

reactive acid chlorides such as di- and trichloroacetyl chloride, phosgene or malonic acid dichloride **1**^[1]. The ketone enol ethers **2** react—except with malonic acid dichloride— analogously; with **1**, the 4-hydroxy-2*H*-pyran-2-ones **6** and/or phloroglucinols **7** are obtained (Table 1). Since the pyranones **6** can be converted into the phloroglucinols **7**^[2] the reaction of **2** with **1** enables a generally applicable synthesis of phloroglucinol and its derivatives in very good yields.

The extension of this reaction to enol ethers of cyclic ketones **8** leads to the bicycles **9** and/or **10** and/or the [n](2,4)phloroglucinophanes **11**, which allow interesting conclusions to be drawn about the structure and reaction behavior of metacyclophanes owing to the possibility of tautomerism in the arene moiety (Table 1). Aqueous work-

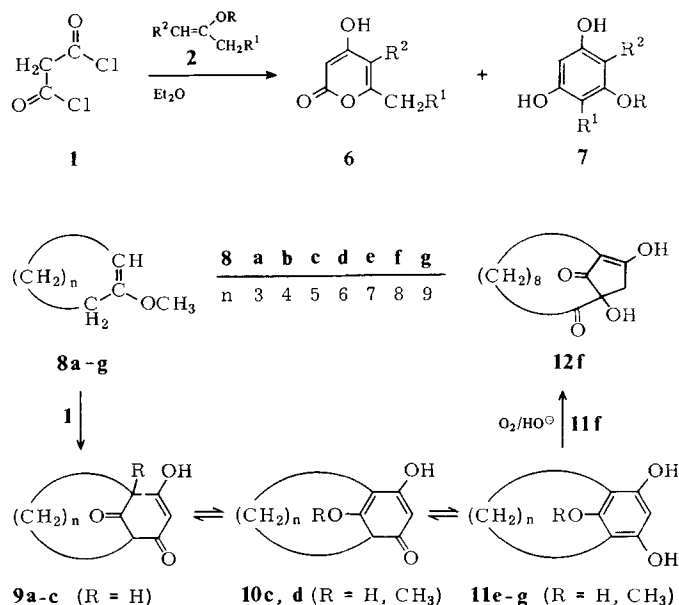


Table 1. 4-Hydroxy-2*H*-pyran-2-ones **6** and phloroglucinols **7** (selection).

2	R	R ¹	R ²	6	+	7
						(Yield [%])
2a	CH ₃	H	H	5a	(43)	7a (52)
2b	C ₂ H ₅	H	H	6a	(42)	7b (43)
2c	CH(CH ₃) ₂	H	H	6a	(24)	7c (65)
2d	C(CH ₃) ₃	H	H	—		7d (79)
2e	CH ₃	H	C ₂ H ₅	6b	(11)	7e (80)
2f	CH ₃	CH ₃	CH ₃	6c	(30)	7f (53)
2g	CH ₃	C ₂ H ₅	H	6d	(15)	7e (16)

A Novel Route to Phloroglucinols – Synthesis, Structure, and Reactions of [n](2,4)Phloroglucinophanes**

By Franz Effenberger*, Karl-Heinz Schönwälder, and
John J. Stezowski

Dedicated to Professor Hermann Stetter on the occasion
of his 65th birthday

Aldehyde enol ethers can be acylated to β-dicarbonyl-
and 1,3,5-tricarbonyl-compounds in very good yields with

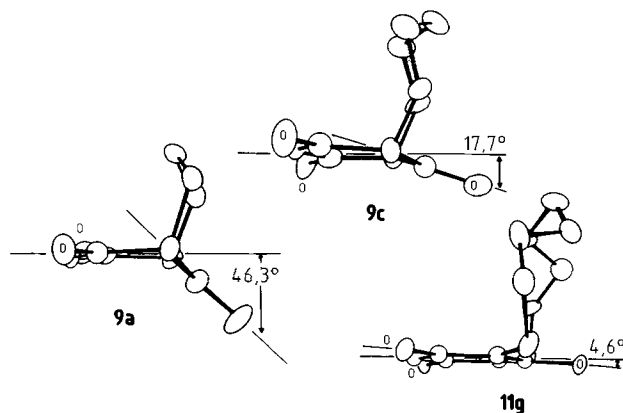
[*] Prof. Dr. F. Effenberger, Dr. K.-H. Schönwälder,
Priv.-Doz. Dr. J. J. Stezowski
Institut für Organische Chemie der Universität
Pfaffenwaldring 55, D-7000 Stuttgart 80 (Germany)

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sistance with the structure determinations.

up of **8a–c** and **1** affords the bicycles **9a–c** (yields 84, 88, and 91%, respectively), while work-up of **8a, b** and **1** in methanol furnishes the 9,9- and 10,10-dimethylketals of **9a, b**, respectively. In the reaction of **8c–g** with **1** the hydrochlorides of the methyl ethers of **10c, d** and **11e–g** can be obtained (yields 70, 31, 18, 55, 28%).

The expected competition between the tautomers **9–11** can be deduced from the side views of the X-ray crystallographically determined structures of **9a** (*n*=3), **9c** (*n*=5), and **11g** (*n*=9), where in each case R=H. In **9a** there is a strain-free coupling of 4-cyclohexene-1,3-dione and cyclohexanone in the chair form and in **9c** a combination of 4-cyclohexene-1,3-dione with cyclooctanone in the energetically less favorable chair-chair conformation. In **11g** the twelve-membered ring is almost strain-free and orthogonally coupled with the arene.

The compounds **9**–**11** show different chemical behavior, depending on ring size and ring strain. The hydrochlorides of **10c** ($R=CH_3$) and **11f**, **g** ($R=CH_3$) with



$n=5, 8, 9$ can be cleaved to the corresponding hydroxy compounds **9c** and **11f**, **g** ($R=H$) even with water, whereas in the case of **10d** ($R=CH_3$) and **11e** ($R=CH_3$), with $n=6, 7$, no cleavage of ether takes place even under drastic conditions (conc. HBr). Comparable with the conversion of deoxyhumulone into humulone and its rearrangement to isohumulone^[14] is the reaction of **11f** ($R=H$), whose autoxidation and rearrangement to the obviously more stable bicycle **12f**, however, takes place much more rapidly; this can be explained in terms of a decrease in strain on going from an 11- to a 12-membered ring.

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1, 1663-67-8; **2a**, 116-11-0; **2b**, 926-66-9; **2c**, 4188-63-0; **2d**, 4188-70-9; **2e**, 53110-70-3; **2f**, 41623-41-0; **2g**, 61142-47-0; **6a**, 675-10-5; **6b**, 83436-27-5; **6c**, 31246-34-1; **6d**, 18742-94-4; **7a**, 2174-64-3; **7b**, 28334-98-7; **7c**, 64507-45-5; **7d**, 83436-28-6; **7e**, 83436-29-7; **7f**, 23848-22-8; **8a**, 931-51-1; **8b**, 50438-50-1; **8c**, 50438-51-2; **8d**, 70578-46-0; **8e**, 13659-75-1; **8f**, 57620-91-4; **8g**, 32400-32-1; **9a**, 83436-30-0; **9a** · 9,9-dimethylketal, 83436-31-1; **9b**, 83436-32-2; **9b** · 10,10-dimethylketal, 83436-34-4; **9c**, 83436-33-3; **10d** ($R=CH_3$), 83436-36-6; **10d** ($R=CH_3$) · HCl, 83436-35-5; **11e** ($R=CH_3$), 83436-38-8; **11e** ($R=CH_3$) · HCl, 83436-37-7; **11f** ($R=H$), 83436-40-2; **11f** ($R=CH_3$) · HCl, 83436-39-9; **11a** ($R=H$), 83436-42-4; **11a** ($R=CH_3$) · HCl, 83436-41-3; **12f**, 83436-43-5;

[1] a) F. Effenberger, R. Meier, K.-H. Schönwälder, T. Ziegler, *Chem. Ber.* 115 (1982) 2766; b) P. Fischer: "Enol Ethers—Structure, Synthesis and Reactions" in S. Patai: *The Chemistry of Functional Groups*, Suppl. E, Part 1, p. 76, Wiley, New York 1980.

[2] U. Huber, DOS 2 705 874 (1977); *Chem. Abstr.* 87 (1977) 167718 y.

[14] a) R. Stevens, *Chem. Rev.* 67 (1967) 19; b) E. Collins, G. D. John, P. V. Shannon, *J. Chem. Soc. Perkin Trans. I* 1975, 96.