ON THE REACTION OF 2,2,6,6-TETRAMETHYL-3,5-HEPTANEDIONE ("DIPIVALOYLMETHANE") WITH OXALYL CHLORIDE [1,2a]

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Dedicated cordially to Prof. Dr. Hans Georg von Schnering on the occasion of his 60th birthday.

Abstract– Refluxing of dipivaloylmethane (**1**) in an excess of oxalyl chloride gives a mixture containing the 5-chloro-furanone derivatives (**2**), (**3**), and (**4**), which then can be completely converted into the 5-tert-butyl-4-pivaloylfuran-2,3-dione (**5**). Compounds (**2-5**) are hydrolyzed to the carboxylic acid (**6**), which in reverse is easily recyclized to **5** .

4-Benzoyl-5-phenylfuran-2,3-dione[3] has been found to be a versatile synthon in building new heterocyclic systems via thermolysis reactions,[4] cycloaddition reactions accompanied by novel rearrangements,[5] or addition of several nucleophiles.[6] Furthermore, under flash vacuum pyrolysis conditions a surprising 1,3-aryl shift with the so formed dibenzoylketene has been detected.[7] The diaryl substituted furandione is prepared smoothly by reaction of dibenzoylmethane with oxalyl chloride in good yield, no intermediates or byproducts are isolable.[3] If other 1,3-diketones are employed in this reaction, various products such as chlorinated or O-acylated derivatives are usually obtained instead of the expected furandiones.[2,8] In order to extend our investigations on the remarkable reactivity[4-7] of 4-benzoyl-5-phenylfuran-2,3-dione[3] to alkyl substituted analogs we now tried to prepare 5-tert-butyl-4-pivaloylfuran-2,3-dione (**5**), starting from the corresponding ketone and oxalyl chloride. Here we describe the complex reaction sequence from dipivaloylmethane (**1**) with oxalyl chloride finally leading to the desired furandione (**5**) [8] in high yield.

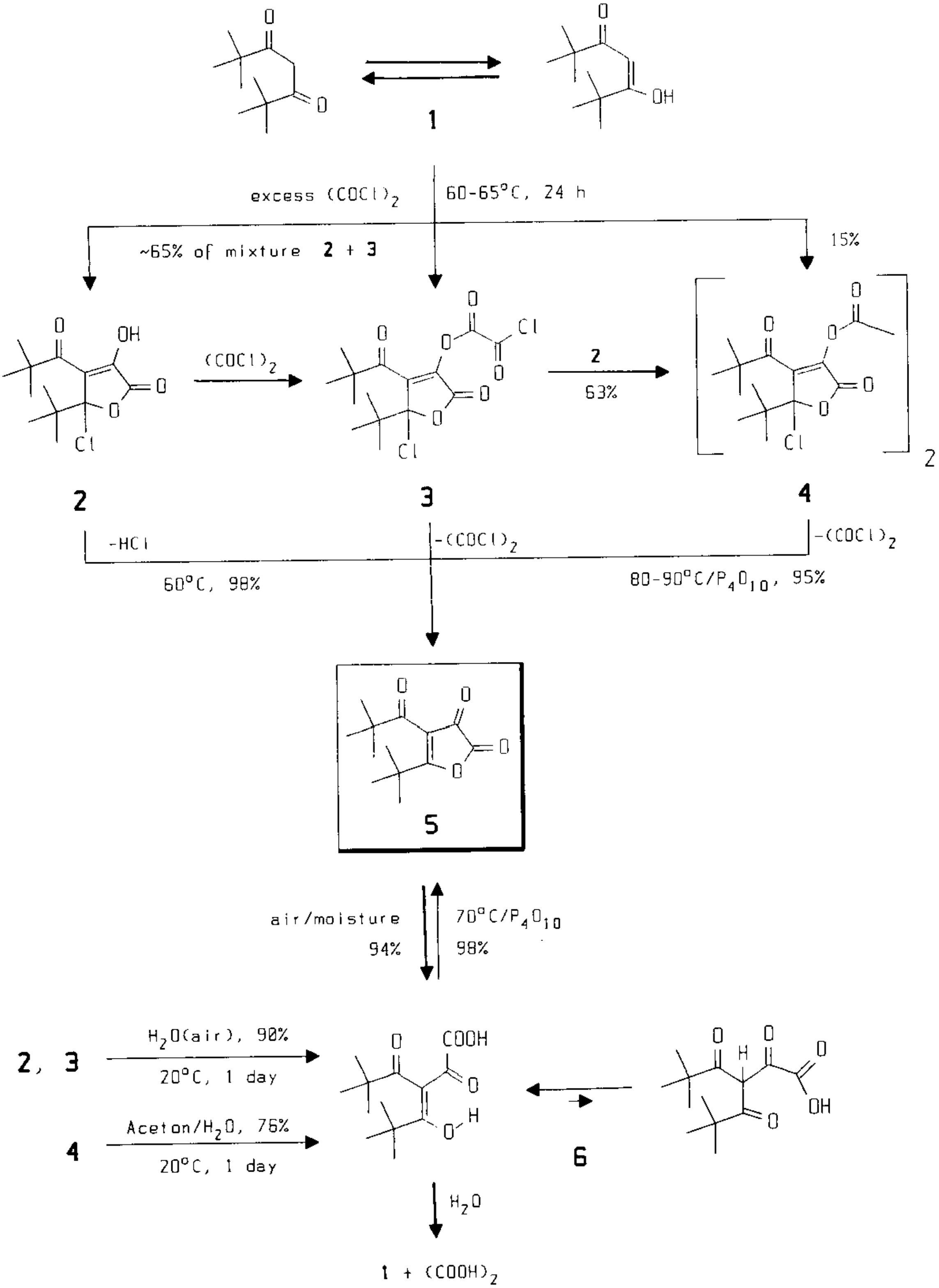
From refluxing the ketone (**1**) in oxalyl chloride for 24 h and evaporating the reaction mixture, a pale yellow residue is obtained, representing a mixture of the 5-chlorofuranone derivatives (**2**), (**3**) and (**4**). Out of these, **2** and **3** can be completely converted into the expected yellow furandione (**5**),[8] either by 10 min boiling in petroleum ether (bp 40-60 °C) or in the solid state by heating in a bulb tube oven at 60-70 °C until the evolution of HCl ceased. The crude **5** is still contaminated with the oxalic ester derivative (**4**) and purified by recrystallization from petroleum ether (for spectroscopic data of **5**, see ref. 8). If the primary residue, consisting of **2**, **3**, and **4**, is dissolved in hot petroleum ether and cooled down immediately, the mixture of **2** and **3** crystallizes and can be separated from **4**, since the latter remaines in solution. **4** itself may also be converted into the furandione (**5**) by heating up to 80-90°C in a drying tube (P_4O_{10}, 10 mm Hg, 1d). Hence the overall yield of **5** is about 75%.

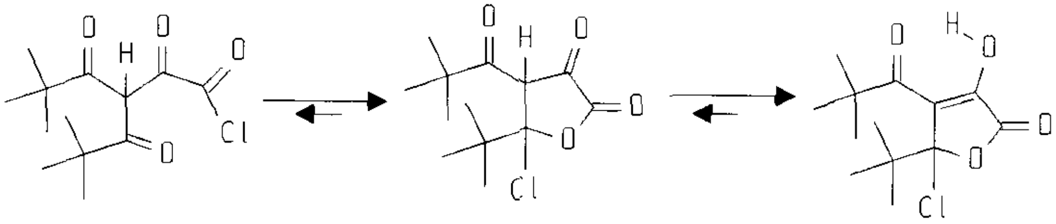
If the mixture of **2** and **3** is refluxed in oxalyl chloride for 30 min, **2** is completely converted into **3**, which is characterized by ir and ^{13}C nmr spectral data.[10] Moreover the close structural analogy of **3** and **4** is easily deduced from their ^{13}C nmr spectra.[10] As expected, the signals of all carbons are nearly identical with an additional one for the COCl-moiety (158.5 ppm)[11] in **3**. The experimental evidence for the presence of **2** comes from the ir spectrum, which, besides overlapping C=O bands of compounds (**2**), (**3**), and (**4**) at 1820-1780, 1700 and 1650 cm^{-1} exhibits a strong OH absorption band at 3250 cm^{-1}, which disappears completely after treatment with additional oxalyl chloride.

Compounds (**2**), (**3**), and (**5**) can easily be hydrolized by moisture at 20 °C to the α-keto acid (**6**), which is also obtained from **4** using an acetone/H_2O solution. From the ^1H nmr of **6** [10] the enolic form should be dominating in solution. Recyclization of **6** to **5** is done again in a drying tube (P_4O_{10}, 70°C). Extensive hydrolysis results in cleavage of the central C-C bond finally to give dipivaloylmethane (**1**) and oxalic acid.

Formation of the primary reaction products (**2**), (**3**), and (**4**) should be initiated by a C-acylation at the activated CH_2 group of **1** leading to intermediate (**2**), which preferably should exist in its isomeric enolic cyclized form. This is well known[12] from several γ-keto acid chlorides e. g. levulinic acid chloride, and made evident from the corresponding ^{13}C nmr spectrum (sp^3 carbon at 104.6 ppm). The furanone (**3**) obviously comes from additional acylation of **2**, the dimeric furanone **4** is the result of combining **2** and **3**. This could be confirmed by an independent experiment.

The target molecule (**5**) finally is obtained via some remarkable unusual fragmentation reactions thus eliminating HCl (from **2**) or oxalyl chloride (from **3** and **4**).


1
excess (COCl)2
60-65°C, 24 h
~65% of mixture 2 + 3
15%
OH
Cl
(COCl)2
2
63%
2
3
4
-HCl
60°C, 98%
-(COCl)2
-(COCl)2
80-90°C/P4O10, 95%
5
air/moisture
94%
70°C/P4O10
98%
2, 3
H2O(air), 90%
20°C, 1 day
4
Aceton/H2O, 76%
20°C, 1 day
COOH
6
H
OH
H2O
1 + (COOH)2



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8. Recently a slightly different procedure to synthesize 5 has been reported: R.W. Saalfrank and Th. Lutz, Angew. Chem., 1990, **102**, 1064. Starting with commercial available diketone (**1**) (Aldrich) and oxalyl chloride (Fluka) as used in our experiments we could not obtain **5** following the procedure described. However, the melting points (97°C and 94°C reported) as well as the ^{13}C nmr data (**5**: 208.3, 191.5, 179.8, 154.8, 121.6, 46.6, 38.3; reported values: 206.3, 189.3, 177.5, 152.7, 119.6, 44.8, 36.6 ppm) are in acceptable agreement. On the other hand, the ir data (KBr) exhibit a significant discrepancy: **5**: 1835, 1684, 1634 cm^{-1} (C=O); reported : 1740, 1670, 1645 cm^{-1}. Since the highest C=O absorbtion band of similar 4,5-unsaturated furan-2,3-diones usually is found within the region of 1850-1830 cm^{-1}, [3,9] this remarkable difference might be due to hydrolysis of the dione eventually during determination of the ir spectrum. In fact, the ir data reported by Saalfrank for the furan-2,3-dione are close to those of the corresponding acid **6**.[10]
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10. **3**: mp: 75°C (petroleum ether); ir (KBr): 2990-2890 (CH), 1820, 1790, 1670 (C=O); ^{13}C nmr ($CDCl_3$): 205.9 (acyl-C), 160.2 (C2), 158.5 (COCl),[11] 150.9, 150.7 (C3, ester-C), 135.5 (C4), 106.8 (C5), 45.5, 42.5 (t-Bu-C). **4**: mp: 160°C (toluene); ir (KBr): 2990-2880 (CH), 1810, 1790, 1700, 1655 (C=O); ^{13}C nmr ($CDCl_3$): 206.5 (m, acyl-C), 160.9 (s, C2), 151.4, 150.8 (s, C3, ester-C), 136.0 (s, C4), 106.8 (m, C5), 46.1, 42.8 (m, t-Bu-C); ms (CI, CH_4): 603 (M^{+}+1). **6**: mp: 138°C (ethanol); ir (KBr): 3500-3200 (OH), 2990-2880 (CH), 1750, 1685, 1655 (C=O); ^{1}H nmr ($CDCl_3$): 1.00 (s, 3 CH_3), 1.32 (s, 3 CH_3), 7.87 (br, OH). All compounds gave satisfying elemental analyses.
11. For comparison: The signal of oxalyl chloride is found at 159.3 ppm (H. O. Kalinowski, S. Berger, and S. Braun, '^{13}C-Nmr Spektroskopie,' G. Thieme Verlag 1984, p. 192.
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