613. *Hydride Ions in Organic Reactions. Part II.*[1] *Preparation of Phenalenium Salts by the Reaction of Phenalenes with Quinones in the Presence of Acids.*

By D. H. Reid and R. G. Sutherland.

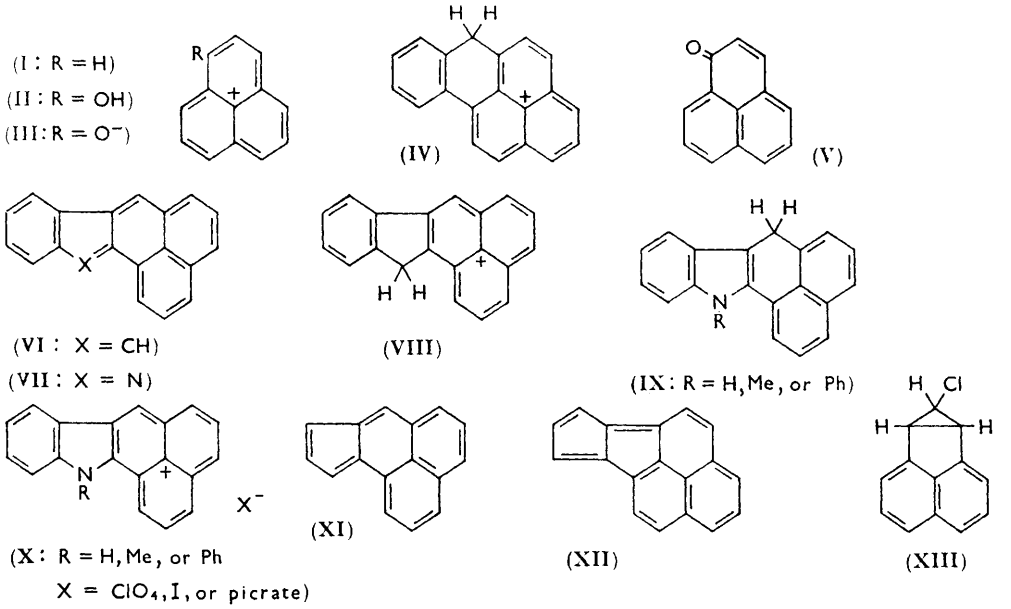
A general synthesis of phenalenium salts involving hydride-transfer from phenalenes to quinones in the presence of acids is reported. The stability of the phenalenium salts is briefly discussed.

The first suggestion [2] that the phenalenium cation (I) might be stable was qualitatively in terms of a resonance stabilisation resulting from the high degree of symmetry of the ion. Simple Hückel molecular-orbital calculations later predicted [3] that the conjugate acids of hydrocarbons containing the phenalenium grouping should be particularly stable, and they were exemplified by reference to benzo[*a*]pyrene, which is one of the most basic of the benzenoid hydrocarbons and dissolves reversibly in concentrated sulphuric acid to form the cation (IV). The stability of the phenalenium unit also accounts for the following: (*a*) Phenalen-1-one (V) is abnormally basic,[4] dissolving reversibly in concentrated hydrochloric acid to form the 1-hydroxyphenalenium cation (II). Its abnormally low infrared carbonyl stretching frequency [5] (1637 cm.$^{-1}$) and high dipole moment [6] (3·99 D) are indicative of considerable polarisation to the limiting phenalenium oxide structure (III). (*b*) Indeno[2,1-*a*]phenalene [7] (VI) is one of the most basic hydrocarbons known. Its order of basicity is that of the azulenes and heptalene. Its conjugate acid is the 12*H*-indeno[2,1-*a*]phenalenium cation (VIII). (*c*) 7,12-Dihydronaphtho[1,8a,8-*ab*]-carbazoles (IX) aromatise readily in acidic solutions to the salts (X).[8] In view of the

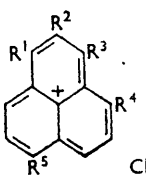
[1] Part I, *J.*, 1959, 2773.
[2] Boekelheide and Larrabee, *J. Amer. Chem. Soc.*, 1950, **72**, 1245.
[3] Gold and Tye, *J.*, 1952, 2181.
[4] Bamberger and Philip, *Annalen*, 1887, **240**, 178; Cook and Hewett, *J.*, 1934, 365.
[5] Cromwell and Hudson, *J. Amer. Chem. Soc.*, 1953, **75**, 872.
[6] Zhdanov, Osipov, Shelapin, and Kogan, *Doklady Akad. Nauk S.S.S.R.*, 1959, **128**, 719.
[7] Aitken and Reid, *J.*, 1956, 3487.
[8] Reid, *Tetrahedron*, 1958, **3**, 339.

importance of the phenalenium structure for the aromaticity and aromatic reactivity of indeno[2,1-*a*]phenalene (VI) and naphtho[1,8a,8-*ab*]carbazole (VII), and for predicting the properties of cyclopenta[*a*]phenalene [7,8] (XI) and pentaleno[1,2,3-*cd*]phenalene [8] (XII), a number of substituted phenalenium salts were prepared for investigation.

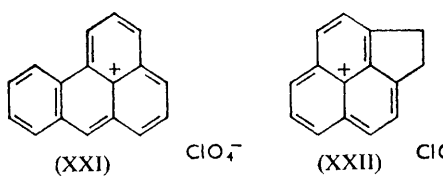
The preparation of phenalenium perchlorate (XIV) by treatment of the chloro-compound (XIII) with silver perchlorate was the first successful attempt [9] to synthesise a



simple phenalenium salt. The first step in the synthesis was the addition of ethyl diazoacetate to acenaphthylene. The scope of the synthesis is limited by the inaccessibility of substituted acenaphthylenes. Previously [1] we reported the preparation of phenalenium perchlorate and its 1,4,7-trimethyl derivative (XVIII) by the action of triphenylmethyl perchlorate on phenalene (XXX) and 1,4,7-trimethylphenalene, respectively. In this paper we describe a new method of preparation of phenalenium salts from phenalenes by hydride-abstraction with quinones in the presence of perchloric acid,[10] and an extension of our earlier work [1] with triphenylmethyl perchlorate.

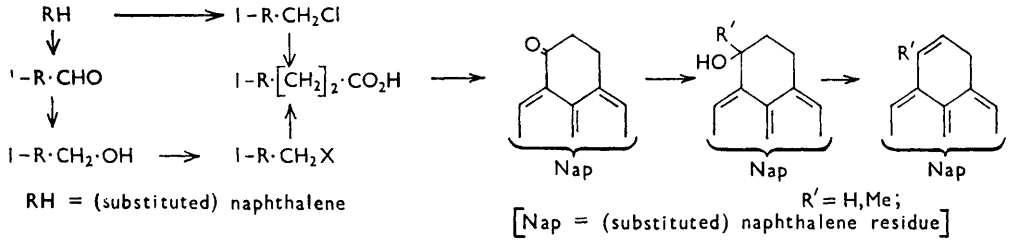


	R¹	R²	R³	R⁴	R⁵
(XIV)	H	H	H	H	H
(XV)	Me	H	H	H	H
(XVI)	Me	Me	H	H	H
(XVII)	Me	H	Me	H	H
(XVIII)	Me	H	H	Me	Me
(XIX)	MeO	H	H	H	H
(XX)	H	MeO	H	H	MeO



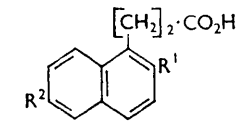
[9] Pettit, *J. Amer. Chem. Soc.*, 1960, **82**, 1972; *Chem. and Ind.*, 1956, 1306.
[10] Reid, Fraser, Molloy, Payne, and Sutherland, *Tetrahedron Letters*, 1961, 530.

Synthesis of Phenalenes.—With the exception of benzo[*b*]phenalene (benzanthrene), the required phenalenes were synthesised from substituted naphthalenes by the following general scheme. 1-Halogenomethylnaphthalenes, prepared by chloromethylation or, indirectly, by successive formylation (Vilsmeier method), reduction with lithium aluminium hydride, and treatment with phosphorus trichloride or tribromide, were converted into β-1-naphthylpropionic acids by the malonic ester synthesis. Cyclisation of the acids with hydrogen fluoride gave in most cases 2,3-dihydrophenalenones as the only product. These with lithium aluminium hydride or Grignard reagents yielded 2,3-dihydrophenalen-1-ols which on dehydration, in some cases during the preparation of the phenalenium salts, gave the required phenalenes.

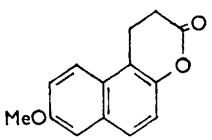


In the synthesis of 1,5-dimethoxyphenalenium perchlorate (XX), cyclisation of β-(2,6-dimethoxy-1-naphthyl)propionic acid (XXIII) gave, in addition to the ketone (LI), a small amount of the benzochromen (XXV) owing to lactonisation and demethylation at the 2-methoxy substituent. Lactone formation was not observed, however, in the cyclisation of the acid (XXIV). In the synthesis of 1,2-dihydrocyclopenta[*cd*]phenalenium perchlorate (XXII), cyclisation of β-acenaphthen-5-ylpropionic acid (XXVI) gave, in addition to the ketone (XXVII), small amounts of its dehydrogenation product (XXVIII), and the indanone (XXIX) arising from cyclisation at position 4.*

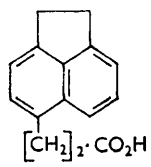
The structure of the substituted phenalenes was not uniquely determined in some cases owing to prototropy in the phenalene system. As many as six structural isomers are possible for a monosubstituted phenalene, corresponding to the number of chemically different positions which the methylene group may occupy. Benzanthrene is known to be benzo[*b*]phenalene (XXXIX). The monomethylphenalene corresponding to 1-methyl-



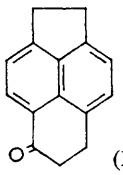
(XXIII: $R^1 = R^2 = OMe$)
(XXIV: $R^1 = OMe, R^2 = H$)



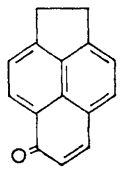
(XXV)



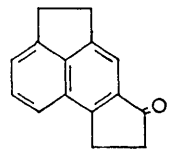
(XXVI)



(XXVII)



(XXVIII)



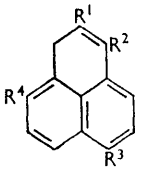
(XXIX)

phenalenium perchlorate (XV), prepared in the present work by the dehydration of the alcohol (XLV), has been shown [12] to be either 4- (XXXVI) or 9-methylphenalene (XXXI),

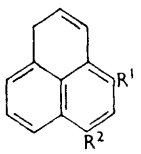
* Cyclisation of the acid (XXVI) with hydrogen fluoride has been reported [11] to give the ketone (XXVII) alone.

[11] Fieser and Jones, *J. Amer. Chem. Soc.*, 1942, **64**, 1666.
[12] Boekelheide and Larrabee, *J. Amer. Chem. Soc.*, 1950, **72**, 1250.

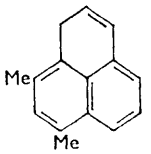
irrespective of its mode of preparation. The structure of the dimethylphenalene corresponding to 1,2-dimethylphenalenium perchlorate, prepared by the dehydration of (XLI), is provisionally formulated as (XXXIII).



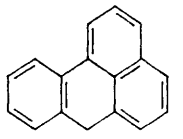
	R^1	R^2	R^3	R^4
(XXX)	H	H	H	H
(XXXI)	H	H	H	Me
(XXXII)	H	Me	Me	Me
(XXXIII)	Me	Me	H	H
(XXXIV)	H	H	H	MeO
(XXXV)	H	o-Cl·C_6H_4	H	MeO



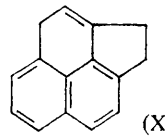
(XXXVI : R^1 = Me, R^2 = H)
(XXXVII : R = R^2 = Me)



(XXXVIII)



(XXXIX)



(XL)

Dehydration of the alcohol (XLVI) gave a hydrocarbon possessing a surprisingly high melting point (151—153°), stability to the atmosphere, and insolubility in light petroleum and acetonitrile. Its molecular weight nevertheless corresponded to that of a dimethylphenalene, and reaction with tetrachloro-*o*-benzoquinone and perchloric acid [10] gave 1,3-dimethylphenalenium perchlorate (XVII), also obtained directly from (XLVI) with the same reagent. Reduction with lithium aluminium hydride of 1,3-dimethylphenalenium perchlorate prepared directly from the alcohol (XLVI) regenerated this hydrocarbon, to which we tentatively assign structure (XXXVII) or (XXXVIII).

The steric requirement of the five-membered ring in the phenalene corresponding to 1,2-dihydrocyclopenta[*cd*]phenalenium perchlorate (XXII), prepared by dehydration of the alcohol (XLVIII), will tend to pull the 2a and 8a positions of the acenaphthene unit together. We suggest therefore that the six-membered ring non-adjacent to the five-membered ring will become benzenoid, and that the hydrocarbon possesses structure (XL).

The phenalene from the reduction of 1,4,7-trimethylphenalenium perchlorate (XVIII) [1] is 3,6,9-trimethylphenalene (XXXII). Its nuclear magnetic resonance spectrum shows the presence of a methylene group and unsplit methyl signals, thus clearly excluding the alternative structure. It is the first phenalene capable of existence in more than one prototropic form whose structure has been established with certainty.

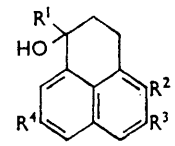
For the preparation of phenalenium salts the relative positions of the methylene group and the substituent(s) is unimportant. The same cation results irrespectively of the site from which the hydride ion is lost.

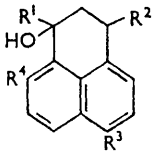
Preparation and Stability of Phenalenium Salts.—Hydride-abstraction by quinones in the presence of perchloric acid [10] was used to prepare the salts (XIV)—(XXII). Reaction is best carried out in acetic acid or acetonitrile, with stoicheiometric amounts of the hydrocarbon and the quinone in the presence of an excess of the acid. The efficiency of a number of quinones as hydride-acceptors was tested qualitatively, with phenalene as the substrate. Increased yields and greater purity of product attended the use of quinones with high redox potentials. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone ($E^\circ \sim 1$ v) is the most efficient hydride-acceptor examined. It is very soluble in the reaction solvents but has the disadvantage that its sparingly soluble quinol is not readily separated from the phenalenium salts. *o*-Chloranil (tetrachloro-1,2-benzoquinone) was the most useful quinone owing to its high redox potential (E° 0·87 v), its high solubility in acetic acid and acetonitrile, and the high solubility of its quinol in ether.

Phenalenium perchlorate (XIV), though possessing a high delocalisation energy,[3,9] is

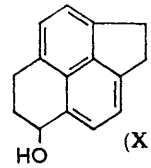
reactive towards even weakly nucleophilic reagents and is instantly hydrolysed by water.[1,9] Derivatives substituted by electron-releasing groups would be expected to be thermodynamically more stable and less reactive towards nucleophiles than the parent salt. The properties of the phenalenium salts examined justified broadly this expectation,

	R^1	R^2	R^3	R^4
(XLI)	H	Me	Me	H
(XLII)	H	MeO	H	H
(XLIII)	H	MeO	H	MeO
(XLIV)	o-Cl·C_6H_4	MeO	H	H

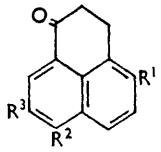




	R^1	R^2	R^3	R^4
(XLV)	H	Me	H	H
(XLVI)	Me	Me	H	H
(XLVII)	H	Me	Me	Me



(XLVIII)



	R^1	R^2	R^3
(XLIX)	H	H	H
(L)	H	o-Cl·C_6H_4	H
(LI)	MeO	H	MeO

with two exceptions. First, 1-methylphenalenium perchlorate (XV) could not be isolated from the reaction of 4(9)-methylphenalene with either *o*-chloranil and perchloric acid or triphenylmethyl perchlorate. The reaction solutions deposited a green solid insoluble in polar solvents. The isolation in high yield of 2,3,5,6-tetrachloroquinol and triphenylmethane, respectively, from the mother-liquors showed that hydride-abstraction had indeed occurred. It appears likely that the formation of the ion (XV) is immediately followed by the loss of a proton, giving the unknown 1-methylenephenalene which is at once polymerised by the acid. Secondly, 1,2-dihydrocyclopenta[*cd*]phenalenium perchlorate (XXII) was precipitated immediately as yellow needles during reaction of the hydrocarbon (XL) with triphenylmethyl perchlorate, but decomposed too rapidly to allow its isolation. The instability of the cation in the perchlorate (XXII) may be the result of distortion of the phenalenium unit occasioned by the geometrical requirements of the five-membered ring.

1,2- (XVI) and more so 1,3-dimethylphenalenium perchlorate (XVII) were more stable than the parent salt. Both are stable crystalline solids in a dry inert atmosphere, but alter rapidly in solution to green insoluble solids resembling that from 1-methylphenalenium perchlorate. 1,4,7-Trimethylphenalenium perchlorate (XVIII), much more stable than the salts (XIV), (XVI), or (XVII), can be recrystallised from hot acetonitrile or acetic acid without decomposition. Iodide ion does not attack the 1,4,7-trimethylphenalenium cation at a noticeable rate, and 1,4,7-trimethylphenalenium iodide (XVIII; I for ClO_4), the only known phenalenium salt containing an anion other than the perchlorate ion, was readily obtained as a stable salt by anion exchange with sodium iodide.

The preparation of methoxy-substituted phenalenium perchlorates presented difficulties initially. It has been shown [13] that dehydration of the alcohol (XLIV) gives the 2,3-dihydrophenalen-1-one (L) by isomerisation and demethylation of the primary dehydration product (XXXV). It was therefore not unexpected that in the dehydration of 2,3-dihydro-4-methoxyphenalen-1-ol (XLII) we obtained 2,3-dihydrophenalenone (XLIX) in

[13] Badger, Carruthers, and Cook, *J.*, 1949, 1768.

place of the desired 9-methoxyphenalene (XXXIV). On the assumption that 9-methoxyphenalene (XXXIV) had first been formed the dehydration and hydride-abstraction steps were combined. Perchloric acid, used with the quinones or, in the dehydrogenation by triphenylmethyl perchlorate,[14] supplied by the equilibrium $Ph_3C^+ClO_4^- + AcOH \rightleftharpoons Ph_3C{\cdot}OAc + H^+ + ClO_4^-$, served as the dehydrating agent. 1-Methoxyphenalenium perchlorate (XIX) was obtained by this procedure in 88% yield. Hydride-abstraction from the primary dehydration product (XXXIV) is thus much faster than the prototropic rearrangement of the double-bond system of (XXXIV). 1,5-Dimethoxyphenalenium perchlorate (XX) was similarly prepared from (XLIII) in 79% yield. Both the methoxy-compounds (XIX) and (XX) are crystallisable salts so stable that they can be isolated in the presence of the equivalent amount of water liberated during preparation by dehydration of the alcohols (XLII) and (XLIII). 1,4,7-Trimethylphenalenium perchlorate (XVIII) and 1,3-dimethylphenalenium perchlorate (XVII) are also stable under similar conditions, and were obtained in 89 and 84% yield, respectively, by the action of *o*-chloranil and perchloric acid on the alcohols (XLVII) and (XLVI). Phenalenium perchlorate, 1-methylphenalenium perchlorate, and 1,2-dimethylphenalenium perchlorate could not be thus prepared, but were extensively hydrolysed.

The effect of annelation on the phenalenium structure was examined. Benzo[*a*]-phenalenium perchlorate (XXI) was readily obtained from benzanthrene as purple needles which decompose rapidly in air. It is much less stable than phenalenium perchlorate.

In conclusion, the order of stability of the perchlorates to heat, solvolysis, and air is 1-methoxyphenalenium $\sim$ 1,4,7-trimethylphenalenium $\sim$ 1,5-dimethoxyphenalenium $\gg$ 1,3-dimethylphenalenium $>$ 1,2-dimethylphenalenium $>$ phenalenium $>$ benzo[*a*]-phenalenium $>$ 1,2-dihydrocyclopenta[*cd*]phenalenium $>$ 1-methylphenalenium.

Except in the case of 1,4,7-trimethyl- (XVIII), 1-methoxy- (XIX), and 1,5-dimethoxy-phenalenium perchlorate (XX), reliable spectral measurements of the salts could not be made owing to their ready decomposition in solution.

Experimental

M. p.s were determined on a Kofler-type heating stage. Visible spectra were measured with a Unicam S.P. 600 spectrophotometer. Infrared spectra was recorded with a Grubb-Parsons type G.S.2A instrument.

Materials.—Acetic acid was of " AnalaR " grade. Acetonitrile was purified by boiling it for 1 hr. with phosphoric anhydride, then distilled through a Vigreux column (50 cm.), and redistilled likewise before use. Light petroleum was of boiling range 40—60°. Perchloric acid refers to 70—72% (w/w) perchloric acid of " AnalaR " grade.

General Procedure.—Analyses. Unless otherwise stated, determination of the percentage of ClO_4 was carried out as follows: a known weight of the perchlorate was shaken for 10 min. with an excess of 0·1M-sodium hydroxide, and the resulting solid was filtered off and washed with water. The combined filtrates were clarified by shaking them with a small amount of pure activated charcoal and were filtered through a sintered-glass funnel, with subsequent thorough washing with more water. The excess of sodium hydroxide in the filtrates was determined by titration against 0·1M-hydrochloric acid. The difference between the two titres corresponds to the perchlorate content of the salt.

Recovery of quinol, tetrachlorocatechol, or 2,3,5,6-tetrachloroquinol. After filtration and washing of the phenalenium salt with ether the combined filtrates were diluted with more ether before the addition of water. The ether phase, washed free from acetic acid with water, was extracted exhaustively with 10% sodium hydroxide solution. The alkaline extracts were washed once with water and acidified with concentrated hydrochloric acid. The precipitated quinol was filtered off, washed with water, dried, and recrystallised from acetic acid.

Recovery of triphenylmethane. After filtration and washing of the phenalenium salt with

[14] Bonthrone and Reid, *Chem. and Ind.*, 1960, 1192.

ether the combined filtrates were washed successively with water, sodium hydrogen carbonate solution, and water, and dried (K_2CO_3) before removal of the solvent. The residual oil in light petroleum was filtered through a column of alumina. The residue from the eluates, crystallised from light petroleum or ethanol, gave pure triphenylmethane.

Phenalenium Perchlorate (XIV) *by the Action of Quinones and Perchloric Acid on Phenalene.*—*Benzoquinone.* A solution of phenalene (830 mg., 5 mmoles) in acetic acid (5 ml.) was added to a solution of 1,4-benzoquinone (540 mg., 5 mmoles) and perchloric acid (1 ml.) in acetic acid (20 ml.), all at room temperature. The resulting greenish-yellow solution at once deposited phenalenium perchlorate (1080 mg., 81%) [1,9,10] as pale yellow needles which were filtered, washed with dry ether, and dried over phosphoric anhydride and potassium hydroxide. Work must be rapid owing to the sensitivity of the salt to the atmosphere. Phenalenium perchlorate does not melt but decomposes slowly on being heated. Quinol (493 mg., 91%), m. p. 172°, was recovered from the mother-liquors.

Chloranil. (*a*) Phenalene (830 mg., 5 mmoles) in acetic acid (20 ml.) was added to a solution of chloranil (1230 mg., 5 mmoles) and perchloric acid (1 ml.) in acetic acid (150 ml.) at 50°.[10] Phenalenium perchlorate (995 mg., 75%) crystallised at once, and after the addition of dry ether (200 ml.) was collected and washed with ether. 2,3,5,6-Tetrachloroquinol (1090 mg., 90%) was recovered from the mother-liquors. (*b*) When acetonitrile was used in place of acetic acid the yields of phenalenium perchlorate and 2,3,5,6-tetrachloroquinol were 587 mg. (44%) and 1040 mg. (84%), respectively.

Tetrachloro-1,2-benzoquinone. A solution of tetrachloro-1,2-benzoquinone (738 mg., 3 mmoles) and perchloric acid (1 ml.) in acetic acid (15 ml.) was added to one of phenalene (498 mg., 3 mmoles) in acetic acid (5 ml.), both solutions at room temperature. Phenalenium perchlorate (634 mg., 80%) crystallised as yellow needles. Dry ether (20 ml.) was added before filtration and washing with dry ether.

1,2-Naphthaquinone. Addition of a solution of 1,2-naphthaquinone (475 mg., 3 mmoles) and perchloric acid (1 ml.) in acetic acid (35 ml.) to one of phenalene (498 mg., 3 mmoles) in acetic acid (5 ml.) produced a blood-red colour which faded as phenalenium perchlorate (343 mg., 43%) crystallised. Dry ether (60 ml.) was added before filtration.

9,10-Phenanthraquinone. A solution of 9,10-phenanthraquinone (625 mg., 3 mmoles) and perchloric acid (1 ml.) in acetic acid (50 ml.), added to phenalene (498 mg., 3 mmoles) in acetic acid at room temperature, gave a greenish-brown solution. Dry ether (100 ml.) was added to complete the precipitation of phenalenium perchlorate (428 mg., 54%).

2,3-Dicyano-1,4-benzoquinone. Addition of a solution of 2,3-dicyano-1,4-benzoquinone (474 mg., 3 mmoles) and perchloric acid (1 ml.) in acetic acid (12 ml.) to one of phenalene (498 mg., 3 mmoles) in acetic acid (5 ml.) gave a green solution which, upon the addition of dry ether, deposited phenalenium perchlorate (687 mg., 88%) as yellow needles.

Attempted Synthesis of 1-Methylphenalenium Perchlorate (XV).—*β-1-Naphthylbutyric acid.* The method of Boekelheide and Larrabee [12] is inconvenient for the large-scale preparation of this acid and the following procedure was adopted. Phosphorus tribromide (35 ml.) was added to a solution of 1-1′-hydroxyethylnaphthalene [15] (172 g.) in ether (1000 ml.) at 5°. The solution was left at room temperature for 1 hr., washed with water until free from acid, dried (Na_2SO_4), and evaporated. Dry benzene (50 ml.) was added to the residual oil and immediately removed at reduced pressure. The crude bromide in dry benzene (1000 ml.) was added to an ice-cold solution of diethyl malonate (380 ml.) in dry ethanol (2 l.) in which sodium (46 g.) had previously been dissolved. The mixture was set aside at 0° for 48 hr., then boiled for 4 hr. Solvent was distilled off and the cold semi-solid residue was shaken with ether (1·5 l.) and water (1·5 l.). The aqueous phase was washed with a fresh portion of ether, and the combined ether extracts were washed with water, dried (Na_2SO_4), and evaporated. Fractional distillation of the residual oil gave the malonic ester as a pale brown oil, b. p. 182—186°/0·5 mm.

This ester was boiled for 3 hr. with potassium hydroxide (168 g.), methanol (50 ml.), and water (1000 ml.). The solution, when cooled, washed with ether, and acidified with concentrated hydrochloric acid, deposited the malonic acid as an oil which was extracted in ether (3 × 500 ml.). Solvent was evaporated after the extracts had been washed with water (3 × 300 ml.) and dried (Na_2SO_4), and the residual oil was decarboxylated at 180° (bath-temperature) for 30 min. Crystallisation of the solid residue from acetone–light petroleum

[15] Pickard and Kenyon, *J.*, 1914, 1126.

gave β-1-naphthylbutyric acid (177 g., 83%) as colourless plates, m. p. 109—110° (lit.,[12] 109—110°).

The acid was converted successively into 2,3-dihydro-3-methylphenalenone, 2,3-dihydro-3-methylphenalen-1-ol (XLV), and 4(9)-methylphenalene [(XXXVI) or (XXXI)] as already described.[12]

Dehydrogenation of 4(9)*-methylphenalene* [(XXXVI) *or* (XXXI)] *with chloranil–perchloric acid.* A solution of chloranil (246 mg., 1 mmole) and perchloric acid (1 ml.) in acetic acid (90 ml.) was added to a solution of 4(9)-methylphenalene (180 mg., 1 mmole) in acetic acid (10 ml.) at room temperature. The solution became yellow, then deep green, and deposited a green solid. Dry ether (50 ml.) was added before filtration. The solid (94 mg.) was insoluble in the common polar organic solvents. The filtrates yielded 2,3,5,6-tetrachloroquinol (162 mg., 65%), m. p. *ca.* 230° (sublimation).

Dehydrogenation of 4(9)*-methylphenalene* [(XXXVI) *or* (XXXI)] *with triphenylmethyl perchlorate.* The same green solid (174 mg.) separated from the dark solution obtained when triphenylmethyl perchlorate (343 mg., 1 mmole) in acetic acid (80 ml.) was added to a solution of 4(9)-methylphenalene (180 mg., 1 mmole) in acetic acid (10 ml.). Triphenylmethane (208 mg., 86%) was recovered from the mother-liquors.

Synthesis of 1,2*-Dimethylphenalenium Perchlorate* (XVI).—β-(2,3-Dimethyl-1-naphthyl)-propionic acid was prepared from 1-chloromethyl-2,3-dimethylnaphthalene [16] by the malonic ester synthesis as described by Buu-Hoï and Cagniant.[17]

2,3*-Dihydro-*4,5*-dimethylphenalen-*1*-one.* This ketone has been prepared by the ring-closure of β-(2,3-dimethyl-1-naphthyl)propionic acid chloride with aluminium chloride.[17] The following method is superior. The acid (73 g.) was added portionwise to anhydrous liquid hydrogen fluoride (600 ml.) and the deep red solution was set aside at 0° for 5 hr. Addition to water gave a yellow oil which rapidly crystallised and was extracted into ether (2500 ml.). The ether extracts were washed successively with water, 15% potassium hydroxide solution, and water before being dried (Na_2SO_4). Removal of the solvent and crystallisation of the residual solid from ether gave 2,3-dihydro-4,5-dimethylphenalen-1-one (62·8 g., 94%) as yellow needles, m. p. 113—114° (lit.,[17] 114°).

2,3*-Dihydro-*4,5*-dimethylphenalen-*1*-ol.* The foregoing ketone (5·83 g.) in benzene (80 ml.) was added dropwise to a stirred solution of lithium aluminium hydride (430 mg.) in ether (200 ml.). The mixture was boiled for 1 hr. before the cautious addition of water to the cooled, stirred solution. It was then poured into an excess of ice-cold dilute hydrochloric acid. Benzene used to wash the acid phase was combined with the organic layer, and the combined extracts were washed free from acid and dried (K_2CO_3) before removal of the solvent. Crystallisation of the pale yellow product from acetone (charcoal) gave 2,3*-dihydro-*4,5*-dimethylphenalen-*1*-ol* (XLI) (5·20 g., 90%) as colourless needles, m. p. 133·5—135·5° (Found: C, 84·7; H, 7·8. $C_{15}H_{16}O$ requires C, 84·9; H, 7·6%).

2,3(?)*-Dimethylphenalene.* Ethanol (5 ml.), saturated with anhydrous hydrogen chloride, was added to a solution of 2,3-dihydro-4,5-dimethylphenalen-1-ol (329 mg.) in ethanol (5 ml.). The resulting solution was boiled for 15 min., then poured into water. The mixture was extracted with ether, and the extracts were washed successively with water (twice), saturated sodium hydrogen carbonate solution (twice), and water, dried (K_2CO_3), and evaporated. The residual oil in light petroleum was purified on a column of alumina (12 × 2·7 cm.) with light petroleum as eluant. The eluates yielded 2,3(?)-dimethylphenalene (XXXIII) as a colourless oil (218 mg., 73%) which crystallised overnight in an evacuated desiccator to plates, m. p. *ca.* 65°, rapidly altered by the atmosphere to a green oil. The hydrocarbon was characterised by its *trinitrobenzene complex*, orange-red needles (from ethanol), m. p. 122—124° (Found: N, 10·1. $C_{21}H_{17}N_3O_6$ requires N, 10·3%).

1,2*-Dimethylphenalenium perchlorate.* A solution of tetrachloro-1,2-benzoquinone (608 g.) and perchloric acid (0·6 ml.) in acetic acid (5 ml.) was added to one of 2,3(?)-dimethylphenalene (474 mg.) in acetic acid (3 ml.) at room temperature. The solution, whose colour had changed from red to dark greenish-brown, deposited 1,2*-dimethylphenalenium perchlorate* (XVI) (528 mg., 74%) as orange-red needles which were at once filtered off, washed with acetic acid followed by dry ether, and dried *in vacuo* over phosphoric anhydride and potassium hydroxide. The

[16] Hewett, *J.*, 1940, 293.
[17] Buu-Hoï and Cagniant, *Rev. Sci.*, 1942, **80**, 271.

salt is stable *in vacuo* for several weeks but decomposes rapidly to insoluble green material on attempted recrystallisation from hot solvents (Found: ClO_4, 34·2, 34·4. $C_{15}H_{13}ClO_4$ requires ClO_4, 34·0%). It does not melt but decomposes gradually on being heated from room temperature.

Synthesis of 1,3-*Dimethylphenalenium Perchlorate* (XVII).—2,3-*Dihydro*-1,3-*dimethylphenalen*-1-*ol*. A solution of 2,3-dihydro-3-methylphenalen-1-one [12] (9·81 g.) in ether (80 ml.) was added to the Grignard reagent from methyl iodide (6·2 ml.) and magnesium (2·49 g.) in ether (300 ml.). The mixture was boiled for 1 hr., then hydrolysed with an excess of ice-cold dilute hydrochloric acid. The ether phase, worked up in the usual manner, gave a pale yellow residue which, after two crystallisations from light petroleum, afforded 2,3-*dihydro*-1,3-*dimethylphenalen*-1-*ol* (XLVI) (7·59 g., 72%) as dense colourless needles with a satin sheen, m. p. 100·5—101·5° (Found: C, 84·6; H, 7·6. $C_{15}H_{16}O$ requires C, 84·9; H, 7·6%).

The combined petroleum mother-liquors were evaporated, and the residue in ethanol (50 ml.) was boiled for 15 min. with ethanol (50 ml.) saturated with hydrogen chloride. The cooled mixture, worked up as described in the succeeding experiment, yielded 4,6(7,9)-dimethylphenalene (1·47 g., 15%) as colourless plates, m. p. 151—153°. The alcohol and hydrocarbon isolated thus correspond to an 87% conversion of the ketone.

4,6(7,9)-*Dimethylphenalene*. Ethanol (20 ml.) saturated with dry hydrogen chloride was added to a solution of 2,3-dihydro-1,3-dimethylphenalen-1-ol (2·12 g.) in ethanol (20 ml.). The mixture was boiled for 15 min., then poured into water (300 ml.). The mixture was extracted with ether (4 × 100 ml.), and the combined extracts were washed with water, dried (Na_2SO_4), and evaporated. The residue in light petroleum (50 ml.) was filtered through a column of alumina (18 × 2·7 cm.) with light petroleum as eluant. 4,6(7,9)-*Dimethylphenalene* [(XXXVII) or (XXXVIII)] (1·53 g., 79%) was obtained from light petroleum (b. p. 60—80°) or ethanol as colourless platelets, m. p. 151—153° [Found: C, 92·6; H, 7·3%; *M* (Rast), 164. $C_{15}H_{14}$ requires C, 92·7; H, 7·3%; *M*, 174].

1,3-*Dimethylphenalenium perchlorate*. (*a*) A solution of tetrachloro-1,2-benzoquinone (246 mg.) and perchloric acid (0·2 ml.) in acetonitrile (5 ml.) was added to a solution of 4,6(7,9)-dimethylphenalene (194 mg.) (from the dehydration of 2,3-dihydro-1,3-dimethylphenalen-1-ol) in acetonitrile (10 ml.). The solution became dark red and after 45 sec. dry ether (50 ml.) was added. 1,3-*Dimethylphenalenium perchlorate* (XVII) (259 mg., 89%) crystallised as orange-yellow needles which were at once filtered off, washed with ether, and dried *in vacuo* over phosphoric anhydride and potassium hydroxide (Found: ClO_4, 34·4, 34·3. $C_{15}H_{13}ClO_4$ requires ClO_4, 34·0%). The salt does not melt but gradually decomposes on being heated from room temperature. It is moderately stable in dry air but decomposes rapidly in solution to insoluble green material. The same salt (239 mg., 82%) (Found: ClO_4, 34·1, 33·8%) was obtained when tetrachloro-1,2-benzoquinone (246 mg.) and perchloric acid (0·2 ml.) in acetonitrile (5 ml.) were added to a solution of the hydrocarbon (194 mg.), prepared by the reduction of 1,3-dimethylphenalenium perchlorate with lithium aluminium hydride (next experiment), in acetonitrile (10 ml.).

(*b*) A solution of tetrachloro-1,2-benzoquinone (492 mg.) and perchloric acid (0·5 ml.) in acetonitrile (5 ml.) was added to one of 2,3-dihydro-1,3-dimethylphenalen-1-ol (423 mg.) in acetonitrile (10 ml.). Dry ether (50 ml.) was added at once to the resulting dark red solution which deposited orange-yellow needles (489 mg., 84%), identical (infrared spectrum) with the product of the preceding experiment (Found: ClO_4, 34·1, 34·4%).

Reduction of 1,3-*Dimethylphenalenium Perchlorate with Lithium Aluminium Hydride*.—The salt (1·27 g.) (prepared from 2,3-dihydro-1,3-dimethylphenalen-1-ol) was added portionwise in 15 min. to a stirred solution of lithium aluminium hydride (465 mg.) in ether (150 ml.). The mixture was boiled for a further 30 min. and cooled to 10° before the dropwise addition of water with stirring. An excess of hydrochloric acid was added and the ether phase was worked up in the usual manner. The residue was chromatographed on a column of alumina (20 × 2·7 cm.) with light petroleum as solvent and eluant. Solvent was evaporated and the residual colourless solid (764 mg.), m. p. 135—145°, was rechromatographed twice in an identical fashion. The product (500 mg., 60%) after successive recrystallisation from light petroleum and ethanol formed colourless plates, m. p. 151—153°, undepressed on admixture with 4,6(7,9)-dimethylphenalene prepared by the dehydration of 2,3-dihydro-1,3-dimethylphenalen-1-ol.

1,4,7-*Trimethylphenalenium Perchlorate* (XVIII).—*From* 2,3-*dihydro*-3,6,9-*trimethylphenalen*-1-*ol* (XLVII). (*a*) A solution of tetrachloro-1,2-benzoquinone (984 mg., 4 mmoles) and

perchloric acid (1 ml.) in acetic acid (20 ml.) at 90° was added to one of 2,3-dihydro-3,6,9-trimethylphenalen-1-ol (904 mg., 4 mmoles) in acetic acid (20 ml.), also at 90°. 1,4,7-Trimethylphenalenium perchlorate (XVIII) (1·093 g., 89%) crystallised at once from the hot solution as copper-coloured needles, unchanged in form after recrystallisation from acetonitrile. The salt decomposes gradually >240°, is stable to the atmosphere and to ethanol containing perchloric acid, and has $\lambda_{max.}$ 412 mμ (log ε 4·49). (*b*) A boiling solution of triphenylmethyl perchlorate (3·43 g., 10 mmoles) in acetonitrile (25 ml.) was added to a hot solution of 2,3-dihydro-3,6,9-trimethylphenalen-1-ol (2·26 g., 10 mmoles) in acetic acid (25 ml.). 1,4,7-Trimethylphenalenium perchlorate (1·925 g., 63%) crystallised as copper-coloured needles, identical spectrally with the product of the preceding experiment.

From 3,6,9-*trimethylphenalene* (XXXII). Boiling solutions of triphenylmethyl perchlorate (3·43 g., 10 mmoles) in acetonitrile (25 ml.) and 3,6,9-trimethylphenalene (2·08 g., 10 mmoles), m. p. 59—60°, in acetic acid (25 ml.) were mixed. 1,4,7-Trimethylphenalenium perchlorate (2·583 g., 84%) crystallised extensively from the boiling solution. The product, filtered and washed with acetonitrile and recrystallised from acetonitrile, formed deep orange needles identical spectrally with the products of the preceding two experiments.

1,4,7-*Trimethylphenalenium Iodide*.—A boiling solution of anhydrous sodium iodide (300 mg., 2 mmoles) in acetonitrile (50 ml.) was added to a boiling solution of 1,4,7-trimethylphenalenium perchlorate (307 mg., 1 mmole) in acetonitrile (50 ml.). 1,4,7-*Trimethylphenalenium iodide* (XVIII; I for ClO_4) (206 mg., 62%) crystallised at once from the boiling solution as grey-black needles, unchanged in form or m. p. after recrystallisation from a large volume of acetonitrile (Found: C, 58·3; H, 4·3; I, 37·0. $C_{16}H_{15}I$ requires C, 57·5; H, 4·5; I, 38·0%). It melts with decomposition on a block preheated to ⩽185°, and decomposes gradually on being heated from room temperature.

Reduction of 1,4,7-*Trimethylphenalenium Perchlorate with Lithium Aluminium Hydride*.—The salt (6·14 g., 20 mmoles) was added rapidly to a stirred solution of lithium aluminium hydride (760 mg., 20 mmoles) in dry ether (250 ml.). Stirring was continued for 90 min. while the salt gradually dissolved, giving a pale yellow solution. The mixture was poured into water, ether (1000 ml.) was added, and the ether phase was washed twice with water and dried (K_2CO_3) before removal of the solvent. The residual orange oil in light petroleum was filtered through alumina (10 × 2·7 cm.). The eluates yielded a colourless oil which crystallised from methanol–acetone (8 : 1) as needles, m. p. 57·5—59°, raised to 59—60° after one recrystallisation from the same solvent. A further 1·464 g. of satisfactory material from the mother-liquors raised the yield of 3,6,9-*trimethylphenalene* (XXXII) to 3·862 g. (93%) (Found: C, 92·1; H, 7·9. $C_{16}H_{16}$ requires C, 92·3; H, 7·7%).

Benzo[a]*phenalenium Perchlorate* (XXI).—A solution of triphenylmethyl perchlorate (756 mg.) in acetic acid (85 ml.) at 60° was added to a solution of benzanthrene [18] (506 mg.) in acetic acid (5 ml.) at room temperature. *Benzo*[a]*phenalenium perchlorate* (XXI) (419 mg., 57%) began to crystallise at once as purple needles from the purple solution which was cooled immediately to room temperature. The salt, filtered rapidly and washed with acetic acid followed by ether, was dried for 1 hr. *in vacuo* over phosphoric anhydride and potassium hydroxide. Benzo[*a*]phenalenium perchlorate decomposes to a black tar on exposure to the atmosphere and was analysed at once by the method applied to phenalenium perchlorate [1] (Found: ClO_4, 31·5, 31·4. $C_{17}H_{11}ClO_4$ requires ClO_4, 31·6%).

Synthesis of 1,2-*Dihydrocyclopenta*[cd]*phenalenium Perchlorate* (XXII).—5-*Hydroxymethylacenaphthene*. This alcohol has been prepared by the catalytic reduction of 5-formylacenaphthene.[11] The following procedure is convenient for its large-scale preparation. 5-Formylacenaphthene (37·9 g.) in benzene (200 ml.) was added to a stirred solution of lithium aluminium hydride (2·47 g.) in ether (800 ml.) at such a rate as to maintain gentle boiling. The solution was boiled for 30 min. before being cooled, hydrolysed, and worked up in the usual manner. 5-Hydroxymethylacenaphthene (33·9 g., 90%) was obtained as colourless needles, having m. p. 153—154° (lit.,[11] 153·8—154·8°) after recrystallisation from benzene.

β-*Acenaphthen-5-ylpropionic acid*. This acid has been prepared (*a*) by reduction of β-acenaphthen-5-ylacrylic acid with sodium amalgam in sodium hydroxide solution,[11] and (*b*) hydrogenation of methyl β-acenaphthen-5-ylacrylate with palladium oxide in methanol, and subsequent hydrolysis.[19] The following convenient procedure was adopted for the

[18] Brown and White, *J.*, 1957, 3755.
[19] Dannenberg and Dannenberg-von Dresler, *Annalen*, 1954, **585**, 1.

preparation of large quantities of the acid. Phosphorus tribromide (4 ml.) was added to a suspension of 5-hydroxymethylacenaphthene (21·1 g.) in dry benzene (200 ml.). The solution was swirled occasionally and the alcohol dissolved rapidly. Water was added after 30 min., and the benzene layer was washed free from acid with water (twice), saturated sodium hydrogen carbonate solution, and water, and dried (Na_2SO_4). Solvent was removed at reduced pressure and the residue was crystallised from acetone–light petroleum (1 : 1). 5-Bromomethylacenaphthene formed colourless prisms (20 g., 72%), m. p. 108—109°, which slowly evolved hydrogen bromide (giving thus incorrect analyses) and became green on storage.

The freshly prepared bromide (21·3 g.) in dry benzene (50 ml.) was added to a solution of diethyl malonate (40 ml.) in ethanol (400 ml.) in which sodium (7 g.) had been dissolved. Both solutions were at 0°. The mixture was kept at 0° for 72 hr., then boiled for 4 hr. The solvent was distilled off and the residue was boiled for 4 hr. with potassium hydroxide (80 g.) and water (400 ml.). The cooled solution was washed with ether (twice), filtered, warmed to 80°, and acidified with concentrated hydrochloric acid. α-Carboxy-β-acenaphthen-5-ylpropionic acid (22·45 g., 96%) was obtained as colourless crystals, m. p. 181—183·5° (decomp.).

The foregoing acid (42 g.) was heated at 180—190° for 30 min., or until decarboxylation was complete. Crystallisation of the residue from benzene gave β-acenaphthen-5-ylpropionic acid (XXVI) (31·9 g., 90%) as colourless needles, m. p. 188—190° (lit., 192°,[11] 188—189° [19]).

Cyclisation of β-acenaphthen-5-ylpropionic acid. The acid (26·65 g.), added to liquid hydrogen fluoride (250 ml.), gave a red solution which was kept at room temperature for 25 min., then poured on crushed ice (400 g.). Organic material was extracted into ether (3 × 250 ml.), and the combined extracts were washed successively with water (five times), 10% aqueous sodium hydroxide (twice), and water (twice), and dried (K_2CO_3) and evaporated at reduced pressure. The residual oil crystallised to a pale yellow solid, m. p. 78—87°, which could not be purified by fractional crystallisation or sublimation. It was absorbed from a solution in benzene (85 ml.) on alumina (27 × 2·7 cm.). Initial development with benzene–light petroleum (1 : 1) brought through a pale yellow band whose eluates gave 2,5,6,7-tetrahydro-5-oxo-1*H*-cyclopenta[*cd*]phenalene (XXVII) (14·5 g., 60%) as pale yellow prisms after one recrystallisation from benzene–light petroleum (1 : 1), m. p. 97—98°, ν_{CO} (Nujol) 1672 cm.$^{-1}$ [lit.,[19] m. p. 98—99°, ν_{CO} (KBr disc) 1675 cm.$^{-1}$]. A very pale orange band, subsequently eluted with benzene, yielded 5,7,8,9-tetrahydro-7-oxo-4*H*-cyclopenta[*e*]acenaphthylene (XXIX) (830 mg., 3·4%) as colourless leaflets, m. p. 189—190°, ν_{CO} (in Nujol) 1690 cm.$^{-1}$ [lit.,[19] m. p. 187—188°; ν_{CO} (in KBr) 1689 cm.$^{-1}$]. Continued elution with ether brought through golden eluates from a deep yellow band which afforded 2,5-dihydro-5-oxo-1*H*-cyclopenta[*cd*]-phenalene (XXVIII) (280 mg., 1·1%) as golden-yellow needles, m. p. 160—163° with blackening >150°, ν_{CO} (Nujol) 1639, 1623 cm.$^{-1}$ [lit.,[19] m. p. 174° with blackening >158°; ν_{CO} (in KBr) 1634, 1618 cm.$^{-1}$].

*Reduction of 2,5,6,7-tetrahydro-5-oxo-*1H*-cyclopenta*[cd]*phenalene with lithium aluminium hydride.* The ketone (13·23 g.) in benzene (50 ml.) was added to a stirred solution of lithium aluminium hydride (960 mg.) in ether (200 ml.) at a rate sufficient to maintain gentle boiling. The mixture was boiled for 45 min., then hydrolysed with ice-cold dilute hydrochloric acid and worked up in the usual manner. Solvent was removed and the residue, crystallised from ethanol–light petroleum (charcoal), yielded colourless crystals (11·2 g.), m. p. 150—159°. Subsequent slow fractional crystallisation from ethanol–light petroleum gave successively 2,5,6,7-*tetrahydro-*1H*-cyclopenta*[cd]*phenalen-5-ol* (XLVIII) (7·1 g., 54%), m. p. 150—152° after recrystallisation from benzene–chloroform (Found: C, 85·5; H, 6·7. $C_{15}H_{14}O$ requires C, 85·7; H, 6·7%), and 1,2-dihydro-4*H*-cyclopenta[*cd*]phenalene (3·83 g., 32%), m. p. 92—93°, identical with the product of the succeeding experiment.

1,2-*Dihydro-*4H*-cyclopenta*[cd]*phenalene.* 2,5,6,7-Tetrahydro-1*H*-cyclopenta[*cd*]phenalen-5-ol (2 g.) and ethanol (20 ml.) saturated with dry hydrogen chloride were boiled for 20 min. The deep blue solution was poured into water, and the resulting mixture was extracted with light petroleum (3 × 150 ml.). The extracts were washed free from acid, dried (K_2CO_3), and evaporated. The residual oil was purified on alumina (25 × 2·7 cm.) with light petroleum as solvent and eluant. 1,2-*Dihydro-*4H*-cyclopenta*[cd]*phenalene* (XL) (1·58 g., 87%) was obtained as colourless needles, m. p. 92—93° (Found: C, 93·7; H, 6·5. $C_{15}H_{12}$ requires C, 93·7; H, 6·3%). It gives a negative Vanscheidt test.

Dehydrogenation of 1,2-*dihydro-*4H*-cyclopent*[cd]*phenalene.* (*a*) A solution of tetrachloro-1,2-benzoquinone (598 mg.) and perchloric acid (0·2 ml.) in acetonitrile (8 ml.) was added to a

solution of 1,2-dihydro-4*H*-cyclopenta[*cd*]phenalene (466 mg.) in acetonitrile (10 ml.). A dark green solid (287 mg.), insoluble in the common polar organic solvents, was precipitated at once from the dark green solution. Tetrachlorocatechol (462 mg., 77%), m. p. 189—192°, was isolated from the mother-liquors. (*b*) Triphenylmethyl perchlorate (2·44 g.), 1,2-dihydro-4*H*-cyclopenta[*cd*]phenalene (1·17 g.), and acetonitrile (15 ml.) were warmed until a homogeneous solution was obtained. After 10 min. the colour of the solution had changed from orange to pale green. Addition of ether (10 ml.) to the cooled solution precipitated 1,2-dihydrocyclopenta[*cd*]phenalenium perchlorate as yellow needles which decomposed rapidly to a green solid on attempted isolation. Triphenylmethane (1·269 g., 73%) was isolated from the mother-liquors.

Synthesis of 1-*Methoxyphenalenium Perchlorate* (XIX).—2-Methoxynaphthalene (116 g.), formylated with phosphorus oxychloride (153 g., 89 ml.) and *N*-formyl-*N*-methylaniline (132 g., 85 ml.) as in the preparation of 1-formyl-2-ethoxynaphthalene,[20] gave 1-formyl-2-methoxynaphthalene (93 g., 68%) as pale yellow needles, m. p. 82° (lit.,[21] 83·5°). The aldehyde (24·1 g.) in dry ether (500 ml.) was reduced with lithium aluminium hydride (1·81 g.) in dry ether (250 ml.) in the manner described for the reduction of 1-formyl-2,6-dimethoxynaphthalene. 1-*Hydroxymethyl*-2-*methoxynaphthalene* (18·7 g., 77%) crystallised from ether as colourless plates, m. p. 100—101° (Found: C, 76·6; H, 6·5. $C_{12}H_{12}O_2$ requires C, 76·6; H, 6·4%).

The foregoing alcohol (18·8 g.) in dry ether (280 ml.) was treated at 0° with phosphorus tribromide (3·4 ml.). After 30 min. water was added. The ether phase was washed successively with water (twice), saturated sodium hydrogen carbonate solution, and water, dried (Na_2SO_4), and evaporated. Crystallisation of the residual solid from a small volume of ether gave 1-*bromomethyl*-2-*methoxynaphthalene* (17·5 g., 70%) as prisms, m. p. 126—129° (Found: Br, 31·4. $C_{12}H_{11}BrO$ requires Br, 31·8%).

A solution of 1-bromomethyl-2-methoxynaphthalene (15·85 g.) in dry benzene (180 ml.) was added to a cold solution of diethyl malonate (100 ml.) in dry ethanol (500 ml.) in which sodium (4·39 g.) had been dissolved. The mixture was kept at 0° for 72 hr., then boiled for 4 hr., and the solvent was removed by distillation. The residue was boiled for 3 hr. with 40% sodium hydroxide solution (300 ml.) before being worked up as described for the preparation of α-carboxy-β-(2,6-dimethoxy-1-naphthyl)propionic acid. α-Carboxy-β-(2-methoxy-1-naphthyl)-propionic acid (16·98 g., 99%) was isolated as plates, m. p. 154—156° (lit.,[13] 174—175°). This acid was converted into β-(2-methoxy-1-naphthyl)propionic acid (XXIV) and thence into 2,3-dihydro-4-methoxyphenalen-1-one as described by Badger, Carruthers, and Cook.[13]

2,3-*Dihydro*-4-*methoxyphenalen*-1-*ol*. A solution of 2,3-dihydro-4-methoxyphenalen-1-one (10·74 g.) in ether (200 ml.) was added to a stirred solution of lithium aluminium hydride (870 mg.) in ether (200 ml.). The mixture was boiled for 2 hr., then hydrolysed with water, and the ether phase was worked up in the usual manner. 2,3-*Dihydro*-4-*methoxyphenalen*-1-*ol* (XLII) (9·1 g., 85%) recrystallised from benzene and benzene–light petroleum (charcoal–alumina) as colourless needles, m. p. 104—105° (Found: C, 78·7; H, 6·4. $C_{14}H_{14}O_2$ requires C, 78·5; H, 5·2%).

1-*Methoxyphenalenium perchlorate*. (*a*) A solution of tetrachloro-1,2-benzoquinone (492 mg., 2 mmoles) and perchloric acid (0·35 ml.) in acetic acid (20 ml.) was added to a solution of 2,3-dihydro-4-methoxyphenalen-1-ol (428 mg., 2 mmoles) in acetic acid (20 ml.). 1-*Methoxyphenalenium perchlorate* (XIX) (516 mg., 88%) separated from the deep red solution as orange-red needles, having m. p. 177·5—180·5° after recrystallisation from acetic acid (Found: C, 56·7; H, 3·4; Cl, 11·3. $C_{14}H_{11}ClO_5$ requires C, 57·1; H, 3·8; Cl, 12·0%), $\lambda_{max.}$ 469, 453, and 410 mμ (log ε 3·82, 3·85, and 4·21). The salt dissolves readily in polar solvents, and is stable to the atmosphere and in hot solvents. (*b*) Triphenylmethyl perchlorate (8·14 g.), 2,3-dihydro-4-methoxyphenalen-1-ol (5·04 g.), and acetic acid (120 ml.) were boiled for 10 min. 1-Methoxyphenalenium perchlorate (5·62 g., 82%) crystallised from the cooled deep red solution as orange-red needles, identical with the product of the preceding experiment.

Dehydration of 2,3-*Dihydro*-4-*methoxyphenalen*-1-*ol*.—The alcohol (290 mg.) and anhydrous ethanol (30 ml.) saturated with dry hydrogen chloride were boiled for 15 min. The solution was poured into water, and the resulting emulsion was extracted with ether (3 × 100 ml.). The ether extract was washed with water (five times), dried (Na_2SO_4), and evaporated, and the residual oil in benzene–light petroleum (1 : 1) was adsorbed on alumina (22 × 2·7 cm.). Elution

[20] *Org. Synth.*, **20**, 11.
[21] Gattermann, *Annalen*, 1907, **357**, 366.

with benzene followed by benzene–ether (20 : 1) gave pale yellow eluates from which the solvent was removed at reduced pressure. Successive sublimation of the residue at 0·5 mm. and crystallisation from benzene–light petroleum gave 2,3-dihydrophenalen-1-one (XLIX) (203 mg., 82%) as pale yellow prisms, identical (m. p. and infrared spectrum) with an authentic specimen.[22] The 2,4-dinitrophenylhydrazone was identical (m. p. and infrared spectrum) with an authentic specimen.

Synthesis of 1,5-*Dimethoxyphenalenium Perchlorate* (XX).—β-(2,6-*Dimethoxy*-1-*naphthyl*)-*propionic acid*. A solution of 1-formyl-2,6-dimethoxynaphthalene [23] (28·5 g.) in ether (200 ml.) was added slowly to a stirred solution of lithium aluminium hydride (1·78 g.) in ether (200 ml.). The mixture was boiled for 1 hr. Water was added cautiously with vigorous stirring before the mixture was poured on ice and an excess of hydrochloric acid. The ether phase, worked up in the usual manner, afforded 1-*hydroxymethyl*-2,6-*dimethoxynaphthalene* which recrystallised from ethanol as leaflets (24·2 g., 84%), m. p. 124—125° (Found: C, 71·8; H, 6·4. $C_{13}H_{14}O_3$ requires C, 71·6; H, 6·5%).

Phosphorus tribromide (3 ml.) was added to a solution of the foregoing alcohol (11·1 g.) in ether (200 ml.). The mixture was thereafter worked up as in the preparation of 1-bromomethyl-2-methoxynaphthalene. 1-*Bromomethyl*-2,6-*dimethoxynaphthalene* (12·5 g., 83%) crystallised from ether as prisms, m. p. 106—107° (decomp.) (block preheated to 105°) (Found: Br, 28·0. $C_{13}H_{13}O_2$ required Br, 28·4%).

A cold solution of 1-bromomethyl-2,6-dimethoxynaphthalene (12·5 g.) in dry benzene (30 ml.) was added to an ice-cold solution of diethyl malonate (20 ml.) in dry ethanol (400 ml.) in which sodium (3·32 g.) had been dissolved. The mixture was kept at 0° for 72 hr., then boiled for 4 hr. Solvent was distilled off and the residual oil was boiled for 4 hr. with potassium hydroxide (50 g.) and water (200 ml.). The cooled solution was washed twice with ether, filtered, heated to 80°, and treated with an excess of concentrated hydrochloric acid. Filtration and recrystallisation from aqueous acetone gave α-*carboxy*-β-(2,6-*dimethoxy*-1-*naphthyl*)*propionic acid* (11·1 g., 86%) as leaflets, m. p. 169—171° (Found: C, 63·9; H, 5·2. $C_{16}H_{16}O_6$ requires C, 63·2; H, 5·3%). This acid (17 g.) was heated at 170° (internal temperature) for 35 min. or until decarboxylation was complete. Crystallisation of the resulting solid from acetone afforded β-(2,6-*dimethoxy*-1-*naphthyl*)*propionic acid* (XXIII) (12 g., 84%) as leaflets, m. p. 152—154° (Found: C, 69·9; H, 6·5. $C_{15}H_{16}O_4$ requires C, 69·2; H, 6·2%).

2,3-*Dihydro*-4,8-*dimethoxyphenalenone*.—β-(2,6-Dimethoxy-1-naphthyl)propionic acid (4·9 g.) was added to liquid hydrogen fluoride (200 ml.). After 30 min. at room temperature the dark red solution was hydrolysed. Organic material was extracted into ether, and the ether extracts were washed successively with water (four times), 10% potassium hydroxide solution, and water before being dried (K_2CO_3). Solvent was removed, and the residue crystallised from benzene–light petroleum ether (1 : 1) as yellow needles (4·7 g.), m. p. 90—97°, which showed infrared carbonyl absorption (in Nujol) at 1675 (ketone) and 1730 cm.$^{-1}$ (δ-lactone). The combined products (8·77 g.) from two such runs were heated at 100° with 10% potassium hydroxide solution (100 ml.). The orange-red solution was decanted from undissolved solid. This process was repeated thrice, or until the alkaline extracts were almost colourless. Acidification of the extracts precipitated a small amount of a solid which was taken up in ether. The ether extract, worked up in the usual way, gave a small quantity of a gum which failed to crystallise and was discarded. The washed alkali-insouble solid was dissolved in ether, and solvent was removed from the dried (K_2CO_3) solution. The residual solid in benzene–light petroleum (1 : 1) was adsorbed on alumina (20 × 2·7 cm.). Elution with the same solvent mixture gave yellow eluates. Evaporation and recrystallisation of the residue from benzene–light petroleum (2 : 1) gave 2,3-dihydro-4,8-dimethoxyphenalen-1-one (LI) (8·04 g.) as yellow prisms, m. p. 100—101° (Found: C, 74·3; H, 5·8. $C_{13}H_{14}O_3$ requires C, 74·4; H, 5·8%).

2,3-*Dihydro*-4,8-*dimethoxyphenalen*-1-*ol*. A solution of 2,3-dihydro-4,8-dimethoxyphenalenone (6·1 g.) in benzene (100 ml.) was added to a stirred solution of lithium aluminium hydride (472 mg.) in ether (200 ml.). After being boiled for 2 hr. the mixture was worked up in the manner described for the preparation of 2,3-dihydro-4,5-dimethylphenalen-1-ol. 2,3-*Dihydro*-4,8-*dimethoxyphenalen*-1-*ol* (XLIII) (5·29 g., 88%) crystallised from light petroleum–acetone (4 : 1) (charcoal) as colourless fluffy needles, m. p. 140·5—142·5° (Found: C, 73·9; H, 6·5. $C_{15}H_{16}O_3$ requires C, 73·8; H, 6·7%).

[22] Fieser and Gates, *J. Amer. Chem. Soc.*, 1940, **62**, 2335.
[23] Buu-Hoï and Lavit, *J.*, 1955, 2776.

1,5-*Dimethoxyphenalenium perchlorate*. (*a*) A solution of tetrachloro-1,2-benzoquinone (246 g., 1 mmole) and perchloric acid (0·2 ml.) in acetic acid (10 ml.) was added to a solution of 2,3-dihydro-4,8-dimethoxyphenalen-1-ol (244 mg., 1 mmole) in acetic acid (10 ml.), both solutions being at room temperature. The solution became deep red at once. Addition of dry ether (30 ml.) caused 1,5-dimethoxyphenalenium perchlorate (XX) (259 mg., 79%) to crystallise as reddish-brown needles which decomposed gradually $>187°$. Recrystallisation was from a small volume of acetic acid. The salt resisted repeated attempts to obtain a satisfactory analysis (Found: C, 54·6; H, 4·2; Cl, 10·1. Calc. for $C_{15}H_{13}ClO_6$: C, 55·5; H, 4·0; Cl, 10·9%); it had $\lambda_{max.}$ 416 mμ (log ε 4·27).

(*b*) Triphenylmethyl perchlorate (412 mg.), 2,3-dihydro-4,8-dimethoxyphenalen-1-ol (291 mg.), and acetic acid (30 ml.) were boiled for 1 min. Reddish-bronze needles (294 mg., 75%) crystallised, identical with the product of the preceding experiment.

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