Formation of Cyclopent[*hi*]acephenanthrylene from 1,2-, 1,3-, 1,4- and 2,3-Triphenylenedicarboxylic Acid Derivatives on Flash Vacuum Pyrolysis at >900°C

Mircea D. Banciu,[A] *Roger F. C. Brown,*[A] *Karen J. Coulston,*[A] *Frank W. Eastwood,*[A] *Craig Jurss,*[A] *Irene Mavropoulos,*[A] *Michaela Stanescu*[A] *and Ulfert E. Wiersum*[B]

[A] Chemistry Department, Monash University, Clayton, Vic. 3168.
[B] Akzo Nobel Central Research, Velperweg 76,
6800 SB Arnhem, The Netherlands.

The processes involved in the conversion of triphenylene, $C_{18}H_{12}$, into cyclopent[*hi*]acephenanthrylene, $C_{18}H_{10}$, under flash vacuum pyrolytic conditions at 900–1100°C have been investigated by pyrolysing triphenylene-1,2- and -2,3-dicarboxylic anhydrides and diallyl triphenylene-1,3- and -1,4-dicarboxylates to give the corresponding didehydrotriphenylenes in the gas phase. These didehydro intermediates are converted into mixtures of cyclopent[*hi*]acephenanthrylene and triphenylene in different yields and proportions. Pyrolysis of 9,10-diethynylphenanthrene, $C_{18}H_{10}$, yields cyclopent[*hi*]acephenanthrylene in good yield. Pyrolysis of 1-nitrotriphenylene and allyl triphenylene-2-carboxylate to give the triphenylen-1-yl and -2-yl radicals leads to formation of the same products. Mechanisms involving radical rearrangements ($C_{18}H_{11}$ species) and benzyne–cyclopentadienylidenecarbene and ethyne–ethenylidene rearrangements ($C_{18}H_{10}$ species) are discussed.

The conversion of triphenylene (1) into cyclopent[*hi*]-acephenanthrylene (7) on flash vacuum pyrolysis (f.v.p.) at 1000°C was first described by Neilen and Wiersum.[1–3] At Monash we have confirmed that this reaction takes place, although in our apparatus a tempera- ture of 1100°C and a packed pyrolysis tube were found to be necessary before significant conversion was observed. The mechanism that had been proposed[1,2] involved sequential loss of the 1- and 2-hydrogen atoms leading to 1,2-didehydrotriphenylene (3), fol-
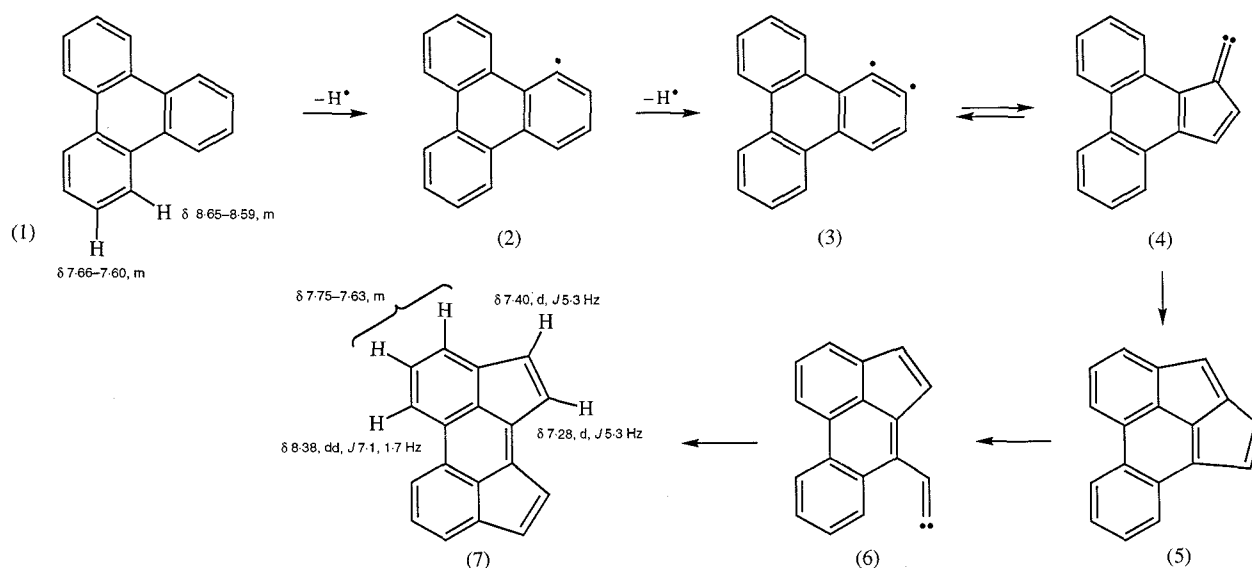

Scheme 1

lowed by ring contraction to the cyclopentadienyli-denecarbene derivative (4) and carbene insertion to give the highly strained cyclopent[*fg*]acephenanthrylene (5), which, by ring cleavage to the ethenylidene derivative (6) and alternative ring closure, formed cyclopent[*hi*]acephenanthrylene (7) (Scheme 1). To test this proposal we have pyrolysed triphenylene-1,2-dicarboxylic anhydride (14) to form the 1,2-didehydrotriphenylene intermediate (3) directly, and have examined a number of other possible mechanistic pathways by pyrolysing other suitable precursors.
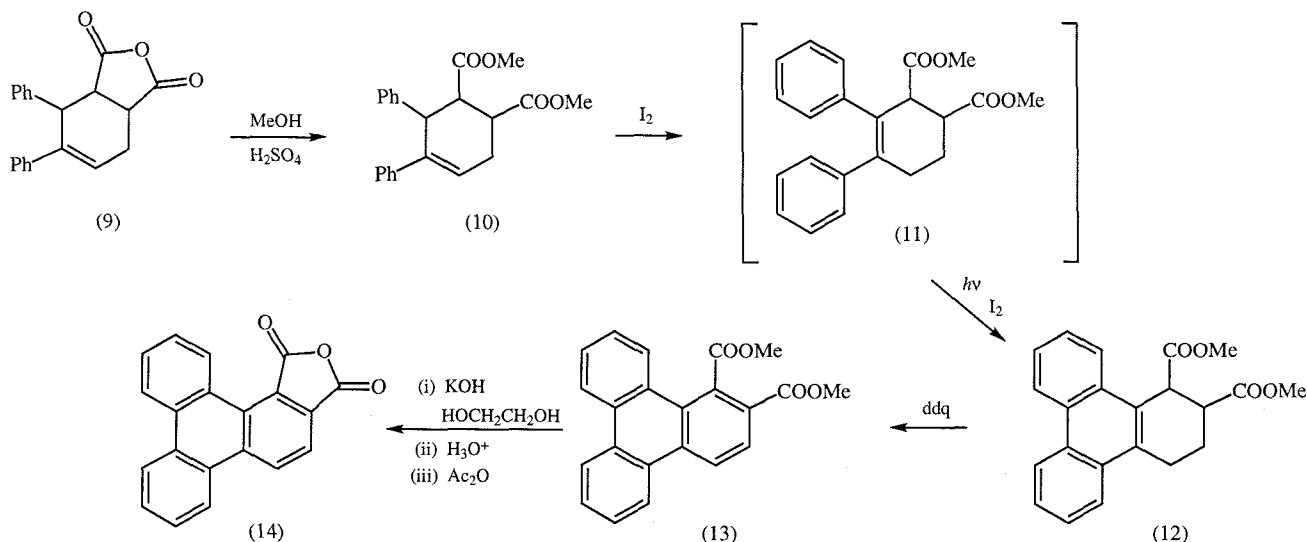
Synthesis of Precursors

9,10-Diethynylphenanthrene (8) was prepared by reaction of lithium acetylide[4] with 9,10-phenanthra-quinone to form 9,10-diethynyl-9,10-dihydrophenan-threne-9,10-diol,[5,6] which underwent reductive elimi-nation with stannous chloride to give the required compound.[7]
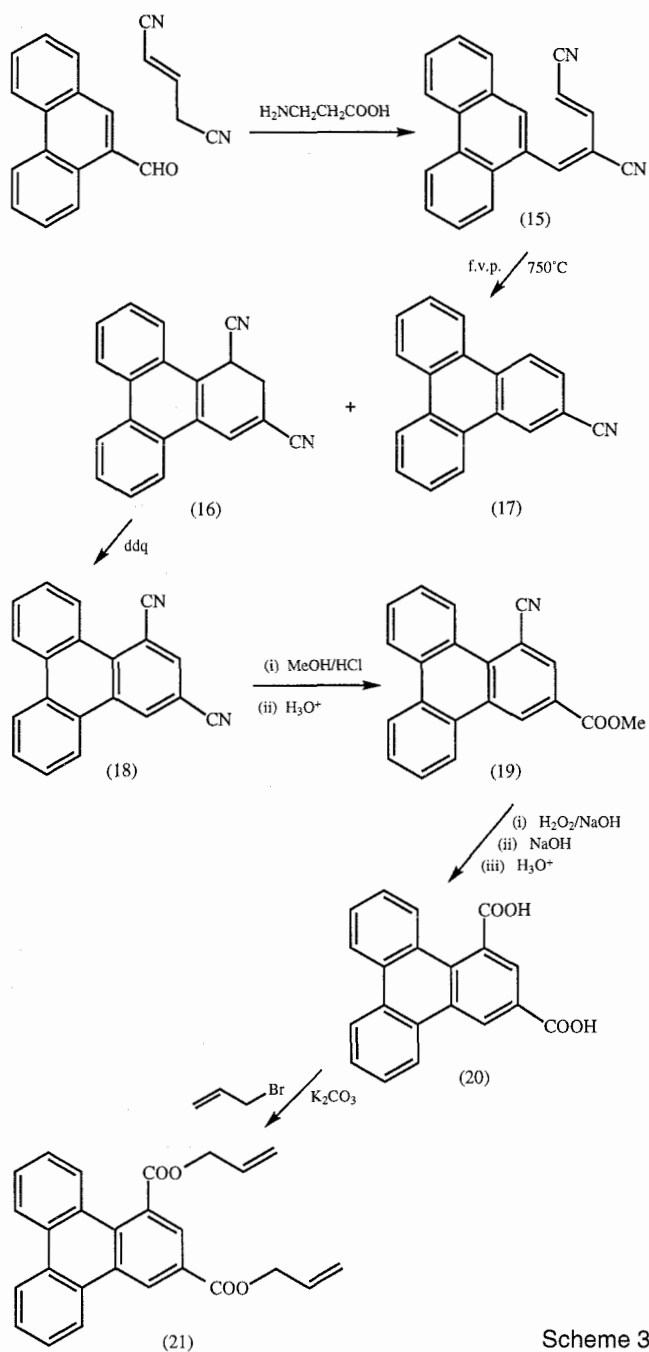

(8)
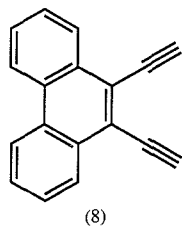
Triphenylene-1,2-dicarboxylic anhydride (14) was prepared by a method based on the photocyclization and dehydrogenation of a (*Z*)-stilbene to a phenanthrene derivative. 3,4-Diphenyl-1,2,3,6-tetrahydrophthalic anhydride[8] (9) was prepared by Diels–Alder addi-tion of maleic anhydride to 1,2-diphenylbuta-1,3-diene and converted into the dimethyl ester (10). Dehydrogenation of this ester yielded dimethyl 3,4-diphenylphthalate which was stable to irradiation and

gave none of the required triphenylene derivative. The 1,2,3,6-tetrahydro ester (10) could not be isomerized to dimethyl 1,2,5,6-tetrahydro-3,4-diphenylphthalate (11), but, based on the supposition that the dou-ble bond could migrate under the catalytic influ-ence of iodine, the diester (10) was irradiated in the presence of iodine. In two experiments the required dimethyl 1,2,3,4-tetrahydrotriphenylene-1,2-dicarboxylate (12) was obtained without difficulty in fair yield. However, on attempting to repeat this work some months later, we could obtain the product (12) only in low yield after prolonged irradiation and careful chromatographic separation. Dehydrogenation of the cyclized ester (12) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (ddq) gave dimethyl triphenylene-1,2-dicarboxylate (13), which was hydrolysed to the diacid and dehydrated with acetic anhydride to yield triphenylene-1,2-dicarboxylic anhydride (14) (Scheme 2).

Diallyl triphenylene-1,3-dicarboxylate (21) was pre-pared by first condensing phenanthrene-9-carbaldehyde with pent-2-enedinitrile (glutacononitrile)[9] in the pres-ence of *β*-alanine to give 4-(9′-phenanthrylmethylidene)-pent-2-enedinitrile (15). This compound on f.v.p. at 750°C gave 1,2-dihydrotriphenylene-1,3-dicarbonitrile (16), together with some triphenylene-2-carbonitrile (17). Dehydrogenation of the dihydro compound (16) with ddq in boiling chlorobenzene gave triphenylene-1,3-dicarbonitrile (18). Hydrolysis of this hindered dinitrile was difficult and was only achieved in rea-sonable yield by first reacting it with methanol and hydrogen chloride to give an imino ether hydrochlo-ride which was converted with aqueous acid into methyl 4-cyanotriphenylene-2-carboxylate (19). Treat-ment of this compound with alkaline hydrogen perox-ide followed by vigorous alkaline hydrolysis gave, on acidification, triphenylene-1,3-dicarboxylic acid (20) which was esterified by reaction with potassium
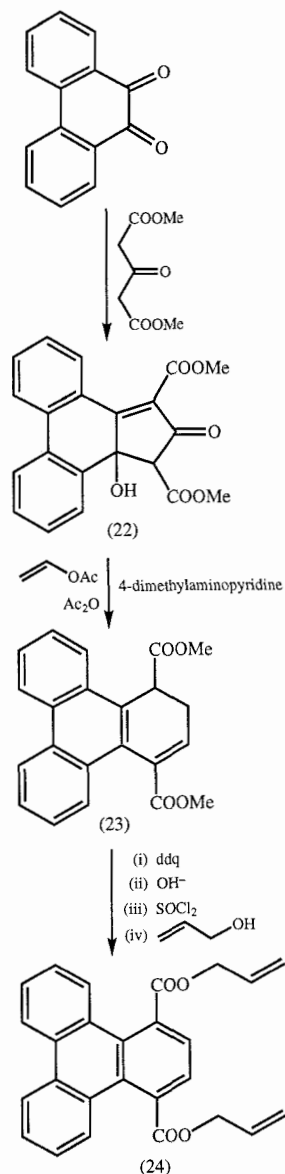

Scheme 2

(15)

(16) + (17)

(18) → (19)

(20)

(21)   Scheme 3

Diallyl triphenylene-1,4-dicarboxylate (24) was prepared by an inverse demand Diels–Alder addition. Condensation of 9,10-phenanthraquinone with dimethyl 3-oxopentanedioate gave the known dimethyl 11b-hydroxy-2-oxo-2,11b-dihydro-1*H*-cyclopenta[*l*]phenanthrene-1,3-dicarboxylate[11] (22), which on reaction with vinyl acetate, acetic anhydride and 4-dimethylaminopyridine yielded, unexpectedly, dimethyl 1,2-dihydrotriphenylene-1,4-dicarboxylate (23). Dehydrogenation of this compound with ddq in boiling chlorobenzene gave dimethyl triphenylene-1,4-dicarboxylate which was hydrolysed to the diacid and esterified by reaction of the acid chloride with allyl alcohol to give diallyl triphenylene-1,4-dicarboxylate (24) (Scheme 4).

Triphenylene-2,3-dicarboxylic anhydride (27) was prepared from phenanthro[9,10-*c*]furan[12] (25) which with maleic anhydride underwent Diels–Alder addition to give the epoxy anhydride (26). This product was

(22)

(23)

(24)

Scheme 4

carbonate and allyl bromide in dimethylformamide solution[10] to give diallyl triphenylene-1,3-dicarboxylate (21) in 20% yield (Scheme 3). Alkaline hydrolysis of the pyrolysate containing triphenylene-2-carbonitrile (17) and 1,2-dihydrotriphenylene-1,3-dicarbonitrile (16) gave triphenylene-2-carboxylic acid and a trace of triphenylene-1,3-dicarboxylic acid which were separated after conversion into the allyl esters. The small amount of dicarboxylic acid presumably arose by initial dehydrogenation due to the presence of air since the bulk of the dihydro compound (16) was destroyed. The monoester was used as a precursor for the triphenylen-2-yl radical.

a mixture of stereoisomers but on heating with acetic anhydride it was converted into a single stereoisomer. Dehydration of this product with polyphosphoric acid at 170°C gave triphenylene-2,3-dicarboxylic anhydride (27) (Scheme 5).
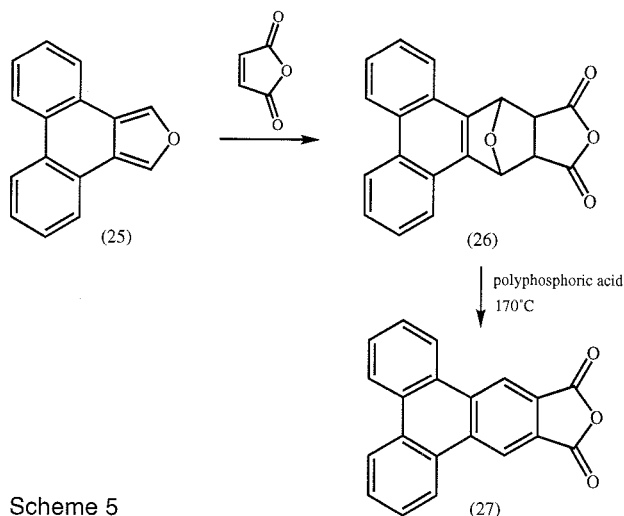
Scheme 5

Analysis of Pyrolysates

The synthesis of cyclopent[*hi*]acephenanthrylene (cpap) (7) has been described by Mulder *et al.*,[13] and the ¹H n.m.r. spectrum of the compound has been reported in detail. F.v.p. of 9,10-diethynylphenanthrene (8) at 900°C gave a pyrolysate which was essentially pure cpap. The ¹H n.m.r. spectrum of this sample was used as the standard and the spectroscopic data are shown beside the structure in Scheme 1. Triphenylene (1) was generally present in the pyrolysates and the ¹H resonance ranges for this compound are also shown in Scheme 1.

The resonances at δ 8·38, 7·40 and 7·28 were characteristic of cpap and were well separated from those of other compounds in the pyrolysates. The multiplet at δ 7·75–7·63, attributed to H2 and H3 of cpap, was partially obscured by the high field multiplet of triphenylene at δ 7·66–7·60. The low field multiplet of triphenylene at δ 8·65–8·59 was well separated from other resonances and the integrated signal could be used for determination of the relative proportions of the two products. In pyrolysates obtained from triphenylene at 1100°C the resonances due to cpap were easily discernible when 3% of the compound was present.

Results of Pyrolyses

Pyrolysis of triphenylene-1,2-dicarboxylic anhydride (14) at 900°C gave a pyrolysate consisting principally of cpap (7) and triphenylene (1) with only traces of other materials present. The ratios of the two products for this and other cases are given in Table 1. In all pyrolyses at 900°C and higher some blackening within the tube was evident and this decomposition

of part of the material provides a source of hydrogen atoms. The formation of triphenylene is considered to involve abstraction of hydrogen from this source by a didehydrotriphenylene or triphenylenyl radical. The mechanism of the transformation of the anhydride (14) into cpap (7) is shown in Scheme 6. It is postulated to involve loss of CO_2 and CO to give the 1,2-didehydrotriphenylene (3) followed by ring contraction and insertion to give the highly strained, non-planar cyclopent[*fg*]acephenanthrylene (5), which undergoes ring opening and closure to form cpap (7). An alternative mode of ring opening to 5-ethynylacephenanthrylene, analogous to the ring opening of cyclopent[*bc*]acenaphthylene to 1-ethynylacenaphthylene,[14] was not observed. Thus, the original proposal that the conversion of triphenylene (1) into cpap (7) could occur by sequential loss of H1 and H2 is a plausible hypothesis.

If, however, the initial loss of H1 is assisted by crowding with H12 (H1, H12 interatomic distance is 190 pm)[15] the loss of a second hydrogen atom could take place at H4. The resulting 1,4-didehydrotriphenylene (31) would be expected to undergo Bergman cleavage[16] to give 9,10-diethynylphenanthrene (8) which has been shown to cyclize efficiently to cpap at 900°C. Pyrolysis of diallyl triphenylene-1,4-dicarboxylate (24) gave cpap and triphenylene in a ratio of 1:1. Although the ratio of cpap to triphenylene is smaller in this case than it is in the case of the 1,2-anhydride,[15] the initiating process in this reaction involves loss of allyl radicals, and, in general, pyrolysates arising from such precursors showed more extraneous aromatic products than those from anhydrides. This is attributed to the addition of allyl radicals to intermediates followed by aromatization of the products.

Evidence from other studies suggested that there exist other mechanisms for the high temperature rearrangement of 1,2-, 1,3-[17] and 1,4-didehydro aromatic species and the two further possibilities for didehydro species in a single ring of triphenylene were examined. Pyrolysis of diallyl triphenylene-1,3-dicarboxylate (21) and of triphenylene-2,3-dicarboxylic anhydride (27) gave the same two products with the ratio of cpap to triphenylene being 0·33:1 and 1·3:1 respectively. Pyrolysis of 1-nitrotriphenylene[18] at 1100°C, which would be expected to result in loss of NO_2 and formation of the triphenylen-1-yl radical (2), gave cpap and triphenylene in a ratio of 0·4:1. Pyrolysis of 2-nitrotriphenylene[18] at 1100°C gave triphenylene but no trace of cpap. On the other hand, pyrolysis of allyl triphenylene-2-carboxylate at 900°C, which would be expected to give the triphenylen-2-yl radical (28), resulted in the formation of cpap and triphenylene in a ratio of 0·14:1.

The Mobility of Hydrogen Atoms in Triphenylene

Lithiation of triphenylene (1) with butyllithium followed by addition of D_2O as described by Ashe

et al.[19] gave deuterated triphenylene. The mass spectrum showed the product to be predominantly dideuterated as had been found previously.[19] [1]H and [2]H n.m.r. spectroscopic measurements showed that H α (H 1,4,5,8,9,12) was made up of 72% [1]H and 28% [2]H, and that H β (H 2,3,6,7,10,11) consisted of 95% [1]H and 5% [2]H. The ratio of [1]H α to [1]H β was 43:57 as determined directly from the integrated signals. F.v.p. of samples of deuterated triphenylene through a

packed tube followed by recovery of the compound and measurement of the [1]H n.m.r. spectrum showed that this ratio remained constant within experimental error: 800°C, H α to H β 42:58 (97% recovery); 900°C, 42:58 (87); 1000°C, 42:58 (80); 1100°C, 43:57 (27). The [1]H n.m.r. spectrum of the sample recovered from the 1100°C pyrolysis showed a small amount of cpap to be present.

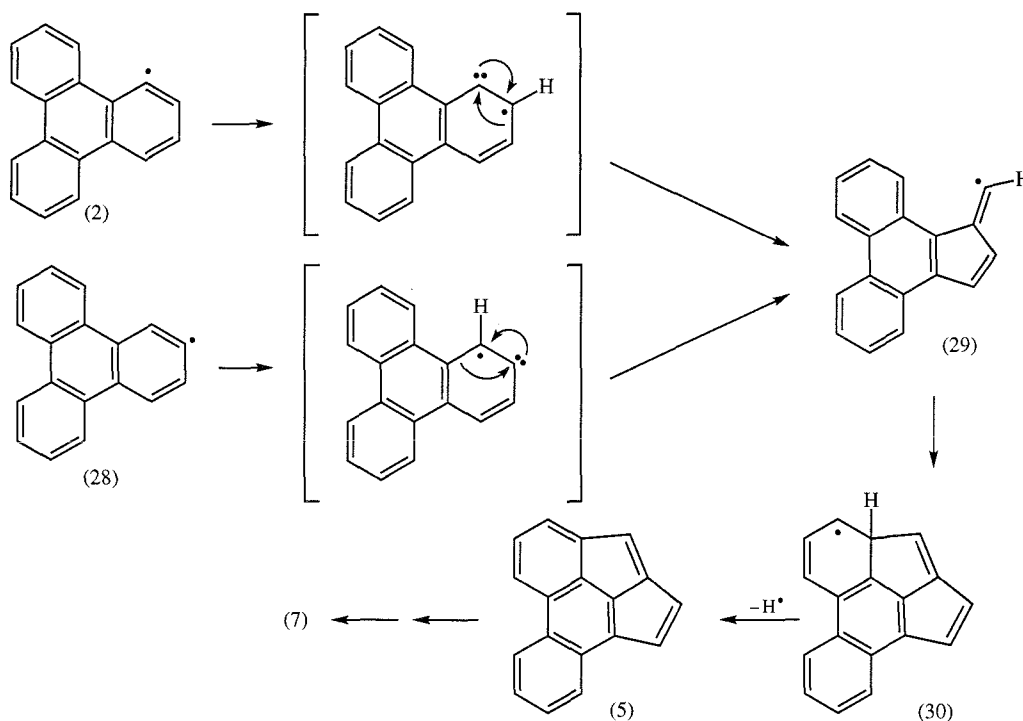F.v.p. of unlabelled triphenylene at 1100°C under the same conditions gave triphenylene containing about

Table 1. Results of f.v.p. of precursors through an unpacked tube

| Compound pyrolysed | | | Pyrolysis conditions | | Sublimation | | | | Ratio of cpap |
Name	No.	Mass (mg)	Temp. (°C)	Pressure (mm)	temp. (°C)	Time (min)	Pyrolysate (mg)	Yield[A] (%)	to triphenylene
9,10-Diethynylphenanthrene	(8)	14[B]	900	0·03	70–85	45	6	86	C
Triphenylene-1,2-dicarboxylic anhydride	(14)	15	900	0·04	200	60	10	88	3:1
Diallyl triphenylene-1,3-dicarboxylate	(21)	9[D]	900	0·05	180	40	1·5	33	0·33:1
Diallyl triphenylene-1,4-dicarboxylate	(24)	100	900	0·03	150–170	60	35	60[E]	1:1
Triphenylene-1,3-dicarboxylic anhydride	(27)	13	950	0·05	270	40	3	30	1·3:1
1-Nitrotriphenylene		24[F]	1100	0·10	110–125	90	16	80	0·4:1
Allyl triphenylene-2-carboxylate		50	900	0·04	140	90	25	69	0·14:1

[A] Yield calculated as $C_{18}H_{12}$.   [B] Unsublimed residue 7 mg.   [C] Pyrolysate contained cpap only and no triphenylene.   [D] Unsublimed residue 3 mg.   [E] The cpap was isolated by chromatography in 24% yield.   [F] Unsublimed residue 4 mg.
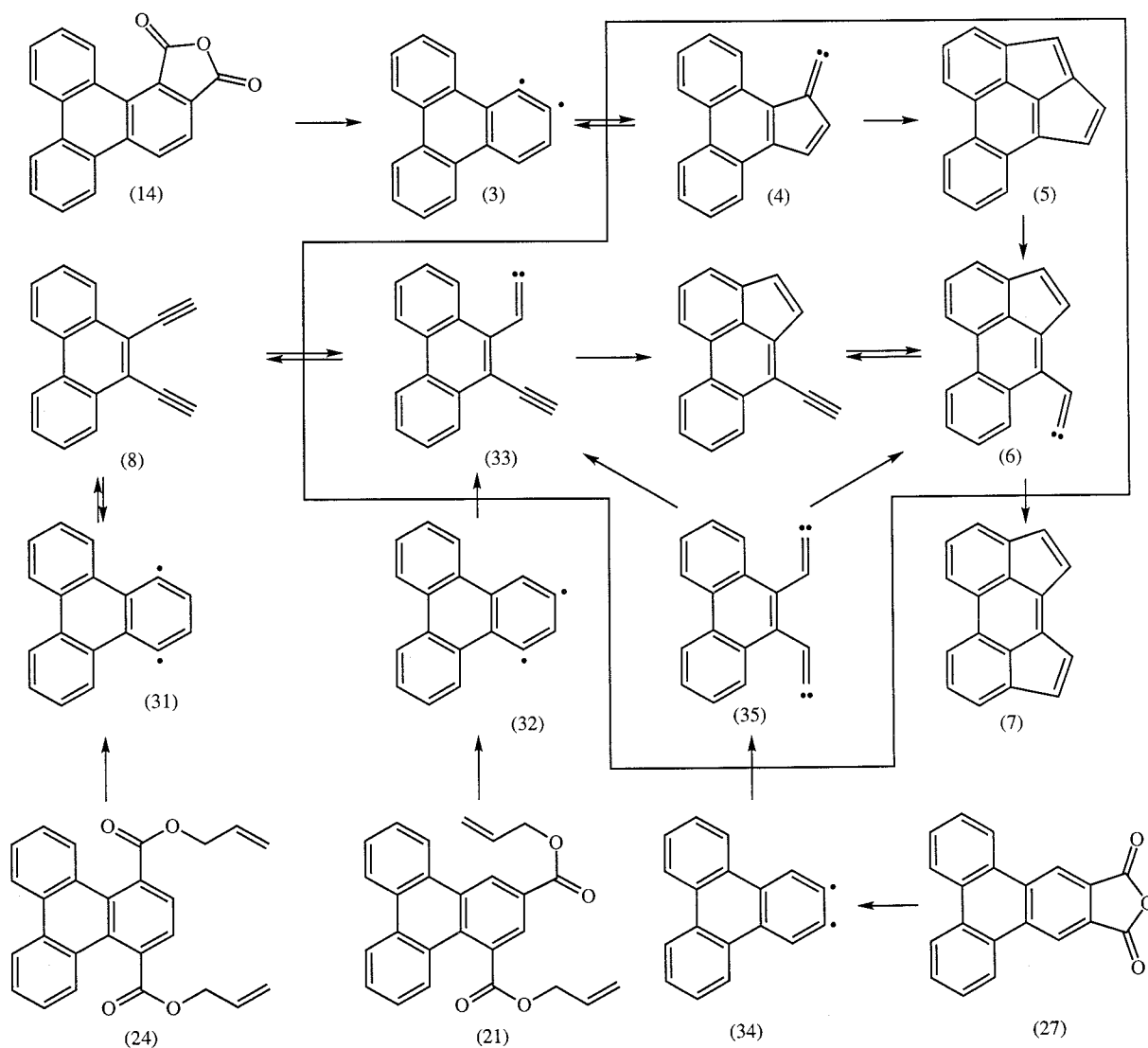
Scheme 6

Scheme 7

3% cpap as determined by [1]H n.m.r. spectroscopy. Copyrolysis of an approximately equimolecular mixture of benzoyl peroxide and triphenylene at 1100°C under the same conditions, which would be expected to produce two phenyl radicals per triphenylene molecule in the gas phase, resulted in a pyrolysate containing principally triphenylene and biphenyl. The cpap was present in this pyrolysate in about 3% yield relative to triphenylene. We conclude that under the conditions employed there is no intermolecular hydrogen abstraction by the phenyl radicals and no promotion of dehydrogenation and rearrangement. It appears from these experiments that the interchange of hydrogen atoms between the α- and β-positions in triphenylene does not take place with any facility, even at 1100°C under our conditions. We would argue that the vibrational energy required to induce any shift of hydrogen is probably similar to that required to cause loss of one and then another hydrogen atom.

Mechanisms Involving Free Radical Species ($C_{18}H_{11}$)

The triphenylen-1-yl radical (2) was formed by f.v.p. of 1-nitrotriphenylene at 1100°C and it gave a markedly greater yield of cpap than was formed by pyrolysis of triphenylene under the same conditions. The triphenylen-2-yl radical (28) was formed by f.v.p. of allyl triphenylene-2-carboxylate at 900°C and it also gave a considerable yield of cpap. We argue that both radicals provide entry points to the main reaction pathway leading to cpap.

The crowding of two hydrogen atoms in the bay region of triphenylene[15] is expected to facilitate the loss

of one hydrogen atom when sufficient vibrational energy is available, and this loss would result in the formation of the highly reactive but less crowded triphenylen-1-yl radical. This radical and also the triphenylen-2-yl radical (28) can be considered as reacting in two ways: pathway a, involving rearrangement of the radical followed by loss of a hydrogen atom; pathway b, involving loss of a hydrogen atom followed by rearrangement.

Pathway a. It is proposed that the triphenylen-1-yl radical (2) may undergo ring contraction to a five-membered ring carrying an exocyclic ylidenemethyl radical (=HC•) (29). Addition of this radical to the adjacent aromatic ring may result in a delocalized radical species (30) which may lose a hydrogen atom to give cyclopent[fg]acephenanthrylene (5) which is considered to be on the pathway to cpap. The triphenylen-2-yl radical (28) may undergo ring contraction to the same exocyclic radical intermediate (29) as is proposed for the triphenylen-1-yl radical (Scheme 7). Ring contraction of an aryl radical is proposed on the basis of the following evidence which will be presented in a separate paper. F.v.p. of benzoyl peroxide at 1100°C yields biphenyl and other aromatic species but no biphenylene is formed. F.v.p. of phthalic anhydride or Ninhydrin at 1100°C gives pyrolysates containing biphenylene. We conclude that at 1100°C the phenyl radical does not lose a hydrogen atom and form 1,2-didehydrobenzene. F.v.p. of allyl biphenyl-2-carboxylate at 1100°C yields cyclopent[a]indene and this may involve ring contraction of a substituted phenyl radical.

Pathway b. Loss of a hydrogen atom from each radical species may occur in different ways.

(i) The triphenylen-1-yl radical can lose H 2 to give 1,2-didehydrotriphenylene which can rearrange to cpap.

(ii) The triphenylen-1-yl radical can lose H 4 to give 1,4-didehydrotriphenylene which can rearrange to cpap.

(iii) If the degenerate rearrangement of the triphenylen-1-yl radical (2) into the triphenylen-12-yl radical requires little activation energy, then the loss of any other bay-region hydrogen atom can result in rearrangement to 1,4-didehydrotriphenylene and conversion into cpap (Scheme 8).
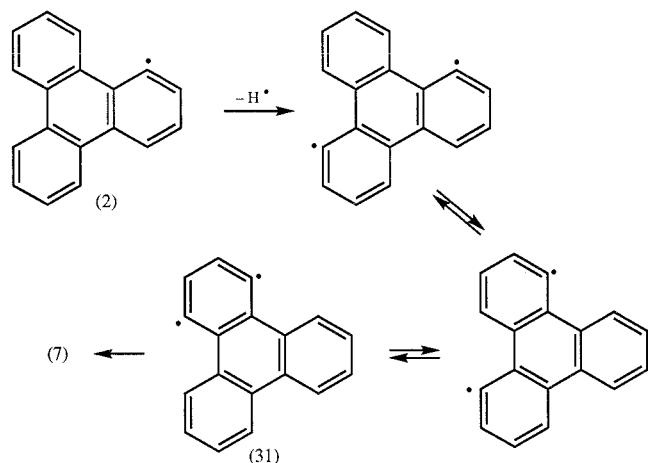
Scheme 8

(iv) The triphenylen-2-yl radical (28) can lose H 1 to give 1,2-didehydrotriphenylene which can rearrange to cpap.

The loss of hydrogen atoms from monoradicals is presumably not restricted to the adjacent hydrogens, and the mobility of hydrogen atoms has not been established in either monoradicals or didehydro species. However, the 1,3- and 2,3-didehydro-triphenylenes have been shown to yield cpap and triphenylene although in different proportions. If the hydrogen atoms in these species are sufficiently mobile that a 1,2- or 1,4-didehydrotriphenylene is formed then either species will rearrange to cpap. An alternative proposal is that there are new forms of cleavage or rearrangement of the carbocyclic rings, and these are discussed in the next section.

Mechanisms Involving Didehydro Species (C₁₈H₁₀)

The conversion of 9,10-diethynylphenanthrene (8) into cpap is considered to involve sequential rearrangement of the ethyne groups to ethenylidene and cyclization by insertion. Compound (8) can in theory be converted reversibly into 1,4-didehydrotriphenylene (31) which might be expected to abstract hydrogen and yield triphenylene. Triphenylene, however, was not detected in the pyrolysate and one must conclude that the route to cpap involves transition states of lower energy.

Pyrolysis of diallyl triphenylene-1,4-dicarboxylate (24) gave cpap and triphenylene in a ratio of 1:1. The diester (24) would be expected to fragment in a series of steps to 1,4-didehydrotriphenylene (31) and during this process there is opportunity for the radicals to abstract hydrogen and form triphenylene. The 1,4-didehydrotriphenylene once formed can undergo Bergman ring opening to 9,10-diethynylphenanthrene (8) and this would be converted into cpap.

Pyrolysis of triphenylene-1,2-dicarboxylic anhydride (14) at 900°C is expected to lead directly to 1,2-didehydrotriphenylene (3) which would undergo a type of ring contraction and insertion process, which has been observed previously,[13] to give cyclopent[fg]acephenanthrylene (5) followed by ring opening and alternative closure to cpap.

The 1,3-diester (21) is expected to fragment by loss of an allyl radical and CO_2 to yield a monoradical, and repetition of the same process would yield the 1,3-didehydrotriphenylene (32). The mono- or di-radical species can abstract hydrogen to give triphenylene. In principle, the species (32) can be cleaved to yield the acetylenic carbene (33)[17] which will be converted into cpap.

Pyrolysis of triphenylene-2,3-dicarboxylic anhydride (27) yields cpap and triphenylene in a ratio of 1·3:1, a somewhat greater ratio than in the case of the 1,4-diester (1:1). This difference in ratio may be due to the much cleaner fragmentation possible in the anhydride which should lead, albeit at a higher fragmentation temperature, to the 2,3-didehydrotriphenylene (34). Cleavage of the 2,3 carbon–carbon bond would lead directly to the highly energetic biscarbene (35) which would equilibrate to cyclized and ethenyl species and rearrange to cpap. All these suggested mechanisms are represented in Scheme 6.

The 1,2-, 1,3-, 1,4- and 2,3-didehydrotriphenylenes are formed and rearrange at temperatures below 1100°C and give a much greater yield of cpap than is formed by pyrolysis of triphenylene at 1100°C under the same conditions of residence time. We conclude that these didehydro species provide separate entry routes to the principal reaction pathway leading to cpap. If hydrogen atoms in these species are sufficiently mobile then the didehydro species will be interconvertible and provide a direct pathway to cpap. If this is not the case then an explanation for the observed phenomena can be found in cleavage of the 2,3-bond to yield ethynyl and ethenylidene species which are interconvertible and provide a pathway to cpap as illustrated in Scheme 6.

A further process that can be considered is a ring contraction involving one radical centre while a second radical centre elsewhere in the didehydrotriphenylene species is not immediately involved. The rearrangement of 1,3-didehydrotriphenylene (32) is shown in Scheme 9 as an example, but the mechanism is applicable to other didehydro species.
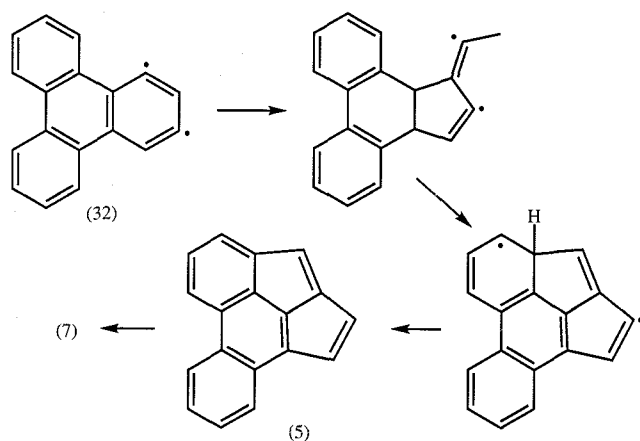
Scheme 9

Conclusion

The pyrolytic dehydrogenation and rearrangement of triphenylene to cpap (7) is a high-energy process most probably initiated by formation of the triphenylen-1-yl radical (2). The process may continue by ring contraction of this radical and cyclization to a new $C_{18}H_{11}$ species which would lose a hydrogen atom to give the highly strained cyclopent[*fg*]acephenanthrylene (5); this in turn would rearrange to cpap. Alternatively, the radical may be converted into 1,2-didehydrotriphenylene (3) which would rearrange to cpap through the same highly strained intermediate (5). A pathway which avoids the intermediacy of (5) involves loss of a second bay-region hydrogen atom and formation of 9,10-diethynylphenanthrene (8), followed by rearrangement to cpap. It should be possible to differentiate these alternative routes experimentally by isotopic labelling. Production of any didehydrotriphenylene under pyrolytic conditions is expected to lead to formation of cpap.

Experimental

Melting points were determined by using a Reichert hot stage melting point apparatus and are uncorrected. Microanalyses were performed by National Analytical Laboratories Pty Ltd, Blackburn, Victoria, and Chemical and Micro Analytical Services Pty Ltd, Essendon North, Victoria. Infrared spectra were recorded on a Perkin–Elmer 1640 Fourier-transform i.r. spectrometer. ^{1}H and ^{13}C n.m.r. spectra were recorded on Bruker AC-200, AM-300 and DRX 400 spectrometers. Values shown for coupling constants J are frequency differences taken directly from spectra. Mass spectra were measured with a VG Trio-1 spectrometer at 70 eV. Silica gel used for flash chromatography was Merck Kieselgel 60, particle size $0 \cdot 040$–$0 \cdot 063$ mm (230–400 mesh), Art. 9385. Light petroleum refers to the fraction of b.p. 60–80°. Gas–liquid chromatogram/mass spectra were recorded with a Hewlett–Packard gas–liquid chromatograph coupled to a V.G. Trio-1 spectrometer via an S.G.E. open split interface of ratio 50 : 1.

The pyrolytic apparatus consisted of a horizontal silica tube (300 by 25 mm i.d.) heated with an external electric furnace. The temperature was measured with a thermocouple placed on the external wall of the tube, and the pressure with a Dynavac TM 8 gauge mounted above the collecting cold finger,

cooled with liquid nitrogen, at the exit end. The material to be pyrolysed was sublimed into the heated tube by warming with an air oven. Pyrolysis conditions are expressed in the form (tube temperature, pressure, sublimation temperature, time to complete sublimation). Pyrolysis conditions are given in Table 1.

1-Nitrotriphenylene and 2-nitrotriphenylene were prepared by nitration of triphenylene with nitric acid in acetic anhydride.[18]

9,10-Diethynylphenanthrene (8)

Phenanthrene-9,10-dione was added to lithium acetylide[4] as described by Sukumaran and Harvey.[5] The resulting 9,10-diethynyl-9,10-dihydrophenanthrene-9,10-diol (86% yield) crystallized from benzene in colourless needles, m.p. 204–207°C (lit.[6] 205–207°C). ν_{max} (Nujol) 3522, 3447 cm^{-1}. Mass spectrum m/z 260 (M, 25%). The diol was reduced with stannous chloride in hydrochloric acid to give a crude product which was purified by radial chromatography (silica; light petroleum) to give the title compound (12% yield) as yellow crystals, m.p. 125–127°C (lit.[7] 130°C). ν_{max} 3278, 2104 cm^{-1}. ^{1}H n.m.r. spectrum δ (CDCl$_3$, 200 MHz) $8 \cdot 70$–$8 \cdot 63$, m, H 4,5; $8 \cdot 51$–$8 \cdot 45$, m, H 1,8; $7 \cdot 78$–$7 \cdot 63$, m, H 2,3,6,7; $3 \cdot 83$, s, $2 \times C \equiv C$-H. Mass spectrum m/z 226 (M, 100%). The ultraviolet spectrum was the same as that reported previously.

Dimethyl 3,4-Diphenyl-1,2,3,6-tetrahydrobenzene-1,2-dicarboxylate (10)

A mixture of 3,4-diphenyl-1,2,3,6-tetrahydrophthalic anhydride[8] (9) ($3 \cdot 0$ g, 10 mmol), methanol (100 ml) and conc. sulfuric acid (2 ml) was heated under reflux for 12 h. The solution was concentrated under vacuum to c. 50 ml and water (20 ml) was added. The mixture was warmed to dissolve the precipitated solid and on cooling the crystalline ester ($1 \cdot 7$ g), m.p. 124–125°C, was collected. The mother liquor was extracted with dichloromethane and the combined extracts were washed with aqueous sodium bicarbonate and water and dried (Na$_2$SO$_4$). Evaporation of the solvent gave further ester ($1 \cdot 0$ g) (total yield 77%). The *ester* (10) crystallized from methanol in colourless plates, m.p. 129–130°C (Found: C, $75 \cdot 3$; H, $6 \cdot 0$. $C_{22}H_{22}O_4$ requires C, $75 \cdot 4$; H, $6 \cdot 3\%$). ν_{max} 1739 cm^{-1}. ^{1}H n.m.r. spectrum δ (CDCl$_3$, 200 MHz) $7 \cdot 25$–$6 \cdot 97$, m, aromatic; $6 \cdot 35$–$6 \cdot 26$, m, H 5; $4 \cdot 52$–$4 \cdot 42$, m, H 3; $3 \cdot 65$, s, OCH$_3$; $3 \cdot 70$–$3 \cdot 50$, overlapping m, 1H; $3 \cdot 18$, s, OCH$_3$; $3 \cdot 27$–$3 \cdot 03$, overlapping m, 2H; $2 \cdot 77$–$2 \cdot 35$, m, 1H. ^{13}C n.m.r. spectrum δ (CDCl$_3$, $75 \cdot 47$ MHz) $173 \cdot 69$, $171 \cdot 87$, $2 \times$CO; $141 \cdot 40$, $139 \cdot 74$, $136 \cdot 80$, $3 \times$quat. C; $129 \cdot 37$, C 5; $127 \cdot 94$, $127 \cdot 83$, $127 \cdot 77$, $126 \cdot 32$, $126 \cdot 25$, $126 \cdot 22$, $10 \times$aromatic CH; $51 \cdot 98$, $50 \cdot 98$, $47 \cdot 13$, C 1,2,3; $45 \cdot 68$, $41 \cdot 35$, $2 \times$OCH$_3$; $25 \cdot 56$, C 6. Mass spectrum m/z 350 (M, 15%), 290 (100), 258 (22), 231 (94), 230 (45), 229 (26), 216 (26), 215 (42), 202 (23), 153 (31), 152 (36), 129 (42), 128 (41), 115 (62), 91 (56).

Dehydrogenation of the ester (10) with ddq in chlorobenzene gave *dimethyl 3,4-diphenylbenzene-1,2-dicarboxylate*, m.p. 126°C (Found: C, $76 \cdot 2$; H, $5 \cdot 3$. $C_{22}H_{18}O_4$ requires C, $76 \cdot 3$; H, $5 \cdot 2\%$). ^{1}H n.m.r. spectrum δ (CDCl$_3$, 200 MHz) $8 \cdot 07$, d, J $8 \cdot 2$ Hz, H 6; $7 \cdot 52$, d, J $8 \cdot 2$ Hz, H 5; $7 \cdot 22$–$7 \cdot 0$, m, aromatic; $3 \cdot 91$, s, OCH$_3$; $3 \cdot 56$, s, OCH$_3$. Mass spectrum m/z 346 (M, 96%).

Dimethyl 1,2,3,4-Tetrahydrotriphenylene-1,2-dicarboxylate (12)

Note that experiment (A) was conducted twice but could not thereafter be reproduced.

(A) In a silica tube the ester (10) (300 mg) was dissolved in benzene (5 ml) and cyclohexane (30 ml). Iodine (5 mg or 10 mg) was added and the solution was flushed continuously with a slow stream of nitrogen. With internal water cooling, the solution was irradiated externally (254–366 nm) for 20 h. The resulting solution was washed with aqueous sodium thiosulfate and water, dried (Na$_2$SO$_4$) and the solvent evaporated.

Crystallization of the residue from methanol gave the title ester (12) as colourless crystals (250 mg, 83%), m.p. 135–136°C.

(B) In a silica tube the ester (10) (300 mg) was dissolved in benzene (5 ml) and cyclohexane (70 ml) and iodine (210 mg) was added. Nitrogen was bubbled through the solution for 5 min and the system was sealed. With internal water cooling, the solution was irradiated externally with lamps giving radiation over the range 254–366 nm for 5 days. The crude product was isolated as described in method (A) and was shown by t.l.c. (ethyl acetate/light petroleum, 1:4) to contain starting material (R_F 0·42) and the title ester (12) (R_F 0·34), together with other compounds. The title *ester* (12) was separated by flash chromatography (silica; ethyl acetate/light petroleum, 1:5 changing to 1:1) and obtained as colourless crystals (0·16 g, 52%), m.p. 135–136°C (Found: C, 76·1; H, 5·6. $C_{22}H_{20}O_4$ requires C, 75·9; H, 5·8%). ν_{max} 1740 cm^{-1}. ^{1}H n.m.r. spectrum δ (CDCl$_3$, 200 MHz) 8·76–8·61, m, 2H; 8·15–7·97, m, 2H; 7·74–7·54, m, 4H; 4·89, d, J 5·1 Hz, H 1; 3·88, s, OCH$_3$; 3·86, s, OCH$_3$; 3·61–3·41, m, H 2; 3·42–2·92, m, 2×H 4; 2·58–2·26, m, 2×H 3. ^{13}C n.m.r. spectrum δ (CDCl$_3$, 75·47 MHz) 173·95, 172·52, 2×CO; 131·10, 130·93, 130·89, 129·98, 129·69, 126·65, 6×quat. C; 127·05, 126·86, 126·57, 125·94, 123·81, 123·09, 122·97, 122·84, 8×aromatic CH; 52·33, 52·07, 2×OCH$_3$; 44·31, 43·04, C 1,2; 26·20, 20·40, C 4,3. Mass spectrum m/z 348 (M, 15%), 289 (12), 288 (34), 230 (29), 229 (100), 228 (39), 226 (17), 215 (24).

Dimethyl Triphenylene-1,2-dicarboxylate (13)

A solution of the diester (12) (0·23 g, 0·6 mmol) and ddq (0·29 g, 1·2 mmol) in chlorobenzene (15 ml) was heated under reflux for 24 h. The mixture was cooled, filtered and the residue washed well with benzene. The filtrate was evaporated under vacuum and the residue was purified by flash chromatography (silica; ethyl acetate/light petroleum, 1:4) to give the *ester* (13) (196 mg, 86%), m.p. 145–146°C (Found: C, 76·9; H, 4·5. $C_{22}H_{16}O_4$ requires C, 76·7; H, 4·7%). ν_{max} 1730, 1720, 1702 cm^{-1}. ^{1}H n.m.r. spectrum δ (CDCl$_3$, 300 MHz) 8·71, d, J 8·87 Hz, 1H; 8·64–8·55, m, 3H; 8·38, dd, J 8·40, 0·99 Hz, 1H; 8·13, d, J 8·74 Hz, 1H; 7·55, ddd, J 8·44, 7·05, 1·42 Hz, 1H; 4·04, s, OCH$_3$; 3·98, s, OCH$_3$. ^{13}C n.m.r. spectrum δ (CDCl$_3$, 50·32 MHz) 171·66, 167·09, 2×CO; 134·15, 133·10, 131·03, 130·77 (×2), 128·64 (×2), 128·51, 8×quat. C; 128·76, 128·12, 127·69, 127·35, 126·45, 124·10, 124·00, 123·54, 123·27, (one peak obscured) 10×CH; 53·05, 52·79, 2×OCH$_3$. Mass spectrum m/z 344 (M, 41%), 313 (22), 298 (50), 281 (39), 270 (18), 254 (25), 226 (100), 225 (35), 224 (35), 213 (17).

Triphenylene-1,2-dicarboxylic Anhydride (14)

A suspension of the ester (13) (0·17 g, 0·5 mmol) and potassium hydroxide (0·2 g) in ethane-1,2-diol (10 ml) was heated under reflux for 20 h. The mixture was cooled, water (20 ml) was added and the resulting solution was extracted twice with ether. On acidification of the aqueous solution with hydrochloric acid, the dicarboxylic acid precipitated slowly. It was collected, washed well with water, and obtained as colourless crystals (150 mg, 95%), m.p. 248–254°C. ν_{max} (Nujol) 3555, 3446, 1698 cm^{-1}. ^{1}H n.m.r. spectrum δ [CDCl$_3$/(CD$_3$)$_2$SO, 300 MHz] 8·80, d, J 8·39 Hz, 1H; 8·70, d, J 8·66 Hz, 1H; 8·66–8·52, m, 3H; 8·12, d, J 8·65 Hz, 1H; 7·77–7·61, m, 3H; 7·61–7·48, m, 1H. Mass spectrum m/z 298 (M − H$_2$O, 56%). The diacid (145 mg, 0·46 mmol) in acetic anhydride (5 ml) was heated under reflux for 2 h and the mixture was cooled to 0°C. The resulting yellow crystals were collected and washed with ethyl acetate. The *anhydride* (14) (118 mg, 86%) was recrystallized from ethyl acetate with difficulty but it sublimed satisfactorily (220°C/0·01 mm), m.p. 252–253°C (Found: C, 80·8; H, 3·2. $C_{20}H_{10}O_3$ requires C, 80·5; H, 3·4%). ν_{max} 1855, 1820, 1770 cm^{-1}. ^{1}H n.m.r. spectrum δ [CDCl$_3$/(CD$_3$)$_2$SO,

300 MHz] 9·30–9·23, m, H 3,12; 8·75–8·68, m, H 5,8,9; 8·21, d, J 8·35 Hz, H 4; 7·88–7·68, m, H 6,10,11. Mass spectrum m/z 298 (M, 86%), 270 (24), 226 (100), 224 (40), 113 (28), 112 (45), 106 (22).

4-(9'-Phenanthrylmethylidine)pent-2-enedinitrile (15)

Phenanthrene-9-carbaldehyde (2·5 g, 12 mmol) and pent-2-enedinitrile[8] (glutacononitrile, mixture of *E* and *Z* isomers; 1·28 g, 14 mmol) were dissolved in benzene (150 ml) and a solution of β-alanine (1·0 g) in glacial acetic acid (20 ml) was added. The mixture was heated under reflux for 2 h with a Dean–Stark apparatus. The cooled solution stood at room temperature for 18 h, during which time an oily sludge of β-alanine adhered to the bottom of the flask and a yellow crystalline solid remained suspended in the benzene. This suspension was decanted, the solid was collected (1·3 g, m.p. 188–200°C) and the benzene filtrate was evaporated under vacuum to yield additional crystalline product. Recrystallization from benzene/light petroleum gave a mixture of stereoisomers of the *title product* (15) as yellow crystals (3·3 g, 97%), m.p. 212–214°C with a further apparent m.p. 226°C (Found: C, 84·4; H, 4·3; N, 9·9. $C_{20}H_{12}N_2$ requires C, 85·7; H, 4·3; N, 10·0%). ν_{max} 2220 (CN), 1608, 1579 cm^{-1}. ^{1}H n.m.r. spectra of samples purified in different ways showed that the proportions of the stereoisomers varied. The spectrum of one isomer had δ (CDCl$_3$, 300 MHz) 8·76, d, J 8·1 Hz, and 8·68, d, J 8·2 Hz, H 4',5'; 8·38, s, H 10'; 8·13, s, C 9'−CH=; 8·00, d, J 7·9 Hz, and 7·93, d, J 8·0 Hz, H 1',8'; 7·80–7·64, m, H 2',3',6',7'; 7·32, d, J 16·0 Hz, H 2; 6·01, d, J 16·1 Hz, H 3. Mass spectrum m/z 280 (M, 100%), 279 (77), 254 (28), 253 (94), 252 (22), 251 (34), 240 (85), 227 (22), 126 (23), 113 (39), 112 (31), 100 (20).

1,2-Dihydrotriphenylene-1,3-dicarbonitrile (16)

The mixture of isomers of the dinitrile (15) (0·5 g) was pyrolysed through an empty quartz tube (750°C, 0·04 mm, 200°C, 4 h) to give a pyrolysate varying in colour from yellow to dark red. The pyrolysate was washed down with dichloromethane under an atmosphere of nitrogen and the solvent was evaporated under vacuum to give a deep red residue (0·42 g, 84%). Separation by flash chromatography (silica; dichloromethane) gave the *title compound* (16) which crystallized from benzene/light petroleum in colourless crystals (0·30 g), m.p. 255–257°C (Found: C, 84·5, 84·9; H, 4·4, 4·2; N, 9·9, 10·0%; M$^{+\bullet}$, 280·100±0·003. $C_{20}H_{12}N_2$ requires C, 85·7; H, 4·3; N, 10·0%; M$^{+\bullet}$, 280·100). ν_{max} 2208 (CN), 765, 725, 668 cm^{-1}. ^{1}H n.m.r. spectrum δ (CDCl$_3$, 400 MHz) 8·82–8·76, m, H 8,9; 8·27, d, J 3·1 Hz, H 4; 8·25–8·20, m, and 8·18–8·13, m, H 5,12; 7·84–7·72, m, H 6,7,10,11; 4·90, dd, J 7·4, 1·8 Hz, H 1; 3·14, dd, J 17·0, 1·75 Hz, H 2α; 2·97, ddd, J 17·0, 7·3, 3·1 Hz, H 2β. ^{13}C n.m.r. spectrum δ (CDCl$_3$, 100·62 MHz) 137·86, C 4; 128·62, 128·14, 128·10, 127·95, 123·87, 123·65, 123·36, 123·34, 8×aromatic CH; 131·72, 130·41, 127·81, 127·62, 126·15, 125·04, 6×quat. C; 118·53, 118·32, 2×CN; 107·36, C 3; 27·76, C 2; 24·96, C 1. Mass spectrum m/z 280 (M, 100%), 279 (55), 278 (25), 253 (31), 252 (15), 251 (25), 240 (24), 126 (24), 113 (24), 112 (30).

Dehydrogenation of this compound with ddq in boiling chlorobenzene gave triphenylene-1,3-dicarbonitrile (18), m.p. 244–245°C, the properties of which are described below. There was also obtained from the column triphenylene-2-carbonitrile (17) which crystallized from benzene/light petroleum as colourless crystals, m.p. 226–228°C. The properties of this compound are given below.

Triphenylene-1,3-dicarbonitrile (18) and Triphenylene-2-carbonitrile (17)

The crude pyrolysate obtained as described above [0·4 g, containing approx. 1 mmol of the dinitrile (16)] and ddq (0·25 g, 1·1 mmol) were dissolved in chlorobenzene (20 ml) and the

mixture was heated under reflux for 6 h. The mixture was cooled and filtered and the residual solid was washed well with benzene. The filtrate and washings were combined and evaporated under vacuum to give a dark residue which was separated by flash chromatography (silica; dichloromethane/light petroleum, then dichloromethane) to yield *triphenylene-2-carbonitrile* (17) which was crystallized from benzene/light petroleum (0·06 g), m.p. 226–228°C (Found: C, 89·9; H, 4·4; N, 5·5. $C_{19}H_{11}N$ requires C, 90·1; H, 4·4; N, 5·5%). ν_{max} 2227 (CN), 759, 722 cm^{-1}. ^{1}H n.m.r. spectrum δ (CDCl$_3$, 300 MHz) 8·90, d, J 1·25 Hz, H1; 8·69–8·62, m, 3H, and 8·61–8·52, m, 2H, H4,5,8,9,12; 7·82, dd, J 8·55, 1·4 Hz, H3; 7·76–7·66, m, H6,7,10,11. Mass spectrum m/z 253 (M, 100%), 251 (21), 126 (18), 113 (16), 112 (23). This was followed by *triphenylene-1,3-dicarbonitrile* (18) which crystallized from benzene/light petroleum in colourless crystals (0·30 g, 60%), m.p. 244–245°C (Found: C, 86·0; H, 3·7; N, 10·4. $C_{20}H_{10}N_2$ requires C, 86·3; H, 3·6; N, 10·1%). ν_{max} 2236 (CN), 754, 718 cm^{-1}. ^{1}H n.m.r. spectrum δ (CDCl$_3$, 400 MHz) 9·62, ddd, J 8·4, 1·2, 0·45 Hz, H12; 9·15, dd, J 1·7, 0·5 Hz, H2; 8·72, dm, J 8·2 Hz, 8·68, dm, J 8·1 Hz, and 8·55, dm, J 8·1 Hz, H5,8,9; 7·87, ddd, J 8·3, 7·0, 1·3 Hz, 1H, and 7·84–7·73, m, 3H, H6,7,10,11. ^{13}C n.m.r. spectrum δ (CDCl$_3$, 100·62 MHz) 137·11, 131·83, 130·68, 129·74, 128·52, 127·89, 126·56, 123·73, 123·66, 123·49, 10×aromatic CH; 133·58, 132·00, 131·94, 130·55, 127·25, 126·50, 6×quat. C; 119·67, 117·41, 2×CN; 110·64, 109·75, C1,3. Mass spectrum m/z 278 (M, 100%), 277 (16), 139 (18).

Methyl 4-Cyanotriphenylene-2-carboxylate (19)

Triphenylene-1,3-dicarbonitrile (18) (0·19 g, 0·68 mmol) was dissolved in a mixture of dichloromethane (20 ml) and methanol (10 ml), and hydrogen chloride gas was bubbled through the mixture for 3 h. The reaction mixture was stirred at room temperature for 18 h and hydrogen chloride was again bubbled through the mixture for 18 h. The mixture, which at this stage contained a heavy precipitate, was stirred at room temperature for a further 6 h, the dichloromethane was evaporated under vacuum and water was added to the residual methanolic mixture. The mixture was heated at 60°C for 1 h, then cooled in ice and the precipitated solid was collected by filtration. This material was purified by flash chromatography (silica; dichloromethane) to give the *title ester* (19) as colourless crystals (0·18 g, 85%), m.p. 202–203°C (Found: C, 81·0; H, 4·25; N, 4·6. $C_{21}H_{13}NO_2$ requires C, 81·0; H, 4·5; N, 4·5%). ν_{max} 2226 (CN), 1719 cm^{-1} (C=O). ^{1}H n.m.r. spectrum δ (CDCl$_3$, 300 MHz) 9·59, dd, J 8·1, 1·5 Hz, H5; 9·44, d, J 1·8 Hz, H1; 8·67–8·57, m, H3,8,9,12; 7·83–7·66, m, H6,7,10,11; 4·07, s, OCH$_3$. ^{13}C n.m.r. spectrum δ (CDCl$_3$, 50·32 MHz) 165·18, CO; 136·00, 129·88, 129·20, 128·87, 128·04, 127·47, 126·31, 123·57, 123·42, 123·28, 10×aromatic CH; 133·30, 131·52, 131·10, 130·04, 129·19, 127·68, 126·83, 108·32, 8×quat. C; 120·78, CN; 52·81, OCH$_3$. Mass spectrum m/z 311 (M, 100%), 281 (16), 280 (73), 252 (56), 251 (82), 249 (15), 225 (23), 224 (22), 140 (34), 126 (37), 125 (19), 113 (27), 112 (77).

Diprop-2-enyl Triphenylene-1,3-dicarboxylate (21)

The ester (19) (0·2 g, 0·64 mmol) was suspended in a mixture of aqueous potassium hydroxide (30%, 3 ml) and methanol (5 ml). Hydrogen peroxide (30%, 5 ml) was added in small portions over 6 h while the mixture was stirred at 60°C. The mixture was then evaporated under vacuum to dryness, potassium hydroxide (3·0 g) and 1,2-ethanediol (10 ml) were added and the mixture was heated under reflux for 18 h. It was then cooled, water (50 ml) was added and the mixture was extracted with dichloromethane. The aqueous solution was filtered, acidified with hydrochloric acid and the precipitated solid collected.

This product was redissolved in aqueous sodium bicarbonate, filtered and reprecipitated with hydrochloric acid to give the product (0·07 g, 35%) relatively free of silicates. The acid (20) (0·03 g, 0·1 mmol) was dissolved in N,N-dimethylformamide (1 ml), anhydrous potassium carbonate (0·1 g) and allyl bromide (0·1 ml) were added, and the mixture was stirred at 20°C for 18 h. Water and ether were added and the ethereal extract was washed well with water, dried (Na$_2$SO$_4$) and the ether evaporated to give the crude ester. Purification by flash chromatography (silica; dichloromethane/light petroleum, 1 : 1, then dichloromethane) gave the *ester* (21) (9 mg, 24%), m.p. 113–115°C (Found: M$^{+\bullet}$, 396·137±0·004. $C_{26}H_{20}O_4$ requires M$^{+\bullet}$, 396·136). ν_{max} 1733 cm^{-1}. ^{1}H n.m.r. spectrum δ (CDCl$_3$, 200 MHz) 9·43, d, J 1·7 Hz, H4; 8·73–8·58, m, H5,8,9; 8·45, d, J 1·7 Hz, H2; 8·13, dd, J 8·4, 1·1 Hz, H12; 7·75–7·65, m, H6,7,10; 7·53, ddd, J 8·2, 7·0, 1·3 Hz, H11; 6·23–5·84, m, 2×=CH; 5·55–5·21, m, 2×=CH$_2$; 4·95, 4·88, 2m, 2×OCH$_2$. ^{13}C n.m.r. spectrum δ (CDCl$_3$, 50·32 MHz) 170·96, 165·51, 2×CO; 132·06, 131·28, 128·76 (2×C), 128·45, 128·33, 127·87, 127·12, 126·36, 123·68, 123·44, 123·28, 12×aromatic CH; 131·58, 131·44, 131·16, 130·27, 128·93, 127·67 (2×C), 111·56 (?), 8×quart. C; 119·58, 118·82, 2×=CH$_2$; 66·63, 66·13, 2×OCH$_2$. Mass spectrum m/z 396 (M, 100%), 355 (24), 340 (17), 339 (57), 271 (20), 270 (82), 254 (23), 227 (19), 226 (59), 225 (29), 224 (33), 213 (27), 113 (15).

Hydrolysis and Esterification of the Nitrile Pyrolysate

The crude pyrolysate (0·4 g, c. 1·4 mmol), obtained from the dinitrile (15) and potassium hydroxide (2·5 g) were dissolved in 1,2-ethanediol (20 ml) and the mixture was heated under reflux for 20 h. The mixture was cooled, diluted with water and extracted with dichloromethane. The aqueous phase was acidified with hydrochloric acid and the precipitated acid was collected (0·6 g, contained silica). The crude product was dissolved in N,N-dimethylformamide (10 ml), and potassium carbonate (1·2 g) and allyl bromide (1·2 ml) were added and the mixture was stirred at 20°C for 20 h. Water and ether were added and the ether extract was separated, washed with water, dried (Na$_2$SO$_4$) and evaporated. The crude ester was separated by flash chromatography (silica; dichloromethane/light petroleum, 1 : 1, then dichloromethane) to give *prop-2-enyl triphenylene-2-carboxylate* (0·18 g) which crystallized from methanol, m.p. 129–130°C (Found: M$^{+\bullet}$, 312·115±0·003. $C_{22}H_{16}O_2$ requires M$^{+\bullet}$, 312·115). ν_{max} 1718 cm^{-1}. ^{1}H n.m.r. spectrum δ (CDCl$_3$, 300 MHz) 9·36, d, J 1·5 Hz, H1; 8·75–8·62, m, H4,5,8,9,12; 8·27, dd, J 8·7, 1·6 Hz, H3; 7·74–7·64, m, H6,7,10,11; 6·21–6·07, m, =CH; 5·50, apparent dd, J 17·2, 1·5 Hz, and 5·36, apparent dd, J 10·5, 1·2 Hz, =CH$_2$; 4·95, m, OCH$_2$. ^{13}C n.m.r. spectrum δ (CDCl$_3$, 50·32 MHz) 166·32, CO; 133·17, 130·58, 129·79, 129·40, 129·34, 128·87, 128·26, 7×quat. C; 132·33, 128·21, 127·66, 127·45, 127·33, 127·21, 125·40, 123·90, 123·46, 123·36, 123·32, 123·22, 12×CH; 118·41, =CH$_2$; 65·77, OCH$_2$. Mass spectrum m/z 312 (M, 75%), 256 (22), 255 (100), 228 (26), 227 (55), 226 (90), 224 (17), 128 (23), 113 (55), 112 (15).

Diprop-2-enyl triphenylene-1,3-dicarboxylate (0·06 g), m.p. 113–115°C, was also eluted from the column.

Dimethyl 1,2-Dihydrotriphenylene-1,4-dicarboxylate (23)

The diester* (22) (61% yield; m.p. 178–179°C; ν_{max} (Nujol) 3443, 1753, 1728, 1699 cm^{-1}; m/z 364) (2·0 g, 5·5 mmol) and 4-dimethylaminopyridine (100 mg) were added to a mixture of acetic anhydride (20 ml) and vinyl acetate (20 ml) and the mixture was heated under reflux for 4 h. The mixture was cooled, the volatile material was evaporated under vacuum and the residue was dissolved in chloroform. The result-

---

* Dimethyl 11b-hydroxy-2-oxo-2,11b-dihydro-1*H*-cyclopenta[*l*]phenanthrene-1,3-dicarboxylate.

ing solution was washed with aqueous sodium bicarbonate, dried (Na₂SO₄) and the solvent evaporated. The residue was purified by flash chromatography (silica; chloroform) and the product crystallized from chloroform/light petroleum to give the *dihydro diester* (23) as colourless crystals (1·34 g, 60%), m.p. 135–136°C (Found: C, 75·4; H, 5·2. $C_{22}H_{18}O_4.0\cdot25H_2O$ requires C, 75·3; H, 5·2%). ν_{max} (Nujol) 1723, 1727w cm⁻¹. ¹H n.m.r. spectrum δ (CDCl₃, 300 MHz) 8·73–8·64, m, H 8,9; 8·08–8·00, m, H 5; 7·66–7·55, m, H 6,7,10,11; 7·53–7·46, m, H 12; 7·21, dd, J 7·40, 2·94 Hz, H 3; 4·46, apparent d, J 5·84 Hz, H 1; 3·71, s, OCH₃; 3·59, s, OCH₃; 3·16, ddd, J 16·53, 7·25, 1·73 Hz, H 2; 2·61, ddd, J 16·53, 7·03, 3·13 Hz, H 2. Mass spectrum *m/z* 346 (M, 18%), 255 (100), 228 (85), 227 (36), 226 (65), 113 (32).

Dimethyl Triphenylene-1,4-dicarboxylate

A solution of the dihydro diester (23) (1·2 g, 3·0 mmol) in chlorobenzene (30 ml) was mixed with a solution of ddq (1·0 g, 4·4 mmol) in chlorobenzene (30 ml) and the mixture was heated under reflux for 16 h. It was then cooled and filtered and the precipitate washed with chlorobenzene. The filtrate and washings were combined and stirred with aqueous sodium bisulphite for 2 h. The liquids were separated and the chlorobenzene solution was filtered, washed with brine, dried (Na₂SO₄) and evaporated under vacuum. The residue was purified by flash chromatography (silica; chloroform) and the product crystallized from light petroleum. The *title diester* was obtained as colourless needles (1·09 g, 91%), m.p. 131–132°C (Found: C, 76·4; H, 4·7. $C_{22}H_{16}O_4$ requires C, 76·7; H, 4·7%). ν_{max} 1720 cm⁻¹. ¹H n.m.r. spectrum δ (CDCl₃, 300 MHz) 8·54, dd, J 7·94, 0·83 Hz, H 8,9; 7·95, dd, J 8·23, 1·09 Hz, H 5,12; 7·82, s, H 2,3; 7·64, ddd, J 8·26, 7·04, 1·21 Hz, H 6,11; 7·53, ddd, J 8·07, 7·25, 1·23 Hz, H 7,10; 3·88, s, 2×OCH₃. Mass spectrum *m/z* 344 (M, 100%), 343 (49), 313 (38), 281 (27), 253 (23), 226 (29), 225 (34), 224 (32), 156 (24), 113 (30), 112 (39), 107 (24).

Triphenylene-1,4-dicarboxylic Acid

Aqueous potassium hydroxide (30 ml, 10%) was added to a solution of dimethyl triphenylene-1,4-dicarboxylate (450 mg) in 1,2-dimethoxyethane (30 ml) and the mixture was refluxed for 16 h. The mixture was cooled and acidified with conc. hydrochloric acid to pH 1. The precipitated material was collected, dissolved in aqueous sodium bicarbonate, the solution extracted with dichloromethane and the aqueous solution acidified. The precipitated product was recrystallized from propan-2-ol/water to give the *title acid* as colourless crystals (300 mg, 73%), m.p. 331–334°C (Found: C, 75·7; H, 3·8. $C_{20}H_{12}O_4$ requires C, 75·9; H, 3·8%). ν_{max} (Nujol) 1682 cm⁻¹ (C=O). ¹H n.m.r. spectrum δ (D₂O/Na₂CO₃, Me₃SiCD₂CD₂CO₂Na, 200 MHz) 8·68–8·53, m, H 5,8,9,12; 7·75–7·57, m, H 6,7,10,11; 7·64, overlapping s, H 2,3. Mass spectrum *m/z* 316 (M, 100%), 315 (76), 299 (22), 227 (25), 226 (65), 225 (37), 224 (53), 215 (20), 213 (29), 149 (17), 135 (18), 112 (27), 107 (63).

Diprop-2-enyl Triphenylene-1,4-dicarboxylate (24)

Triphenylene-1,4-dicarboxylic acid (100 mg, 0·3 mmol) was heated in thionyl chloride for 2 h and the excess reagent was evaporated under vacuum (aspirator). The residual yellow solid was dissolved in allyl alcohol (5 ml) and the mixture was heated under reflux for 5 h. The excess allyl alcohol was evaporated under vacuum and the residue dissolved in dichloromethane. The solution was washed with sodium bicarbonate solution, dried (Na₂SO₄) and the solvent evaporated under vacuum. The *diallyl ester* (24) crystallized from chloroform/light petroleum in colourless crystals (100 mg, 80%), m.p. 102–104°C. ¹H n.m.r. spectrum δ (CDCl₃, 300 MHz) 8·55, dd, J 7·78, 1·00 Hz,

H 8,9; 8·01, dd, J 8·26, 0·90 Hz, H 5,12; 7·65, ddd, J 8·24, 7·09, 1·12 Hz, H 6,11; 7·51, ddd, J 8·06, 7·22, 1·17 Hz, H 7,10; 6·00–5·82, m, =CH; 5·31, m, =CH₂; 4·84–4·81, m, CH₂. Mass spectrum *m/z* 396 (100%), 355 (16), 339 (24), 314 (18), 313 (25), 297 (32), 270 (45), 255 (25), 254 (20), 226 (56), 225 (48), 224 (74), 213 (23).

1,2,3,4-Tetrahydro-1,4-epoxytriphenylene-2,3-dicarboxylic Anhydride (26)

1,4-Dihydro-1,4-epoxytriphenylene was prepared from 9-bromophenanthrene and furan by the method of Best *et al.*[12] (76% yield, m.p. 179–181°C (lit. 180–181°C)). This was hydrogenated to give 1,2,3,4-tetrahydro-1,4-epoxytriphenylene (84% yield). The compound changed form at 161°C and melted at 171°C (lit. m.p. 164°C). Mass spectrum *m/z* 246 (M, 15%), 219 (18), 218 (100), 189 (26). This epoxide (0·3 g, 1·2 mmol) was pyrolysed through an empty silica tube (600°C, 0·03 mm, 140°C, 1·5 h) and the colourless pyrolysate was washed with dichloromethane from the cold finger and trap inlet onto maleic anhydride (0·12 g, 1·2 mmol). The solution was left at room temperature overnight and it was then evaporated under vacuum. The residual solid was recrystallized from ethyl acetate/light petroleum, c. 1:1, to give colourless crystals (0·37 g, 96%), m.p. 194–197°C. A ¹H n.m.r. spectrum showed it to be a mixture of *endo* and *exo* products. This mixture was heated under reflux in acetic anhydride and then reisolated. A single stereoisomer of the *anhydride* (26) was obtained as colourless crystals, m.p. 215–216°C (Found: C, 76·3; H, 3·5. $C_{20}H_{12}O_4$ requires C, 75·9; H, 3·8%). ν_{max} 1862, 1850, 1775s, 1712 cm⁻¹. ¹H n.m.r. spectrum δ (CDCl₃, 200 MHz) 8·80–8·73, m, H 8,9; 8·02–7·96, m, H 5,12; 7·81–7·68, m, H 6,7,10,11; 6·43, s, H 1,4; 3·31, s, H 2,3. ¹³C n.m.r. spectrum δ (CDCl₃, 75·47 MHz) 169·79, 2×CO; 139·18, 130·63, 124·84, 6×quat. C; 127·74, 127·63, 124·03, 123·89, 8×arom. CH; 82·53, C 1,4; 50·89, C 2,3. Mass spectrum *m/z* 316 (M, 4%), 219 (17), 218 (100), 189 (43).

Triphenylene-2,3-dicarboxylic Anhydride (27)

The epoxy anhydride (26) (0·10 g, 0·3 mmol) was heated with polyphosphoric acid (3 ml) at 170°C for 4 h. The red-brown semi-solid mixture was cooled and water was added. The precipitated solid was collected, washed well with water, dried, and then washed with dichloromethane. The resulting product was a brown powder (70 mg) which was purified by sublimation (270°C, 0·1 mm) to give the *title anhydride* (27) as yellow crystals (35 mg, 37%), m.p. >330°C (Found: C, 80·8; H, 3·0. $C_{20}H_{10}O_3$ requires C, 80·5; H, 3·4%). ν_{max} 1854, 1832s, 1790s cm⁻¹. ¹H n.m.r. spectrum δ [(CD₃)₂SO, 200 MHz] 9·53, s, H 1,4; 9·36, dd, J 7·82, 1·0 Hz, H 5,12; 8·93, dd, J 7·65, 1·65 Hz, H 8,9; 7·94–7·77, m, H 6,7,10,11. Mass spectrum *m/z* 298 (M, 74%), 254 (28), 227 (18), 226 (100), 225 (25), 224 (43), 200 (17), 199 (54), 113 (44), 112 (38).

Pyrolyses

Pyrolyses of the precursors listed in Table 1 were conducted under the conditions specified there. Pyrolyses of deuterated triphenylene (15-mg samples) were conducted through a packed tube (800, 900, 1000 and 1100°C, 0·03 mm, 130°C, 1 h) to yield 14, 13, 12 and 4 mg of pyrolysate at the respective temperatures. At 1000 and 1100°C there was some blackening within the pyrolysis tube. Triphenylene (30 mg) and benzoyl peroxide were copyrolysed at 1100°C/0·08 mm during 75 min by simultaneous volatilization from separate flasks heated at 130 and 80–100°C respectively. The pyrolysate (13 mg) was washed from the end of the tube and the condenser with CDCl₃ and examined by ¹H n.m.r. spectroscopy.

Acknowledgments

References

1 Neilen, R. G. H., and Wiersum, U. E., 7th International Symposium on Novel Aromatic Compounds, Victoria, Canada, July 1992.

2 Wiersum, U. E., *Janssen Chim. Acta*, 1992, **10**(3), 3.

3 Neilen, R. G. H., and Wiersum, U. E., *Chem. Commun.*, 1996, 149.

4 Midland, M. M., McLoughlin, J. I., and Werley, R. T., *Org. Synth.*, 1990, **68**, 14.

5 Sukumaran, K. B., and Harvey, R. G., *J. Org. Chem.*, 1981, **46**, 2740.

6 Criegee, V. R., Hoger, E., Huber, G., Kruck, P., Marktscheffel, F., and Schellenberger, H., *Justus Liebigs Ann. Chem.*, 1956, **599**, 81.

7 Morimoto, M., Akiyama, S., Misumi, S., and Nakagawa, M., *Bull. Chem. Soc. Jpn*, 1962, **35**, 857.

8 Etienne, A., and Weill-Raynal, J., *Bull. Soc. Chim. Fr.*, 1953, 1142.

9 Johnson, F., Panella, J. P., Carlson, A. A., and Hunneman, D. H., *J. Org. Chem.*, 1962, **27**, 2473.

10 Cadogan, J. I. G., Hutchinson, H. S., and McNab, H., *Tetrahedron*, 1992, **48**, 7747.

11 Yang-Lan, S., Mueller-Johnson, M., Oehldrich, J., Wichman, D., Cook, J. M., and Weiss, U., *J. Org. Chem.*, 1976, **41**, 4053; Kubiak, G., Cook, J. M., and Weiss, U., *Tetrahedron Lett.*, 1985, **26**, 2163.

12 Best, W. M., Collins, P. A., McCulloch, R. K., and Wege, D., *Aust. J. Chem.*, 1982, **35**, 843; Stringer, M. B., and Wege, D., *Tetrahedron Lett.*, 1980, **21**, 3831.

13 Mulder, P. P. J., Boere, B. B., Cornelisse, J., and Lugtenberg, J., *Recl Trav. Chim. Pays-Bas*, 1993, **112**, 255.

14 Adeney, M., Brown, R. F. C., Coulston, K. J., Eastwood, F. W., and James, I., *Aust. J. Chem.*, 1991, **44**, 967; Brown, R. F. C., Eastwood, F. W., and Wong, N. R., *Tetrahedron Lett.*, 1993, **34**, 1223.

15 Ahmed, F. R., and Trotter, J., *Acta Crystallogr.*, 1963, **16**, 503; Schettino, V., *J. Mol. Spectrosc.*, 1970, **34**, 78; Ferraris, G., Jones, D. W., and Yerkess, J., *Z. Kristallogr.*, 1973, **138**, 113; Cioslowski, J., Liu, G., Martinov, M., Piskorz, P., and Moncrieff, D., *J. Am. Chem. Soc.*, 1996, **118**, 5261.

16 Jones, R. R., and Bergman, R. G., *J. Am. Chem. Soc.*, 1972, **94**, 660; Bergman, R. G., *Acc. Chem. Res.*, 1973, **6**, 25; Lockhart, T. P., Comita, P. B., and Bergman, R. G., *J. Am. Chem. Soc.*, 1981, **103**, 4082; Lockhart, T. P., and Bergman, R. G., *J. Am. Chem. Soc.*, 1981, **103**, 4090.

17 Fischer, I. P., and Lossing, F. P., *J. Am. Chem. Soc.*, 1963, **85**, 1018.

18 Bavin, P. M. G., and Dewar, M. J. S., *J. Chem. Soc.*, 1956, 164; Martin, R. H., Defay, N., and Geerts Evrard, F., *Tetrahedron*, 1963, **19**, 1091.

19 Ashe, A. J., Kampf, J. W., and Savla, P. M., *J. Org. Chem.*, 1990, **55**, 5558.