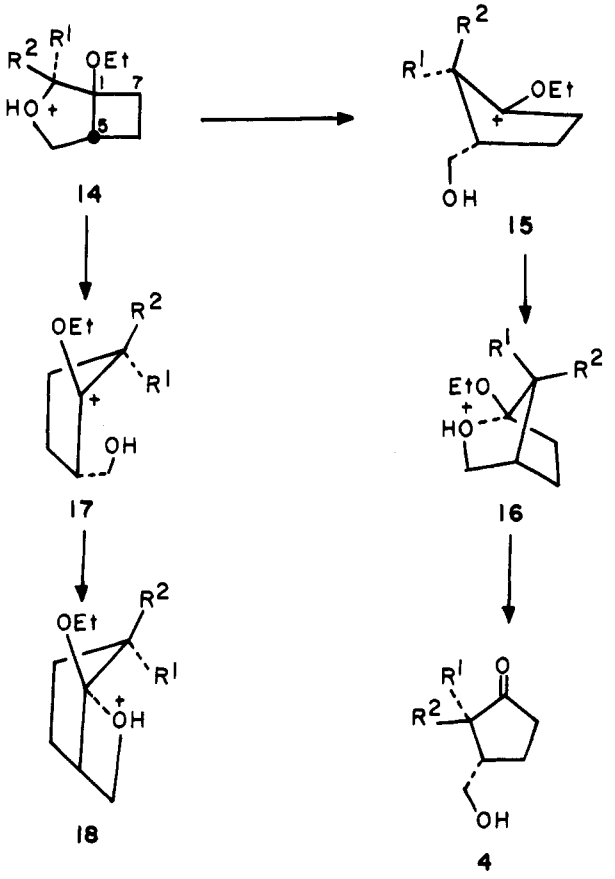
Table 1. Synthesis of Vicinially Substituted Cyclopentanones

entry	ketones	vinyl carbinols (% yield)	dienes (% yield)	photoadducts (% yield)	cyclopentanones (% yield)	keto esters (% yield)
1	**1a**	**2a** (70)	**3a** (93)	**4a** (67)	**5a** (74)	**6a** (74)
2	**1b**	**2b** (81)	**3b** (71)	**4b** (88)	**5b** (88)[a]	
3	**1c**	**2c** (71)	**3c** (83)	**4c:8c** 3.8:1 (53)	**5c:9c** 3.8:1 (62)	**6c:10c** 3.8:1 (74)
4	**1d**	**2d** (76)	**3d** (92)	**4d:8d** 5:1 (61)	**5d:9d** 5:1 (66)	**6d:10d** 5:1 (67)
5	**1e**	**2e** (85)	**3e** (95)	**4e:8e** 19:1 (54)	**5e:9e** 19:1 (30)	**6e:10e** 19:1 (73)
6	**1f**	**2f** (71)	**3f** (95)	**4f** (71)	**5f** (75)	**6f** (73)
7	**1g**	**2g** (69)	**3g** (99)	**4g** (60)	**5g** (25)	
8	**1h**	**2h** (89)	**3h** (94)			
9	**1i**	**2i** (67)	**3i** (88)	**4i** (73)		

[a] Reference 12.

Scheme 4



quirement in the pinacol rearrangement[20] has been shown to be an antiperiplanar conformation of the migrating C–C bond and the leaving group. A Drieding model of the cyclobutane derivatives **4** reveals that it is the C_1–C_7 bond which is antiperiplanar to the leaving group. However, exclusive migration of the C_1–C_5 bond in the rearrangement of **4** and **8** suggests the involvement of a mechanism (Scheme 4) which offset the effect of stereoelectronic requirement. As during the rearrangement the configuration at C_2 of the cyclobutane derivatives **4** and **8** is retained in the products **5** and **9**, a concerted migration of the C_1–C_5 bond in the protonated species **14** leads to the formation of the carbonium ion **15**. The cation **15** is then stabilized by the OH group through formation of a 6-membered cyclic transition state **16** which rapidly collapses to the cyclopentanone derivatives **5**. In case of C_1–C_7 bond migration, the stabilization of the resulting cation **17** by the OH group requires unfavorable formation of the strained oxetane[21] intermediate **18** and is thus inhibited. Thus, the regioselectivity observed in bond migration is the result of the assistance provided by a neighboring group[22] that is generated during the rearrangement.

To conclude, a proper choice of the starting acyclic ketones would allow stereocontrolled synthesis of vicinally substituted cyclopentanones with desired α-*gem* substitution through the general four-step sequence developed above. The approach would be of immense potential in cyclopentanoid natural products synthesis.

Experimental Section

Melting points were measured in open capillary tubes in sulfuric acid bath. All mp's and bp's reported are uncorrected. The organic extracts were dried over anhydrous Na_2SO_4 unless otherwise stated. Column chromatography was performed on silica gel (60–120 mesh). Petroleum refers to the fraction of petroleum ether boiling in the range 60–80 °C. IR spectra were recorded as neat for liquids and as KBr pellet for solids. Unless otherwise stated ^{1}H NMR spectra were recorded at 60 MHz in CCl_4 solution. Mass spectra were recorded at 70 eV. Elemental analyses were performed in the microanalytical laboratory of this department.

Reaction of Ketones with (Ethoxyvinyl)lithium. The general procedure is illustrated with the reaction of diethyl ketone.

2-Ethoxy-3-ethylpenten-3-ol (2a). To a solution of ethyl vinyl ether (7.56 g, 105 mmol) in anhydrous THF (20 mL) cooled to −70 °C under argon atmosphere, was added t-BuLi (16 mL, 30 mmol, 12% solution in pentane) dropwise with magnetic stirring. After addition, the reaction mixture was allowed to warm to −10 °C and stirred for 15 min at that temperature. It was cooled again to −70 °C and to it a solution of diethyl ketone (**1a**, 1.72 g, 20 mmol) in THF (10 mL) was added slowly over a period of 15 min. The reaction mixture was stirred at −70 °C for 30 min and allowed to attain room temperature slowly. The reaction mixture was quenched by slow addition of 15% aqueous NH_4Cl and then extracted with ether (2 × 50 mL). The ether extract was dried (K_2CO_3) and concentrated. The residual liquid in presence of 1–2% of NEt_3 was distilled under reduced pressure to afford a clear liquid, **2a** (1.56 g, 70%): bp 38–40 °C (0.2 mm); ^{1}H NMR δ 0.80 (6H, t, J = 7 Hz), 1.30 (3H, t, J = 7 Hz), 1.50–1.80 (5H, m), 3.74 (2H, q, J = 7 Hz), 3.98 (1H, d, J = 2 Hz), 4.18 (1H, d, J = 2 Hz).

(20) Mundy, B. P.; Otzenbenger, R. D. *J. Chem. Ed.* **1971**, *48*, 431.

(21) Searles, S. In *Comprehensive Heterocyclic Chemistry*, Katritzky, A. R., Chairman, Ed. Board; Pergamon Press: New York, 1984; Vol. 7, Part 5, p 370.

(22) A carbonyl group assisted regioselective C–C bond migration in pinacol rearrangement of a cyclobutanone derivative has been reported: Shimada, J.; Hashimoto, K.; Kim, B. H.; Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1984**, *106*, 1759.

2-Ethoxy-3-methyl-1-buten-3-ol (2c): bp 80–82 °C (10 mm); ^{1}H NMR δ 0.80 (3H, t, J = 7 Hz), 1.27 (3H, s), 1.33 (3H, t, J = 7 Hz) merged with a m centered at 1.54 (3H), 3.73 (2H, q, J = 7 Hz), 3.87 (1H, d, J = 2 Hz), 4.17 (1H, d, J = 2 Hz).

2-Ethoxy-3-methyl-5-phenyl-1-penten-3-ol (2d): bp 107–110 °C (0.1 mm); ^{1}H NMR δ 1.33 (s) merged with t at 1.33 (J = 7 Hz) (total 6H), 1.57–2.83 (5H, m), 3.73 (2H, q, J = 7 Hz), 3.90 (1H, d, J = 2 Hz), 4.23 (1H, d, J = 2 Hz), 7.10 (5H, s).

2-Ethoxy-3-methyl-4-phenylbuten-3-ol (2e): bp 100–102 °C (0.2 mm); ^{1}H NMR δ 1.30 (3H, s) merged with a t at 1.33 (3H, J = 7 Hz), 1.83 (1H, br s), 2.90 (2H, AB_q, J = 14 Hz), 3.77 (2H, q, J = 7 Hz) merged with a d at 3.83 (1H, J = 2 Hz), 4.08 (1H, d, J = 2 Hz), 7.20 (5H, s).

2-Ethoxy-3-(4-methylcyclohexyl)buten-3-ol (2f): bp 80–82 °C (0.2 mm); ^{1}H NMR δ 0.67–1.10 (3H, m), 1.23 (3H, s) merged with a t at 1.33 (3H, J = 7 Hz), 1.57–2.07 (11H, m), 3.77 (2H, q, J = 7 Hz), 3.90 (1H, d, J = 2 Hz), 4.18 (1H, d, J = 2 Hz).

2-Ethoxy-3-(1,4-dimethylcyclohexyl)buten-3-ol (2g): bp 142–145 °C (0.5 mm); ^{1}H NMR δ 0.90 (s) merged within a m at 0.67–1.03 (total 6H), 1.25 (s) and 1.37 (t, J = 7 Hz) merged within a m at 1.07–1.70 (total 15H), 1.90–2.13 (1H, br s), 3.70 (2H, q, J = 7 Hz), 3.93 (1H, d, J = 2 Hz), 4.10 (1H, d, J = 2 Hz).

2-Ethoxy-3-*p*-tolylbuten-3-ol (2h): bp 100–102 °C (0.2 mm); ^{1}H NMR δ 1.23 (3H, t, J = 7 Hz), 1.53 (3H, s), 2.30 (3H, s), 2.37–2.63 (1H, m), 3.70 (2H, q, J = 7 Hz), 4.00 (1H, d, J = 2 Hz), 4.27 (1H, d, J = 2 Hz), 6.87–7.40 (4H, m).

2-Ethoxy-4-methylpenten-3-ol (2i): bp 73–74 °C (0.5 mm); ^{1}H NMR δ 0.85 (3H, d, J = 6 Hz), 0.88 (3H, d, J = 6 Hz), 0.97 (3H, s), 1.33 (3H, t, J = 7 Hz), 1.53–2.13 (2H, m), 3.60 (1H, d, J = 6 Hz) merged with a q at 3.73 (2H, J = 7 Hz), 3.90 (1H, d, J = 2 Hz), 4.03 (1H, d, J = 2 Hz).

Transformation of the Vinylcarbinols to the Diallyl Ether Derivatives. The general procedure is illustrated by the synthesis of **3a**.

3-(Allyloxy)-2-ethoxy-3-ethylpent-1-ene (3a). NaH (0.96 g, 16 mmol, 40% in oil) was placed in a three-neck round-bottom flask under nitrogen atmosphere and washed repeatedly with petroleum to make it free from adhering oil. To it was added sequentially THF (20 mL) and a solution of the carbinol **2a** (1.56 g, 7.9 mmol) in THF (10 mL). The mixture was gently refluxed for 2 h with stirring and then cooled to room temperature, and to it was added HMPA (5 mL) followed by allyl bromide (1.94 g, 16 mmol). After this mixture was refluxed for 2 h, it was cooled in ice, cold water (20 mL) was added slowly, and then it extracted with ether (3 × 50 mL). The ether extract was washed with aqueous $NaHCO_3$, water, dried (K_2CO_3), and then concentrated. The residual liquid in presence of 1–2% of NEt_3 was distilled under reduced pressure to afford a colorless liquid **3a** (1.82 g, 93%): bp 78–80 °C (0.2 mm); ^{1}H NMR δ 0.72 (6H, t, J = 7 Hz), 1.28 (3H, t, J = 7 Hz), 1.53–1.80 (4H, m), 3.73 (2H, q, J = 7 Hz) partly merged within a m centered at 3.76 (2H), 4.03 (1H, d, J = 2 Hz), 4.26 (1H, d, J = 2 Hz), 4.93–6.11 (3H, m).

3-(Allyloxy)-2-ethoxy-3-methylpent-1-ene (3c): bp 52–54 °C (0.5 mm); ^{1}H NMR δ 0.82 (3H, t, J = 7 Hz), 1.27 (3H, s), 1.33 (3H, t, J = 7 Hz), 1.40–1.90 (2H, m), 3.73 (2H, q, J = 7 Hz), partly merged within a m centered at 3.80 (2H), 3.97 (1H, d, J = 2 Hz), 4.20 (1H, d, J = 2 Hz), 4.90–6.26 (3H, m).

3-(Allyloxy)-2-ethoxy-3-methyl-5-phenylpent-1-ene (3d): bp 140–143 °C (0.1 mm); ^{1}H NMR δ 1.27 (3H, s), 1.33 (3H, t, J = 7 Hz), 1.70–2.80 (4H, m), 3.71 (2H, q, J = 7 Hz) partly merged with a m centered at 3.93 (3H), 4.25 (1H, d, J = 2 Hz), 4.90–6.23 (3H, m), 7.13 (5H, s).

3-(Allyloxy)-2-ethoxy-3-methyl-4-phenylbut-1-ene (3e): bp 120–123 °C (0.2 mm); ^{1}H NMR δ 1.20 (3H, s), 1.30 (3H, t, J = 7 Hz), 2.90 (2H, s), 3.70 (2H, q, J = 7 Hz) partly merged within a m centered at 3.90 (3H), 4.07 (1H, d, J = 2 Hz), 4.90–6.23 (3H, m), 7.17 (5H, s).

3-(Allyloxy)-2-ethoxy-3-(4-methylcyclohexyl)but-1-ene (3f): bp 100–105 °C (0.2 mm); ^{1}H NMR δ 0.63–1.03 (6H, m), 1.10–2.07, (13H, m), 3.67 (2H, q, J = 7 Hz), partly merged with a m at 3.70–3.87 (2H), 3.97 (1H, d, J = 2 Hz), 4.10 (1H, d, J = 2 Hz), 4.83–6.17 (3H, m).

3-(Allyloxy)-2-ethoxy-3-(1,4-dimethylcyclohexyl)but-1-ene (3g): bp 107–110 °C (0.1 mm); ^{1}H NMR δ 0.90 (s) merged with a m at 0.60–1.03 (total 6H), 1.07–2.00 (15 H, m), 3.63 (2H, q, J = 7 Hz) partly merged with a m centered at 3.83 (2H), 3.97–4.17 (2H, m), 4.83–6.10 (3H, m).

3-(Allyloxy)-2-ethoxy-3-*p*-tolylbut-1-ene (3h): bp 133–135 °C (0.4 mm); ^{1}H NMR δ 1.17 (3H, t, J = 7 Hz), 1.60 (3H, s), 2.33 (3H, s), 3.43–3.90 (4H, m), 4.00 (1H, d, J = 2 Hz), 4.47 (1H, d, J = 2 Hz), 4.90–6.23 (3H, m), 6.93–7.43 (4H, m).

3-(Allyloxy)-2-ethoxy-4-methylpent-1-ene (3i): bp 102–104 °C (0.5 mm); ^{1}H NMR δ 0.86 (3H, d, J = 6 Hz), 0.90 (3H, d, J = 6 Hz), 1.30 (3H, t, J = 7 Hz), 1.57–2.17 (1H, m), 3.23 (1H, d, J = 6 Hz), 3.70 (2H, q, J = 7 Hz), 3.80–4.23 (4H, m), 4.90–6.20 (3H, m).

Irradiation of Diallyl Ether Derivatives. The general procedure is illustrated by cycloaddition of the diallyl ether **3a**.

(1*SR*,5*RS*)-1-Ethoxy-2,2-diethyl-3-oxabicyclo[3.2.0]-heptane (4a). A solution of the diallyl ether derivative **3a** (0.9 g, 4.5 mmol) in anhydrous ether (250 mL) was irradiated in presence of cuprous triflate (300 mg) through a quartz immersion well with a medium-pressure mercury vapor Hanovia lamp (450 W) for 7 h. The ether solution was washed with aqueous NH_4OH, water and dried. Removal of ether followed by column chromatography of the residual liquid with petroleum–ethyl acetate (19:1) as eluent afforded the pure photoadduct **4a** (600 mg, 76%) as a clear liquid: ^{1}H NMR δ 0.73 (3H, t, J = 7 Hz), 0.77 (3H, t, J = 7 Hz), 1.17 (3H, t, J = 7 Hz), 1.40–1.83 (4H, m), 1.97–2.43 (4H, m), 2.70–3.03 (1H, m), 3.37–3.87 (4H, m); ^{13}C NMR {^{1}H} (25 MHz) δ ($CDCl_3$) 6.6 (q), 8.1 (q), 15.9 (q), 19.8 (t), 20.2 (t), 23.1 (t), 24.1 (t), 42.1 (d), 60.4 (t), 69.8 (t), 86.3 (s), 91.1 (s). Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.37; H, 11.06.

(1*SR*,2*SR*,5*RS*)-1-Ethoxy-2-ethyl-2-methyl-3-oxabicyclo-[3.2.0]heptane (4c) and (1*SR*,2*RS*,5*RS*)-1-ethoxy-2-ethyl-2-methyl-3-oxabicyclo[3.2.0]heptane (8c) were obtained as a mixture of colorless liquids: ^{1}H NMR δ 0.91 (3H, t, J = 7 Hz), 0.98 (s, Me of **8c**), 1.05 (s, Me of **4c**) (total 3H), 1.15 (3H, t, J = 7 Hz), 1.20–1.73 (3H, m). 1.77–2.43 (3H, m), 2.47–2.93 (1H, m), 3.23–3.93 (4H, m). Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.27; H, 10.73.

(1*SR*,2*SR*,5*RS*)-1-Ethoxy-2-methyl-2-(2-phenylethyl)-3-oxabicyclo[3.2.0]heptane (4d) and (1*SR*,2*RS*,5*RS*)-1-ethoxy-2-methyl-2-(2-phenylethyl)-3-oxabicyclo[3.2.0]-heptane (8d) were obtained as a mixture of colorless liquids: ^{1}H NMR δ 1.10 (s, Me of **8d**), 1.17 (s, Me of **4d**), (total 3H), 1.13 (3H, t, J = 7 Hz), 1.30–2.90 (9H, m), 3.23–4.00 (4H, m), 7.13 (5H, s). Anal. Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 77.93; H, 9.16.

(1*SR*,2*SR*,5*RS*)-1-Ethoxy-2-benzyl-2-methyl-3-oxabicyclo[3.2.0]heptane (4e) and (1*SR*,2*RS*,5*RS*)-1-ethoxy-2-benzyl-2-methyl-3-oxabicyclo[3.2.0]heptane (8e) were obtained as a mixture of colorless liquids: ^{1}H NMR δ 0.80 (s, Me for **8e**), 0.97 (s, Me for **4e**), (total 3H), 1.23 (3H, t, J = 7 Hz), 1.40–2.53 (6H, m), 2.57–2.93 (1H, m), 3.33–4.27 (4H, m), 7.16 (5H, m); ^{13}C NMR {^{1}H} (25 MHz) (of the major isomer from the mixture) δ ($CDCl_3$) 15.7 (q), 19.0 (q), 19.7 (t), 23.8 (t), 36.5 (t), 42.4 (d), 59.7 (t), 69.9 (t), 83.3 (s), 90.5 (s), 125.6 (d), 127.5 (d), 130.5 (d), 138.4 (s). Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.55; H, 8.87.

(1*SR*,2*SR*,5*RS*)-1-Ethoxy-2-methyl-2-(4-methylcyclohexyl)-3-oxabicyclo[3.2.0]heptane (4f) was obtained as a clear liquid: ^{1}H NMR (200 MHz) δ ($CDCl_3$) 0.86 (3H, d, J = 6.4 Hz), 1.07 (3H, s), 1.21 (3H, t, J = 7 Hz), 1.33–2.40 (14H, m), 2.79–2.97 (1H, m), 3.47–3.90 (4H, m). Anal. Calcd for $C_{16}H_{28}O_2$: C, 76.14; H, 11.18. Found: C, 75.89; H, 11.34.

(1*SR*,2*SR*,5*RS*)-1-Ethoxy-2-(1,4-dimethylcyclohexyl)-2-methyl-3-oxabicyclo[3.2.0]heptane (4g) was obtained as a clear liquid: ^{1}H NMR δ 0.97 (s) and 1.07 (s) merged within a m at 0.73–2.43 (total 25H), 2.73–3.10 (1H, m), 3.37–4.43 (4H, m). Anal. Calcd for $C_{17}H_{30}O_2$: C, 76.64; H, 11.35. Found: C, 77.07; H, 11.33.

(1*SR*,2*SR*,5*RS*)-1-Ethoxy-2-isopropyl-3-oxabicyclo[3.2.0]-heptane (4i) was obtained as a clear liquid: ^{1}H NMR δ 0.90 (3H, d, J = 5 Hz), 1.02 (3H, d, J = 5 Hz), 1.27 (3H, t, J = 7 Hz), 1.37–2.40 (5H, m), 2.77–4.17 (6H, m).

Rearrangement of Oxabicyclo[3.2.0]heptanes. The general procedure is illustrated by the rearrangement of the cyclobutane derivative **4a**.

2,2-Diethyl-3-(hydroxymethyl)cyclopentanone (5a). Trifluoromethanesulfonic acid (0.1 mL, 1.13 mmol) was added to a solution of the photoadduct **4a** (220 mg, 1.11 mmol) in CH_2Cl_2 (3 mL) at −78 °C. The reaction mixture was slowly allowed to warm to room temperature and stirred for additional 2 h. It was then diluted with ether (10 mL) and washed with 10% aqueous NaOH solution and brine and dried. Removal of solvent followed by column chromatography of the residual mass with petroleum−ether (3:2) as eluent afforded the cyclopentanone derivative **5a** (140 mg, 74%) as a clear liquid: IR 1730, 3440 cm^{-1}; ^1H NMR δ 0.77 (3H, t, J = 7 Hz), 0.83 (3H, t, J = 7 Hz), 1.23−2.47 (9H, m), 2.90 (1H, br s), 3.53−3.93 (2H, m); ^{13}C NMR {^1H} (25 MHz) δ ($CDCl_3$) 8.3 (q), 8.4 (q), 22.1 (t), 22.4 (t), 25.5 (t), 36.6 (t), 44.8 (d), 54.0 (s), 62.7 (t), 222.3 (s): ms *m/z* (%) 170 (M^+, 21), 142 (36), 123 (32), 111 (100), 110 (54), 97 (25), 96 (29), 95 (42), 85 (80), 84 (32), 81 (59), 69 (49), 67 (42), 57 (40), 54 (99).

(2*RS*,3*SR*)-2-Ethyl-2-methyl-3-(hydroxymethyl)cyclopentanone (5c) and (2*SR*,3*SR*)-2-ethyl-2-methyl-3-(hydroxymethyl)cyclopentanone (9c) were obtained as a mixture of clear liquids: IR 1730, 3440 cm^{-1}; ^1H NMR δ 0.87 (s, Me of **5c**), 1.03 (s, Me of **9c**) merged within 0.63−2.53 (total 11H), 3.57−3.73 (2H, m).

(2*RS*,3*SR*)-2-Methyl-2-(2-phenylethyl)-3-(hydroxymethyl)cyclopentanone (5d) and (2*SR*,3*SR*)-2-methyl-2-(2-phenylethyl)-3-(hydroxymethyl)cyclopentanone (9d) were obtained as a mixture of clear liquids: IR 1730, 3440 (br) cm^{-1}; ^1H NMR δ 0.90 (s, Me of **5d**), 1.11 (s, Me of **9d**), 1.43−2.80 (9H, m), 3.08 (1H, br s), 3.47−3.77 (2H, m), 7.06 (5H, s); ^{13}C NMR {^1H} (25 MHz) (of **5d** from the mixture) δ ($CDCl_3$) 17.0 (q), 22.2 (t), 30.6 (t), 36.7 (t), 38.7 (t), 44.8 (d), 63.1 (t), 125.6 (d), 128.1 (d), 141.9 (s), 223.0 (s). Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.70; H, 8.93.

(2*RS*,3*SR*)-2-Benzyl-2-methyl-3-(hydroxymethyl)cyclopentanone (5e) and (2*SR*,3*SR*)-2-Benzyl-3-methyl-3-(hydroxymethyl)cyclopentanone (9e). TfOH (0.43 mL, 4.9 mmol) was added to a solution of a mixture of the photoadducts **4e** and **8e** (0.6 g, 2.4 mmol) in TFA (5 mL, 65 mmol), and the mixture was heated at 80 °C for 3 h under N_2 atmosphere. It was cooled to room temperature, diluted with ether, washed with water, 10% aqueous NaOH solution, and brine, and dried. After removal of solvent, the resulting liquid was heated at 80 °C with 20% aqueous KOH solution (5 mL) for 1 h. After cooling to room temperature the mixture was extracted with ether (3 × 20 mL). The ether layer was washed with brine (3 × 10 mL) and dried. Removal of solvent followed by column chromatography of the residual mass with petroleum−ether (3:2) as eluent afforded a mixture of the cyclopentanone derivatives **5e** and **9e** (160 mg, 30%): IR 1735, 3450 (br) cm^{-1}; ^1H NMR δ 0.98 (s, Me for **5e**), 1.25 (s, Me for **9e**), 1.27−2.47 (6H, m), 2.83 (2H, AB_q, J = 14 Hz), 3.47−3.80 (2H, m), 7.10 (5H, m); ^{13}C NMR {^1H} (25 MHz) (of **5e**) δ ($CDCl_3$) 18.2 (q), 22.3 (t), 37.4 (t), 42.5 (t), 43.2 (d), 52.1 (s), 63.3 (t), 126.2 (d), 127.9 (d), 130.3 (d), 137.7 (s), 223.1 (s).

(2*RS*,3*SR*)-2-Methyl-2-(4-methylcyclohexyl)-3-(hydroxymethyl)cyclopentanone (5f) was obtained as a clear liquid: IR 1730, 3440 (br) cm^{-1}; ^1H NMR (200 MHz) δ ($CDCl_3$) 0.84 (3H, d, J = 6.6 Hz), 0.88 (3H, s), 1.04−1.81 (5H, m), 1.97−2.44 (11H, m), 3.55 (1H, A of ABX, J_{AB} = 10.3 Hz, J_{AX} = 8.3 Hz), 3.84 (1H, q, B of ABX, J_{AB} = 10.3 Hz, J_{BX} = 4.3 Hz). Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.64; H, 11.04.

(2*RS*,3*SR*)-2-(1,4-Dimethylcyclohexyl)-2-methyl-3-(hydroxymethyl)cyclopentanone (5g) was obtained as a clear liquid: IR 1730, 3440 (br) cm^{-1}; ^1H NMR (200 MHz) δ ($CDCl_3$) 0.88 (3H, d, J = 6 Hz), 0.90 (3H, s), 0.97 (3H, s), 1.40−1.80 (9H, m), 2.00−2.65 (6H, m), 3.54 (1H, A of ABX, J_{AB} = 10.3 Hz, J_{AX} = 9.4 Hz), 3.94 (1H, B of ABX, J_{AB} = 10.3 Hz, J_{BX} = 3.8 Hz); ms *m/z* 238 (M^+, 1), 165 (5), 128 (40), 111 (23), 97 (100), 69 (38), 54 (28).

Transformation of the Hydroxycyclopentanones to the Cyclopentanone Carboxylates. The general procedure is illustrated by the conversion of the keto alcohol **5a** to the keto ester **6a**.

Methyl 2,2-Diethyl-1-oxo-cyclopentane-3-−carboxylate **(6a).** To a magnetically stirred ice-cold solution of the alcohol **5a** (140 mg, 0.8 mmol) in acetone (4 mL) was added dropwise Jones reagent (4 mL, 0.7 M) and stirring was continued for additional 1 h. The reaction mixture after dilution with water was extracted with ethyl acetate (2 × 20 mL). The organic extract was washed with aqueous sodium bicarbonate. The aqueous part after acidification with cold 6 N HCl was extracted with ethyl acetate (3 × 20 mL). The organic extract was washed with brine (2 × 10 mL) and dried. Removal of solvent afforded a white solid (120 mg), mp 98 °C. The crude acid was treated with etheral diazomethane. The liquid mass thus obtained was filtered through a short column of neutral alumina to afford the keto ester **6a** (120 mg, 74%) as a colorless liquid: IR 1745 cm^{-1}; ^1H NMR δ 0.80 (6H, t, J = 7 Hz), 1.10−2.40 (8H, m), 2.70−3.17 (1H, m), 3.70 (3H, s); ms *m/z* 198 (M^+, 11), 170 (47), 142 (28), 141 (22), 138 (32), 112 (29), 111 (100), 110 (33), 97 (43), 96 (49), 95 (21), 81 (42), 69 (39), 67 (30), 54 (82).

(2*RS*,3*SR*)-Methyl-2-Ethyl-2-methyl-1-oxocyclopentane-3-carboxylate (6c) and (2*SR*,3*SR*)-Methyl 2-Ethyl-2-methyl-1-oxocyclopentane-3-carboxylate (10c). Oxidation of a mixture of the keto alcohols **5c** and **9c** afforded the corresponding acids: mp 76 °C; IR 1710, 1740 cm^{-1}. Treatment of the crude acid thus obtained with diazomethane afforded a mixture of the keto esters **6c** and **10c** as a clear liquid: IR 1730−40 cm^{-1}; ^1H NMR δ 0.80 (3H, t, J = 7 Hz), 0.83 (s, Me of **6c**), 1.10 (s, Me of **10c**), 1.23−2.37 (6H, m), 2.77−3.10 (1H, m), 3.67 (3H, s); ms *m/z* 184 (M^+, 25), 156 (54), 153 (24), 128 (36), 127 (23), 124 (59), 98 (32), 97 (100), 96 (53), 83 (59), 82 (75), 67 (34), 54 (80).

(2*RS*,3*SR*)-Methyl 2-Methyl-1-oxo-2-(2-phenylethyl)cyclopentane-3-carboxylate (6d) and (2*SR*,3*SR*)-Methyl 2-Methyl-1-oxo-2-(2-phenylethyl)cyclopentane-3-carboxylate (10d). Oxidation of a mixture of the keto alcohols **5d** and **9d** afforded the corresponding acids, mp 88 °C. Treatment of the crude acids thus obtained with diazomethane furnished a mixture of the keto esters **6d** and **10d**: IR 1735 cm^{-1}; ^1H NMR δ 0.92 (s, Me of **6d**), 1.13 (s, Me of **10d**), 1.60−2.63 (8H, m), 2.73−3.17 (1H, m), 3.70 (3H, s), 7.17 (5H, s); ms *m/z* 260 (M^+, 3), 156 (50), 98 (7), 97 (100), 91 (31).

(2*RS*,3*SR*)-Methyl 2-Benzyl-2-methyl-1-oxocyclopentane-3-carboxylate (6e) and (2*SR*,3*SR*)-Methyl 2-Benzyl-2-methyl-1-oxocyclopentane-3-carboxylate (10e). Oxidation of a mixture of the keto alcohols **5e** and **9e** afforded the corresponding acids: mp 155 °C; IR 1705, 1740 cm^{-1}. Treatment of the crude acid thus obtained with diazomethane afforded a mixture of the keto esters **6e** and **10e**: IR 1740 cm^{-1}; ^1H NMR δ 0.96 (s, Me of **6e**), 1.13 (s, Me of **10e**), 1.10−2.47 (4H, m), 2.90 (2H, AB_q, J = 14 Hz) merged with a m centered at 2.87 (1H), 3.73 (3H, s), 7.12 (5H, s); ms *m/z* 246 (M^+, 27), 186 (6), 145 (7), 129 (8), 128 (9), 92 (11), 91 (100), 65 (7).

(2*RS*,3*SR*)-Methyl 2-methyl-2-(4′-methylcyclohexyl)-1-oxocyclopentane-3-carboxylate (6f) was obtained as a colorless liquid: IR 1740 cm^{-1}; ^1H NMR 0.87 (s) merged within a m at 0.70−2.57 (total 20H), 2.87−3.23 (1H, m), 3.63 (3H, s); ms *m/z* 252 (M^+, 2), 156 (47), 98 (8), 97 (100), 95 (9), 81 (9), 54 (19).

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Supplementary Material Available: Copies of ^1H NMR spectra of **2a,c−i, 3a,c−i, 4i, 5a,c,e,g, 6a,c−f,** ^{13}C NMR spectra of **4a,e, 5a,d,e** and mass spectra of **5a,g** and **6a,c−f** (38 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.

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