

New Oxidative Cyclizations of 1,3,4,6-Tetraketones.  
Synthesis and Structure of  
(*Z*)-2-Acyl-5-alkyl(aryl)-1,4-dioxaspiro[2.4]hept-5-en-7-ones

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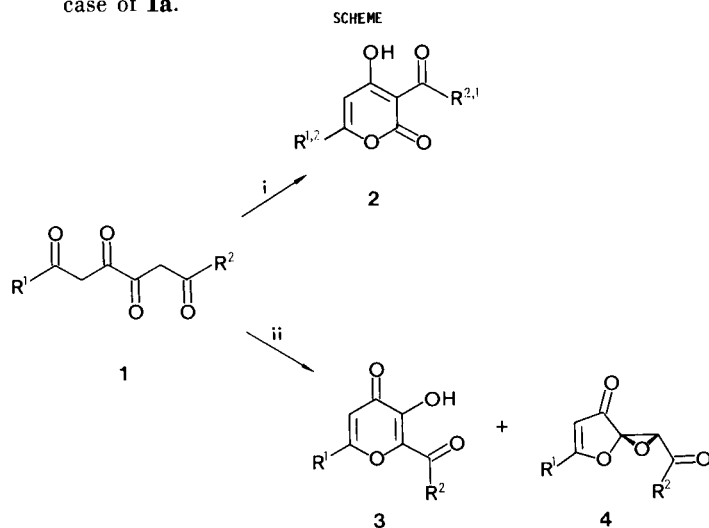
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Iodosobenzene diacetate oxidation of 1,3,4,6-tetraketones **1a-c** yielded (*Z*)-2-acyl-5-alkyl(aryl)-1,4-dioxaspiro[2.4]hept-5-en-7-ones (**4a-c**) in addition to 2-acyl-6-alkyl(aryl)-3-hydroxy-4-pyrones (**3a-c**). The structure of new spiro-heterocycles **4** was inferred from chemical and spectroscopic data, and the stereochemistry was fully defined by a single-crystal X-ray analysis. Alternative cyclization pathways can be rationalized as proceeding through carbocation intermediates derived from both forms of the ring-chain tautomerism of 1,3,4,6-tetraketones **1**.

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Tetracarbonyl compounds have been studied extensively because they are the smallest polycarbonyl systems that can provide reasonable models of polyketide-type biosyntheses (2). The investigation of the chemistry of inverted tetraketide assembly **1** has been primarily concerned with biogenetic-type reactions (3,4). Instances of considerable interest are oxidative transformations of the array leading to isomerides of tetraacetic lactone. An unexpected cyclization to dehydroacetic acids **2**, accompanied by rearrangement, has been observed in oxidation of **1** with lead tetraacetate (5,6). Another type of cyclization is exemplified by specific conversion into regioisomers **3** of dehydroacetic acids (7). In addition to **3a**, however, a third isomeric product, **4a** (30%), mp 165° dec, has been encountered in the case of **1a**.

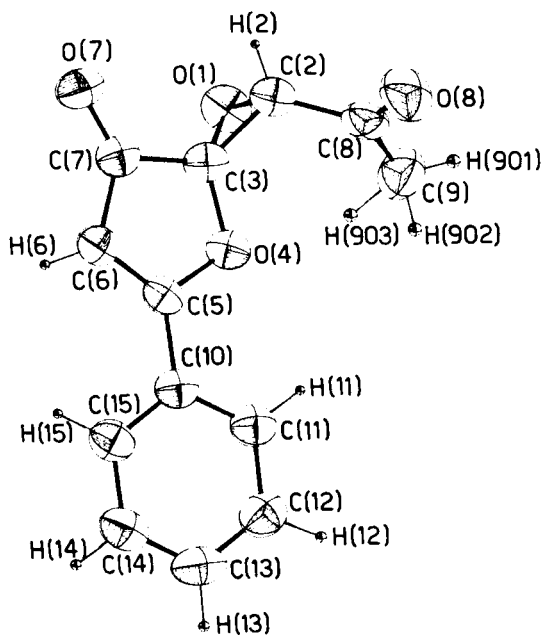


**a:** R<sup>1</sup> = R<sup>2</sup> = Ph; **b:** R<sup>1</sup> = Ph, R<sup>2</sup> = Me; **c:** R<sup>1</sup> = R<sup>2</sup> = *t*-Bu. **i,** Pb(OAc)<sub>4</sub>/AcOH; **ii,** PhI(OAc)<sub>2</sub>/AcOH.

The earliest experiments showed a non-specific response of **4a** to usual carbonyl reagents. It was tempting to assume a bicyclic structure, since free  $\alpha$ -diketone grouping could not be demonstrated by conversion to a quinoxaline derivative. The ready decomposition and delayed reaction with ferric chloride indicated lability of the ring system. On the other hand, the low-yield conversions to **2a** (11%), by treatment with boron trifluoride, and to **3a** (11%), in the presence of aqueous alkalis, were reminiscent of several known transformations of aurone epoxides (8). The interpretation of all experimental evidence, taken in conjunction with the spectral characteristics (see Experimental Part), lead us to propose (*Z*)-2-benzoyl-5-phenyl-1,4-dioxaspiro[2.4]hept-5-en-7-one structure for the product **4a**. The stereochemical arrangement could not be argued persuasively from the spectral data. However, it was assumed that the (*Z*)-configuration of the epoxide ring is sterically favourable.

Although the oxidations of a number of tetraketones have been investigated (5-7), these reactions do not, as yet, form a coherent picture. The novel cyclization has now been extended to the synthesis of **4a-c**. Wishing to explore the regiocontrol of competing cyclization reactions in formation of oxygen heterocycles, we have oxidized an unsymmetrical tetraketone, 1-phenylheptane-1,3,4,6-tetrone (**1b**), with iodosobenzene diacetate. Careful working up of the reaction mixture gave only **3b** (14%) and **4b** (42%) among the four possible products; no traces of regioisomeric compounds were detected.

In order to remove any equivocation about the structural assignment, we decided to take advantage of the propensity which the compound **4b** showed to produce well formed crystals and carried out an X-ray crystallographic structure determination. The atomic parameters which de-

Figure. ORTEP Drawing of the Structure of **4b**

fine the crystal structure of **4b** are recorded in Table I, and bond distances, bond and torsion angle data are collected in Tables II-III. The structure of **4b** is depicted by ORTEP drawing shown in the Figure.

The regioselectivity of iodosobenzene diacetate stood in marked contrast to the regioselective pattern in oxidations with lead tetraacetate (6). Different oxidation pathways, however, suggest that the molecular geometry of the oxidant is the main factor determining the distinct transition state. Tetrahedral lead tetraacetate could act as a bidentate reagent capable of forming a cyclic lead(IV) ester with hydroxyfuranone tautomeric species. Diaxially oriented oxygens in the trigonal bipyramid configuration of iodosobenzene diacetate, however, do not permit formation of an analogous intermediate. The monodentate reagent can thus attack **1** in either forms of the ring-chain tautomeric equilibrium (4). The lifetime of the cationic species and the position of the equilibrium must certainly play a decisive role in formation of oxygen heterocycles **3** and **4**. The proportions of the two are influenced by subtle interplay of steric and/or electronic factors.

Similar conclusions arose from the iodosobenzene di-

Table I  
Positional and Thermal Parameters for **4b**

Atom	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
C(2)	1853(10)	1602(2)	5960(5)	26(2)	56(3)	41(3)	1(2)	5(2)	-4(2)
C(3)	1814(10)	1223(2)	4880(5)	23(2)	54(3)	42(2)	2(2)	4(2)	1(2)
C(5)	4031(11)	916(1)	3032(4)	32(2)	45(2)	36(2)	0(2)	-1(2)	-6(2)
C(6)	4005(14)	548(2)	3941(5)	62(3)	45(3)	42(3)	1(2)	9(2)	-4(2)
C(7)	2555(11)	704(2)	5183(5)	41(3)	53(3)	42(2)	-2(2)	4(2)	1(2)
C(8)	2814(13)	2099(2)	5638(5)	47(3)	60(3)	51(3)	1(2)	23(2)	-11(2)
C(9)	1171(17)	2348(3)	4387(8)	78(4)	56(3)	75(4)	5(3)	19(3)	13(3)
C(10)	5305(10)	955(2)	1623(4)	29(2)	53(3)	34(2)	-3(2)	-3(2)	-2(2)
C(11)	5288(13)	1388(2)	920(5)	43(3)	56(3)	41(3)	-1(2)	0(2)	-1(2)
C(12)	6406(13)	1413(2)	-426(5)	53(3)	64(3)	44(3)	-11(3)	-1(2)	4(3)
C(13)	7562(13)	1013(2)	-1040(6)	46(3)	88(4)	39(3)	-13(3)	9(2)	-2(3)
C(14)	7630(13)	588(2)	-334(6)	51(3)	66(3)	52(3)	0(3)	12(2)	-14(3)
C(15)	6547(12)	553(2)	1010(5)	45(3)	55(3)	46(3)	1(2)	6(2)	-6(2)
O(1)	-1117(7)	1417(1)	5237(4)	20(2)	66(2)	60(2)	2(1)	1(1)	-9(2)
O(4)	2668(7)	1323(1)	3508(3)	33(2)	50(2)	35(2)	6(1)	-1(1)	0(1)
O(7)	1999(10)	503(1)	6291(4)	83(3)	62(2)	47(2)	3(2)	22(2)	8(2)
O(8)	4934(10)	2275(1)	6448(4)	71(3)	79(3)	74(3)	-24(2)	5(2)	-24(2)
H(2)	223(12)	149(2)	696(5)	4					
H(6)	471(12)	23(2)	379(5)	5					
H(901)	89(15)	265(2)	451(6)	7					
H(902)	235(14)	239(2)	364(6)	7					
H(903)	114(14)	206(2)	372(6)	7					
H(11)	456(13)	168(2)	136(5)	5					
H(12)	620(13)	175(2)	-89(5)	6					
H(13)	824(12)	102(2)	-197(6)	5					
H(14)	817(13)	30(2)	-81(5)	5					
H(15)	653(12)	25(2)	152(5)	5					

Positional parameters are given as fractions of the unit cell edges (C and O  $\times 10^4$ , H  $\times 10^3$ ). The anisotropic thermal parameters are given in the  $10^3$  scale and the isotropic temperature factors are given in the  $10^2$  scale. Estimated standard deviations are given on the same scale in parentheses.

Table II  
Bond Lengths and Bond Angles

Bond	Å	Angle	Deg
C(9)–C(8)	1.446(9)	C(9)–C(8)–C(2)	120.5(5)
O(8)–C(8)	1.182(6)	C(9)–C(8)–O(8)	122.4(6)
C(2)–C(8)	1.494(8)	C(2)–C(8)–O(8)	117.2(4)
C(2)–O(1)	1.416(5)	C(8)–C(2)–C(3)	120.7(4)
C(2)–C(3)	1.468(7)	C(8)–C(2)–O(1)	119.1(4)
C(3)–O(1)	1.424(6)	C(3)–C(2)–O(1)	59.2(3)
C(3)–C(7)	1.506(8)	C(2)–O(1)–C(3)	62.3(3)
C(3)–O(4)	1.417(6)	C(2)–C(3)–O(1)	58.6(3)
C(5)–O(4)	1.380(5)	C(2)–C(3)–O(4)	120.5(4)
C(5)–C(6)	1.341(6)	O(2)–C(3)–C(7)	126.1(4)
C(5)–C(10)	1.505(6)	O(4)–C(3)–C(7)	106.9(4)
C(6)–C(7)	1.462(7)	O(4)–C(3)–O(1)	118.9(4)
C(7)–O(7)	1.237(6)	O(1)–C(3)–C(7)	118.9(4)
C(10)–C(11)	1.382(8)	C(3)–O(4)–C(5)	107.7(3)
C(10)–C(15)	1.401(8)	O(4)–C(5)–C(6)	112.7(4)
C(11)–C(12)	1.416(7)	O(4)–C(5)–C(10)	116.4(3)
C(12)–C(13)	1.382(8)	C(6)–C(5)–C(10)	130.9(4)
C(13)–C(14)	1.363(8)	C(5)–C(6)–C(7)	108.8(5)
C(14)–C(15)	1.409(8)	C(3)–C(7)–C(6)	103.7(4)
C(9)–H(901)	0.87(6)	C(3)–C(7)–O(7)	122.7(5)
C(9)–H(902)	0.92(6)	C(6)–C(7)–O(7)	133.6(5)
C(9)–H(903)	1.02(6)	C(5)–C(10)–C(11)	120.5(4)
C(2)–H(2)	0.98(5)	C(5)–C(10)–C(15)	120.4(4)
C(6)–H(6)	0.96(6)	C(11)–C(10)–C(15)	119.1(4)
C(11)–H(11)	0.99(6)	C(10)–C(11)–C(12)	119.5(5)
C(12)–H(12)	1.04(5)	C(11)–C(12)–C(13)	121.1(5)
C(13)–H(13)	0.96(6)	C(12)–C(13)–C(14)	119.3(5)
C(14)–H(14)	0.97(6)	C(13)–C(14)–C(15)	120.8(5)
C(15)–H(15)	0.98(5)	C(14)–C(15)–C(10)	120.2(5)
		H(2)–C(2)–C(3)	114(3)
		H(2)–C(2)–O(1)	110(3)
		H(2)–C(2)–C(8)	119(3)
		H(6)–C(6)–C(5)	126(3)
		H(6)–C(6)–C(7)	125(3)
		C(8)–C(9)–H(901)	115(3)
		C(8)–C(9)–H(902)	116(3)
		C(8)–C(9)–H(903)	94(3)
		H(901)–C(9)–H(902)	94(5)
		H(901)–C(9)–H(903)	150(5)
		H(902)–C(9)–H(903)	66(5)

Table III  
Torsional Angles (Deg)

C(10)–C(11)–C(12)–C(13)	-1.0(7)	C(5)–C(6)–C(7)–O(7)	-179.8(4)
C(11)–C(12)–C(13)–C(14)	-0.1(6)	C(5)–O(4)–C(3)–C(2)	149.5(4)
C(12)–C(13)–C(14)–C(15)	-0.2(6)	C(5)–C(4)–C(3)–O(1)	-142.0(4)
C(13)–C(14)–C(15)–C(10)	1.6(7)	C(6)–C(7)–C(3)–C(2)	-148.2(4)
C(14)–C(15)–C(10)–C(11)	-2.7(7)	C(6)–C(7)–C(3)–O(1)	141.3(4)
C(15)–C(10)–C(11)–C(12)	2.4(7)	O(7)–C(7)–C(3)–C(2)	30.4(4)
C(14)–C(15)–C(10)–C(5)	177.7(4)	O(7)–C(7)–C(3)–O(1)	-40.0(4)
C(15)–C(10)–C(5)–C(6)	4.7(7)	C(7)–C(3)–C(2)–O(1)	-104.8(4)
C(15)–C(10)–C(5)–O(4)	-176.0(4)	C(7)–C(3)–O(1)–C(2)	116.8(4)
C(10)–C(5)–O(4)–C(3)	-176.3(3)	C(4)–C(3)–C(2)–C(8)	-0.4(4)
C(10)–C(5)–C(6)–C(7)	178.4(4)	C(3)–O(1)–C(2)–C(8)	110.3(4)
C(5)–O(4)–C(3)–C(7)	-3.8(4)	C(3)–C(2)–C(8)–C(9)	55.1(4)
C(5)–C(6)–C(7)–C(3)	-1.4(5)	C(3)–C(2)–C(8)–O(8)	-125.3(4)
O(4)–C(3)–C(7)–C(6)	3.2(4)	O(1)–C(2)–C(8)–O(8)	165.3(4)
O(4)–C(3)–C(7)–O(7)	-178.2(4)	O(1)–C(2)–C(8)–C(9)	-14.3(4)

acetate oxidation of **1c**. The operation of a bulk-effect in acyclic intermediate is seen in the low yield of **3c** (4%). The steric crowding is somewhat relieved in the cyclic carbonium ion intermediate and the ease of formation of epoxide **4c** (51%) is then an entropy effect. While in this case electronic effects differ little along the series and the substantially changed **3/4** ratio stems almost wholly from steric influences in transition state, the same clearly cannot be true for oxidation of **1c** with lead tetraacetate. The reaction yielded **2c** (52%), as the only isolable product, despite an increase in the size of substituents. Lead tetraacetate oxidations (5,6) are less sensitive to changes in substituents and this may be held to favour the involvement of an initial bicyclic lead(IV) ester, for this is of low steric demand.

## EXPERIMENTAL

All melting points are uncorrected. Infrared spectra were taken on a Perkin-Elmer 257 spectrometer as potassium bromide disks. Ultraviolet spectral data were obtained with a Perkin-Elmer 124 spectrophotometer. The <sup>1</sup>H-nmr spectra were recorded on a Varian T-60 instrument, and the <sup>13</sup>C-nmr spectra on a Varian XL-100FT NMR spectrometer. Off-resonance decoupling served to distinguish between the primary, secondary, tertiary and quaternary carbons. Chemical shifts are given in δ units (ppm) relative to internal tetramethylsilane. Multiplicity is indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; umc, unresolved multiplet centre. Mass spectra were recorded on a Varian MAT CH-7 spectrometer at 70 eV, 100 μA, and 70-90°C. Microanalyses were performed on a Perkin-Elmer 240 Elemental analyser. Tetraketones **1a-c** were prepared according to original procedures (9). Solvents and reagents were routinely purified before use. Light petroleum refers to the fraction boiling at 30-50°.

Iodosobenzene Diacetate Oxidations. General Procedure.

The procedure described previously (7) was used on a 0.01 mole scale with slight modifications. Iodosobenzene diacetate (6.5 g) was gradually added to a stirred suspension of finely powdered tetraketone **1** in glacial acetic acid (50 ml). The reaction mixture was stirred for 6-8 hours (iodimetric test) at room temperature. The solvent was removed under reduced pressure, and then the residue was dried in a high vacuum (10<sup>-3</sup> Torr, 50°). The crude products **3** and **4** were separated by specific methods noted below.

2-Benzoyl-3-hydroxy-6-phenyl-4-pyrone (**3a**) and (Z)-2-Benzoyl-5-phenyl-1,4-dioxaspiro[2.4]hept-5-en-7-one (**4a**).

Separation of **3a** (33%), described recently (7), and **4a** (30%) was effected by fractional crystallization from ethanol. Recrystallized compound **4a**, mp 165° dec, gave no immediate colouration with methanolic ferric chloride. A brown-red colour appeared on heating or prolonged standing; uv (ethanol): λ max nm (log ε) 252 (4.20), 315 (4.15); ir (potassium bromide): ν max 1703, 1695, 1603, 1589, 1567, 1488, 1449, 1342, 1210, 766, 760, 686 cm<sup>-1</sup>; <sup>1</sup>H-nmr (deuteriochloroform): δ 8.1-7.3 (um, 10H, phenyls), 6.18 (s, 1H, =CH-), 4.77 (s, 1H, epoxide); <sup>13</sup>C-nmr (deuteriochloroform): δ 194.9 (s, CO), 191.5 (s, C-7), 185.1 (s, C-5), 134.5, 134.3, 134.0, 129.0, 128.8, 128.6, 128.5, 127.4 (phenyls), 100.9 (d, C-6), 86.5 (s, C-3), 62.3 (d, C-2); ms: m/e (relative intensity) 292 (4.3, M<sup>+</sup>), 264 (3.5), 188 (1.1), 187 (2.9), 162 (3.5), 158 (1.4), 147 (2.3), 146 (1.2), 131 (1.1), 130 (4.6), 105 (100.0), 102 (25.0), 90 (3.4), 89 (3.7), 77 (47.5), 69 (4.6).

Anal. Calcd. for C<sub>18</sub>H<sub>12</sub>O<sub>4</sub>: C, 73.95; H, 4.14. Found: C, 73.88; H, 4.08.

2-Acetyl-3-hydroxy-6-phenyl-4-pyrone (**3b**) and (Z)-2-Acetyl-5-phenyl-1,4-dioxaspiro[2.4]hept-5-en-7-one (**4b**).

Fractional crystallization from dichloromethane/light petroleum afforded **3b** (14%) and **4b** (42%). Compound **3b** was obtained as colourless prisms, mp 165-166°, which gave a brown-red colour with methanolic ferric chloride; ir (potassium bromide):  $\nu$  max 3200, 1680, 1615, 1600  $\text{cm}^{-1}$ ;  $^1\text{H-nmr}$  (deuteriochloroform):  $\delta$  9.8 (bs, 1H, OH), 7.9-7.6 (um, 5H, phenyl), 6.90 (s, 1H, =CH-), 2.70 (s, 3H, COMe); ms:  $m/e$  230 ( $\text{M}^+$ ).

*Anal.* Calcd. for  $\text{C}_{13}\text{H}_{10}\text{O}_4$ : C, 67.82; H, 4.38. Found: C, 67.66; H, 4.60.

Colourless prisms of **4b**, mp 143-144° dec, showed a characteristic delayed reaction with ferric chloride; ir (potassium bromide):  $\nu$  max 1722, 1703, 1608, 1592, 1575, 1493, 1457, 1450, 1341, 1296, 1262, 1247, 1227, 1040, 1027, 932, 906, 883, 822, 776, 689  $\text{cm}^{-1}$ ;  $^1\text{H-nmr}$  (deuteriochloroform):  $\delta$  7.9-7.5 (um, 5H, phenyl), 6.27 (s, 1H, =CH-), 4.00 (s, 1H, epoxide), 2.41 (s, 3H, COMe);  $^{13}\text{C-nmr}$  (deuteriochloroform):  $\delta$  200.8 (s, CO), 191.5 (s, C-7), 184.4 (s, C-5), 134.0, 129.2, 127.3, 127.2 (phenyl), 100.9 (d, C-6), 86.4 (s, C-3), 62.1 (d, C-2), 26.7 (q, Me); ms:  $m/e$  230 ( $\text{M}^+$ ).

*Anal.* Calcd. for  $\text{C}_{13}\text{H}_{10}\text{O}_4$ : C, 67.82; H, 4.38. Found: C, 67.76; H, 4.43.

6-*t*-Butyl-3-hydroxy-2-pivaloyl-4-pyrone (**3c**) and (*Z*)-5-*t*-Butyl-2-pivaloyl-1,4-dioxaspiro[2.4]hept-5-en-7-one (**4c**).

Fractional crystallization from carbon tetrachloride afforded **3c** (4%) and **4c** (51%). Compound **3c** was recrystallized from ethanol to give light yellow prisms, mp 141-142°, which gave a red colour with ferric chloride solution; ir (potassium bromide):  $\nu$  max 3200, 2975, 1683, 1630, 1617  $\text{cm}^{-1}$ ;  $^1\text{H-nmr}$  (deuteriochloroform):  $\delta$  9.7 (bs, 1H, OH), 6.43 (s, 1H, =CH-), 1.29 (s, 9H,  $\text{COCMe}_3$ ), 1.19 (s, 9H,  $\text{CMe}_3$ ); ms:  $m/e$  252 ( $\text{M}^+$ ).

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{20}\text{O}_4$ : C, 66.64; H, 7.99. Found: C, 66.70; H, 7.99.

Fine needles of **4c**, mp 135-137° dec, also showed characteristic delayed reaction with ferric chloride; ir (potassium bromide):  $\nu$  max 2980, 1722 sh, 1717, 1586, 1473, 1334, 1255, 1230, 1080, 1069, 1008, 951, 920, 880, 802, 791  $\text{cm}^{-1}$ ; uv (methanol):  $\lambda$  max nm (log  $\epsilon$ ) 275 (3.80);  $^1\text{H-nmr}$  (deuteriochloroform):  $\delta$  5.70 (s, 1H, =CH-), 4.37 (s, 1H, epoxide), 1.27 (s, 9H,  $\text{COCMe}_3$ ), 1.21 (s, 9H,  $\text{CMe}_3$ );  $^{13}\text{C-nmr}$  ( $\text{DMSO-d}_6$ ):  $\delta$  203.1 (s, CO), 200.0 (s, C-5), 192.6 (s, C-7), 101.3 (d, C-6), 85.7 (s, C-3), 59.8 (d, C-2), 43.0 (s,  $\text{COCMe}_3$ ), 34.8 (s,  $\text{CMe}_3$ ), 26.6 (q,  $\text{CMe}_3$ ), 25.2 (q,  $\text{CMe}_3$ ); ms:  $m/e$  252 ( $\text{M}^+$ ).

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{20}\text{O}_4$ : C, 66.64; H, 7.99. Found: C, 66.53; H, 7.93.

Conversion of **4a** to 3-Benzoyl-6-phenyl-2*H*-pyran-2,4(3*H*)-dione (**2a**).

To a solution of **4a** (2.92 g, 0.01 mole) in dry dioxane (20 ml), boron trifluoride etherate (0.1 ml, 47%) was added, and the reaction mixture was refluxed for 5 hours under anhydrous conditions. After removal of the solvent, the residue was dissolved in 5% aqueous sodium bicarbonate (20 ml), and then in turn is filtered, acidified with hydrochloric acid to pH 2, and extracted with chloroform. The extract was washed with water, dried, and evaporated to dryness. Crystallization from ethanol yielded 0.3 g (11%) of colourless needles, mp 171°, identical in all respects with **2a** (6).

Conversion of **4a** to 2-Benzoyl-3-hydroxy-6-phenyl-4-pyrone (**3a**).

To a solution of **4a** (1.2 g, 0.004 mole) in dioxane (20 ml) 0.01 *N* aqueous sodium hydroxide (8 ml) was added. The mixture was stirred for 5 hours at 60°, and then in turn was diluted with water (50 ml), acidified to pH 2 with hydrochloric acid, and extracted with chloroform. The dried extract was evaporated to dryness and the residue was repeatedly crystallized from ethanol to give 0.13 g (11%) of needles, mp 176-177°, identical in all respects with **3a** (7).

6-*t*-Butyl-3-pivaloyl-2*H*-pyran-2,4(3*H*)-dione (**2c**).

As in the original preparation of dehydroacetic acid (5), tetraketone **1c** (2.54 g, 0.01 mole) was subjected to oxidation with lead tetraacetate (10 g) in glacial acetic acid (30ml), and worked up to give **2c** (1.3 g, 52%). For the analysis the substance was sublimed in vacuum, mp 95°; ir (potassium bromide):  $\nu$  max 2975, 1740, 1703, 1640, 1611, 1580, 1550, 1393  $\text{cm}^{-1}$ ;  $^1\text{H-nmr}$  (deuteriochloroform):  $\delta$  17.13 (s, 1H, OH), 5.98 (s, 1H, =CH-), 1.39 (s, 9H,  $\text{COCMe}_3$ ), 1.29 (s, 9H,  $\text{CMe}_3$ ); ms:  $m/e$  252 ( $\text{M}^+$ ).

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{20}\text{O}_4$ : C, 66.64; H, 7.99. Found: C, 66.46; H, 8.13.

#### X-Ray Crystallographic Measurements.

Slow crystallization from carbon tetrachloride provided a sample of (*Z*)-2-acetyl-5-phenyl-1,4-dioxaspiro[2.4]hept-5-en-7-one (**4b**) for single crystal X-ray diffraction analysis; *crystal data*: crystals of **4b**,  $\text{C}_{13}\text{H}_{10}\text{O}_4$ ,  $M = 230.22$ , are monoclinic, space group  $P2_1/c$ , with  $a = 4.169(2)$ ,  $b = 28.051(2)$ ,  $c = 9.396(4)\text{Å}$ ,  $\beta = 98.9(3)^\circ$ ,  $V = 1085.64\text{Å}^3$ ,  $D_m = 1.398\text{gem}^{-3}$ ,  $D_c = 1.408\text{gem}^{-3}$ ,  $Z = 4$ ,  $\mu = 8.91\text{cm}^{-1}\text{CuK}\alpha$ .

Intensity data were measured on a Philips PW-1100 four-circle automatic diffractometer using  $\text{CuK}\alpha$  radiation with a graphite monochromator ( $\lambda = 1.5418\text{Å}$ ), within the interval  $6.5^\circ \leq 2\theta \leq 166.8^\circ$ . The intensities of 1378 independent reflections with  $I > 5\sigma(I)$ , corrected for Lorentz and polarization effects, were used in structure determination. The structure was solved by direct methods using the program MULTAN (10), and refined by full-matrix least-squares procedure to  $R = 0.079$  ( $R_w = 0.099$ ) for 1275 reflections with  $\sin\theta/\lambda < 0.6$ , using anisotropic temperature factors for non-hydrogen atoms and fixed isotropic thermal parameters for hydrogen atoms.

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