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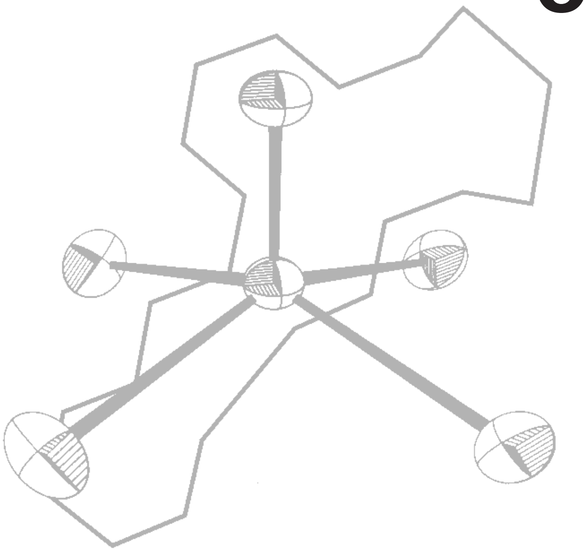

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Synthesis of Precursors for the Pyrolytic Formation of Pentatetraenones

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3-(9′,10′-Dihydro-9′,10′-ethanoanthracen-11′-ylidene)prop-2-enoyl chloride and its [12′,12′-$^2H_2$] and [1-^{13}C] isotopomers have been prepared and pyrolysed. Argon matrix infrared spectroscopy showed ν_2 bands at 2207·7, 2207·0, and 2168·5 cm^{-1} respectively for the three pentatetraenone isotopomers. The pyrolysate of the 12′-methyl substituted precursor showed a band at 2205 cm^{-1} which was tentatively assigned to methylpentatetraenone. The 12′-ethenyl substituted precursor gave a pyrolysate showing ketene bands but also yielded 9,10-dihydro-9,10[1′,2′]-benzenoanthracene.

The geometries of ethenone[1] and those of the more flexible cumulenones, namely propadienone[2] and butatrienone,[3] have been determined and their spectroscopic properties have been compared with those calculated by a variety of methods. Argon matrix infrared spectroscopic evidence that the next member of the series, pentatetraenone, H_2C_5O, had been prepared was presented in 1988.[4] This first synthesis of pentatetraenone was achieved by pyrolytic methods using five different precursors. The frequencies assigned to the high-intensity C=C=C=O vibration ν_2 2207 cm^{-1} and the corresponding band for the $H_2C_4{}^{13}C{=}O$ isotopomer at 2168 cm^{-1} were compared with those calculated for the molecule by using models based on force constants taken from ethenone, allene and tricarbon monoxide. The numbering system for the vibration modes is according to C_{2v} symmetry. Recently, East[5] has discussed the various methods used for determining the 'kinkiness' of cumulenones and has concluded that, based on calculations for the frequency of the ν_2 band, there is strong evidence that pentatetraenone had been prepared in this earlier work.

The five precursors used in that work were difficult to synthesize and each on fragmentation gave rise to cyclopentadiene, a compound with a permanent dipole moment and consequently a microwave absorption spectrum. It may be possible in the future to define the geometry of pentatetraenone by determining its microwave spectrum in a pyrolysate stream and we sought to prepare a precursor which could be made in sufficient quantity to permit its use in a flow system and which would fragment to yield hydrogen chloride, anthracene, and pentatetraenone. In this paper we describe the synthesis of precursors which appear to fragment in this manner.

9,10-Dihydro-9,10-ethanoanthracene-11-carbonyl chloride (1) was converted into the allenic ester (2) by using the method of Lang and Hansen.[6] Best results were obtained by adding methyl (triphenylphosphoranylidene)ethanoate and triethylamine to a solution of the acid chloride in boiling ethanol-free chloroform. The resulting ester (2) could not readily be purified and was unstable and it was hydrolysed to the stable allenic acid (3). The acid chloride (4), which was prepared from the acid and oxalyl chloride, served as the pyrolytic precursor. The synthesis was repeated with methyl (triphenylphosphoranylidene)[1-^{13}C]ethanoate which had been diluted to 50 atom % ^{13}C to give the labelled allenic acid chloride (5).

To obtain the dideuterated precursor (8), methyl propenoate was heated in deuterium oxide in the presence of potassium chloroplatinate and hydroquinone.[7] The crude deuterated product was extracted into xylene and reacted directly with anthracene. The resulting ester was hydrolysed and the 9,10-dihydro-9,10-ethanoanthracene-11-carboxylic acid (6) was found to be deuterated at the 11-position (53%) and at the 12-position (50%), as estimated by ^1H n.m.r. spectroscopy. After conversion of the acid (6) into the allenic acid (7), the 12′-position remained 50% deuterated. The allenic acid (7) was then converted into the acid chloride (8).

Pyrolysis of the unlabelled precursor (4) at 650° in a flow of argon, collection as a matrix at 10 K and measurement of the infrared spectrum gave strong absorption at 2207·7 cm^{-1} which was attributed to ν_2 of pentatetraenone. This band was not detected

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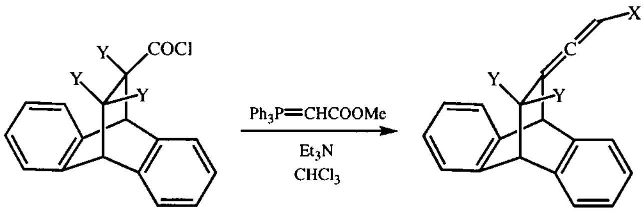
when the acid chloride was pyrolysed at 550°, and when the precursor was pyrolysed at 750° the matrix showed a band at 2207 cm^{-1} of only low intensity. Similarly, pyrolysis at 650° of the [1-^{13}C] isotopomer (5) containing 50 atom % ^{13}C gave a matrix showing bands at 2207·4 and 2168·5 cm^{-1} which were assigned to the ν_2 bands of pentatetraenone and [1-^{13}C]pentatetraenone respectively. Pyrolysis of the 12′,12′-dideuterated compound (8) at 650° gave a matrix with strong absorption at 2207·0 cm^{-1}. We consider that this compound fragmented to a mixture of pentatetraenone and dideuterated pentatetraenone. The absorption due to the ν_2 band would appear to be only perturbed to a minor degree by the remote deuterium atoms so that there is little observed change in the absorption due to the mixture.

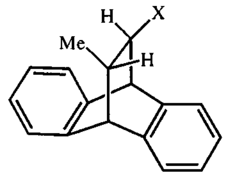
An attempt to obtain a continuous flow of pentatetraenone in a microwave study failed. Heating the precursor to induce slow volatilization into the pyrolysis tube caused decomposition (the slow introduction of a mull of the precursor in vacuum grease is proposed as a solution to this problem).

The initial attempt to synthesize methylpropadienone, $CH_3CH{=}C{=}C{=}O$, by pyrolysis of 5-ethylidene-2,2-dimethyldioxan-4,6-dione resulted in a complex mixture but trapping the pyrolysate in the gas phase with aniline led to the isolation of but-3-enanilide, arising from vinylketene.[8] Studies on the pyrolysis of 5-cyclopentylidene-2,2-dimethyldioxan-4,6-dione by Wentrup *et al.*[9] and of the 5-ethylidene derivative by Maquestiau *et al.*[10] showed that fragmentation of such compounds was complex. The ethylidene derivative fragmented to vinyl(carboxy)ketene (ν_{max} 2135 cm^{-1}) which decarboxylated to methylpropadienone (ν_{max} 2093 cm^{-1}). The facile pyrolytic conversion of methylpropadienone into vinylketene (ν_{max} 2118 cm^{-1}) was confirmed.[10] Similar results were obtained on pyrolysis of 5-isopropylidene-2,2-dimethyldioxan-4,6-dione which on fragmentation gave isopropenyl(carboxy)ketene (ν_{max} 2125 cm^{-1}) which decarboxylated to yield dimethylpropadienone (ν_{max} 2088 cm^{-1}). Conversion of dimethylpropadienone into isopropenylketene (ν_{max} 2109 cm^{-1}) was found to require vigorous conditions.[10] Methylbutatrienone, $CH_3CH{=}C{=}C{=}C{=}O$, is not a known compound but dimethylbutatrienone (ν_{max} 2224, 2216 cm^{-1}) has been prepared by pyrolysis of a specific precursor.[11] We have sought to synthesize methylpentatetraenone using elimination of hydrogen chloride and anthracene as described above for pentatetraenone.

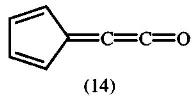


(1) Y = H
(6) Y = D

	X	Y
(2)	COOMe	H
(3)	COOH	H
(4)	COCl	H
(5)	(50%) ^{13}COCl	H
(7)	COOH	D
(8)	COCl	D



(9) X = COCl
(11) X = COC(PPh₃)COOMe



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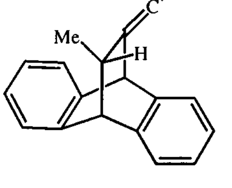
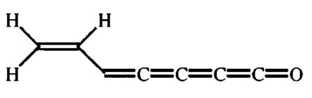


(10) X = COOMe
(12) X = COOH
(13) X = COCl



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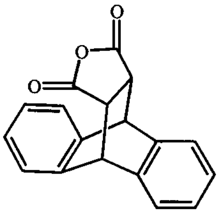

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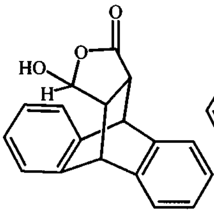

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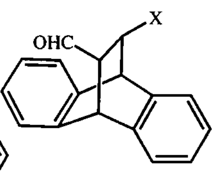
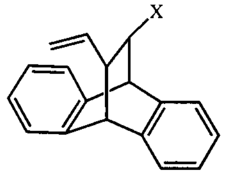
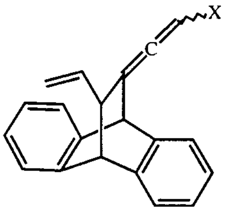


(18) X = COOH
(19) X = COOMe



(20) X = COOMe
(21) X = COOH
(22) X = COCl
(24) X = COC(PPh₃)COOMe



(23) X = COOMe
(25) X = COOH
(26) X = COCl
(27) X = (50%) ^{13}COCl

trans-12-Methyl-9,10-dihydro-9,10-ethanoanthracene-11-carboxylic acid (9) was prepared from but-2-enoic acid and anthracene and converted via the acid chloride into a mixture of *E*- and *Z*-allenic esters (10). In this reaction there was also formed some of the triphenylphosphorane (11). The ester (10) was hydrolysed to a mixture of the *E*- and *Z*-acids (12), which was converted into a mixture of acid chlorides (13) with oxalyl chloride.

Pyrolysis of the acid chlorides (13) in a stream of argon, deposition of a matrix at 10 K and measurement of the infrared spectrum showed an absorption band at 2205·1 cm^{-1}. We suggest that this could be due to methylpentatetraenone. However, the possibility that this compound could rearrange to vinylbutatrienone (hexa-1,2,3,5-tetraen-1-one) (15) cannot be disregarded. There is also the possibility that a 1,5-hydrogen shift could give rise to hexa-1,5-dien-3-yn-1-one. An alternative 1,5-hydrogen shift could lead to the aldehyde hexa-2,4-diynal.

In a study on the pyrolytic generation of cyclopentadienylideneethenone (14) (ν_{max} 2089 cm^{-1}) it was found that the precursors derived from Meldrum's acid (2,2-dimethyldioxan-4,6-dione) when pyrolysed showed not only the band at 2089 but also one at 2225 cm^{-1}.[12] This latter frequency was shifted downwards by 40 cm^{-1} on ^{13}C substitution of the carbonyl carbon atom. This ketene could not be identified but because the isotopic shift was comparable with that observed (39 cm^{-1}) on ^{13}C substitution in pentatetraenone (39 cm^{-1}) it was suggested that fragmentation of the cyclopentadiene ring might lead to vinylpentatetraenone (15). We have explored the possibility of preparing this compound using the ethenyl precursor (26).

9,10-Dihydro-9,10-ethanoanthracene-11,12-dicarboxylic anhydride (16) was reduced with disodium tetracarbonylferrate sesquidioxanate[13] to the lactol (17). Dissolution of the lactol in aqueous potassium hydroxide and acidification gave the *trans* formyl carboxylic acid (18). Conversion of this acid into the methyl ester (19) followed by methylenation by a Wittig reaction gave the *trans* ethenyl-substituted ester (20). This ester was hydrolysed under alkaline conditions and the resulting acid (21) converted into the acid chloride (22) with oxalyl chloride. Reaction of the acid chloride (22) with methyl (triphenylphosphoranylidene)ethanoate and triethylamine in chloroform gave a 43% yield of the required allenic ester (23) together with a 40% yield of the triphenylphosphorane (24). Hydrolysis of the allenic ester with lithium hydroxide and acidification gave a mixture of the *E*- and *Z*-isomers of the ethenyl allenic acid (25). Treatment of this mixture with oxalyl chloride gave the mixture of acid chlorides (26) used as the pyrolytic precursor. The synthesis was repeated with methyl (triphenylphosphoranylidene)[1-^{13}C]ethanoate containing 50 atom % ^{13}C which resulted in the precursor mixture (27).

Pyrolysis of the precursor (26) gave unsatisfactory results but pyrolysis of the precursor (27) containing 50% ^{13}C in the carbonyl group gave clearer spectra. Bands due to CO_2 and a small amount of $^{13}CO_2$ were evident and those due to CO (2138·5 cm^{-1}) and ^{13}CO (2091·3 cm^{-1}) were of equal intensity. The pyrolysate obtained at 550° showed a small band at 2154·3 cm^{-1}. The pyrolysates obtained at 650 and at 750° showed sharp bands at 2154·2 and 2106·6 cm^{-1}. These bands were attributed to an unlabelled and labelled ketene and the decrease in frequency on labelling of 47·7 cm^{-1} suggests that the product could be a pentatetraenone derivative. After measurement of each spectrum the CsI plate was allowed to warm to room temperature and the pyrolysate was examined by g.c.–m.s. The same two products were identified in each pyrolysate. The compounds were anthracene and 9,10-dihydro-9,10[1′,2′]-benzenoanthracene.

On the basis of these findings we suggest that long-chain ketenes are formed in these pyrolyses. However, we cannot say with certainty whether vinylpentatetraenone is formed. What we can say is that none of the ketene absorption bands observed in this work correspond to the band at 2225 cm^{-1} observed in the earlier work.[12] It is clear also that besides elimination of the ketene with formation of anthracene there is a cyclization involving loss of HCl and CO which leads to the formation of a benzene ring and yields 9,10-dihydro-9,10[1′,2′]-benzenoanthracene which is stable to pyrolysis under the conditions used. However, there is no evidence concerning the reaction pathway.

Conclusion

The results indicate that these new precursors provide a simple method for obtaining pentatetraenones. However, structural assignments based solely on matrix infrared spectrometric measurements are not considered to be definitive.

Experimental

Melting points were determined by using a Reichert hot-stage melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin–Elmer 1640 Fourier-transform i.r. spectrometer. ^1H and ^{13}C n.m.r. spectra were recorded on Bruker AC-200 and AM-300 spectrometers. Values shown for coupling constants J are frequency differences taken directly from spectra. Carbon resonances were assigned with the assistance of a J-MODXH pulse sequence. Mass spectra were measured with a VG Trio-1 spectrometer at 70 eV. Accurate mass values were determined on a VG Micromass 7070F spectrometer. Silica gel used for flash chromatography was Merck Kieselgel 60, particle size 0·040–0·063 mm (230–400 mesh), Art. 9385. Light petroleum refers to the fraction of b.p. 55–68°. Gas–liquid chromatogram/mass spectra (g.c.–m.s.) were recorded with a Hewlett–Packard gas liquid chromatograph coupled to a VG Trio-1 spectrometer via an S.G.E. open split interface of ratio 50 : 1.

In matrix experiments argon–precursor mixtures were passed through a quartz tube (420 by 20 mm i.d.) heated with an external furnace (Lindberg tube 55035). The temperature was monitored with a chromel/alumel thermocouple midway along the external wall of the tube. The exit from the tube turned 90° and was joined through a 10-mm tap to a sample chamber containing a copper-mounted CsI plate cooled with a CTI Cryodyne 21 refrigerator. The deposition rate was controlled by the flow of argon (Hoke vernier needle valve) and monitored by pressure measurement. After deposition was complete the sample chamber was isolated and the CsI plate rotated 90° for infrared spectroscopic measurement. Volatile samples were mixed with argon and placed in a 100-ml reservoir attached to a 1000-ml reservoir on the vacuum line. Solids or low vapour pressure liquids were placed in a small glass vial near the entrance to the pyrolysis tube and volatilized by heating in a stream of argon. Infrared measurements were made on a Bruker IF6 120 HR interferometer using the spectral range 4000–650 cm^{-1}.

9,10-Dihydro-9,10-ethanoanthracene-11-carboxylic Acid

Methyl 9,10-dihydro-9,10-ethanoanthracene-11-carboxylate, m.p. 117–118°, ν_{max} 1729 cm^{-1} [^1H n.m.r. δ (200 MHz, $CDCl_3$) 7·33–7·15, m, 4H, 7·14–7·06, m, 4H, aromatic; 4·68, d, J 2·5 Hz, H10; 4·34, t, J 2·7 Hz, H9; 3·59, s, OCH_3; 2·93–2·84, m, H11; 2·21–1·93, m, $(H12)_2$. ^{13}C n.m.r. δ (50 MHz, $CDCl_3$)

173·97, C=O; 143·85, 143·57, 142·39, 139·95, C 4a, C 8a, C 9a, C 10a; 126·18, 126·11, 125·70 (2C), 124·68, 123·62, 123·42, 123·22, C 1–8; 51·87, OCH_3; 46·75, C 11; 43·96, 43·77, C 9, C 10; 30·70, C 12. Mass spectrum, *m/z* 264 (M, 1·5%), 178 (100)], was prepared in 66% yield by reaction of anthracene with methyl propenoate.[14] Hydrolysis of the ester with potassium hydroxide gave the title acid, m.p. 191–192° (lit.[15] 191–193°), in 88% yield. The acid was more readily prepared by heating anthracene (4·0 g, 22 mmol) and propenoic acid (3·03 g, 33 mmol) in toluene (10 ml) under reflux for 48 h. The cooled mixture was extracted with aqueous sodium hydroxide (100 ml, 10%) and the aqueous extract was washed with ether (2×50 ml). The alkaline solution was acidified to pH 1 with concentrated hydrochloric acid and allowed to stand at room temperature overnight. The precipitated acid was collected by filtration, washed with water and dried (5·10 g, 91%), m.p. 191–192°, $\nu_{\max}$ 1703 cm^{-1}. ^{1}H n.m.r. δ (200 MHz, $CDCl_3$) 11·1, br s, OH; 7·37–7·20, 4H, 7·19–7·07, 4H, aromatic; 4·72, d, *J* 2·3 Hz, H 10; 4·38, t, *J* 2·4 Hz, H 9; 2·90–2·88, m, H 11; 2·19–1·97, m, $(H\,12)_2$. ^{13}C n.m.r. δ (50 MHz, $CDCl_3$) 179·80, C=O; 143·68, 143·62, 142·27, 139·60, C 4a, C 8a, C 9a, C 10a; 126·25, 126·19, 125·65, 125·75, 125·02, 123·63, 123·48, 123·13, C 1–8; 46·45, C 11; 43·99, 43·96, C 9, C 10; 30·46, C 12. Mass spectrum, *m/z* 250 (M, 4%), 178 (100).

9,10-Dihydro-9,10-ethanoanthracene-11-carbonyl Chloride (1)

The acid obtained above was treated with oxalyl chloride and dimethylformamide in dichloromethane under an atmosphere of nitrogen as described by Friedrich and Schuster[15] and Brosshard *et al.*[16] Crystallization of the product from hexane gave the acid chloride (1) (94% yield), m.p. 116–118° (lit.[15] 120–123°). $\nu_{\max}$ (Nujol) 1804 cm^{-1}. ^{1}H n.m.r. δ (200 MHz, $CDCl_3$) 7·37–7·22, m, 4H, 7·17–7·10, m, 4H, aromatic; 4·84, d, *J* 2·3 Hz, H 10; 4·36, t, *J* 2·7 Hz, H 9; 3·35–3·26, m, H 11; 2·16–2·06, m, $(H\,12)_2$. Mass spectrum, *m/z* 268 (M, 2%), 178 (100).

3-(9′,10′-Dihydro-9′,10′-ethanoanthracen-11′-ylidene)prop-2-enoic Acid (3)

A solution of triethylamine (8·71 ml, 61·4 mmol) and methyl (triphenylphosphoranylidene)ethanoate (20·27 g, 61·4 mmol) in ethanol-free chloroform (150 ml) was added dropwise over 1·5 h to a boiling solution of the acid chloride (15·0 g, 56·0 mmol) in ethanol-free chloroform (250 ml) under an atmosphere of nitrogen. The resulting red solution was heated under reflux while the reaction was monitored by infrared measurements and t.l.c. It was found that the allenic ester was decomposing before all the acid chloride had reacted and after 1 h the heating was stopped. The solution was evaporated under vacuum to one-third of the initial volume and then washed with water (3×150 ml). The chloroform solution was dried ($CaCl_2$) and evaporated under vacuum to give a mixture of oil and crystals. Ether was added, the solution was filtered to remove the precipitated triphenylphosphine oxide, and the ether was evaporated under vacuum. The product was purified by flash chromatography (silica; dichloromethane) to give the intermediate ester (2) as a yellow oil (10·4 g, 65%). $\nu_{\max}$ 3022, 2950, 2845, 1964 (C=C=C), 1715 (C=O), 1480, 1436, 1293, 1166, 1025, 769 cm^{-1}. The ^{1}H n.m.r. spectrum and the mass spectrum showed the ester to be contaminated with triphenylphosphine oxide. The ester decomposed readily and it was hydrolysed immediately.

The ester (10·4 g, 36·6 mmol) was added to a solution of lithium hydroxide monohydrate (3·10 g, 135 mmol) in water (80 ml) and 1,2-dimethoxyethane (80 ml) and the mixture was stirred at room temperature for 48 h. Ether (50 ml) and water (50 ml) were added and a small amount of white precipitate which formed was removed by filtration. The aqueous phase was separated and acidified to pH 1 with concentrated hydrochloric acid. The precipitated material was isolated by extraction of the mixture with ether. The ethereal extracts were combined, dried ($MgSO_4$), and evaporated under vacuum to give a yellow crystalline solid. The product was recrystallized from ether/light petroleum to give the title *acid* (3) as a pale yellow powder (3·94 g, 40%), m.p. 212–214° (Found: *m/z*, 274·099±0·003. $C_{19}H_{14}O_2$ requires *m/z*, 274·099). $\nu_{\max}$ (Nujol) 1963 (C=C=C), 1680 cm^{-1} (C=O). ^{1}H n.m.r. δ (200 MHz, $CDCl_3$) 7·39–7·29, m, 4H, 7·16–7·10, m, 4H, aromatic; 5·56, t, *J* 3·8 Hz, H 2; 4·89, s, H 10′; 4·47, t, *J* 2·6 Hz, H 9′; 2·68–2·62, m, $(H\,12')_2$. ^{13}C n.m.r. δ (50 MHz, $CDCl_3$) 209·60, C 3; 171·80, C=O; 143·29, 143·10, 141·10, 140·42, C 4′a, C 8′a, C 9′a, C 10′a; 126·60 (2C), 126·56, 126·43, 126·04, 123·91, 123·75, 123·70, C 1′–8′; 105·01, C 11′; 89·29, C 2; 49·70, 44·24, C 9′, C 10′; 33·70, C 12′. Mass spectrum, *m/z* 274 (M, 1%), 178 (100).

3-(9′,10′-Dihydro-9′,10′-ethanoanthracen-11′-ylidene)prop-2-enoyl Chloride (4)

Oxalyl chloride (0·02 ml, 0·20 mmol) was added to a solution of the allenic acid (3) (20 mg, 0·07 mmol) in dichloromethane (0·35 ml). The mixture was allowed to stand for 2 h whereupon the excess of oxalyl chloride and dichloromethane were evaporated under vacuum without heating. The title *acid chloride* (4) was obtained quantitatively as a yellow powder, m.p. 160–161° (Found: *m/z*, 292·065±0·001. $C_{19}H_{13}{}^{35}ClO$ requires *m/z*, 292·065). $\nu_{\max}$ (Nujol) 1953 (C=C=C), 1757 cm^{-1} (C=O). ^{1}H n.m.r. δ (200 MHz, $CDCl_3$) 7·37–7·25, m, 4H, 7·21–7·16, m, 4H, aromatic; 5·86, m, H 2; 5·03, s, H 10′; 4·56, m, H 9′; 2·75–2·58, m, $(H\,12)_2$. ^{13}C n.m.r. δ (50 MHz, $CDCl_3$) 214·25, C 3; 165·86, C=O; 143·17, 143·00, 139·92, 139·49, C 4′a, C 8′a, C 9′a, C 10′a; 126·76, 126·62, 126·48, 126·22, 124·11, 123·91, 123·84, 123·72, C 1′–8′; 106·91, C 2; 49·52, 43·99, C 9′, C 10′; 34·14, C 12′. Mass spectrum, *m/z* 294 (6·4%) 292 (M, 21), 179 (64), 178 (100).

Methyl (Triphenylphosphoranylidene)[1-^{13}C]ethanoate

Methyl bromo(1-^{13}C)ethanoate (1·1 g, 7 mmol, 99·4 atom % ^{13}C) and triphenylphosphine (1·9 g, 7·2 mmol) in ether yielded the quaternary bromide (2·6 g, 88%) which on treatment with aqueous sodium hydroxide gave methyl (triphenylphosphoranylidene)(1-^{13}C)ethanoate (1·8 g, 94% yield, 99·4 atom % ^{13}C), m.p. 168–169°. This was mixed with an equal quantity of the unlabelled ylide to give 3·6 g of the title *ylide* (50 atom % ^{13}C). $\nu_{\max}$ 1618, 1582 cm^{-1}. ^{13}C n.m.r. δ (50 MHz, $CDCl_3$) 171·89, 171·64 (relative intensities 8·1 : 10·4), C=O. Mass spectrum, *m/z* 335 (M, 5%, $C_{20}{}^{13}CH_{19}O_2P$), 334 (10), 333 (20), 304 (10), 303 (28), 302 (75), 301 (100).

3-(9′,10′-Dihydro-9′,10′-ethanoanthracen-11′-ylidene)[1-^{13}C]prop-2-enoic Acid

Reaction of the acid chloride (1) (700 mg, 2·5 mmol) with methyl (triphenylphosphoranylidene)[1-^{13}C]ethanoate (1·0 g, 4·1 mmol) in chloroform in the presence of triethylamine (0·8 ml, 4·0 mmol) as previously described gave the labelled ester (2) as a colourless oil (500 mg, 67%). $\nu_{\max}$ 1964 (C=C=C), 1717 (C=O), 1671 cm^{-1} (^{13}C=O). ^{1}H n.m.r. δ (200 MHz, $CDCl_3$) 7·37–7·19, m 4H, 7·17–7·10, m, 4H, aromatic; 5·61, t, *J* 3·8 Hz, H 2; 4·88, s, H 10′; 4·48, t, *J* 2·4 Hz, H 9′; 3·65, s (flanked by d, *J* 4 Hz), CH_3; 2·69–2·62, m, $(H\,12')_2$. ^{13}C n.m.r. δ (50 MHz, $CDCl_3$) 208·76, C 3; 166·55 (intense), C=O; 143·28, 143·18, 141·02, 140·58, C 4′a, C 8′a, C 9′a, C 10′a; 126·43, 126·38, 126·33, 126·28, 123·99, 123·77, 123·59 (2C), C 1′–8′; 104·00, C 11′; 89·32 (flanked by d, *J* 80 Hz), C 2; 51·48, 49·74, C 9′, C 10′; 44·20, CH_3; 35·55, C 12′. Mass spectrum, *m/z* 289 (M, 1%, $C_{19}{}^{13}CH_{16}O_2$), 288 (1, $C_{20}H_{16}O_2$), 179 (40), 178 (100).

Hydrolysis of the ester and crystallization of the product from diethyl ether/light petroleum gave the title *acid* (labelled (3)) as pale yellow crystals, m.p. 212–214° (Found: *m/z*, 275·102±0·005. $C_{18}{}^{13}CH_{14}O_2$ requires *m/z*, 275·102). ν_{max} 1963 (C=C=C), 1705 (C=O), 1668 cm^{-1} (^{13}C=O). ^{1}H n.m.r. δ (200 MHz, $CDCl_3$) 7·35–7·23, m, 4H, 7·18–7·06, m, 4H, aromatic; 5·57, t, *J* 3·8 Hz, H 2; 4·90, s, H 10′; 4·47, t, *J* 2·6 Hz, H 9′; 3·38, s, OH (D_2O exch.); 2·68–2·62, m, (H 12′)$_2$. ^{13}C n.m.r. δ (50 MHz, $CDCl_3$) 210·08, C 3; 171·06 (intense), C=O; 143·17 (2C), 140·80, 140·32, C 4′a, C 8′a, C 9′a, C 10′a; 126·49 (2C), 126·45, 126·32, 123·96, 123·79, 123·64, 123·59, C 1′–8′; 89·09 (flanked by d, *J* 80 Hz), C 2; 104·90, C 11′; 49·61, 44·14, C 9′, C 10′; 33·60, C 12′. Mass spectrum, *m/z* 275 (M, 2%), 274 (2), 179 (30), 178 (100).

3-(9′,10′-Dihydro-9′,10′-ethanoanthracen-11′-ylidene)[1-^{13}C]prop-2-enoyl Chloride (5)

The acid (3) (50 atom % ^{13}C) was converted, as previously described, into the *acid chloride* (5) which was obtained as a yellow powder, m.p. 158–160° (Found: *m/z*, 293·068±0·003. $C_{18}{}^{13}CH_{13}O^{35}Cl$ requires *m/z*, 293·068). ν_{max} (Nujol) 1955 (C=C=C), 1749 (C=O), 1711 cm^{-1} (^{13}C=O). ^{1}H n.m.r. δ (200 MHz, $CDCl_3$) 7·39–7·24, m, 4H, 7·19–7·13, m, 4H, aromatic; 5·83, m, H 2; 5·00, s, H 10′; 4·53, m, H 9′; 2·71, m, (H 12′)$_2$. ^{13}C n.m.r. δ (50 MHz, $CDCl_3$) 214·24, C 3; 165·87 (intense), ^{13}C=O; 143·16, 143·00, 139·92, 139·49, C 4′a, C 8′a, C 9′a, C 10′a; 126·76, 126·70, 126·62, 126·54, 124·11, 123·91, 123·84, 123·72, C 1′–8′; 106·91, C 11′; 96·36 (flanked by d, *J* 80 Hz), C 2; 49·52, 43·99, C 9′, C 10′; 34·14, C 12′.

Polydeuterated Methyl 9,10-Dihydro-9,10-ethanoanthracene-11-carboxylate

Methyl propenoate (3·4 g, 40·0 mmol), potassium chloroplatinate (0·2 g, 0·50 mmol) and hydroquinone (0·1 g) were added to deuterium oxide (19 ml) and the mixture was stirred and heated at 90° in a stainless steel autoclave for 16 h.[7] The cooled mixture was extracted with xylene (80 ml), the xylene layer separated, a small amount of polymer was discarded and the solution was dried (Na_2SO_4) and used directly for the next preparation. Anthracene (3·00 g, 170 mmol) was added to the xylene solution and the mixture was heated in an autoclave at 210° for 12 h.[14] The resulting solution was evaporated under vacuum and the residue recrystallized from methanol to yield the title ester (5·2 g, 42%), m.p. 115–116°. ν_{max} 1708 cm^{-1} (C=O). ^{1}H n.m.r. δ (200 MHz, $CDCl_3$) 7·33–7·14, m, 4H, 7·14–7·02, m, 4H, aromatic; 4·66, d, *J* 2·9 Hz, H 10; 4·32, s, H 9; 3·59, s, 0·45H (85% ^{2}H), OCH_3; 2·93–2·88, m, 0·35H (65% ^{2}H), H 11; 2·20–1·98, m, 1H (50% ^{2}H), H 12. ^{13}C n.m.r. δ (50 MHz, $CDCl_3$) 178·78, C=O; 143·71, 143·64, 142·31, 139·66, C 4a, C 8a, C 9a, C 10a; 126·28, 126·21, 125·78 (2C), 125·01, 123·66, 123·51, 123·19, C 1–8; 51·91 (low intensity), OCH_3; 46·77 (low intensity), C 11; 43·99, 43·77, C 9, C 10; 33·20 (low intensity), C 12. Mass spectrum, *m/z* 268, 267 (2·5%, $C_{18}H_{13}{}^{2}H_3O_2$), 266, 265, 264 (abundance ratio 3 : 17 : 9 : 5 : 13), 178 (100).

[11,12,12-^{2}H$_3$]-9,10-Dihydro-9,10-ethanoanthracene-11-carboxylic Acid

The deuterium-labelled ester (5·0 g, 19·0 mmol) was hydrolysed with aqueous ethanolic potassium hydroxide. The acidic product was recrystallized from diethyl ether/light petroleum to give the title *acid* as colourless crystals (2·5 g, 53%), m.p. 188–190° (Found: *m/z*, 253·119±0·003. $C_{17}H_{11}{}^{2}H_3O_2$ requires *m/z*, 253·118). ν_{max} (Nujol) 3300–3000 (OH), 1700 cm^{-1} (C=O). ^{1}H n.m.r. δ (200 MHz, $CDCl_3$) 7·33–7·23, m, 4H, 7·16–7·04, m, 4H, aromatic; 4·66, s, H 10; 4·33, s, H 9; 2·90–2·88, m, 0·47H (53% ^{2}H), H 11; 2·11–1·97, m, 1H (50% ^{2}H), (H 12)$_2$. ^{13}C n.m.r. δ (50 MHz, $CDCl_3$) 174·85, C=O; 142·43 (2C), 139·30, C 4a, C 8a, C 9a, C 10a (three detected); 126·37, 126·30, 125·87 (2C), 125·11, 123·74, 123·69, 123·27, C 1–8; 46·61, C 11; 43·89, 43·68, C 9, C 10; C 12 was not observed. Mass spectrum, *m/z* 254, 253 (2·3%, $C_{17}H_{11}{}^{2}H_3O_2$), 252, 251, 250 (abundance ratio 7 : 38 : 19 : 6 : 9), 178 (100).

[12,12-^{2}H$_2$]-9,10-Dihydro-9,10-ethanoanthracene-11-carbonyl Chloride (6)

The acid prepared above (400 mg) was converted into the *acid chloride* (6) (420 mg, 98%) as previously described (Found: *m/z*, 270·077±0·003. $C_{17}H_{11}{}^{2}H_2{}^{35}ClO$ requires *m/z*, 270·078). ν_{max} 1804 cm^{-1} (C=O). ^{1}H n.m.r. δ (200 MHz, $CDCl_3$) 7·37–7·26, m, 4H, 7·24–7·10, m, 4H, aromatic; 4·84, d, *J* 2·5 Hz, H 10; 4·36, t, *J* 2·3 Hz, H 9; 3·35–3·26, m, 0·89H (11% ^{2}H), H 11; 2·15–2·05, m, 1H (50% ^{2}H), (H 12)$_2$. ^{13}C n.m.r. δ (50 MHz, $CDCl_3$) 174·45, C=O; 143·57, 143·13, 141·12, 138·52, C 4a, C 8a, C 9a, C 10a; 126·79, 126·69, 126·17, 126·11, 125·17, 123·96, 123·66, 123·42, C 1–8; 56·09, C 11; 46·94, 43·47, C 9, C 10; 31·77 (low intensity), C 12. Mass spectrum, *m/z* 273, 272, 271, 270 (M, 4·5%), 269, 268 (abundance ratio 5 : 16 : 25 : 49 : 32 : 15), 204 (17), 178 (100).

3-([12′,12′-^{2}H$_2$]-9′,10′-Dihydro-9′,10′-ethanoanthracen-11′-ylidene)prop-2-enoic Acid (7)

Reaction of the deuterated acid chloride (6) (1·4 g, 5·2 mmol) with methyl (triphenylphosphoranylidene)ethanoate (3·6 g, 11 mmol) and triethylamine (1·8 ml, 9·3 mmol) in ethanol-free chloroform as previously described gave the deuterated ester (860 mg, 58%) as a pale yellow oil. ν_{max} 1963 (C=C=C), 1731 cm^{-1} (C=O). ^{1}H n.m.r. δ (200 MHz, $CDCl_3$) 7·38–7·20, m, 4H, 7·16–7·05, m, 4H, aromatic; 5·61, br s, H 2; 4·89, s, H 10′; 4·47, br s, H 9′; 3·65, s, OCH_3; 2·65–2·55, m, 1H (50% ^{2}H), (H 12′)$_2$. ^{13}C n.m.r. δ (50 MHz, $CDCl_3$) 208·80, C 3; 166·70, C=O; 143·17, 143·15, 141·03, 140·59, C 4′a, C 8′a, C 9′a, C 10′a; 126·42, 126·38, 126·33, 126·28, 126·14, 123·98, 123·78, 123·58, C 1′–8′; 89·31, C 2; 51·83, OCH_3; 49·74, C 11′; 44·21, 44·12, C 9′, C 10′; 31·25 (low intensity), C 12′.

This ester was hydrolysed with lithium hydroxide as previously described and the acidic product was crystallized from diethyl ether/light petroleum to give the title *acid* (7) as a yellow powder (450 mg, 56%), m.p. 215–216° (Found: *m/z*, 276·111±0·003. $C_{19}H_{12}{}^{2}H_2O_2$ requires *m/z*, 276·111). ν_{max} (Nujol) 1963 (C=C=C), 1672 cm^{-1} (C=O). ^{1}H n.m.r. δ (200 MHz, $CDCl_3$) 7·36–7·29, m, 4H, 7·17–7·11, m, 4H, aromatic; 5·53, m, H 2; 4·89, s, H 10′; 4·47, m, H 9′; 2·65–2·56, m, 1H (50% ^{2}H), (H 12′)$_2$. ^{13}C n.m.r. δ (50 MHz, $CDCl_3$) 208·71, C 3; 168·27, C=O; 143·38, 143·24, 141·23, 140·71, C 4′a, C 8′a, C 9′a, C 10′a; 126·41, 126·35, 126·33, 126·30, 124·05, 123·82, 123·81, 123·60, C 1′–8′; 104·02, C 11′; 90·08, C 2; 49·73, 44·13, C 9′, C 10′; 33·49 (low intensity), C 12′. Mass spectrum, *m/z* 278, 277, 276 (M, 1·4%), 275, 274 (abundance ratios, 4 : 11 : 30 : 23 : 33), 178 (100).

3-([12′,12′-^{2}H$_2$]-9′,10′-Dihydro-9′,10′-ethanoanthracen-11′-ylidene)prop-2-enoyl Chloride (8)

The deuterated acid (7) (20 mg) was converted by the method previously described into the title *acid chloride* (8) which was obtained as a yellow powder (21 mg, 98%), m.p. 160–161° (Found: *m/z*, 294·078±0·001. $C_{19}H_{11}{}^{2}H_2{}^{35}ClO$ requires *m/z*, 294·077). ν_{max} (Nujol) 1952 (C=C=C), 1755 cm^{-1} (C=O). ^{1}H n.m.r. δ (200 MHz, $CDCl_3$) 7·39–7·20, m, 4H, 7·19–7·11, m, 4H, aromatic; 5·83, m, H 2; 5·00, s, H 10′; 4·53, m, H 9′; 2·73–2·69, m, 1H (50% ^{2}H), (H 12′)$_2$. ^{13}C n.m.r. δ (50 MHz, $CDCl_3$) 214·26, C 3; 165·89, C=O; 143·18, 143·02, 139·94, 139·51, C 4′a, C 8′a, C 9′a, C 10′a; 126·78, 126·72, 126·56, 126·50, 124·13, 123·87, 123·85, 123·70, C 1′–8′; 106·92, C 11′; 96·37, C 2; 49·52, 43·84, C 9′, C 10′; 34·15 (low intensity), C 12′. Mass spectrum, *m/z* 297, 296, 295, 294 (M, 2·2%), 293, 292 (abundance ratio 3 : 7 : 9 : 24 : 12 : 18), 178 (100).

Pentatetraenone: Pyrolysis of Acid Chlorides (4), (5) and (8)

The deposition line was evacuated and the furnace heated to 400° for 4 h. The requisite allenic acid chloride (20–50 mg) was prepared in a glass vial and introduced into the line. The system was evacuated to 0·04 mmHg, the furnace heated to the required temperature and the CsI plate cooled to *c.* 10 K. The precursor was sublimed at 120–170° in a stream of argon and pyrolysed at 550–750°/0·025 mmHg and the pyrolysate deposited on the plate during 50 min. The infrared spectrum was recorded.

H_2C_5O, precursor (4) (650°). ν_{max} 3756·6m, 3723·5m, 3711·1w, 3326·4s(br), 2925·5m, 2345·1s, 2340·3s, 2339·1 (CO_2), 2207·7s (C=C=C=O), 2149·4s, 2139·8 (CO), 1862·1m, 1781·5s, 1623·7s, 1607·8s, 1471·8m, 1269·7s, 1260·0s, 1107·0m, 914·3s, 908·9m, 878·1w, 837·4s, 836·4s, 835·4s, 754·2m, 711·4m cm^{-1}. At 550° no band was detected at 2707·7 cm^{-1}. At 750° the intensity of the band at 2207·7 cm^{-1} was very weak.

$H_2C_4{}^{13}CO$, precursor (5) (650°). ν_{max} 3756·8m, 2880·0s, 2869·6s, 2863·3s, 2815·4s, 2787·0s, 2347·0s, 2345·0s, 2340·2s, 2339·1s (CO_2), 2279·5s, 2274·7s, 2273·7s ($^{13}CO_2$), 2207·4s (C=C=C=O), 2168·5s (C=C=^{13}C=O), 2154·3s, 2138·3s (CO), 2091·2w, 1787·5s, 1742·6s, 1626·5w, 1589·9w, 1450·2m, 1440·2m, 1317·7m, 1189·2s, 1168·6m, 1149·8m, 1116·3m, 1101·8w, 959·0m, 880·5s, 767·0s, 731·5s cm^{-1}.

D_2C_5O, precursor (8) (650°). ν_{max} 3064·8w, 2888·5w, 2868·6m, 2862·5s, 2843·6w, 2809·8s, 2786·1s, 2344·8s, 2340·3s (CO_2), 2207·0s (C=C=O), 2153·7s, 2138·3s (CO), 2072·3w, 2036·3w, 2013·5w, 1601·6w, 1318·0w, 880·7s, 729·9s cm^{-1}. At 750° no band was detected at 2207·7 cm^{-1}.

trans-*12-Methyl-9,10-dihydro-9,10-ethanoanthracene-11-carbonyl Chloride (9)*

trans-12-Methyl-9,10-dihydro-9,10-ethanoanthracene-11-carboxylic acid was prepared in 20% yield from anthracene (10 g), but-2-enoic acid (3·87 g) and hydroquinone (0·3 g) dissolved in benzene (35 ml) and heated at 200° for 20 h. It crystallized from heptane, m.p. 195–196° (lit.[17] 191–193, lit.[18] 115°). The ^{1}H n.m.r. spectrum was the same as that described by Ripoll *et al.* [18] δ (200 MHz, $CDCl_3$) 7·29–7·21, m, 7·15–7·04, m, H 1–8; 4·54, d, *J* 2·2 Hz, 3·97, d, *J* 2·2 Hz, H 9, H 10; 2·34–2·15, m, H 11, H 12; 0·91, d, *J* 6·7 Hz, CH_3. ^{13}C n.m.r. (50 MHz, $CDCl_3$) 179·83, C=O; 144·61, 142·22, 140·93, 139·28, C 4a, C 8a, C 9a, C 10a; 126·10, 125·95 (2C), 125·75, 125·69, 125·33, 123·24, 123·00, C 1–8; 52·54, 50·79, C 9, C 10; 46·48, C 11; 37·52, C 12; 21·07, $C\mathbf{C}H_3$. Mass spectrum, *m/z* 264 (M, 4%), 178 (100).

A solution of the acid (2·2 g, 8·3 mmol) in dichloromethane (10 ml) under an atmosphere of nitrogen was treated with oxalyl chloride (2·18 ml, 25 mmol) and the mixture was allowed to stand for 2 h. The excess of reagent and solvent were evaporated and the acid chloride (9) was obtained quantitatively as a colourless oil. ν_{max} 1798 (C=O) cm^{-1}. ^{1}H n.m.r. δ (200 MHz, $CDCl_3$) 7·35–7·20, m, 7·18–7·05, m, H 1–8; 4·73, d, *J* 2·2 Hz, H 10; 4·03, d, *J* 2·3 Hz, H 9; 2·68, dd, *J* 5·4, 2·2 Hz, H 11; 2·50–2·35, m, H 12; 0·98, d, *J* 6·9 Hz, CH_3. ^{13}C n.m.r. δ (50 MHz, $CDCl_3$) 175·00, C=O; 144·00, 141·11, 140·90, 138·37, C 4a, C 8a, C 9a, C 10a; 126·77, 126·57, 126·41, 126·22, 125·99, 125·51, 123·80, 123·48, C 1–8; 64·46, C 11; 50·81, 47·35, C 9, C 10; 38·53, C 12; 21·11, CH_3. Mass spectrum, *m/z* 282 (M, 0·03%), 178 (100).

Methyl (E)- *and* (Z)-*3-(12′-Methyl-9′,10′-dihydro-9′,10′-ethanoanthracen-11′-ylidene)prop-2-enoate (10)*

A solution of methyl (triphenylphosphoranylidene)ethanoate (3·0 g, 9·2 mmol) and triethylamine (1·3 ml, 9·2 mmol) in ethanol-free chloroform (10 ml) was added dropwise to a boiling solution of the acid chloride (9) (2·2 g, 7·8 mmol) in ethanol-free chloroform (40 ml) under an atmosphere of nitrogen. The mixture was then heated under reflux for a further 2·5 h, cooled and evaporated under vacuum without heating. The residue was separated by flash chromatography (SiO_2; dichloromethane) to yield first the title *mixture* of *E* and *Z* esters (10) (286 mg, 12%) as a yellow oil (Found: *m/z*, 302·130±0·003. $C_{21}H_{18}O_2$ requires *m/z*, 302·130). ν_{max} 1960s (C=C=C), 1810w, 1716s cm^{-1} (C=O). ^{1}H n.m.r. δ (200 MHz, $CDCl_3$) 7·35–7·23, m, 7·18–7·02, m, H 1′–8′; 5·67, d, *J* 4·1 Hz, 5·60, d, *J* 3·7 Hz, H 2; 4·84, s, H 10′; 4·13, d, *J* 2·0 Hz, H 9′; 3·63, s, 3·58, s, OCH_3; 3·22–2·77, m, H 12′; 0·92, d, *J* 6·9 Hz, 0·90, d, *J* 6·9 Hz, CH_3. ^{13}C n.m.r. δ (50 MHz, $CDCl_3$) 209·69, 209·36, C 3; 166·57, 166·39, C=O; 144·07, 141·60, 140·62, 140·57, 140·53, 140·21 (2C), 139·95, C 4′a, C 8′a, C 9′a, C 10′a; 126·50, 126·41, 126·35, 126·27 (2C), 126·18, 126·09, 126·05, 125·84, 125·68, 124·01, 123·68, 123·64, 123·51, 123·47, 123·21, C 1′–8′; 110·88, 110·74, C 11′; 90·32, 90·22, C 2; 51·75, 51·01, OCH_3; 49·79, 49·69, C 9′, C 10′; 39·70, 38·98, C 12′; 19·78, CH_3. Mass spectrum, *m/z* 302 (M, 2%), 243 (8), 228 (8), 226 (10), 178 (100).

The second compound isolated was methyl (*E*)-3-(12′-methyl-9′,10′-dihydro-9′,10′-ethanoanthracen-11′-yl)-3-oxo-2-triphenylphosphoranylidenepropanoate (11), obtained as colourless *crystals*, m.p. 236–238° (Found: *m/z*, 580·215±0·006. $C_{39}H_{33}O_3P$ requires *m/z*, 580·217). ν_{max} 1664 (C=O), 1557 cm^{-1}. ^{31}P n.m.r. δ (120 MHz, $CDCl_3$) 19·46, $Ph_3P=C$. ^{1}H n.m.r. δ (200 MHz, $CDCl_3$) 7·62–7·28, m, 3×phenyl; 7·25–6·90, m, H 1′–8′; 4·82, d, *J* 1·9 Hz, H 9′; 3·90, d, *J* 2·0 Hz, H 10′; 3·31, dd, *J* 5·6, 2·0, H 11′; 3·27, s, OCH_3; 2·66–2·51, m, H 12′; 0·74, d, *J* 6·9 Hz, CH_3. ^{13}C n.m.r. δ (50 MHz, $CDCl_3$) 195·19, 195·13, C=O; 167·89, 167·58, C=O; 145·37, 144·33, 141·95, 139·90, C 4′a, C 8′a, C 9′a, C 10′a; 133·15, 132·95, 131·36, 131·30, 128·39, 128·14, 125·65, 125·54, 125·36, 124·95, 124·62, 124·56, 123·08, 122·98, C 1′–8′ and phenyl CH; 127·84, 125·98, phenyl quat. C; 56·23, 56·09, OCH_3; 51·35, 49·78, 49·76, 49·73, C 9′, C 10′; 34·22, 34·19, C 12′; 20·88, CH_3. Mass spectrum, *m/z* 580 (M, 8%), 362 (24), 361 (96), 293 (27), 262 (100), 183 (38), 178 (66).

(E)- *and* (Z)-*3-(12′-Methyl-9′,10′-dihydro-9′,10′-ethanoanthracen-11′-ylidene)prop-2-enoic Acid (12)*

The ester (10) (250 mg, 0·83 mmol) was added to lithium hydroxide monohydrate (65 mg, 2·5 mmol), water (4 ml) and 1,2-dimethoxyethane (4 ml) and the resulting mixture stirred at room temperature for 30 h. The alkaline solution was diluted with water and extracted with ether, separated, and the aqueous phase was filtered and acidified with concentrated hydrochloric acid to pH 1. After 2 days the colourless crystalline precipitate was collected, washed with water and dried to give the title *acid* (12) (137 mg, 57%), m.p. 151–152° (Found: *m/z*, 288·116±0·006. $C_{20}H_{16}O_2$ requires *m/z*, 288·115). ν_{max} 1957 (C=C=C), 1698 cm^{-1} (C=O). ^{1}H n.m.r. δ (200 MHz, $CDCl_3$) 7·38–7·21, m, 7·19–7·05, m, H 1′–8′; 5·1, d, *J* 4·1 Hz, 5·0, d, *J* 3·7 Hz, H 2; 4·85, s, H 10′; 4·10, br s, H 9′; 2·92–2·81, m, H 12′; 0·92, d, *J* 6·9 Hz, 0·90, d, *J* 6·9 Hz, CH_3. ^{13}C n.m.r. δ (50 MHz, $CDCl_3$) 210·85, 210·75, C 3; 170·87, 170·61, C=O; 144·11, 144·00, 140·65, 140·34, 139·95, 139·71, C 4′a, C 8′a, C 9′a, C 10′a; 126·69, 126·49, 126·41, 126·21, 125·88, 125·71, 124·03, 123·74, 123·70, 123·56, 123·51, 123·29, C 1′–8′; 111·29, C 11′; 90·04, 89·97, C 2; 51·82, 51·00, 49·70, 49·59, C 9′, C 10′; 39·95, 39·23, C 12′; 19·82, 19·63, ?; 15·26, CH_3. Mass spectrum, *m/z* 288 (M, 1%), 178 (100).

(E)- *and* (Z)-*3-(12′-Methyl-9′,10′-dihydro-9′,10′-ethanoanthracen-11′-ylidene)prop-2-enoyl Chloride (13)*

The acid (12) (60 mg, 0·20 mmol) in dichloromethane (2 ml) was treated with oxalyl chloride (0·8 ml, 0·80 mmol) and allowed to stand for 2 h at room temperature under an atmosphere of nitrogen. The excess of reagent and solvent were evaporated under vacuum without heating. The title acid chloride (13) (62 mg, 98%) was obtained as a yellow oil. ν_{max} 1952 (C=C=C), 1751 (C=O) cm^{-1}. ^{1}H n.m.r. δ (200 MHz, $CDCl_3$) 7·36–7·30, m, 7·23–7·14, m, H 1′–8′; 5·90, d, *J* 3·6 Hz, 5·84, d, *J* 3·5 Hz, H 2; 4·95, s, H 10′; 4·21, br s, H 9′; 3·02–2·96, m, H 12′; 1·00, d, *J* 6·9 Hz, 0·95, d, *J* 6·9 Hz, CH_3. ^{13}C n.m.r. δ (50 MHz, $CDCl_3$) 214·82, C 3; 165·70, C=O; 143·79, 143·62, 140·42, 140·23, 139·22, 139·00, 138·71, C 4′a, C 8′a, C 9′a, C 10′a; 126·48, 126·43, 126·25, 126·17, 125·73, 125·57, 123·91, 123·69, 123·63, 123·54, 123·37, 123·27, C 1′–8′; 112·26, C 11′; 97·02, C 2; 50·72, 50·67, 49·42, 49·38, C 9′, C 10′; 40·60, 39·92, C 12′; 19·57, 19·25, CH_3.

Pyrolysis of the Acid Chloride (13)

The deposition line was evacuated and the furnace heated to 400° for 16 h. The mixture of (*E*)- and (*Z*)-prop-2-enoyl chlorides (13) (60 mg, 0·20 mmol) was introduced into the line in a glass vial and the system was evacuated to 0·03 mmHg, the furnace heated to 650° and the CsI plate cooled to *c.* 10 K. The precursor was sublimed at 60–80° in a flow of argon (0·05 mmHg) and the precursor/argon mixture pyrolysed at 650°/0·02 mmHg and deposited during 45 min. The infrared spectrum was recorded (4000–650 cm^{-1}). ν_{max} 3323·1w, 3064·5w, 2888·1w, 2869·6w, 2852·9w, 2815·1m, 2783·4s, 2340·9s, 2205·1m, 2154·2s, 2149·2s, 2138·5s, 2091·3m, 1974·6w, 1947w, 1815·5m, 1318·0m, 878·6s, 837·7s, 755·5s, 728·7s cm^{-1}.

9,10,11,15-Tetrahydro-9,10[3′,4′]-furanoanthracene-12,14-dione (16)

The crude anhydride was prepared by the method of Bachmann and Scott[19] and recrystallized from ethyl acetate/acetic anhydride (9 : 1) by using a Soxhlet apparatus to give the anhydride (16) (97% yield), m.p. 264–265° (lit.[19] 264–264·5°). ν_{max} 1862, 1781 cm^{-1}. Mass spectrum, *m/z* 276 (5%, M), 178 (100).

Reaction of the anhydride with methanol in the presence of sulfuric acid gave the *cis* dimethyl ester (90% yield), m.p. 149–150° (lit.[19] 150–151°). ν_{max} 1748 cm^{-1} (C=O). Mass spectrum, *m/z* 322 (M, 2%), 178 (100).

*14-Hydroxy-9,10,14,15-tetrahydro-9,10[3′,4′]-furanoanthracene-12(11*H*)-one (17)*

Disodium tetracarbonylferrate sesquidioxanate (*c.* 21 mmol) was prepared by the method of Finke and Sorrell,[13] washed repeatedly with dry hexane and suspended in anhydrous tetrahydrofuran (120 ml) under an atmosphere of nitrogen. The anhydride (16) (5·6 g, 20 mmol) was added directly to the suspension and the mixture was stirred for 2 h. The reaction mixture was then acidified with hydrochloric acid (4 M, 150 ml) and stirred for 30 min. The mixture was concentrated under vacuum to remove most of the tetrahydrofuran and then extracted with ether until the aqueous phase was no longer red. The ethereal extracts were combined, dried (Na_2SO_4) and evaporated to give a red-brown residue. The residue was washed with a small amount of chloroform and the solid collected. Recrystallization from chloroform/diethyl ether yielded the title lactol (17) (4·89 g, 88%) as a colourless powder, m.p. 246° (lit.[20] 246°). ν_{max} (Nujol) 3295 (OH), 1734 cm^{-1} (C=O). The ^{1}H n.m.r. spectrum was as previously described.[18] ^{13}C n.m.r δ (50 MHz, $CDCl_3$) 175·162, C=O; 142·61, 141·72, 140·36, 139·56, C 4a, C 8a, C 9a, C 10a; 126·49, 126·37, 126·20, 126·03, 125·23, 124·60, 124·17, 123·82, C 1–8; 100·59, C 14; 49·02, C 11; 47·30, C 15; 44·74, 44·64, C 9, C 10. Mass spectrum, *m/z* 278 (M, 5%), 178 (100).

trans-*12-Formyl-9,10-dihydro-9,10-ethanoanthracene-11-carboxylic Acid (18)*

The lactol (17) (290 mg, 1·0 mmol) was dissolved in aqueous potassium hydroxide (10%) until the pH was >11 and the mixture was stirred until all the material had dissolved. Hydrochloric acid (1 M) was then added dropwise until no more material precipitated. The colourless precipitate was collected, washed with water and dried to give the title *formyl acid* (18) (220 mg, 76%), m.p. 185–187° (Found: *m/z*, 278·095±0·002. $C_{18}H_{14}O_3$ requires *m/z*, 278·094). ν_{max} (Nujol) 2728 (CHO), 1735 (HC=O), 1698 cm^{-1} (C=O). ^{1}H n.m.r. δ (200 MHz, $CDCl_3$) 9·61, s, CHO; 8·7–7·6, br s, OH (D_2O exchange); 7·37–7·23, m, 4H, 7·18–7·07, m, 4H, H 1–8; 4·78, d, *J* 2·5 Hz, H 9 (H 10); 4·75, d, *J* 2·5 Hz, H 10 (H 9); 3·39, dd, *J* 5·1, 2·5 Hz, H 12; 3·28, dd, *J* 5·1, 2·5 Hz, H 11. ^{13}C n.m.r. δ (50 MHz, $CDCl_3$) 199·62, CHO; 177·56, C=O; 142·09, 141·92, 140·59, 139·60, C 4a, C 8a, C 9a, C 10a; 126·86, 126·66, 126·59, 125·26, 125·04, 124·27, 123·79, 123·53, C 1–8; 55·31, C 12; 46·21, C 11; 45·18, 44·62, C 9, C 10. Mass spectrum, *m/z* 278 (M, 2%), 178 (100).

Methyl trans-*12-Formyl-9,10-dihydro-9,10-ethanoanthracene-11-carboxylate (19)*

The formyl acid (18) (2·3 g, 8·3 mmol) was dissolved in tetrahydrofuran (50 ml) and excess of ethereal diazomethane was added. The excess of diazomethane was quenched with acetic acid and the solvent was evaporated to yield an orange oil. Purification by flash chromatography (Al_2O_3; ethyl acetate/light petroleum, 1 : 4) gave the title *ester* (19) as an orange oil (2·0 g, 83%) (Found: *m/z*, 292·110±0·003. $C_{19}H_{16}O_3$ requires *m/z*, 292·110). ν_{max} 2722m (CHO), 1731 cm^{-1} (C=O). ^{1}H n.m.r. δ (200 MHz, $CDCl_3$ (base-washed)) 9·62, s, CHO; 7·37–7·23, m, 4H, 7·18–7·07, m, H 1–8; 4·77, m, H 9, H 10; 3·62, s, OCH_3; 3·36, m, H 11, H 12. ^{13}C n.m.r. δ (50 MHz, $CDCl_3$ (base-washed)) 199·70, CHO; 172·58, C=O; 142·12, 141·83, 140·80, 139·68, C 4a, C 8a, C 9a, C 10a; 126·70, 126·53, 126·48, 126·44, 124·86, 124·38, 123·87, 123·49, C 1–8; 55·36, C 12; 52·34, OCH_3; 46·44, C 11; 454·23, 45·62, C 9, C 10. Mass spectrum, *m/z* 292 (M, 1%), 178 (100).

Methyl trans-*12-Ethenyl-9,10-dihydro-9,10-ethanoanthracene-11-carboxylate (20)*

n-Butyllithium (1·8 M in hexane, 9·45 ml, 17·01 mmol) was added dropwise from an airtight syringe during 10 min to a stirred suspension of methyltriphenylphosphonium bromide (6·2 g, 17 mmol) in dry diethyl ether (20 ml) under an atmosphere of nitrogen at −78°. The mixture was then allowed to stir at room temperature for 3 h. The resulting phosphorane solution was cooled to −78° and a solution of the formyl ester (19) (4·32 g, 14·5 mmol) in dry diethyl ether (10 ml) was added slowly. The yellow reaction mixture was warmed to −40° and when it changed to an off-white colour (*c.* 5 min) it was cooled to −50° and stirred for 1 h before being allowed to warm to room temperature over a 2-h period. It was then stirred at room temperature for a further 16 h. The white slurry which resulted was quenched with water (25 ml) and the ethereal layer was separated. The aqueous layer was extracted with dichloromethane (3×100 ml) and the extracts and ethereal solution were combined, dried (Na_2SO_4) and evaporated. The resulting brown oil was purified by flash chromatography (SiO_2; dichloromethane/light petroleum, 2 : 1) to give the title ester (20) as a colourless viscous oil (3·00 g, 72%). ν_{max} 3072, 3023, 2951, 1735 cm^{-1} (C=O). ^{1}H n.m.r. δ (200 MHz, $CDCl_3$) 7·34–7·24, m, 4H, 7·15–7·07, 4H, H 1–8; 5·43–5·25, m, =CH–; 5·13–4·91, m, =CH_2; 4·64, d, *J* 2·4 Hz, H 9; 4·16, d, *J* 2·4 Hz, H 10; 3·61, s, OCH_3; 3·04–2·95, m, H 12; 2·53, dd, *J* 5·3, 2·4 Hz, H 11. ^{13}C n.m.r. δ (50 MHz, $CDCl_3$) 173·18, C=O; 143·57, 142·35, 142·32, 140·68, C 4a, C 8a, C 9a, C 10a; 140·54, =CH–; 126·15, 125·96, 125·94, 125·83, 125·29, 124·79, 123·28, 123·19, C 1–8; 115·44, =CH_2; 51·82, OCH_3; 51·04, C 11; 49·91, C 12; 46·85, 46·56, C 9, C 10. Mass spectrum, M not observed, *m/z* 178 (100%).

trans-*12-Ethenyl-9,10-dihydro-9,10-ethanoanthracene-11-carboxylic Acid (21)*

The ester (20) (2·70 g, 9·3 mmol) was hydrolysed in a mixture of water (10 ml), ethanol (60 ml) and potassium hydroxide (2·0 g) by heating under reflux for 20 h. The hot solution was filtered, cooled and acidified to pH 2 with hydrochloric acid (4 M) and the white precipitate was collected and washed with water. Recrystallization from aqueous ethanol gave the *monohydrate* of the title acid (21) as nearly colourless crystals, m.p. 210–212° (Found: C, 77·9; H, 5·6. $C_{19}H_{16}O_2.H_2O$ requires C, 77·5; H, 6·2%). The acid was sublimed six times at 180°/0·04 mmHg to give colourless *crystals* (Found: C, 82·5; H, 5·9. $C_{19}H_{16}O_2$ requires C, 82·6; H, 5·8%). $\nu_{\max}$ (hydrate) 3448s(br) (OH), 1702 cm^{-1} (C=O). ^{1}H n.m.r. δ (200 MHz, $CDCl_3$) 7·43–7·23, m, 4H, 7·17–7·08, m, 4H, H 1–8; 5·43–5·24, m, =CH–; 5·13–4·92, m, =CH_2; 4·64, d, J 2·3 Hz, H 10; 4·25, d, J 2·3 Hz, C 9; 2·96, sept., H 12; 2·54, dd, J 5·5, 2·3 Hz, H 11. ^{13}C n.m.r. δ (50 MHz, $CDCl_3$) 178·00, C=O; 143·67, 142·28, 140·60, 139·45, C 4a, C 8a, C 9a, C 10a; 140·36, =CH–; 126·26, 126·06 (2C), 125·90, 125·39, 125·16, 123·35, 123·18, C 1–8; 115·67, =CH_2; 50·93, C 11; 49·97, C 12; 46·59 (2C), C 9, C 10. Mass spectrum, M not observed, m/z 178 (100%).

trans-*12-Ethenyl-9,10-dihydro-9,10-ethanoanthracene-11-carbonyl Chloride (22)*

A solution of the acid (21) (25 mg, 0·09 mmol) in dichloromethane (10 ml) under an atmosphere of nitrogen was treated with oxalyl chloride (13 mg, 0·01 mmol) and the mixture was allowed to stand at room temperature for 2 h. The volatile constituents were evaporated under vacuum and the *acid chloride* (22) was obtained as a pale yellow oil in quantitative yield (Found: m/z, 294·081±0·003. $C_{19}H_{15}{}^{35}ClO$ requires m/z, 294·081). $\nu_{\max}$ 1794 cm^{-1} (C=O). ^{1}H n.m.r. δ (200 MHz, $CDCl_3$) 7·36–7·24, 4H, 7·18–7·11, 4H, H 1–8; 5·38–5·20, =CH–; 5·20–4·96, =CH_2; 4·83, d, J 2·0 Hz, C 10; 4·18, d, J 2·1 Hz, C 9; 3·07–2·93, m, H 11, H 12. ^{13}C n.m.r. δ (50 MHz, $CDCl_3$) 173·85, C=O; 143·08, 140·96, 140·62, 138·32, C 4a, C 8a, C 9a, C 10a; 139·19, =CH–; 126·80, 126·56, 126·39, 126·30, 126·19, 125·23, 123·72, 123·48, C 1–8; 116·78, =CH_2; 62·91, C 11; 50·04, C 12; 47·39, 47·20, C 9, C 10. Mass spectrum, m/z 294 (M, 2%), 178 (100).

Mixture of E- *and* Z-*Isomers of 3-(12′-Ethenyl-9′,10′-dihydro-9′,10′-ethanoanthracen-11′-ylidene)prop-2-enoic Acid (25)*

A solution of methyl (triphenylphosphoranylidene)ethanoate (0·64 g, 1·9 mmol) and triethylamine (0·26 ml, 1·9 mmol) in ethanol-free chloroform was added dropwise to a boiling solution of the acid chloride (22) (266 mg, 1·0 mmol) in ethanol-free chloroform (12 ml) under an atmosphere of nitrogen. When all the solution had been added, heating was continued for 5 h after which the mixture was cooled and the solvent was evaporated under vacuum to give a red residue. Water was added and the mixture was extracted with ether (3×20 ml). A solid (triphenylphosphine oxide) which precipitated from the aqueous phase was collected and washed with ether. The ethereal extracts and washings were combined, washed with water, dried ($MgSO_4$) and evaporated to give a mixture of oil and crystals. Flash chromatography (SiO_2; ethyl acetate/light petroleum, 1 : 1) yielded two products. The first was a mixture of the *E*- and *Z*-isomers of methyl 3-(12′-ethenyl-9′,10′-dihydro-9′,10′-ethanoanthracen-11′-ylidene)prop-2-enoate (23) obtained as a yellow oil (120 mg, 43%). $\nu_{\max}$ 1963 (C=C=C), 1718 cm^{-1} (C=O). ^{1}H n.m.r. δ (200 MHz, $CDCl_3$) 7·43–7·22, m, 7·20–7·04, m, H 1′–8′; 5·67–5·59, m, ethenyl =CH–; 5·41–4·94, m, =CH_2, H 2; 4·89, s, H 10′; 4·29, d, J 2·4 Hz, H 9′; 3·62, 3·59, 2s (*c*. 1 : 1), 2×OCH_3; 3·48–3·38, m, H 12′. ^{13}C n.m.r. δ (50 MHz, $CDCl_3$) 210·59, 210·22, C 3; 166·36, 166·32, C=O; 143·19, 143·12, 140·64, 140·59, 140·38, 140·32, C 4a′, C 8a′, C 9a′, C 10a′; 137·95, 137·70, ethenyl =CH–; 126·61, 126·54, 126·51, 126·47, 126·24, 126·17, 125·55, 125·42, 124·00, 123·79, 123·70, 123·66, 123·57, 123·35, C 1′–8′; 116·16, ethenyl =CH_2; 108·52, 107·82, C 11′; 90·38, 90·10, C 2; 51·82, 51·72, OCH_3; 50·54, 50·34, 49·70, 49·60, C 9′, C 10′; 49·15, 48·68, C 12′. Mass spectrum, m/z 314 (M, 5%), 178 (100). The second was *methyl 3-(12′-ethenyl-9′,10′-dihydro-9′,10′-ethanoanthracene-11′-yl)-3-oxo-2-triphenylphosphoranylidenepropanoate* (24), which was obtained as a yellow powder (240 mg, 40%), m.p. 114–116° (Found: m/z, 592·214±0·003. $C_{40}H_{33}O_3P$ requires m/z, 592·215). $\nu_{\max}$ 1662 cm^{-1} (C=O). ^{1}H n.m.r. δ (200 MHz, $CDCl_3$) 7·63–7·32, m, phenyl H; 7·27–6·91, m, H 1′–8′; 5·44–5·26, m, ethenyl =CH–; 4·92–4·78, H 10′, =CH_2; 4·07, d, J 2·2 Hz, H 9′; 3·66, dd, J 5·7, 2·2 Hz, H 11′; 3·27, s, OCH_3; 3·26–3·18, m, H 12′. ^{13}C n.m.r. δ (50 MHz, $CDCl_3$) 194·36, 194·30, C 3=O; 167·90, 167·49, C 1=O; 144·55, 144·46, 141·46, 140·04, C 4a′, C 8a′, C 9a′, C 10a′; 142·48, ethenyl =CH–; 133·24, 133·05, 131·39, 131·33, 128·34, 128·09, 3×phenyl CH; 127·68, 125·82, phenyl quat.; 125·79, 125·66, 125·11, 124·99, 124·81, 124·58, 123·16, 123·05, C 1′–8′; 113·77, =CH_2; 54·39, 54·25, OCH_3; 50·28, C 11′; 49·76, 49·36, C 9′, C 10′; 44·56, 44·53, C 12′. Mass spectrum, m/z 592 (M, 5%), 361 (20), 262 (45), 183 (20), 178 (100).

The ester (23) (130 mg, 0·41 mmol) was added to a solution of lithium hydroxide monohydrate (46 mg, 20 mmol) in water (1·85 ml) and 1,2-dimethoxyethane (1·85 ml) and the mixture was stirred for 20 h. Ether (3 ml) and water (3 ml) were then added and the ethereal layer was separated, dried ($MgSO_4$) and evaporated to yield unreacted ester (20 mg, 15%). The aqueous phase was acidified with hydrochloric acid (50 ml, 10%) to pH 1 and extracted with ether (3×30 ml). The ether extracts were combined, washed with water, dried ($MgSO_4$) and evaporated under vacuum to give the crude acid (70 mg, 56%) as a yellow oil which crystallized on standing. The product was purified by flash chromatography (SiO_2; dichloromethane followed by ethyl acetate) to give the title acid (25) as pale yellow crystals, m.p. 168–172°. $\nu_{\max}$ 3449br (OH), 1962 (C=C=C), 1702 cm^{-1} (C=O). ^{1}H n.m.r. δ (200 MHz, $CDCl_3$) 10·0, br s, OH; 7·36–7·19, m, 7·18–7·09, m, H 1′–8′; 5·61–5·54, m, ethenyl =CH–; 5·45–4·92, m, =CH_2, H 2; 4·90, s, H 10′; 4·29, d, J 2·3 Hz, H 9′; 3·49–3·38, m, H 12′. ^{13}C n.m.r. δ (50 MHz, $CDCl_3$) 212·02, 211·81, C 3; 171·88, 171·54, C=O; 143·33, 143·18, 140·62, 140·53, 140·37, 140·18, 140·16, C 4a′, C 8a′, C 9a′, C 10a′; 137·90, 137·71, ethenyl =CH–; 126·89, 126·73, 126·66, 126·58, 126·42, 126·21, 125·71, 125·56, 124·18, 123·95, 123·88, 123·77, 123·52, C 1′–8′; 116·50, 116·45, =CH_2; 109·01, 108·25, C 11′; 90·42, 90·15, C 2; 50·66, 50·44, 49·67, 49·58, C 9′, C 10′; 49·50, 48·99, C 12′. Mass spectrum, m/z 300 (M, 4%), 178 (100).

Mixture of E- *and* Z-*Isomers of 3-(12′-Ethenyl-9′,10′-dihydro-9′,10′-ethanoanthracen-11′-ylidene)prop-2-enoyl Chloride (26)*

The acid (25) (20 mg, 0·06 mmol) was dissolved in dichloromethane (0·2 ml) and oxalyl chloride (0·02 ml, 0·2 mmol) was added under an atmosphere of nitrogen. The mixture was allowed to stand for 2 h and then the solvent and excess of reagent were evaporated under vacuum at 0° to give the title *acid chloride* (26) as a yellow oil (Found: m/z, 318·081±0·003. $C_{21}H_{15}{}^{35}ClO$ requires m/z, 318·081). $\nu_{\max}$ 1955 (C=C=C), 1772, 1750 cm^{-1} (C=O). ^{1}H n.m.r. δ (200 MHz, $CDCl_3$) 7·43–7·29, m, 7·24–7·08, m, H 1′–8′; 5·89–5·82, m, ethenyl =CH–; 5·39–4·94, m, =CH_2, H 2, H 10′; 4·35, apparent t, J 2·1 Hz, H 9′; 3·55–3·40, m, H 12′. ^{13}C n.m.r. δ (50 MHz, $CDCl_3$) 215·72, 215·65, C 3; 165·54, 165·31, C=O; 143·00, 142·76, 140·22, 139·96, 139·42, 139·25, 139·09, C 4a′, C 8a′, C 9a′, C 10a′; 137·14, 137·077, ethenyl =CH–; 126·67, 126·61, 126·54, 126·44, 126·23, 126·14, 125·50, 125·36, 125·07, 123·99, 123·81, 123·73, 123·60, 123·44, 123·32, C 1′–8′; 116·67, 116·54, =CH$_2$; 110·58, 110·22, C 11′; 97·19, 97·11, C 2; 50·36, 50·30, 50·09, 49·88, 49·50, 49·28, 49·21, C 9′, C 10′; 47·23, 47·04, C 12′. Mass spectrum, *m/z* 320 (0·5%), 318 (M, 1·5), 178 (100).

Mixture of E- *and* Z-*Isomers of 3-(12′-Ethenyl-9′,10′-dihydro-9′,10′-ethanoanthracen-11′-ylidene)[1-^{13}C]prop-2-enoic Acid*

Methyl (triphenylphosphoranylidene)[1-^{13}C]ethanoate (1·5 g, 4·0 mmol, 50 atom % ^{13}C) was allowed to react with the acid chloride (22) (530 mg, 2·0 mmol) under the conditions described for the unlabelled reagent and the products were separated. Methyl 3-(12′-ethenyl-9′,10′-dihydro-9′,10′-ethanoanthracen-11′-ylidene)[1-^{13}C]prop-2-enoate was obtained as a yellow oil (57 mg, 12%). $\nu_{\max}$ 1963 (C=C=C), 1717 (C=O), 1673 cm^{-1} (^{13}C=O). ^{1}H n.m.r. δ (200 MHz, CDCl$_3$) 7·36–7·32, m, 7·18–7·05, m, H 1′–8′; 5·64–5·58, m, ethenyl =CH–; 5·45–4·89, m, =CH$_2$, H 2; 4·88, s, H 10′; 4·28, d, *J* 2·3 Hz, H 9′; 3·62, 3·59, 2t (intensity *c.* 1 : 1), 2×OCH$_3$; 3·46–3·76, m, H 12′. ^{13}C n.m.r. δ (50 MHz, CDCl$_3$) 210·76, 210·39, C 3; 166·55, 166·29 (intense), C=O; 143·33, 143·26, 140·99, 140·79, 140·73, 140·53, 140·45, C 4a′, C 8a′, C 9a′, C 10a′; 138·09, 137·85, ethenyl =CH–; 126·76, 126·69, 126·65, 126·55, 126·38, 126·31, 125·70, 125·56, 124·17, 123·94, 123·85, 123·80, 123·73, 123·49, C 1′–8′; 116·32, ethenyl =CH$_2$; 108·622 (flanked by d, *J* 2·6 Hz), 107·69 (flanked by d, *J* 2·6 Hz), C 11′; 90·52 (flanked by d, *J* 40 Hz), 90·25 (flanked by d, *J* 40 Hz), C 2; 51·98, 51·95, 51·89, 50·70, 50·49, C 9′, C 10′; 49·85, 49·75, 49·30, 48·82, C 12′. Mass spectrum, *m/z* 315 (M, 4%), 314 (3), 255 (50), 178 (100).

Methyl 3-(12′-ethenyl-9′,10′-dihydro-9′,10′-ethanoanthracen-11′-yl)-3-oxo-2-triphenylphosphoranylidene[1-^{13}C]propanoate was obtained as colourless crystals (700 mg, 60%), m.p. 114–116° (Found: *m/z*, 593·221±0·006. C$_{39}{}^{13}$CH$_{33}$O$_3$P requires *m/z*, 593·218). $\nu_{\max}$ 1663 (C=O), 1623 cm^{-1} (^{13}C=O). ^{1}H n.m.r. δ (200 MHz, CDCl$_3$) 7·60–7·31, 3×phenyl CH; 7·25–6·93, H 1′–8′; 5·39–5·25, ethenyl =CH–; 4·90–4·77, ethenyl =CH$_2$, H 10′; 4·06, d, *J* 2·0 Hz, H 9′; 3·65, dd, *J* 5·6, 2·0 Hz, H 11′; 3·26, apparent t, OCH$_3$; 3·23–3·16, m, H 12′. ^{13}C n.m.r. δ (50 MHz, CDCl$_3$) 194·21, 194·16, 194·11, 194·06, C 3=O; 167·64, 167·33 (intense), C 1=O; 147·75, 145·05, 144·66, 144·38, 144·28, 142·00, 141·28, 140·14, 139·87, C 4a′, C 8a′, C 9a′, C 10a′; 142·31, ethenyl =CH–; 133·06, 132·86, 131·22, 131·16, 128·17, 127·92, phenyl CH; 127·50, 125·64, phenyl quat.; 125·61, 125·48, 125·33, 124·95, 124·82, 124·65, 124·53, 124·42, 122·99, 122·87, 122·61, C 1′–8′; 113·61, ethenyl =CH$_2$; 54·20, 54·07, OCH$_3$; 50·11, 49·59, C 11′; 49·19, 48·30, 45·99, C 9′, C 10′; 44·38, 44·35, C 12′. Mass spectrum, *m/z* 593 (M, 7%), 362 (32), 361 (25), 262 (73), 183 (38), 178 (100).

The ester (23) (40 mg, 0·13 mmol, 50 atom % ^{13}C) was hydrolysed as previously described and the title acid was obtained as yellow crystals (25 mg, 64%, 50 atom % ^{13}C), m.p. 170–172°. $\nu_{\max}$ 3432br (OH), 1960 (C=C=C), 1700 (C=O), 1673 cm^{-1} (^{13}C=O). ^{1}H n.m.r. δ (200 MHz, CDCl$_3$) 7·36–7·28, m, 7·25–7·13, m, C 1′–8′; 5·61–5·55, m, ethenyl =CH–; 5·44–4·92, m, ethenyl =CH$_2$, H 2; 4·90, s, H 10′; 4·30, d, *J* 2·1 Hz, H 9′; 3·54–3·39, m, H 12′. ^{13}C n.m.r. δ (50 MHz, CDCl$_3$) 211·81, 211·63, C 3; 171·22, 170·84 (intense), C=O; 143·20, 143·06, 140·48, 140·39, 140·24, 140·05, C 4a′, C 8a′, C 9a′, C 10a′; 137·77, 137·58, ethenyl =CH–; 126·77, 126·61, 126·53, 126·46, 126·30, 125·58, 125·44, 124·04, 123·83, 123·76, 123·68, 123·63, 123·39, C 1′–8′; 116·38, 116·31, ethenyl =CH$_2$; 108·96, 108·91, 108·26, 108·22, C 11′; 90·18 (flanked by d, *J* 40 Hz), 89·94 (flanked by d, *J* 40 Hz), C 2; 50·53, 50·33, 50·03, 49·55, 49·47, C 9′, C 10′; 49·38, 48·87, C 12′. Mass spectrum, *m/z* 301 (M, 1·5%), 300 (1·3), 178 (100).

Mixture of E- *and* Z-*Isomers of 3-(12′-Ethenyl-9′,10′-dihydro-9′,10′-ethanoanthracen-11′-ylidene)[1-^{13}C]prop-2-enoyl Chloride (27)*

The title *acid chloride* (27) was prepared as previously described and obtained as a yellow oil (Found: *m/z*, 319·085±0·003. C$_{20}{}^{13}$CH$_{15}{}^{35}$ClO requires *m/z*, 319·085). $\nu_{\max}$ 1961 (C=C=C), 1838, 1777 (C=O), 1738 cm^{-1} (^{13}C=O). ^{1}H n.m.r. δ (200 MHz, CDCl$_3$) 7·43–7·29, m, 7·24–7·08, m, H 1′–8′; 5·89–5·82, ethenyl =CH–; 5·35–4·95, m, ethenyl =CH$_2$, H 2, H 10′; 4·35, apparent t, *J* 2·1 Hz, H 9′; 3·55–3·40, m, H 12′. ^{13}C n.m.r. δ (50 MHz, CDCl$_3$) 200·99, C 3; 165·83, 165·61 (intense), C=O; 143·28, 143·03, 140·49, 140·23, 139·35, C 4a′, C 8a′, C 9a′, C 10a′; 137·43, 137·35, ethenyl =CH–; 127·31, 126·95, 126·89, 126·82, 126·72, 126·51, 126·27, 125·78, 125·63, 125·52, 125·34, 125·20, 124·27, 124·01, 123·87, 123·72, 123·04, 122·54, C 1′–8′; 116·94, 116·81, ethenyl =CH$_2$; 98·15, 97·46, 97·39, 96·58, C 2; 50·64, 50·58, 50·37, 49·78, 49·55, C 9′, C 10′; 47·55, 46·79, C 12′. Mass spectrum, *m/z* 319 (M, 5%), 318 (4), 276 (50), 241 (70), 240 (35), 239 (50), 178 (100).

Pyrolysis of Acid Chlorides (26) and (27)

The deposition line was evacuated and the furnace heated to 400° for 16 h. The requisite acid chloride (20 mg, 0·06 mmol) was introduced into the line in a glass vial and the system was evacuated to 0·04 mmHg, the furnace heated to the required temperature and the CsI plate cooled to *c.* 10 K. The precursor was sublimed at 60–180° in a flow of argon (0·07 mmHg) and pyrolysed and deposited during 1 h. The infrared spectrum was recorded (4000–650 cm^{-1}, 0·5 cm^{-1} resolution).

Precursor (26) (650°/0·02 mmHg). $\nu_{\max}$ 3724·1s, 3698·8s, 3635·8s, 3545·2s, 2852·4m, 2347·5s (CO$_2$), 2327·3, 2281·9w, 2188·2w, 2138·7m (CO), 2104·3s(br), 2092·2m(br), 1764·2w, 1620·8m, 1602·3s, 1110·0w, 1038·0w, 883·4m, 731·8s, 662·2s cm^{-1}.

The same procedure was used for precursor (27) except that after measurement of the infrared spectrum, the CsI plate was warmed to room temperature and the products were analysed by gas chromatography–mass spectrometry.

Precursor (27) (550°/0·02 mmHg). $\nu_{\max}$ 2963·4m, 2887·9s, 2868·6s, 2963·1, 2853·4s, 2814·9s, 2785·5s, 2756·3s, 2345·0s (CO$_2$), 2340·2s (CO$_2$), 2279·5s (^{13}CO$_2$), 2275·6s (^{13}CO$_2$), 2154·3w, 2138·5s (CO), 1779·5s, 1701·6s, 1506·6m, 1478·1m, 1455·3m, 1385·7m, 1336·7m, 1318·0m, 1262·3m, 1080·3s, 1067·1s, 1049·9s, 755·7s cm^{-1}. G.c.–m.s.: product A (t_{R} 11·90 min), *m/z* 178 (M, 100%), 176 (20), 152 (10); product B (t_{R} 16·08 min), *m/z* 254 (M, 75%), 253 (100), 252 (40), 250 (20), 126 (14), 113 (20).

At 650°/0·02 mmHg. $\nu_{\max}$ 2962·9w, 2927·8w, 2888·0m, 2869·4s, 2963·4s, 2815·0s, 2785·9s, 2345·1s (CO$_2$), 2339·1s (CO$_2$), 2279·6s (^{13}CO$_2$), 2273·7s (^{13}CO$_2$), 2154·2m, 2138·5s (CO), 2106·6m, 2091·3s (^{13}CO), 1256·7m, 1095·6w, 883·7m, 783·2m, 726·1m cm^{-1}. G.c.–m.s.: product A (t_{R} 11·89 min), *m/z* 178 (M, 100%), 177 (20), 176 (55), 152 (24), 151 (22), 150 (20), 89 (55), 88 (30), 76 (40); product B (t_{R} 16·07 min), 254 (M, 70%), 253 (100), 252 (40), 250 (20), 126 (14).

At 750°/0·02 mmHg. $\nu_{\max}$ 2961·88w, 2920·4w, 2888·0s, 2870·6m, 2863·2s, 2815·3s, 2345·0s (CO$_2$), 2340·2s (CO$_2$), 2339·1s (CO$_2$), 2279·5m (^{13}CO$_2$), 2273·7 (^{13}CO$_2$), 2154·3, 2138·4s (CO), 2106·6m, 2091·3s (^{13}CO), 878·6m, 837·5m, 783·6m, 728·1m cm^{-1}. G.c.–m.s.: product A (t_{R} 11·89 min), *m/z* 178 (M, 100%), 177 (30), 176 (50), 152 (30), 151 (28), 150 (25), 89 (80), 88 (54), 87 (18), 76 (65), 75 (32), 74 (15), 63 (25); product B (t_{R} 16·04 min), *m/z* 254 (M, 70%), 253 (100), 252 (40), 250 (20), 126 (14).

Product A was identified as anthracene and product B as 9,10-dihydro-9,10[1′,2′]-benzenoanthracene (triptycene).

Ethyl 3-(12′-Ethenyl-9′,10′-dihydro-9′,10′-ethanoanthracen-11′-yl)-3-oxo-2-triphenylphosphoranylidenepropanoate (24)

A solution of the acid chloride (22) (400 mg, 1·5 mmol) in dry tetrahydrofuran (15 ml) was added dropwise to a boiling solution of methyl (triphenylphosphoranylidene)ethanoate (1·0 g, 3·2 mmol) and triethylamine (0·2 ml, 1·5 mmol) in tetrahydrofuran (20 ml). Heating was continued for 6 h and then the mixture was allowed to cool. The precipitated material was removed by filtration and the filtrate was evaporated under vacuum. Purification of the residue by flash chromatography (SiO_2; ethyl acetate/light petroleum, 1 : 1) gave the title *ester* (24) (660 mg, 80%) as colourless crystals, m.p. 217–219° (Found: *m/z*, 606·234±0·006. $C_{41}H_{35}O_3P$ requires *m/z*, 606·232). $\nu_{\max}$ (Nujol) 1651 (C=O), 1557 cm^{-1}. ^{31}P n.m.r. δ (120 MHz, $CDCl_3$) 18·08, Ph_3P=C. ^{1}H n.m.r. δ (200 MHz, $CDCl_3$) 7·62–7·31, m, phenyl H; 7·25–6·87, m, H 1′–8′; 5·43–5·25, m, ethenyl =CH–; 4·90–4·76, m, H 10′, =CH_2; 4·06, d, J 2·3 Hz, H 9′; 3·89–3·69, m, H 11′, OCH_2–; 3·23–3·14, m, H 12′; 0·67, t, J 7·2 Hz, CH_3. ^{13}C n.m.r. δ (50 MHz, $CDCl_3$) 194·51, 194·45, C 3=O; 167·56, 167·21, C 1=O; 144·50, 144·48, 141·54, 140·20, C 4′a, C 8′a, C 9′a, C 10′a; 142·59, ethenyl =CH–; 133·21, 133·01, 131·32, 131·26, 128·39, 3×phenyl CH; 128·08, 126·22, phenyl quat.; 125·78, 125·62, 125·11, 124·95, 124·81, 124·58, 123·36, 123·09, C 1′–8′; 113·77, ethenyl =CH_2; 58·41, OCH_2–; 50·39, C 11′; 49·38, C 9′, C 10′; 44·46, C 12′; 13·81, CH_3. Mass spectrum, *m/z* 606 (M, 28%), 375 (57), 303 (34), 262 (100), 178 (99).

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References

[1] East, A. L. L., Allen, W. D., and Klippenstein, S. J., *J. Chem. Phys.,* 1995, **102**, 8506; Kwiatkowski, J. S., and Leszczynski, J., *Theochem*, 1995, **324**, 43.

[2] Brown, R. D., Godfrey, P. D., and Champion, R., *J. Mol. Spectrosc.*, 1987, **123**, 93.

[3] Brown, R. D., Godfrey, P. D., Ball, M. J., Godfrey, S., McNaughton, D., Rodler, M., Kleibömer, B., and Champion, R., *J. Am. Chem. Soc.*, 1986, **108**, 6534.

[4] Brown, R. F. C., Coulston, K. J., Eastwood, F. W., Irvine, M. J., and Pullin, A. D. E., *Aust. J. Chem.*, 1988, **41**, 225.

[5] East, A. L. L., *J. Chem. Phys.*, 1998, **108**, 3574.

[6] Lang, R. W., and Hansen, H.-J., *Helv. Chim. Acta*, 1980, **63**, 438.

[7] Masaaki, K., Uno, T., Kobayashi, M., and Osuga, N., (Mitsubishi Rayon Co. Ltd) *Eur. Pat. Appl.* EP 186106 (*Chem. Abstr.*, 1986, **105**, 114619a).

[8] Brown, R. F. C., Eastwood, F. W., and Harrington, K. J., *Aust. J. Chem.*, 1974, **27**, 2373.

[9] Wentrup, C., Gross, G., Berstermann, H.-M., and Lorencak, P., *J. Org. Chem.*, 1985, **50**, 2877.

[10] Maquestiau, A., Pauwels, P., Flammang, R., Lorencak, P., and Wentrup, C., *Org. Mass Spectrom.*, 1986, **21**, 259.

[11] Brown, R. F. C., Coulston, K. J., Eastwood, F. W., and Irvine, M. J., *Aust. J. Chem.*, 1991, **44**, 87.

[12] Brown, R. F. C., Browne, N. R., Coulston, K. J., Eastwood, F. W., Irvine, M. J., Pullin, A. D. E., and Wiersum, U. E., *Aust. J. Chem.*, 1989, **42**, 1321.

[13] Finke, R. G., and Sorrell, T. N., *Org. Synth.*, Collect. Vol. 6 (Ed. W. E. Noland), p. 807 (John Wiley: New York 1988).

[14] Bartlett, P. D., and Tate, F. A., *J. Am. Chem. Soc.*, 1953, **73**, 91.

[15] Friedrich, L. E., and Schuster, G. B., *J. Am. Chem. Soc.*, 1972, **94**, 1193.

[16] Bosshard, H. H., Mory, R., Schmid, M., and Zollinger, Hch., *Helv. Chim. Acta*, 1959, **42**, 1653.

[17] Diels, O., and Alder, K., *Justus Liebigs Ann. Chem.*, 1931, **486**, 191.

[18] Ripoll, J. L., Lebrun, H., and Thuillier, A., *Tetrahedron*, 1980, **36**, 2497.

[19] Bachmann, W. E., and Scott, L. B., *J. Am. Chem. Soc.*, 1948, **70**, 1458.

[20] Reid, W., and Schinzel, H., *Liebigs Ann. Chem.*, 1982, 1569.