An Isolable but Highly Reactive *o*-Quinodimethane; 1,1a,2,3,4,4a-Hexahydro-9,10-diphenyl-1,4-methanoanthracene

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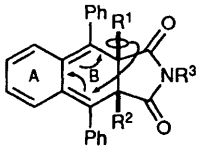
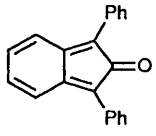
The relatively stable *o*-quinodimethane **7** has been prepared by photodecarbonylation of the 1,3-diphenylinden-2-one–norbornene adduct **5**. Reactions of **7** with phenyltriazolinedione, sulphur dioxide and triplet oxygen all occur to the less hindered face of the diene system terminating at the α,α′-positions of the *o*-quinodimethane. The same face of the same diene system is involved in forming the major carbonyl iron complex, **12**, of **7**. Both thermolysis and acid-catalysed rearrangement of **7** give the dihydronaphthalene **10**. The 1,5-sigmatropic hydrogen shift of **7** that would give **10** is slow at 140 °C.

Although *o*-quinodimethane itself dimerises at −150 °C, a few derivatives are isolable.[1] Our own interest arose with the derivatives **1** and **2**[2] which are isolated in pure form without special precautions and have a good shelf life. Their stability is associated with steric blocking of the ring-B diene system by the ring-B substituents. This prevents dimerisation, reaction with air and even the addition of dienophiles to the ring-B diene system. Inclusion of the normally reactive diene system of *o*-quinodimethane in a six-membered ring prevents conrotatory ring-closure to a benzocyclobutene and the imide ring in **1** and **2** probably inhibits electrocyclic ring-opening to an *o*-divinylbenzene. The low migratory aptitude of alkyl groups and imide carbonyl groups in 1,5-sigmatropy may also contribute to the stability of **1** and **2**; an attempt to prepare **3** gave instead the product of the 1,5-hydrogen shift shown, **3** (arrows), as well as the naphthalene produced by dehydrogenation. Herein we describe the preparation and properties of the *o*-quinodimethane **7** which is isolable, albeit in impure form, and retains high *o*-quinodimethane reactivity in ring-B, but is slow to undergo 1,5-hydrogen shift.



1 $R^1 = R^2 = R^3 = Me$
2 $R^1, R^2 = (CH_2)_4$; $R^3 = Me$
3 $R^1 = R^2 = H$; $R^3 = Ph$



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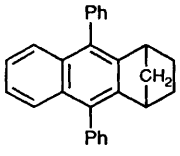

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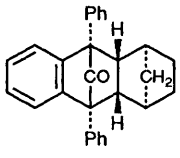

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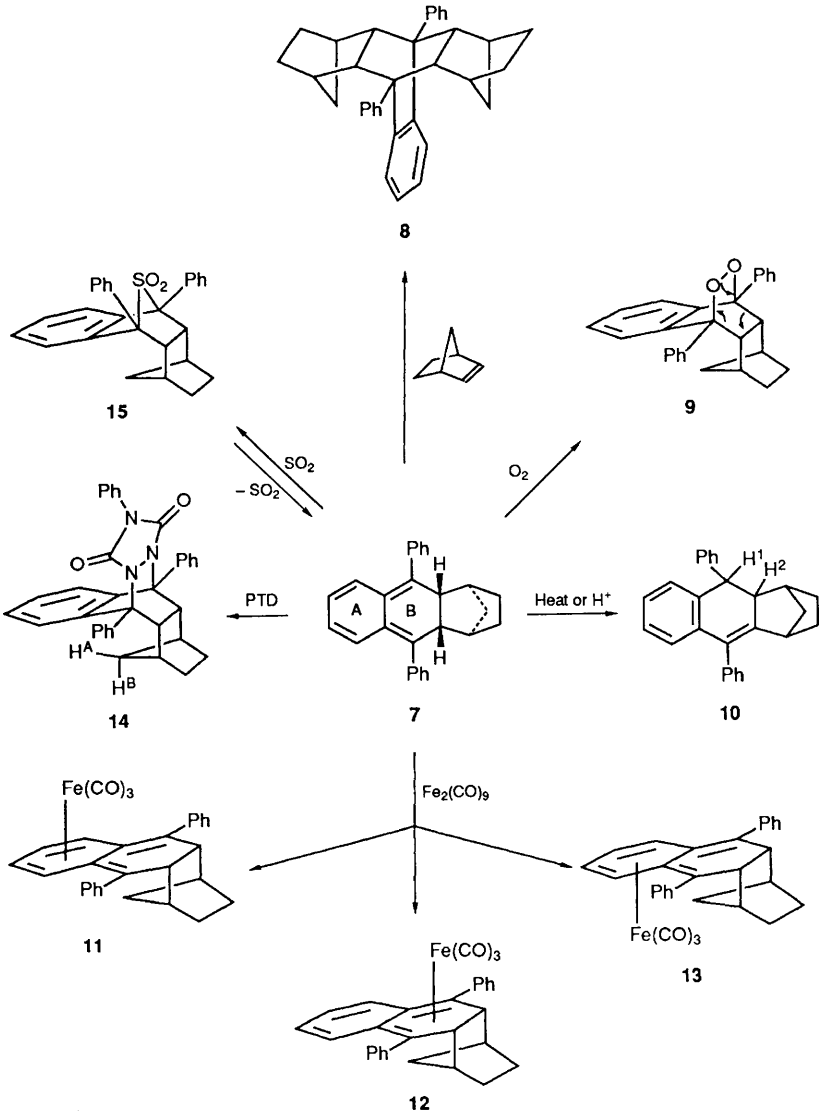
1,3-Diphenylinden-2-one **4** was generated by dissociation of its dimer[3] in the presence of norbornene at 111 °C to give mainly the *endo*-adduct **5**. Photolysis of **5** in deoxygenated acetonitrile produced a deep orange solution of the *o*-quinodimethane **7** together with the dihydronaphthalene **10** and the naphthalene **6**. Although it was possible to crystallise **7** from the reaction mixture, and recrystallise from acetonitrile in a N_2-atmosphere, the impurities were persistent; comparison of the AA′BB′ pattern at δ_H 5.91 ($CDCl_3$)[2,4] assigned to the ring-A protons of **7** with the total integral for aromatic protons (δ_H 7.0–7.9) indicated the content of **7** to vary in the range 60–70%. A slightly broadened singlet due to the ring junction protons in **7** (δ 3.25) is also clearly recognisable and the absence of noticeable coupling in this signal agrees with location of the *o*-quinodimethane *exo* on the norbornane framework, *i.e.* retention of configuration at the ring-junction in going from **5** to **7**. The UV–vis spectrum of **7** was conveniently measured by photolysis of **5** in deoxygenated acetonitrile in a UV cell fitted with a serum cap. The orange colour is due to a broad absorption band (370–530 nm) with λ_{max} 454 nm showing indistinct vibrational structure similar to that shown by *o*-quinodimethane itself.[5] Comparison with the λ_{max} for **1**,[2] 415 nm, shows that the phenyl groups in **7** conjugate much more effectively with the *o*-quinonoid system. Here the phenyl groups can depart from the positions orthogonal to the *o*-quinodimethane which they are forced to occupy in **1** and **2**. Accordingly steric protection of the ring-B diene system is much less in **7** which thus presents an opportunity to explore, with an isolable *o*-quinodimethane, those reactions thought to be characteristic of transient *o*-quinodimethanes. These reactions are outlined in Scheme 1.

Reaction of **1** with 2,3-diazanaphthoquinone results in addition to the ring-A diene system.[2] However, in **7** the ring-B diene system is readily attacked by phenyltriazolinedione (PTD) upon the less hindered face to give the adduct **14**. The stereochemistry of **14** is consistent with the highfield position of H^A and H^B (−1.15 and +0.35 δ respectively). In the adduct **5** the related methylene protons appear at −0.68 and +0.25 δ. Our initial experiments to produce **5** were conducted in a sealed stainless steel bomb in an oil bath at 150 °C (5 h). Under these conditions the adduct, **8**, of **7** with norbornene, was formed (9.6%) together with **5** and its *exo*-isomer. Presumably under the reaction conditions **5** undergoes thermal decarbonylation to **7** which reacts with a further molecule of norbornene.

Both *o*-quinodimethane[6a] and its 1,2,3,4-tetramethyl derivative[6b] react with sulphur dioxide. A sulphinic ester formed by Diels–Alder addition to the sulphur–oxygen double bond is believed to be the product of kinetic control, whilst a sulphone formed by a cheletropic process at the sulphur atom is the product of thermodynamic control. However even below 0 °C compound **7** added sulphur dioxide to give the sulphone **15**. The resonances of the methylene protons at +0.43 and −0.90 δ indicate the stereochemistry shown in **15**, and the IR bands at 1304 and 1135 cm^{-1} indicate a sulphone rather than a sulphinate which would show single strong band at 1105 cm^{-1}.

It was noted by Cava and McGrady[7] that triethylamine

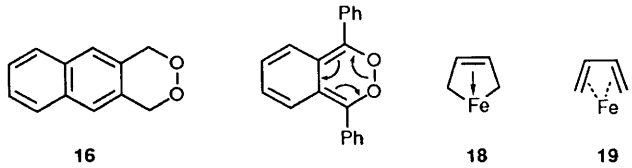


Scheme 1

catalysed sulphur dioxide elimination from certain strained sulphones. Similar addition of triethylamine to a solution of **15** rapidly regenerated the *o*-quinodimethane **7**. In the absence of triethylamine, it was necessary to heat the sulphone **15** at 90 °C to cause loss of SO_2 and regeneration of **7**.

Although the reaction of certain *cisoid* dienes with triplet (ground state) oxygen is known, the process is normally inefficient unless catalysed.[8] However 2,3-naphthoquinodimethane gives the peroxide **16** but *o*-quinodimethane itself fails to afford a similar peroxide.[9] On the other hand singlet oxygen adds readily to 1,3-diphenylbenzo[*c*]furan,[10a] 1,2,3-triphenylisoindole,[10b] and 1,4-diphenyl-2-benzopyran-3-one.[10c] When oxygen was passed through a solution of **7** in the absence of light the orange colour was discharged and the peroxide **9** was isolated in 54% yield by chromatography. Possible mechanisms for the spin-forbidden addition of triplet oxygen to dienes have been suggested by Barton and his collaborators.[8] When briefly heated, **9** decomposed to give *o*-dibenzoylbenzene and norbornene. Possible mechanisms are a direct fragmentation **9** (arrows) or a reverse Diels–Alder process to give **17** which subsequently undergoes electrocyclic ring-opening **17** (arrows). Although it may seem less likely there is precedent[10c] for the involvement of **17** in a related fragmentation.

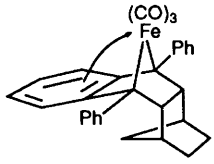
Several complexes of *o*-quinodimethanes have been prepared[11] but apart from our own work[11c] it is unclear whether their formation involves free *o*-quinodimethanes as intermediates. A further question which we have previously touched upon is the nature of the bonding in these complexes[11a,c] Bonding in metal–diene complexes can be represented by the extreme valence bond structures **18** and **19**.[12a] Although the



16 **17** **18** **19**

latter is generally preferred, the overall effect of the $Fe(CO)_3$ group is to donate electrons to the diene ligand and hence some filling of the diene LUMO occurs.[12b] The occupancy of the LUMO will increase as the LUMO energy drops. Since *o*-quinodimethanes have low energy LUMOs the structure **18** might be particularly important for their carbonyl iron complexes. In an attempt to clarify these questions, **7** was treated with enneacarbonyldiiron. The complexes **11**, **12** and **13** were formed in good yield. Complexes **11** and **12** were obtained as a mixture following chromatography and the major component **12** was obtained in pure form by crystallisation. The nature of the minor complex **11** was deduced from the ^1H NMR spectrum of the mixture. The ring-A protons of **11** and **13** appear as 2 H

multiplets in the regions δ 5.00–6.00 and 3.50–4.00. The corresponding protons in **12** appear in the aromatic region suggesting a substantial contribution by the σ-bonded resonance form **20**. However the hybridisation at the diene termini bonded to



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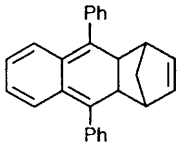
iron cannot be the same as in the compounds **14**, **15** and **9**. Unlike these compounds, the complex **12** shows no highfield proton resonances; broad ill-resolved signals extend only to as highfield as δ 0.5. The geometry of the complex is therefore closer to that represented by structure **12**. This agrees with earlier NMR evidence on related complexes.[11a]

We have noted that the *o*-quinodimethane **7** is slow to undergo 1,5-sigmatropic hydrogen shift. When heated in boiling xylene (140 °C) it slowly decomposed. In contrast, a fast 1,5-shift at 20 °C as shown in **3** (arrows) was supposed to prevent isolation of **3**. At 180 °C in boiling *o*-dichlorobenzene, **7** gave the dihydronaphthalene **10**. Although the imide carbonyl groups in **3** might well accelerate 1,5-hydrogen shift the possibility that these rearrangements are acid catalysed should not be overlooked. A trace of CF_3CO_2H in $CDCl_3$ causes rapid conversion of **7** into **10** at 20 °C and chlorinated solvents frequently retain traces of hydrogen chloride.* The vicinal coupling between H^1 and H^2 in **7** is 8 Hz in better agreement with a *cis*- than a *trans*-1,2-dihydronaphthalene.[13] This accords with a suprafacial 1,5-shift in **7** but does not rule out an acid-catalysed process because proton attack on the less hindered face of the *o*-quinodimethane **7** would also give *cis*-**10**.

Other reactive *o*-quinodimethanes which can be observed and characterised by trapping with PTD are **21** (λ_{max} 456 nm) and **22** (λ_{max} 439 nm). The observation of **21** is noteworthy, for it was observed following photo-decarboxylation of the *exo*-adduct **23**. We have found that photodecarboxylation is slower than



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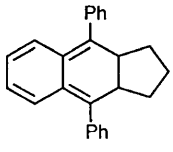

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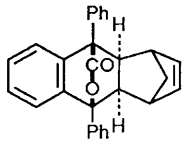

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photodecarbonylation and that *exo*-adducts fragment more slowly than *endo*-adducts. Moreover **21** would be expected to fragment to 1,4-diphenylnaphthalene and cyclopentadiene. Indeed 1,4-diphenylnaphthalene was formed together with the PTD adduct of **21** in our trapping experiment. Evidently this fragmentation and other photoreactions of **21** are sufficiently slow to allow its observation despite its slow formation from **23**.

Experimental

For general details see ref. 2. Irradiations were conducted in a silica flask. All reactions were conducted in a N_2-atmosphere. *J* Values are recorded in Hz.

Dissociation of the 1,3-*Diphenylinden-2-one Dimer in the Presence of Bicyclo*[2.2.1]*heptene*.—(a) *In xylene at* 150 °C. The 1,3-diphenylinden-2-one dimer (100 mg, 0.177 mmol), bicyclo-[2.2.1]heptene (1.5 g, 16 mmol) and xylene (3 ml) were heated in a steel bomb in an oil bath at 150 °C (5 h). Evaporation of the solvent and chromatography of the residue on silica using benzene–petroleum (4:1) afforded the *bis-bicyclo*[2.2.1]*heptene adduct* **8** (15 mg, 9.6%), m.p. 278–279 °C, from chloroform–ethanol (Found: C, 92.15; H, 7.9. $C_{34}H_{34}$ requires C, 92.3; H, 7.7%), δ_H 7.80–7.10 (14 H, m, aromatic), 2.30–2.00 (8 H, m), 1.50–1.00 (8 H, m), 0.27 (2 H, d, *J* 9), −0.15 (2 H, d, *J* 9), *m*/*z* 442 (M), 348 and 280 (4.5, 100 and 16.9%) (Found: M, 442.226. $C_{34}H_{34}$ requires M, 442.266). Continued elution of the column gave the *exo*-adduct† (20 mg, 15%), m.p. 163–167 °C(d), from chloroform–ethanol (Found: C, 89.4; H, 6.7. $C_{28}H_{24}O$ requires C, 89.3; H, 6.4%), ν_{max}/cm^{-1} 1768, δ_H 7.95–7.35 (10 H, m, aromatic), 7.25–6.60 (4 H, m, aromatic), 2.50 (2 H, s), 2.38 (2 H, s), 1.85 (1 H, d, *J* 9), 1.70–1.37 (2 H, m), 1.37–1.05 (2 H, m) and 0.89 (1 H, d, *J* 9); *m*/*z* 348 (M − CO), 307 and 280 (100, 31.5 and 32.7%) (Found: M, 376, 183. $C_{28}H_{24}O$ requires M, 376.183). Continued elution of the column gave the *endo*-adduct **5** (65 mg, 48%), m.p. 233–238 °C(d), from chloroform–ethanol (Found: C, 89.05; H, 6.45%), ν_{max}/cm^{-1} 1785, δ_H 7.52–7.22 (10 H, m, aromatic), 7.22–6.62 (4 H, m, aromatic), 2.71 (2 H, s), 2.24 (2 H, br s), 1.32 (4 H, brs), 0.25 (1 H, d, *J* 11) and −0.68 (1 H, d, *J* 11); *m*/*z* 348 (M − CO), 307 and 280 (100, 29.6 and 32.7%) (Found: M, 376.184. $C_{28}H_{24}O$ requires M, 376.183).

(b) *In toluene*. The 1,3-diphenylinden-2-one dimer (300 mg, 0.532 mmol), bicyclo[2.2.1]heptene (2 g, 0.0213 mol) and dry, deoxygenated toluene (10 ml) were boiled under reflux in a nitrogen atmosphere (18 h). Evaporation of the solvent and chromatography of the residue on silica using benzene–petroleum (3:2) gave the *exo*-adduct (25 mg, 6.3%). Continued elution of the column gave the *endo*-adduct **6** (360 mg, 90%). Both products were identical with samples previously prepared.

Trapping of the o-*Quinonoid* 7

(a) *With* 4-*Phenyl*-1,2,4-*triazoline*-3,5-*dione*.—A solution of the *endo*-1,4-diphenyl-2-benzopyran-3-one–bicyclo[2.2.1]heptene adduct[14] (45 mg, 0.115 mmol) in dry, deoxygenated benzene (10 ml) was irradiated for 3 min (100 W, medium pressure Hg lamp). The resulting yellow solution (λ_{max} 454 nm) was titrated with a solution of 4-phenyl-1,2,4-triazoline-3,5-dione (23 mg, 0.131 mmol) in dry, deoxygenated benzene (10 ml) to a colourless end point. This process was repeated for a total irradiation time of 7 h. Evaporation of the solvent and chromatography of the residue on silica in benzene–ether (9:1) gave the *adduct* **14** (30 mg, 49%), m.p. 297–299 °C, from benzene–petroleum (Found: C, 80.3; H, 5.6; N, 7.8. $C_{35}H_{29}N_3O_2$ requires C, 80.3; H, 5.6; N, 8.0%), ν_{max}/cm^{-1} 1770 and 1720, δ_H 7.90–7.00 (19 H, m, aromatic), 3.15 (2 H, s), 2.40 (2 H, s), 1.58 (4 H, s), 0.35 (1 H, d, *J* 10), −1.15 (1 H, d, *J* 10); *m*/*z* 523 (M), 348, 307 and 280 (10.7, 100, 7.3 and 20.1%) (Found: M, 523.224. $C_{35}H_{29}N_3O_2$ requires M, 523.226).

(b) *With Bicyclo*[2.2.1]*heptene*.—A solution of the *endo*-bicyclo[2.2.1]heptene adduct **5** (50 mg, 0.13 mmol) in dry, deoxygenated benzene (10 ml) was irradiated for 20 min (100 W, medium pressure lamp). Bicyclo[2.2.1]heptene (1.5 g) was added to the resulting yellow solution and the mixture was heated under reflux for 30 min. The yellow colour remained and no bis-adduct **8** was detected by TLC. The mixture was irradiated for a further 15 h, when starting material was detectable by TLC. Evaporation of the solvent at 100 °C under reduced pressure and chromatography of the residue on silica in

* The sample of *o*-dichlorobenzene was freshly distilled.
† The term *exo*-refers to addition to the indenone. For *o*-quinodimethanes only addition to the *exo*-face of norbornene is observed.

benzene–petroleum (1:19), gave the *bis-adduct* **8** (20 mg, 29.5%). The IR and ^{1}H NMR spectra and m.p. were identical with those of previously prepared material.

(c) *With Oxygen.*—A solution of the *endo*-bicyclo[2.2.1]-heptene adduct **5** (50 mg, 0.13 mmol) in dry, deoxygenated benzene (10 ml) was irradiated for 2 h (1 kW, medium pressure lamp). Oxygen was bubbled through the deep orange solution until no colour remained. Evaporation of the solvent and chromatography of the residue on silica using benzene–petroleum (4:1) gave the *dioxygen adduct* **9** (35.2 mg, 54.2%) m.p. 190–195 °C (from benzene–petroleum) (Found: C, 85.55; H, 6.5. $C_{27}H_{24}O_2$ requires C, 85.2; H, 6.4%); δ_H 8.00–7.00 (14 H, m, aromatic), 3.10 (2 H, s), 2.30 (2 H, br s), 1.57 (4 H, s), 0.40 (1 H, d, *J* 10) and −0.64 (1 H, d, *J* 10); *m/z* 348 (M − O_2), 286, 280, 270, 209, 181 and 105, (100, 25.4, 20.8, 25.8, 49, 7.8 and 38.5%) (Found: M, 380.179. $C_{27}H_{24}O_2$ requires M, 380.177).

Thermolysis of dioxygen adduct **9** *in* o-*dichlorobenzene.* The dioxygen adduct **9** (25 mg, 0.066 mmol) and *o*-dichlorobenzene (3 ml) were heated at 170–180 °C (oil bath temperature) for 15 min. Evaporation of the solvent at 100 °C under high vacuum and crystallisation of the residue from methylene dichloride–ethanol gave *o*-dibenzoylbenzene (15 mg, 80%) (m.p. and IR spectrum identical with those of authentic material).

(d) *With Sulphur Dioxide.*—A solution of the *endo*-bicyclo-[2.2.1]heptene adduct **5** (50 mg, 0.13 mmol) in deoxygenated acetonitrile (5 ml) was irradiated for 2 h (1 kW, medium pressure lamp). The resulting deep orange solution was cooled to 0 °C and sulphur dioxide bubbled through the solution until a white precipitate was deposited which when filtered off gave the *sulphone* **15** (33 mg, 60%), m.p. 145–149 °C, from methylene dichloride–petroleum (Found: C, 78.15; H, 5.95; S, 7.95. $C_{27}H_{24}SO_2$ requires C, 78.6; H, 5.8; S, 7.8%), ν_{max}/cm^{-1} 1304 and 1135, δ_H 7.83–7.45 (10 H, m, aromatic), 7.45–6.88 (4 H, m, aromatic, AA′BB′), 2.60 (2 H, s), 2.22 (2 H, s), 1.60 (4 H, s), 0.43 (1 H, d, *J* 10) and −0.90 (1 H, d, *J* 10), *m/z* 348 (M − SO_2), 307 and 280 (100, 41.7 and 61.5%).

Reaction of the sulphone **15** *with triethylamine and trapping with* N-*phenylmaleimide.* Triethylamine (1 ml) was added to a stirred solution of the sulphone **15** (22.9 mg, 0.055 mmol) in deoxygenated benzene (5 ml) under nitrogen. Immediately a deep yellow colour developed (λ_{max} 452 nm) which was assigned to the *o*-quinonoid **7**. After 5 min *N*-phenylmaleimide (40 mg, 0.23 mmol) was added and the solution stirred for a further 16 h. Evaporation of the solvent and chromatography of the residue on silica using benzene gave a mixture of the exo- and endo-N-*phenylmaleimide adducts* (20 mg, 70%), m.p. 281–283 °C (from benzene–petroleum) (Found: C, 85.35; H, 5.8; N, 2.5. $C_{37}H_{31}NO_2$ requires C, 85.2; H, 6.0; N, 2.7%).

Thermolysis of the sulphone **15**. The sulphone **15** (12.3 mg, 0.0298 mmol) in deoxygenated *p*-cymene (2 ml) was warmed to 90 °C (oil bath temperature) to give a deep yellow solution (λ_{max} 453 nm) the colour of which was assumed to be due to the *o*-quinonoid **7**. Further warming of the solution to 200 °C (oil bath temperature) and examination of the solution by TLC showed the major component to be the dihydronaphthalene **10**. This was isolated by chromatography and characterised by IR comparison with authentic material.

(e) *With Enneacarbonyldiiron.*—A solution of the *endo*-1,3-diphenylinden-2-one–bicyclo[2.2.1]heptene adduct **5** (50 mg, 0.13 mmol) in dry, deoxygenated toluene (10 ml) was irradiated for 2 h (1 kW, medium pressure lamp). Enneacarbonyldiiron (0.5 g) was added to the resulting deep orange solution which was then stirred at room temperature for 2 h. The solution was filtered and evaporated at 25 °C under reduced pressure and the residue was chromatographed on silica in petroleum–benzene (19:1) to give a mixture of **11** and **12** (44 mg, 67.8%). The *major isomer* **12** was obtained by crystallisation from benzene–petroleum, m.p. 187–190 °C (Found: C, 73.5; H, 5.15. $C_{30}H_{24}FeO_3$ requires C, 73.8; H, 4.9%), ν_{max}/cm^{-1} 2060, 1990 and 1973, δ_H 8.00–7.00 (14 H, m, aromatic), 2.32 (2 H, s), 2.0 (2 H, s), 1.40–0.50 (6 H, m); *m/z* 488 (M), 460 (M − CO), 432 (M − 2CO), 404 (M − 3CO), 348 [M − Fe(CO)$_3$] and 280 (1.5, 7.7, 14.5, 100, 8 and 17.2%) (Found: M, 488.1081 requires M, 488.107). By comparison of the ^{1}H NMR spectra of the mixture and the pure complex **12**, the following signals were assigned to the minor complex **11**, δ_H 5.35 (2 H, m), 3.80 (2 H, m) and 2.75 (2 H, s). Further elution of the column gave **13** (7 mg, 10.7%), m.p. 218–222 °C (from benzene–petroleum) (Found: C, 73.55; H, 4.9. $C_{30}H_{24}FeO_3$ requires C, 73.8; H, 4.9%), ν_{max}/cm^{-1} 2060, 2016 and 1975; δ_H 7.60–7.10 (10 H, m, aromatic), 5.40–5.10 (2 H, m, ring A protons), 4.05–3.85 (2 H, m, ring A protons), 2.68 (2 H, s), 2.04 (2 H, br s) and 1.50–0.80 (6 H, m); *m/z* 460 (M − CO), 432 (M − 2CO), 404 (M − 3CO), 348 [M − Fe(CO)$_3$] and 280 (7.2, 17.1, 100, 10.8 and 14.3%) (Found: M, 488.107. $C_{30}H_{24}FeO_3$ requires M, 488.107).

Thermolysis of the o-*quinonoid* **7**. A solution of the *endo*-1,3-diphenylinden-2-one–bicyclo[2.2.1]heptene adducts (50 mg, 0.13 mmol) in deoxygenated acetonitrile (10 ml) was irradiated for 2 h (1 kW, medium pressure lamp). The solvent was removed in a high vacuum at 25 °C. The residue in deoxygenated *o*-dichlorobenzene (5 ml) was immersed in an oil bath at 200 °C for 2 min. Evaporation of the solvent under high vacuum at 100 °C and chromatography of the residue on silica in petroleum–benzene (19:1) gave the *dihydronaphthalene* **10** (25 mg, 51%), m.p. 126–128 °C (from chloroform–methanol) (Found: C, 92.75; H, 7.15. $C_{27}H_{24}$ requires C, 93.1; H, 6.9%), δ_H 7.60–6.90 (14 H, m, aromatic), 4.15 (1 H, d, *J* 8), 2.80 (1 H, d, *J* 8), 2.56 (1 H, br s), 2.37 (1 H, br s), 1.90–1.20 (4 H, br m), 0.80 (1 H, d, *J* 10) and 0.30 (1 H, d, *J* 10); *m/z* 348 (M), 346 (M − 2H), 318 and 280 (100, 23.8, 17.1 and 19.2%). (Found: M, 348.187. $C_{27}H_{24}$ requires M, 348.188).

Reaction of o-*quinodimethane* **7** *with trifluoroacetic acid.* A solution of the *endo*-bicyclo[2.2.1]heptene adduct **5** (30 mg, 0.08 mmol) in dry, deoxygenated benzene (10 ml) was irradiated for 2 h (1 kW, medium pressure lamp). Evaporation of the solvent gave an orange residue which was dissolved in $CDCl_3$ (0.5 ml) and the ^{1}H NMR spectrum obtained. Three drops of a trifluoroacetic acid–$CDCl_3$ mixture (3 drops of CF_3CO_2H in 0.5 ml of $CDCl_3$) was added to the sample which was shaken for 3 min and the ^{1}H NMR spectrum re-recorded. The AA′BB′ signal for the four ring-A protons in the *o*-quinonoid **7** had disappeared and the spectrum now resembled that of the dihydronaphthalene **10**. Evaporation of the solvent and chromatography of the residue on silica using petroleum–benzene (19:1) gave the dihydronaphthalene **10** identical with an authentic sample (IR and m.p. comparison).

Attempts to Prepare a Pure Sample of the o-*Quinonoid* **7** *and Record its* ^{1}H NMR *Spectrum.*—(i) A solution of the *endo*-bicyclo[2.2.1]heptene adduct **5** (50 mg, 0.13 mmol) in deoxygenated acetonitrile (10 ml) was irradiated for 2 h (1 kW, medium pressure lamp). Crystallisation was promoted by scratching; the orange crystalline material was filtered off and recrystallised twice from deoxygenated acetonitrile under nitrogen. The resulting orange crystalline material was dried in a high vacuum at room temperature, m.p. *ca.* 120 °C (d) (Found: C, 92.65; H, 7.0. $C_{27}H_{24}$ requires C, 93.1; H, 6.9%); *m/z* 348 (M), 347 (M − H), 346 (M − 2 H), 320, 319, 318 and 280 (100, 11.9, 38.4, 4.5, 12.9, 28.6 and 49.5%) (Found: M, 348.187. $C_{27}H_{24}$ requires M, 348.188). However the ^{1}H NMR integration of the aromatic protons was too large in comparison to that of the four ring-A protons and therefore not consistent with pure *o*-quinodimethane **7**.

(ii) A stirred solution of the *endo*-bicyclo[2.2.1]heptene adduct **5** (50 mg, 0.13 mmol) in deoxygenated acetonitrile (5 ml) was irradiated for 2 h. (1 kW, medium pressure lamp). The resulting orange crystalline material was filtered off and recrystallised from deoxygenated acetonitrile under nitrogen. The recrystallised sample was dried in a high vacuum at 25 °C and its ^{1}H NMR spectrum obtained in $CDCl_3$. The resulting solution was titrated to a colourless endpoint with 4-phenyl-1,2,4-triazoline-3,5-dione. Evaporation of the solvent and chromatography of the residue on silica in benzene–petroleum (1:19) gave a mixture of dihydronaphthalene **10** and naphthalene **6** (7.7 mg) identified by ^{1}H NMR. The solvent polarity was steadily increased to benzene–ether (9:1) to elute the 4-phenyl-1,2,4-triazoline-3,5-dione adduct **14** (22.2 mg) (IR and m.p. comparison with authentic material).

(iii) A solution of the *endo*-bicyclo[2.2.1]heptene adduct **5** (50 mg, 0.13 mmol) in deoxygenated acetonitrile (5 ml) was irradiated for 20 h (100 W, medium pressure lamp). The resulting crystalline precipitate (14.3 mg) was filtered off, dried in a high vacuum at 25 °C, dissolved in $CDCl_3$ and its ^{1}H NMR spectrum obtained. This showed the presence of *ca.* 20% of the *o*-quinonoid **7** which was titrated with 4-phenyl-1,2,4-triazoline-3,5-dione to a colourless end point. Evaporation of the solvent and chromatography of the residue on silica in petroleum–benzene (19:1) gave the *naphthalene* **6** (8 mg), m.p. 242 °C (from benzene–petroleum) (Found: C, 93.5; H, 6.25. $C_{27}H_{22}$ requires C, 93.65; H, 6.35%), δ_H 7.80–7.00 (14 H, m, aromatic), 3.34 (2 H, m) and 2.00–1.00 (6 H, m); *m/z* 346 (M), 318 (M − C_2H_4) and 241 (100, 92.2 and 36.4%) (Found: M, 346.172. $C_{27}H_{22}$ requires M, 346.172).

Trapping of the o-*Quinonoid* **22** *with* 4-*Phenyl*-1,2,4-*triazoline*-3,5-*dione*.—A solution of the *endo*-1,3-diphenylinden-2-one–cyclopentene adduct [14] (50 mg, 0.143 mmol) in dry deoxygenated benzene (3 ml) was irradiated for 3 min (100 W, medium pressure lamp). The resulting yellow solution (λ_{max} 439 nm) was titrated with a solution of 4-phenyl-1,2,4-triazoline-3,5-dione (25.6 mg, 0.146 mmol) in dry, deoxygenated benzene (10 ml) to a colourless end point. This process was repeated for a total irradiation time of 6.5 h. Evaporation of the solvent and chromatography of the residue on silica using benzene–ether (4:1) gave a 1:1 *adduct* (42 mg, 59.4%), m.p. 274–278 °C (from benzene–petroleum) (Found: C, 79.85; H, 5.5; N, 8.6. $C_{31}H_{27}N_3O_2$ requires C, 79.6; H, 5.5; N, 8.5%); ν_{max}/cm^{-1} 1768 and 1715, δ_H 8.00–6.80 (19 H, m, aromatic), 3.80–3.40 (2 H, m), 2.40–1.92 (2 H, m) and 1.30–0.75 (4 H, m); *m/z* 497, 322, 321, 320 and 280 (6.2, 86.7, 99, 100 and 9.8%) (Found: M, 497.210. $C_{31}H_{27}N_3O_2$ requires M, 497.210).

Trapping of the o-*Quinonoid* **21** *with* 4-*Phenyl*-1,2,4-*triazoline*-3,5-*dione*.—A solution of the *exo*-1,4-diphenyl-2-benzopyran-3-one–bicyclo[2.2.1]heptadiene adduct [14] (50 mg, 0.128 mmol) in dry, deoxygenated benzene (5 ml) was irradiated for 5 min (100 W, medium pressure lamp). The resulting pale yellow solution (λ_{max} 456 nm) was titrated with a solution of 4-phenyl-1,2,4-triazoline-3,5-dione to a colourless end point. This process was repeated for a total irradiation time of 15.5 h. Evaporation of the solvent and chromatography of the residue on silica using benzene–ether (4:1) gave a mixture of 1,4-diphenylnaphthalene and starting material (12 mg). Continued elution of the column gave a 1:1 *adduct* (20 mg), m.p. 277–280 °C (from benzene–petroleum) (Found: C, 80.6; H, 5.3; N, 7.8. $C_{35}H_{27}N_3O_2$ requires C, 80.6; H, 5.2; N, 8.0%), ν_{max}/cm^{-1} 1768 and 1710, δ_H 8.00–7.70 (3 H, m, aromatic) 7.70–7.43 (6 H, m, aromatic) 7.43–7.00 (10 H, m, aromatic), 6.41 (2 H, s, olefinic), 3.05 (2 H, s), 2.98 (2 H, s), 0.50 (1 H, d, *J* 6) and −1.15 (1 H, d, *J* 6); *m/z* 521 (M) and 346, 280 and 203 (5.6, 5.8, 100 and 7.0%).

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