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THE PRODUCTS DERIVED FROM THE ACID-CATALYZED DEHYDRATION OF 4-HYDROXY-2,3,4-TRIPHENYL-2-CYCLOPENTENONE

M. K. CONNER,* J. M. DUNSTON,* E. LEGOFF,† and P. YATES

Departments of Chemistry, Michigan State University, East Lansing, Michigan 48823, USA
and University of Toronto, Toronto 5, Ontario, Canada

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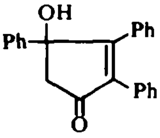
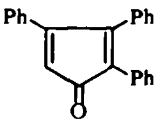
Abstract—Acid-catalyzed dehydration of 4-hydroxy-2,3,4-triphenyl-2-cyclopentenone (1) affords a mixture of dimers and a dehydrodimer of 2,3,4-triphenylcyclopentadienone (2). The structures of three of these dimers have been established as 2,3-dihydro-3,3', 4,4', 5,5'-hexaphenyl-2,2'-bis(cyclopentadienone) (3), (*E*)-3,3', 4,4', 5,5'-hexaphenyl[bi-3-cyclopentenylidene]-2,2'-dione (5), and 3a,3b,6a,10b-tetrahydro-1,2,5,6,6a-pentaphenylbenz[*e*]-*as*-indacene-3,4-dione (11). The structure of the dehydrodimer has been established as 4-hydroxy-1,2,5,6,6a-pentaphenylbenz[*e*]-*as*-indacen-3(6a*H*)-one (14). Dehydrogenation of 5 with chloranil gives 3,3',4,4',5,5'-hexaphenyl-2,2'-bis(cyclopentadienone) (7), which on thermal rearrangement gives 14.

THE acid-catalyzed dehydration of 4-hydroxy-2,3,4-triphenyl-2-cyclopentane (1) has been reported to yield a blue and yellow compound.[1,2] The blue compound was considered to be 2,3,4-triphenylcyclopentadienone (2), but no structure was assigned to the yellow compound.[2] We have found that the dehydration of 1 yields complex mixtures of products, from which we have been able to isolate in a pure state four products: red, white, blue and yellow. The last two correspond to the blue and yellow compounds previously isolated.



1



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When 1 was treated for 5 min with boiling 2% sulfuric acid in acetic acid a 35% yield of a red crystalline compound, $C_{46}H_{32}O_2$, was isolated together with a 3% yield of the blue compound. The red compound is assigned the tetrasubstituted cyclopentadienone structure 3 (Scheme 1) on the basis of its composition, spectra, and chemical transformations. The single CO-stretching bond in its IR spectrum at 1702 cm^{-1} is characteristic of both the cyclopentenone (2,3,4-triphenyl-2-cyclopentenone absorbs at 1699 cm^{-1}) and arylated cyclopentadienone rings of 3 (tetraphenylcyclopentadienone absorbs at 1704 cm^{-1}). The long wavelength band at

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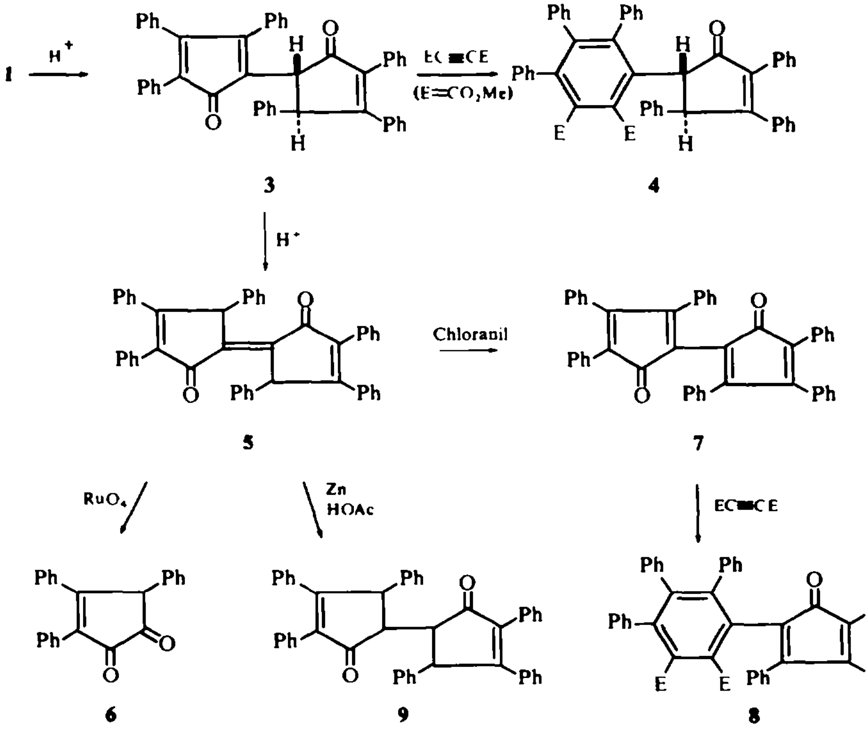
* Taken in part from the Ph.D. theses of M.K.C., Michigan State University, 1969, and J.M.D., University of Toronto, 1965.

† To whom inquiries should be addressed; presented at the International Symposium on the Chemistry of Nonbenzenoid Aromatic Compounds, Sendai, Japan, August, 1970.

490 nm (ε 1200) in its UV spectrum is also characteristic of an arylated cyclopentadienone [*cf* tetraphenylcyclopentadienone: 512 nm (ε 1320)[3]]. Its NMR spectrum has a 30-proton multiplet at τ 2·6–3·6, attributable to the phenyl protons, and a two-proton doublet of doublets at τ 4·72 and 3·61 (J = 4 Hz), attributable to the methine protons in the cyclopentenone ring; the magnitude of the coupling constant establishes that these protons are vicinal and have a *trans* relationship (*vide infra*).

As expected for a cyclopentadienone, the red compound 3 reacts with dimethyl acetylenedicarboxylate to give a colourless product, whose composition corresponds to the formation of a 1:1 adduct followed by extrusion of carbon monoxide. This product can be formulated as 4 (Scheme 1).

Treatment of 3 with hot dilute sulfuric acid or passage of a solution of 3 through alumina gives in a high yield a yellow isomer, shown to be identical with the yellow compound obtained in low yield by dehydration of 1 with sulfuric acid in acetic acid according to the method of Pauson and Williams.[2] The yellow compound is assigned structure 5 (Scheme 1) on the basis of its composition, spectra, and chemical transformations. The single CO-stretching band in its IR spectrum at 1672 cm^{-1} is in accord with the cross-conjugated dienone systems in 5, as are the long wavelength maxima in its UV spectrum at 342 (ε 13,500) and 460 nm (ε 400). Its NMR spectrum has a 30-proton multiplet at τ 2·8–3·1, attributable to the phenyl protons, and a two-proton singlet at τ 4·22, attributable to the methine protons and in accord with their situation in identical environments.

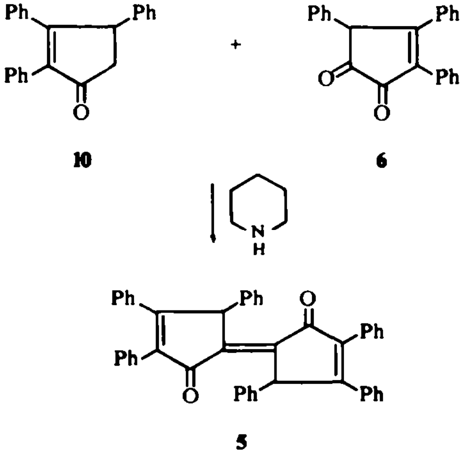


Scheme 1

Oxidation of the yellow compound with ruthenium tetroxide leads to the formation of 3,4,5-triphenyl-3-cyclopentene-1,2-dione (**6**). Dehydrogenation with chloranil gives a black crystalline compound, $C_{46}H_{30}O_2$, that is formulated as **7** (see Scheme 1), the first reported example of a bis-cyclopentadienone in which the 5-membered rings are directly joined. It shows a CO-stretching band at 1705 cm^{-1} in its IR spectrum and a maximum at 546 nm (ε 2900) in its UV spectrum in good accord with the structural formulation. On treatment with dimethyl acetylenedicarboxylate, **7** gives a red product, whose composition corresponds to **8**, derived from loss of carbon monoxide from the 1:1 adduct.

Reduction of **5** with zinc and acetic acid gives a colourless compound, $C_{46}H_{34}O_2$, formulated as **9**. Its IR spectrum with a single CO-stretching band at 1697 cm^{-1} and its UV spectrum with a maximum at 297 nm (ε 23,400), are in accord with the presence of two 2,3,4-triphenyl-2-cyclopentenone moieties [*cf* 2,3,4-trimethyl-2-cyclopentenone (10): 295 nm (ε 11,500)]. Its NMR spectrum shows a 30-proton multiplet at τ 2·7–2·95, attributable to the phenyl protons, and a four-proton doublet of doublets at τ 6·80 and 5·47 (J = 2·5 Hz), attributable to the 2 (2′) and 3 (3′) protons, respectively. The magnitude of the coupling constant establishes that the pairs of protons on each cyclopentenone ring are vicinal and have a *trans* relationship. The latter conclusion follows from consideration of the ranges of dihedral angles between the vicinal C—H bonds of a cyclopentenone ring, which indicate that the coupling constant between *cis* protons will be 6–10 Hz, while that between *trans* protons will be 2–6 Hz (*cf* the NMR spectrum of **10**, where the coupling constants between the C-4 proton and the protons at C-5 are 2·5 and 7·5 Hz). The stereochemistry of **9** is not completely defined since it is unknown whether the two cyclopentenone rings are joined in a *meso* or *dl*-fashion.

The structural assignment of **5** to the yellow compound was confirmed by its independent synthesis by base-catalyzed condensation of **10** with 3,4,5-triphenyl-3-cyclopentene-1,2-dione (**6**) (Scheme 2).

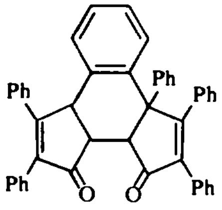


Scheme 2

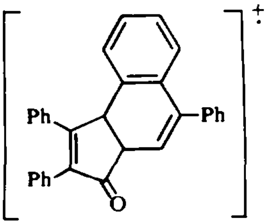
The yellow compound is expected to have the more stable of the two possible configurations about the interannular double bond, i.e., the "E" configuration[4] shown in **5**, since these should be capable of equilibration via enol formation.*

Treatment of **1** for 20 min with boiling 1·2% sulfuric acid in acetic acid gives as major products the blue compound, the yellow compound **5**, and a colourless compound, $C_{46}H_{32}O_2$, isomeric with **3** and **5**; none of the red compound **3** was isolated, but another red isomer was obtained in very low yield. The colourless compound is assigned structure **11** on the basis of its composition and spectra. Its IR spectrum has a strong band at 1700 cm^{-1} in accord with the presence of the 2,3-diphenyl-2-cyclopentenone systems. Its NMR spectrum shows, in addition to signals attributable to aromatic protons, three one-proton signals—a doublet of doublets at τ 6·04 (J = 1·5 and 7 Hz), a doublet at τ 5·63 (J = 1·5 Hz), and a doublet at τ 5·19 (J = 7 Hz) —in accord with the presence of three adjacent methine protons. The mass spectrum of the colorless compound shows in addition to the molecular ion peak (base peak) peaks with m/e 410 and 204 which can readily be assigned to ions **12** and **13** on the basis of structure **11**. Its UV spectrum shows a maximum at 293 nm (ε 11,500); although this maximum has an intensity corresponding to a single simple 2,3-diphenyl-2-cyclopentenone chromophore, it is much broader than the maximum at 295 nm spectrum of **10**; it would also be expected that steric factors would reduce the intensities of the 2,3-diphenyl-2-cyclopentenone chromophores in the spectrum of **11**.

When **7** was heated in boiling benzophenone it was transformed into an isomeric, blue compound (70%) that was identical with the blue compound obtained by



11



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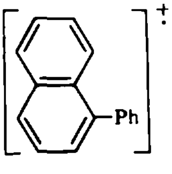

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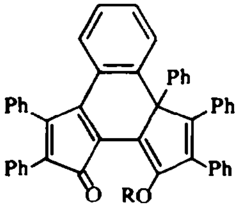
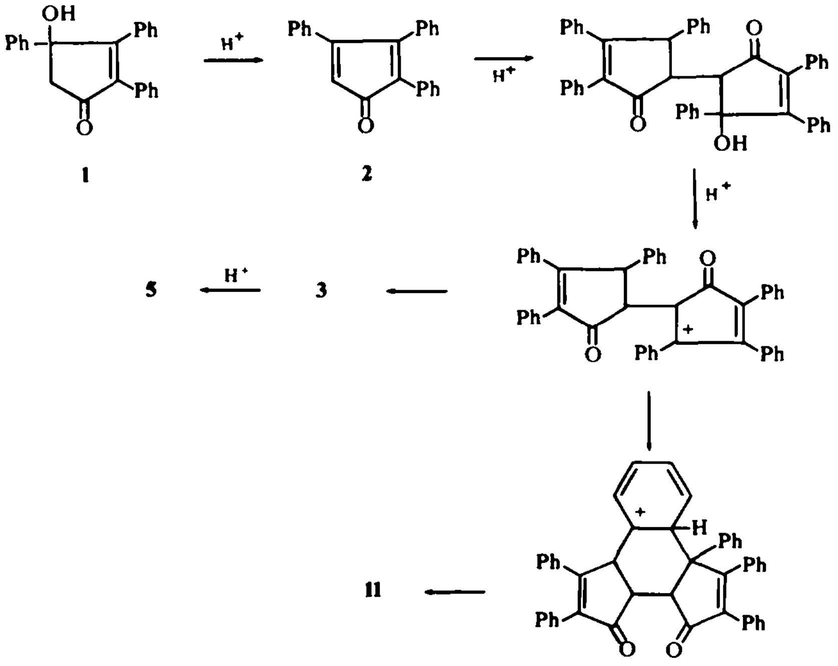
* Since the submission of this paper, Atkinson[5] has reported the independent assignment of structure **5** to the yellow compound. He subjected **5** to reduction with zinc and acetic acid under milder conditions than those used in the present work and obtained not a *trans-trans* **9**, but a *cis-cis* and a *cis-trans* isomer.

† A tentative assignment of stereochemistry may be made to **11**, *viz*, each cyclopentenone ring *cis*-fused to the six-membered ring and an *anti*-relationship between the cyclopentenone rings.

dehydration of 1. This compound was also obtained in low yield by oxidation of 11 with DDQ. The origin of the blue compound from these several sources, its spectra, and its reactions leads to its formulation as 14, rather than 2. This reformulation requires revision of the molecular formula of the blue compound to $C_{46}H_{30}O_2$; this formula was confirmed by elemental analyses of its acetate (15) and trimethylsilyl derivative (16) and the high resolution mass spectra of the latter and of its phenylhydrazone. The IR, UV and NMR spectra of 14 and 15 are in accord with the structural assignments but will not be discussed here since they have recently been discussed by Atkinson,[6] who has independently concluded that the blue compound has structure 14. The deep purple trimethylsilyl derivative 16 resembles the acetate 15 in showing a CO-stretching band in its IR spectrum at 1701 cm^{-1} and a long wavelength maximum in its UV spectrum at 522 nm (ε 5400), analogous to bands in the spectra of tetraphenylcyclopentadienone.



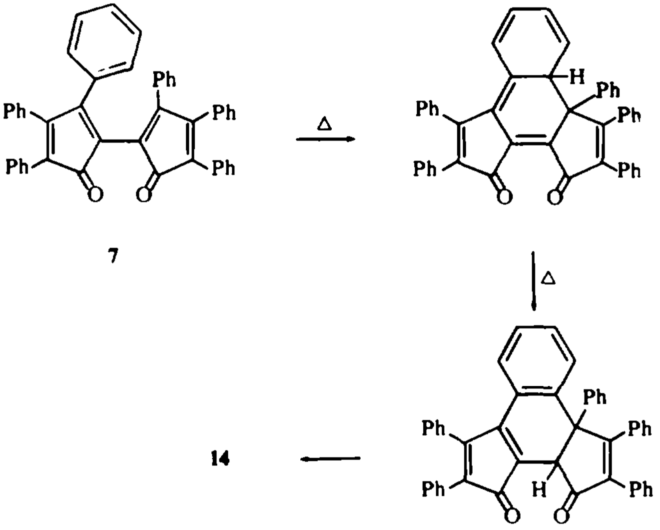
14: R = H
15: R = CH_3CO
16: R = $(CH_3)_3Si$



Scheme 3

The formation of the isomers **3**, **5** and **11** on dehydration of **1** can be interpreted in terms of the intermediacy of 2,3,4-triphenylcyclopentadienone (**2**) as shown in Scheme 3.

The thermal rearrangement of **7** to **14** can be envisaged as occurring as shown in Scheme 4. The formation of **14** during the acid-catalyzed dehydration of **1** probably involves the oxidation of either **3** or **5** to **7**, which is converted to **14** by an acid-catalyzed rearrangement analogous to that depicted in Scheme 4. Compound **11** is not converted to **14** under the conditions used for the dehydration of **1**, and thus oxidation does not occur at this stage.



Scheme 4

EXPERIMENTAL

Solns in organic solvents were dried over $MgSO_4$ unless otherwise specified. IR spectra were recorded in $CHCl_3$ soln unless otherwise specified. UV spectra were recorded in cyclohexane soln unless otherwise specified. Nmr spectra were recorded in $CDCl_3$ soln with a Varian A-60 or a Jeolco C-60H spectrometer. Mass spectra were recorded at 70 eV with a Hitashi RMU-6 or an AEIMS-902 spectrometer. Elemental analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Michigan, or Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Dehydration of 4-hydroxy-2,3,4-triphenyl-2-cyclopentenone

(i) *Formation of 2,3-dihydro-3,3′,4,4′,5,5′-hexaphenyl-2,2′-bis(cyclopentadienone* (3) *and 4-hydroxy-*1,2,5,6,6a-*pentaphenylbenz*[e]-as-*indacen*-3(6aH)-*one* (14). A soln of **1** (10·0 g; 31 mmol) in AcOH (50 ml) and H_2SO_4 (1 ml) was boiled under reflux for 5 min. The mixture was poured into water, and the solid that separated was dried and taken up in ether. The ethereal soln was filtered and evaporated to give a green solid residue, which was chromatographed on silica acid. Elution with CCl_4-benzene (5:1) gave 300 mg (3%) of the blue compound **14**. Further elution with CH_2Cl_2-benzene (5:6) gave 3·4 g (36%) of **3** which was obtained as red crystals, mp 207–209°, after recrystallization from $CHCl_3$-MeOH; ν_{max} 1702 cm^{-1}; λ_{max} (log ε) 245 (4·70), 269 (4·51), 332 (3·06), 490 nm (3·08); τ 2·6–3·6 (m, 30 H), 5·28 (d, $J = 4$ Hz, 1 H), 6·39 (d, $J = 4$ Hz, 1 H); *m/e* (rel. abund.) 616(100), 598(9), 588(13), 570(4), 539(6), 525(4), 521(3), 511(23), 510(3), 498(8), 493(4), 433(4), 308(46), 280(12), 267(12), 178(19). (Found: C, 89·47; H, 5·26. $C_{46}H_{32}O_2$ requires: C, 89·58; H, 5·23%).

(ii) Formation of (E)-3,3′,4,4′,5,5′-*hexaphenyl(bi-3-cyclopentenylidene)-2,2′-dione* (**5**), 3a,3b,6a,10b-*tetrahydro*-1,2,5,6,6a-*pentaphenylbenz*[e]-as-*indacene*-3,4-*dione* (**11**), *and* **14**. To a soln of **1** (8·25 g; 25 mmol) in AcOH (85 ml) was added H_2SO_4 (1 ml). The soln was boiled under reflux for 15 min, when a yellow solid separated on the walls of the flask. After being boiled for a further 5 min, the dark mixture was added to water, and the whole was extracted 3 times with ether. The combined blue-black ethereal extracts were washed 4 times with water, twice with $NaHCO_3$ aq, and once again with water. During the extractions yellow solid (2·00 g) remained undissolved at the phase interface in the ethereal layer and was collected by filtration of this layer. The solid was washed 4 times with ether and the washings were combined with the filtrate.

Fractional crystallization of the yellow solid from $CHCl_3$ resolved it into two compounds, each of which was purified by recrystallization from benzene. The less soluble fraction yielded **5** (600 mg) as fine, yellow needles, mp 334–335° (dec to red liquid); $\nu_{max}^{CCl_4}$ 1672 cm^{-1}, λ_{max}^{EtOH} (log ε) 271 (4·50), 363 nm (4·24) (unchanged in EtOH-1%KOH): λ_{max}(log ε) 267 (4·46), 342 (4·13), 460 nm (2·60); τ 2·75–3·1 (m, 30 H), 4·22 (s, 2 H); *m/e* (rel. abund.) 616 (60), 588 (5), 511 (10), 308 (32), 178 (50), 105 (100), 102 (20). (Found: C, 89·38; H, 5·38. $C_{46}H_{32}O_2$ requires: C, 89·58; H, 5·23%).

The more soluble fraction from the fractional crystallization of the yellow solid yielded **11** (1·2 g) as thick, colorless needles, mp 262–263° (dec to red liquid); ν_{max} 1700 cm^{-1}; $\lambda_{max}^{CHCl_3}$ 293 nm (log ε 4·06); τ 2·6–3·15 (m, 27 H), 3·35–3·6 (m, 2 H), 5·19 (d, J = 7 Hz, 1 H), 5·63 (d, J = 1·5 Hz, 1 H), 6·04 (dd, J = 1·5 and 7 Hz, 1 H); *m/e* (rel. abund.) 616 (100), 410 (22), 382 (6), 333 (11), 305 (6), 230 (5), 204 (18), 178 (12), 105 (6). (Found: C, 89·75; H, 5·33. $C_{46}H_{32}O_2$ requires: C, 89·58; H, 5·23%).

Evaporation of the solvent from the combined ethereal filtrate and washings gave a dark green solid. This was crystallized from EtOH to give **14** (520 mg), which after recrystallization from 95% EtOH was obtained as blue needles, mp 285–287° (lit.[2] mp 292–294°); $\nu_{max}^{CCl_4}$ 3225, 1688 cm^{-1}; λ_{max}^{EtOH} (log ε) 267 (4·20), 300 (4·28), 610 nm (3·28); τ − 0·2 (s, 1 H), 2·55–3·0 (m, 29 H).

The ethanolic mother liquor from the crystallization of **14** was evaporated, and the residue was dissolved in light petroleum-benzene (1:1) and chromatographed on silica gel. Elution with light petroleum benzene (2:3) gave additional **14** (760 mg; total yield 16%). A second yellow fraction yielded further **5** (180 mg; total yield 10%). Elution with benzene and benzene-ether gave a red gum, which gave on addition of acetone further crystalline **11** (470 mg; total yield 21%).

The orange-red acetone mother liquor was left to stand exposed to the atmosphere. During 6 weeks the solvent evaporated, and the residue was treated with EtOH. The insoluble rose solid was collected by filtration and twice recrystallized from light petroleum benzene to give fine, matter deep rose-red needles (100 mg, 1%), mp 174–175°; ν^{CCl} 4 1712, 1661 cm^{-1}; λ_{max}^{EtOH} (log ε) 289 (4·62), 517 nm (3·23); τ 2·5–3·1 (m); *m/e* (rel. abund.) 616 (43), 614 (49), 435 (47), 336 (100), 178 (71), 165 (94), 149 (68), 105 (100). (Found: C, 89·48; H, 5·16. $C_{46}H_{32}O_2$ requires: C, 89·58; H, 5·23%).

Reaction of 3 *with dimethyl acetylenedicarboxylate; formation of* 4

A soln of **3** (200 mg; 0·32 mmol) and dimethyl acetylenedicarboxylate (300 mg; 2·1 mmol) in benzene (10 ml) was boiled under reflux for 12 hr. The solvent was evaporated, and the residue was chromatographed on silica acid with benzene-CH_2Cl_2 (5:6) as eluent. Crystallization of the principal fraction from MeOH gave **4** (150 mg, 61%) as colourless crystals, mp 264–265°; ν_{max} 1735, 1701 cm^{-1}; τ 2·7–3·4 (m, 30 H), 5·14 (d, J = 4 Hz, 1 H), 5·85 (d, J = 4 Hz, 1 H), 6·38 (s, 3 H), 6·60 (s, 3 H); *m/e* 730. (Found: C, 83·45; H, 5·20. $C_{51}H_{38}O_5$ requires: C, 83·81; H, 5·24%).

Conversion of **3** *to* **5**. A benzene soln of 500 mg of **3** was passed through a column of F-20 alumina. A single fraction was collected, which gave **5** (0·45 g, 90%) upon removal of the solvent as a yellow solid, identical with the sample obtained by dehydration of **1**.

Treatment of **3** with hot dil H_2SO_4 also gave **5**.

Oxidation of 5 *with ruthenium tetroxide; formation of* 3,4,5-*triphenyl*-3-*cyclopentene*-1,2-*dione* (6)

A soln of **5** (300 mg; 0·48 mmol) in $CHCl_3$ (20 ml; washed well with water to remove traces of EtOH) was added dropwise to a mixture of $CHCl_3$ (10 ml) water (30 ml) ruthenium dioxide (10 mg) and sodium periodate (0·64 g). The resulting mixture was stirred overnight at room temp and then filtered. The chloroform and aqueous layers were separated, and the former was dried and stripped of solvent under reduced pressure. The residue was chromatographed on silicic acid in benzene-CH_2Cl_2 (5:6). From the first yellow fraction 140 mg (47%) of **5** was recovered. The second fraction gave 85 mg (48% based on unrecovered **5**) of **6** as orange needles, mp 160–162° (lit.[7] mp 162–163·5°); ν_{max} 1760, 1705 cm^{-1}; *m/e* 324. Its IR spectrum was identical with that of an authentic sample[7] and a mixture mp was undepressed.

Dehydrogenation of **5** *with chloranil; formation of 3,3′,4,4′,5,5′-hexaphenyl-2,2′-bis(cyclopentadienone* (**7**)

A mixture of **5** (100 mg; 0·16 mmol) and chloranil (200 mg; 0·81 mmol) in xylene (10 ml) was boiled under reflux for 4 hr. The solvent was removed under reduced pressure, and $CHCl_3$ was added to the residue. The soln was filtered from insoluble material, and the solvent was evaporated. The residue was chromatographed on neutral alumina with benzene to give **1** (60 mg; 60%) which was obtained as black crystals, mp 288–289°, after recrystallization from $CHCl_3$-i-PrOH; ν_{max} 1705 cm^{-1}; $\lambda_{max}^{C_6H_6}$ (log ε) 332 (4·23), 546 nm (3·46); *m/e* 614. (Found: C, 90·15; H, 5·09. $C_{46}H_{30}O_2$ requires: C, 89·87; H, 4·92%).

When **5** was heated with N-bromosuccinimide in CCl_2, for 20 hr, **7** was formed in 10% yield.

Reaction of **7** *with dimethyl acetylenedicarboxylate; formation of* **8**

A mixture of **1** (50 mg; 0·080 mmol) and dimethyl acetylenedicarboxylate (200 mg; 1·40 mmol) in benzene (5 ml) was boiled under reflux for 24 hr. The bright red soln was stripped of solvent to give a red oil, which was chromatographed to silica acid with benzene-CH_2Cl_2 (5:6). A red oil was obtained which crystallized after addition of MeOH to give 48 mg (83%) of red crystals. Recrystallization from MeOH gave **8** as bright red crystals, mp 174–175°; ν_{max} 1730, 1710 cm^{-1}; λ_{max} (log ε) 248 (4·63), 325 (3·93), 480 nm (3·01); *m/e* (rel. abund.) 728 (8), 697 (100). (Found: C, 83·91; H, 5·06. $C_{51}H_{36}O_5$ requires: C, 84·05; H, 4·98%).

Reduction of **5** *with zinc and acetic acid; formation of 2,2′,3,3′-tetrahydro-3,3′,4,4′,5,5′-hexaphenyl-2,2′-bis(cyclopentadienone)* (**9**

A suspension of **5** (250 mg; 0·40 mmol) and Zn dust (250 mg; 3·82 mg-atom) in AcOH (35 ml) was boiled under reflux until all of the organic compound had dissolved (3 days). The yellow soln was decanted into water, and the mixture was extracted 3 times with $CHCl_3$. The combined extracts were washed 5 times with water and dried. Removal of solvent under reduced pressure left a yellow gum, which was treated with CCl_4. The soln was filtered from a small amount of **9** (11 mg) and evaporated. The residue was dissolved in light petroleum benzene (1:1) and chromatographed on silica gel. Elution with light petroleum benzene (3:2) gave a small amount of yellow gum; elution with benzene gave **9** (128 mg). Two recrystallizations of the total crude **9** from light petroleum benzene gave colourless needles (125 mg, 50%), mp 268·5–269·5°; $\nu_{max}^{CH_2Cl_2}$ 1697 cm^{-1}; $\lambda_{max}^{CHCl_3}$ 297 nm (log ε 4·37); τ 2·75–2·95 (m, 30 H), 5·47 (d, J = 2·5 Hz, 2 H), 6·80 (d, J = 2·5 Hz, 2 H). (Found: C, 89·70; H, 5·62. $C_{46}H_{34}O_2$ requires: C, 89·28; H, 5·54%).

Synthesis of **5** *from* **6** *and 2,3,4-triphenyl-2-cyclopentenone* (**10**)

To a soln of **10**[7] (342 mg; 1·10 mmol) and **6** (356 mg; 1·10 mmol) in 95% ethanol (60 ml) was added 4 drops of piperidine and 3 drops of hexamethylphosphoramide. The soln was boiled under reflux for 10 days, after which time small yellow needles of **5** had separated. The major portion of the solution was decanted, and the crystals of **5** (60 mg, 9%) were collected and washed with $CHCl_3$: mp *ca* 323° dec, undepressed on admixture with a sample of **5** prepared from **1**; the IR spectra of the two samples were identical.

Rearrangement of **7** *to* **14**

A mixture of **7** (100 mg) and benzophenone (500 mg) was boiled gently under reflux. Within 15 min an intense blue soln resulted. The soln was cooled, and MeOH (10 ml) was added. Upon standing the soln deposited 70 mg (70%) of deep blue crystals of **14**, mp 286–287°; λ_{max} (log ε) 265 (4·20), 305 (4·25), 345 (4·25), 345 (3·34), 620 nm (3·34); its IR and nmr spectra were identical with those of a sample of **14** prepared from **1**, and a mixture mp was undepressed. (Found: C, 90·38; H, 5·23. $C_{46}H_{30}O_2$ requires: C, 89·87; H, 4·92%).

Dehydrogenation of **11** *with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone* (DDQ); *formation of* **14**

A mixture of **11** (90 mg; 0·14 mmol) and DDQ (200 mg; 0·88 mmol) in xylene (25 ml) was boiled under reflux for 48 hr. The mixture was cooled and filtered. The filtrate was stripped of solvent under reduced pressure, and the residue was chromatographed on silica gel; elution with hexane-benzene (2:3) gave a blue fraction that yielded **14** (9 mg, 10%). Two recrystallizations from hexane-benzene gave **14** as blue crystals, mp 278–280°, undepressed on admixture with a sample of **14** prepared from **1**; the IR spectra of the two samples were identical.

Acetylation of **14**; *formation of* **15**

A mixture of **14** (100 mg) Ac_2O (5 ml) and pyridine (2 ml) was boiled under reflux under N_2 for 30 min. When the mixture was poured into water, the acetate **15** crystallized and was filtered off. Recrystallization from hexane gave **15** (60 mg, 62%) as purple crystals, mp 300–301°; ν_{max} 1760, 1701 cm^{-1}; λ_{max} (log ε) 290 (4·46), 525 nm (3·39). (Found: C, 87·59; H, 5·02. $C_{48}H_{32}O_3$ requires: C, 87·78; H, 4·91%).

Trimethylsilylation of **14**; *formation of* **16**

A mixture of **14** (100 mg) and bis(trimethylsilyl)acetamide (1 ml) in acetonitrile (8 ml; freshly distilled from P_2O_5) was boiled under reflux under N_2 for 30 min. Upon standing at room temp the mixture deposited **16** (89 mg, 82%) as purple crystals, mp 257–258°; ν_{max} 1701 cm^{-1}; λ_{max} (log ε) 255 (4·57), 295 (4·73), 522 nm (3·72); *m/e* 686·2600 (parent ion requires: 686·2641). (Found: C, 85·41; H, 5·57. $C_{49}H_{38}O_2Si$ requires: C, 85·68; H, 5·58%).

Phenylhydrazone of **14**

A mixture of **14** (250 mg) and phenylhydrazine (500 mg) in AcOH (30 ml) was boiled under reflux for 20 hr. The mixture was poured into water, and the aqueous mixture was extracted with benzene. The extract was washed with water and dried over Na_2CO_3. The solvent was evaporated, and the residue was washed with EtOH and then crystallized from $CHCl_3$-EtOH to give the phenylhydrazone of **14** (80 mg, 28%) as reddish-black crystals, mp 284–285°; ν_{max} 3300, 1590, 1485 cm^{-1}; λ_{max} (log ε) 261 (4·40), 4·15 nm (4·15); *m/e* 704·2764 (parent ion requires: 704·2827).

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