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Products from Furans. 4.[1a] Selective Oxidation of 2-Furfuryl Alcohol Derivatives, in the Presence of Aryl Thioethers, with *N*-Bromosuccinimide (NBS). A New Procedure for the Preparation of 2*H*-Pyran-3(6*H*)-ones

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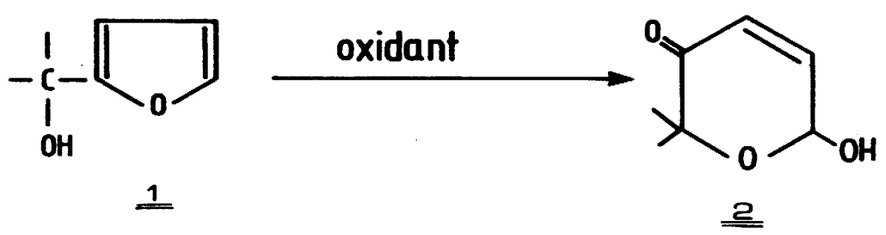
A new general fast method (as fast as a titration) for converting 2*H*-furfuryl alcohols to 2*H*-pyran-3(6*H*)-ones by the use of NBS as an oxidant is presented. NBS oxidizes selectively the furfuryl alcohols without affecting thioether substituents.

A variety of methods have been reported for the synthesis of 2*H*-pyran-3(6*H*)-ones **2** by oxidation of 2-furfuryl alcohol derivatives[2] **1**. *m*-Chloroperbenzoic acid (MCPBA),[3] peracetic acid,[3] and pyridinium chlorochromate[4] (PCC) were used as oxidants, while the use of Br_2 in methanol,[5] Br_2 in water[6] and anodic oxidation[7] has also been reported, as well as the mechanism of the above oxidation.[8]

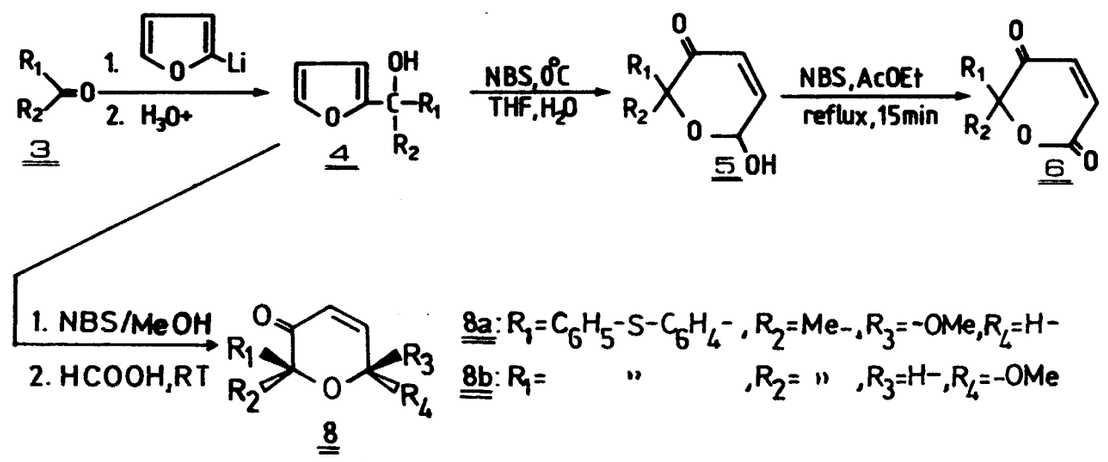


1 **2**

2*H*-Pyran-3(6*H*)-one derivatives are of great interest since they are biologically active (antimicrobials;[3,9] anticoccidials[3,9]) and, on the other hand, have been used as intermediates in the synthesis of sugar analogues,[10-12] maltol,[6] tirantamycines,[13] pheromones,[14] anticanceer compounds,[15] and several other products.[2]

We would like to report here a novel oxidation procedure using NBS as the oxidant for the synthesis of the above pyranones which is simple, gives high yields, and is considerably cheaper than the MCPBA method. By the use of NBS method, we were able to synthesize 6-hydroxy-2-[*p*-(phenylthio)phenyl)]-2-methyl-2*H*-pyran-3(6*H*)-one (**5a**) and 6-hydroxy-2-[*p*((phenylthio)oxy)phenyl]-2-methyl-2*H*-pyran-3(6*H*)-one (**5b**) which were target molecules for new anticoccidials and which could not be synthesized by the use of other oxidative agents mentioned before.

Scheme I



3 **4** **5** OH **6** **8**

General Procedure

The procedure we have used is the following: 1 equiv of furfuryl alcohol **4** was dissolved in THF–H_2O (4:1) and cooled to 0 °C (Scheme I). Then a stoichiometric amount of NBS was carefully added portionwise. Every new portion of NBS was added only when the color of bromine from the previous addition of NBS disappeared and the temperature was restored to 0 °C. A slight excess of NBS indicated the end of the reaction. After the usual workup, the reaction mixture yielded the pyranone **5** (Table I).

The described method gives only one product without any polymerization or production of byproducts (single spot on TLC). The following conditions are critical in order to avoid byproducts and optimize yields:

(a) The temperature should be maintained below 5 °C.

(b) The excess of NBS should be destroyed before the evaporation of the organic layer.

(c) NBS must be added in solid state, so that the subsequently liberated in situ bromine can be consumed immediately.

Several byproducts may be produced if the above experimental conditions are not followed. Excess of NBS, for example, in relatively higher temperature gives 2-[*p*-(phenylsulfonyl)phenyl]-2-methyl-2*H*-pyran-3,5-dione (**6**, $R_1 = CH_3$, $R_2 = C_6H_5SO_2C_6H_4$) from the furfuryl alcohol **4c**. Compound **6** may be the only product (single spot on TLC) if conditions depicted in Scheme I are followed. The same product (identified by superimposed IR and NMR) is derived by oxidation of **5c** with John's reagent.

Treatment of **4a** with NBS in the usual way, with methanol (95%) instead of THF–H_2O as the solvent and subsequent addition of formic acid, yielded the cis and trans isomers of 6-methoxy-2-[*p*-(phenylthio)phenyl]-2-methyl-2*H*-pyran-3(6*H*)-one (**8a** and **8b**) in the ratio 1:3.

(1) (a) For parts I–III, see ref. 9c, 8, 9b. (b) Taken in part from the Ph.D. Thesis of E.A.C. See ref 9a.

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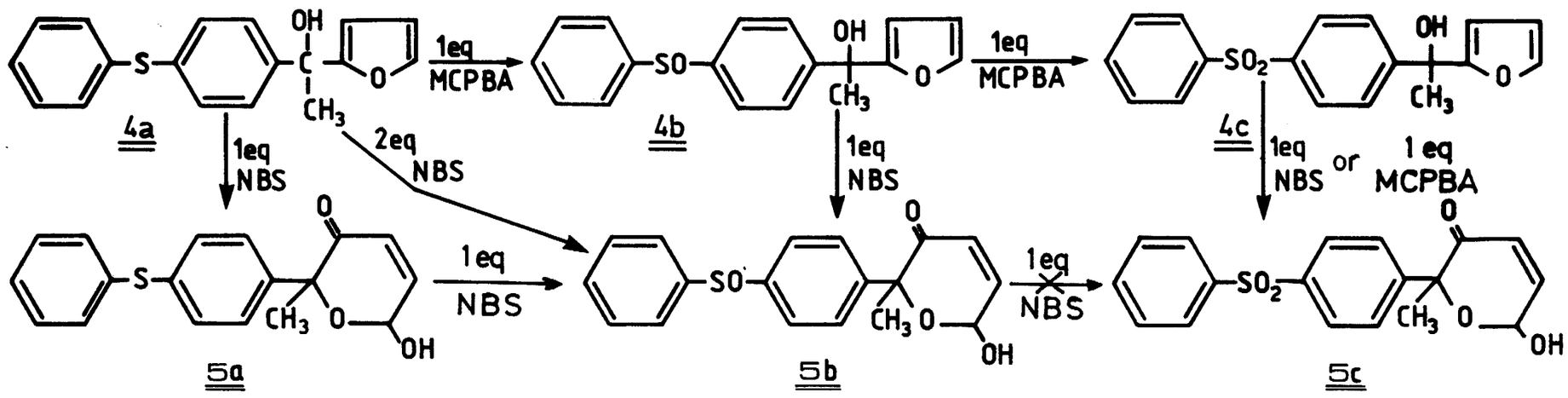
Table I. (Refer to Scheme I)

reactant no.	R_1	R_2	oxidant (equiv)	product no.	R_1	R_2	yield, %[a]
4a	CH_3	4-$PhSC_6H_4$	NBS (1)	**5a**	CH_3	4-$PhSC_6H_4$	78
4a	CH_3	4-$PhSC_6H_4$	NBS (2)	**5b**	CH_3	4-$PhSOC_6H_4$	64
4a	CH_3	4-$PhSC_6H_4$	MCPBA (3)	**5c**	CH_3	4-$PhSO_2C_6H_4$	72
4b	CH_3	4-$PhSOC_6H_4$	NBS (1)	**5b**	CH_3	4-$PhSOC_6H_4$	67
4c	CH_3	4-$PhSO_2C_6H_4$	NBS (1)	**5c**	CH_3	4-$PhSO_2C_6H_4$	69
4d	CH_3	H	NBS (1)	**5d**	CH_3	H	65
4e	H	3,4-methylenedioxyphenyl	NBS (1)	**5e**	H	3,4-methylenedioxyphenyl	77
4f		$(CH_2)_5$	NBS (1)	**5f**		$(CH_2)_5$	76

[a] Total yield for two steps based on the corresponding ketone **3**.

Scheme II



The above is a one-pot synthesis of 6-methoxypyranones directly from the corresponding furfuryl alcohol. It is also a convenient way to prepare the trans isomer of **8**, since the reported procedure[9b] is expensive and time consuming, and gives low yields.

Selectivity against Aryl Thioethers

In planning to prepare compound **5d** we had in mind that MCPBA would react preferably with the sulfur atom rather than with the furan ring; that is why we have selected as a new oxidant NBS for the same reaction. Indeed, we have found a different mode of action between the above two oxidants (see Scheme II).

So, the reaction of 1 equiv of MCPBA with **4a** gives the sulfoxide **4b**, which subsequently with another equiv of MCPBA gives the sulfone **4c**, and finally an overall excess of MCPBA (3:1) yields the pyranone **5c** (see Experimental Section). It is obvious from the above that MCPBA first oxidizes the sulfur atom to its highest oxidation state and afterwards reacts with the furan ring.

On the other hand, the furfuryl alcohol **4a** may be converted to the corresponding pyranone **5a**, by the use of a stoichiometric amount of NBS. An additional equivalent of NBS oxidizes the sulfur atom, yielding **5b**. Further oxidation of the sulfoxide group gives poor results. Thus, the sulfone **5c** cannot be synthesized directly from **5a** with NBS.

From the above it is assumed that NBS gives preferably an 1,4-addition[8] to the furan ring before its reaction with water and formation of the hypobromide, which oxidizes the sulfur atom.

Conclusion

Compounds **5a** and **5b** cannot be prepared by the known oxidation procedures but only by the NBS one. The latter is a general fast method (as fast as a titration) for converting 2-furfuryl alcohols to 2*H*-pyran-3(6*H*)-ones.

Experimental Section

General Methods. All melting points were determined on a Buchi apparatus and are uncorrected NMR spectra were determined on a Varian 60-MHz spectrophotometer (Model 360 EM) with Me_4Si as an internal reference (δ 0.00). The coupling constants are given in hertz. IR spectra were recorded on a Perkin-Elmer Model 283B infrared spectrophotometer. Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory.

Materials. Commercial NBS 98% (Merck), MCPBA 80% (EGA-CHIMIE), *n*-BuLi as a solution in *n*-hexane 15% m/v (Merck), and cyclohexanone (**3f**, Merck) were used without further purification. THF (Merck) was distilled above CaH_2 before use. Acetophenones **3a–c** were prepared from diphenyl sulfide (Merck) according to the Szmant and Palopoli method.[16] Heliotropine (**3e**) was donated from Vioryl SA and was recrystallized from ether–AcOEt before use. The furfuryl alcohols **4c**, **4d**, **4e**, and **4f** were prepared as described in 9b, 5, 15, and 14a, respectively, and they were characterized as crude oils from their NMR and IR spectra and were used without further purification.

α-Methyl-α-[*p*-(phenylthio)phenyl]furfuryl Alcohol (4a). **3a** (45.6 g, 0.2 mol) in 100 mL of THF was poured in a solution of furyllithium (prepared from 150 mL of *n*-BuLi 15% m/v (0.5 mol) and 70 mL of furan in 200 mL of THF) at 0 °C, under N_2. The reaction mixture was mildly stirred for 6 h under N_2 at room temperature and stand overnight. After the usual workup,[9b] the reaction yielded 50 g (84%) of crude **4a** as a brown-yellow oil: IR (oil) 2990 (CH_3), 3030, 1585, 1960, 805, 690 (Ar), 3410 (br d, OH), 1020, 885, 740 (furan), 750 (C–S) cm^{-1}; NMR ($CDCl_3$) δ 7.1 (s, 9 H, Ar), 3.2 (br, 1 H, disappeared on addition of D_2O, OH), 1.7 (s, 3 H, angular methyl), 7.0 (m, 1 H, furan), 6.0 (m, 2 H, furan).

α-Methyl-α-[*p*-((phenylthio)oxy)phenyl]furfuryl Alcohol (4b). **3b** (10 g, 0.04 mol) and 30 mL of *n*-BuLi 15% m/v (0.11 mol) were reacted as before, yielding 11 g (86%) of crude **4ab** as a yellow oil: IR (oil) 2990, 2940 (CH_3), 3060, 1590, 1965 (Ar), 3360 (br d, OH), 1015, 885, 740, (furan), 1045 (SO) cm^{-1}; NMR ($CDCl_3$) δ 7.3 (m, 9 H, Ar), 3.7 (br d, 1 H, disappeared on addition of D_2O, OH), 1.7 (s, 3 H, angular methyl), 7.1 (dd, 1 H, furan), 6.0 (m, 2 H, furan).

Preparation of 2*H*-Pyran-3(6*H*)-ones 5 Using NBS. The corresponding furfuryl alcohol **4** (1 equiv) was dissolved in THF–H_2O (4:1) and cooled to 0 °C. A stoichiometric amount of NBS was then added portionwise while the temperature was being kept to 0 °C. After the reaction was over (TLC), the reaction mixture was successively washed with KI (10%), $Na_2S_2O_4$ (15%), and $NaHCO_3$ (10%), and the product was extracted with CH_2Cl_2 or ether. The organic layer was separated, washed with water, dried ($MgSO_4$), and evaporated under reduced pressure, yielding the corresponding pyranone **5** as a crude oil. Further purification of the product was achieved by column chromatography.

6-Hydroxy-2-[*p*-(phenylthio)phenyl]-2-methyl-2*H*-

(16) Szmant, H.; Palopoli, F. *J. Am. Chem. Soc.* **1950**, *72*, 1757–1760.

pyran-3(6*H*)-one (5a). **4a** (14 g, 0.043 mol) in 80 mL of THF and 20 mL of H_2O were reacted with 10 g (0.056 mol) of NBS according to the general procedure. The crude product was chromatographed on silica gel with ether–hexane (40:60) as the eluant. Evaporation of the solvents yielded 13 g of **5a** as a slight yellow oil (yield 78% based on the ketone **3a**): IR (oil) 2940 (CH_3), 3060, 1960, 820, 745 (Ar), 3430 (br d, OH), 1690 (C=O), 1220, 1040 (COC), 750 (CS) cm^{-1}; NMR ($CDCl_3$) δ 7.1 (m, 9 H, Ar), 4.6 (br d, 1 H disappeared on addition of D_2O, OH), 6.6 (dd, 1 H, double bonds, J_{db} = 10, J_{vic} = 1.7), 5.9 (dd, 1 H, double bond, J_{db} = 10, $J_{allylic}$ = 1.4), 5.3 (dd, 1 H, allylic, J_{vic} = 1.7, $J_{allylic}$ = 1.4), 1.6 (s, 3 H, angular methyl). **5a** ($C_{18}H_{16}O_3S$) was analyzed as methyl carbamate.[9b] Anal. Calcd for $C_{20}H_{19}NO_4S$: C, 65.02; H, 5.18; N, 3.79. Found: C, 64.74; H, 5.08; N, 3.56.

6-Hydroxy-2-[*p*-(phenylsulfinyl)phenyl]-2-methyl-2*H*-pyran-3(6*H*)-one (5b) (from 4b). **4b** (6 g, 0.017 mol) and 4 g (0.02 mol) of NBS were reacted in 40 mL of THF and 10 mL H_2O, according to the general method described before. The crude product was chromatographed on silica gel with ether–AcOEt (9:1) as the eluant. Evaporation of the solvents gave 5 g of **5b** as a yellow oil (yield 67% based on **3b**): IR (oil) 2995, 2940 (CH_3), 3060, 1590, 1970, 750 (Ar), 3350 (br d, OH), 1690, (C=O), 1250, 1010 (COC), 1040 (SO) cm^{-1}; NMR ($CDCl_3$) δ 7.1 (m, 9 H, Ar), 3.1 (br d, 1 H, disappeared on addition of D_2O, OH), 6.6 (dd, 1 H, double bond, J_{db} = 10, J_{vic} = 1.2), 6.0 (dd, 1 H, double bond, $J_{allylic}$ = 1.2), 5.1 (dd, 1 H, allylic), 1.7 (s, 3 H, angular methyl).

5b ($C_{18}H_{16}O_4S$) was analyzed as methyl carbamate.[9b] Anal. Calcd for $C_{20}H_{19}NO_5S$: C, 65.78; H, 5.52; N, 3.65. Found: C, 65.49; H, 5.27; N, 3.37.

6-Hydroxy-2-[*p*-(phenylsulfinyl)phenyl]-2-methyl-2*H*-pyran-3(6*H*)-one (5b) (from 4a). **4a** (3.5 g, 0.011 mol) and 5.5 g (0.03 mol) of NBS were treated as described above, yielding 2.7 g of pure **5b** (yield 64% based on **3a**).

6-Hydroxy-2-[*p*-(phenylsulfonyl)phenyl]-2-methyl-2*H*-pyran-3(6*H*)-one (5c) (from 4a). The known procedure was followed[9b] with a threefold excess of MCPBA, yielding product **5c** in overall yield 72% (based on **3a**).

6-Hydroxy-2-methyl-2*H*-pyran-3(6*H*)-one (5d). **4d** (10 g, 0.08 mol) and 20 g (0.1 mol) of NBS were reacted as before. After the reaction was over (TLC) the mixture was evaporated under reduced pressure at low temperature (0–5 °C). The product was extracted with ether and filtrated on a column of silica gel with ether hexane (70:30) as the eluant, yielding 8.1 g (65% based on the acetylfuran) of **5d** as a clear oil, which was identical by NMR, IR, and TLC comparison with a sample of **5d** made by known methods.[5]

6-Hydroxy-2-(3,4-methylenedioxyphenyl)-2*H*-pyran-3-(6*H*)-one (5e). **4e** (3.3 g, 0.015 mol) and **4e** and 4 g (0.02 mol) of NBS were reacted in 40 mL of THF and 10 mL of H_2O according to the described method, yielding 2.7 g (yield 77% based on **3e**) of **5e**, as a white solid, which was identical by NMR, IR, and TLC comparison with a sample of **5e** made by the MCPBA method[15] [mp 119–120 °C dec; IR (KBr) 1702 (conj C=O), 3455 (OH), 1632 (C=C), 1083 (COC), 3080, 1612, 1505, 825 (Ar), 2940, 2880 (CH_2) cm^{-1}; NMR (CD_3COCD_3) δ 7.1 (dd, 1 H, double bond, J_{db} = 10.1), 6.9 (m, 3 H, Ar), 6.1 (d, 1 H, double bond), 6.0 (s, 2 H CH_2O), 5.8 (dd, 1 H, allylic, J_{vic} = 3.44, $J_{allylic}$ = 0, $J_{6\text{-OH}}$ = 5.7), 5.5 (s, 1 H, HC(2)), 3.1 (br, OH)].

2-Hydroxy-1-oxaspiro[5.5]undec-3-en-5-one (5f). **4f** (2.5 g, 0.015 mol) and 4 g (0.02 mol) of NBS were reacted in 40 mL of THF and 10 mL of H_2O according to the described method, yielding 2.1 g (yield 76%) of **5f** as a colorless oil, which was identical by NMR, IR, and TLC comparison with a sample of **5f** made by the MCPBA method[14a] [IR (oil) 3420, 2940, 2880, 1690, 1140, 1030, 1455, 820 cm^{-1}; ($CDCl_3$) δ 1.5 (br d, 10 H, cyclohexane), 4.4 (br d, 1 H, OH), 6.6 (dd, 1 H, double bond, J_{db} = 10.0, J_{vic} = 1.7), 5.8 (dd, 1 H, double bond, $J_{allylic}$ = 0.5), 5.4 (m, 1 H, allylic)].

6-Methoxy-2-[*p*-(phenylthio)phenyl]-2-methyl-2*H*-pyran-3(6*H*)-one (8). **4a** (3.5 g, 0.01 mol) as dissolved in 30 mL of CH_3OH (95%) and cooled to 0 °C. NBS (1.8 g, 0.01 mol) was added portionwise. After the reaction was over (TLC), 0.4 mL of HCOOH 98% was added, and the reaction was stirred at room temperature for 20 min. The reaction mixture was neutralized and extracted with ether, and the combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure to give a yellow liquid. Column chromatography with silica gel and ether–hexane (80:20) as the eluant gave two products. The one with the higher R_f value, **8a** (white oil, 2.7 g, yield 74%), was identified by NMR[17] to be the trans isomer of **8** and the other one, **8b** (recrystallized from ether, white crystals, 0.7 g, yield 19%), the cis isomer of **8**.

8a: IR (oil) 3070, 1590, 1940, 690 (Ar), 2840 (OMe), 1690 (conj ketone), 1210, 1110 (COC), 2995, 2960 (angular methyl) cm^{-1}; NMR ($CDCl_3$) δ 7.5 (s, 9 H, Ar), 3.3 (s, 3 H, OMe), 6.4 (dd, 1 H, double bond, J_{db} = 10, J_{vic} = 1.5), 5.7 (dd, 1 H, double bond, $J_{allylic}$ = 1.0), 4.8 (t, 1 H, allylic), 1.5 (s, 3 H, angular methyl).

8b: mp 86–87 °C; IR (KBr) 3080, 3060, 1585, 790 (Ar), 2835 (OMe), 1680 (conj ketone), 1210, 1010 (COC), 740 (CS) cm^{-1}; NMR ($CDCl_3$) δ 7.2 (s, 9 H, Ar); 3.3 (s, 3 H, OMe), 6.7 (dd, 1 H, double bond, J_{db} = 10, J_{vic} = 2.5), 6.0 (dd, 1 H, double bond, $J_{allylic}$ = 1.2), 5.3 (dd, 1 H, allylic), 1.6 (s, 3 H, angular methyl).

2-[*p*-(Phenylsulfonyl)phenyl]-2-methyl-2*H*-pyran-3,5-dione (6). NBS (0.6 g, 0.003 mol) was added to a solution of 0.95 g (0.0027 mol) of **5c** in 10 mL of AcOEt. The reaction mixture is refluxed for 15 min. After workup in the conventional manner and two recrystallizations from AcOEt, we took 0.8 g (yield 81%) of **6** as a pale yellow crystal solid, mp 110–112 °C: IR 1735 (conj ester), 1692 (conj ketone), 750 (CS), 1220, 1040 (COC), 2940 (CH_3), 3060, 1960, 820, 745 (Ar) cm^{-1}; NMR δ 7.8 (m) and 7.3 (m, 9 H, Ar), 1.8 (s, 3 H, angular methyl), 6.6 (q, 2 H, double bonds, AB system, J_{A+B} = 9.6).

Reaction of 4a with MCPBA (Referring to Scheme II). **4a** (1 mequiv) was dissolved in 5 mL of CH_2Cl_2 and cooled to 15 °C, and 0.5 mequiv of MCPBA was added portionwise. TLC showed two spots corresponding to **4a** (starting material) and to **4b**. After an additional amount of 0.5 mequiv of MCPBA was added, TLC showed three spots corresponding to **4a–c**. Subsequent addition of 0.5 mequiv of MCPBA gave on TLC two spots corresponding to **4b** and **4c** while upon the addition of a new portion of 0.5 mequiv of MCPBA, TLC gave mainly one spot, **4c**. Traces of **4b** and **5c** were also detected.

Finally, the reaction yields **5c** upon the addition of another portion of 1 mequiv of MCPBA and stirring at room temperature for 3 h.

Registry No. **3a**, 10169-55-8; **3b**, 65085-80-5; **4a**, 102285-64-3; **4b**, 102285-65-4; **4c**, 81830-82-2; **4d**, 4208-64-4; **4e**, 102285-66-5; **4f**, 36169-67-2; **5a**, 102285-67-6; **5b**, 102285-68-7; **5c**, 102285-69-8; **5d**, 41728-14-7; **5e**, 102285-70-1; **5f**, 36067-19-3; **6**, 102285-73-4; **8a**, 102285-71-2; **8b**, 102285-72-3.

(17) The assignment of the configuration of 2-aryl-substituted 2*H*-pyran-3(6*H*)-ones was based on the quotient of $J_{vic}/J_{allylic}$, according to the findings in ref 9b.