557. *Hydride Ions in Organic Reactions. Part I. Dehydrogenation by Triphenylmethyl Perchlorate.*

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The use of triphenylmethyl perchlorate as a dehydrogenating agent has been investigated. Reaction is considered to proceed by successive elimination of a hydride ion and a proton, the key step being removal of the hydride ion. Necessary structural features in the substrate are discussed.

Application of the reagent in a new synthesis of perinaphthenylium salts is described.

Considerable recent evidence shows that the key step in various organic oxidation–reductions involves transfer of hydrogen as hydride ion. These reactions include a number of dehydrogenations in which loss of two hydrogen atoms occurs, usually in two steps. The common, distinguishing feature of the general dehydrogenation is step (1) in which an electrophilic dehydrogenating agent (E^+) removes a hydride ion from the substrate (R_3CH). Subsequent loss of a proton from an acidic site in the resulting carbonium ion (R_3C^+) normally completes the dehydrogenation. Reaction may, however, not proceed beyond the initial step if the intermediate cation (R_3C^+) is very stable; this may indeed be capable of isolation as its salt (see below).

$$(1)\quad R_3CH + E^+ \rightleftharpoons R_3C^+ + EH$$

$$(2)\quad R_3C^+ \longrightarrow \text{Final product} + H^+$$

Reactions which proceed according to this mechanism include the following:

(*a*) Dehydrogenation of dihydro-aromatic compounds by quinones. This has been the subject of detailed studies[1] by Braude and Linstead and their collaborators and finds use in preparative organic chemistry.

(*b*) Formation[2] of styrenes as intermediates in the Friedel–Crafts reactions of ethyl- and higher alkyl-benzenes with excess of acid chloride and aluminium chloride. Good evidence has been presented[3] that the dehydrogenating agent is the acylium cation present in excess. Under similar conditions certain derivatives of indane and tetralin are transformed into indenes and 1,2-dihydronaphthalenes, respectively.[4]

(*c*) Oxidation of alcohols to aldehydes or ketones, when dissolved in acidic systems capable of generating carbonium ions from the same or a different alcohol.[5] Thus acetone is formed from isopropyl alcohol in 50% sulphuric acid containing triphenylmethanol. Isotopic studies using labelled isopropyl alcohol proved that a hydride ion is transferred from the secondary alcohol to the triphenylmethyl cation formed by the action of sulphuric acid on triphenylmethanol. Related reactions which undoubtedly proceed by a similar mechanism include the oxidation of alcohols and ethers by tribiphenylylmethanol and sulphuric acid,[6] and of ethyl alcohol with xanthhydrol and hydrobromic acid[7] or with methoxytriphenylmethanols and hydrochloric acid.[8]

In the reactions considered under (*c*) the dehydrogenating agent, a carbonium ion, is first formed in the reaction system. In one case, that of the formation of tropylium salts by the action of triphenylmethyl salts on cycloheptatrienes,[9] a preformed carbonium ion has been used to remove the hydride ion. This process corresponds to the initial step (1) of the general dehydrogenation scheme given above. The possibility that preformed carbonium ions in the form of their salts might be used to dehydrogenate suitable substrates to relatively stable intermediate cations [step (1)] capable of further losing a proton with formation of a neutral product containing two fewer hydrogen atoms [step (2)] does not seem to have been considered. The work described in this paper is concerned with preliminary investigations on the general use of triphenylmethyl perchlorate as a dehydrogenating agent in this connection.

Triphenylmethyl perchlorate is most conveniently prepared by essentially the method of Hofmann and Kirmreuther[10] in which 70% perchloric acid is added to a solution of triphenylmethanol in acetic anhydride and acetic acid at room temperature. This procedure is conveniently adaptable to large-scale practice. The best dehydrogenation procedure consists in heating the substrate with triphenylmethyl perchlorate in boiling acetic acid for a time depending on the compound. Reaction is usually complete by the time the mixture has reached its reflux temperature and in no successful case was more than 15 minutes' boiling necessary. In several instances reaction was rapid at room temperature, but even then it was found expedient to raise the temperature of the mixture to the boiling point owing to the low solubility of triphenylmethyl perchlorate in cold acetic acid. In most cases clean products were readily obtained in high yield; this was not always so when acetonitrile and nitromethane were tried as solvents. Representatives from the following classes of compounds were chosen as substrates.

Hydrocarbons.—9,10-Dihydroanthracene was converted into anthracene in almost quantitative yield. The carbonium ion (I) is relatively stable, being a derivative of the diphenylmethyl cation.[11]

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[1] Braude, Jackman, and Linstead, *J.*, 1954, 3548, 3564.

[2] Baddeley and Wrench, *J.*, 1956, 4943.

[3] Baddeley and Pickles, *J.*, 1953, 3726.

[4] Baddeley, Wrench, and Williamson, *ibid.*, p. 2110; *J.*, 1957, 2855.

[5] Bartlett and McCollum, *J. Amer. Chem. Soc.*, 1956, **78**, 1441.

[6] Schmidlin and Garcia-Banùs, *Ber.*, 1912, **45**, 3188.

[7] Fosse, *Compt. rend.*, 1901, **133**, 100, 881; Fosse and Bertrand, *ibid.*, 1904, **139**, 601.

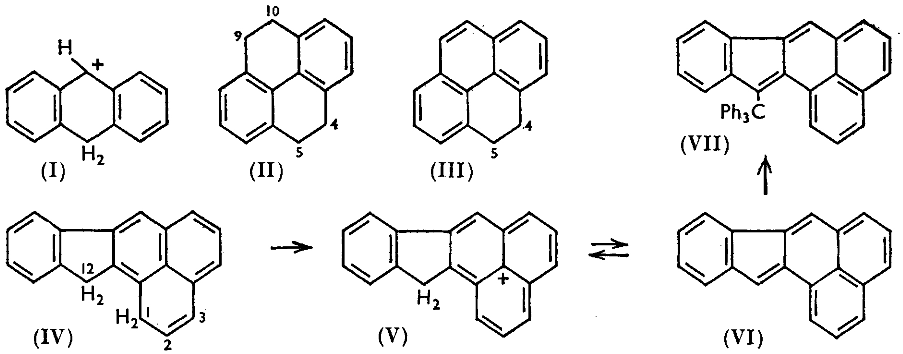
[8] Kauffmann and Pannwitz, *Ber.*, 1912, **45**, 766.

[9] Dauben, Gadecki, Harmon, and Pearson, *J. Amer. Chem. Soc.*, 1957, **79**, 4557; Dauben and Honnen, *ibid.*, 1958, **80**, 5570.

[10] Hofmann and Kirmreuther, *Ber.*, 1909, **42**, 4856.

[11] Gold and Tye, *J.*, 1952, 2172.

4,5:9,10-Tetrahydropyrene (II) might be expected to be dehydrogenated in two stages, first to 4,5-dihydropyrene (III) and thence to pyrene. On treatment with triphenylmethyl perchlorate it gave, however, pyrene as the main transformation product together with starting material, indicating that 4,5-dihydropyrene is dehydrogenated very much more rapidly than the tetrahydro-derivative (II).



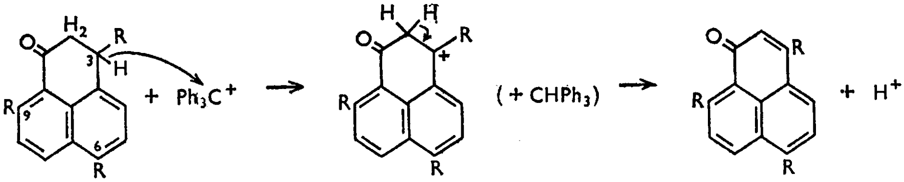
(I) (II) (III) (VII)

(IV) (V) (VI)

1,12-Dihydroindeno[2,1-*a*]perinaphthene[12] (IV), in view of the unusually high stability[13] of the perinaphthenylium cation (XVIII; R = H), would be expected to give 12*H*-indeno[2,1-*a*]perinaphthenylium (V) as the intermediate carbonium ion, identical with the cation generated when indeno[2,1-*a*]perinaphthene (VI) dissolves in strong acids.[13a] Reaction occurred immediately at room temperature, to give indeno[2,1-*a*]perinaphthene (VI) as expected, together with its 12-triphenylmethyl derivative (VII) formed by subsequent rapid substitution. The two products were readily separated by extraction of their mixture in benzene with 77% (w/w) sulphuric acid in which the triphenylmethyl derivative is insoluble.

Ketones.—Results obtained on application of the reagent to cyclic ketones have persuaded us that dehydrogenation by triphenylmethyl perchlorate constitutes the best method for converting perinaphthanones into perinaphthenones.

Perinaphthan-1-one (VIII; R = H) and 3,6,9-trimethylperinaphthan-1-one (VIII; R = Me) gave perinaphthenone (IX; R = H) in 80% yield and 3,6,9-trimethylperinaphthenone (IX; R = Me) in 81% yield, respectively. The case of (VIII; R = Me) is noteworthy since all attempts[14] to prepare 3,6,9-trimethylperinaphthenone by oxidation of 1,4,7-trimethylperinaphthene (XVII; R = Me) (tautomeric with 3,6,9-trimethylperinaphthene) failed, as did attempts to dehydrogenate (VIII; R = Me) by other reagents. These failures were unexpected in view of the ease with which perinaphthene (XVII; R = H) is oxidised to perinaphthenone[15] Loss of a hydride ion is considered to take place at $C_{(3)}$ of the perinaphthan-1-one nucleus (VIII) since a positive charge at



(VIII) (VIIIa) (IX)

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[12] Aitken and Reid, unpublished work.

[13] (*a*) Aitken and Reid, *J.*, 1956, 3487; (*b*) Reid, " Azulene and Related Substances," Chem. Soc. Special Publ. No. 12, 1958, p. 69; (*c*) Pettit, *Chem. and Ind.*, 1956, 1306; see also the synthesis described in this paper.

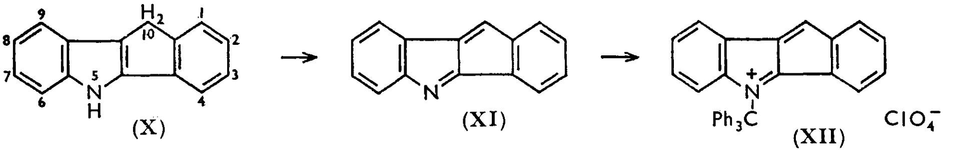
[14] Bonthrone and Reid, unpublished work.

[15] Lock and Gergely, *Ber.*, 1944, **77**, 461.

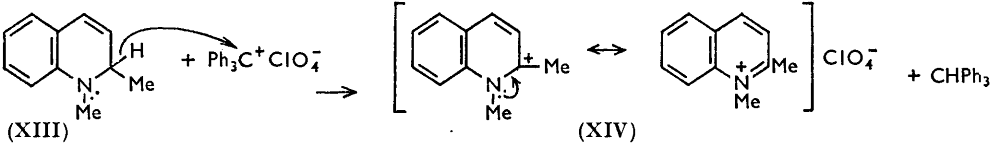
this site is resonance-stabilised by the adjacent aromatic nucleus. The considerable aromatic character of perinaphthenones provides the driving force for the subsequent loss of a proton from the intermediate cation (VIIIa).

Heterocycles.—5,10-Dihydroindolo[2,3-*a*]indene (X) was converted into a derivative of the hitherto unknown indeno[1,2-*b*]indole (XI). The dehydrogenation product (XI) itself was not isolated but was at once quaternised by the excess of reagent to give the 5-triphenylmethyl perchlorate (XII). This result seems surprising in view of the known lack of aromatic character of the corresponding carbocycle, 1,2:4,5-dibenzopentalene.[16]

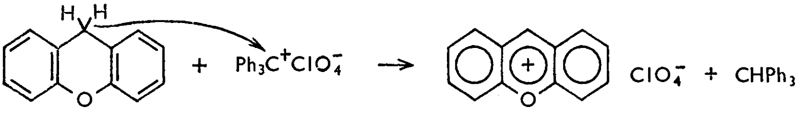
Finally, 1,2-dihydro-1,2-dimethylquinoline (XIII) gave quinaldine methoperchlorate (XIV) in quantitative yield, and xanthen (XV) was readily converted into xanthylium perchlorate (XVI).



(X) (XI) (XII)



(XIII) (XIV)



(XV) (XVI)

Discussion.—It is necessary to mention briefly the important factors upon which a successful dehydrogenation depends. These are implicit in the dehydrogenation scheme given at the beginning of this paper. For the initial step (1) they are (i) the electrophilic strength of the reagent E^+, (ii) the stability of EH, and (iii) the stability of the intermediate carbonium ion R_3C^+. The first two factors are constant for a given reagent and are henceforth ignored. The stability of the intermediate carbonium ion R_3C^+ is, then, all-important for a successful first step. For the final step (2) the acidity of the intermediate carbonium ion R_3C^+, determined by the relative stabilities of R_3C^+ and its conjugate base (the dehydrogenation product), is the decisive factor.

In the case of all successful dehydrogenations cited, except that of 5,10-dihydroindeno[1,2-*b*]indole, the substrate forms a stable carbonium ion (R_3C^+) as is readily envisaged. The driving force for the final step (2) is the additional resonance energy attending the loss of a proton.

The dehydrogenations of 1,2-dihydro-1,2-dimethylquinoline and xanthen require further discussion. The intermediate cations (XIV) and (XVI) cannot further lose a proton but are highly stabilised by participation of the 2*p*-electrons of the heteroatoms in the cyclical resonance and are themselves the final products. These reactions and the recently reported analogous preparation [9] of tropylium salts by abstraction of a hydride ion from cycloheptatrienes represent special cases of our general dehydrogenation scheme in which the intermediate carbonium ion (R_3C^+) is unusually stable.

These considerations, together with the known stability of the perinaphthenylium cation,[13] prompted us to attempt the synthesis of perinaphthenylium salts by allowing triphenylmethyl perchlorate and perinaphthenes to interact in acetic acid solution. Perinaphthene (XVII; R = H) gave perinaphthenylium perchlorate (XVIII; R = H)

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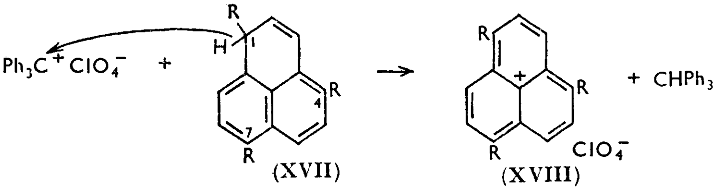
[16] Blood and Linstead, *J.*, 1952, 2263.

smoothly in good yield as yellow needles which become bluish-green and finally black on exposure to the atmosphere, and are hydrolysed instantly in water to perinaphthene, perinaphthenone, and perchloric acid. In contrast, 1,4,7-trimethylperinaphthenylium perchlorate (XVIII; R = Me), prepared similarly from 1,4,7-trimethylperinaphthene (XVII; R = Me), formed bronze-coloured needles, stable to the atmosphere, readily recrystallised from boiling acetic acid or acetonitrile without decomposition, and not readily solvolysed by water or alcohols.



We are now trying to elaborate this reaction into a convenient general preparation of perinaphthenylium salts. Other similar reactions will be reported later.

EXPERIMENTAL

M. p.s were determined on a Kofler-type heating stage. Chromatography was on activated alumina. Light petroleum was of boiling range 60—80° unless otherwise stated. Acetic acid was of " AnalaR " grade.

Dehydrogenation with Triphenylmethyl Perchlorate.—Stoicheiometric quantities of substrate and triphenylmethyl perchlorate were used unless otherwise indicated.

9,10-*Dihydroanthracene.* The hydrocarbon (180 mg.), triphenylmethyl perchlorate (343 mg.), and acetic acid (10 ml.) were boiled for 4 min. The cooled solution, whose colour had changed successively from deep yellow-green through deep green to very pale green, deposited anthracene (160 mg., 90%) as colourless plates, m. p. and mixed m. p. 215—218° (with sublimation).

4,5:9,10-*Tetrahydropyrene.* The hydrocarbon (1·03 g.; m. p. 132—135°), triphenylmethyl perchlorate (1·72 g.), and acetic acid (10 ml.) were boiled for 5 min., the initially deep yellow-brown and opaque solution becoming pale yellow and transparent. It was poured into water, and the mixture was extracted with light petroleum (2 × 300 ml.). The extracts were washed until free from acid and dried (K_2CO_3) before removal of the solvent, and the residual oil was dissolved in a hot mixture of ethanol (10 ml.) and benzene (8 ml.). Triphenylmethane (1·033 g., 89%), m. p. 92·5—94°, crystallised from the cooled solution. Benzene (2 ml.) was added to the mother-liquors, followed by picric acid (1·15 g.), and the mixture was boiled briefly to redissolve solid matter. Pyrene picrate (1·003 g., 93%; based on triphenylmethyl perchlorate used) crystallised from the cooled solution as orange-red needles, m. p. 222—224° (lit., m. p. 224°). After decomposition of the picrate (640 mg.) with dilute aqueous ammonia and working up in the usual manner, pyrene (190 mg., 62%) was obtained as colourless plates, m. p. and mixed m. p. 148—150°.

Dihydroindeno[2,1-a]*perinaphthene.* A solution of triphenylmethyl perchlorate (160 mg.) in acetic acid (40 ml.), at <20°, was added to a solution of dihydroindeno[2,1-*a*]perinaphthene (120 mg.) in acetic acid (40 ml.), also at <20°. The solution became red immediately and was left at room temperature for 3 hr. 12-*Triphenylmethylindeno*[2,1-a]*perinaphthene* (VII) separated from the solution as brown crystals (60 mg.), m. p. >320°, which dissolved in organic solvents to red solutions. Recrystallisation was from benzene (Found: C, 94·9; H, 4·7. $C_{39}H_{26}$ requires C, 94·7; H, 5·3%). It is insoluble in 77% (w/w) sulphuric acid.

The acetic acid mother-liquor was poured into water and extracted with benzene (300 ml.). The benzene extract was washed until free from acetic acid before being extracted with 77% (w/w) sulphuric acid (3 × 100 ml.). The acid extracts were washed with benzene (150 ml.) before dilution in water (2 l.), and the precipitated reddish-brown solid was taken up in ether (500 ml.). The ether solution was washed until free from acid with water and saturated sodium hydrogen carbonate solution before drying (K_2CO_3) and removal of solvent. The residue in benzene was filtered through a column (8 × 2·7 cm.) of alumina and the deep red eluates were evaporated to dryness. On addition of 1,3,5-trinitrobenzene to the residue dissolved in absolute ethanol the trinitrobenzene complex of indeno[2,1-*a*]perinaphthene crystallised as black needles (25 mg.), m. p. and mixed m. p. with an authentic specimen [13a] 175—176°.

Perinaphthan-1-*one*. Triphenylmethyl perchlorate (686 mg.), perinaphthan-1-one (364 mg.), and acetic acid (30 ml.) were boiled for 10 min., or until dissolution was complete. The solution was poured into water (250 ml.), and the resulting emulsion was extracted with benzene (2 × 100 ml.). The benzene extracts were washed until free from acetic acid before extraction with concentrated hydrochloric acid (3 × 50 ml.). The acid extracts were washed once with benzene (50 ml.) before dilution in water (500 ml.). The precipitated solid was extracted with benzene (2 × 200 ml.). The combined benzene extracts were washed successively with water, saturated sodium hydrogen carbonate, and water, and dried (Na_2SO_4) before removal of solvent. The pale yellow residue, after sublimation at 150°/0·5 mm. followed by one crystallisation from light petroleum (b. p. 60—80°)-benzene (1 : 1), afforded perinaphthenone (IX; R = H) as yellow needles (290 mg., 80%), m. p. and mixed m. p. 155·5—156·5°.

The benzene solution from which perinaphthenone had been extracted by concentrated hydrochloric acid was washed successively with water, saturated sodium hydrogen carbonate solution, and water, and dried (Na_2SO_4) before removal of solvent. The residue crystallised from ethanol as colourless plates (300 mg., 62%), m. p. 93·5—94°, undepressed on admixture with triphenylmethane.

3,6,9-*Trimethylperinaphthan*-1-*one*. A mixture of 3,6,9-trimethylperinaphthan-1-one (448 mg.), triphenylmethyl perchlorate (686 mg.), and glacial acetic acid (50 ml.) was boiled for 15 min., then was worked up as described for the dehydrogenation of perinaphthan-1-one. After sublimation at 150°/0·1 mm. followed by one crystallisation from light petroleum (b. p. 60—80°) the crude product afforded 3,6,9-*trimethylperinaphthen*-1-*one* (IX; R = Me) (360 mg., 81%) as yellow needles, m. p. 106—107° (Found: C, 86·6; H, 6·4. $C_{16}H_{14}O$ requires C, 86·4; H, 6·4%). Triphenylmethane (340 mg., 70%), m. p. 93—94°, was isolated from the original reaction mixture.

5,10-*Dihydroindeno*[1,2-b]*indene*. A boiling solution of triphenylmethyl perchlorate (185 mg.) in acetic acid (25 ml.) was added to one of 5,10-dihydroindolo[1,2-*a*]indene (110 mg.) in acetic acid (15 ml.), also at the b. p., the solution becoming blue. The solution was boiled for 1 min. and allowed to cool to room temperature. 5-*Triphenylmethylindeno*[1,2-b]*indolium perchlorate* (XII) separated from the cooling solution as black crystals, m. p. >320° (Found: C, 73·6; H, 4·3; Cl, 5·8; N, 2·5. $C_{34}H_{24}O_4NCl$ requires C, 74·8; H, 4·4; Cl, 6·5; N, 2·6%), insoluble in benzene and non-polar solvents and dissolving in acetone or nitromethane to greenish-blue solutions.

1,2-*Dihydro*-1,2-*dimethylquinoline*. Triphenylmethyl perchlorate (343 mg.) was added to a solution of 1,2-dihydro-1,2-dimethylquinoline [17] (160 mg.) in acetic acid (6 ml.). The mixture was boiled for 1 min. during which a transient red colour developed and faded. The cooled solution deposited quinaldine methoperchlorate (XIV) (255 mg., 98%) as colourless prisms, m. p. and mixed m. p. 152—154°.

Xanthen. Xanthen (182 mg.), triphenylmethyl perchlorate (343 mg.), and acetic acid (10 ml.) were heated for 2 min. *Xanthylium perchlorate* (XVI) began to separate from the boiling solution as yellow plates. The product, filtered from the cooled solution, recrystallised from acetic acid as bronze plates (190 mg., 68%), m. p. (capillary) 225—226° to a red liquid (Found: C, 55·2; H, 3·3; Cl, 12·9. $C_{13}H_9O_4Cl$ requires C, 55·6; H, 3·2; Cl, 12·6%).

Preparation and Properties of Perinaphthenylium Perchlorate (XVIII; R = H).—A solution of triphenylmethyl perchlorate (686 mg.) in acetic acid (90 ml.) was added to one of perinaphthene (370 mg.) in acetic acid (10 ml.). Perinaphthenylium perchlorate began to separate from solution almost at once as yellow needles. After 5 min. it was filtered off, washed with anhydrous ether followed by dry light petroleum, and transferred immediately to a vacuum-desiccator. The perchlorate obtained (357 mg., 61%) was dried *in vacuo* for 5 hr. over phosphoric oxide and potassium hydroxide.

Owing to its instability to the atmosphere in which it blackens the perchlorate had to be analysed at once. Determination of the percentage of ClO_4 present was therefore carried out as follows: the dried perchlorate (357 mgm.) was hydrolysed with water (100 ml.), and the resulting yellow solid was filtered off through a sintered-glass funnel, with subsequent thorough washing with more water (100 ml.). The combined solutions containing perchloric acid were

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[17] Bradley and Jeffrey, *J.*, 1954, 2770.

titrated against 0·05N-sodium hydroxide (Bromothymol Blue). A second determination was carried out on 328 mg. of perchlorate (Found: ClO_4, 37·2, 37·0. $C_{13}H_9O_4Cl$ requires ClO_4, 37·6%). *Perinaphthenylium perchlorate* is insoluble in non-polar solvents but dissolves readily in acetic acid, acetonitrile, and nitromethane, giving yellow solutions. It does not melt but decomposes slowly on heating.

The organic material filtered off after hydrolysis of the perchlorate (685 mg.) was dissolved in benzene (150 ml.) and extracted exhaustively with concentrated hydrochloric acid as described for the dehydrogenation of perinaphthan-1-one. The hydrochloric acid extracts thus gave perinaphthenone (180 mg., 39% based on perinaphthenylium perchlorate), m. p. 154—156°. The benzene solution from which perinaphthenone had been extracted with concentrated hydrochloric acid was washed in turn with water, saturated sodium hydrogen carbonate solution, and water before drying (Na_2SO_4) and evaporation of the solvent. The residual oil was taken up in light petroleum and purified through a column (15 × 2·8 cm.) of alumina, light petroleum being used as eluant. Solvent was evaporated from the colourless eluates (200 ml.), and the residual oil, dissolved in ethanol (30 ml.), was treated with 1,3,5-trinitrobenzene (110 mg.). The trinitrobenzene complex of perinaphthene crystallised as orange needles (150 mg., 15% based on perinaphthenylium perchlorate), m. p. 151—152° (decomp.), unchanged after recrystallisation from ethanol (lit.,[18] m. p. 159°). The perinaphthenone and perinaphthene thus isolated accounted for 54% of the perinaphthenylium perchlorate used in the experiment.

Preparation and Properties of 1,4,7-*Trimethylperinaphthenylium Perchlorate* (XVIII; R = Me).—Triphenylmethyl perchlorate (1·75 g.) in acetic acid (200 ml.) was added to a solution of 1,4,7-trimethylperinaphthene (1·06 g.) in acetic acid (20 ml.). 1,4,7-*Trimethylperinaphthenylium perchlorate* began to crystallise immediately from the resulting solution as yellow needles (570 mg., 37%). The salt, recrystallised from acetonitrile, was obtained as copper-coloured needles, decomp. >240° (Found: C, 63·3; H, 5·1; Cl, 11·1. $C_{16}H_{15}O_4Cl$ requires C, 62·7; H, 4·9; Cl, 11·6%). The compound is insoluble in non-polar organic solvents but in acetic acid or acetonitrile readily gives yellow solutions. It is stable to the atmosphere and is not readily solvolysed by water or alcohols.

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[18] Boekelheide and Larrabee, *J. Amer. Chem. Soc.*, 1950, **72**, 1245.