# Synthesis and Reactions of 1,6-Diaryl-2,5-bis(diazo)-1,3,4,6-tetraoxohexanes

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The title compounds were obtained in about 50% yields by reaction of the corresponding diaryltetraoxohexanes with dinitrogen trioxide. A mechanism to account for their formation is proposed. Thermal decompositions of bis-diazo-compounds in the solid state or in suspension in various media afforded derivatives of α,α'-diaroyl-succinic acids (6) and, in one case, a pyrazole. Ketens are postulated as intermediates. In an inert medium, a bis-keten is suggested to react intramolecularly to give the bis-enol-lactone of (6) ; its structure was established by X-ray crystallography. This bis-enol-lactone was shown to be formed by pyrolysis of diesters of (6), contrary to earlier reports.

As part of an approach to synthesis of vicinal hexaketones, we have investigated the reactions of 1,6-diaryl-1,3,4,6-tetraoxohexanes † (1) with dinitrogen trioxide (N_2O_3). Contrary to expectation, these reactions produced, under
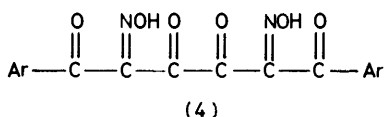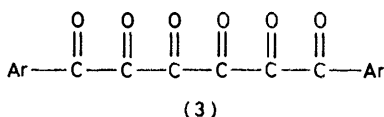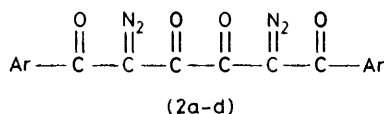

(1)

a; Ar = Ph

b; Ar = p-MeOC$_6$H$_4$

c; Ar = p-MeC$_6$H$_4$

d; Ar = p-ClC$_6$H$_4$

(2a—d)

(3)
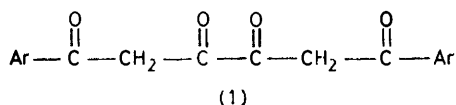
(4)

controlled conditions, respectable yields of the bis-(diazo)tetraketones (2). The purpose of the present report is to describe the synthesis and thermal decompositions of these interesting diazo-compounds. Details of the X-ray crystallographic analysis of a product (5a) are also presented.

RESULTS AND DISCUSSION

Synthesis of Bis(diazo)tetraketones.—Since the first report by Wieland and Bloch [1] in 1904, a convenient procedure for synthesis of vicinal triketones [2] has in-

† These highly enolic compounds are named as tetraketones for convenience.

volved reaction of readily available β-diketones with N_2O_3 in methylene chloride at low temperature, followed by warming to room temperature and isolation of the product. For this purpose, N_2O_3 has been generated by reaction of nitric acid with arsenious oxide,[1] by reaction of sulphuric acid with sodium nitrite,[3] or by mixing equal volumes of NO and NO_2.[4] The major by-product was the α-oximino-β-diketone; in one case [1] a trace of an α-diazo-β-diketone was also observed.

The mild conditions and simplicity of this procedure made it seem an attractive method for conversion of doubly β-diketonic systems (1) into the corresponding diarylhexaketones (3). In the present work the oxides of nitrogen generated by addition of concentrated nitric acid to sodium nitrite [5] were used. This method has the advantage of allowing very rapid generation of nitrogen oxides and turned out to be crucial in obtaining reproducible results. In the event, saturation of a cold (−30 °C) methylene chloride solution of (1a) with nitrogen oxides gave a blue solution which was allowed to warm to room temperature for 1 h with evolution of brown oxides of nitrogen, and then concentrated under vacuum. The faintly yellow solid which separated (51% yield) was clearly not the desired hexaketone hydrate. On the basis of analytical and spectroscopic data, in particular the characteristic diazo-absorption at 2 130 cm⁻¹, it was assigned the structure 1,6-diphenyl-2,5-bis-(diazo)-1,3,4,6-tetraoxohexane (2a). The bis-dioxime [6] (4a) of (3) was obtained in 21% yield from the mother liquors; the remaining product was a complex mixture. Similar results were obtained with the di-p-methoxy-(1b), di-p-methyl- (1c), and di-p-chloro-compounds (1d). Further evidence for the structures of the diazo-compounds was provided by their thermal decompositions as described later.

The overall change observed in these reactions is quite remarkable. From a simple stoicheiometric point of view, it involves replacement of the two hydrogens of a methylene group by a diazo-function according to the

$$\mathord{>}CH_2 + 2N_2O_3 \longrightarrow \mathord{>}C{=}N_2 + 2HNO_3$$

equation shown. A mechanism to account for the observed results is shown in the Scheme.

The first step proposed is nitrosation [7] of starting β-

diketone by electrophilic attack of N_2O_3 (or N_2O_4) to give (I); the intermediacy of (I) is supported by isolation of its tautomer, the oxime. In addition to tautomerization, (I) may react with an excess of NO, if present, to give the diazonium nitrate (II). Conversion of nitroso-compounds to diazonium nitrates by reaction with excess of NO was first reported to occur with aromatic nitroso-

initially formed nitroso-compound (I) became dominant in the absence of an appreciable concentration of NO. This Scheme has a variety of interesting implications which we hope to investigate.

Reactions of Bis(diazo)tetraketones.—The bis(diazo)-tetraketones (2) underwent violent decomposition upon attempted determinations of their melting points.
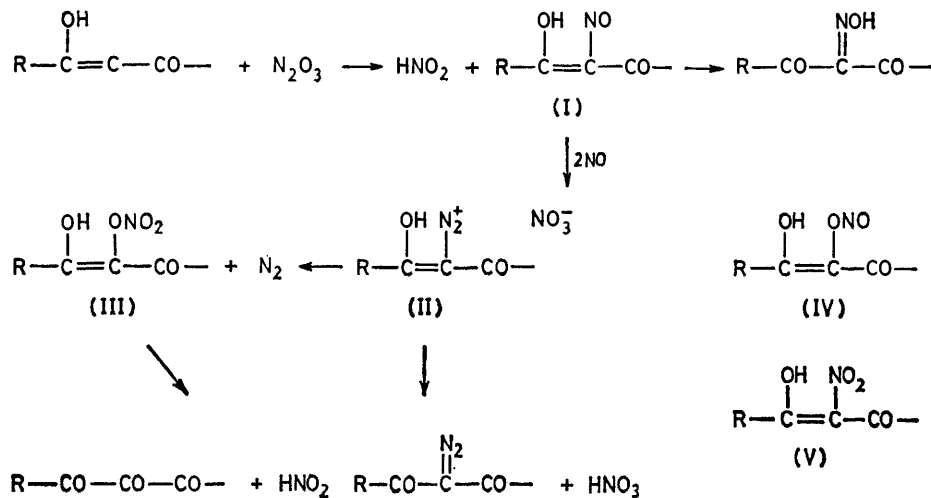
SCHEME

compounds[8] and more recently with acetylenic[9] and alkyl or cycloalkyl[10] nitroso-compounds. This reaction has been suggested[10a] to involve addition of two molecules of NO to the nitroso-compound followed by formation of a cyclic intermediate and fragmentation:
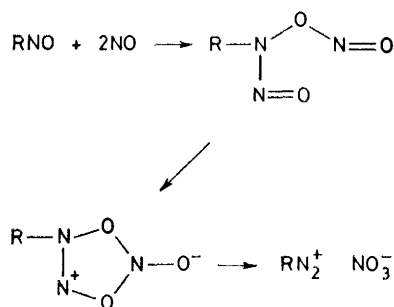
In the special case of a diazonium nitrate of type (II), simple loss of an acidic proton yields the observed α-diazo-β-diketone. We assume that the necessary NO is available from the equilibrium $N_2O_3 \rightleftharpoons NO + NO_2$. The Scheme also suggests a possible route for formation of triones (as observed by earlier workers) *via* decomposition of (II) to give the nitrate ester (III) followed by elimination of nitrous acid.[11] Other possible precursors of trione could be nitrate ester (IV) or nitro-compound (V).

Some support for the proposed Scheme derives from the observation that slow addition of acid (nitric or sulphuric) to sodium nitrite, that is, slow generation of oxides of nitrogen, afforded dioximes (4) as the only isolable products. Presumably, tautomerization of the

Interestingly, these decomposition points were very reproducible when using purified diazo-compounds. Small preparative-scale explosions furnished high melting, highly fluorescent orange solids (5); yields were quite variable due to mechanical losses. A more convenient, if less dramatic, procedure involved refluxing a toluene suspension of (2) for a few minutes and cooling to obtain crystalline (5); yields were in the range 64—89%. The structure of (5a) was established by X-ray crystallographic analysis (see later) to be the bis(enol-lactone) of α,α'-dibenzoylsuccinic acid (6a).

Examination of the literature revealed a number of reports[12] that heating esters of (6a) at *ca.* 300 °C gave a high-melting, orange solid which was called ' naphthacene diquinone dihydride ' and assigned structure (7). Curiously, (7) was reported to be stable to base even though it would have been expected to isomerize to the thermodynamically more stable tautomer (8), a known compound.[13] This anomaly was resolved when the preparation of supposed (7) from diethyl α,α'-dibenzoyl-succinate (12a) was repeated and the product shown to be identical to (5a). Accordingly, the compound $C_{18}H_{13}$-NO_4, m.p. 202—203 °C, reported earlier[12a] from reaction of ' naphthacene diquinone dihydride ' with ammonia is presumably one of the double-bond isomers of the ketoamide monolactone (9a) and the product $C_{28}H_{22}N_4$-O_2, m.p. 320 °C, obtained with phenylhydrazine[12a] is one one of the isomers (DL or *meso*) of the bicyclic compounds (10) or (11).

Attempted determination of the structure of (5a) by chemical methods before the X-ray analysis was completed also encountered difficulties due to formation of

mixtures of isomeric products. For example, heating (5a) with aniline yielded a crystalline material whose combustion and mass spectral analyses indicated that it was the product of addition of one molecule of aniline to (5a), presumably a keto-anilide-lactone. However, repeated
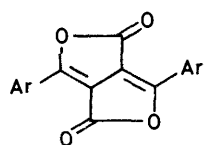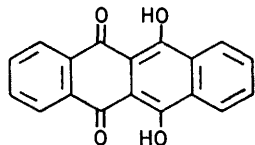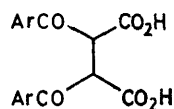

(5)

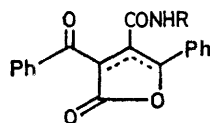a; Ar = Ph
b; Ar = p-MeOC₆H₄
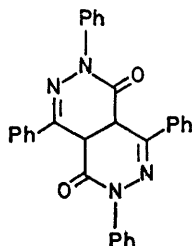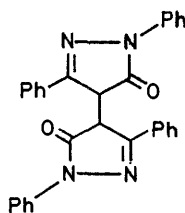c; Ar = p-MeC₆H₄
d; Ar = p-ClC₆H₄

(6a–d)

(9)

a, R = H
b, R = Ph

(7)

(8)
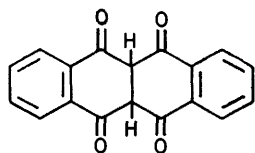
(10)

(11)

crystallization did not give sharp-melting material and the product appears to be a mixture of double-bond isomers as represented by structure (9b). A similar problem was encountered when the bis-diazo-compound (2a) was heated in the presence of aniline. On the basis of analytical and spectroscopic data the product was a mixture of the bisanilides (12a) of *meso-* and DL-α,α'-dibenzoylsuccinic acid (6a); no (5a) was formed in this reaction.

Refluxing (2a) in n-butyl alcohol also resulted in rapid decomposition; (5a) again was completely absent from the reaction product. The major components were the n-butyl esters (12b) (total 74%) of (6a) from which the *meso*-isomer could be crystallized. Its structure was established by comparison with a sample synthesized from n-butyl benzoylacetate. The isomeric esters were

interconverted by heating above 150 °C or by passage through a column of silica gel. The configurations of (12b) were assigned by comparison of n.m.r. spectra with spectra of the known [14] ethyl esters (12c) of *meso-* and DL-(6a). The higher-melting *meso*-ethyl ester exhibited signals (triplet and quartet) for the O-ethyl protons at higher field than in the lower melting DL-isomer, while the signals for the α,α'-protons and the *ortho*-protons of the benzoyl groups were at lower field in the *meso*-isomer. Mixtures of the two isomers could by analysed conveniently from the integrals of the two-proton singlets at δ 5.65 (*meso*) and 5.58 (DL). Similar variations in chemical shift were observed with the n-butyl esters. No evidence for significant concentrations of enolic forms was observed in the n.m.r. spectra although the facile equilibrations described above presumably proceed *via* keto-enol equilibria. The absence of significant concentration of enolic forms in diethyl α,α'-diacetylsuccinate has been noted recently.[15]
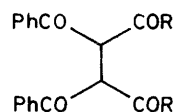
(12)

a; R = NHPh
b; R = OBuⁿ
c; R = OEt
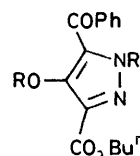
(13a)

R = H, Me
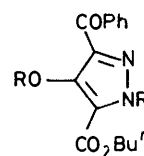
(13b)

R = H, Me

A second product containing two nitrogen atoms was isolated in 12% yield from the n-butyl alcohol reaction. It is assigned one of the isomeric structures (13a or b) on the basis of analytical and spectroscopic data, and was converted into a dimethyl derivative by reaction with diazomethane.

Numerous examples of photochemical and thermal (catalysed and uncatalysed) Wolff rearrangements of α-diazo-β-diketones to acyl ketens have been reported.[16] The results described above can be explained by assuming consecutive Wolff rearrangements of (2a). In the presence of alcohol or amine, the initially formed monoketen (14) would react to form ester or amide (15) which would then rearrange to a new keten (16) and thence proceed to product. Compound (14) could also cyclize to the pyrazole derivative (17), the precursor of (13). In the absence of a reactive species which traps keten, as in the solid state or in toluene, (14) would undergo a second Wolff rearrangement to give the bis-keten [17] (18) which would cyclize as shown to (5). *A priori*, each Wolff rearrangement could proceed in two ways, either *via* migration of an acyl or of a phenyl group, leading to three possible bis-ketens, two symmetrical and one unsymmetrical. Consecutive phenyl migrations would result in formation of bis-keten (19) which would be expected to cyclize to the known pulvinic acid lactone (20), an isomer of (5). The latter compound was synthesized [18] in order to determine if it were present in the

product from heating (2a) in toluene. No positive evidence for the presence of (20) was found; on the basis of t.l.c. and u.v. spectra it cannot have constituted more than 1% of the total reaction product. Thus the results obtained indicate a considerable preference for acyl over phenyl group migration in these keto-carbenes.

by irradiation of (2a) in various solvents. The catalytic method resulted only in recovery of (2a), probably because the very low solubility of (2a) required use of very dilute solutions. This insolubility was also the cause of difficulties in the photolysis of (2a) since it necessitated irradiation at 254 nm where (2a) has

Ar = Ph
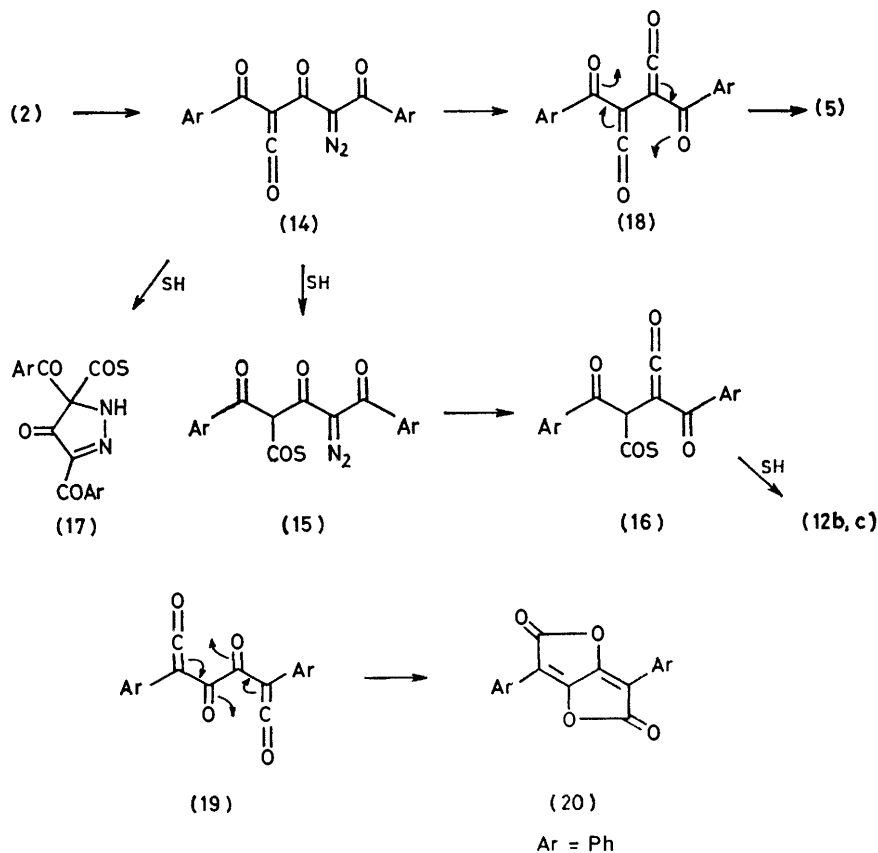
An alternative mechanism for formation of bis-keten (18) can also be considered. Open-chain compounds having terminal diazoketone functions have been shown[19] to cyclize to 2-ene-1,4-diones in a synthetically useful reaction, and αα'-bis(diazo)ketones have been suggested[20] to undergo cyclization to afford cyclopropenones as reactive intermediates. A similar process occurring with (2) would afford the cyclobutenedione (21). Subsequent electrocyclic ring opening[21] of (21) would

appreciable absorption, even in dilute solution. Complex product mixtures were formed, undoubtedly because reaction products also absorbed at this wavelength and underwent further photo-reactions.

Thus no experimental distinction between the two possible modes of decomposition of (2) is possible at present. However, it should be emphasized that (5a) was not formed * in reactions in the presence of aniline or n-butyl alcohol. This result is in agreement with a
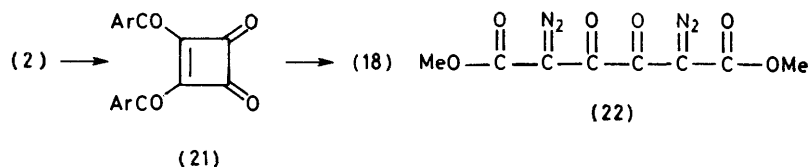
lead only to the bis-keten (18) and thus account for the fact that (20) was not formed. This would require that (13) be formed by a minor reaction path. Attempts were made to effect decomposition of (2a) at room temperature and thus allow detection of (21). These were performed using bis-chloro-π-allylpalladium[22] and

stepwise mechanism; it seems unlikely that intramolecular reaction of the bis-keten (18) to give (5a) would not compete to even a small extent with an intermolecular reaction with amine or alcohol.

* The strong fluorescence of (5a) permits its detection at extremely low concentration.

TABLE 1

Positional parameters for non-hydrogen atoms ($\times 10^4$) and for hydrogen atoms ($\times 10^3$) and vibrational parameters for non-hydrogen atoms ($\times 10^3$) with estimated standard deviations in parentheses

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	2 562(4)	4 092(2)	1 146(4)	40(2)	31(2)	59(3)	7(1)	−9(2)	−2(1)
O(2)	4 575(5)	5 311(2)	2 069(4)	48(2)	46(2)	80(3)	−5(2)	−16(2)	1(2)
C(1)	2 821(7)	5 012(3)	1 266(6)	47(3)	42(3)	42(4)	3(2)	1(2)	−1(2)
C(2)	−705(6)	4 637(2)	−312(6)	39(2)	35(2)	38(4)	−1(2)	−4(2)	2(2)
C(3)	434(7)	3 878(3)	192(6)	40(2)	38(3)	40(4)	1(2)	5(2)	1(2)
C(4)	−127(6)	2 965(2)	−13(5)	39(2)	32(3)	36(3)	−1(2)	−2(2)	−1(2)
C(5)	−2 285(8)	2 699(3)	−809(6)	45(3)	35(3)	55(4)	2(2)	−5(2)	4(2)
C(6)	−2 847(9)	1 839(3)	−1 003(7)	43(3)	46(3)	71(4)	−1(2)	−7(3)	−4(2)
C(7)	−1 181(11)	1 225(4)	−392(8)	81(4)	32(3)	67(5)	−7(3)	7(3)	−15(3)
C(8)	962(8)	1 462(3)	371(7)	53(3)	37(3)	65(5)	0(2)	−2(3)	10(3)
C(9)	1 511(8)	2 336(3)	572(6)	45(3)	40(3)	52(4)	−3(2)	−5(2)	−2(2)
H(5)	−338(6)	308(3)	−117(5)	3(1)					
H(6)	−433(8)	173(3)	−146(6)	6(1)					
H(7)	−154(8)	84(3)	−61(6)	4(2)					
H(8)	201(8)	113(3)	74(6)	7(2)					
H(9)	295(7)	248(3)	110(5)	5(1)					

The reactions of a related compound, dimethyl 2,5-bis(diazo)-3,4-dioxoadipate (22), in which the two aroyl groups of (2) are replaced by methoxycarbonyl groups, have been described. Photolysis [23] of (22) in methanol
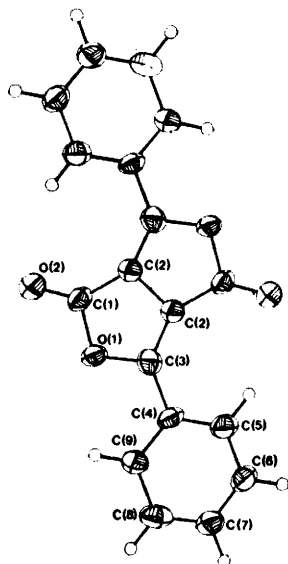

FIGURE Molecular structure and atomic numbering of the bislactone of α,α′-dibenzoylsuccinic acid (5a)

solution yielded tetramethyl ethane-1,1,2,2-tetracarboxylate, presumably by way of a bis-keten (or successive mono-ketens). Thermal reactions (100—110 °C) gave a variety of products.[24] A pyrazole was formed in the presence of amines, and a pyridazine in isopropyl alcohol. Reactions in the presence of aromatic species, such as toluene, gave products incorporating a molecule of the aromatic substrate in contrast to the results obtained in the present work.

X-*Ray Crystallographic Analysis of the Bis-enol-lactone* (5a).—The molecular structure and numbering of (5a) is shown in Figure 1; Table 1 lists final positional and vibrational parameters. Corresponding interatomic distances and angles are given in Tables 2 and 3, respectively. The molecule occupies the space-group special positions (inversion centre) (0; 0; $\frac{1}{2}$) and (0; $\frac{1}{2}$; 0). The

bislactone moiety is planar (out-of-plane displacements are in the range 0.0—0.001 Å) making a dihedral angle of 5.6° with the planar phenyl rings. The effect of conjugation between the alternating single [C(2)–C(2)*] and double bonds [C(2)–C(3), C(2)*–C(3)*] is quite apparent with the shortening of the 'single' bond (1.422 Å) and the lengthening of the 'double' bond (1.365 Å); these values are the same as in other molecules exhibiting conjugation.[25] The shortening of C–O single bonds (1.386, 1.415 Å) is typical for O–C(sp^2) bonds.[26]

TABLE 2

Bond lengths involving C and O atoms (Å) (e.s.d.s lie in the range 0.005—0.009 Å)

O(1)–C(1)	1.415	C(4)–C(5)	1.378
O(1)–C(3)	1.386	C(4)–C(9)	1.384
O(2)–C(1)	1.205	C(5)–C(6)	1.359
C(1)–C(2 *) †	1.445	C(6)–C(7)	1.383
C(2)–C(2 *) †	1.422	C(7)–C(8)	1.350
C(2)–C(3)	1.365	C(8)–C(9)	1.377
C(3)–C(4)	1.438		

† C(2 *) is related to C(2) by an inversion centre.

TABLE 3

Bond angles involving C and O atoms (°) (e.s.d.s lie in the range 0.3—0.6°)

C(3)–O(1)–C(1)	110.4	C(9)–C(4)–C(3)	120.3
O(2)–C(1)–O(1)	119.0	C(9)–C(4)–C(5)	118.8
C(2 *) †–C(1)–O(1)	105.1	C(6)–C(5)–C(4)	121.6
C(2 *) †–C(1)–O(2)	135.9	C(7)–C(6)–C(5)	118.3
C(2 *) †–C(2)–C(3)	109.6	C(8)–C(7)–C(6)	121.7
C(4)–C(3)–O(1)	117.4	C(9)–C(8)–C(7)	119.7
C(4)–C(3)–C(2)	134.5	C(8)–C(9)–C(4)	120.0
C(5)–C(4)–C(3)	120.9		

† C(2 *) is related to C(2) by an inversion centre.

EXPERIMENTAL

I.r. spectra were determined in potassium bromide pellets and n.m.r. spectra in deuteriochloroform solutions at 60 MHz using tetramethylsilane as internal standard unless noted otherwise.

1,6-*Diphenyl-2,5-bis(diazo)-1,3,4,6-tetraoxohexane* (2a).— A solution of 1,6-diphenyl-1,3,4,6-tetraoxohexane [27] (1a) (4 g) in methylene chloride (750 ml) was cooled to −30 °C [some (1a) crystallized]. The gases generated by addition of 70% nitric acid (40 ml) over 7 min to an excess of solid sodium nitrite were bubbled into the cold solution with

shaking; the yellow colour became deep blue. The solution was removed from the cooling bath and after 1 h was concentrated under reduced pressure at 25—30 °C to *ca.* 200 ml. Benzene (30 ml) was added and concentration continued to about 50 ml. The green to red paste which separated was filtered off and washed with benzene (3 × 10 ml) to give (2a) as a faintly yellow solid. Concentration of the filtrate to *ca.* 15 ml gave an additional 0.3 g (total yield 51%). An analytical sample was prepared by dissolving the crude product at room temp. in methylene chloride and adding hexane; violent decomposition at 155 °C; $\nu_{max.}$ 2 130 and 1 640 cm^{-1}; $\lambda_{max.}$ (CH$_2$Cl$_2$) 257 nm (ε 32 000) (Found: C, 61.8; H, 3.05; N, 16.3. C$_{18}$H$_{10}$N$_4$O$_4$ requires C, 62.43, H, 2.91, N, 16.18%).

Dilution of the filtrate with hexane after isolation of (2a) gave the 2,5-dioxime (4a) (1.0 g, 21%), m.p. 125—127 °C (lit.,[6] m.p. 130 °C), of diphenyl hexaketone. The filtrate from isolation of (4a) showed at least six components upon t.l.c. analysis on silica gel. Repetition of the above procedure with addition of nitric or sulphuric acid to sodium nitrite over a 60-min period gave the dioxime (4a) as the only isolable product.

The following compounds were similarly prepared: 1,6-*Di*-(p-*methoxyphenyl*)-2,5-*bis*(*diazo*)-1,3,4,6-*tetraoxohexane* (2b) from (1b) as described above in 46% yield, violent decomposition at 155.5 °C; $\nu_{max.}$ 2 150 and 1 655 cm^{-1}; $\lambda_{max.}$ (CH$_2$Cl$_2$) 275 nm (ε 27 000) (Found: C, 58.75; H, 3.4; N, 13.9. C$_{20}$H$_{14}$N$_4$O$_6$ requires C, 59.11; H, 3.47; N, 13.79%). 1,6-*Di*-(p-*tolyl*)-2,5-*bis*(*diazo*)-1,3,4,6-*tetraoxohexane* (2c), from (1c) as described above in 45% yield, violent decomposition at 155.5 °C; $\nu_{max.}$ 2 140 and 1 670 cm^{-1}; $\lambda_{max.}$ (CH$_2$Cl$_2$) 264 nm (ε 42 000); δ 2.40 (6 H), 7.30 (4 H, d, *J* 7 Hz), and 7.63 (4 H, d, *J* 7 Hz) (Found: C, 63.85; H, 3.75; N, 15.2. C$_{20}$H$_{14}$N$_4$O$_4$ requires C, 64.17; H, 3.77; N, 14.97%): 1,6-*Di*-(p-*chlorophenyl*)-2,5-*bis*(*diazo*)-1,3,4,6-*tetraoxohexane* (2d). Prepared from (1d) as described above in 26% yield, violent decomposition at 163.5 °C; $\nu_{max.}$ 2 145 and 1 665 cm^{-1}; $\lambda_{max.}$ (CH$_2$Cl$_2$) 261 nm (ε 55 000) (Found: C, 51.8; H, 2 05; N, 13.65; Cl, 16.55. C$_{18}$H$_8$Cl$_2$N$_4$O$_4$ requires C, 52.07; H, 1.94; N, 13.49; Cl, 17.09%).

Bis-(*enol-lactone*) (5a) *of* αα'-*Dibenzoylsuccinic Acid.*—(a) *From* (2a). A suspension of the bis(diazo)tetraketone (2a) (0.88 g) in toluene (100 ml) was heated rapidly to reflux with stirring. Vigorous evolution of gas began at *ca.* 100 °C and the solid dissolved rapidly to give a strongly fluorescing orange solution. After a 10-min reflux, the solution was concentrated to *ca.* 15 ml and the resulting orange solid filtered off to give (5a) (0.42 g). The filtrate was taken to dryness and the residue crystallized from chloroform–hexane to give additional (5a) (0.05 g, total yield 59%). An analytical sample of (5a) was crystallized from chloroform–methanol, m.p. 289—290 °C; $\nu_{max.}$ 1 785 and 1 635 cm^{-1}; $\lambda_{max.}$ (CH$_2$Cl$_2$) 285 (ε 7 400), 402 (22 500), 427 (43 000), and 456 nm (47 000); *m/e* 290 (*M*$^+$), 262, 234, 105, and 77 (Found: C, 74.65; H, 3.85. C$_{18}$H$_{10}$O$_4$ requires C, 74.48; H, 3.42%).

(5a) could also be obtained by heating (2a) without solvent at 150—160 °C. Yields ranged from 25—50%; mechanical losses were considerable.

(b) *From diethyl* α,α'-*dibenzoylsuccinate* (12c). A mixture of DL- and *meso*-(12c) was heated as described [12] to give an orange solid, m.p. 290—291 °C, identical by mixed m.p. and comparison of i.r. spectra with (5a).

Bis(*enol-lactone*) (5b) *of* αα'-*Di*-(p-*methoxybenzoyl*)*succinic Acid.*—Compound (5b) (85%) was prepared as described

above from (2b). An analytical sample was crystallized from toluene, m.p. 295—298 °C (decomp.); $\nu_{max.}$ 1 765 and 1 620 cm^{-1}; $\lambda_{max.}$ (CH$_2$Cl$_2$) 253 (ε 31 000), 302 (11 500), 425 (sh) (30 000), 452 (68 000), and 483 (90 000) (Found: C, 68.5; H, 4.15. C$_{20}$H$_{14}$O$_6$ requires C, 68.57; H, 4.03%).

Bis(*enol-lactone*) (5c) *of* αα'-*Di*-(p-*methylbenzoyl*)*succinic Acid.*—Compound (5c) (76%) was prepared as described above from (2c). An analytical sample was crystallized from toluene, m.p. 304—305.5 °C; $\nu_{max.}$ 1 785 and 1 630 cm^{-1}; $\lambda_{max.}$ (CH$_2$Cl$_2$) 243 (32 000), 263 (10 600), 293 (8 000), 385 (sh) (9 300), 408 (26 000), 433 (53 000), and 463 (60 000); δ 2.50 (6 H), 7.40 (4 H, d, *J* 7 Hz), and 8.25 (4 H, d, *J* 7 Hz) (Found: C, 75.4; H, 4.4. C$_{20}$H$_{14}$O$_4$ requires C, 75.46; H, 4.43%).

Bis(*enol-lactone*) (5d) *of* αα'-*Di*-(p-*chlorobenzoyl*)*succinic Acid.*—Compound (5d) (77%) was prepared as described above from (2d). An analytical sample was crystallized from toluene, m.p. 298—299 °C; $\nu_{max.}$ 1 782 and 1 640 cm^{-1}; $\lambda_{max.}$ (CH$_2$Cl$_2$) 248 (ε 33 000), 265 (sh) (15 000), 295 (11 000), 387 (sh) (11 300), 410 (30 000), 436 (60 000), and 466 (67 000) (Found: C, 60.3; H, 2.35. C$_{18}$H$_8$O$_4$Cl$_2$ requires C, 60.19; H, 2.25%).

Reaction of (2a) *with Aniline.*—A suspension of (2a) (0.24 g) in a mixture of toluene (5 ml) and aniline (1 ml) was boiled for 10 min. Upon cooling a solid (0.15 g), m.p. 206—210 °C separated; an additional quantity (0.04 g) was obtained from the mother-liquor. Crystallization from chloroform–benzene gave white crystals of (12a) melting in the range 210—220 °C; $\nu_{max.}$ 3 290, 3 180, 1 670, 1 600, and 1 585 cm^{-1}; $\lambda_{max.}$ (CH$_2$Cl$_2$) 258 nm (ε 34 000) (Found: C, 75.10; H, 4.65; N, 5.5. C$_{30}$H$_{24}$N$_2$O$_4$ requires C, 75.61; H, 5.08; N, 5.88%).

The filtrate showed at least five spots on t.l.c. analysis, but none of the highly fluorescent spot characteristic of (5a) was observed.

Reaction of (5a) *with Aniline.*—A sample (0.23 g) of (5a) in a mixture of toluene (5 ml) and aniline (1 ml) was heated on a steam-bath for 1 h; the characteristic fluorescence of (5a) had completely disappeared. The yellow crystals which separated off were recrystallized from chloroform–benzene to give (9b) (0.09 g), m.p. 226—227 (decomp.) $\nu_{max.}$ 2 800—3 300, 1 720, 1 650, 1 610, and 1 600 cm^{-1}; $\lambda_{max.}$ (CH$_3$OH) 294 (ε 14 000) and 397 (37 000); *m/e* 383 (*M*$^+$) (Found: C, 74.7; H, 4.6; N, 4.0. C$_{24}$H$_{17}$NO$_4$ requires C, 75.18; H, 4.47; N, 3.65%).

Additional crystalline material (0.11 g), obtained by dilution of the mother-liquors with hexane, had m.p. 200—212 °C, not changed by repeated crystallization from chloroform–benzene; the i.r. spectrum was very similar to that of the higher-melting compound described above.

Reaction of (2a) *with n-Butyl Alcohol.*—A suspension of (2a) (0.304 g) in n-butyl alcohol (10 ml) was heated to boiling. Vigorous evolution of gas ensued and the solid had completely dissolved after 9 min; boiling was continued for an additional 5 min. T.l.c. analysis (silica gel, chloroform) showed no trace of a fluorescent spot corresponding to the bis-lactone (5a). The yellow solution was concentrated on a rotary evaporator and the residue chromatographed on silica gel (10 g). Elution with chloroform (50 ml) until a yellow zone reached the bottom of the column and concentration gave a fraction (0.283 mg, 74%) which consisted of a 1 : 1 mixture of *meso*- and DL-(12b) by n.m.r. analysis. Two crystallizations from hexane gave *meso*-(12b) (0.028 g), m.p. 86—88 °C, identical by i.r. analysis with material described below.

The yellow zone was eluted from the column with chloroform (50 ml) and gave, after concentration, a semi-solid (0.109 g). Crystallization from methylene chloride–hexane gave crystalline (13) (0.047 g, 12%), m.p. 151—153 °C. The analytical sample of (13) was obtained by crystallization from a small volume of acetone as white crystals, m.p. 157—158 °C; $\nu_{max.}$ 3 320, 3 200, 1 672, 1 625, and 1 300 cm^{-1}; $\lambda_{max.}$ (MeOH) 235 (54 000), 270 (sh) (7 600), and 280 (sh) (600); δ ([$^2H_6$]DMSO) 0.4—0.8 (3 H), 0.9—1.7 (4 H), 3.9—4.2 (2 H, superimposed on broad signal 3.5—4.5 2 H), 7.3—7.6 (3 H), and 7.8—8.2 (2 H); m/e 288 (M^+) (Found: C, 62.45; H, 5.65; N, 9.65. $C_{15}H_{16}N_2O_4$ requires C, 62.49; H, 5.59; N, 9.72%).

The mother-liquors from crystallization of (13) showed five spots on t.l.c. analysis (silica gel, chloroform); attempted preparative-scale thick-layer chromatography did not yield any pure, characterizable substances.

Reaction of a suspension of (13) (0.065 g) in ether (3 ml) with an excess of diazomethane followed by preparative thick-layer chromatography (silica gel, chloroform) gave the dimethyl derivative (0.040 g) as a colourless oil, homogeneous by t.l.c., which could not be induced to crystallize; $\nu_{max.}$ 1 713, 1 653, 1 235 cm^{-1}; δ 0.9—1.2 (3 H, 1.4—2.0 (2 H), 3.95 (3 H), 4.30 (3 H), 4.76 (2 H, t, J 6 Hz), 7.4—7.7 (3 H), and 8.1—8.3 (2 H); m/e 312 (M^+).

Preparation of meso *and Racemic Di-n-butyl* α,α′-*Dibenzoylsuccinate* (12b).—n-Butyl benzoylacetate (13.05 g) was added dropwise with stirring during 2 h to a suspension of sodium hydride (2.66 g of 55% dispersion in oil) in anhydrous ether (250 ml) under nitrogen. The vigorous evolution of hydrogen which accompanied the addition ceased 15 min after addition was completed. Iodine (6.89 g) was then added to the stirred solution; a white precipitate separated. After stirring for 5 h at room temperature, water (100 ml) containing potassium hydrogensulphite (1 g) was added, the layers were separated, and the ether layer washed with water and saturated salt solution. After drying and concentration, the colourless oil was dissolved in hexane (25 ml) and allowed to stand for several hours. The white crystals were filtered to give di-n-butyl *meso*-α,α′-dibenzoylsuccinate (12b) (5.74 g, 44%), m.p. 79—82 °C. Crystallization from hexane (20 ml) afforded 4.50 g, m.p. 89—90 °C. An analytical sample of *meso*-(12b) was prepared by two additional crystallizations from hexane, 89—90 °C; $\nu_{max.}$ 1 740 and 1 680 cm^{-1}; $\lambda_{max.}$ (MeOH) 252 (ε 28 000) and 289 (sh) (2 650) nm; addition of one drop of 10% potassium hydroxide solution gave $\lambda_{max.}$ 282 nm (ε 12 000); δ 0.5—1.7 with strong lines at 0.70, 0.80 (m, 14 H), 3.93 (t, J 6 Hz, 4 H), 5.70 ($W_\frac{1}{2}$ 1.5 Hz, 2 H), 7.3—7.8 (m; 6 H), and 8.15—8.4 (m; 4 H); m/e 438 (M^+) (Found: C, 71.40; H, 7.05. $C_{26}H_{30}O_6$ requires C, 71.21; H, 6.90%).

The filtrate from the first crystallization of *meso*-(12b) was concentrated to give a clear oil (7.47 g); the n.m.r. spectrum indicated that it consisted of the racemic isomer plus oil from the sodium hydride dispersion. It was chromatographed rapidly on silica gel (see below) eluting with 5% methylene chloride in pentane. The first fraction (25 ml) consisted of 1.2 g of clear oil. Subsequent fractions (5.60 g, 43%) were partly crystalline. Crystallization from hexane gave an additional quantity (2 g) of *meso*-(12b). The mother-liquors in a small volume of methanol were left at −20 °C for two days and then decanted from a small quantity of crystals. Concentration of the solution gave a pure sample

* For details of Supplementary Publication, see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1979, Index issue.

of racemic di-n-butyl α,α′-dibenzoylsuccinate (12b) which could not be induced to crystallize; $\nu_{max.}$ (film) 1 730 and 1 680 cm^{-1}; $\lambda_{max.}$ (MeOH) 252 (24 500) and 280 (sh) (2 900) nm; addition of one drop of 10% potassium hydroxide solution gave $\lambda_{max.}$ 281 (ε 9 500) nm; δ 0.6—1.8 with strong lines at 0.83, 0.90 (m, 14 H), 4.10 (t, J 6 Hz, 4 H), 5.60 ($W_\frac{1}{2}$ 1.5 Hz, 2 H), 7.3—7.8 (m, 6 H), and 8.1—8.3 (m, 4 H); m/e 438 (M^+).

All attempts to crystallize DL-(12b) failed. It was isomerized to a 1 : 1 mixture (by n.m.r. analysis) of DL and *meso* by passage through a column of silica gel or upon attempted short-path distillation at 130 °C and 0.05 mmHg.

Crystal Data on Bis(enol-lactone) (5a).—$C_{18}H_{10}O_4$, $M = $ 290.3. Monoclinic, $a = 5.777(5)$, $b = 15.295(7)$, $c = 7.453$-(4) Å, $\beta = 96.69°(2)$, $U = 654.1$ Å^3, $D_c = 1.475$ g cm^{-3}, $Z = 2$, $D_m = 1.481$ g cm^{-3}, Cu-K_α radiation ($\lambda = 1.541$ 8 Å). Space group $P2_1/C$ (C_{2h}^5, No. 14).

Yellow prismatic crystals were obtained by recrystallization from chloroform–methanol solution. A small prismatic crystal (0.2 × 0.1 × 0.1 mm) was used for intensity measurements. Intensities were measured on a PW 1 100 Philips four-circle, computer-controlled diffractometer with graphite monochromated Cu-K_α radiation, using the ω—θ scanning technique. (ω = 3.0—62.0°, Δω = 1.0°, scan speed = 0.025° s^{-1}, background measured for 20 s). Of 789 independent reflections measured, 196 were < 1.5 σ(F_o).

The crystal structure was solved by MULTAN 77 [28] and refined by full-matrix least-square analysis [29] with anisotropic thermal parameters for C and O atoms, isotropic for H atoms.

Scattering factors for C and O were taken from Cromer and Mann,[30] and for H from Stewart, Davidson, and Simpson.[31] The final R value was 0.063 and $R' = 0.075$ {$w = 0.79/[\sigma^2(F_o) + 0.02(F_o)^2]$}. The list of observed and calculated structure factors is contained in Supplementary Publication No. SUP 22856 (5 pp.).*

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