CONFORMATION DEPENDENT CYCLIZATIONS OF 1,3,3,5-TETRAPHENYLPENTANE-1,5-DIONE

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The molecular and crystal structure of 1,3,3,5-tetraphenylpentane-1,5-dione (*I*) obtained from direct methods and anisotropically refined by the least-squares method shows that the two 3,3-phenyl groups force the molecule into a conformation suitable for formation of cyclic products and intermediates. Compound *I* crystallizes in the $P\bar{1}$ group with lattice parameters a = 8.444(1), b = 10.195(2), c = 14.618(2) Å, α = 75.52(2)°, β = 73.22(1)°, γ = 65.47(1)°. Photochemically and thermally found was the system *I* $\underset{\Delta}{\overset{h\nu}{\rightleftharpoons}}$ *II*. The reaction of 1,5-dione *I* with phenylmagnesium bromide gives the 2,3-dihydropyran derivative *III*, whereas complex hydrides give a mixture of *IV* and *VI*. On treatment with magnesium, the diketone *I* gives diol *VIII*. Chlorine (Cl_2) reacts with compound *I* to give the mono-, di-, and tetrachloro derivatives *XII*, *XIII*, and *XIV*, respectively. Bromine (Br_2) produces 3,5-dibromo-4*H*-pyran derivative *XVIII*, whereas I_2 only catalyzes the formation of 4*H*-pyran *V*. The formylation of dione *I* with dimethylformamide and $POCl_3$ gives the 4*H*-pyran-3-carbaldehyde *XX*. Probable mechanisms of the reactions investigated and the stereochemistry of compounds *VI*, *VIII*, *XIII*, and *XIV* are discussed.

The dependences between conformational structure of reactants and topological course of their reactions belong to generally interesting topics of contemporary organic chemistry. These dependences can easily be shown with such compounds as the 1,3,3,5-tetraphenylpentane-1,5-dione (*I*) which undergoes smooth heterocyclizations to photochromic pyran derivatives[1-11] and – less often – also transformations to non-heterocyclic products[1-3]. The present communication tries to demonstrate that the cyclizations of dione *I* really depend on the conformation of its molecules.

We started from the idea that the prevailing conformation of compound *I* in solution is identical or almost identical with the "frozen" configuration of its molecules in crystalline phase. This presumption is supported by the NMR spectra of the compound measured in various solvents at various temperatures which do not reveal the presence of other conformations. Therefore, first of all we investigated the molecular structure of dione *I* by means of X-ray diffraction analysis. Figure 1 represents the molecular skeleton of *I* and Fig. 2 gives the arrangement of molecules in the unit cell. It can be seen

that, in contrast to the earlier published[12,13] crystal structures of 1,5-pentanediones, the molecule of dione *I* assumes a rolled up conformation in which the carbonyl groups (C1–O2 and C5–O1) are relatively near to each other, which situation is enforced undoubtedly by steric requirements of the two phenyl groups attached to C3 atom. Both C=O bonds exhibit the expected lengths (3.265 and 3.266 Å), the nonbonding distance between C1 and C5 being, in accordance with the respective atomic radii, shorter (3.201 Å) than that between O1 and O2 (3.730 Å).

The generally accepted experimental test of the solid state structure-reactivity relations undoubtedly is based on photochemical reactions in crystalline phase[14]. We have found that irradiation of the crystals of compound *I* with a 400 W high-pressure mercury discharge lamp initiates its photoisomerization into 2,4,4,6-tetraphenyl-2,3-dihydropyran-2-ol (*II*). The transformation $I \xrightarrow{h\nu} II$ at analogous conditions takes place also in benzene solutions of the 1,5-dione where compound *II* was proved by means of NMR spectra. In this case, however, the reaction mixture is more complex (especially at higher conversion degrees of compound *I*), since it contains products of the Norrish-type transformations[15]. The formation of hemiacetal *II* was also observed after irradiation with sunlight both in benzene solution and in crystalline state. On the other hand, in darkness the formation of hemiacetal *II* was observed neither in solid phase nor in solution.

The formation of hemiacetal *II* cannot be interpreted by primary photoenolization[16,17]. As the photoisomerization investigated is connected with a migration of one hydrogen centre from carbon to oxygen, we were interested in the non-bonding

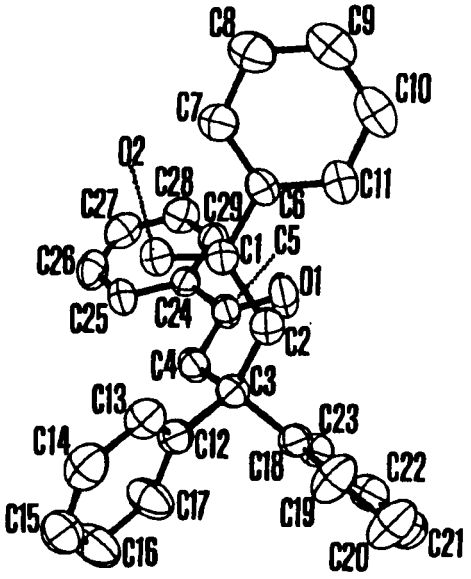


FIG. 1
The ORTEP plot of a single molecule of 1,5-dione *I* with the numbering scheme

interatomic distances given in Table I. It is obvious that the distance between two hydrogen atoms (H2C2, H2C4) and the corresponding oxygen atoms O1 and O2 (2.416 and 2.436 Å, respectively) is smaller than the sum of the van der Waals radii of oxygen and hydrogen (2.72 Å, refs[18,19]), hence the main topochemical requirement for intramolecular abstraction of hydrogen in a photochemical transformation[14] is fulfilled. Thus the above-mentioned formation of compound *II* can be classified as a gamma-hydrogen abstraction going via the triplet excited state $^3(n\,\pi^*)$ of the starting substance. It was shown[20 - 22] that the phototransformations of 1,5-diarylpentane-1,5-diones proceed via the corresponding 1,4-biradical intermediate. In our case, obviously, the favourable spatial arrangement enables an easy closure of this intermediate with formation of the heterocycle. In a sense, the mechanism of the photohemiacetalization found by us approaches the concerted mechanism (Scheme 1).

The hemiacetal *II* isolated by chromatography is not thermostable. Within 14 h it is quantitatively transformed into the starting 1,5-dione *I* at 100 °C in solid phase. These

TABLE I
Intramolecular distances of the O1, O2 atoms from the neighbouring hydrogens in 1,5-dione *I*

O · · · H	Distance, Å	O · · · H	Distance, Å
O1–H1C2	3.843(6)	O2–H1C2	2.885(7)
O1–H2C2	2.416(7)	O2–H2C2	3.047(6)
O1–H1C4	2.946(6)	O2–H1C4	3.836(5)
O1–H2C4	3.101(6)	O2–H2C4	2.436(6)

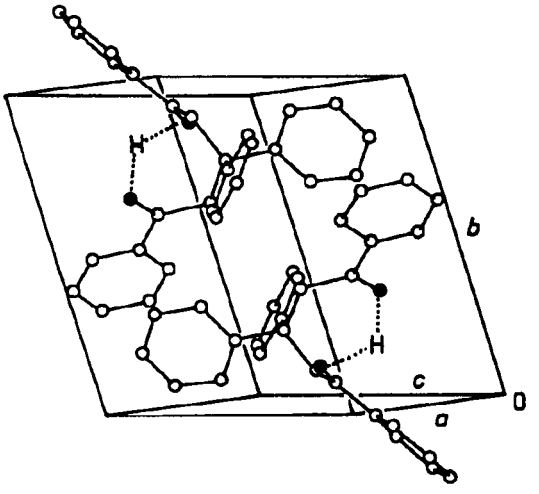
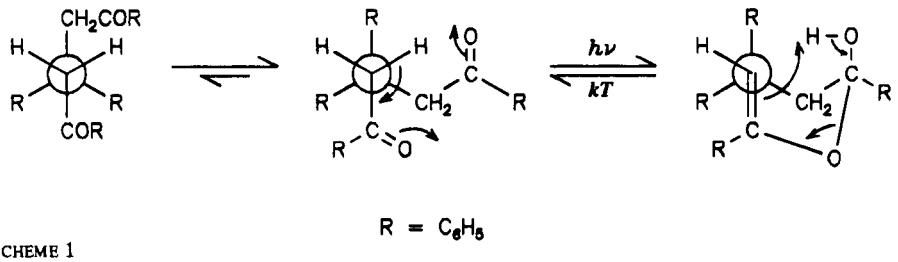


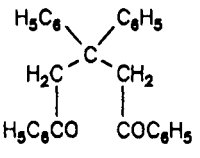
FIG. 2
Unit cell contents (crystal packing)

findings make it possible to formulate the reverse isomerization *II* → *I* as a thermal process (Scheme 1). From the findings it also follows that the earlier described[1 - 3,7,8]

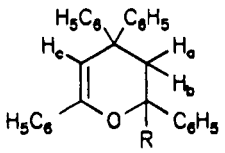


SCHEME 1

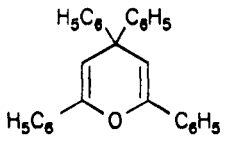
heterocyclization of 1,5-dione *I* into 2,4,4,6-tetraphenyl-4*H*-pyran (*V*), i.e. *I* → *V* + H_2O, must be catalyzed by compounds with dehydration selectivity. In this case, the hemiacetal *II* is transient, being formed via catalyzed monoenolization of diketone *I*, and it cannot be proved in the reaction mixture, since its dehydration is rapid due to the catalysis. Nevertheless, the conformation dependences of both the photochemical and the thermal transformations can be considered very similar, since the enolization of compound *I* apparently will not much change the shapes of reacting molecules mainly affected by the sterical requirements of 3,3-phenyl groups. This presumption is verified also by the other transformations of the 1,5-dione *I*.



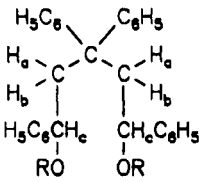
I



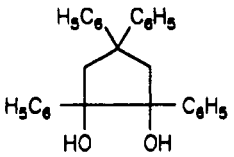
II, R = OH
III, R = C_6H_5
IV, R = H_d



V



VI, R = H
VII, R = $COCH_3$



VIII

A rather long time ago, Peres de Carvalho[3] performed the reaction of dione *I* with phenylmagnesium bromide and, in contrast to the analogous reaction with ethylmagnesium bromide, obtained no heterocyclization product but only 1,1,3,3,5,5-hexaphenylpentane-1,5-diol. We have reproduced these experiments and found that in reality the predominant product is 2,2,4,4,6-pentaphenyl-2,3-dihydropyran (*III*) formed undoubtedly by operation of at least one intramolecular heterocyclization step[11].

The borohydride and aluminohydride reductions as well as the reduction of 1,5-dione *I* with diisobutylaluminium hydride lead to a mixture of diastereoisomeric 1,3,3,5-tetraphenylpentane-1,5-diols (*VI*), the conformational effects in the formation of product *VI* being manifested by a high degree of stereoselectivity of the process. A similar result can be observed in the pinacol reduction of dione *I* with magnesium giving 1,2,4,4-tetraphenylcyclopentane-1,2-diol (*VIII*). From Table II it is obvious that the *meso*-form is the predominant or exclusive product with both the dihydroxy derivatives *VI* and *VIII*. The relative configuration of OH groups was verified by estimating the magnetic non-equivalence of carbon nuclei of both 3,3-phenyl groups in the NMR spectra of the pure *meso*-form *VI* and the therefrom prepared diacetoxy derivative *VII*. The non-equivalence of phenyl nuclei at 4-position was also observed in the case of *cis*-cyclopentan-1,2-diol *VIII*. In the NMR spectrum of the *dl*-form *VI* both the 3,3-phenyl groups are equivalent. In the case of ^{1}H NMR spectra of diastereoisomers *VI*, the proton signals of both forms exhibit analogous relations between chemical shifts as those found earlier[23] with 3,3-dimethyl-1,5-pentanedione.

The stereoselectivity found in formation of diol *VI* can be interpreted on the basis of the hypothesis about the likely equilibrium between the primary heterocyclic products *IXa* $\rightleftharpoons$ *IXb*. In the case of simple borohydride and aluminohydride reduction (M = B or Al), the negative charge at the atomic centre M evokes strong repulsion interactions which energetically favour the stereoisomer *IXa* with one axial phenyl substituent. In the reduction of compound *I* with diisobutylaluminium hydride, apparently the oxo

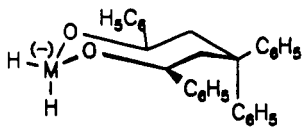
TABLE II
Stereoselective transformations of 1,5-diketone *I*

Reagent	Product	Product ratio, %[a]	
		meso-form	racemic-form
$NaBH_4$	*VI*	97	3
$LiAlH_4$	*VI*	84	16
$(i\text{-}Bu)_2AlH$	*VI*[b]	64	28
Mg	*VIII*	100	–

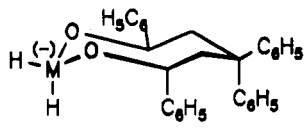
[a] Estabilished from ^{1}H NMR spectra; [b] 8% of 2,3-dihydropyran *IV* has been also observed.

compound *Xa* is the primary intermediate which can react with another molecule of the reducing agent in two ways. The attack of carbonyl group from the side of the more efficiently shielding ligand sphere of aluminium leads to the minor racemic form of diol *VI*, whereas the sterically more favourable attack from the other side of molecule *Xa* leads to the predominant *meso*-form of diol *VI*. At the same time, the higher conformational mobility of the intermediate *Xa* – as compared with the intermediates *IXa*, *IXb* – can explain the lower degree of stereoselectivity (Table II). On the other hand, the complete stereoselectivity of formation of the cyclic *cis*-diol *VIII* can be interpreted as a result of preference of the biradical *XI* with diaxial electron-atracting singlet-occupied orbitals. The idea of existence of the intermediate *Xa* also enables explanation of the formation of the dihydropyran derivative *IV* on the basis of an intramolecular nucleophilic attack of carbonyl group, i.e. according to the scheme

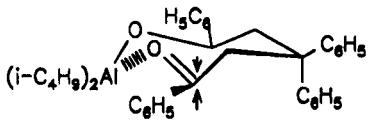
$$Xa \rightarrow Xb \rightarrow IV + (i\text{-}C_4H_9)_2AlOH \text{ and / or}$$
$$Xb + 3\ H_2O \rightarrow Xc + 2\ (CH_3)_3CH + Al(OH)_3 \text{ and } Xc \rightarrow IV + H_2O\ .$$



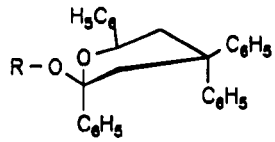
IXa



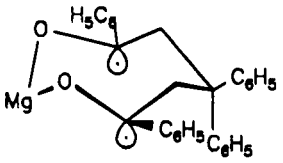
IXb



Xa

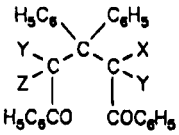


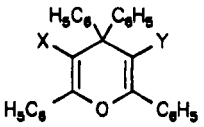
Xb, R = $(i\text{-}C_4H_9)_2Al$
Xc, R = H



XI

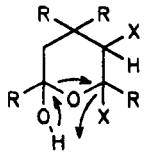
We also examined the reactions of carbon disulfide solutions of compound *I* with heavy halogens at ca 20 °C. As expected, the lowest selectivity was observed in the chlorination: from its products it was possible to obtain both 2,4-dichloro-1,3,3,5-tetraphenylpentane-1,5-dione (*XIII*) and 2,2,4,4-tetrachloro-1,3,3,5-tetraphenylpentane-1,5-dione (*XIV*) on preparative scale and to prove spectrally the presence of the monochloro derivative *XII*. After the bromination, Carvalho[3] isolated 2,4-dibromo-1,3,3,5-tetraphenylpentane-1,5-dione (*XVI*). When reproducing this experiment, we found beside the compound *XVI* also a comparable amount of 3,5-dibromo-2,4,4,6-tetraphenyl-4*H*-pyran (*XVIII*). All attempts at iodination with I_2 only resulted in heterocyclization of compound *I* giving 4*H*-pyran derivative *V*.

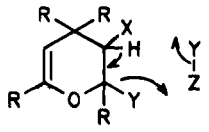




XII, X = Cl; Y = Z = H
XIII, X = Z = Cl; Y = H
XIV, X = Y = Z = Cl
XV, X = Br; Y = Z = H
XVI, X = Z = Br; Y = H

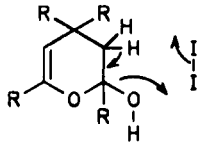
XVII, X = Br; Y = H
XVIII, X = Y = Br
XIX, X = Y = Cl
XX, X = H; Y = CHO
XXI, X = H; Y = $CH=\overset{(+)}{N}(CH_3)_2\ Cl^{(-)}$





XXII, R = C_6H_5; X = Cl or Br

XXIII, R = C_6H_5; X = Y = Z = Br
XXIV, R = C_6H_5; X = $CH=\overset{(+)}{N}(CH_3)_2\ Cl^{(-)}$; Y = Cl; Z = H



XXV, R = C_6H_5

The diastereoisomerism of the halogenation products from *XIII* and *XVI* could not be unequivocally elucidated by means of the spectral methods adopted. The ^{1}H NMR and ^{13}C NMR spectra measured at usual conditions are average data of dynamic equilibria between the respective diastereoisomers. The signals of 2- and 4-protons at δ 6.58 and δ 6.68 of both the 2,4-dihalogen derivatives *XIII* and *XVI* at lower temperatures have a broadened diffusion shape, and their half-widths are reduced with increasing temperature. It is likely that an intermediate step of this stereotautomerism can be an equilibrium formation of enol forms and/or hemiacetals from both diastereoisomeric pairs of 2,4-dihalo-1,5-diones.

The interpretation of the findings given starts from the presumption that the primary substrate, which is halogenated, more probably is the hemiacetal *II* than the short-living enol form of diketone *I*. Chlorine (Cl_2) and bromine (Br_2) are obviously added to the double bond of the molecule *II*, the products of non-heterocyclic nature (*XII* – *XIV*, *XVI*) being then formed by reaction pathways starting from the cycloelimination decompositions of primary adducts *XXII* (*II* + X_2 → *XXII* → *XII* or *XV* + HX, where X = Cl or Br). On the other hand, the formation of the halogenated heterocycle *XVIII* can be explained by an electrocyclic decomposition of the supermolecule *XXIII* (*II* + 2 Br_2 → *XXIII* → *XVII* + Br_2 + HBr → *XVIII* + 2 HBr), the last step of the scheme given corresponding to the bromination of 4*H*-pyran *V* described in ref.[24]. Due to steric hindrance, I_2 does not add to the double bond of compound *II* and acts only as a catalyst of dehydration via the supermolecule *XXV* (*II* + I_2 → *XXV* → *V* + HI + HOI; HI + HOI → H_2O + I_2).

Peres de Carvalho[3] gives 1,1,5,5-tetrachloro-1,3,3,5-tetraphenylpentane as the product of reaction of 1,5-dione *I* with phosphorus pentachloride in xylene at enhanced temperatures. When reproducing this experiment (Procedure *A*), we found that the reaction mixture contained six compounds (HPLC analysis), and we succeeded in chromatographical isolation of 3,5-dichloro-2,4,4,6-tetraphenyl-4*H*-pyran (*XIX*) only. However, if the reaction of compound *I* with the reagent mentioned is carried out without solvent (Procedure *B*), then its course is more selective, and the product *XIX* can easily be isolated. Once again, the interpretation of the course of the corresponding chemical transformations can be derived from the hemiacetal *II* (*II* + PCl_5 → *V* + $POCl_3$ + 2 HCl; *V* + PCl_5 → *XIX* + HCl + PCl_3).

The inclination of 1,5-dione *I* to heterocyclizations makes itself felt also in attempts at application of the Vilsmeier–Haack formylation by action of DMF and $POCl_3$ (Procedure *A*). The product isolated was 3-formyl-2,4,4,6-tetraphenyl-4*H*-pyran (*XX*) whose formation from hemiacetal *II* (2 *II* + $POCl_3$ → 2 *V* + HPO_3 + 3 HCl; *V* + $ClCH{=}N(CH_3)_2^+Cl^-$ + HCl → *XXIV* → *XXI* + 2 HCl; *XXI* + H_2O → *XX* + $(CH_3)_2NH_2^+Cl$) was supported by independent formylation (Procedure *B*) of the 4*H*-pyran derivative *V* giving the identical 3-carbaldehyde *XX*.

EXPERIMENTAL

The temperature data are not corrected. The melting temperatures were measured with a Boetius apparatus. The ^1H NMR and ^{13}C NMR spectra were measured with a Bruker AM-400 apparatus with TMS as internal standard. The parameters for the proton spectra (400.134 MHz): digital resolution 0.184 Hz/point, pulse width 4 μs (45°), temperature 297 K; for the carbon spectra (100.61 MHz): digital resolution 0.9 Hz/point, temperature 297 K, APT technique. The IR spectra were measured with a Perkin–Elmer 325 spectrometer. The reaction course was monitored by means of HPLC using a Separon™ column SGX C18 (3 × 150 mm), the size of particles 5 μm (Tessek, Czechoslovakia) in a 9 : 1 (v/v) MeOH–H_2O system or by means of TLC using Silufol plates (Kavalier, Czechoslovakia).

Compound *I* was prepared by alkaline (sodium amide) ketolization[1,8] of 0.2 mol acetophenone and 0.1 mol benzophenone in ether. The reaction mixture was decomposed and worked up to give the product in 55% yield, m.p. 187 – 188 °C (benzene). For $C_{29}H_{24}O_2$ (404.5) calculated: 86.14% C, 5.94% H; found: 86.19% C, 5.99% H.

A crystal of the dimensions 0.65 × 0.3 × 0.2 mm was measured on a four-circle diffractometer CAD4 (Enraf–Nonius) at 25 °C using MoKα radiation (λ = 0.71073 Å) monochromatized by a graphite monochromator. The lattice parameter values were refined from a set of 20 reflections (Θ = 18 – 21°). The intensities were measured ω/2Θ scan. The scanning velocity varied from 2.06 to 16.48°/min. In the region of reciprocal space $0 \leq h \leq 10$, $-13 \leq k \leq 13$, $-19 \leq l \leq 19$, altogether 6 666 reflections were measured. The intensity of three standard reflections exhibited the maximum fluctuation of only 0.3% during the measurements. The correction for absorption and extinction was neglected.

The phase problem was solved by direct methods. The positions of hydrogens were calculated from the theoretical positions and then refined isotropically. When refining 377 parameters by the full-matrix least squares approach we minimized the function $\sum w(|F_o| - |F_c|)^2$. The final weight scheme had the form of $w = 1$ if $F_o \leq 566.8$ and $w = 2\ (566.8/F_o)$ if $F_o \geq 566.8$. For 3 145 observed reflections selected on the basis of the condition $I > 3\sigma(I)$, the refinement gave the final values of $R = 0.048$ and $wR = 0.060$. The highest value of the ratio of parameter shift/e.s.d. was 0.02. The calculations were carried out with a PDP 11/73 computer using an SPD program set[25]. The basic crystallographic data thus obtained are as follows: $a = 8.444(1)$ Å, $b = 10.195(2)$ Å, $c = 14.618(2)$ Å, $\alpha = 75.52(2)°$, $\beta = 73.22(1)°$, $\gamma = 65.47(1)°$, $V = 1\ 083.7(2)$ Å^3, $Z = 2$, $\rho_o = 1\ 230$ kg m^{-3}, $\rho_c = 1\ 240$ kg m^{-3}, space group $P\bar{1}$, μ(MoKα) = 0.07 mm^{-1}, and $F(000) = 428$. The final coordinates of non-hydrogen atoms are given in Table III and the corresponding bond lengths and angles in Tables IV and V. The molecule *I* in the unit cell can be fitted with 5 planes whose characteristics inclusive of mutual dihedral angles are given in Table VI. These planes correspond approximately to those of phenyl cycles. It was shown that the atoms O1, O2, C1, and C5 (Fig. 1) do not lie in a common plane.

4*H*-Pyran was prepared[8] from 1,5-dione *I* by treatment with P_4O_{10} in xylene.

2,4,4,6-Tetraphenyl-2,3-dihydropyran-2-ol (*II*)

A crystalline film of compound *I* (0.12 g, 0.3 mmol) obtained by evaporation of its benzene solution on a glass surface (30 cm^2) was irradiated with a 400 W high-pressure mercury discharge lamp at 10 – 15 °C 40 min (20% conversion). This procedure was carried out four times at the same conditions, and the combined products were submitted to column chromatography (100 g SiO_2, 40 – 100 μm, benzene). The first chromatographical fractions contained 50 mg (52%) compound *II*, m.p. 124 – 127 °C (heptane); at the melting temperature the compound isomerizes to the starting 1,5-dione *I*, which on further heating again crystallizes and melts at 183 – 186 °C. For $C_{29}H_{24}O_2$ (404.5) calculated: 86.14% C, 5.94% H; found: 86.25% C, 6.11% H. IR spectrum ($CHCl_3$): 3 540 (OH); 1 650, 1 598 (C=C–O); 1 565, 1 495, 1 450 (C=C$_{arom}$). ^1H NMR spectrum ($CDCl_3$): 2.77 d, 1H (H_a, $J_{ab} = 14.2$); 3.14 dd, 1H (H_b, $J_{ab} = 14.2$, $J_{bc} = 1.8$); 3.25 s, 1H (OH); 6.05 d, 1H (H_c, $J_{bc} = 1.8$); 7.09 – 7.50 m, 14H (Ph); 7.57, 7.66, 7.77 m, 6H (*o*-Ph, ^3J =

TABLE III

The fractional atomic coordinates (. 10^4) of non-hydrogen atoms of 1,5-dione *I* and their equivalent thermal parameters (. 10^4)

$U_{eq} = (U_{11} + U_{22} + U_{33} + 2(U_{12}\cos\gamma + U_{13}\cos\beta + U_{23}\cos\alpha))/3$

Atom	*x*	*y*	*z*	U_{eq}, Å^2
O1	-451(2)	3609(2)	3509(1)	551.3(5)
O2	1665(2)	1397(2)	1490(1)	544.9(5)
C1	1739(2)	839(2)	2321(1)	364.3(5)
C2	2754(2)	1156(2)	2888(1)	374.3(5)
C3	3297(2)	2502(2)	2501(1)	338.3(5)
C4	1791(2)	3845(2)	2110(1)	376.8(5)
C5	-102(2)	4170(2)	2675(1)	362.2(6)
C6	863(2)	-240(2)	2803(1)	329.0(5)
C7	-43(3)	-542(2)	2277(1)	411.7(6)
C8	859(3)	-1545(2)	2676(2)	516.1(7)
C9	-810(3)	-2233(2)	3610(2)	552.1(7)
C10	70(3)	-1940(2)	4149(2)	532.5(7)
C11	901(3)	-940(2)	3751(1)	425.4(6)
C12	4930(2)	2248(2)	1653(1)	356.9(5)
C13	5699(2)	1037(2)	1191(2)	401.4(6)
C14	7172(3)	893(2)	426(2)	470.5(6)
C15	7890(3)	1944(3)	123(2)	521.2(7)
C16	7133(3)	3159(3)	575(2)	630.5(7)
C17	5678(3)	3302(2)	1328(2)	558.7(6)
C18	3829(2)	2752(2)	3344(1)	354.9(5)
C19	5312(3)	1701(3)	3671(2)	549.0(7)
C20	5864(3)	1842(3)	4427(2)	648.0(8)
C21	4950(3)	3059(3)	4883(2)	517.4(6)
C22	3488(3)	4109(2)	4571(2)	466.6(6)
C23	2923(2)	3965(2)	3814(2)	395.3(6)
C24	-1567(2)	5238(2)	2190(1)	332.8(4)
C25	-1288(3)	5942(2)	1249(2)	428.6(6)
C26	-2723(3)	6940(3)	852(2)	535.6(6)
C27	-4430(3)	7231(3)	1390(2)	545.7(7)
C28	-4721(3)	6543(3)	2315(2)	517.4(7)
C29	-3310(3)	5544(2)	2719(1)	414.1(5)

8.3, 8.4, 8.8, ^4J = 1.8, 1.7, 1.4). ^{13}C NMR spectrum ($CDCl_3$): 45.23 (C4); 46.60 (C3); 98.41 (C2); 104.06 (C5); 135.65 (i-Ph6); 146.32 (i-Ph2); 146.32 (C6); 148.67 and 148.86 (i-Ph4); 125.16, 125.65, 126.16, 126.86, 126.93, 127.92, 128.26, 128.29, 128.35, 128.38, 128.55, 128.78 CH (Ph). Mass spectrum, *m/z* (%): 404 (M^+, 5), 311 (5), 285 (13), 224 (10), 196 (13), 178 (10), 167 (15), 147 (10), 122 (13), 105 (100), 91 (8), 85 (7), 83 (18), 77 (42), 69 (15), 57 (12), 51 (15), 43 (12). Moreover, 298 mg of the starting substance was isolated.

2,2,4,4,6-Pentaphenyl-2,3-dihydropyran (*III*)

The Grignard reagent prepared from 0.6 g (25 mmol) magnesium and 4 g (25 mmol) bromobenzene in 30 ml abs. THF was added dropwise to a solution of 1 g (2.5 mmol) compound *I* in 30 ml abs. THF during 1 h. The reaction mixture was stirred at 20 °C 12 h, whereafter it was decomposed by pouring into saturated ammonium chloride solution and extracted with chloroform. Combined extracts were dried with $MgSO_4$ and the solvent was evaporated under reduced pressure. The raw product was submitted to column chromatography (80 g SiO_2 40 – 100 μm, heptane–benzene 7 : 3) to give 0.70 g (61%) compound *III*, m.p. 113 – 115°C (ethanol–benzene). For $C_{35}H_{28}O$ (464.6) calculated: 90.48% C, 6.08% H; found: 90.13% C, 6.09% H. IR spectrum ($CHCl_3$): 3 090, 3 067, 3 018 (CH_{arom}); 1 653, 1 600 (C=C–O); 1 574, 1 493, 1 450 ($C=C_{arom}$). ^{1}H NMR spectrum ($CDCl_3$): 3.60 s, 2H (H3); 5.89 s, 1H (H5); 6.97 – 7.08 m, 12H (*m,p*-Ph2; *m, p*-Ph4); 7.11 m, 4H (*o*-Ph2); 7.26 m, 4H (*o*-Ph4, ^3J = 8.1, ^4J = 2.0); 7.35 t, 1H (*p*-Ph6, ^3J = 7.1);

TABLE IV
Bond lenghts involving only non-hydrogen atoms in the molecule of 1,5-dione *I*

Atoms[a]	Distance, Å	Atoms[a]	Distance, Å
C1–C6	1.496(3)	C15–C16	1.374(4)
C1–O2	1.213(2)	C16–C17	1.376(3)
C1–C2	1.510(4)	C17–C12	1.384(4)
C3–C2	1.552(3)	C18–C19	1.386(3)
C3–C4	1.550(2)	C19–C20	1.374(4)
C3–C12	1.543(2)	C20–C21	1.378(4)
C3–C18	1.536(3)	C21–C22	1.364(3)
C5–O1	1.219(2)	C22–C23	1.384(4)
C5–C4	1.510(3)	C23–C18	1.387(3)
C5–C24	1.490(2)	C24–C25	1.387(3)
C6–C7	1.387(4)	C25–C26	1.389(3)
C7–C8	1.384(4)	C26–C27	1.375(3)
C8–C9	1.374(3)	C27–C28	1.363(3)
C9–C10	1.379(5)	C28–C29	1.379(3)
C10–C11	1.390(4)	C29–C4	1.394(2)
C11–C6	1.393(3)	O1 ··· O2	3.730(7)[b]
C12–C13	1.378(3)	O1 ··· C1	3.265(6)[b]
C13–C14	1.394(3)	O2 ··· C5	3.266(7)[b]
C14–C15	1.364(4)	C1 ··· C5	3.201(5)[b]

[a] See Fig. 1; [b] non-bonding distance.

7.41 t, 2H (*m*-Ph6, ^3J = 7.2); 7.89 m, 2H (*o*-Ph6, ^3J = 7.2, ^4J = 1.9). ^{13}C NMR spectrum ($CDCl_3$): 45.06 (C3); 45.92 (C4); 82.06 (C2); 105.12 (C5); 135.95 (i-Ph6); 144.41 (i-Ph2); 148.50 (i-Ph4); 149.02 (C6); 125.10, 125.62, 125.97, 126.63, 127.88, 127.95, 128.45, 128.49 CH (Ph). Mass spectrum, *m/z* (%): 464 (M^+, 5), 387 (5), 368 (10), 344 (8), 284 (20), 270 (25), 269 (100), 207 (10), 191 (20), 180 (15), 179 (16), 167 (17), 166 (20), 105 (26), 91 (12), 77 (14), 69 (10), 54 (11).

Reduction of 1,5-Diketone *I*

Reduction with $NaBH_4$: A solution of 0.5 g (1.24 mmol) compound *I* in a mixture of 20 ml abs. benzene and 5 ml ethanol was treated with 47 mg (1.24 mmol) $NaBH_4$. The reaction mixture was stirred at room temperature 10 days, whereafter 100 ml water was added and the mixture was extracted with chloroform. Combined extracts were dried with $MgSO_4$ and the solvent was evaporated under reduced pressure to give 0.44 g (86%) mixture of isomers *VI*.

Reduction with $LiAlH_4$: A solution of 0.5 g (1.24 mmol) compound *I* in 20 ml abs. THF was treated with a solution of 47 mg (1.24 mmol) $LiAlH_4$ in 7 ml THF added dropwise under nitrogen during 1 h. The mixture was stirred at room temperature 2 h, whereafter it was decomposed with water. After addition of 2 ml acetic acid, the emulsion obtained was extracted with chloroform, combined extracts were dried with $MgSO_4$, and the solvent was evaporated under reduced pressure to give 0.45 g (88%) mixture of diols *VI*.

Reduction with diisobutylaluminium hydride: A solution of 0.5 g (1.24 mmol) compound *I* in 20 ml abs. benzene was treated with a solution of 0.43 g (2.98 mmol) diisobutylaluminium hydride in 3.7 ml toluene added dropwise under dry nitrogen during 1 h. The mixture was stirred at room temperature 2 h, whereafter it was decomposed with water and acidified with 2 ml acetic acid. The organic layer was sepa-

TABLE V
Bond angles involving only non-hydrogen atoms in the molecule of 1,5-dione *I*

Atoms[a]	Angle, °	Atoms[a]	Angle, °
C6–C1–O2	119.7(2)	C13–C12–C17	117.4(2)
C6–C1–C2	118.0(4)	C12–C13–C14	120.8(2)
O2–C1–C2	122.2(2)	C13–C14–C15	120.7(2)
C12–C3–C18	107.4(2)	C14–C15–C16	119.1(2)
C12–C3–C2	113.2(2)	C15–C16–C17	120.2(3)
C12–C3–C4	105.5(1)	C23–C18–C19	116.7(2)
C18–C3–C2	105.7(2)	C18–C19–C20	122.1(2)
C18–C3–C4	113.4(2)	C19–C20–C21	120.3(2)
C2–C3–C4	111.7(2)	C20–C21–C22	118.6(3)
O1–C5–C24	119.9(2)	C21–C22–C23	121.2(2)
C7–C6–C11	118.7(2)	C24–C5–C4	118.1(2)
C8–C7–C6	120.8(2)	C25–C24–C29	118.6(2)
C7–C8–C9	120.0(3)	C24–C25–C26	120.2(2)
C8–C9–C10	120.2(2)	C25–C26–C27	120.1(2)
C11–C10–C9	120.1(2)	C26–C27–C28	120.2(2)
O1–C5–C4	122.1(2)	C27–C28–C29	120.4(2)

[a] See Fig. 1.

rated and the aqueous layer was extracted with benzene. Combined organic portions were dried with $MgSO_4$ and the solvents were evaporated under reduced pressure to give 0,43 g mixture of diols *VII* and 2,3-dihydropyran *IV*. The column chromatography (200 g silica gel, 30 – 60 μm, petroleum ether–chloroform 95 : 5) and recrystallization of the individual fractions from heptane gave 21 mg (4%) 2,3-dihydropyran *IV*, m.p. 174.5 – 175.5 °C; 70 mg (14%) *dl*-form *VI*, m.p. 201 – 202 °C; 165 mg (32%) *meso*-form *VI*, m.p. 170 – 170.5 °C.

TABLE VI

Least squares planes fitted through atoms in the molecule of 1,5-dione *I*.
Each plane is defined by eq. $AX + BY + CZ + D = 0$, where X, Y and Z are Cartesian coordinates

Plane No.	Coefficients *A, B, C, D*	Atom[a]	Deviation[b] Å	χ^2-Test	No.[c]	Dihedral angles of planes, °
1	0.5071	C6	0.006(2)	26	2	114.7(1)
	−0.7951	C7	−0.007(2)		3	75.0(1)
	−0.3328	C8	0.004(2)		4	60.9(1)
	−0.6677	C9	−0.001(2)			
		C10	−0.000(2)			
		C11	−0.003(2)			
2	−0.6662	C12	−0.001(2)	3	3	83.6(1)
	0.3707	C13	−0.001(2)		4	74.9(1)
	−0.6471	C14	0.003(2)			
	−4.4502	C15	−0.003(3)			
		C16	0.001(3)			
		C17	0.001(3)			
3	0.6670	C18	0.000(2)	3	4	114.6(1)
	0.3710	C19	0.002(2)			
	−0.6461	C20	−0.003(3)			
	2.0906	C21	0.001(2)			
		C22	0.003(2)			
		C23	−0.002(2)			
4	−0.5062	C24	−0.004(2)	9		
	−0.7944	C25	0.001(2)			
	−0.3355	C26	0.001(2)			
	−6.1569	C27	−0.000(2)			
		C28	−0.002(2)			
		C29	0.002(2)			

[a] See Fig. 1; [b] from the plane; [c] the second plane.

2,3-Dihydropyran *IV*: for $C_{29}H_{24}O$ (388.5) calculated: 89.66% C, 6.23% H; found: 89.96% C, 5.97% H. IR spectrum ($CHCl_3$): 3 095, 3 070, 3 010 (CH_{arom}); 1 640, 1 598 (C=C–O); 1 575, 1 495, 1 425 (C=C_{arom}). ^1H NMR spectrum ($CDCl_3$): 2.64 dd, 1H (H_a, J_{ab} = 13.6, J_{ad} = 11.6); 2.77 ddd, 1H (H_b, J_{ab} = 13.6, J_{bc} = 2.1, J_{bd} = 1.6); 4.98 dd, 1H (H_d, J_{ad} = 11.5, J_{bd} = 1.6); 5.87 d, 1H (H_c, J_{bc} = 2.1); 7.12 – 7.43 m, 18H (Ph); 7.71 m, 2H (*o*-Ph6, ^3J = 8.4, ^4J = 1.6). ^{13}C NMR spectrum ($CDCl_3$): 44.06 (C3); 47.27 (C4); 75.10 (C2); 104.61 (C5); 135.70 (i-Ph6); 141.59 (i-Ph2); 148.74 and 148.78 (i-Ph4); 151.33 (C6); 125.10, 126.05, 126.15, 126.23, 127.15, 127.80, 128.20, 128.35, 128.46 CH (Ph). Mass spectrum, *m/z* (%): 389 (3), 388 (M^+, 5), 297 (5), 384 (16), 383 (20), 207 (6), 205 (8), 194 (17), 193 (100), 179 (22), 178 (17), 167 (12), 165 (5), 115 (16), 105 (60), 91 (52), 77 (33), 51 (5).

dl-Form *VI*: for $C_{29}H_{28}O_2$ (408.5) calculated: 85.26% C, 6.91% H; found: 85.26% C, 7.00% H. IR spectrum (CCl_4): 3 620, 3 500, 3 300 (OH); 3 100, 3 060, 3 032 (CH_{arom}); 1 500, 1 450, 1 440 (C=C). ^1H NMR spectrum ($CDCl_3$): 2.37 d, 2H (H_b, J_{ab} = 14.7); 3.33 dd, 2H (H_a, J_{ab} = 14.7, J_{ac} = 9.4); 3.78 s, 2H (OH); 4.40 d, 2H (H_c, J_{ac} = 9.4); 7.02 – 7.31 m, 20H (Ph). ^{13}C NMR spectrum ($CDCl_3$): 47.71 (C2); 49.80 (C3); 71.62 (C1); 125.20 (*o*-Ph1); 126.17 (*p*-Ph3); 127.13 (*p*-Ph1); 128.01 (*m*-Ph1); 128.20 (*o*-Ph3); 128.41 (*m*-Ph3); 146.46 (i-Ph1); 148.76 (i-Ph3).

meso-Form *VI*: for $C_{29}H_{28}O_2$ (408.5) calculated: 85.26.% C, 6.91% H; found: 85.26% C, 6.87% H. IR spectrum (CCl_4): 3 620, 3 550, 3 400 (OH); 3 092, 3 067, 3 015 (CH_{arom}); 1 475, 1 453, 1 447 (C=C_{arom}). ^1H NMR spectrum ($CDCl_3$): 1.32 s, 2H (OH); 2.77 dd, 2H (H_a, J_{ab} = 14.3, J_{ac} = 8.2); 2.84 dd, H (H_b, J_{ab} = 14.3, J_{bc} = 2.6); 4.64 dd, 2H (H_c, J_{ac} = 8.2, J_{bc} = 2.6); 7.05 – 7.35 m, 20H (Ph). ^{13}C NMR spectrum ($CHCl_3$): 47.75 (C2); 49.08 (C3); 71.61 (C1); 125.61 (*o*-Ph1); 126.19 and 126.60 (*p*-Ph3); 127.15 (*p*-Ph1); 127.96 (*m*-Ph1); 128.21 and 128.34 (*o*-Ph3); 128.34 and 128.60 (*m*-Ph3); 146.03 (i-Ph1); 148.51 and 148.61 (i-Ph3).

meso-1,3,3,5-Tetraphenylpentane-1,5-diyl Diacetate (*VII*)

Subsequently added were 0.22 (3.1 mmol) acetyl chloride and a solution of 0.5 g (1.2 mmol) *meso*-1,5-diol *VI* in 3 ml abs. pyridine into 2 ml pyridine cooled with ice with exclusion of moisture. The reaction mixture was stirred at room temperature 24 h, whereafter it was poured onto ice cubes. The precipitate formed was collected by suction, washed with water, dried, and recrystallized twice from heptane to give 0.31 g (52%) compound *VII*, m.p. 176 – 178 °C. For $C_{33}H_{32}O_4$ (492.6) calculated: 80.46% C, 6.55% H; found: 80.37% C, 6.73% H. IR spectrum ($CHCl_3$): 3 100, 3 058, 3 030 (CH_{arom}); 1 727 (C=O); 1 600, 1 494, 1 447 (C=C_{arom}); 1 227 (C–O–C). ^1H NMR spectrum ($CDCl_3$): 1.43 s, 6H (CH_3); 2.64 dd, 2H (H_b, J_{ab} = 14.7, J_{bc} = 1.4); 3.09 dd, 2H (H_a, J_{ab} = 14.7, J_{ac} = 8.8); 5.64 dd, 2H (H_c, J_{ac} = 8.8, J_{bc} = 1.4); 7.12 – 7.33, 20H (Ph). ^{13}C NMR spectrum ($CDCl_3$): 20.62 (CH_3); 43.85 (C2); 48.48 (C3); 72.92 (C1); 125.99 and 126.44 (*p*-Ph3); 126.30 (*o*-Ph1); 127.70 (*p*-Ph1); 127.82 and 127.89 (*o*-Ph3); 128.11 and 128.34 (*m*-Ph3); 128.52 (*m*-Ph1); 124.14 (i-Ph1); 147.47 and 147.69 (i-Ph3); 169.86 (C=O).

cis-1,2,4,4-Tetraphenylcyclopentane-1,2-diol (*VIII*)

A suspension of 0.36 g (15.0 mmol) magnesium chips in 60 ml ether was stirred under nitrogen, and 1.27 g (5.0 mmol) iodine was added thereto in small portions. The mixture was refluxed until clear. After cooling, a solution of 1 g (2.5 mmol) compound *I* in 25 ml abs. THF was added drop by drop and the reaction mixture was refluxed 12 h (bath temperature 70 °C). After cooling the mixture was decomposed by pouring into saturated solution of ammonium chloride and extracted with chloroform. The combined extracts were dried with $MgSO_4$ and the solvent was evaporated under reduced pressure. The oily residue was covered with a thin layer of ethanol, whereupon it solidified. Its recrystallization from hexane gave 0.73 g (73%) compound *VIII*, m.p. 193 – 194 °C. For $C_{29}H_{26}O_2$ (406.5) calculated: 85.68% C, 6.45% H; found: 86.03% C, 6.49% H. IR spectrum (CCl_4): 3 600, 3 535 (OH); 3 093, 3 068, 3 010 (CH_{arom}); 1 495, 1 447 (C=C_{arom}). ^1H NMR spectrum ($CDCl_3$): 3.17 s, 2H (OH); 3.40 and 3.57 AB system, 4H (H3, H5;

J_{AB} = 14.8); 6.20 – 7.06 m, 10H (Ph1, Ph2); 7.14 t, 1H and 7.18 t, 1H (*p*-Ph4, ^3J = 7.4 and 7.2); 7.26 – 7.38 m, 4H (*m*-Ph4); 7.45 m, 2H and 7.61 m, 2H (*o*-Ph4). ^{13}C NMR spectrum ($CDCl_3$): 50.21 (C-3,5); 51.41 (C4); 85.84 (C-1,2); 125.91 and 125.94 (*p*-Ph4); 126.30 and 126.38 (*o*-Ph4); 126.40 (*o*-Ph1, *o*-Ph2); 126.86 (*p*-Ph1, *p*-Ph2); 127.19 (*m*-Ph1, *m*-Ph2); 128.68 and 128.75 (*m*-Ph4); 142.30 (i-Ph1, i-Ph2); 149.88 and 150.64 (i-Ph4).

Reactions of 1,5-Dione *I* with Chlorine (Cl_2)

Dry chlorine gas was introduced into a suspension of 1.0 g (2.5 mmol) compound *I* in 30 ml carbon disulfide at 20 °C for 1 h. The reaction mixture was stirred for another 5 h and then left to stand overnight. The solvent was evaporated, and the oily residue was dissolved in cyclohexane and submitted to column chromatography on silica gel. The first fractions gave the mixture of *XII* (20%) and *XIII* (80%). 2-Chloro-1,3,3,5-tetraphenylpentane-1,5-dione (*XII*): ^{1}H NMR spectrum ($CDCl_3$): 4.36 q, 2H (CH_2, ^2J = 15.1); 6.95 s, 1H (CHCl); 7.23 – 7.45 m, 16H (Ph); 7.75 d, 2H and 7.94 d, 2H (*o*-Ph, ^3J = 7.3 and 7.4). ^{13}C NMR spectrum ($CDCl_3$): 46.31 (C4); 59.05 (C3); 60.50 (C2); 126.80 and 126.88 (*p*-Ph3); 127.28 and 127.70 (*m*-Ph3); 128.02 and 128.36 (*o*-Ph3); 128.59 (*m*-Ph5); 128.78 (*o*-Ph1); 129.34 (*o*-Ph5); 130.18 (*o*-Ph1); 132.94 (*p*-Ph5); 133.23 (*p*-Ph1); 136.20 (i-Ph1); 137.70 (i-Ph5); 143.32 and 143.59 (i-Ph3); 198.00 (C1); 198.96 (C5). 2,4-Dichloro-1,3,3,5-tetraphenylpentane-1,5-dione (*XIII*), yield 550 mg after crystallization of the mixture, colourless solid, m.p. 146 – 147 °C (benzene–cyclohexane). For $C_{29}H_{22}O_2Cl_2$ (473.4) calculated: 73.58% C, 4.68% H, 14.98% Cl; found: 73.60% C, 4.72% H, 14.95% Cl. IR spectrum ($CHCl_3$): 1 680 (C=O). ^{1}H NMR spectrum ($CDCl_3$): 6.56 s, 2H (CHCl); 7.19 – 7.52 m, 12H (H_{arom}-*meta*, *para*); 7.61 – 7.62 m, 4H (H_{arom}-*ortho*); 7.69 – 7.71 m, 4H (H_{arom}-*ortho*). ^{13}C NMR spectrum ($CDCl_3$): 53.44 (C3); 60.00 (C2); 127.06 (*o*-Ph1); 127.56 (*p*-Ph3); 128.51 (*o*-Ph3); 128.67 (*m*-Ph1); 131.87 (*m*-Ph3); 133.36 (*p*-Ph1); 135.91 (i-Ph1); 139.36 (i-Ph3); 193.66 (C1). Mass spectrum, *m/z* (%): 476 (3), 474 (10), 472 (M^+, 17), 439 (7), 437 (23), 436 (12), 420 (4), 404 (10), 403 (30), 402 (15), 401 (15), 400 (15), 331 (10), 330 (30), 321 (27), 320 (26), 319 (50), 297 (45), 283 (30), 191 (20), 105 (100), 77 (100), 51 (5).

The later fractions contained 250 mg colourless 2,2,4,4-tetrachloro-1,3,3,5-tetraphenylpentane-1,5-dione (*XIV*), m.p. 139 – 140°C (benzene–cyclohexane). For $C_{29}H_{20}O_2Cl_4$ (542.3) calculated: 64.23% C, 3.72% H, 26.15% Cl; found: 64.28% C, 3.80% H, 26.05% Cl. IR spectrum ($CHCl_3$): 1 690 (C=O). ^{1}H NMR spectrum ($CDCl_3$): 7.25 – 7.40 m, 12H (*m*, *p*-Ph); 7.40 – 7.68 m, 4H and 7.68 – 7.70 m, 4H (*o*-Ph). Mass spectrum, *m/z* (%): 542 (M^+, 0.1), 508 (4), 506 (4), 474 (3), 472 (5), 471 (5), 470 (4), 437 (6), 436 (7), 435 (6), 434 (5), 401 (4), 400 (6), 399 (4), 367 (15), 365 (7), 355 (10), 354 (5), 353 (15), 331 (13), 330 (9), 319 (18), 318 (6), 317 (20), 283 (12), 250 (8), 248 (15), 223 (18), 214 (22), 178 (17), 139 (5), 106 (40), 105 (100), 77 (100), 51 (10).

Reaction of 1,5-Diketone *I* with Bromine (Br_2)

A solution of 0.8 g (5 mmol) Br_2 in 10 ml carbon disulfide was added dropwise to a suspension of 1.0 g (2.5 mmol) compound *I* in 30 ml CS_2 at 20 °C. The further procedure was the same as in the previous case. The chromatography of the oily product on a silica gel column with tetrachloromethane as the eluent gave – in the first fractions – 700 mg (52%) 3,5-dibromo-2,4,4,6-tetraphenyl-4*H*-pyran (*XVIII*), m.p. 228 °C (benzene–heptane) which was identical with the substance prepared in another way[24]. For $C_{29}H_{20}OBr_2$ (544.3) calculated: 63.99% C, 3.70% H, 29.35% Br; found: 64.00% C, 3.90% H, 29.00% Br. Later fractions gave 350 mg (26%) 2,4-dibromo-1,3,3,5-tetraphenylpentane-1,5-dione (*XVI*), m.p. 139 – 141°C (refs[3,26] give m.p. 132 – 134 °C). For $C_{29}H_{22}O_2Br_2$ (562.3) calculated: 61.94% C, 3.94% H, 28.42% Br; found: 61.99% C, 4.01% H, 28.48% Br. IR spectrum ($CHCl_3$): 1 685 (C=O). ^{1}H NMR spectrum ($CDCl_3$): 6.68 s (broad), 2H (CHBr); 7.23 – 7.51 m, 12H (Ph); 7.63 – 7.66 m, 4H and 7.76 – 7.79 m, 4H (*o*-Ph). Mass spectrum, *m/z* (%): 560 (M^+, 0.1), 482 (2), 480 (2), 465 (15), 463 (15), 402 (5), 401 (5), 400 (5), 384 (5), 297 (20), 279 (8), 267 (7), 191 (5), 165 (5), 105 (100), 77 (35), 51 (5).

Reaction of 1,5-Diketone *I* with Iodine (I_2)

A solution of 1.0 g (2.5 mmol) compound *I* and 0.2 g (0.8 mmol) I_2 in 180 ml toluene was submitted to azeotropic distillation until the reaction water was completely removed (30 h). Then the solvent was evaporated and the residue was covered with a layer of petroleum ether. The crystals formed were collected by suction. Yield 450 mg (47%) 2,4,4,6-tetraphenyl-4*H*-pyran (*V*), m.p. 172 – 173 °C (heptane) whose identity was confirmed by comparison with the authentic substance[8]. In another experiment the iodination of diketone *I* was atempted using the same conditions as those of the bromination. After evaporation of solvent and recrystallization from a benzene–heptane mixture, 0.82 g starting diketone *I* was isolated.

Reaction of 1,5-Diketone *I* with Phosphorus Pentachloride

Procedure A: A mixture of 1.0 g (2.5 mmol) compound *I* and 4.2 g (20 mmol) PCl_5 was heated in 20 ml xylene with exclusion of moisture 3 h (the bath temperature 160 °C). After cooling, the reaction mixture was poured onto ice cubes and extracted with chloroform. The combined extracts were dried with $MgSO_4$ and the solvent was evaporated under reduced pressure. The oily residue was submitted to column chromatography (150 g silica gel, 40 – 100 μm, benzene–heptane 1 : 5) to give 0.42 g (38%) compound *XIX*, m.p. 221 – 222 °C (benzene–heptane) (ref.[24] gives m.p. 222.5 – 223 °C).

Procedure B: A mixture of 1.0 g (2.5 mmol) compound *I* and 4.1 g (20 mmol) PCl_5 was ground and heated on a 120 °C bath with exclusion of moisture 1 h. After cooling, the reaction mixture was decomposed with ice. The precipitate formed was collected by suction, washed with water, dried, and recrystallized from heptane–benzene to give 0.70 g (62%) compound *XIX*, m.p. 219 – 221 °C.

3-Formyl-2,4,4,6-tetraphenyl-4*H*-pyran (*XX*)

Procedure A: A suspension of 1.0 g (2.5 mmol) compound *I* in 1.0 ml (12.5 mmol) abs. DMF was stirred with cooling (ice bath), and 3.5 ml (37.5 mmol) $POCl_3$ was added drop by drop. The reaction mixture was stirred at 20 °C 1 h and then on a 100 °C bath 7 h. The unreacted $POCl_3$ was removed by vacuum distillation and the residue was cooled and poured onto ice. The aqueous solution was neutralized with saturated solution of Na_2CO_3 to pH 7 and extracted with chloroform. The combined extracts were dried with $MgSO_4$, the solvent was evaporated under reduced pressure, and the oily residue was submitted to column chromatography (50 g silica gel, 40 – 100 μm, benzene) to give 0.58 g (56%) compound *XX*, m.p. 150 – 152 °C (methanol).

Procedure B: The reaction was caried out and the mixture was worked up in the same way as in procedure *A*. The reaction of 1.0 g (2.6 mmol) 4*H*-pyran *V* with a reagent obtained from 1.0 ml (12.9 mmol) DMF and 3.6 ml (38.7 mmol) $POCl_3$ gave 0.63 g (58%) compound *XX*, m.p. 151 – 152 °C (methanol). For $C_{30}H_{22}O_2$ (414.5) calculated: 86.93% C, 5.35% H; found: 86.92% C, 5.27% H. IR spectrum ($CHCl_3$): 3 060, 3 040, 3 016 (CH_{arom}); 1 674 (C=O); 1 605, 1 590, 1 573 (skeletal vibrations). ^1H NMR spectrum ($CDCl_3$): 5.75 s, 1H (H5); 7.20 – 7.65 m, 20H (Ph); 9.52 s, 1H (CH=O). ^{13}C NMR spectrum ($CDCl_3$): 48.60 (C4); 109.53 (C5); 117.94 (C3); 124.54 (*o*-Ph6); 126.29 (*p*-Ph4); 127.88 (*o*-Ph2); 128.34 (*m*-Ph6); 128.50 (*o*-Ph4); 128.98 (*p*-Ph6); 129.21 (*m*-Ph4); 130.40 (*m*-Ph2); 130.94 (*p*-Ph2); 132.14 (i-Ph6); 132.45 (i-Ph2); 144.85 (C6); 145.88 (i-Ph4); 167.09 (C2); 191.01 (C=O).

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