JOC Notes

Complete Control of Regioselectivity in the Intramolecular [2 + 2] Photocycloaddition of 2-Alkenyl-3(2*H*)-furanones by the Length of the Side Chain

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Received September 11, 2002

Abstract: The 2-(ω-alkenyl)-substituted 2-methyl-3(2*H*)-furanones **2a** and **2b** were prepared from biacetyl (**3**) in four reaction steps and in overall yields of 20% and 21%, respectively. They underwent a clean intramolecular [2 + 2] photocycloaddition upon irradiation at $\lambda = 350$ nm. Whereas compound **2a** reacted in the expected manner and yielded 7-oxabicyclo[3.2.1.0^{3,6}]octane **7** (87% yield), the regioselectivity in the photocycloaddition of compound **2b** was completely reversed. The reaction led to compound **8** (92% yield) with the unusual 9-oxabicyclo[4.2.1.0^{3,8}]nonane skeleton, the structure of which was established by single-crystal X-ray crystallography.

In 1983, a new monoterpene glycoside was isolated from *P. lactiflora* and was named lactiflorin.[1] The same compound has been isolated more recently from the related species *P. anomala* var. *intermedia* (C. A. Mey.) O. & B. Fedtsch.[2] On the basis of spectral data two structures[2,3] have been proposed for lactiflorin which mainly differ in the tricyclic monoterpene backbone. One of the proposed structures is depicted in Figure 1 as formula **1**. It exhibits a 7-oxabicyclo[4.2.1.0^{3,8}]nonane skeleton that could be accessible by an intramolecular [2 + 2] photocycloaddition of a cyclic oxaenone.[4] Along these lines, 2-(3-butenyl)-2-methyl-3(2*H*)-furanone **2b** appeared to be a suitable test substrate to evaluate the regio- and stereochemistry of the photocycloaddition. Previous work by Margaretha et al.[5] had revealed that

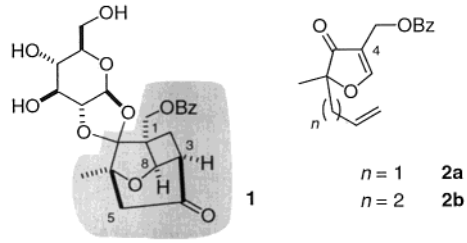
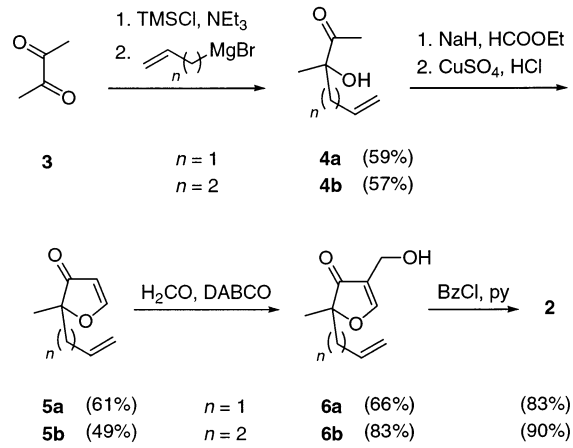


FIGURE 1. Suggested[2] structure for lactiflorin (**1**) and irradiation precursors **2a** and **2b**.

SCHEME 1. Preparation of Compounds 2a and 2b from Biacetyl (3)



the photocycloaddition of a 2-(2-propenyl)-substituted 3(2*H*)-furanone (vide infra) proceeds with the desired regioselectivity, i.e., by a C−C bond formation between the terminal alkene carbon atom and the carbon atom C-4 of the heterocycle. In this note, we report on the preparation of compounds **2a** and **2b** and their intramolecular [2 + 2]-photocycloaddition reactions. Contrary to our initial considerations, compound **2b** delivered a 9-oxabicyclo[4.2.1.0^{3,8}]nonan-7-one but *not* the desired 7-oxabicyclo[4.2.1.0^{3,8}]nonane skeleton.

Starting from biacetyl (**3**), one carbonyl group of which was protected via its silyl enol ether, addition of the appropriate Grignard reagent yielded the alcohols **4a** and **4b** (Scheme 1). Their conversion to the 3(2*H*)-furanones **5** was conducted as previously described[5] by a Claisen condensation and a subsequent acid-promoted cyclization. The hydroxymethyl group was installed by a Baylis−Hillman reaction.[6] To the best of our knowledge 3(2*H*)-furanones have not yet been used as substrates in this type of reaction.[7] In our study, an aqueous solution (30% w/w) of formaldehyde was employed as the source of the electrophile (4 equiv).[8] Various catalysts (DMAP, PBu_3, DABCO, DBU) were tested to achieve a chemoselective and fast transformation. DBU[9] promoted an

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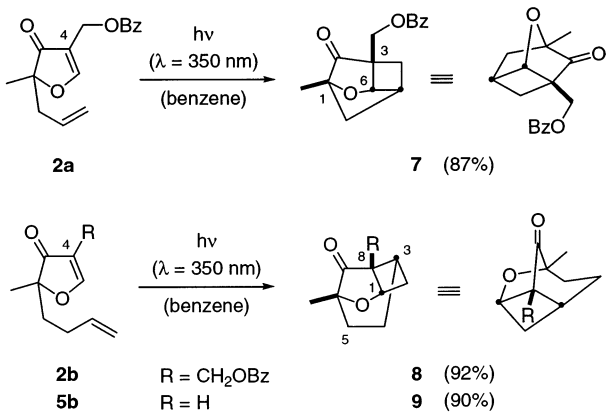
10.1021/jo0264372 CCC: $25.00
Published on Web 02/01/2003

SCHEME 2. Intramolecular [2 + 2] Photocycloaddition of Compounds 2a, 2b, and 5b



extremely fast reaction but delivered several side products, which were difficult to separate from the desired product. Side reactions were also observed with varying amounts of DMAP or PBu_3. The use of DABCO (0.2 equiv) in THF turned out to be superior. It allowed a clean conversion to the desired products, although the reaction velocity was not fully satisfactory. Routinely, the reactions were stopped after 48 h at about 50% conversion. The separation of the products **6** was easy, and the starting materials **5** could be recovered. The yields given in Scheme 1 for the transformation **5** → **6** are based on recovered starting material. A subsequent benzoylation of the corresponding primary alcohols **6** with benzoyl (Bz) chloride and pyridine in CH_2Cl_2 delivered the desired photocycloaddition substrates.

Irradiation in benzene at $\lambda = 350$ nm (Rayonet RPR 3500 Å) converted compound **2a** exclusively into the tricyclic product **7** (Scheme 2). The regioselectivity was proven by comparison of the spectral data with those of the previously reported parent 7-oxabicyclo[3.2.1.$0^{3,6}$]-octan-2-one.[5] The hydrogen atom H-6 accounts for a doublet at 5.05 ppm with a coupling constant of $J_{HH} =$ 4.3 Hz. By a COSY experiment the hydrogen atom H-5 was identified as the atom responsible for the J_{HH} coupling to H-6, and it was unambiguously proven by a HMQC experiment that this hydrogen atom is attached to a tertiary carbon atom (C-5). As previously alluded to, this regioselectivity was expected on the basis of the charge distribution in the excited state (T_1).[4a,10]

The intramolecular photocycloaddition of substrate **2b** proceeded smoothly and yielded a single product. The NMR data of the product did, however, not match the expected structure. The hydrogen atom next to the furan oxygen atom, which resonates at 4.56 ppm and which is the direct analogue to H-6 in compound **7**, did not produce a doublet. It rather gave a doublet of doublets with $J_{HH} = 4.5$ Hz and $J_{HH} = 5.2$ Hz. This result and additional two dimensional NMR experiments strongly suggested structure **8**. A HMBC experiment, for instance, revealed a $^2J_{CH}$ or $^3J_{CH}$ coupling of the CH_2OBz protons to two quaternary (C-7, C-8) and two tertiary (C-1, C-3) carbon atoms. Final proof for the structure assignment was obtained by single-crystal X-ray crystallography (Figure 2).[11]

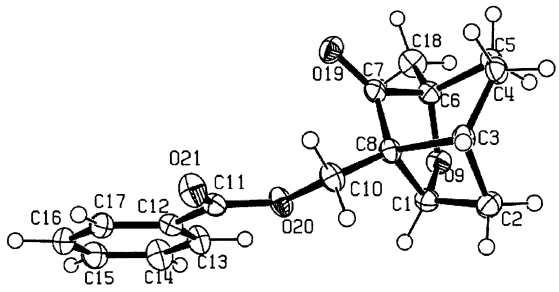


FIGURE 2. A molecule of compound **8** in the crystal.

To study the influence of the substituent in 4-position of the 3(2*H*)-furanone on the regioselectivity the unsubstituted substrate **5b** was submitted to the conditions of a [2 + 2] photocycloaddition. NMR data revealed that the regioselectivity of this reaction is the same as that observed for **2b**, and structure **9** was consequently assigned to the product. Again, the reaction proceeded quantitatively and without the formation of any side products. In this respect, the intramolecular [2 + 2] photocycloaddition allows for a rapid and high yielding access to the hitherto unknown parent 9-oxabicyclo-[4.2.1.$0^{3,8}$]nonane skeleton.

The question why this mode of C−C bond formation is so strongly favored and why the regioselectivity is completely reversed while going from **2a** to **2b** or from

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(11) (a) Crystal structure analysis of **8**: $C_{17}H_{18}O_4$, $M_r = 286.31$, triclinic, space group *P*$\bar{1}$, $a = 7.408(2)$, $b = 10.275(5)$, $c = 10.768(3)$ Å, $\alpha = 68.44(3)°$, $\beta = 84.42(2)°$, $\gamma = 69.68(3)°$, $V = 714.4(5)$ Å^3; $Z = 2$; $\rho_{calc} = 1.331$ g cm^{-3}, $F_{000} = 304$, $\mu = 0.094$ mm^{-1}. A suitable single crystal for the X-ray diffraction study was obtained from a EA/P solution at 4 °C. The selected crystal was coated with perfluorinated ether, fixed in a capillary, and transferred to the diffractometer and the cold nitrogen flow. Preliminary examination and data collection were carried out on a four-circle diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å; sealed tube). Data collection were performed at 153 K within the θ range of $2.03° < \theta < 25.98°$. A total of 5579 reflections were integrated and corrected for Lorentz and polarization effects. After merging ($R_{int} = 0.0254$), 2795 [2406: $I_o > 2\sigma(I_o)$] independent reflections remained and all were used to refine 262 parameters. The structure was solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. All hydrogen atom positions were found in the difference Fourier map calculated from the model containing all non-hydrogen atoms. The hydrogen positions were refined with individual isotropic displacement parameters. Full-matrix least-squares were carried out by minimizing $w(F_o^2 - F_c^2)^2$ and converged with $R1 = 0.0360$ [$I_o > 2\sigma(I_o)$], $wR2 = 0.0989$ [all data], $GOF = 1.044$ and shift/error < 0.001. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-197904. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk); a CIF file is available as Supporting Information. (b) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *SIR92*. *J. Appl. Crystallogr.* **1994**, *27*, 435. (c) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2001. (d) Sheldrick, G. M. *SHELXL-97*; Universität Göttingen: Göttingen, Germany, 1998.

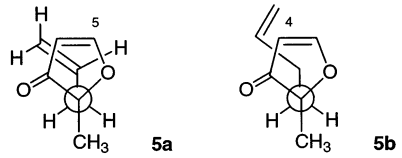

FIGURE 3. Possible conformations of compounds **5a** and **5b** resulting in a regioselective [2 + 2] photocycloaddition.

5a to **5b** is not fully clear. There is analogy to the work by McMurry et al., who studied the photocycloaddition of 5-(*ω*-alkenyl)-substituted 3-phenylcyclopent-2-enones.[12] If the substituent was a 2-propenyl group, they obtained bicyclo[3.2.1.$0^{3,6}$]octan-2-ones exclusively, whereas the irradiation (Hanovia 450 W, Pyrex filter) of the 3-butenyl-substituted 3-phenylcyclopen-2-enone gave a 2:1 mixture of bicyclo[4.2.1.$0^{3,8}$]nonan-7-one and bicyclo[4.2.1.$0^{3,8}$]-nonan-9-one. Upon further irradiation the product ratio changed in favor of the nonan-7-one as the result of a photochemically induced equilibration. The authors invoke conformational and stereoelectronic factors[13] that govern the outcome of the reaction. In our case, we did not observe any other regioisomer throughout the reactions, and a conformation as depicted for 3(2*H*)-furanone **5a** in Figure 3 is most likely to be involved in the product formation **2a** → **7**. In line with previous results obtained with **5a**,[5] the first C−C bond is formed between carbon atom C-5 of the ring and the internal carbon atom (CH) of the side chain to yield a 1,4-biradical, which subsequently collapses to the product. Given a similar conformation for compound **5b** (and for **2b**), the first C−C bond can only be established between carbon atom C-4 of the ring and the internal carbon atom, leading exclusively to the opposite regioisomer.[14]

In summary, the intramolecular photocycloaddition of the 2-propenyl-substituted 3(2*H*)-furanones **2b** and **5b** produced the 9-oxabicyclo[4.2.1.$0^{3,8}$]nonan-7-ones **8** and **9** in almost quantitative yields (90−92%). The regioselectivity is opposite to the selectivity observed with the nor-analogues **2a** and **5a**. Possible synthetic applications of the products are currently being studied.

Experimental Section

General. For general remarks, see ref 15. All solvents, ethyl acetate (EA), pentane (P), and diethyl ether, for column chromatography were distilled prior to use. Benzene used as solvent in irradiation experiments was thoroughly degassed immediately prior to use by pump and freeze methodology. Allylmagnesiumbromid and homoallylmagnesiumbromid were prepared according to standard procedures.[16] Compounds **4a**[17] and **5a**[5] have been previously described. All other chemicals were commercially available and were used without further purification.

3-Hydroxy-3-methyl-hept-6-en-2-one (4b) was prepared from biacetyl (**3**, 3.50 mL, 40 mmol) according to a previously published procedure.[17] The product was purified by distillation (2 mbar, 57−60 °C) to give product **4b** (3.24 g, 22.8 mmol, 57%) as a colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.36 (s, 3 H), 1.75 (br s, 1 H), 1.85−1.70 (m, 2 H), 2.21 (s, 3 H), 2.35−2.11 (m, 2 H), 4.91−4.95 (dm, J = 9.5 Hz, 1 H), 4.96−5.03 (dm, J = 17.2 Hz, 1 H), 5.68−5.82 (m, 1 H); ^{13}C NMR (62.9 MHz) δ 23.6 (q), 25.4 (q), 27.7 (t), 38.4 (t), 78.5 (s), 115.0 (t), 137.7 (d), 212.1 (s). Anal. Calcd for $C_8H_{14}O_2$ (142.20): C, 67.57; H, 9.92. Found: C, 67.50; H, 10.00.

2-But-3-enyl-2-methyl-furan-3-one (5b) was prepared from **4b** (3.30 g, 23.2 mmol) according to a previously published procedure.[5] The product was purified by distillation (15 mbar, 70−72 °C) to give compound **5b** (1.72 g, 11.4 mmol, 49%) as a colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.33 (s, 3 H), 1.75−2.20 (m, 4 H), 4.89−4.93 (dm, J = 9.4 Hz, 1 H), 4.93−5.00 (dm, J = 16.4 Hz, 1 H), 5.62 (d, J = 3.3 Hz, 1 H), 5.62−5.76 (m, 1 H), 8.17 (d, J = 3.3 Hz, 1 H); ^{13}C NMR (62.9 MHz) δ 21.6 (q), 27.2 (t), 35.4 (t), 89.5 (s), 105.9 (d), 115.1 (t), 137.1 (d), 176.6 (d), 207.2 (s). Anal. Calcd for $C_9H_{12}O_2$ (152.19): C, 71.03; H, 7.95. Found: C, 70.46; H, 8.01.

General Procedure A for Baylis−Hillman Reaction of 3(2*H*)-Furanones. To a solution of the 3(2*H*)-furanone (6.58 mmol) in THF (15 mL) were added formaldehyde (30% w/w, 2.26 mL, 22.6 mmol) and DABCO (148 mg, 1.07 mmol), and the resulting mixture was stirred at ambient temperature for 48 h. After evaporation of the solvent the crude product was purified by column chromatography.

2-Allyl-4-hydroxymethyl-2-methyl-furan-3-one (6a) was prepared from **5a** according to general procedure A. The product was purified by column chromatography (silica, P/CH_2Cl_2/EA = 10/5/2 as eluent) to give 453 mg (3.28 mmol, 50%) of unchanged **5a** and 364 mg (2.17 mmol, 33%) of the desired product **6a** as a colorless oil: ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.32 (s, 3 H), 2.41 (d, J = 7.3 Hz, 2 H), 2.96 (br s, 1 H), 4.27 (s, 2 H), 5.06−5.08 (dm, J = 9.0 Hz, 1 H), 5.08−5.11 (dm, J = 17.8 Hz, 1 H), 5.57−5.65 (m, 1 H), 8.14 (s, 1 H); ^{13}C NMR (62.9 MHz) δ 20.9 (q), 40.5 (t), 53.2 (t), 90.1 (s), 118.2 (s), 119.8 (t), 130.5 (d), 174.0 (d), 206.3 (s). HRMS (EI) calcd for $C_9H_{12}O_3$ 168.07864, found 168.07864.

2-But-enyl-4-hydroxymethyl-2-methyl-furan-3-one (6b) was prepared from **5b** according to general procedure A. The product was purified by column chromatography (silica, P/CH_2Cl_2/EA = 10/5/2 as eluent) to give 530 mg (3.48 mmol, 53%) of unchanged **5b** and 471 mg (2.59 mmol, 40%) of the desired product **6b** as a colorless oil: ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.37 (s, 3 H), 1.80−2.13 (m, 4 H), 2.15 (br s, 1 H), 4.33 (d, J = 0.7 Hz, 2 H), 4.92−4.96 (dm, J = 11.5 Hz, 1 H), 4.95−5.02 (dm, J = 17.5 Hz, 1 H), 5.69−5.77 (m, 1 H), 8.16 (s, 1 H); ^{13}C NMR (90.6 MHz) δ 21.5 (q), 27.3 (t), 35.5 (t), 53.6 (t), 90.6 (s), 115.2 (s), 118.3 (t), 137.1 (d), 173.8 (d), 206.6 (s). HRMS (EI) calcd for $C_{10}H_{14}O_3$ 182.09430, found 182.09438.

General Procedure B for Benzoylation of Alcohols. A solution of the alcohol (0.5 mmol) in CH_2Cl_2 (5 mL) was stirred at 0 °C. Pyridine (42 μL, 0.52 mmol) and benzoyl chloride (61 μL, 0.52 mmol) were then added dropwise. The resulting mixture was allowed to warm to room temperature and stirred for another 3 h. CH_2Cl_2 (10 mL) and a saturated NH_4Cl solution (10 mL) were added. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were washed with a saturated NaCl solution (10 mL) and dried (Na_2SO_4). After filtration and evaporation of the solvent the crude product was purified by column chromatography.

Benzoic acid 5-allyl-5-methyl-4-oxo-4,5-dihydrofuran-3-ylmethylester (2a) was prepared from **6a** according to general procedure B. The product was purified by column chromatography (silica, P/CH_2Cl_2/EA = 20/1/1 as eluent) to give 114 mg (0.42 mmol, 83%) of **2a** as a colorless oil: ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.36 (s, 3 H), 2.44 (d, J = 7.3 Hz, 2 H), 4.94 (s, 2 H), 5.01−5.04 (dm, J = 10.0 Hz, 1 H), 5.06−5.12 (dm, J = 17.0 Hz, 1 H), 5.57−5.64 (m, 1 H), 7.38−7.42 (m, 2 H), 7.50−7.58 (m, 1 H), 7.95−8.05 (m, 2 H), 8.39 (s, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$) δ 20.8 (q), 40.6 (t), 54.4 (t), 90.3 (s), 78.5 (s), 114.2 (s), 119.8 (t),

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128.3 (d), 129.6 (d), 129.9 (s), 130.3 (d), 133.0 (d), 166.6 (s), 176.7 (s), 204.5 (s). Anal. Calcd for $C_{16}H_{16}O_4$ (272.30): C, 70.57; H, 5.92. Found: C, 70.39; H, 6.03.

Benzoic acid 5-but-3-enyl-5-methyl-4-oxo-4,5-dihydrofuran-3-ylmethylester (2b) was prepared from **6b** according to general procedure B. The product was purified by column chromatography (silica, P/CH_2Cl_2/EA = 20/1/1 as eluent) to give 129 mg (0.45 mmol, 90%) of **2a** as a colorless oil. ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.38 (s, 3 H), 1.82−2.18 (m, 4 H), 4.90−4.93 (dm, J = 10.5 Hz), 4.93−4.98 (dm, J = 17.0 Hz, 1 H), 4.97 (s, 2 H), 5.65−5.75 (m, 1 H), 7.40−7.44 (m, 2 H), 7.53−7.57 (m, 1 H), 8.00−8.04 (m, 2 H), 8.42 (s, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$) δ 21.5 (q), 27.2 (t), 35.5 (t), 54.5 (t), 90.9 (s), 114.4 (s), 115.2 (t), 128.4 (d), 129.6 (d), 129.9 (s), 133.1 (d), 137.0 (d), 166.7 (s), 177.0 (s), 204.9 (s). Anal. Calcd for $C_{17}H_{18}O_4$ (286.32): C, 71.31; H, 6.34. Found: C, 71.09; H, 6.14.

General Procedure C for [2 + 2] Photocycloaddition of Enones. The appropriate 3(2*H*)-furanone (0.50 mmol) was dissolved in benzene (10 mL) and irradiated at 350 nm (light source Rayonet RPR 3500 Å) at room temperature for 8 h. The solvent was then removed in vacuo ,and the residue was purified by column chromatography.

Benzoic acid 1-methyl-2-oxo-7-oxa-tricyclo[3.2.1.0^{3,6}]oct-3-ylmethylester (7) was prepared from **2a** according to general procedure C. The product was purified by column chromatography (silica, P/CH_2Cl_2/Et_2O = 20/1/1 as eluent) to give 118 mg (0.44 mmol, 87%) of **7** as a colorless oil: ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.51 (d, J = 12.2 Hz, 1 H), 1.52 (s, 3 H), 1.79 (d, J = 12.5 Hz, 1 H), 1.83−1.88 (m, 1 H), 2.21−2.30 (m, 1 H), 2.93−2.99 (m, 1 H), 4.44 (d, J = 11.8 Hz, 1 H), 4.50 (d, J = 11.8 Hz, 1 H), 5.05 (d, J = 4.3 Hz, 1 H), 7.42−7.46 (m, 2 H), 7.54−7.59 (m, 1 H), 8.01−8.04 (m, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$) δ 13.3 (q), 30.6 (t), 36.4 (d), 41.2 (t), 53.9 (s), 61.4 (t), 79.6 (d), 85.1 (s), 128.4 (d), 129.7 (d), 129.8 (s), 133.1 (d), 166.3 (s), 210.3 (s). Anal. Calcd for $C_{16}H_{16}O_4$ (272.30): C, 70.57; H, 5.92. Found: C, 70.21; H, 5.81.

Benzoic acid 6-methyl-7-oxo-9-oxa-tricyclo[4.2.1.0^{3,8}]non-8-ylmethylester (8) was prepared from **2b** according to general procedure C. The product was purified by column chromatography (silica, P/CH_2Cl_2/Et_2O = 20/1/1 as eluent) to give 131 mg (0.46 mmol, 92%) of **8** as a colorless solid: ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.34 (s, 3 H), 1.56−1.70 (m, 2 H), 2.05−2.20 (m, 2 H), 2.41−2.51 (m, 1 H), 2.81−2.88 (m, 1 H), 2.91−2.99 (m, 1 H), 4.56 (dd, J = 5.2 Hz, 4.5 Hz, 1 H), 4.58 (d, J = 11.8 Hz, 1 H), 4.65 (d, J = 11.8 Hz, 1 H), 7.41−7.46 (m, 2 H), 7.54−7.60 (m, 1 H), 7.99−8.04 (m, 2 H); ^{13}C NMR (90.6 MHz, $CDCl_3$) δ 19.3 (q), 23.1 (t), 32.3 (t), 40.1 (t), 42.8 (d), 53.7 (s), 60.3 (t), 72.4 (d), 81.2 (s), 128.4 (d), 129.6 (d), 129.7 (s), 133.2 (d), 166.4 (s), 214.3 (s). Anal. Calcd for $C_{17}H_{18}O_4$ (286.31): C, 71.31; H, 6.34. Found: C, 71.38; H, 6.30.

6-Methyl-9-oxa-tricyclo[4.2.1.0^{3,8}]nonan-7-one (9) was prepared from **5b** according to general procedure C. The product was purified by column chromatography (silica, P/CH_2Cl_2/Et_2O = 20/1/1 as eluent) to give 69 mg (0.45 mmol, 90%) of **9** as a colorless oil: ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.25 (s, 3 H), 1.56−1.62 (m, 2 H), 2.02−2.11 (m, 2 H), 2.36−2.46 (m, 1 H), 2.71−2.78 (m, 1 H), 3.07−3.13 (m, 2 H), 4.52 (dt, J = 5.2 Hz, 4.1 Hz, 1 H); ^{13}C NMR (90.6 MHz, $CDCl_3$) δ 19.3 (q), 23.2 (t), 34.1 (t), 40.4 (d), 40.7 (t), 46.7 (d), 70.1 (d), 80.2 (s), 216.7 (s). Anal. Calcd for $C_9H_{12}O_2$ (152.19): C, 71.03; H, 7.95. Found: C, 70.86; H, 7.82.

Acknowledgment. Support of this research by the Deutsche Forschungsgemeinschaft (Ba 1372-6/2) and by the Fonds der Chemischen Industrie is gratefully acknowledged.

Supporting Information Available: IR and MS data for all new compounds;^{13}C NMR spectra of compounds **6a**, **6b**, and **9**; crystal data and details of the structure in the solid state together with PLATON graphics of compound **8**; crystallographic data for **8** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0264372