

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 recycled to 5.

4-Benzoyl-5-phenylfuran-2,3-dione³ 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 reactivity⁴⁻⁷ of 4-benzoyl-5-phenylfuran-2,3-dione³ 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.

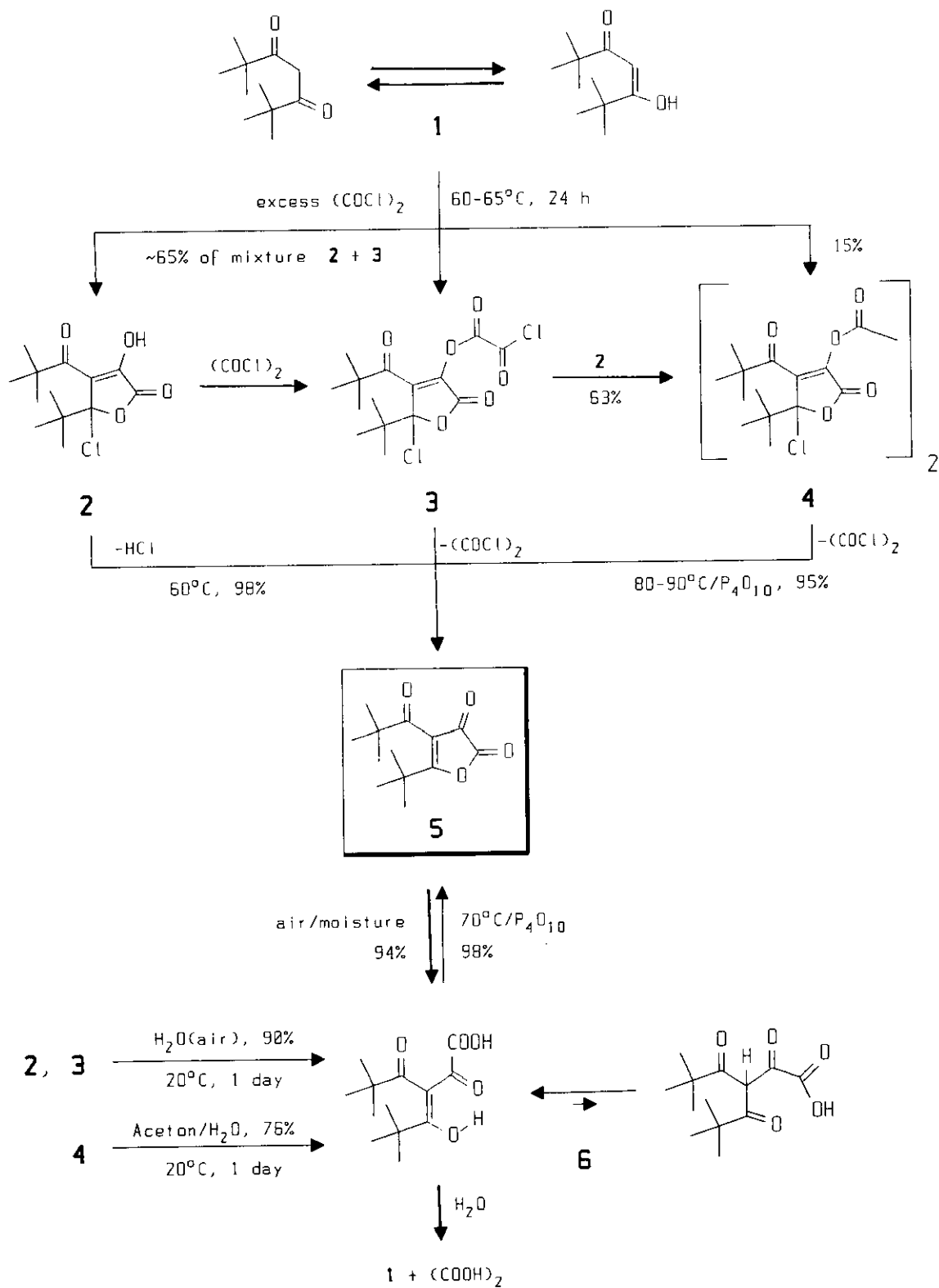
From refluxing the ketone (**1**) in oxalyl chloride for 24 h and evaporating the reaction mixture, a pale yellow residue is obtained, representing a mixture of the 5-chlorofuranone derivatives (**2**), (**3**) and (**4**). Out of these, **2** and **3** can be completely converted into the expected yellow 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 remains in solution. **4** itself may also be converted into the furandione (**5**) by heating up to 80-90°C in a drying tube (P₄O₁₀, 10 mm Hg, 1d). Hence the overall yield of **5** is about 75%.

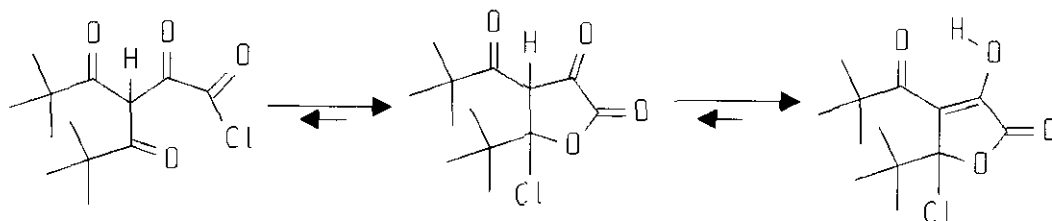
If the mixture of **2** and **3** is refluxed in oxalyl chloride for 30 min, **2** is completely converted into **3**, which is characterized by ir and ¹³C nmr spectral data.¹⁰ Moreover the close structural analogy of **3** and **4** is easily deduced from their ¹³C nmr spectra.¹⁰ As expected, the signals 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 hydrolyzed by moisture at 20 °C to the α-keto acid (**6**), which is also obtained from **4** using an acetone/H₂O 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 (P₄O₁₀, 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 CH₂ group of **1** leading to intermediate (**2**), which preferably should exist in its isomeric enolic cyclized form. This is well known¹² from several γ-keto acid chlorides e. g. levulinic acid chloride, and made evident from the corresponding ¹³C nmr spectrum (sp³ 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**).





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REFERENCES AND NOTES

1. Reactions with Cyclic Oxalyl Compounds, 33. For Part 32 see: E. Terpetschnig, G. Penn, G. Kollenz, K. Peters, E.-M. Peters, and H. G. von Schnering, *Tetrahedron*, 1991, in press.
2. a) Diploma Thesis, C. O. Kappe, Univ. Graz 1989; b) R. D. Clark and C. H. Heathcock, *Synthesis*, 1974, 47; *ibid.*, 1976, 555; *J. Org. Chem.*, 1976, 41, 636.
3. E. Ziegler, G. Kollenz, and H. Igel, *Monatsh. Chem.*, 1971, 102, 1769.
4. G. Kollenz, H. Igel, and E. Ziegler, *Monatsh. Chem.*, 1972, 103, 450; G. Kollenz, E. Ziegler, and W. Ott, *Org. Prep. Proced. Int.*, 1973, 5, 261; E. Ziegler, G. Kollenz, and W. Ott, *Synthesis*, 1973, 679; G. Kollenz, E. Ziegler, W. Ott, and G. Kriwetz, *Z. Naturforsch.*, 1977, 32B, 701; E. Ziegler, G. Kollenz, G. Kriwetz, and W. Ott, *Liebigs Ann. Chem.*, 1977, 1751.
5. G. Kollenz, W. Ott, E. Ziegler, K. Peters, H. G. von Schnering, and H. Quast, *Liebigs Ann. Chem.*, 1980, 1801; G. Kollenz, W. Ott, E. Ziegler, E.-M. Peters, K. Peters, H. G. von Schnering, V. Formacek, and H. Quast, *ibid.*, 1984, 1137; G. Kollenz, G. Penn, W. Ott, K. Peters, E.-M. Peters, and H. G. von Schnering, *Chem. Ber.*, 1984, 117, 1310; G. Kollenz, G. Penn, G. Dolenz, Y. Akcamur, K. Peters, E.-M. Peters, and H.G. von Schnering, *ibid.*, 1984, 117, 1299; W. Ott, E. Terpetschnig, H. Sterk, and G. Kollenz, *Synthesis*, 1987, 176; G. Kollenz, G. Penn, W. Ott, K. Peters, E.-M. Peters and H. G. von Schnering, *Heterocycles*, 1987, 26, 625; W. M. F. Fabian and G. Kollenz, *J. Mol. Struct.*, 1989, 187, 199; G. Kollenz, H. Sterk, and G. Hutter, *J. Org. Chem.*, 1991, 56, 235.
6. W. Ott, E. Ziegler, and G. Kollenz, *Synthesis*, 1976, 477; Y. Akcamur, G. Penn, E. Ziegler, H. Sterk, G. Kollenz, K. Peters, E.-M. Peters, and H. G. von Schnering, *Monatsh. Chem.*, 1986, 117, 231; Y. Akcamur and G. Kollenz, *Org. Prep. Proced. Int.*, 1987, 19, 52; E. Terpetschnig, W. Ott, G. Kollenz, K. Peters, E.-M. Peters, and H. G. von Schnering, *Monatsh. Chem.*, 1988, 119,

- 367; Y. Akcamur, B. Altural, E. Saripinar, G. Kollenz, C. O. Kappe, K. Peters, E.-M. Peters, and H. G. von Schnering, J. Heterocycl. Chem., 1988, 25, 1419; Zs. Juhasz-Riedl, G. Hajos, G. Kollenz, and A. Messmer, Chem. Ber., 1989, 122, 1935; B. Altural, Y. Akcamur, E. Saripinar, I. Yildirim, and G. Kollenz, Monatsh. Chem., 1989, 120, 1015; B. Altural and G. Kollenz, Monatsh. Chem., 1990, 121, 677.
7. C. Wentrup, H. W. Winter, G. Gross, H. P. Netsch, G. Kollenz, W. Ott, and A. G. Biedermann, Angew. Chem., Int. Ed. Engl., 1984, 23, 800.
 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 ¹³C 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 absorption 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
 9. S. Murai, K. Hasegawa, and N. Sonoda, Angew. Chem., Int. Ed. Engl., 1975, 14, 636; Yu. C. Andreichikov, Yu. A. Nelimova, G. D. Plakhina, R. F. Saraeva, and S. P. Tendryakova, Khim. Geterosikl. Soedin., 1975, 1468.
 10. **3**: mp: 75°C (petroleum ether); ir (KBr): 2990-2890 (CH), 1820, 1790, 1670 (C=O); ¹³C nmr (CDCl₃): 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); ¹³C nmr (CDCl₃): 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 (Cl, CH₄): 603 (M⁺+1). **6**: mp: 138°C (ethanol); ir (KBr): 3500-3200 (OH), 2990-2880 (CH), 1750, 1685, 1655 (C=O); ¹H nmr (CDCl₃): 1.00 (s, 3 CH₃), 1.32 (s, 3 CH₃), 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, ¹³C-Nmr Spektroskopie, G. Thieme Verlag 1984, p. 192.
 12. W. J. Elliot and J. Fried, J. Org. Chem., 1978, 43, 2708.