Acetolysis of 2-(2,3-Dihydro-1*H*-cyclopenta[*l*]phenanthren-2-yl)ethyl Derivatives: Participation by the 9,10-Bond of Phenanthrene to give an Analogue of a Classical Norbornyl Cation

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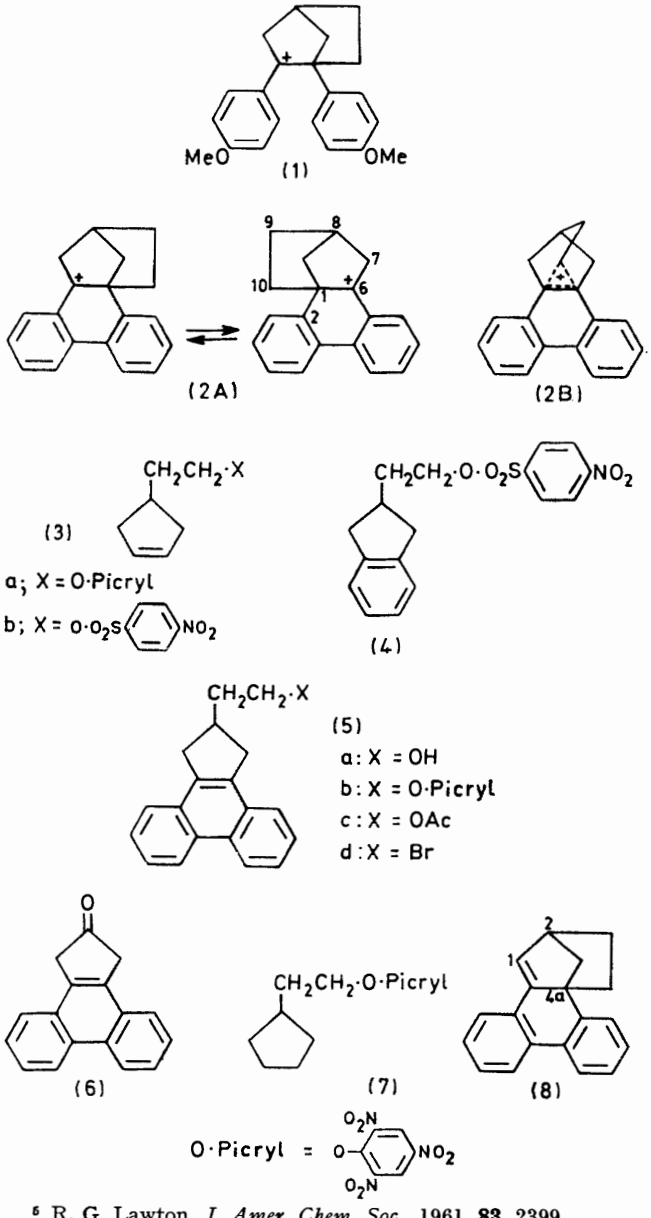
Kinetic and product studies of the title reaction indicate participation by the 9,10-bond of the phenanthrene ring. Preparative acetolysis of the bromide (5d) catalysed by silver acetate, gives 3,4-dihydro-2*H*-2,4a-methanotriphenylene (8) as a major product. This dissolves in fluorosulphonic acid to give a red solution, the ^{1}H n.m.r. and electronic absorption spectra of which are consistent with the presence of the classical norbornyl cation (2A). Nucleophilic capture of the cation by acetic acid occurs predominantly at the bridge carbon atom, and is accompanied by ring opening to regenerate the cyclopentaphenanthrenylethyl skeleton.

THE application of short-time-scale spectroscopic techniques to the structure of the norbornyl cation is a relatively recent development. Perhaps the first clear success was the use, by Olah's group, of Raman spectroscopy to define norbornyl itself as ' nortricyclene-like ',[1] this being a key step in the ultimate structure determination.[2]

Stimulated by Sargent's provocative review,[3] we had considered the possibility of using u.v. and visible spectroscopy to examine analogues of the norbornyl system. A precedent already existed in the work of Schleyer *et al.*[4] on the 1,2-bis(methoxyphenyl)norbornyl and related cations. For these, a variety of spectroscopic and chemical evidence pointed to a pair of rapidly equilibrating classical structures. A complication with this system, however, appeared to be the possibility, in the classical formulation, of free rotation of the aryl substituent attached to C-1. In view of this, and the efficient electron-releasing properties of the aryl substituent on C-2, it seems unremarkable that the classical structures should most accurately represent these cations [*e.g.* the ion (1)].

The system chosen for the present study, namely (2A) [or (2B)], was different in that the aryl substituents at C-1 and C-2 are not independent, being constrained in such a way that they simultaneously present one face to the mobile 9,10-ethano-bridge. Furthermore, the delocalisation of charge across the phenanthrene system which should occur in either structure (2A) or (2B), should minimise complications from electrophilic substitution.[4] It was envisaged that, irrespective of n.m.r. data, the electronic spectrum of cation (2), by comparison with the electronic spectra of 9-protonated phenanthrenes, should enable a distinction to be drawn between the two alternatives for its structure. No satisfactory model is available for the bridged structure (2B). However, it seems *a priori* unlikely, on grounds both of electronic structure and of symmetry, that (2A) and (2B) would have similar electronic spectra.

The π-route to norbornanes involving solvolysis of cyclopentenylethyl derivatives (3) is well known,[5,6] but experiments with the benzologue (4), have, in contrast,



[1] G. A. Olah, A. Commeyras, and C. Y. Lui, *J. Amer. Chem. Soc.*, 1968, **90**, 3882.
[2] G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, 1969, **91**, 6883.
[3] G. D. Sargent, *Quart. Rev.*, 1966, **20**, 301.
[4] P. von R. Schleyer, D. C. Kleinfelter, and H. G. Richey, *J. Amer. Chem. Soc.*, 1963, **85**, 479; see also discussion by H. C. Brown, *Chem. in Britain*, 1966, **2**, 199.
[5] R. G. Lawton, *J. Amer. Chem. Soc.*, 1961, **83**, 2399.
[6] P. D. Bartlett and G. D. Sargent, *J. Amer. Chem. Soc.*, 1965, **87**, 1297.

yielded no evidence for participation.[6] Nevertheless, the considerable double bond character of the phenanthrene 9,10-bond encouraged us to prepare the cyclopentaphenanthrenylethanol (5a) from the phenanthrocyclopentenone (6) [7] in order to investigate the possibility of a π-route to the ion (2). We compared the rate of acetolysis of the picrate (5b) [8] with the rates of acetolysis of the cyclopentane derivatives (3a) and (7). The kinetic data are summarised in Table 1. The rate of

TABLE 1

Kinetic data on the acetolysis of the picrates (5b), (3a), and (7)

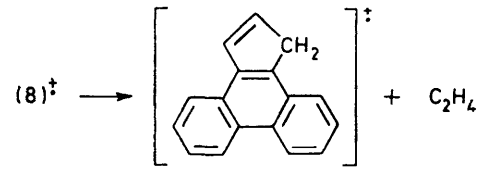
Picrate	T/°C	k/s	k_{rel} (at 111·6 °C)	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal K^{-1} mol^{-1}
(7)	115·5	$3·49 \times 10^{-6}$	1	29·1 ± 0·5	−9·1 ± 1·6
	122·3	$6·72 \times 10^{-6}$			
	127·3	$1·17 \times 10^{-5}$			
	130·3	$1·42 \times 10^{-5}$			
	145·3	$5·47 \times 10^{-5}$			
(5b)	99·5	$1·05 \times 10^{-5}$	13·5	27·3 ± 0·5	−7·9 ± 1·5
	115·5	$5·20 \times 10^{-5}$			
	122·3	$8·90 \times 10^{-5}$			
	127·3	$1·44 \times 10^{-4}$			
	130·3	$1·72 \times 10^{-4}$			
(3a)	77·9	$7·51 \times 10^{-6}$	85·4	25·4 ± 0·4	−9·2 ± 1·1
	83·1	$1·53 \times 10^{-5}$			
	89·6	$2·63 \times 10^{-5}$			
	107·2	$1·38 \times 10^{-4}$			
	110·3	$1·80 \times 10^{-4}$			

acetolysis of the picrate (5b) was found to be midway between those for the two model compounds, a result strongly suggestive of intramolecular participation. However, the activation parameters do not show any clear demarcation between the picrate (7) on the one hand, and compounds (5b) and (3a) on the other.

Our experience with the picrate acetolysis procedure has been entirely in accord with the claims of convenience and reproducibility for this method.[8,9] A possible difficulty for the phenanthrene system could arise from inter- or intra-molecular charge transfer. We could find no spectroscopic evidence to suggest this in the dilute solutions in buffered acetic acid employed for the kinetic experiments. If it had occurred it might, in any case, have been expected to make the picrate a poorer leaving group and thus to have had a retarding effect on the reaction.

Acetolysis of the picrate (3a) has not previously been reported, but appears to parallel that of other cyclopentenylethyl derivatives [5,6,10] in giving *exo*-norbornyl acetate as the only detectable product (but see also ref. 11).

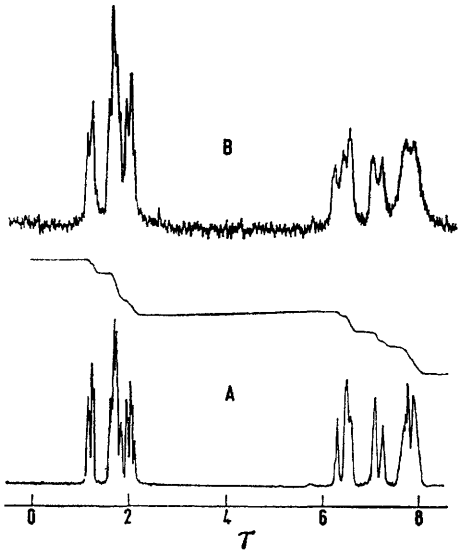
Preparative acetolysis of (5b) gave unrearranged acetate (5c) (75%) as the major product, together with small quantities of at least three other compounds, none of which has been unambiguously identified. Product evidence for the participation of the phenanthrene nucleus was however obtained in the silver acetate-catalysed acetolysis of the corresponding bromide (5d). Reaction was complete after 45 min at reflux, when the major product was a hydrocarbon identified as the norbornene derivative (8) (75%). This compound was characterised by n.m.r. and mass spectrometry. The latter showed a peak for the parent ion at *m/e* 244·1255 and base peak at *m/e* 216 consistent with the fragmentation indicated in the annexed formulae. The olefin (8) may be the kinetically controlled product from the ion (2) in acetic acid, for when it was subjected to prolonged heating in this solvent in the presence of sodium acetate, *i.e.* the conditions employed for the preparative acetolysis of the picrate (5b), it was converted into the acetate (5c), together with small quantities of the unidentified products found in that acetolysis. If the sodium acetate was replaced by a trace of toluene-*p*-sulphonic acid, addition of acetic acid to give (5c) was rapid, consistent with nucleophilic capture of cation (2) at C-10 (*i.e.*, the reverse of the π-route to the norbornane skeleton, *cf.* ref. 12).



When the hydrocarbon (8) is dissolved in fluorosulphonic acid, a red solution is obtained, the n.m.r. spectrum of which is readily interpretable in terms either of the rapidly equilibrating structures (2A), or of their symmetrically bridged counterpart (2B). An interesting feature is the large chemical shift separation (*ca.* 0·6 p.p.m.) between the *endo*- and *exo*-protons at C-7. At −110° in FSO_3H–SO_2ClF, broadening of the spectrum is observed, except for that part which is attributable to the bridgehead proton (at C-8) (Figure). This result strongly favours the classical formulation (2A), an interpretation wholly supported by the u.v. and visible spectra. The latter are very similar to those of model protonated phenanthrenes,[13] and also to the spectra of the recently reported (classical) 9,10,10-trimethylphenanthrenium cation (10) (Table 2).[14] The long-wavelength absorption band of the ion (2) is very broad (ε 3·33 in FSO_3H at 500 nm) thus explaining the imperfect correspondence in $\lambda_{max.}$ for this band. Quenching of fluorosulphonic acid solutions of the ion (2) into acetic acid gave the acetate (5c).

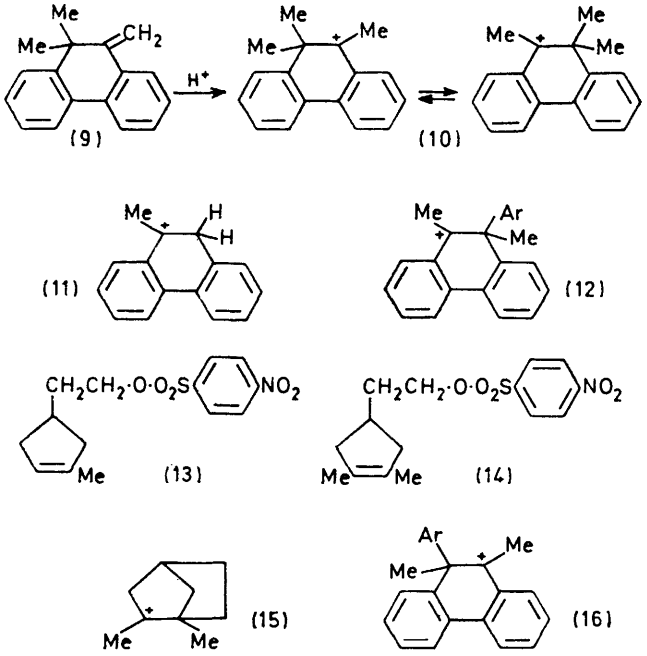
[7] A. C. Cope, L. Field, D. W. H. MacDowell, and M. F. Wright, *J. Amer. Chem. Soc.*, 1956, **78**, 2547; A. C. Cope and D. W. H. MacDowell, *ibid.*, 1958, **80**, 5513.
[8] M. L. Sinnott and M. C. Whiting, *Chem. Comm.*, 1968, 1617.
[9] M. L. Sinnott and M. C. Whiting, *J. Chem. Soc.* (*B*), 1971, 965.
[10] P. D. Bartlett, S. Bank, R. J. Crawford, and G. H. Schmid, *J. Amer. Chem. Soc.*, 1965, **87**, 1288.
[11] L. A. Spurlock and W. G. Cox, *J. Amer. Chem. Soc.*, 1969, **91**, 2961.
[12] L. B. Jones and V. K. Jones, *J. Org. Chem.*, 1971, **36**, 1017.
[13] G. Dallinga, E. L. Mackor, and A. A. Verijn Stuart, *Mol. Phys.*, 1958, **1**, 123; see also W. Th. A. M. van der Lugt, H. M. Buck, and L. J. Oosterhoff, *Tetrahedron*, 1968, **24**, 4941, and C. Reid, *J. Amer. Chem. Soc.*, 1964, **76**, 3264.
[14] V. G. Shubin, D. V. Korchagina, A. I. Rezvukhin, and V. A. Koptyug, *Doklady Akad. Nauk S.S.S.R.*, 1968, **179**, 119.

The cation (2) has also been generated (n.m.r.) by the reaction of the bromide (5d) with silver hexafluoroantimonate in sulphur dioxide. Although our spectroscopic data cannot legitimately be extrapolated to the



90 MHz ^{1}H n.m.r. spectra of cation (2) in FSO_3H–SO_2ClF, A, at −30° and B, −110°

structure of the cationic intermediate involved in the acetolyses, it seems reasonable to refer to the reaction in sulphur dioxide as a 'π-route to a classical norbornyl



cation'. It would be interesting to devise a procedure whereby the kinetics of a homogeneous counterpart of this reaction (*e.g.* promoted by SbF_5) could be determined. Provided that π-participation in the removal of the halogen atom was established, measurements of substituent effects on the rate of such a reaction would permit the symmetry of the transition state to be probed in a reaction which leads to an unsymmetrical ion. In the context of this suggestion, a possible ambiguity in the pioneering studies [6] of this application of substituent effects by Bartlett *et al.* is noteworthy. Because rate data for only two of the three compounds (3b), (13), and (14) were obtained at more than one temperature, the all-important relationship between the rate ratios at that temperature could conceivably be fortuitous. More recent information, both from solvolysis of 1,2-dimethylnorbornyl derivatives,[15] and from direct spectroscopic observation,[16] favours equilibrating classical structures for the 1,2-dimethylnorbornyl cation (15).

TABLE 2

Spectroscopic data for phenanthrenium ions

Ion	$\lambda_{max.}$/nm (log ε)	Ref.
(11) [a]	259 (4·43); 320 (4·01); 510 (3·80)	13
(10) [b]	266 (4·28); 338 (4·00); 530 (3·59)	14
(2) [c]	258 (4·21); 331 (3·60); 496 (3·01)	This work
(2) [d]	191 (4·60); 259 (4·50); 335 (3·93); 460 (3·74)	This work

[a] In HF–BF_3. [b] In 75% H_2SO_4. [c] In 80% H_2SO_4. [d] In FSO_3H.

Finally, it is valuable to compare our results with those obtained by Shubin *et al.* for the cation (10),[14] and for the aryl substituted analogues (16).[17] Line broadening in the ^{1}H n.m.r. spectrum of the ion (2A) becomes important only at temperatures which are sufficiently low to attain the slow exchange limit for the ion (10), and which are, more significantly, lower than the coalescence temperature for the methyl resonances of the ion (16; Ar = Ph). Although the slow exchange limit has not been approached for the ion (2), and quantitative analysis is therefore not yet possible, this qualitative comparison allows the interesting possibility that the alkyl-bridged transition state for equilibration of the ion (2) may be energetically more accessible than the phenyl-bridged counterpart for equilibration of the ion (16; Ar = Ph).

EXPERIMENTAL

M.p.s are uncorrected. The n.m.r. spectra were recorded for solutions in deuteriochloroform unless otherwise stated. 100 MHz spectra and mass spectra were obtained through the P.C.M.U. at Harwell, whom we thank. Light petroleum refers to that fraction with b.p. 60—80°, unless otherwise specified.

2-Bromo-2,3-dihydro-1H-cyclopenta[l]phenanthrene.—Using essentially the method of Cope and his co-workers,[7] 9,10-phenanthraquinone was converted into 2,3-dihydro-

[15] H. L. Goering and K. Humski, *J. Amer. Chem. Soc.*, 1968, **90**, 6213; H. L. Goering, C. Brown, and C. B. Schewene, *ibid.*, p. 6214.

[16] G. A. Olah, J. R. DeMember, C. Y. Liu, and R. D. Porter, *J. Amer. Chem. Soc.*, 1971, **93**, 1442.

[17] V. G. Shubin, D. V. Korchagina, G. I. Borodkin, B. G. Derendjaev, and V. A. Koptyug, *Chem. Comm.*, 1970, 696.

2-hydroxy-1*H*-cyclopenta[*l*]phenanthrene, m.p. 187—188° (from ethanol) (lit.,[7] 187—188°). This alcohol was converted into its *methanesulphonate* by treating a solution in dry pyridine with freshly distilled methanesulphonyl chloride in dry methylene chloride. The product (91%), m.p. 161·5—162·5° (from ethanol), showed $\nu_{max.}$ 1325—1345 and 1165 cm^{-1} (sulphonyl group), τ 1—1·5 (2H, m), 2—2·25 (6H, m), 4·1br (1H, t), 6·3br (4H, d), and 6·9 (3H, s). To this derivative (5 g) in dry acetone (250 ml) was added anhydrous lithium bromide (3 mol. equiv.), and the mixture was boiled under reflux for 24 h, giving *2-bromo-2,3-dihydro-1H-cyclopenta[l]phenanthrene*, m.p. 162·5—163° (from ethanol) (Found: C, 68·3; H, 4·3. $C_{17}H_{13}Br$ requires C, 68·6; H, 4·4%), τ 0·85—1·05 (2H, m), 1·8—2·2 (6H, m), 4·85br (1H, t), and 6·0br (4H, d).

Cyclopentaphenanthrenylethyl Alcohol (5a).—Powdered sodium hydride (0·4 g) was added to dry dimethoxyethane (10 ml), and the mixture was stirred under dry nitrogen while diethyl malonate (2·8 g) in dry dimethoxyethane (20 ml) was added (30 min). The resulting clear solution was stirred for 1 h after which the above bromo-compound (5 g) in dry dimethoxyethane (20 ml) was added in one portion, and the mixture was then heated to 80° for 48 h and cooled; water (20 ml) was added and dimethoxyethane was removed by distillation under reduced pressure. The residue was distributed between water (250 ml) and methylene chloride (500 ml). Solvent was removed from the dried methylene chloride solution, the residue was dissolved in a minimum of methylene chloride and chromatographed on a column (4 ft × 2 in) of silica gel (450 g; 60—120 mesh). Elution with methylene chloride gave two major fractions, of which the first was unchanged bromide and the second was diethyl 2,3-dihydro-1*H*-cyclopenta[*l*]phenanthren-2-ylmalonate, $\nu_{max.}$ 1725 cm^{-1}, τ 1·25—2·5 (8H, m), 5·82 (4H, q), 6·2—7·1 (6H, m), and 8·75 (6H, t). The crude diester (3·5 g) was hydrolysed by heating with aqueous potassium hydroxide (30 ml; 40%) on a steam bath for 30 min. The crude dicarboxylic acid (1 g) [$\nu_{max.}$ 1710br, m.p. (decomp.) *ca.* 209°] was dissolved in pyridine (50 ml; dried over KOH), and the solution was boiled under reflux overnight, cooled, poured into water (100 ml), and the mixture was acidified (dilute HCl). The precipitated 2,3-dihydro-1*H*-cyclopenta-[*l*]phenanthren-2-ylacetic acid had m.p. 242—244° (from ethanol). A portion of the crude acid was methylated (CH_2N_2) and the n.m.r. spectrum of the product compared with that of the dimethyl ester of the corresponding malonic acid similarly prepared. This comparison showed, by examination of the OMe resonances which were not coincident, that decarboxylation was complete. Methylation of the monocarboxylic acid (5·2 g) in methanol (50 ml), by diazomethane in ether, followed by removal of the solvent gave the methyl ester, m.p. 164° (from benzene–light petroleum). This was dissolved in dry tetrahydrofuran (400 ml) and dry methylene chloride (100 ml), and was slowly added to lithium aluminium hydride (5 g) under nitrogen in dry ether (50 ml). The mixture was stirred overnight, boiled under reflux for 1 h, cooled, and excess of lithium aluminium hydride was destroyed by the addition of wet ether. The *2-(2,3-dihydro-1H-cyclopenta[l]phenanthren-2-yl)ethanol* was purified by column chromatography on silica gel, eluting with methylene chloride, and was crystallised from benzene–light petroleum, m.p. 166·5—168° [Found: C, 86·5; H, 6·9%; *M*, 262 (m.s.). $C_{19}H_{18}O$ requires C, 87·0; H, 6·9%; *M*, 262], $\nu_{max.}$ 3300 (OH) cm^{-1}, τ 1·2—1·4 (2H, m), 2·1—2·5 (6H, m), 6·15 (2H, t, CH_2O), 6·35—7·4 (5H, m), 8·1 (2H, m), 8·57br (1H, s, OH). The acetate, m.p. 116—118° was prepared by acetylation with acetic anhydride and crystallisation from ethanol.

2-(2,3-Dihydro-1H-cyclopenta[l]phenanthren-2-yl)ethyl Bromide.—The above alcohol was converted into its methanesulphonate, and this was converted into the corresponding *bromide*, m.p. 123—124·5° (Found: C, 70·2; H, 5·5. $C_{19}H_{17}Br$ requires C, 70·15; H, 5·3%), following the procedures already described for the preparation of 2-bromo-2,3-dihydro-1*H*-cyclopenta[*l*]phenanthrene. The corresponding *chloride* was similarly prepared from the methanesulphonate by use of lithium chloride in acetone, m.p. 128—130° (Found: C, 81·1; H, 6·1; Cl, 12·4. $C_{19}H_{17}Cl$ requires C, 81·3; H, 6·1; Cl, 12·6%).

2-(Cyclopent-3-enyl)ethanol.—This was prepared by a slight modification of the method of Wilt *et al.*[18]

2-Cyclopentylethanol.—This was prepared by a modification of the procedure given by Lawton.[5]

Picryl Fluoride.—This compound is now commercially available, and a ' more reliable ' preparation (43—50%) has recently been described by Sinnott and Whiting.[9] Our experience with earlier published procedures was slightly different from theirs, and merits comment. We were unable to secure picryl fluoride by the method of Sharma *et al.*[19] or by that of Vorozhtsov and Yakobson.[20] However, the method of Shaw and Seaton [21] gave reproducible yields approaching 60%.

Cyclopentaphenanthrenylethyl Picrate (5b).—The alcohol (5a) was converted to the corresponding picrate by the general method outlined by Sinnott and Whiting.[8] The *picrate* (5b) (74%) was obtained as orange-yellow plates, m.p. 202—204° (decomp.) (Found: C, 63·6; H, 4·3; N, 8·9. $C_{25}H_{19}N_3O_7$ requires C, 63·4; H, 4·0; N, 8·9%), $\nu_{max.}$ 3110, 1615, 1540, and 1340 cm^{-1} (picryl group), τ 1·05 (2H, s), 1·1—1·3 (2H, m), 2·0—2·4 (6H, m), 5·5 (2H, t, CH_2O), 6·1—7·2 (5H, m), and 7·6—7·9 (2H, m). This and other picrates were stored in the dark over P_2O_5.

2-(Cyclopent-3-enyl)ethyl Picrate.—Following the general procedure described above, cyclopentenylethyl alcohol was converted into its *picrate*, m.p. 69·5° (from benzene–light petroleum) (Found: C, 48·6; H, 4·1; N, 13·1. $C_{13}H_{13}N_3O_7$ requires C, 48·3; H, 4·0; N, 13·0%), τ 1·16 (2H, s), 4·35br (2H, s), 5·75 (2H, t), and 7·2—8·4 (7H, m).

2-Cyclopentylethyl Picrate.—Cyclopentylethanol was similarly converted into its *picrate*, m.p. 67—68° (from benzene–light petroleum) (Found: C, 48·0; H, 4·9; N, 13·1. $C_{13}H_{15}N_3O_7$ requires C, 48·0; H, 4·65; N, 12·9%), τ 1·13 (2H, s), 5·72 (2H, t), and 8·1—8·6 (11H, m).

Acetolysis Studies.—(a) *Kinetics.* Solutions of the appropriate picrate (*ca.* $1·5 \times 10^{-4}$M) were prepared in reagent-grade acetic acid which was 0·125M in sodium acetate, and samples (4 ml) were sealed in glass ampoules and heated in a thermostatically controlled oil bath the temperature of which was maintained constant within ±0·2 °C, and was measured with a calibrated thermometer. Samples were withdrawn at intervals, quenched by rapid cooling, and their spectra were recorded against blanks (unheated reaction mixture stored just above its m.p.). The progress

[18] J. W. Wilt, S. N. Massie, and R. B. Dabek, *J. Org. Chem.*, 1970, **35**, 2803.
[19] H. L. Sharma, V. N. Sharma, and R. L. Mital, *Canad. J. Chem.*, 1966, **44**, 1327.
[20] N. N. Vorozhtsov and G. G. Yakobson, *J. Gen. Chem. (U.S.S.R.)*, 1961, **31**, 345.
[21] G. C. Shaw and D. L. Seaton, *J. Org. Chem.*, 1961, **26**, 5227.

of the reaction was followed at 390 nm, and linear first-order plots were obtained over at least two half lives, with generally excellent reproducibility (*cf.* ref. 9). The results are summarised in Table 1. A slight dependence of the rate on the concentration of sodium acetate was noted in a control experiment, consistent with a small salt effect.

(b) *Products:* (i) 2-(*cyclopent-3-enyl*)*ethyl picrate.* A solution of the picrate (0·5 g) in reagent-grade acetic acid (20 ml) containing anhydrous sodium acetate (0·206 g) was shielded from the light, and boiled under reflux for 72 h, after which time t.l.c. showed that all the initial picrate had disappeared. Water (100 ml) was added to the cooled solution, and the acetic acid was neutralised by cautious addition of sodium hydrogen carbonate. The resulting solution was extracted with chloroform (3 × 100 ml), the extracts were dried (K_2CO_3), and the solvent was removed. The residue (210 mg, 91%) was indistinguishable (i.r., n.m.r.) from authentic *exo*-norbornyl acetate.

(ii) *Cyclopentaphenanthrenylethyl picrate.* A mixture of the picrate (788 mg) and anhydrous sodium acetate (0·206 g) was dissolved in glacial acetic acid (20 ml) and the mixture was boiled under reflux for 72 h, shielded from direct light. Water (100 ml) was added to the cooled solution, and the mixture was extracted with methylene chloride (3 × 50 ml). The solution was washed with aqueous sodium hydrogen carbonate, dried (K_2CO_3), and the solvent was removed. Examination of the residue by t.l.c. showed it to contain a substantial proportion of a compound chromatographically indistinguishable from cyclopentaphenanthrenylethyl acetate, together with several minor components. Column chromatography on neutral alumina gave the acetate (376 mg, 74%) indistinguishable from authentic material, and traces of other more polar substances which have not been identified.

(iii) *Cyclopentaphenanthrenylethyl bromide, catalysed by silver acetate.** To a stirred mixture of silver acetate (4·0 g) in reagent grade acetic acid (50 ml), protected from light, was added cyclopentaphenanthrenylethyl bromide (4·0 g.). The solution was boiled under reflux, and the progress of the reaction was monitored by t.l.c. Disappearance of the bromide was essentially complete after 45 min, when the mixture was cooled, and insoluble silver salts were removed. Water (250 ml) was added and the solution extracted with ether (3 × 100 ml). The combined extracts were washed with aqueous sodium hydrogen carbonate, dried (K_2CO_3), and the solvent was removed. T.l.c. revealed two major products together with traces of two minor components. The total product was therefore chromatographed on neutral alumina. Elution with light petroleum (b.p. 40—60°) gave the major product as a crystalline solid (2·26 g). Elution with light petroleum–toluene (1 : 1) then gave cyclopentaphenanthrenylethyl acetate (0·73 g) and a second minor, unidentified, product (35 mg). The major product crystallised from methanol as prisms, m.p. 110—110·5°. It was identified as 3,4-*dihydro*-2H-2,4a-*methanotriphenylene* by spectroscopy. The mass spectrum showed a parent ion at *m/e* 244·1255 (calc. for $C_{19}H_{16}$, *m/e* 244·1252) and a base peak at $M - 28$ (see text). The u.v. spectrum showed maxima at 254·5 and 263·5 nm and a broad featureless maximum at 300 nm, in contrast to the characteristic fine structure found in the long-wavelength absorption of the phenanthrene precursors. The n.m.r. spectrum showed absorptions at τ 2·1—2·8 (8H, m, aromatic), 3·55 (1H, d, *J* 3·1 Hz, 1-H), 6·81 (1H, m, 2-H), and 7·9—9·2 (6H, m); the coupling between 1-H and 2-H was confirmed by a double resonance experiment. When this hydrocarbon (20 mg), acetic acid (2 ml), and anhydrous sodium acetate (20 mg) were boiled under reflux for 72 h, the hydrocarbon was converted into cyclopentaphenanthrenylethyl acetate (5c) and traces of additional products similar (t.l.c.) to those obtained from the picrate acetolysis. Almost quantitative conversion into acetate was achieved in *ca.* 2 h by heating the hydrocarbon in acetic acid containing *ca.* 0·1% of toluene-*p*-sulphonic acid.

The hydrocarbon dissolved in fluorosulphonic acid or in 80% sulphuric acid to give orange-red solutions, the electronic spectral characteristics of which are recorded in Table 2. The 90 MHz ^1H n.m.r. spectrum of the solution in fluorosulphonic acid at room temperature exhibited resonances at τ 1·19 (2H, d), 1·55—1·85 (4H, m), 2·05 (2H, t), 6·40br (2H, d, *J* 15 Hz), 6·53br (1H, s, 4-H), 7·10br (2H, d, *J* 15 Hz), and 7·65—8·0 (4H, m). The chemical shifts are relative to internal methylene chloride taken as τ 4·67. The AB pattern centred at τ 6·4 and 7·1 was established by a double-resonance experiment (at 60 MHz). Essentially the same spectrum was obtained from a solution prepared by condensing dry sulphur dioxide onto a mixture of the bromide (5d) and excess silver hexafluoroantimonate. At −110° in FSO_3H–SO_2ClF, the spectrum was considerably broadened, with the notable exception of the peak due to 4-H.

When the solution in fluorosulphonic acid was quenched into acetic acid, the principal identifiable product (i.r., t.l.c.) was the ring-opened acetate (5c).

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* Following the method of Sherrod and Bergman.[22]

[22] S. A. Sherrod and R. G. Bergman, *J. Amer. Chem. Soc.*, 1971, **93**, 1938.