106. Photochemical Synthesis of Cyclic 2-(2,2-Dimethylpropylidene)-1,3-dicarbonyl Compounds

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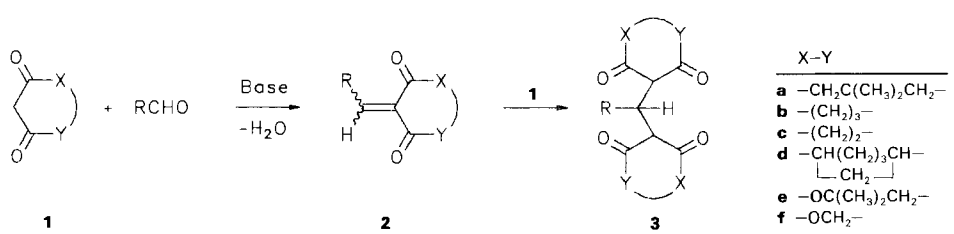
(2.V.89)

Photolysis (λ = 254 nm) of 4-(*t*-Bu)-substituted [*b*]-fused bi- and tricyclic pyrandiones **5** affords title compounds **4** in good yields as well as small amounts of spiroalkanediones **8**. The alkyl-substitution pattern at C(4) of the pyran ring in **5** determines the relative amount of α- *vs.* β-cleavage products obtained from the primarily formed acyl-vinyloxy biradical.

Cyclic 1,3-dicarbonyl compounds **1** react with aldehydes to give either *Knoevenagel* (1:1) condensation products **2** or *Michael* (2:1) addition products **3**. The differential ability of compounds **2** to react as *Michael* acceptors has been correlated with their pK_L values as electrically neutral organic *Lewis* acids [1]. Due to their high reactivity as *Michael* acceptors [1] [2] in inter- [3] [4] or intramolecular [5] cycloadditions, and due to the ease of tautomerization to – usually unstable – dienols, with R = alkyl with an α-H-atom [6–8], only very few of such compounds **2a–f** *(Scheme 1)* have been isolated [3] [9] [10].

Scheme 1



We have recently reported preliminary results [11] of the photochemical synthesis of 2-(2,2-dimethylpropylidene)-5,5-dimethylcyclohexane-1,3-dione (**4a**) from pyrandione **5a** *via* homolysis of the lactone O–CO bond and subsequent ketene elimination from biradical **6a**. We have now synthesized bi- and tricyclic pyrandiones **5b–f** from 5-(2,2-dimethylpropylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**7**) [12] and cyclic 1,3-dicarbonyl compounds **1b–f** and found that photolysis of **5** does indeed offers a general synthetic path to title compounds **4**. In addition, we report that acyl-vinyloxy biradicals **6** do not exclusively eliminate ketene but to a minor extent (10–15%) also decarbonylate to give 1-(*tert*-butyl)-spiroalkanediones **8** *(Scheme 2)*.

Scheme 2

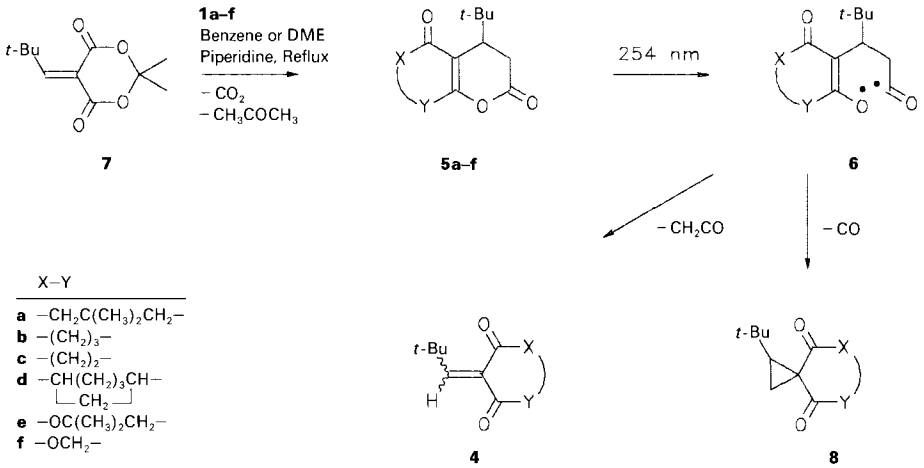


Table 1. *Spectroscopic Data of Compounds* **5**

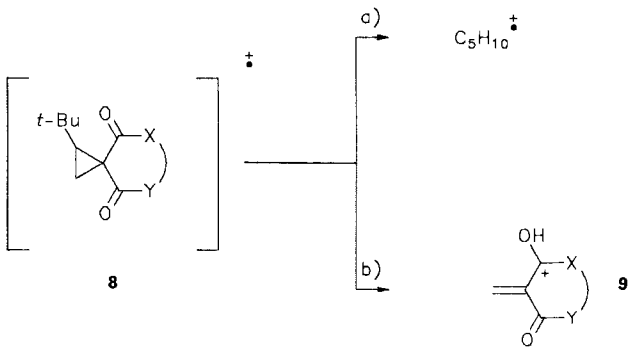
Compound	UV	IR	^{1}H-NMR	^{13}C-NMR	MS
5a[a])	252 (4.13)	1790, 1670, 1645	2.91 (*m*, 2 H); 2.55–2.20 (*m*, 5 H); 1.17, 1.13 (2*s*, 3 H); 0.88 (*s*, 9 H)	196.2; 168.0; 165.8; 115.6; 50.6; 41.2; 37.0; 35.3; 31.9; 31.0; 28.3; 27.7; 27.4	250 (5, M^+), *166*
5b[a])	251 (3.94)	1790, 1670, 1645	2.88 (*dd*, J = 8.0, 1.1); 2.82 (*dd*, J = 16.8, 1.1); 2.56 (*m*, 2 H); 2.42 (*dd*, J = 16.8, 8.0); 2.30 (*m*, 2 H); 2.02 (*m*, 2 H); 0.82 (*s*, 9 H)	196.8; 167.8; 167.4; 116.4; 36.7; 36.6; 35.0; 30.8; 27.5; 27.1; 20.2	222 (5, M^+), *138*
5c[b])	240 (4.08)	1795, 1705, 1655	2.42 (*d*, J = 17.6); 2.21 (*d*, J = 7.9); 1.86 (*m*, 4 H); 1.63 (*dd*, J = 17.6, 7.9); 0.73 (*s*, 9 H)	199.9; 179.9; 174.9; 119.4; 38.5; 35.1; 33.9; 30.7; 27.2; 25.0	208 (10, M^+), *124*
5d[c])[d])	258 (4.04)	1785, 1665, 1635	2.99 (*dd*, J = 8.0, 1.1); 2.91 (*dd*, J = 17.0, 1.1); 2.73–2.55 (*m*, 2 H); 2.41 (*dd*, J = 17.0, 8.0); 2.19–1.32 (*m*, 8 H); 0.86 (*s*, 9 H)	198.8; 167.6; 166.7; 116.3; 41.4; 36.6; 34.6; 33.9; 31.7; 31.0; 27.8; 26.9; 24.5; 18.2	262 (9, M^+), *178*
5e[e])	240 (3.80)	1800, 1725, 1680	2.78 (*d*, J = 8.1); 2.51 (*d*, J = 16.8); 2.01, 1.67 (*AB*, J = 17.8); 1.80 (*dd*, J = 16.8, 8.1); 0.99, 0.95 (2*s*, 3 H); 0.78 (*s*, 9 H)	166.7; 164.7; 160.5; 106.8; 38.9; 38.1; 35.4; 30.9; 29.3; 27.2; 26.2	252 (1, M^+), *168*
5f[f])	231 (3.88)	1795, 1745, 1680	3.82 (*d*, J = 16.7); 3.73 (*dd*, J = 16.7, 1.8); 2.35 (*dd*, J = 16.5, 1.1); 2.06 (*ddd*, J = 8.3, 1.8, 1.1); 1.65 (*dd*, J = 16.5, 8.3); 0.69 (*s*, 9 H)	171.2; 170.2; 165.7; 105.8; 64.9; 38.8; 35.0; 30.4; 26.8	210 (1, M^+), *57*

[a]) UV (i-PrOH); IR (CCl_4); ^{1}H-NMR ($CDCl_3$); ^{13}C-NMR ($CDCl_3$).
[b]) UV (cyclohexane); IR (CCl_4); ^{1}H-NMR (C_6D_6); ^{13}C-NMR (C_6D_6).
[c]) UV (i-PrOH); IR (CCl_4); ^{1}H-NMR ($CDCl_3$); ^{13}C-NMR ($CDCl_3$).
[d]) 3:1 Mixture of diastereoisomers. NMR data for the major component.
[e]) UV (cyclohexane); IR (CCl_4); ^{1}H-NMR (C_6D_6); ^{13}C-NMR ($CDCl_3$).
[f]) UV (i-PrOH); IR (KBr); ^{1}H-NMR (C_6D_6); ^{13}C-NMR ($CDCl_3$).

The 4-(*t*-Bu)-substituted [*b*]-fused pyran-2,5-diones **5a–f** were obtained from **1a–f**, respectively, and **7** *via Michael* addition and subsequent transesterification [11] [13]: their spectroscopic data is summarized in *Table 1*. As expected, oxo-lactones **1e** and **1f** cyclize selectively *via* enolisation of the ketone C=O bond. GC/MS Monitoring of the photolyses ($\lambda = 254$ nm) of **5a–f** in *t*-BuOH indicates the formation of one[1]) major (*m/z* [*M*(**5**) – CH_2CO]) and a minor product (*m/z* [*M*(**5**) – CO]) in a ratio varying between 5:1 and 8:1. The conversion of **5** is neither affected by naphthalene as quencher nor does it proceed when using xanthone as sensitizer, suggesting that it occurs from the excited singlet state of **5**.

Compounds **4a**, **4b**, and **4d** as well as the diastereoisomeric (*E*/*Z*) mixtures of **4e** and **4f** were isolated in > 95% purity by bulb-to-bulb distillation, while the cyclopentanedione derivative **4c** decomposes under these conditions and was only characterized as crude product. Spirocycloalkanedione **8a** was isolated by preparative GC. The other spiro compounds **8b–f** were characterized by MS directly from the irradiated solutions.

Scheme 3



The two typical fragmentation patterns for the molecular ions of **8** (except for **8f**) are formation of $C_5H_{10}^+$ (*m/z* 70) *(Scheme 3, a)* and formation of ions $\mathbf{9}^+$ by elimination of $C_5H_8 + H^\cdot$ *(Scheme 3, b)*. The spectroscopic data of the photoproducts is summarized in *Table 2*.

To better understand the competitive α- *vs.* β-cleavage of acyl-vinyloxy biradicals **6** (formation of **8** *vs.* formation of **4**), we investigated the photolyses in *t*-BuOH of the 4-unsubstituted and the 4,4-dimethyl-pyrandione **10a** and **10b**, respectively. From **10a**, spiro[2.5]octanedione **11a** is formed selectively and was isolated in 70% yield, while no formation of **11b** from **10b** was observed at all. Most probably, intermediate **12b** undergoes exclusive β-cleavage to yield **13b** which then tautomerizes [7] [8] [11] to **14b**, finally leading to polymeric material only *(Scheme 4)*. This suggests that β-cleavage from the acyl-vinyloxy biradicals **6** and **12** is enhanced by alkyl substituents at C(4) of the pyranone moiety. This is reasonable, since such substituents weaken the bond between the (former) atoms C(4) and C(3) and in addition stabilize the (conjugated olefinic) β-cleavage product.

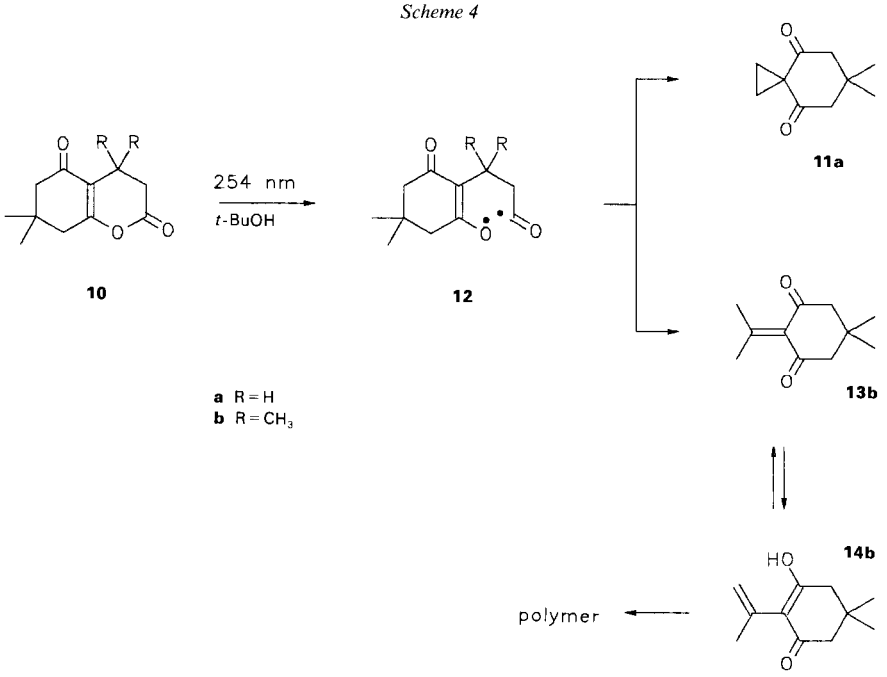
[1]) Diastereoisomers of **4e** and **4f** were not resolved on our 30-m *SE 30* capillary column.

Table 2. *Spectroscopic Data of* **4** *and* **8**

Compound	^{1}H-NMR	MS
4a[a])	7.40 (*s*, 1 H); 2.11 (*s*, 2 H); 2.09 (*s*, 2 H); 1.20 (*s*, 9 H); 0.59 (*s*, 6 H)	208 (33, M^+), *193*
4b[a])	7.45 (*s*, 1 H); 2.28–2.00 (*m*, 6 H); 1.25 (*s*, 9 H)	180 (53, M^+), *165*
4c[a])	7.25 (*s*, 1 H); 2.01–1.82 (*m*, 4 H); 1.18 (*s*, 9 H)	166 (58, M^+), *151*
4d[a])	7.41 (*s*, 1 H); 2.50–2.40 (*m*, 2 H); 1.95–1.65 (*m*, 6 H); 1.21 (*s*, 9 H)	220 (27, M^+), *205*
4e[b])[c])	7.71, 7.60 (*s*, 1 H); 2.72, 2.69 (*s*, 2 H); 1.47, 1.46 (*s*, 6 H); 1.31, 1.29 (*s*, 9 H)	210 (3, M^+), *41*
4f[b])[c])	7.45, 7.40 (*s*, 1 H); 4.71, 4.62 (*AB*, J = 16.3); 1.39, 1.35 (*s*, 9 H)	168 (12, M^+), *153*
8a[b])	2.70 (*d*, J = 14.8); 2.58 (*dd*, J = 14.8, 2.6); 2.57 (*d*, J = 16.3); 2.49 (*dd*, J = 16.3, 2.6); 2.22 (*dd*, J = 9.4, 3.2); 1.99 (*dd*, J = 9.4, 3.2); 1.87 (*t*, J = 9.4); 1.18, 0.97 (*s*, 3 H); 0.96 (*s*, 9 H)	222 (9, M^+), 153 (18)[d]), *70*
8b		194 (8, M^+), *151*, 125 (31)[d]), 70 (50)
8c		180 (10, M^+), 111 (25)[d]), *70*
8d[e])		234 (12, M^+), *191*, 165 (39)[d]), 70 (85)
8e		224 (1, M^+), 155 (18)[d]), *70*
8f		182 (12, M^+), *57*

[a]) ^{1}H-NMR (C_6D_6). [b]) ^{1}H-NMR ($CDCl_3$). [c]) 1:1 Mixture of diastereoisomers. NMR data for both components. [d]) Fragment **9**. [e]) Mixture of diastereoisomers (not resolved).

Scheme 4



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Experimental Part

General. Qual. GC was performed on a 30-m *SE 30* capillary column. Irradiations were performed in a *Rayonet RPR-100* photoreactor on Ar-degassed solns. using 254-nm lamps. UV spectra: in nm (log ε). IR spectra: in cm^{-1}. Chemical shifts in the 400-MHz ^1H- and 100.63-MHz ^{13}C-NMR spectra: in ppm relative to TMS (= 0 ppm). MS: at 70 eV.

Cyclic 1,3-Dicarbonyl Compounds **1**. *Cyclohexane-1,3-dione* (**1a**) and *5,5-dimethylcyclohexane-1,3-dione* (**1b**) are commercially available. *Cyclopentane-1,3-dione* (**1c**) [14], *bicyclo[3.3.1]nonane-2,4-dione* (**1d**) [15], *6,6-dimethyl-5,6-dihydropyran-2,4(3H)-dione* (**1e**) [16], and *tetrahydrofuran-2,4-dione* (**1f**) [17] were synthesized according to the literature methods.

Synthesis of **5a–f**. A soln. of 4.24 g ($2 \cdot 10^{-2}$ mol) of **7** [12], $2 \cdot 10^{-2}$ mol of **1**, and one drop of piperidine in 300 ml of benzene (for **1a** and **1b**) or 1,2-dimethoxyethane (for **1c–1f**) was refluxed for 6 h (for **1a** and **1b**) or 24 h (for **1c–f**). After evaporation of the solvent, the residue was chromatographed (SiO_2, CH_2Cl_2/MeOH 97:3) to afford: *4-(*tert*-butyl)-7,7-dimethyl-3,4,5,6,7,8-hexahydro-2*H*-[1]benzopyran-2,5-dione* (**5a**; 77%; m.p. 105°); *4-(*tert*-butyl)-3,4,5,6,7,8-hexahydro-2*H*-[1]benzopyran-2,5-dione* (**5b**; 79%; m.p. 58°); *4-(*tert*-butyl)-3,4,6,7-tetrahydro-2*H*-cyclopenta[*b*]pyran-2,5-dione* (**5c**; 52%, m.p. 79°); *4-(*tert*-butyl-3,4,5,6,7,8-hexahydro-6,10-methano-2*H*-[1]benzopyran-2,3-dione* (**5d**; 3:1 mixture of diastereoisomers; 75%; m.p. 125°); *4-(*tert*-butyl)-7,7-dimethyl-3,4,7,8-tetrahydro-2*H*,5*H*-pyrano[4,3-*b*]pyran-2,5-dione* (**5e**; 78%; m.p. 139°); *4-(*tert*-butyl)-2,3,4,7-tetrahydro-furo[4,3-*b*]pyran-2,5-dione* (**5f**; 51%; m.p. 160°).

Syntheses of **10a** *and* **10b** were achieved according to procedures in [18] and [19], respectively.

Photolyses of **5a–f**. An Ar-degassed soln. of 10^{-3} mol of **5** in 10 ml of *t*-BuOH was irradiated (λ = 254 nm) for 36 h. GC indicated the formation of two products, the ratio varying between 5:1 and 8:1, and the major product (**4**) having shorter t_R. Evaporation of the solvent and bulb-to-bulb distillation (140–150°/0.1 Torr) afforded compounds **4** as colourless oils: *2-(2,2-dimethylpropylidene)-5,5-dimethylcyclohexane-1,3-dione* (**4a**; 75%); *2-(2,2-dimethylpropylidene)cyclohexane-1,3-dione* (**4b**; 65%); *3-(2,2-dimethylpropylidene)bicyclo[3.3.1]nonane-2,4-dione* (**4d**; 50%); *3-(2,2-dimethylpropylidene)-6,6-dimethyl-3,4,5,6-tetrahydro-2*H*-pyran-2,4-dione* (**4e**; 3:2 mixture of diastereoisomers; 40%); *3-(2,2-dimethylpropylidene)tetrahydrofuran-2,4-dione* (**4f**; 1:1 mixture of diastereoisomers; 55%).

The minor product of the photolysis of **5a** was isolated by prep. GC on a 10% *QF-1* column on *Chromosorb W-AW-DMCS* at 200°. *1-(*tert*-Butyl)-6,6-dimethylspiro[2.5]octane-4,8-dione* (**8a**) was obtained in 5% yield and of > 96% purity.

Photolyses of **10a** *and* **10b**. Irradiation (λ = 254 nm) of 10^{-3} mol of **10a** in 10 ml of *t*-BuOH for 24 h, evaporation of the solvent, and bulb-to-bulb distillation (120°/0.1 Torr) afforded 116 mg (70%) of *6,6-dimethylspiro[2.5]octane-4,8-dione* (**11a**), identified by comparing its spectra with those described in [20].

REFERENCES

[1] F.J. Kunz, P. Margaretha, O.E. Polansky, *Chimia* **1970,** 165.
[2] W.H. Bunnelle, L.A. Meyer, *J. Org. Chem.* **1988,** *53,* 4038.
[3] P.E. Eaton, W.H. Bunnelle, *Tetrahedron Lett.* **1984,** 23.
[4] T. Ogawa, T. Murafuji, H. Suzuki, *Chem. Lett.* **1988,** 849.
[5] L.F. Tietze, M. Bratz, R. Machinek, G. Kiedrowski, *J. Org. Chem.* **1987,** *52,* 1638.
[6] S.I. Zav'yalov, G.V. Kondrat'eva, L.F. Kudryavtseva, *Zh. Obshch. Khim.* **1961,** *31,* 3695.
[7] M.L. Bolte, W.D. Crow, S. Yoshida, *Aust. J. Chem.* **1982,** *35,* 1411.
[8] M.L. Bolte, W.D. Crow, S. Yoshida, *Aust. J. Chem.* **1982,** *35,* 1421.
[9] P. Margaretha, O.E. Polansky, *Monatsh. Chem.* **1970,** *101,* 824.
[10] H. Zimmer, W.W. Hillstrom, J.C. Schmidt, P.D. Seemuth, R. Vögeli, *J. Org. Chem.* **1978,** *43,* 1541.
[11] K. Hobel, P. Margaretha, *Helv. Chim. Acta* **1987,** *70,* 995.
[12] P. Schuster, O.E. Polansky, F. Wessely, *Monatsh. Chem.* **1964,** *95,* 53.
[13] P. Margaretha, *Tetrahedron Lett.* **1970,** 1449.
[14] M. Nilsson, *Acta Chem. Scand.* **1981,** *35,* 667.
[15] T. Yamazaki, K. Matoba, T. Itooka, M. Chintani, T. Momose, O. Muraoka, *Chem. Pharm. Bull.* **1987,** *35,* 3453.
[16] E.M. Arnett, J.A. Harrelson, *J. Am. Chem. Soc.* **1987,** *109,* 809.
[17] D.G. Schmidt, H. Zimmer, *Synth. Commun.* **1981,** *11,* 385.
[18] B.M. Monroe, *J. Heterocycl. Chem.* **1969,** *6,* 917.
[19] S. Gelin, B. Chantegrel, *C. R. Séances Acad. Sci., Ser. C* **1971,** *273,* 635.
[20] K. Ichikawa, O. Itoh, T. Kawamura, *Bull. Chem. Soc. Jpn.* **1968,** *41,* 1240.