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PALLADIUM CATALYZED C-ALLYLATION OF HIGHLY ACIDIC CARBO AND HETEROCYCLIC β-DICARBONYL COMPOUNDS

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Abstract.- Highly acidic carbo and heterocyclic β-dicarbonyl compounds such as barbituric acid, 3,5-dimethyl-2H-1,2,6-thiadiazine 1,1-dioxide, cyclohexane-1,3-dione, tetronic acids, Meldrum acid and 1,2-diphenylpyrazolidine-3,5-dione are efficiently C-allylated with primary and secondary allylating agents under palladium catalysis.

The palladium catalyzed allylation of proton active substrates is a well established method of carbon-carbon bond formation.[1] The acidity of the most frequently used proton active substrates is in the range pK_a 10-24. More acidic substrates have received much less attention. A few cases of palladium catalyzed C-allylation of cyclopentane-1,3-diones and cyclohexane-1,3-diones[2] and of Meldrum's acid[3], compounds with pK_a's around 5, have been reported but the subject is far from having attracted general attention.

We have previously reported[4] in preliminary form that compounds with pK_a values as low as 3.76 (tetronic acid, **4**) can be efficiently C-allylated under palladium catalysis. Moreover, a mechanistic and synthetic study on the palladium catalyzed allylation of triacetic acid lactone has been carried out by our group.[5] In summary, our previous findings point out that cyclic β-dicarbonyl systems of high acidity and high enol content can be efficiently C-allylated by means of thermodynamically conducted reactions under palladium catalysis, conditions under which allylation at oxygen is kinetically favoured although reversible. Such systems are frequently difficult to alkylate at the central carbon atom due to the strong competition from O-alkylation which is irreversible under conventional conditions. Therefore an extension of the palladium method for C-alkylation should be of general interest in synthetic organic chemistry.

We wish to report now our studies on the scope of the method which we have used on a broad selection of highly acidic β-dicarbonyl cyclic systems. Our chosen substrates, their reported pK_a values and their preferred tautomers are: barbituric acid, **1**, pK_a 4.1,[6] 100% triketo form in solid phase and in DMSO;[6] 3,5-dimethyl-2H-1,2,6-thiadiazine 1,1-dioxide, **2**, pK_a 3.27,[7] 100% enamine form;[8] cyclohexane-1,3-dione, **3a**, pK_a 5.25,[9] and its trimethylsilyl ether, **3b**;[10] tetronic acid, **4**, pK_a 3.76,[11] 100% enol form; 3-methyltetronic acid, **5**,[12] 100% enol form; Meldrum's acid, **6**, pK_a 4.83,[13] 100% keto form and 1,2-diphenylpyrazolidine-3,5-dione, **7**,[14a] pK_a 5.4,[14b] 100% keto form.

A few conventional C-alkylations have been reported for **1**,[6] **3a**,[15], **6**[13,16a] and **7**[14c] although dialkylation is frequently an unsolved problem. Alkylation of **2** led to N-alkyl derivatives,[17] and no useful C-alkylations are known for **4** and **5**.[18] Also indirect methods have been reported for the alkylation of **1**,[6,19] **3**[20] and **6**[16b] and **7**.[14c] Finally, the isoprenylation of **1**, **6** and **7** with isoprene under rhodium (I) catalysis has been recently described.[21]

In spite of all the efforts dedicated to the C-alkylation of products of the type represented by **1-7** it seems that the necessity of a general method is still felt.

Our results are collected in the scheme and in the table. Allylation was achieved in all the

cases although polyallylation remains as a problem to be solved for every particular case when working with primary allylating agents. In general it can be said that the resulting monoallylated products are more nucleophilic than the starting substrates thus rendering the control difficult.

The method is so powerful that secondary radicals can be introduced in good yields with good monoallylation control. Thus 3-penten-2-yl and 2-cyclohexen-1-yl derivatives are efficient allylating agents as shown in runs 8-11, 13-17 and 19. Even diallylated products with two secondary radicals in the activated carbon atom are easily obtained (Runs 13-16). This is most unusual and indicates the possibilities of the palladium catalyzed allylation.

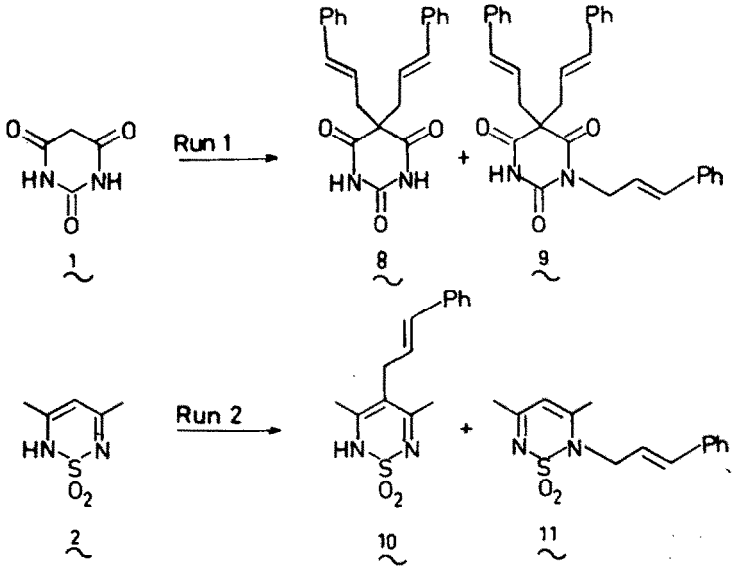
Barbituric acid afforded the polyallylated derivatives 8 and 9 (Run 1). The thiadiazine dioxide 2 afforded the allyl derivatives 10 and 11 although the yields were not good (Run 2). Both 3a and 3b were efficiently allylated (Runs 3-11) under a variety of experimental conditions.

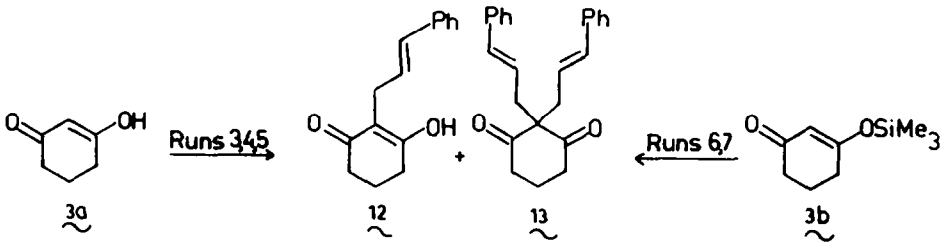
The most remarkable achievement from the viewpoint of the category of the substrates is the allylation of tetronic acid, 4, and its 3-methyl derivative, 5, for which no useful C-alkylation had been previously described. For 4 no control of the monoallylation could be achieved with primary agents (run 12) although it was achieved for secondary ones (Runs 13-17). The lactone 5 was cleanly allylated both with a primary and with a secondary allylating agent (Runs 18 and 19).

For Meldrum's acid, 6, again a good allylation was achieved but lack of control was again experienced. Finally, the pyrazolinedione 7 was treated with 2-butenyl acetate to afford a mixture of the three possible diallylation products, 26, 27 and 28, which were separated and identified.

Several different experimental conditions were considered as indicated in the table: solvent (toluene and THF), catalyst ($Pd(acac)_2$/triphenylphosphine and $Pd(dba)_2$/bis-(diphenylphosphino)ethane), activation of the β-dicarbonyl compound in the form of trimethylsilyl ether, leaving group in the allylation agent (acetate or ethyl carbonate) and the presence of base (DBU) or its absence. From the results presented in the table no general trend emerges in order to define the best set of experimental conditions. However, we believe the given experimental conditions could be a good starting point for any substrate of the type considered different from those studied here.

In order to broaden the scope of the palladium based method of allylation of β-dicarbonyl (and related) compounds we have performed two hydrogenations of the allylic chains in compounds 18 and 23. The hydrogenated oxobutanolides 29 and 30 were obtained in nearly quantitative yields under Pd-C catalysis as indicated. Although no more hydrogenation experiments have been performed, those collected in this paper together with those reported by us elsewhere[4,5] indicate that the present method of allylation should be considered as useful for the introduction of allylic as well as saturated primary and secondary radicals at the activated carbon atom of highly acidic cyclic β-dicarbonyl and related compounds.





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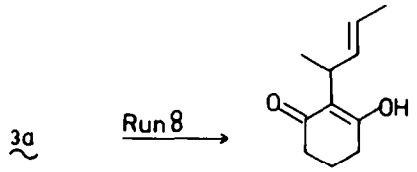

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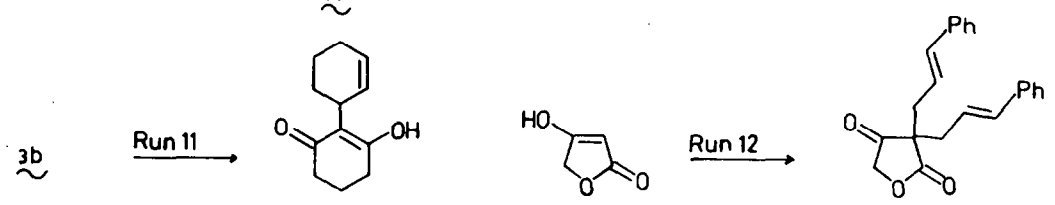
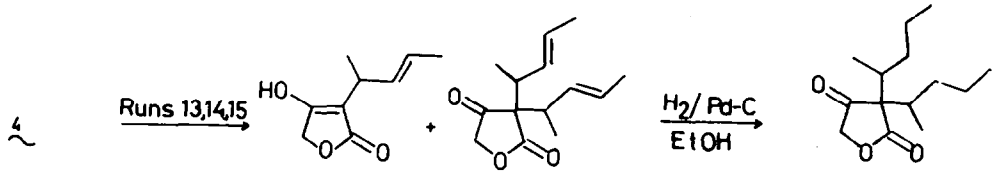
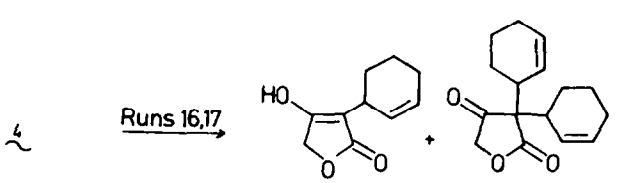


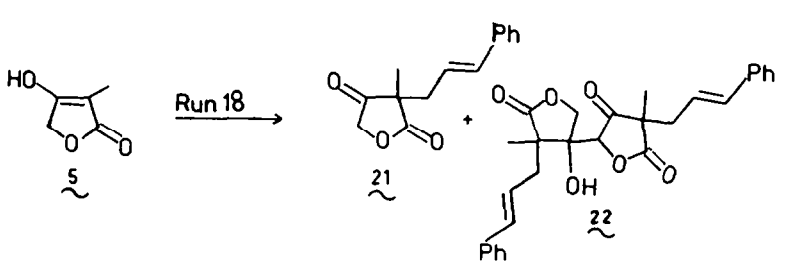
3b 15 4 16



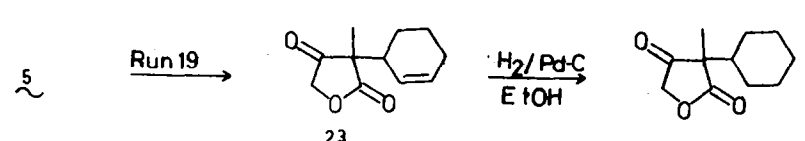
4 17 18 19



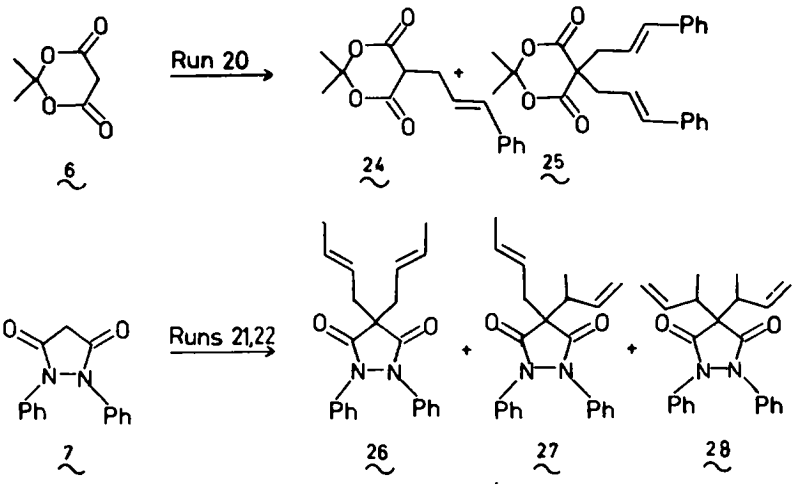
4 19 20



5 21 22



5 23 30



TABLE

Run	Reagents	DBU	Conditions	Cat.[a]	Products (%)[b]
1	1 + PhCH=CHCH$_2$OAc (1:1)	1 eq.	THF/78C/89h	A	8(15), 9(8)
2	2 + PhCH=CHCH$_2$OAc (1:1)	1 eq.	THF/50C/53h	A	10(13), 11(13)
3	3a + PhCH=CHCH$_2$OAc (1:1)	1 eq.	THF/40C/36h	A	12(26), 13(28),[c]
4	3a + PhCH=CHCH$_2$OCOOEt (1:1)	—	THF/40C/36h	A	12(16), 13(30)
5	3a + PhCH=CHCH$_2$OAc (1:1)	1 eq.	Tol./68C/5h	A	12(34), 13(28),[c]
6	3b + PhCH=CHCH$_2$OCOOEt (1:1)	—	THF/70C/4h	B	12(28), 13(23)
7	3b + PhCH=CHCH$_2$OCOOEt (1:1)	—	Tol./82C/1.5h	B	12(35), 13(26)
8	3a + MeCH=CHCH(Me)OCOOEt (1:1)	—	Tol./95C/9h	B	14(9)
9	3b + MeCH=CHCH(Me)OAc (1:1)	—	Tol./90C/7h	B	14(46)
10	3b + MeCH=CHCH(Me)OCOOEt (1:1)	—	Tol./95C/3h	B	14(59)
11	3b + 2-Cyclohexenyl-OCOOEt (1:2)	—	Tol./92C/3h	B	15(87)
12	4 + PhCH=CHCH$_2$OAc (1:2)	1 eq.	THF/62C/26h	A	16(38),[d]
13	4 + MeCH=CHCH(Me)OAc (1:2)	1 eq.	THF/65C/19h	A	17(42), 18(17)
14	4 + MeCH=CHCH(Me)OAc (1:4)	1 eq.	THF/62C/19h	A	17(12), 18(60)
15	4 + MeCH=CHCH(Me)OAc (1:1)	1 eq.	Tol./67C/4h	A	17(24), 18(13)
16	4 + 2-Cyclohexenyl-OAc (1:2)	1 eq.	THF/65C/3h	A	19(57), 20(14)
17	4 + 2-Cyclohexenyl-OCOOEt (1:2)	—	THF/62C/18h	B	19(0), 20(0)
18	5 + PhCH=CHCH$_2$OAc (1:1)	1 eq.	THF/62C/30min	A	21(32), 22(37),[c]
19	5 + 2-Cyclohexenyl-OAc (1:1)	1 eq.	THF/62C/17h	A	23(27)
20	6 + PhCH=CHCH$_2$OAc (1:1.2)	1 eq.	Tol./76C/4h	A	24(19), 25(68)
21	7 + MeCH=CHCH$_2$OAc (1:1)	1 eq.	Tol./65C/2h	A	26(14), 27(24), 28(1)
22	7 + MeCH=CHCH$_2$OAc (1:2)	1 eq.	THF/67C/2h	A	26(22), 27(47), 28(6)

[a] A: $Pd(acac)_2$ (5%) + Ph_3P (20%); B: $Pd(dba)_2$ (5%) + dppe (10%). [b] Yields refer to isolated and pure products. [c] 3-Cinnamylpentane-2,4-dione was also isolated as an oil: 1H-NMR($CDCl_3$) 2.17(s, 6H, keto), 2.26(s, 6H, enol), 2.80(dd, J ca. 6.6 and 6.6 Hz, 2H, keto), 3.20(d, J 3.9Hz, 2H, enol), 3.84(t, J 6.6 Hz, 1H, keto), 5.86-6.66(m, 2H, keto + enol), 7.16-7.51(m, 10H, keto + enol). [d] 3,3-Dicinnamylpentane-2,4-dione[22] was also isolated.

EXPERIMENTAL

5,5-Dicinnamyl-pyrimidine2,4,6-trione, 8, and 1,5,5-tricinnamylpyrimi-dine-2,4,6-trione, 9. (Run 1).

A mixture of barbituric acid, 1, (0.64 g, 5 mmol), DBU (0.761 g, 5 mmol) and anhydrous THF (25 mL) was stirred under argon atmosphere for 1-2 minutes. Then, and in the following order were added Pd(II) acetylacetonate (0.077 g, 0.25 mmol), triphenylphosphine (0.262 g, 1 mmol) and cinnamyl acetate (0.810 g, 5 mmol). The mixture was immersed in an oil bath at 78C and kept under magnetic stirring for 89h. The reaction was monitored by TLC. The cooled mixture was diluted with ethyl acetate and partitioned with 0.1N HCl. The organic layer was washed to neutrality, dried and evaporated. The residue was chromatographed through silica gel. The following products were isolated:

9 (8%): m.p. 157-8C; IR(KBr): 3215, 1746, 1715, 1678 cm^{-1}; 1H-NMR(DMSO-d_6): δ 2.85 (d, J 7.4 Hz, 4H), 4.52 (d, J 5.9 Hz, 2H), 5.74-6.70 (m, 6H), 7.24 (s, 15H), 11.76 (s, 1H); 13C-NMR($CDCl_3$):δ 41.2, 42.9, 57.7, 121.2, 121.8, 126.3, 126.5, 127.8, 128.5, 135.2, 135.8, 136.0, 136.2, 149.2, 170.9, 171.1, ; MS (Chemical ionization with ammonia): m/e 494(M+18). Calcd. for $C_{31}H_{28}N_2O_3$: C, 78.13; H, 5.92; N, 5.88. Found: C, 78.01; H, 5.93; N, 5.97.

8 (15%): m.p. 226-8C; IR(KBr): 3205, 3085, 1758, 1720, 1686 cm^{-1}; 1H-NMR(DMSO-d_6): δ 2.79 (d, J 7.2 Hz, 4H), 6.04 (dt, J 7.2 and 16.1 Hz, 2H), 6.51 (d, J 16.1 Hz, 2H), 7.29 (s, 10H), 11.50(s, 2H); 13C-NMR(DMSO-d_6): δ 55.6, 122.5, 126.1, 127.6, 128.5, 134.2, 136.3, 149.6, 171.8; MS: m/e 360(M, 7), 117(82), 115(100), 91(78). Calcd. for $C_{22}H_{20}N_2O_3$: C, 77.30; H, 5.59; N, 7.77. Found: C, 73.03; H, 5.68; N, 7.51.

The same method was used for allylations of 2, 3a, and 4-7 performed under the conditions indicated in the table. The following compounds were isolated:

4-Cinnamyl-3,5-dimethyl-2H-1,2,6-thiadiazine 1,1-dioxide, 10: oil; IR($CHCl_3$): 3340, 1600, 1510, 1320, 1200, 1170 cm^{-1}; 1H-NMR($CDCl_3$): δ 2.23 (s, 6H), 3.16(d, J 4 Hz, 2H), 6.1-6.3(m, 2H), 7.1-7.4(m, 5H).

2-Cinnamyl-3,5-dimethyl-2H-1,2,6-thiadiazine 1,1-dioxide, 11: m.p. 79-81C; IR(KBr): 1577, 1512, 1394, 1316, 1169 cm^{-1}; 1H-NMR($CDCl_3$): δ 2.26(s, 3H), 2.3(s, 3H), 4.63(d, J 5.3 Hz, 2H), 5.72(s, 1H), 6.21(dt, J 15.8 and 5.3 Hz, 1H), 6.62(d, J 15.8 Hz, 1H), 7.31(s, 5H); 13C-NMR($CDCl_3$): δ 20.4, 25.4, 47.4, 102.9, 123.2, 126.6, 128.3, 128.6, 134.1, 135.7, 157.6, 172.9; MS: m/e276(M, 9), 117(100), 115(45), 91(18). Calcd. for $C_{14}H_{16}N_2O_2S$: C, 60.85; H, 5.83; N, 10.14; S, 11.60. Found: C, 60.71; H, 6.24; N, 9.94; S, 11.11.

2-Cinnamyl-1,3-cyclohexanedione, 12: m.p. 160-2C; IR(KBr): 3600-2400 (broad), 1568, 1364 cm^{-1}; 1H-NMR($CDCl_3$): δ 1.86-2.21(m, 2H), 2.21-2.64(m, 4H), 3.29(d, 6.6 Hz, 2H), 6.20(dt, J 6.6 and 15.8 Hz, 1H), 6.58(d, J 15.8 Hz, 1H), 7.15-7.30(m, 5H); 13C-NMR(DMSO-d_6): δ 20.4, 24.9, 32.3 (broad), 112.4, 125.5, 126.5, 128.3, 128.6, 128.9, 137.4; MS: m/e 228(M, 54), 200(22), 172(31), 157(23), 137(100), 128(34), 129(33), 115(52), 104(20), 91(37), 77(21). Calcd. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 79.12; H, 7.16.

2,2-Dicinnamyl-1,3-cyclohexanedione, 13: m.p. 110-1C; IR(KBr): 1721, 1695 cm^{-1}; 1H-NMR($CDCl_3$):δ 1.65-2.05(m, 2H), 2.56(t, J 6.6 Hz, 4H), 2.72(d, 7.9 Hz, 2H), 5.94(dt, J 7.9 and 15.8 Hz, 2H), 6.43(d, J 15.8 Hz, 2H), 7.26(s, 10H); 13C-NMR($CDCl_3$): δ 16.4, 40.0, 40.1, 68.6, 123.6, 126.1, 127.4, 128.4, 134.2, 136.8, 210.4; MS: m/e 344(M, 1), 128(35), 117(66), 116(22), 115(100), 91(93), 77(21). Calcd. for $C_{24}H_{24}O_2$: C, 83.69; H, 7.02. Found: C, 83.59; H, 7.01.

2-(3-Penten-2-yl)-1,3-cyclohexanedione, **14**: m.p. 106-8C; IR(KBr): 3300-2300(broad), 1563 cm^{-1}; 1H-NMR($CDCl_3$): δ (keto+enol) 1.16(d, J 6.6 Hz, 3H), 1.69-1.83(m, 3H), 1.83-2.13(m, 2H), 2.18-2.56(m, 4H), 3.6-4.1(m, 1H), 5.6-6.0(m, 2H), 6.95(s, 1H); 13C-NMR($CDCl_3$): δ (keto+enol) 17.3, 17.5, 17.7, 18.5, 20.6, 30.2, 33.0, 38.0, 38.9, 39.2, 73.3, 118.7, 124.6, 125.8, 132.6, 135.2, 185.8, 205.9, 206.1; MS: m/e180(M, 22), 165(20), 151(80), 109(55), 95(27), 79(23), 69(28), 67(31), 55(64), 43(59), 41(100). Calcd. for $C_{11}H_{16}O_2$: C, 73.30: H, 8.95. Found: C, 73.52; H, 9.29.

3,3-Dicinnamyl-3H,5H-furan-2,4-dione, **16**: m.p. 99-100C; IR(KBr): 1806, 1757 cm^{-1}; 1H-NMR($CDCl_3$):δ 2.72(d, J 7.9 Hz, 4H), 4.35(s, 2H), 6.03(dt, J 7.9 and 15.8 Hz, 2H), 6.52(d, J 15.8 Hz, 2H), 7.28(s, 10H); 13C-NMR($CDCl_3$):δ 38.2, 54.4, 73.1, 120.8, 126.3, 127.9, 128.5, 136.0, 136.2, 175.7, 210.0; MS: m/e 332(M, 13), 219(50), 128(55), 117(92), 116(30), 115(100), 91(88). Calcd. for $C_{22}H_{20}O_3$: C, 79.50; H, 6.06. Found: C, 79.43; H, 6.30.

4-Hydroxy-3-(3-penten-2-yl)-5H-furan-2-one, **17**: m.p. 118-20C; IR(KBr): 3400-2400 (broad), 1701, 1608 cm^{-1}; 1H-NMR($CDCl_3$):δ 1.30(d, J 6.7 Hz, 3H), 1.89(dd, J 1.3 and 4.0 Hz, 3H), 3.06-3.48(m, 1H), 4.41-4.75(m, 2H), 5.38-5.96(m, 2H), 8.5(broad s, 1H); 13C-NMR($CDCl_3$): δ 17.7, 18.4, 31.0, 67.5, 104.6, 124.9, 132.6, 173.6, 177.6; MS: m/e 168(M, 11), 153(25), 135(47), 111(40), 101(100), 95(63), 79(38), 69(87), 68(29), 67(55), 53(21), 41(72). Calcd. for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.41; H, 6.91.

3,3-(Di-3-penten-2-yl)-3H,5H-furan-2,4-dione, **18** (mixture of isomers): oil; IR(film): 1790, 1745, 975 cm^{-1}; 1H-NMR($CDCl_3$):δ 0.8-1.35(m, 6H), 1.43-1.83(m, 6H), 2.30-2.95 (m, 2H), 4.15-4.35(m, 2H), 5.05-5.75 (m, 4H). This mixture was hydrogenated without further purification to the oxobutanolide **29**.

3-(2-Cyclohexen-1-yl)-4-hydroxy-5H-furan-2-one, **19**: m.p. 167-9C; IR(KBr): 3400-2400(broad), 1714, 1600 cm^{-1}; 1H-NMR($CDCl_3$): δ 1.46-2.0(m, 4H), 2.0-2.3(m, 2H), 3.05-3.35(m, 1H), 4.57(s, 2H), 5.73-6.29(m, 2H), 7.73(broad s, 1H); 13C-NMR(CD_3OD): δ 23.2, 25.6, 28.2, 31.8, 67.8, 104.3, 128.6, 129.3, 174.9, 177.7. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.36; H, 7.06.

3,3-(Di-2-cyclohexen-1-yl)-3H,5H-furan-2,4-dione, **20**: m.p. 88-90C; IR(KBr): 1796, 1748 cm^{-1}; 1H-NMR($CDCl_3$): δ 1.14-2.17(m, 12H), 2.71-3.12(m, 2H), 4.31-4.46(m, 2H), 5.17-6.06(m, 4H); 13C-NMR($CDCl_3$): δ 21.5, 23, 24, 25, 38.5, 58, 73, 124, 132, 175, 211 (most of the peaks were double, thus indicating the presence of more than one isomer). Calcd. for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.66; H, 7.64.

3-Cinnamyl-3-methyl-3H,5H-furan-2,4-dione, **21**: m.p. 93-4C; IR(KBr): 1796, 1749 cm^{-1}; 1H-NMR($CDCl_3$): δ 1.38(s, 3H), 2.7(d, J 7.2 Hz, 2H), 4.27, 4.48, 4.54 and 4.75 (AB system, 2H), 6.02(dt, J 7.2 and 14.3 Hz, 1H), 6.52(d, J 14.3 Hz, 1H), 7.29(s, 5H); 13C-NMR($CDCl_3$): δ 19.0, 39.4, 48.8, 72.4, 121.1, 126.3, 127.9, 128.5, 135.8, 136.2, 177.0, 209.8. Calcd. for $C_{11}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 72.96; H, 6.19.

3-Cinnamyl-4-[(3-cinnamyl-3-methyl-3H,5H-2,4-dioxo)-5-furyl]-4-hydroxy-3-methyl-2-oxotetrahydrofuran, **22**: m.p. 188-91C; IR(KBr): 3363, 1770, 1752 cm^{-1}; 1H-NMR($CDCl_3$+TFAA):δ 1.40(two s, 6H), 2.8 (two d, J ca. 6.7 and 6.7 Hz, 4H), 4.39(d, J ca. 10.8 Hz, 1H), 4.66(d, J ca. 10.8 Hz, 1H), 4.9(s, 1H), 5.78-6.86(m, 4H), 7.2(s, 10H); MS: m/e 460(M, 2), 117(100), 115(27).

3-(2-Cyclohexen-1-yl)-3-methyl-3H,5H-furan-2,4-dione, **23** (mixture of isomers): oil; IR(film): 1800,1750 cm^{-1}; 1H-NMR($CDCl_3$): δ 1.31(s, 3H), 1.35-2.20(m, 6H), 2.45-2.80(m, 1H), 4.52 (deceptive doublet, inner part of an AB system, 2H), 5.35-5.65(m, 1H), 5.75-6.05(m, 1H); 13C-NMR($CDCl_3$):δ 16.1 and 16.4, 21.4 and 21.7, 23.1, 24.1 and 24.6, 42.2, 50.6 and 50.8, 72.4, 123.6 and 123.7, 131.8 and 132.1, 176.8 209.7. This mixture was hydrogenated without further purification to the oxobutanolide **30**.

5-Cinnamyl-2,2-dimethyl-1,3-dioxan-4,6-dione, 24: m.p. 105-6C (Lit.[23] m.p. 108-9C); IR(KBr): 1790, 1740 cm^{-1}; 1H-NMR($CDCl_3$): δ 1.73(s, 3H), 1.78(s, 3H), 3.04(dd, J 3.2 and 6.7 Hz, 2H), 3.65(t, J 3.2 Hz, 1H), 6.23(dt, J 6.7 and 16.0 Hz, 1H), 6.63(d, J 16.0 Hz, 1H), 7.09-7.46(m, 5H); 13C-NMR($CDCl_3$): δ 26.7, 28.3, 29.5, 46.5, 104.9, 124.1, 126.2, 127.5, 128.4, 134.4, 136.8, 164.9; MS: m/e 260(M, 10), 158(33), 130(70), 129(100), 128(40), 115(35), 43(41).

5,5-Dicinnamyl-3,3-dimethyl-1,3-dioxan-4,6-dione, 25: m.p. 131C; IR(KBr): 1765, 1735 cm^{-1}; 1H-NMR($CDCl_3$): δ 1.55(s, 6H), 2.97(d, J 7.3 Hz, 4H), 6.08(dt, J 7.3 and 16.0 Hz, 2H), 6.58(d, J 16.0 Hz, 2H), 7.18-7.41(m, 10H); 13C-NMR($CDCl_3$): δ 29.6, 41.9, 56.2, 105.7, 121.7, 126.2, 127.8, 128.5, 135.8, 136.2, 168.4; MS: m/e 302(30), 300(25), 290(27), 205(100), 155(23), 141(25), 129(42), 128(60), 117(91), 91(64). Calcd. for $C_{24}H_{24}O_4$: C, 76.57; H, 6.43. Found: C, 76.26; H, 6.37.

4,4-Di-(2-buten-1-yl)-1,2-diphenylpyrazolidine-3,5-dione, 26 (mixture of two isomers as determined by GLC): oil; IR(film): 1758, 1725 cm^{-1}; 1H-NMR($CDCl_3$): δ 1.54(d, J 5.4 Hz, 3H), 2.54(d, J 5.9 Hz, 2H), 5.08-5.87(m, 4H), 6.95-7.37(m, 10H); 13C-NMR($CDCl_3$): δ 17.8, 38.4, 55.8, 122.8, 123.5, 126.6, 128.8, 131.3, 136.0, 172.8. Calcd. for $C_{23}H_{24}N_2O_2$: C, 76.64; H, 6.71; N, 7.77. Found: C, 76.61; H, 6.97; N, 7.67.

4-(2-Buten-1-yl)-4-(3-buten-2-yl)-1,2-diphenylpyrazolidine-3,5-dione, 27 (mixture of two isomers as determined by GLC): oil; IR(film): 1755, 1721 cm^{-1}; 1H-NMR($CDCl_3$): δ 1.2(d, J 7.2 Hz, 3H), 1.53(d, J 6 Hz, 3H), 2.49-2.97(m, 3H), 4.97-6.21(m, 5H), 7.02-7.50(m, 10H); 13C-NMR($CDCl_3$): δ 15.7, 17.8, 37.6, 44.0, 57.6, 117.4, 122.6, 123.6, 126.5, 128.7, 131.3, 135.7, 137.4, 172.2, 172.5. Calcd. for $C_{23}H_{24}N_2O_2$: C, 76.64; H, 6.71; N, 7.77. Found: C, 76.93; h, 7.07; N, 7.46.

4,4-Di-(3-buten-2-yl)-1,2-diphenylpyrazolidine-3,5-dione, 28: oil; 1H-NMR($CDCl_3$): δ 1.19(d, J 6.6 Hz, 6H), 2.66-3.11(m, 2H), 4.97-5.33(m, 4H), 5.72-6.26(m, 2H), 7.03-7.48(m, 10H). The small amount available prevented any further characterization.

2-(2-Cyclohexen-1-yl)cyclohexane-1,3-dione, 15. (Run 11).

A mixture of $Pd(dba)_2$ (0.160 g, 0.275 mmol) and bis(diphenylphosphino)ethane (0.223 g, 0.55 mmol) was purged with argon. The following compounds were added in the indicated order and via syringe: anhydrous toluene (15 mL), 3b[10] (1.008 g, 5.5 mmol) in anhydrous toluene (5 mL) and 2-cyclohexen-1-yl ethyl carbonate (1.883 g, 11 mmol). The mixture was immersed in an oil bath at 90-95C and was stirred for 3h (GLC monitoring). The solvent was evaporated and the residue was chromatographed through a silica gel column. Dibenzylideneacetone was eluted first (0.089 g, 69% recovered) and product 15 was eluted second. 15: m.p. 138-9C; IR(KBr): 3400-2200 (broad), 1563 cm^{-1}; 1H-NMR($CDCl_3$): δ 1.08-2.58(m, 12H), 3.51-3.92(m, 1H), 5.67-6.27(m, 2H), 7.15(s, 1H); 13C-NMR($CDCl_3$): δ 20.6, 21.5, 24.9, 28.2, 29.2, 30.4, 36.5, 118.2, 130.6, 132.3, 172.5, 197.4; MS: m/e 192(M, 15), 91(23), 77(22), 55(27), 53(40), 43(30), 42(65), 41(100). Calcd. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.66; H, 8.63.

The same method was used for runs 6, 7, 9 and 10 in which 3b was used as starting material. The experimental conditions are given in the table.

3,3-Di-(2-pentyl)-3H,5H-furan-2,4-dione, 29 (mixture of isomers as determined by GLC).

A mixture of 18 (0.185 g), absolute ethanol (15 mL) and 5% Pd-C (37 mg) was shaked in a hydrogen atmosphere until the absortion of hydrogen ceased. The mixture was filtered through celite, and the solvent was evaporated to afford 0.187 g (100% yield) of 29: oil; IR(film): 1802, 1749 cm^{-1}; 1H-NMR($CDCl_3$): δ 0.71-1.14(m, 12H), 1.14-1.62(m, 8H), 1.87-2.41(m, 2H), 4.39(s, 2H); 13C-NMR($CDCl_3$): δ 13, 14, 20, 23, 27, 33, 34, 36, 39, 59, 73, 176, 212 (some of these peaks showed duplicity thus indicating the presence of isomers). Calcd. for $C_{14}H_{24}O_3$: C, 69.96; H, 10.06. Found: C, 69.68; H, 10.15.

3-Cyclohexyl-3-methyl-3H,5H-furan-2,4-dione, **30**.

It was prepared as above for **29**. Compound **30**: m.p. 83-4C; IR(KBr): 1787, 1748 cm^{-1}; ^1H-NMR($CDCl_3$): δ 1.0-1.3(m, 3H), 1.3(s, 3H), 1.4-2.0(m, 8H), 4.49 and 4.54(central part of the AB system, 2H); ^{13}C-NMR($CDCl_3$): δ 17.0, 25.7, 26.1, 26.2, 27.1, 27.5, 44.5, 51.5, 72.7, 177.0, 211.0. Calcd. for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 66.62; H, 7.93.

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