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Reactions of Cyclic Oxalyl Compounds[1] - 38.
New Isoindigoide Dyes from Heterocyclic 2,3-Diones - Synthesis and Thermal Rearrangement

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Abstract: *The heterocyclic 2,3-diones* ***1*** *and* ***11*** *together with Lawesson reagent (LR) afford novel isoindigoide dyes* ***4*** *and* ***12****, respectively.* ***4a*** *can thermally be isomerized into the pyrano[4,3-c]pyrane* ***6****, accompanied by a significant hypsochromic shift which was corroborated by quantum chemical calculations. The phoshporanylidene derivative* ***13*** *was obtained via Wittig reaction of* ***1***. *All structural assignments were based on X-ray studies of* ***4a*** *and* ***13***.

The chemistry of monocyclic heterocyclic 2,3-diones in general has been widely explored during the last decades.[2] In particular, derivatives of the general structure **1** have found to serve as versatile synthons in a) thermolysis reactions [3] via *in situ* - generating α-oxoketenes, b) cycloaddition reactions [4] across their oxadiene moiety as well as c) reactions with nucleophiles[5] thus affording novel mono- and bicyclic heterocyclic systems and disclosing unexpected rearrangements.[6]

In order to examine if that kind of chemistry can be extended to somewhat modified systems several attempts to change functional groups in **1** and related systems e.g. pyrrol-2,3-diones, have now been made : e.g. transformation of carbonyl groups into the corresponding C=S- moieties using the *Lawesson*- reagent [2,4-bis-(4-methoxyphenyl) 1,3,2,4-dithiadiphosphetane-2,4-disulfide][7], or to establish C=C- double bonds instead of C=O functionalities via the Wittig reaction.[8] Surprisingly, the outcome of these experiments did not follow the expected routes but from all those reactions novel, deeply coloured dyes were obtained as described in the following.

A. Reactions of furan-2,3-diones **1** with Lawesson reagent (LR)
B. Reactions of fused pyrrol-2,3-diones **11** with Lawesson reagent
C. Wittig reaction of furan-2,3-dione **1a**

A. According to the usual experimental procedures applied to achieve sulfurization of carbonyls with aid of Lawesson reagent[7] the furan-2,3-diones **1** and LR were warmed to 60-70°C in dry xylene for 2 hours thus forming a deep red solution. After cooling metallic brilliant bronze-coloured crystals (**4a**) or fine red needles (**4b**) could be obtained in moderate yields (40-50%). Analytical and spectroscopic investigations clearly indicated that instead of any sulfurization bis-furanones **4** representing iso-oxindigoide molecular skeletons had been formed (details see Experimental).

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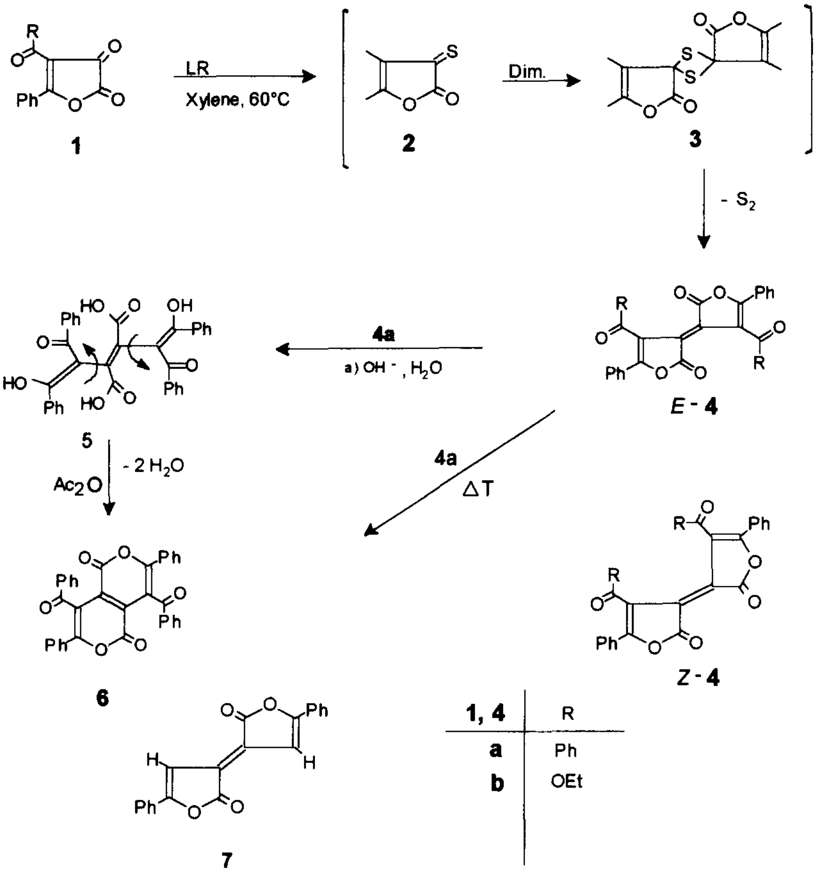


1, 4	R
a	Ph
b	OEt

Scheme 1

The IR data (e.g. **4a** : C=O at 1760, 1650 cm^{-1}) support the presence of a furan-2-one moiety[4a] as well as allow a preliminary distinction between *E*- and *Z*-configuration : Based on the C_{2h} -symmetry of *E*-**4** only one carbonyl absorption band is expected for the lactone moiety, while due to the C_{2v} -symmetry of *Z*-**4** the symmetrical and anti-symmetrical C=O vibration should be active thus leading to two absorptions.[9] The IR-spectrum of **4a** in $CHCl_3$ clearly exhibits one sharp band only at 1775 cm^{-1} . The highly symmetrical nature of **4** also became evident from the ^{13}C NMR spectra : Three signals only appear in the down-field region : δ = 159.2, 163.8 and 189.6 (C-5, C-2, benzoyl-C , **4a**); 160.1, 163.4 and 164.1 ppm (ester-C, C-2, C-5, **4b**). However, final and unambiguous structural confirmation was achieved from an X-ray analysis of **4a** (see Figure 1). As expected, the two furan-2-one rings are nearly within one plane, the bond lenghts of the chromophor O=C-C=C-C=O show no distinct deviations from normal values.

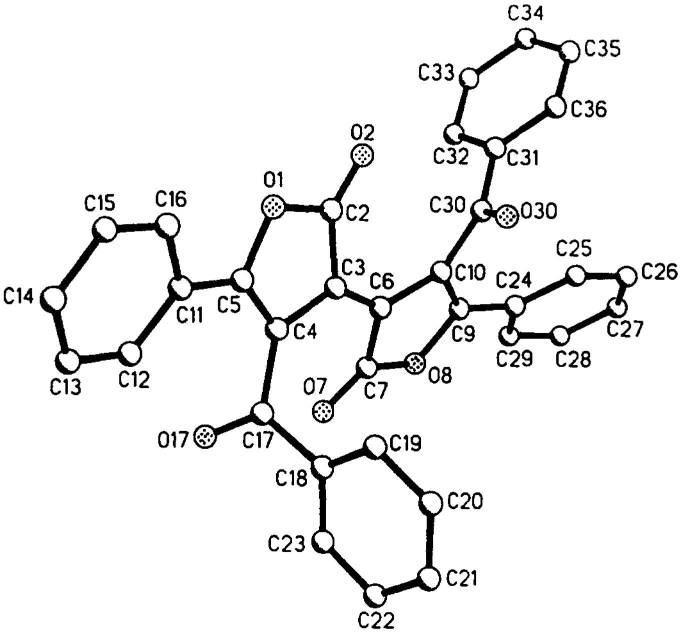


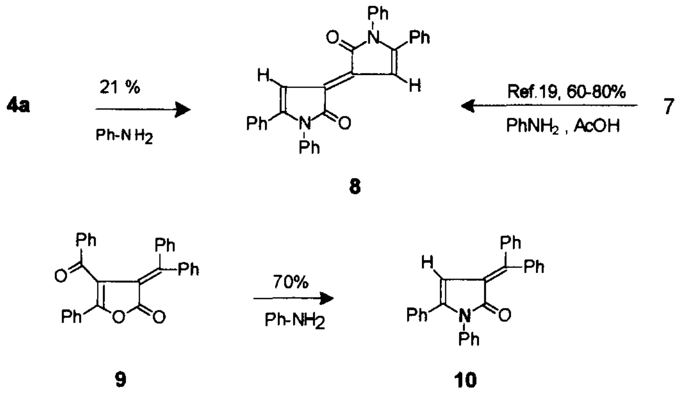
Figure 1. Perspective drawing of the molecule **4a** without H atoms. White and dotted circles represent carbon and oxygen atoms, respectively.

A close structural similarity of the bis-furanones **4** with the long known Pechmann dyes [10] (**7**) is obvious. This analogy in particular is also nicely documented by comparing the UV/VIS-spectra of **4** and **7** (Ar = Ph), selecting the λ_{max}- values (nm) in the visual region only : **4a** ($CHCl_3$) : 518 (lgε 4.36), 545 (lgε 4.33); **4b** ($CHCl_3$) : 508 (lgε 4.45), 540 (lgε 4.30); **7** (Ar=Ph): 502, 538 (no lgε values given).[10c] In acetone, the two maxima indicated are overlapping, e.g. λ_{max} = 545 nm (**4a**) appears as shoulder only.

A reasonable proposal for the reaction pathway from the furandiones **1** to the isoxoindigo dyes **4** is outlined briefly in Scheme 1. Primary sulfurization should lead to the intermediate **2**, its dimerization to the dithietane derivative **3** followed by extrusion of sulfur finally affords the bis-furanones **4**. There were few examples of similar olefination reactions reported, running either via thiono intermediates [11] or starting directly from thiocarbonyls.[12] Furthermore, instead of dithietane[12a] intermediates also thiiranes[12b] have been discussed.

While examining the melting point of **4a** an uncommon behaviour has been observed : At about 260°C the dark crystals in the solid state brighten up into pale red ones before finally melting above 360°C. This obviously indicates an unusual thermal rearrangement. When repeated in a more preparative scale, the rearranged compound **6** was obtained in 85% yield. The results of analytical and spectroscopic investigation clearly revealed **6** as an isomer of **4a** representing a pyrano[4,3-c]pyrane skeleton : The IR absorption of the lactone moiety shifted from 1775 (five-membered ring) to 1740 cm^{-1} (six-membered ring), the signals of the low-field carbons in the ^{13}C NMR spectrum appear at 158.4, 159.8 (C- 1,C-5,C-3,C-7) and 193.3 ppm (PhCO). The change in colour (**4a** : deep red , **6** : bright yellow) is reflected in a dramatic hypsochromic shift of the λ_{max} -value from 545 nm to 407 nm (lgε 4.3). From all those data a thermally initiated *E Z* isomerization *E* - **4a** into *Z*-**4a** seems unlikely or can be excluded, respectively, although some examples of thermally[13] or photochemically[13b,14] effected *E/Z*-isomerization of similar isoindigoide systems are known. Furthermore, Pechmann dyes themselves are also reported to rearrange into the pyrano-pyrane system by heating, exhibiting a similar change of colour

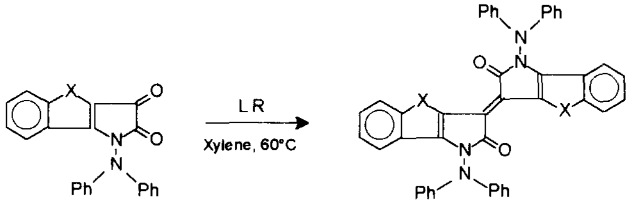
(deep red into yellow-orange)[15] and, recently, the thermal isomerization of indigo at 460°C in the gas phase into dibenzonaphthyridindione was also found.[16] Further experimental proof came from alkaline hydrolysis of **4a** affording an unstable fumaric acid derivative **5** which on heating with acetanhydride recyclized to yield a mixture of **4a** and **6**, respectively, which was unambiguously detected from TLC due to their corresponding R_f-values and characteristical colour : **4a** (purple), **6** (yellow). Due to the benzoylic side-chains **5** obviously has two options on recyclization. A quite similar behaviour was reported from the Pechmann dye (**7**) itself as well as the benzo-analogue isooxindigo[17] : Alkaline hydrolysis of e.g. the bis-furanone **7** gave the corresponding diphenacyl fumaric acid , which re-lactonisized on acidification to the yellow pyrano-pyrane compound, analogous to **6**.[10b,c] The structure of **6** as pyrano[4,3-c]pyrane rather than *Z*-**4a** is further corroborated by comparing the experimental UV/VIS-spectra with those calculated by quantum chemical methods[18] for the possible structures *E*-**4a**, *Z*-**4a** and **6**. The results are 22300, 22100 and 24700 cm^{-1} (*E*-**4a**, *Z*-**4a**, **6**, respectively) to be compared with the experimental values of 19300 (*E*-**4a**) and 24600 cm^{-1} (**6**). Thus, the large hypsochromic shift observed for **6** can only be obtained by the calculation if the pyrano[4,3-c]pyrane structure is assumed. Both, the structure of the transition state as well as the calculated activation energy (570 $kJ.mol^{-1}$) closely resemble those obtained for the related thermal isomerization of indigo[16]. The conclusion given there, namely, proposing a stepwise mechanism for the rearrangement, therefore, should also apply for the present reaction. The conversion *E*-**4a** into **6** appears to be highly exothermic ($\Delta H_R = 90$ $kJ.mol^{-1}$).



Scheme 2

Compound **4a** when reacted in boiling aniline gave the deeply coloured bis-pyrrolone derivative **8** in low yield (21%) but acceptable purity , indicating a conversion of the furanone into the pyrrolone system accompanied by loss of the benzoyl moiety. It is interesting to note, that in spite of absence of the benzoyl group the λ_{max} value in the UV/VIS spectrum of **8** (565 nm) is found at longer wave-length than with **4a**, but this agrees well with the specific position of the benzoyl group in **4a** (perpendicular to the bis-furanone system) as found from the X-ray study. From such a steric arrangement a minor effect on the UV/VIS spectrum would only be expected . The bis-pyrrolone **8** was found to be identical with a compound obtained by Treibs et al.[19] from a similar reaction of the Pechmann dye **7** with aniline, but isolated as dihydrate only (spectroscopic and analytical details see Experimental Section). Transformation of lactones into lactams is a well known procedure[20], formation of comparable pyrrolones from the corresponding furanones - running via isolable open-chain intermediates - has also been described.[21] A similar conversion and debenzoylation reaction has been observed starting with furanone **9**, made via [2+2] cycloaddition of **1** and diphenylketene [4a], affording pyrrolone **10**. This deacylation process in basic medium (aniline) observed during the reactions **4a** to **8** and **9** to **10**, respectively, probably proceeding via open-chain intermediates, could be regarded as *retro*-Claisen reaction.[22]

B. Extending the reaction of furandione **1** with Lawesson reagent to fused pyrrol-2,3-diones **11**, prepared from cyclocondensation reactions of the corresponding hydrazones and oxalyl dichloride [23], similar results were obtained : Instead of the expected sulfurized products again deeply blue coloured isoindigoide dyes **12** could be isolated through column chromatography (silicagel Merck 60 G, eluent $CHCl_3$) in moderate yields (30-45%), their formation should again follow the reaction pathway outlined briefly in Scheme 1 :



11 **12**

11, 12	X
a	CH_2
b	$(CH_2)_2$
c	$(CH_2)_3$

Scheme 3

The analogy of compounds 12 a-c first of all can be deduced from nearly identical UV/VIS spectra (Figure 2), their C_{2h}-symmetry is reflected by the ^{13}C NMR spectrum of 12b as an example, exhibiting one set of signals only for half of the molecule : 168.7 (s, C-2), 144.9 (t, quart. N-phenyl C), 143.7 (m, C-9b), 117.9 (t, C-3a); C-3 could not be identified due to severe signal overlap.

Compounds **12** obviously firmly keep water molecules which is reflected by some deviations in the elemental analyses (see Experimental Part). This behaviour was also observed by Treibs et al.[19] with similar isoindigoide dyes. In contrast to **4** thermolysis of **12** does not afford any isomerized products, neither condensed analogues of **6**, nor aza-propellanes via thermal Fischer - indolization as originally expected.[23] In general, similar enedioxo moieties as found with **4** and **12** connected to heteroatoms O, S or N serve as chromophors in several natural isoindigoide systems, e.g. violacein and analogues[24] and trikendiol[25], as well as synthetic ones.[26]

C. α-Methylene-γ-lactone ring containing natural products have found strong interest due to the unusual variety of their biological activities[27] which also led to a considerable number of synthetic approaches.[28] Among those the Wittig olefination methodology[29] applied to furan-2,3-diones gave contradictory results : while benzofuran-2,3-diones and phosphorus ylides afforded the corresponding 2- or 3-ylidenefuranones[30], with monocyclic furan-2,3-diones phosphoranylidene-cyclopentendiones were formed.[31] When furan-2,3-dione **1a** was treated with methylenetriphenylphosphorane, following the procedures given by Näf et al.[32] and Anderson and Henrick [33],

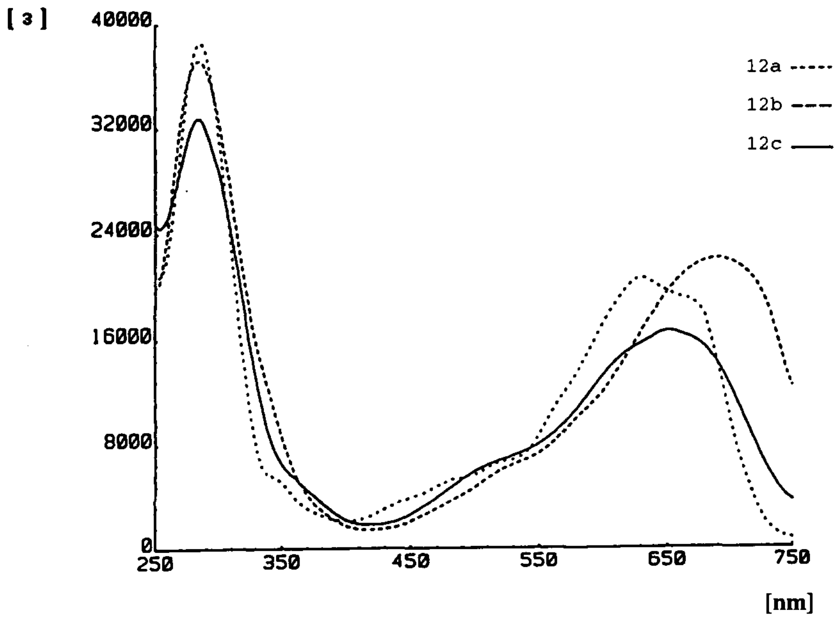
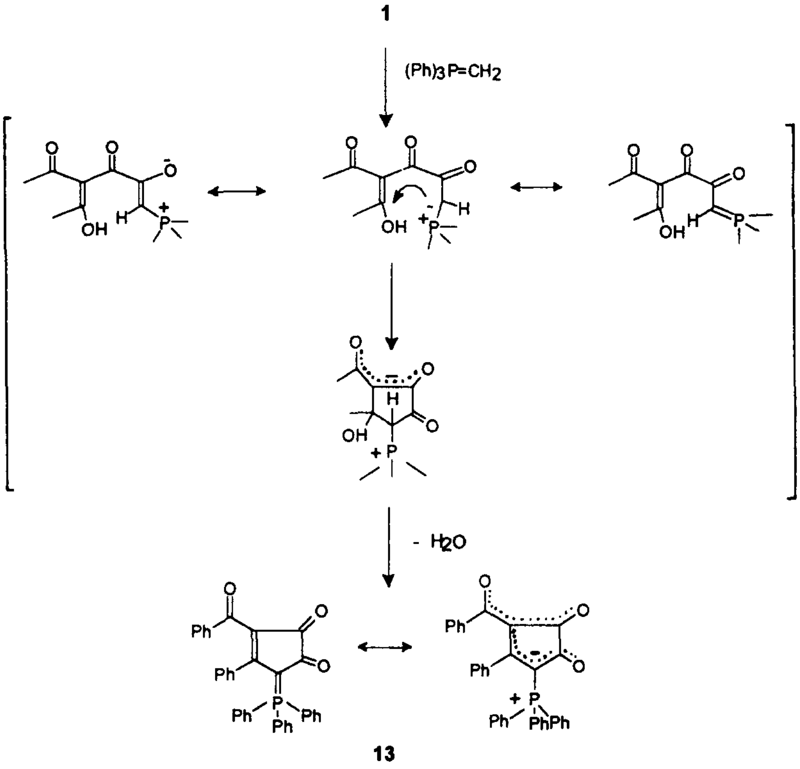


Figure 2 . UV/VIS spectra of **12** in methanol.

respectively, very dark violet crystals (λ_{max} 557 nm, lgϵ 3.67) were obtained, from analytical and spectroscopic investigations and - finally - an X-ray study, unambiguously identified as 4-benzoyl-5-phenyl-1-triphenylphosphoranylidene-4-cyclopentene-2,3-dione **13** (Scheme 4). It is interesting to note, that the X-ray analysis of **13** is one of the very rare examples for cyclic phosphorus ylides. In the IR spectrum the carbonyl absorptions are found at 1700, 1660 and 1600 cm^{-1} , the ^{13}C NMR spectrum exhibits significant signals ($CDCl_3$) at 191 (dt, $^2J_{PC}$ = 5Hz, C-5), 188 (t, benzoyl-C), 185.5 (d, $^3J_{PC}$= 3Hz, C-3), 184 (d, $^2J_{PC}$= 6.5Hz, C-2), 114 (d, $^3J_{PC}$= 2Hz, C-4), 74 ppm (d, J_{PC}= 115Hz, C-1). The chemical shift values as well as P-C coupling constants are in good agreement with corresponding data reported for some open-chain and cyclic acylalkylenetriphenylphosphoranes[34] In the ^{31}P NMR spectrum ($CDCl_3$, reference to H_3PO_4) the P-atom appears at 8 ppm.

The length of the exocyclic P-C bond (175.8 pm) lies slightly out of the usual range for P=C-systems (165 - 175 pm) given by Bart in 1969 [35], this could be explained by intense conjugation with C=O and the cross conjugated C=C-C=O moiety in **13** . In fact, it is very similar to values found for several conjugated ylides[36] and, furthermore, it is settled in between the numbers reported for three cyclic phosphoranylidenes (177 pm[37a] , 173.8[37b] and 172.8 pm[38] , respectively). However, P-C single bonds in C=O-conjugated triphenylphosphoranylidenes have been found up to 184 pm in length.[39] Summarizing these experimental findings it can be estimated, that the P=C form contributes to a rather high extent in resonance stabilization of the novel cyclic ylide **13**. The formation of **13** can be regarded as some kind of *transylidation* [40] that is transformation of methylenetriphenylphosphorane into the cyclic acylidenetriphenylphosphorane **13**, possibly running via resonance stabilized open-chain intermediates followed by recyclization with elimination of water as briefly outlined in Scheme 4.



Scheme 4

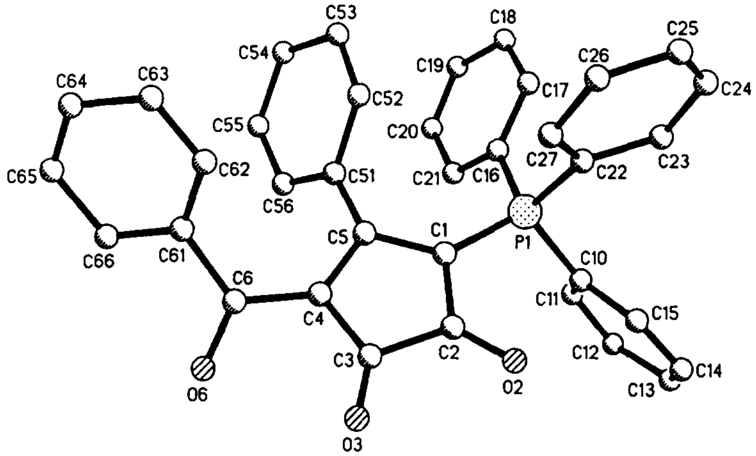


Figure 3. Perspective drawing of the molecule **13** without H atoms. Hatched circles represent oxygen atoms, the dotted circle the phosphorus atom.

EXPERIMENTAL

4-Benzoyl-3-(4-benzoyl-5-phenyl-2(3H)-furanon-3-ylidene)-5-phenyl-2(3H)-furanone (**4a**). 0.56g (2 mmol) of **1a** and 0.45g (1.1 mmol) Lawesson reagent are stirred in 5 ml of dry xylene at 60-70°C for 2 h. By cooling to 20°C a black product precipitates which is recrystallized from acetic acid thus affording brilliant black crystals (0.21g, 40%), mp 260-65°C (brightening), above 360°C (see text p. 2); IR(KBr, $CHCl_3$), UV/VIS see text ; ^{13}C NMR ($CDCl_3$): δ= 189.6 (t, PhC=O), 163.0 (s, C-2), 159.3 (t, C-5), 137.6, 133.4, 132.4, 129.0, 128.0, 126..2; 118.2 . MS (80 eV): m/z 524 (M^{+}, 100), 496 (11). Anal. Calcd. for $C_{34}H_{20}O_6$: C, 77.85; H, 3.85. Found: C, 77.57; H, 3.84%.

4-Ethoxycarbonyl-3-(4-ethoxycarbonyl-5-phenyl-2(3H)-furanon-3-ylidene)-5-phenyl-2(3H)-furanone (**4b**). 0.6g of **1b** and 0.5g of *Lawesson*-reagent react in 10ml of dry xylene at 60-70°C for 2 h. After cooling to room temp. the bright red precipitate is separated by suction and recrystallized from xylene to give 0.26 g red crystals (46%) of **4b**. mp 252-253°C. IR(KBr):1780, 1730 cm^{-1}; UV/VIS see text ; ^{1}H NMR($CDCl_3$): δ= 8.0-7.6 (aromat), 4.4 (qu,OCH_2), 1.3 (t, CH_3); ^{13}C NMR($CDCl_3$): δ= 164.0, 163.4, 160.1 (ester-CO, C-2, C-5), 133.0, 129.0, 128.8, 126.7, 126.2, 113.8, 62.3, 14.1. Anal. Calcd. for $C_{26}H_{20}O_8$: C, 67.82; H, 4.37. Found: C, 68.00; H, 4.38.

4,8-Dibenzoyl-1,5-dioxo-3,7-diphenyl-pyrano[4,3-c]pyrane (**6**). a) 50mg **4a** are heated to 260-270°C for 20 min whilst the colour of the solid changes from black to orange.. Recrystallization from chlorobenzene or dimethylformamide gives 40mg (80%) of **6**, mp above 360°C. IR(KBr): 1740, 1680 cm^{-1} (C=O); UV/VIS see text. ^{13}C NMR (DMSO-d_6): 193.3 (PhC=O), 159.8 158.4 (C-1,C-5,C-3,C-7), 138.9, 135.6, 132.8, 132,6, 130.9, 130.6, 130.5, 130.1, 129.35, 116.5. Anal. Calcd. for $C_{34}H_{20}O_6$: C, 77.85; H, 3.85. Found: C, 77.84; H, 4.01.

Alkaline Hydrolysis and Ring Closure of **4a.**[13c] 0.21g of **4a** and 1.4 ml of ethanolic KOH (10%) were stirred at reflux for 30 min thus forming a flocky orange precipitate. After cooling to room temperature water was added until a clear yellow solution was obtained. Acidification with diluted HCl afforded a yellow, highly instable precipitate (0.2g, 90%) which by no means could be further purified . In accordance with literature[13c] the structure of an open-chain fumaric acid derivative **5** was assigned to that crude product [IR(KBr): 3600-3200, 1760, 1700 cm^{-1}]. After refluxing of **5** in 3.5 ml of acetic anhydride for 1 h, evaporation to dryness and triturating with ether, 0.1 g of an orange-red product were isolated. From the R_f-values and characteristical colours on TLC (solvent : toluene/acetone 9:1) this product was unambiguously identified as a mixture of **4a** (purple) and **6** (yellow).

1,5-Diphenyl-3-(1,5-diphenyl-2(3H)-pyrrolon-3-ylidene)-2(3H)-pyrrolone (**8**).[19] 0.52g (1 mmol) of **4a** are refluxed in 4 ml of aniline for 2 h. After cooling ether is added to precipitate a dark product which then is purified via column chromatography (10g of silica gel 60 (0.06-0.2 mm), eluent $CHCl_3$) to yield 0.1g (21%) of dark-violet crystals, mp 290°C (lit.[19] : 310°C , as dihydrate). IR(KBr): 1690 cm^{-1} (C=O); UV/VIS ($CHCl_3$): λ_{max} = 565 nm (lgϵ 4.32); MS (70eV): m/z 466 (M^{+}, 100), 437 (6), 409 (5), 180 (48), 77 (67). Anal. Calcd. for $C_{32}H_{22}N_2O_2$: C, 82.38; H 4.76; N, 6.01. Found: C, 82.19; H, 5.35; N, 5.44.

3-Diphenylmethylene-1,5-diphenyl-2(3H)-pyrrolone (**10**). 0.21g (0.5 mmole) of furanone **9** [4a] and 5 ml of aniline reflux for 2 h. The excess of aniline is removed by water steam distillation, the residue is triturated with ether affording a crude product which is recrystallized from acetic acid. Yield 0.14g (70%) of thin orange needles, mp 243-245°C. IR(KBr): 1705 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$): δ= 6.1 (s, =CH), 7.1-7.5 (m, aromat); MS (70ev): m/z 399 (M^+, 100), 370 (12), 180(77), 93(53), 77(95). Anal. Calcd. for $C_{29}H_{21}NO$: C, 87.18; H, 5.31; N, 3.51. Found: C, 87.08; H, 5.28; N, 3.33.

Synthesis of isoindigoide Dyes 12 - General Procedure. 1.0 mmole of the corresponding pyrroldione **11**[23] and 0.2g of Lawesson reagent were kept at 60°C in dry xylene for 2 h (with **11a** for 20 min only). After removal of the solvent in vacuo the dark-blue residue is dissolved (or suspended) in $CHCl_3$ and purified on column chromatography (silica gel 60 G (30g), eluent $CHCl_3$).

1,1'-Bis-diphenylamino-1,4,1',4'-tetrahydro-[3,3']bi[indeno[1,2-b]pyrrolyliden]-2,2'-dione (**12a**). From 0.4g **11a** 0.225g (33%) **12a** are obtained as deep-blue powder, mp 190°C (deg.). IR(KBr): 1700, 1585 cm^{-1}; UV/VIS see Figure 2. Anal.Calcd. for $C_{46}H_{32}N_4O_2$: C, 82.11; H, 4.80; N 8.32. Found: C, 81.53; H, 4.85; N, 8.13.

1,1'-Bis-diphenylamino-4,5,4',5'-tetrahydro-1H,1'H-[3,3']bi[naphtho[1,2-b]pyrrolyliden]-2,2'-dione (**12b**). From 0.37g **11b** 0.25g (35%) of **12b** are isolated, mp 153°C. IR(KBr): 1695 ,1590 cm^{-1} ; UV/VIS see Figure 2; ^{13}C NMR see text. Anal. Calcd. for $C_{48}H_{36}N_4O_2$: C, 82.29; H, 5.14; N, 8.00. Found: C, 81.53; H, 5.16; N, 7.60

1,1'-Bis-diphenylamino-1,4,5,6,1',4',5',6'-octahydro-[3,3']-di[benzo[6,7]cyclohepta[1,2-b]pyrrolyliden]-2,2'-dione (**12c**). 0.4g **11c** give 0.35g (46%) of **12c** , mp 165°C. IR(KBr): 1690, 1585 cm^{-1}; UV/VIS see Figure 2. Anal.Calcd. for $C_{50}H_{40}N_4O_2$: C, 82.38; H, 5.54; N, 7.68. Found: C, 81.80; H, 5.98; N, 7.31.

4-Benzoyl-5-phenyl-1-triphenylphosphoranylidene-4-cyclopentene-2,3-dione (**13**). [32,33] 0.55ml n-Butyllithium (2N solution in hexane) is added to 0.39g (1.1 mmol) methyltriphenylphosphonium bromide suspended in 10ml of dry ether under heavy stirring. After 3.5h a suspension of 0.2g **1** in dry ether is added and the reaction mixture is kept for 24h at 20°C. Then the mixture is decomposed by addition of 20 ml of water and extracted by chloroform. The organic layer is dried with sodium sulfate overnight and the product isolated with aid of flash chromatography (silicagel 60H, eluent acetone/$CHCl_3$ = 1:2). The crude **13** is recrystallized from dichloromethane/methanol yielding deep violet crystals (0.25g, 65%), mp 270°C. IR(KBr): 1700, 1660, 1600, 1380 cm^{-1}; UV/VIS ($CHCl_3$): λ_{max} = 555nm (lgε 3.67); ^{13}C and ^{31}P NMR see text. Anal. Calcd. for $C_{36}H_{25}PO_3$: C, 80.59; H, 4.66. Found: C, 80.15; H, 4.88.

Table 1. Crystal parameters for the X-ray diffraction study [46] of compounds **4a** and **13**

Compound	**4a**	**13**
formula	$C_{34}H_{20}O_6$	$C_{36}H_{25}O_3P$
molecular mass	524.53	536.57
a [pm]	1094.1(2)	1594.7(7)
b [pm]	1099.2(1)	1493.4(9)
c [pm]	1197.9(2)	1121.9(5)
α[deg]	86.64(1)	
β[deg]	73.19(1)	
γ[deg]	68.52(1)	
V[pm^3]	1281.6(4).10^6	2672(2).10^6
Z	2	4
d(calc.)[g.cm^{-3}]	1.359	1.334
crystal system	triclinic	orthorhombic
space group	P1	Pna2_1
diffractometer	Siemens P4	Siemens R3m/V
radiation	Mo*K*α	Mo*K*α
monochromator	graphite	graphite
crystal size [mm]	0.4x0.75x0.05	0.75x1.1x0.5
data collection mode	ω-scan	Wyckoff-scan
theta range[deg]	1.75 - 27.5	1.75 - 27.5
recip.latt.segment	h= 0 - 14	h = 0 - 22
	k = -14 - 14	k = 0 - 21
	l = -14 - 15	l = 0 - 15
no.refl.measd.	6196	4395
no.unique refl.	5886	4100
no. refl.F $> 3\sigma(F)$	3357	3535
lin.abs.coeff.[mm^{-1}]	0.09	0.13
abs.correction	ψ-scan	ψ-scan
solution by	direct phase determination	direct phase determination

method of refinement	Full-Matrix LSQ. Hydrogen positions of riding model with fixed isotropic U	Full-Matrix LSQ. Hydrogen positions of riding model with fixed isotropic U
data-to-parameter ratio	9.85	9.79
R, R_w	0.066, 0.062	0.047, 0.037
weighting scheme	$w = 1/\sigma^2(F)$	
largest difference peak	0.24 eÅ^{-3}	
largest difference hole	0.22 eÅ^{-3}	
program used	Siemens SHELXTL PLUS	

REFERENCES

Dedicated with best wishes to Prof.Dr.Miha Tisler, University of Ljubljana, Slovenia, on the occasion of his 70th birthday.

1. Part 37: Kappe, C. O.; Terpetschnig, E.; Penn, G.; Kollenz, G.; Peters, K.; Peters, E.-M.; von Schnering, H.G. *Liebigs Ann. Chem.* **1995**, 537 - 543.
2. Reviews and selected Papers : a) Kollenz, G.; Heilmayer, W. Furan-2,3-diones - Versatile Synthons in Heterocyclic Chemistry. In *Trends in Heterocyclic Chemistry;* Research Trends, Eds.; Trivandrum, India, 1993 , Vol.3, pp.379 - 395.

   b) Andreichikov, Yu. *On the Chemistry of Five-membered 2,3-Dioxoheterocycles.* University of Perm, Russia, 1994, pp.5 - 210.

   c) Sano, T.; AMano, K.; Seki, M.; Hirota, H.; Toda, J.; Kiuchi, F.; Tsuda, Y. *Heterocycles* **1994** (37), 523 - 539. (Part 57 from the series : Dioxopyrrolines).
3. Recent Review: Wentrup, C.; Heilmayer, W.; Kollenz, G. *Synthesis* **1994** (Special Issue), 1219 - 1248.
4. Selected Papers: a) Terpetschnig, E.; Penn, G.; Kollenz, G.; Peters, K.; Peters, E.-M.; von Schnering, H.G. *Tetrahedron* **1991,** 47, 3045 - 3058.

   b) Kollenz, G.; Penn, G.; Ott, W.; Peters, K.; Peters, E.-M.; von Schnering, H.G. *Chem. Ber.* **1984,** 117, 1310 - 1329 and *Heterocycles* **1987,** 26, 625 - 631.
5. Selected Papers: a) Juhasz-Riedl, Zs.; Hajos, G.; Kollenz, G.; Messmer, A.; *Chem. Ber.* **1989,** 122, 1935 - 1938.

   b) Akcamur, Y.; Altural, B.; Saripinar, E.; Kollenz, G.; Kappe, C. O.; Peters, K.; Peters,E.M..; von Schnering, H.G. *J. Heterocycl. Chem.* **1988,** 25, 1419 - 1422.
6. a) Kollenz, G.; Sterk, H.; Hutter, G. *J. Org. Chem.* **1991,** 56, 235 - 239.

b) Heilmayer, W.; Kappe, C. O.; Sterk, H.; Kollenz, G.; Peters, K.; Peters, E.-M.; von Schnering, H. G.; Walz, L. *Chem. Ber.* **1992,** 126, 2061 - 2067.

c) Kollenz, G.; Ott, W.; Ziegler, E.; Peters, K.; von Schnering, H. G.; Formacek, V.; Quast, H. *Liebigs Ann. Chem.* **1984,** 1137 - 1164.

7. a) Pedersen, B. S.; Scheibye, S.; Nilsson, N. H.; Lawesson, S. O. *Bull. Soc. Chim. Belg.* **1978,** 87, 223 - 228.

   b) Scheibye, S.; Shabana, R.; Lawesson, S. O.; Romming, C. *Tetrahedron* **1982,** 38, 993 - 1001.

8. Review : Maercker, A. The Wittig-Reaction. In *Organic Reactions* **1965,** 14, pp.270 - 490.

9. a) Fadini, A.; Schnepel F.M. *Schwingungsspektroskopie - Methoden und Anwendungen;* Thieme Verlag: Stuttgart-New York, **1985,** p. 105.

   b) Jaffe', H.; Orchin, M. *Symmetrie in der Chemie;* A. Hüthig Verlag: Heidelberg, **1967,** p.161.

10. a) von Pechmann, H. *Ber. Dtsch. Chem. Ges.* **1882,** 15, 881 - 892.

    b) Chen Shang Fang; Bergmann, W. *J. Org. Chem.* **1951,** 16, 1231 - 1237.

    c) Review : Klingsberg, E. *Chem. Rev.* **1954,** 54, 59 - 77.

11. El-Kateb, A. A.; Hennawy, I. T.; Shabana, R.; Osman, F. H. *Phosph. Sulfur* **1984,** 20, 329 - 332.

12. a) Campaigne, E.; Reid, W.B. *J. Am. Chem. Soc.* **1946,** 68, 769 - 770.

    b) Klein, O. In *Methoden der Organischen Chemie;* Houben-Weyl-Müller, Eds.; Thieme Verlag: Stuttgart **1972,** Bd. V/1b, p. 418.

    c) Detty, M. R.; Murray, B. J. *J. Org. Chem.* **1982,** 47, 1146 - 1148.

13. a) Vyas, K.; Manohar, H. *J. Chem. Soc. Perkin Trans 2,* **1990,** 1177 - 1180.

    b) Pawlik, A.; Grahn, W.; Reisner, A.; Jones P.G.; Ludger, E. *Angew.Chem.* **1994** , 106, 2058 - 2061; *Angew. Chem. Int.Ed.Engl.* **1994,** 33, 1958 - 1961.

    c) Bogert, M. T.; Ritter, J. J. *J. Am. Chem. Soc.* **1924,** 46, 2871 - 2879.

14. Irie, M.; Kato, M. *J. Am. Chem. Soc.* **1985,** 107, 1024 - 1028.

15. a) Bowden, K.; Etemadi, R.; Ranson, R. R. *J. Chem. Soc. Perkin Trans 2,* **1991,** 743 - 746.

    b) Merkel, H.; Kern, E. GP 1,052,017 **(1959);** *Chem. Abstr.* **1961,** 55, 24046.

16. Haucke, G.; Graneß, G. *Angew. Chem.* **1995,** 107, 116 - 117; *Angew. Chem. Int. Ed. Engl.* **1995,** 34, 67 - 68.

17. a) Chovin, P.; *Bull. Soc. Chim. Fr.* **1944,** 11, 82 - 90.

    b) Chatterjea, J. N.; *J. Ind. Chem. Soc.* **1959,** 36, 69 - 75.

18. Molecular geometries were optimized by the VAMP program package[41] using the AM1 hamiltonian.[42] Electronic excitation energies were calculated by INDO/1[43] using the ZINDO-program package.[44] The solvent effect on UV/VIS spectra was estimated by the SCRF-method.[45]

19. Treibs, A.; Jacob, K.; Dietl, A. *Liebigs Ann. Chem.* **1967,** 702, 112 - 130.

20. Schnell, H.; Nentwig, J.; Wieland, Th. In *Methoden der Organischen Chemie,* Houben-Weyl-Müller, eds.; Thieme Verlag: Stuttgart **1958,** Bd. XI/2, p.539.

21. a) Filler, R.; Hebron, L. H. *J. Am. Chem. Soc.* **1959,** 81, 391 - 393.

    b) Filler, R.; Leipold, H. *J. Org. Chem.* **1962,** 27, 4440 - 4443.

    c) Awad, W. J.; Omran, S. M. A.; Hashem, A. I. *J. Chem. U. A. R.* **1967,** 287 - 300; *Chem. Abstr.* **1968,** 69, 86677.

22. For similar debenzoylation reactions see: a) Ziegler, E.; Kollenz, G.; Ott, W. *Synthesis* **1973,** 679 - 680.

    b) Kollenz, G.; Ziegler, E.; Ott, W.; Igel, H. *Z.Naturforschg.* **1976,** 31b, 1511 - 1514.

23. a) Kollenz, G. *Monatsh. Chem.* **1978,** 109, 249 - 257.
    b) Kollenz, G.; Theuer, R.; Ott, W.; Peters, K.; Peters, E.-M.; von Schnering, H. G. *Heterocycles* **1988,** 27, 479 - 494.
24. a) Laatsch, H.; Thomson, R. H.; Cox, P. J. *J. Chem. Soc. Perkin Trans 2,* **1984,** 8, 1331 - 1339.
    b) Katritzky, A. R.; Caster, K. C.; Rubio, O.; Schwarz, O. *J. Heterocycl. Chem.* **1986,** 23, 1315 - 1325.
25. Loukaci, A.; Guyot, M. *Tetrahedron Lett.* **1994,** 35, 6869 - 6872.
26. a) Yoshida, K.; Yamanaka, Y.; Ueno, Y. *Chem. Lett.* **1994,** 11, 2051 - 2054.
    b) Gompper, R.; Kellner, R.; Polborn, K. *Angew. Chem.* **1992,** 104, 1222 - 1225; *Angew. Chem. Int. Ed. Engl.* **1992,** 31, 1202 - 1205.
    c) Gompper, R.; Hartmann, K.; Polborn, K. *Tetrahedron Lett.* **1994,** 35, 9195 - 9196.
27. Review : Hoffmann, H. M. R.; Rabe, J. *Angew. Chem.* **1985,** 97, 96 - 112; *Angew. Chem. Int. Ed. Engl.* **1985,** 24, 94 - 100.
28. Review: Grieco, P. A., *Synthesis* **1975,** 67 - 82.
29. Wittig, G.; Geißler, G. *Liebigs Ann. Chem.* **1953,** 580, 44 - 57.
30. Takeuchi, Y.; CHoshi, T.; Tomozane, H.; Yoshida, H.; Yamato, M. *Chem. Pharm. Bull.* **1990,** 38, 2265 - 2267.
31. a) Andreichikov, Yu. S.; Kozminykh, E. N.; Kozminykh, V. O. *Zh. Obshch. Khim* **1985,** 55, 1653 - 1654.
    b) Kozminykh, V. O.; Igidov, N. M.; Kozminykh, E. N.; Berezina, E. S. *Phosphor, Sulfur and Silicon* **1993,** 81, 191 - 197.
    c) Capuano, L.; Triesch, T.; Willmes, A. *Chem. Ber.* **1983,** 116, 3767 - 3773.
32. Näf, F.; Decorzant, R.; Thommen, W.; Willhalm, B.; Ohloff, G. *Helv. Chim. Acta* **1975,** 58, 1016 - 1037.
33. Anderson, R. J.; Henrick, C. A. *J. Am. Chem. Soc.* **1975,** 97, 4327 - 4334.
34. a) Gray, G. A. *J. Am. Chem. Soc.* **1973,** 95, 7736 - 7742.
    b) Albright, T. A.; Gordon, M. D.; Freeman, W. J.; Schweizer, E. E. *J. Am. Chem. Soc.* **1976,** 98, 6249 - 6252.
    c) Saalfrank, R.W.; Ackermann, E.; Winkler, H.; Paul, W.; Böhme, R. *Chem. Ber.* **1980,** 113, 2950 - 2958.
35. Bart, J. C. J. *J. Chem. Soc. B* **1969,** 350 - 365.
36. Stephens, F. S. *J. Chem. Soc.* **1965,** 5640 - 5650; 5658 - 5678.
37. a) Bailey, A. S.; Peach, J. M.; Cameron, T. S.; Prout, C. K. *J. Chem. Soc. C* **1969,** 2295 - 2298.
    b) Capuano, L.; Drescher, S.; Huch, V. *Liebigs Ann. Chem.* **1993,** 125 - 129.
38. Kennard, O.; Motherwell, W. D. S.; Coppola, J. C. *J. Chem. Soc. C* **1971,** 2461 - 2464.
39. Antipin, M. Yu.; Kalinin, A. E.; Struchkov, Yu. T.; Aladzheva, I. M.; Mastryukova, T. A.; Kabachnik, M. I. *Zh. Strukt. Khim.* **1980,** 21, 175 - 182; **1978,** 19, 319 - 327.
40. a) Bestmann, H. J. *Angew. Chem.* **1965,** 77, 651 - 666; *Angew. Chem. Int. Ed. Engl.* **1965,** 4, 645 - 660.
    b) House, H. O.; Babad, J. *J. Org. Chem.* **1963,** 28, 90 - 92.
41. Clark, T. VAMP: Erlangen Vectorized Molecular Orbital Package, Version 4.40. Computer-Chemie Zentrum, Universität Erlangen-Nürnberg, Germany 1992.
42. Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.,* **1985,** 107, 3902 - 3909.

43. Ridley, J. E.; Zerner, M. C. *Theor. Chim. Acta* **1973,** 32, 111 - 134.
44. ZINDO, a comprehensive semiempirical quantum chemistry package: Zerner, M. C. Quantum Theory Project, University of Florida, Gainesville, FL, USA.
45. a) Tapia, O.; Goscinski, O. *Mol. Phys.* **1975,** 29, 1653 - 1661.
    b) Karelson, M.; Zerner, M. C. *J. Phys. Chem.* **1992,** 96, 6949 - 6957.
46. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-75344 Eggenstein-Leopoldshafen, on quoting the deposition number CSD-404397 for **4a** and CSD-404398 for **13**, the names of the authors and the journal citation.

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