Reactions of Bicyclic Olefins with Palladium Chloride–Copper Chloride

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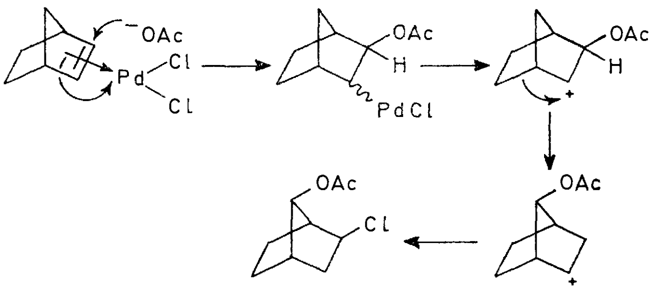
endo- (1) and *exo*-5,6-(*o*-phenylene)norborn-2-ene (2) and *endo*- (3) and *exo*-5,6-(1,8-naphthylene)norborn-2-ene (4) have been prepared and their reactions with a palladium chloride–cupric chloride catalyst system investigated. Products with rearranged and unrearranged structure have been identified. The mechanism of these reactions has been discussed and it has been suggested that the controlling intermediate leading to unrearranged products is an olefincopper complex, whereas the corresponding palladium(II) complexes lead predominantly to rearranged chloroacetates. Species possessing carbonium ion character have been suggested as intermediates in the pathway involving palladium. Carbonium ion formation in the cupric chloride catalysed reactions is much less pronounced. The important role of substituents in determining the rearrangements has been demonstrated and confirmed by the reactions, in acid media, of the derived epoxides of olefins (1) and (2). Solvolytic studies involving a number of derived bromohydrins further emphasised the importance of this factor.

REACTIONS of olefins with palladium salts have been developed into important procedures in organic synthesis.[1] Oxidation of ethylene with palladium chloride in aqueous solution leads to acetaldehyde and the process has been enhanced catalytically with respect to palladium by the addition of cupric chloride.[2,3] This operates by oxidation of the palladium metal produced in the reaction of divalent palladium with formation of cuprous chloride which is subsequently reoxidised by oxygen. In a similar manner vinyl acetate is obtained from palladium acetate and ethylene in acetic acid solution in the presence of cupric acetate and oxygen.[1,4] Although cupric chloride or cupric acetate is used as a reoxidant in these processes, minor side products are also formed which can be made major by increasing the copper(II) concentration. These are chloroacetates, diacetates, and in some cases dichlorides. Reaction of norbornene in glacial acetic acid containing sodium acetate, cupric chloride, and a catalytic quantity of palladium chloride gave a good yield of *exo*-2-chloro-*syn*-7-acetoxynorbornene (Scheme 1).[5] The mechanism of this and the previous reactions have evoked considerable discussions. Formation of a norbornenepalladium chloride π-complex was suggested to be followed by nucleophilic attack by acetate ion to form a β-acetoxyalkylpalladium chloride σ-complex and subsequent heterolytic cleavage to produce an acetoxynorbornyl carbonium ion. Rearrangement and trapping of the carbonium ion with chloride ion leads to the observed product together with 5—10% of the diacetate. Formation of acetaldehyde from ethylene has been demonstrated to involve an intramolecular palladium hydride shift but the mechanism and involvement of carbonium ions has not been clarified.[4]



SCHEME 1

In the course of a series of studies on carbonium ion reactions in rigid systems we had recourse to prepare the olefins *endo*- (1) and *exo*-5,6-(*o*-phenylene)norborn-2-ene (2) and *endo*- (3) and *exo*-5,6-(1,8-naphthylene)norborn-2-ene (4).[6,7] A study of the reactions of these systems with palladium chloride and cupric chloride has been made to investigate both the synthetic possibilities of the rearrangement processes observed and also to provide information on the role of carbonium ions in

[1] J. Tsuji, *Adv. Phys. Org. Chem.*, 1969, **6**, 109; E. W. Stern, *Catalysis Rev.*, 1968, **1**, 74; F. R. Hartley, *Chem. Rev.*, 1969, **69**, 799.

[2] J. Smidt, W. Hafner, R. Hira, R. Sieber, J. Sedlmeier, and A. Sabel, *Angew. Chem. Internat. Edn.*, 1962, **1**, 54.

[3] A. Aguilo, *Adv. Organometallic Chem.*, 1967, **5**, 321.

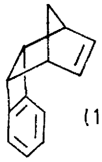
[4] P. M. Maitlis, 'The Organic Chemistry of Palladium,' Academic Press, New York, 1971.

[5] W. C. Baird, jun., *J. Org. Chem.*, 1969, **31**, 2411.

[6] R. Baker and T. J. Mason, *J.C.S. Perkin II*, 1972, 18.

[7] R. Baker and T. J. Mason, *J. Chem. Soc.* (*B*), 1971, 1144.

these reactions.[8] This is particularly appropriate since extensive studies have been made on carbonium ions, with these systems and distinctive rearrangement properties identified. The possibility of the observation of interaction between the *endo*-aromatic groups in (1) and (3) with palladium orientated on the *endo*-side of the molecules was also of particular interest.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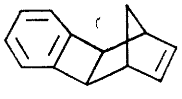
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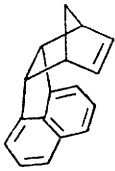
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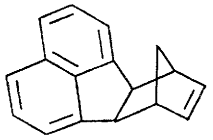
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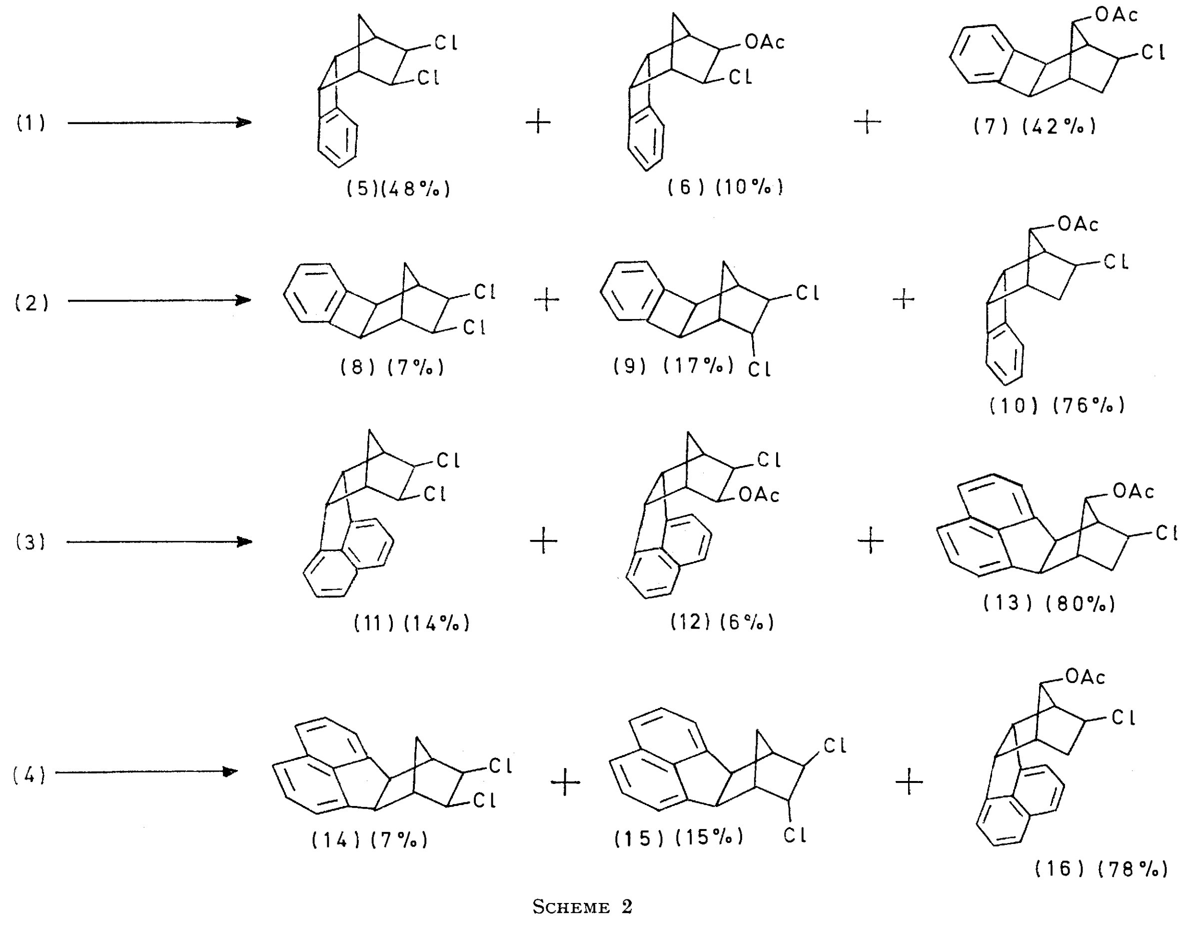
In the course of these studies, a number of rearrangements have been observed which were not typical of those previously reported for these bicyclic systems. Further investigations, involving acid opening of the derived epoxides of (1) and (2) and the solvolysis of disubstituted derivatives has highlighted the role of an electron-withdrawing group β to a positive centre as a determining factor in the course of these reactions.

RESULTS

Reactions with Palladium Chloride and Cupric Chloride in Acetic Acid.—Compounds (1)—(4) reacted in acetic acid containing sodium acetate at 80° for 72 h (Scheme 2). Structures of these products were assigned predominantly by a detailed analysis of their n.m.r. and mass spectral data (Table 1). A comparison of the position of the benzylic protons to the positions of the corresponding signals of *exo*-phenylene- (17) (τ 6·95) and *endo*-phenylene-alcohols (18) (τ 6·50)[9] suggests that the benzo-group in (5) has *endo*-stereochemistry. This finds support in that the α-Cl proton signals occur at τ 6·27 which provides confirmation for a *cis–exo*-arrangement of the chlorine substituents. Benzylic proton signals at τ 6·30, lower than the equivalent protons in (8), together with the α-Cl proton signal at τ 6·30 provide confirmation for the *endo*-configuration of the benzene ring and the *exo*-stereochemistry of the chlorine substituent in (6). A comparison of the position of the α-OAc proton (τ 5·62) with the corresponding signal in (19) (τ 5·37)[10]



SCHEME 2

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[8] C. J. R. Adderley, J. W. Nebzydoski, M. A. Battiste, R. Baker, and D. E. Halliday, *Tetrahedron Letters*, 1971, 3545.

[9] R. Baker and T. J. Mason, *J. Chem. Soc. (C)*, 1970, 596.

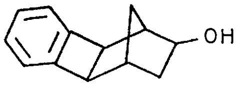
[10] M. Avram, F. Chiraleu, and I. Pogany, *Rev. Roumaine Chim.*, 1970, **15**, 1219.

suggests that the acetoxy-group also possesses *exo*-stereochemistry. In the n.m.r. spectrum of (7) the benzylic proton signals at τ 6·75 together with the α-Cl and α-OAc proton signals at τ 6·03 and 5·80 confirm the *exo*-configuration of the benzene ring with the chlorine substituent in the 2-position and the acetoxy-group in the 7-position, *anti* to the benzene ring. Evidence for the *exo*-configuration of the chlorine substituent is provided by the appearance of the benzylic protons as a singlet. It has been shown that *endo*-substituents engender a difference between the *endo*-benzylic protons in *exo*-phenylene systems causing them to possess different chemical shifts.[9] The bridge position of the acetoxy-substituent is reflected in the mass spectral data; whereas the mass spectrum of (7) exhibits a ratio of ($M^+ - 60$) ion (loss of acetic acid) to parent ion M^+ of 0·6, the corresponding ratio for (6) is 8·3.

TABLE 1

^1H N.m.r. spectra (τ) (CCl_4) of products of reaction of (1)—(4) with palladium chloride and cupric chloride in acetic acid

Compound	Aromatic	Benzylic	α-Cl	α-OAc	Bridgehead	Bridge
(5)	2·77 (4H, s)	6·27 (2H, m)	6·27 (4H, m)		7·24 (2H, m)	7·47, 8·27 (2H, AB, *J* 11 Hz)
(6)	2·82 (4H, m)	6·30 (2H, m)	6·30 (1H, m)	5·62 (1H, dd, *J* 6·0, 1·8 Hz)	7·28 (2H, m)	7·63, 8·32 (2H, complex d, *J* 10·5 Hz)
(7)	2·90 (4H, m)	6·75 (2H, m)	6·03 (1H, m)	5·80 (1H, m)	7·15, 7·49 (2H, m)	7·60—7·90 (2H, m)
(8)	2·94 (4H, m)	6·75 (2H, m)	6·07 (2H, d, *J* 2·0 Hz)		7·44 (2H, s)	8·40, 9·06 (2H, AB, *J* 11 Hz)
(9)	2·90 (4H, m)	6·04 (1H, d, *J* 3·5 Hz) 6·64 (1H, d, *J* 3·5 Hz)	5·66 (1H, dd, *J* 3·0, 4·0 Hz) 6·32 (1H, t, *J* 3·0 Hz)		7·39br (1H, d, *J* 4·0 Hz) 7·46br (1H, s)	8·29, 8·83 (2H, AB, *J* 11 Hz)
(10)	2·88 (4H, m)	6·45 (2H, m)	6·29 (1H, m)	5·22 (1H, m)	7·06 (1H, d, *J* 5·0 Hz) 7·33 (1H, d, *J* 5·0 Hz)	8·00—8·50 (2H, m)
(11)	2·57 (6H, m)	5·94 (2H, m)	6·56 (2H, d, *J* 1·5 Hz)		7·11 (2H, m)	7·52, 8·18 (2H, AB, *J* 10·5 Hz)
(13)	2·58 (6H, m)	6·58 (2H, d, *J* 1 Hz)	5·87 (1H, m)	5·96 (1H, m)	7·06 (1H, m) 7·53 (1H, m)	7·43, 7·64 (2H, m)
(14)	2·63 (6H, m)	6·50 (2H, s)	5·67 (2H, d, *J* 2 Hz)		7·36 (2H, s)	8·17, 9·18 (2H, AB, *J* 10 Hz)
(15)	2·60 (6H, m)	5·81 (1H, d, *J* 6 Hz) 6·40 (1H, d, *J* 6 Hz)	5·66 (1H, m) 6·05 (1H, m)		7·39 (2H, m)	8·31, 9·08 (2H, m)
(16)	2·67 (2H, m)	6·04 (2H, m)	6·81 (1H, m)	5·02 (1H, m)	6·94, 7·21 (2H, m)	8·05, 8·42 (2H, m)



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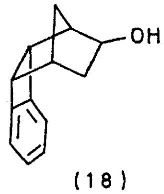

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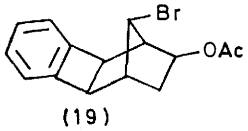
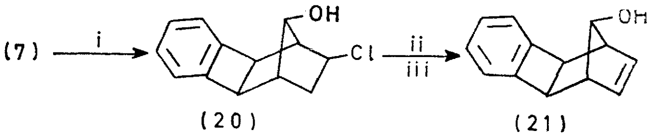


(19)

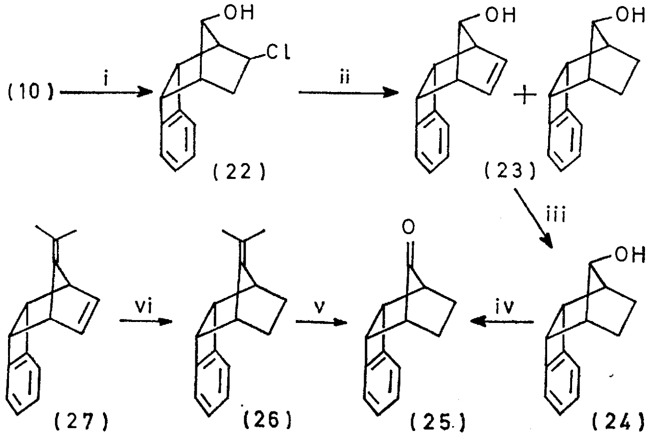
Conclusive evidence for the structure of (7) was provided by its conversion into (21) *via* the chlorohydrin (20) (Scheme 3). Treatment of an ethereal solution of (7) with lithium aluminium hydride gave (20), τ (CCl_4) 2·90 (4H, m, aromatic), 6·08 (1H, m, α-Cl), 6·40br (1H, s, α-OH), 6·80 (2H, s, benzylic), 7·50 (1H, s, bridgehead, *syn*-Cl), 7·70 (3H, m, bridgehead, *anti*-Cl, hydroxy, *exo*-geminal), and 8·16 (1H, m, *endo*-geminal). Dehydrochlorination of (20) afforded (21), τ ($CDCl_3$) 2·90 (4H, m, aromatic), 3·76 (2H, s, vinylic), 6·62 (1H, s, α-OH), 6·84 (2H, s, benzylic), 7·22 (2H, s, bridgehead), and 8·03 (1H, m, hydroxy). A comparison of signals for the benzylic protons of (21) with the corresponding signals of *endo*-olefin (1) (τ 6·46) and *exo*-olefin (2) (τ 6·93), strongly suggests an *exo*-phenylene configuration. Appearance of the α-OH proton at τ 6·62 confirms the *anti*-orientation of the hydroxy-substituent with respect to the benzene ring.



SCHEME 3 Reagents: i, $LiAlH_4$–Et_2O; ii, Bu^tOK–Me_2SO; iii, H^+–H_2O

Reaction of (2) gave the mixture (8)—(10) (Scheme 2). For (8) a symmetrical structure is apparent with the α-Cl protons less shielded than the corresponding protons in (5) and the *endo*-benzylic protons appear at higher field in this case compared with the *exo*-benzylic protons of (5). In the n.m.r. of (9), the *endo*-chlorine substituent is associated with a difference between the two *endo*-benzylic protons.

The mass spectrum of (10) revealed an $M^+ - 60$ ion which was less intense than the parent ion. This implied that, in contrast to (6), the acetoxy-group is in the bridge position. Whilst this spectrum is consistent with (10) it is is not definitive and chemical proof for this structure was obtained by conversion to the known alcohol (24) and ketone (25) (Scheme 4). In the n.m.r. spectrum of (24) occurrence of the benzylic proton signals at τ 6·46 together with that for the α-OH proton at τ 5·93 provide confirmation for the *endo*-configuration of the benzene ring and the bridge position of the hydroxy-substituent. For (25) the i.r. absorption at 1765 cm^{-1} is characteristic of the bridged carbonyl group and the benzylic proton signal at τ 6·26 confirms the *endo*-configuration of the benzene ring. The structure of (25) was also confirmed by preparation from (27) by selective hydrogenation followed by ozonolysis.

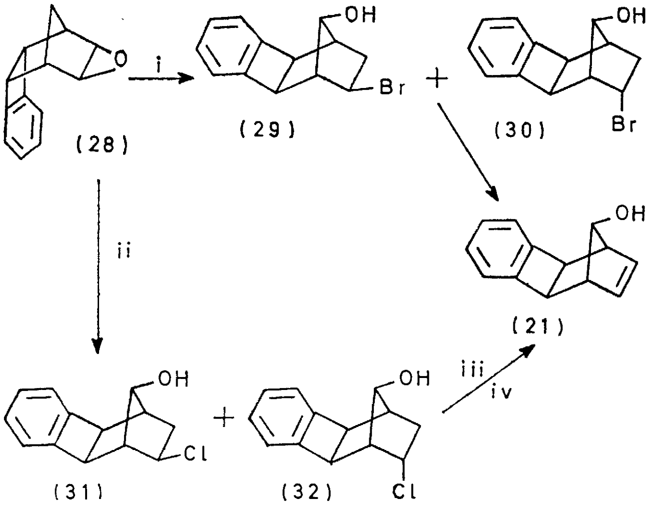


SCHEME 4 Reagents: i, $LiAlH_4$–Et_2O; ii, Li–Bu^tOH–THF; iii, H_2–PtO_2–EtOH; iv, CrO_3–C_5H_5N–CH_2Cl_2; v, O_3–MeOH; vi, H_2–Pd–C

Structure assignment for products from reaction of (3) and (4) was similar.

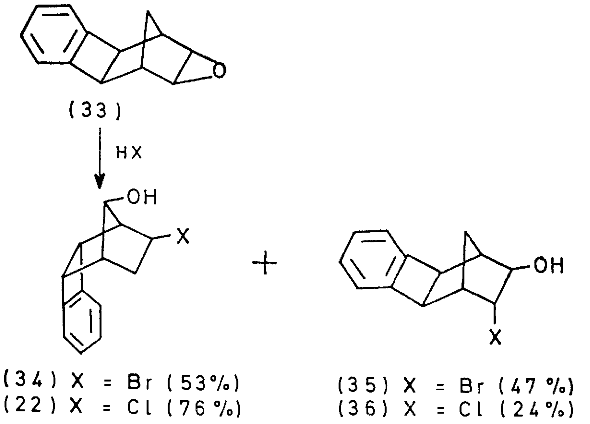
Reactions with Cupric Chloride in Acetic Acid.—Reactions in which palladium chloride was totally excluded revealed that cupric chloride alone could account for formation of unrearranged products. Thus, (1) yielded (5) (69·5%) and (6) (30·5%), and (2) gave a mixture of (8) (37·6%) and (9) (62·4%) on treatment with cupric chloride in acetic acid containing sodium acetate.

Reactions of the exo-*Epoxides of* (1) *and* (2).—Treatment of a chloroform solution of (1) with *m*-chloroperbenzoic acid resulted in formation of (28), τ (CCl_4) 2·97 (4H, m, aromatic), 6·30 (2H, m, benzylic), 7·33 (2H, s, bridgehead), 7·37 (2H, m, α to epoxide), and 8·27 and 8·80 (2H, AB, *J* 16·5 Hz, bridge). The epoxide is assigned *exo*-stereochemistry on the basis of the α-epoxide proton signals at τ 7·37 which are shielded by the benzene ring, indicating they are in the *endo*-configuration. Reaction of (28) with 48% aqueous hydrobromic acid gave a mixture of two rearranged bromohydrins (29) (55%) and (30) (45%). These could not be separated but their structures were assigned by dehydrobromination of the mixture of (21). Similarly, treatment of (28) with 40% aqueous hydrochloric acid gave a mixture comprising two rearranged chlorohydrins (31) and (32).



Reagents: i, HBr–H_2O; ii, HCl–H_2O; iii, Bu^tOK–Me_2SO; iv, H^+–H_2O

Treatment of (2) with *m*-chloroperbenzoic acid gave (33), τ (CCl_4) 3·06 (4H, m, aromatic), 6·79 (2H, s, benzylic), 7·06 (2H, s, α-epoxide), 7·59br (2H, s, bridgehead), and 8·90 and 9·56 (2H, AB, *J* 10 Hz, bridge). Benzylic proton signals at τ 6·79 together with the appearance of the α-epoxide protons as a singlet at τ 7·06 provide confirmation for the assigned *exo*-phenylene–*exo*-epoxide stereochemistry. Reaction with 48% aqueous hydrobromic acid gave the mixture of bromohydrins (34) (53%) and (35) (47%). Benzylic proton signals at τ 6·42, together with those of the α-OH at τ 5·86 and the α-Br proton at 6·42 provide confirmation for the *endo*-configuration of the benzene ring and the bridge and *exo*-geminal arrangement of the hydroxy- and bromo-substituents in (34). In (35), the two benzylic proton signals at τ 6·18 and 6·79 provide evidence for the assigned structure. A similar reaction was observed on treatment of (33) with 40% aqueous hydrochloric acid and a mixture of (22) (76%) and (36) (24%) was formed.

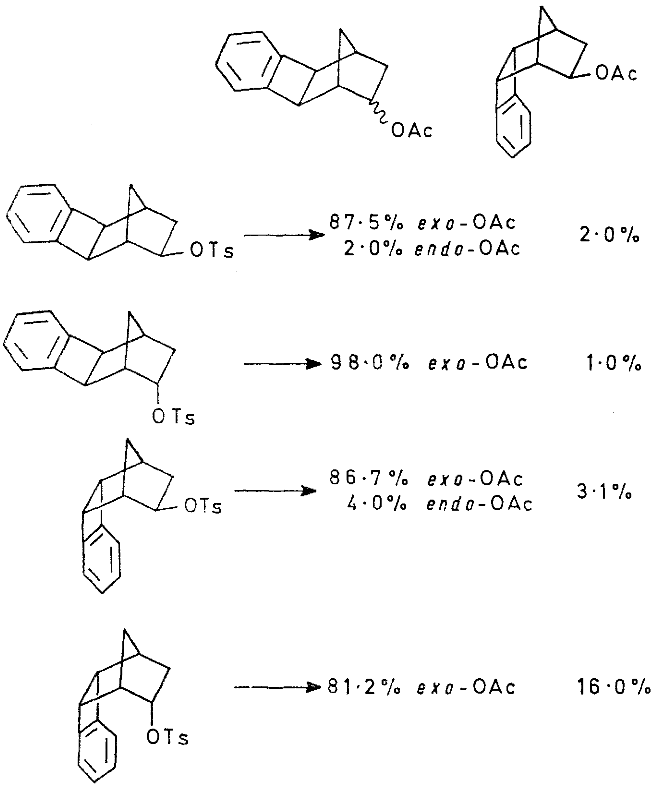


DISCUSSION

In contrast to exclusive product formation with rearranged structure on treatment of norbornene with palladium chloride and cupric chloride in acetic acid containing sodium acetate,[5] the nature of products from a similar treatment of (1)—(4) is dependent upon structure. Both dichloride (5) and chloroacetate (6) with retained *endo*-phenylene stereochemistry together with rearranged chloroacetate (7) are obtained from reaction of (1). *exo*-Olefin (2) gives rise to rearranged chloroacetate (10) as major product; *cis*- and *trans*-dichlorides (8) and (9) are also formed. Similar results are also obtained with the naphthylene-substituted olefins (3) and (4).

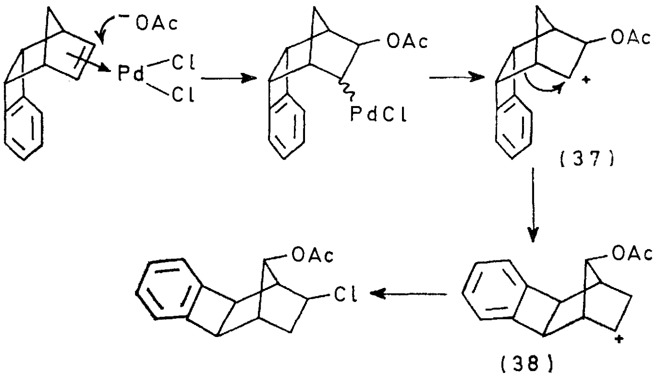
The predominance of rearranged products from both *exo*-substituted olefins (2) and (4) is the most striking feature of these studies. Formation of products with retained *exo*-aryl configuration has been shown to be extremely favoured by these systems in solvolyses [6] and derivatives with *endo*-arylene substitution lead to almost exclusive rearranged products (Scheme 5). Similar trends were found with the analogous *endo*- and *exo*-naphthylene systems. A substantial amount of unrearranged products is found in the present reactions with (1) and, to a lesser extent, with (3).

Reactions of the olefins (1)—(4) with cupric chloride can account for a substantial amount of unrearranged products, as seen by their isolation from reactions in which palladium chloride is excluded. Formation of rearranged structures (7), (10), (13), and (16) requires the presence of a palladium species. The results can thus be interpreted in terms of two competing pathways. One, requiring both palladium(II) and copper(II), leads to rearranged products, whilst the other, involving copper(II) alone, gives rise to structures with retained arylene configuration.



SCHEME 5

A similar mechanism to that for norbornene can be proposed for reaction of (1) (Scheme 6). Heterolytic fission of the carbon–palladium bonds in σ-alkylpalladium species to yield carbonium ions is favoured at high chloride concentration and the role of copper(II) species was suggested to be withdrawal of electrons from the environment of palladium(II).[11] It has also been suggested that in the transition state the two electrons from the carbon–palladium bond are transferred through palladium(II) to copper(II) so that, in effect, palladium(0) is never completely formed and a palladium(II) species is the effective leaving group; this has been described as (39). The carbonium ion (37) will be associated with solvent and also probably exist as an ion pair. Stabilisation of the positive centre could also be possible by neighbouring acetoxy-group participation leading to bridged species (40). Formation of such an intermediate would be more favoured with an *endo*-configuration of the carbon–palladium bond in the σ-complex.[12,13] Subsequent Wagner–Meerwein rearrangement would then yield the carbonium ion (38) leading to rearranged product. Similarly for (2) formation of the chloroacetate (10) required the rearrangement of (41) to (42). At first sight, the intermediacy of (41) in reaction of (2) should lead predominantly to unrearranged chloroacetate and the solvolysis results (Scheme 5) have indicated the larger steric interactions in the *endo*-phenylene substituted derivatives.[9,14] This would appear to suggest that acetoxy-participation is not important, probably owing to the non-coplanarity of *trans*-2,3-substituents in bicyclo[2.2.1] systems. It is apparent that removal of the destabilising interaction between the electron-withdrawing acetoxy-group and the positive centre is the determining factor in the rearrangement. A measure of this destabilisation is found in that the acetolysis rate of *cis*-2-acetoxycyclohexyl *p*-bromobenzenesulphonate is slower than that of cyclohexyl *p*-bromobenzenesulphonate by a factor of 3·8 × 10^4.[12,13] Formation of



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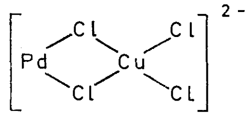

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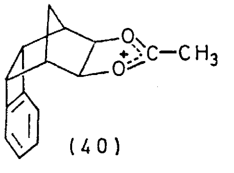

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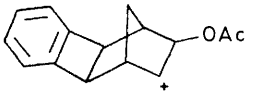

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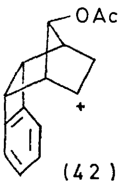

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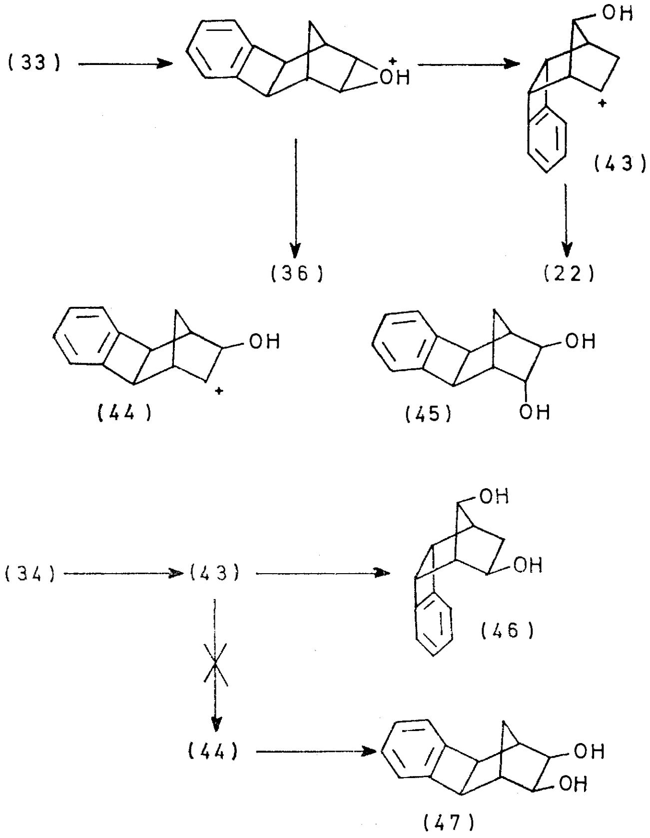
[12] S. Winstein, E. Grunwald, R. E. Buckles, and C. Hanson, *J. Amer. Chem. Soc.*, 1948, **70**, 848.

[13] S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Amer. Chem. Soc.*, 1948, **70**, 821.

[14] R. Baker and J. Hudec, *Chem. Comm.*, 1967, 929.

rearranged chloroacetates (13) and (16) from *endo*- and *exo*-olefins (3) and (4) can be explained in a similar way.

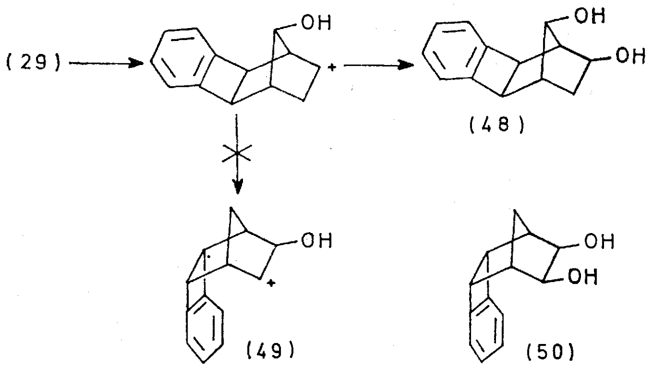
Supporting evidence for the proposed carbonium ion mechanism is obtained by acid opening of epoxides (28) and (33). Formation of rearranged products occurs exclusively in the case of (28), whereas the extent of rearrangement from (33) varies according to the acid used. Protonation of (33) with 40% aqueous hydrochloric acid is followed by Wagner–Meerwein rearrangement or formation of the unrearranged chlorohydrin. Since acid opening of epoxides proceeds substantially by S_N2 attack on the oxonium ion (or opening to the carbonium ion prior to attack) competition can occur between a C-1–C-6 shift and incoming nucleophile (Scheme 7).



SCHEME 7

An important factor in the C-1–C-6 bond migration is the electron-withdrawing hydroxy-group adjacent to the carbonium ion (44).

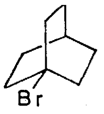
A similar competition between C-1–C-6 bond shift and bromide attack is found on treatment of (33) with 48% aqueous hydrobromic acid. The greater nucleophilicity of bromide in comparison with that of chloride is reflected in the smaller amount of rearranged product obtained from hydrobromic acid opening of (33); 47% of the unrearranged bromohydrin (35) is found compared with 24% of the unrearranged chlorohydrin (36) from reaction of the epoxide with hydrochloric acid. Support for the importance of nucleophilicity of the incoming nucleophile in determining the course of reaction is seen in formation of unrearranged *trans*-diol (45) as the exclusive product from treatment of epoxide (33) with 50% aqueous sodium hydroxide.



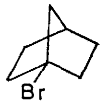
Acid opening of (28) leads to rearranged products exclusively. Absence of unrearranged *endo*-phenylene products is a reflection of steric hindrance experienced by an incoming nucleophile, as a result of the *endo*-5,6-substituent so that the Wagner–Meerwein rearrangement is favoured. Preferential formation of *exo*-halogeno-product again reflects favoured *exo*-approach of nucleophile to the intermediate formed as a result of the rearrangement.

Conclusive evidence for the effect of electron-withdrawing groups on the course of these reaction has been provided by solvolysis studies. Solvolysis of (34) with 10% aqueous silver nitrate gave unrearranged diol (46) as sole product. Formation of diol (47) would require rearrangement to (44) in which the hydroxy-group is adjacent to an electron-deficient centre. Thus, although rearrangement of *endo*-phenylene carbonium ions to those with *exo*-phenylene stereochemistry is an extremely favoured process,[6] the destabilising effect of the β-hydroxy-group, which would be present in (44) appears to be sufficient to prevent such a rearrangement.

Similarly, solvolysis of (29) gives only unrearranged diol (48). Formation of (50) would require the intermediacy of the carbonium ion (49), which would again be destabilised to some extent by a β-hydroxy-group; the Wagner–Meerwein rearrangement would also not be favoured on steric considerations. Even when subjected to heating at 75° for 20 h, (35) remained inert to 10% aqueous silver nitrate solution. It is noteworthy that such extremely unreactive bromides as (51) and (52) do react when subjected to these solvolytic conditions, the former after only 4 h at room temperature.[15]



(51)



(52)

Reactions with Cupric Chloride.—Reactions of olefins (1) and (2) with cupric chloride in the absence of palladium chloride gave only unrearranged products; *cis*- and

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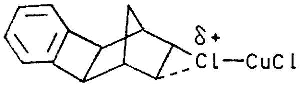
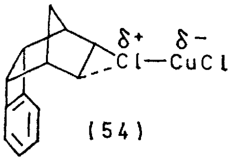
[15] R. C. Fort, jun., and P. von R. Schleyer, *Adv. Alicyclic Chem.*, 1966, **1**, 284.

trans-dichlorides were obtained from reaction with *exo*-olefin (2), whereas reaction with the *endo*-isomer (1) afforded *cis*-dichloride, together with *cis*-chloroacetate. Isolation of *cis*- and *trans*-dichlorides from *exo*-olefin (2) can arise through a loosely bound chloronium ion intermediate (53). Such intermediates have been shown by Koyano to be involved in chlorination of olefins with cupric chloride in the liquid phase.[16–18] Initially, a complex is formed between the olefin and cupric chloride. This is transformed into a cationic chlorine complex which yields dichloride by attack of chloride ion. The cationic intermediate appears to involve only a small bridging interaction since, in the chlorination of *cis*- and *trans*-but-2-ene, a similar mixture of *meso*- and racemic 2,3-dichlorobutane is formed. This implies rotation about the central carbon–carbon bond which is faster than attack of nucleophiles.[17] In cupric chloride chlorination of the olefins (1)—(4), no rotation is possible but it is apparent that the cationic character of the transition state is not sufficient to allow similar rearrangements observed in the reactions in the presence of cupric chloride and palladium chloride. Our interpretation is that although the chloronium ion is only loosely bound, it is sufficient to delocalise charge from the carbon atom to the chlorine and copper atoms in the intermediate. This decrease in electrophilic character of the carbon removes the drive for Wagner–Meerwein rearrangements in reactions of cupric chloride and (1)—(4).



(53)

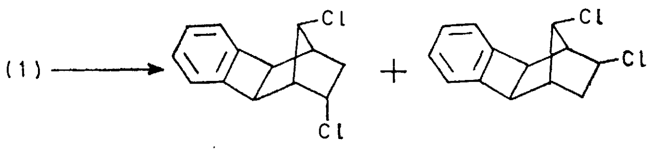


(54)

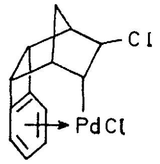
In the phenylene-olefin systems, cupric chloride-promoted breaking of the carbon–chlorine bond in chloronium ion intermediates (53) and (54) is such that the carbonium ion is not sufficiently developed to allow C-1–C-6 shift. Preferential formation of unrearranged *trans*-dichloride (9) from chlorination of *exo*-olefin (2) with cupric chloride is a reflection of the faint bridging present in intermediate chloronium ion (53). The steric influence of the 5,6-substituent is reflected in total conversion of *endo*-olefin (1) to *cis*-products. Formation of both chloroacetate (6) and dichloride (5) suggests that the inhibition of the more favoured *trans*-approach of nucleophile prolongs intermediacy of (54) sufficiently to permit acetate to compete with chloride ion.

The different nature of chlorination with cupric chloride from that with chlorine is reflected in the products. Treatment of *endo*-olefin (1) with chlorine in dichloromethane gave a mixture of totally rearranged dichlorides (55) and (56) in almost equal amounts.[19]

Ratios of unrearranged products from olefins (1) and (2) in the presence of palladium chloride differ from those in its absence. The discrepancy is much larger in the case of *endo*-olefin (1), being only small in the case of *exo*-isomer (2). Conversion into unrearranged products in the presence of palladium chloride is also much larger with olefin (1), amounting to 58%. The unique position of olefin (1) is further exemplified by the predominance of rearranged products from palladium chloride-catalysed reactions of both *endo*- and *exo*-olefins (3) and (4). Inclusion of palladium chloride obviously affects the course of reaction with olefin (1) to a larger extent than can be attributed to the small change in conditions. Decomposition of the π-complex (see Scheme 6) derived from (1) by attack of chloride or acetate ion can eventually lead to an intermediate with ionic character. Trapping by chloride ion occurs extremely readily to form unrearranged *cis*-dichloride (5). This occurs in competition with migration of the C-1–C-6 bond leading to rearranged product (7). It is suggested that the second chloride for formation of (5) originates from a tight or intimate ion pair formed on decomposition of the π-complex, together with the palladium–copper species (39). Thus, trapping of the intermediate occurs before extensive rearrangement takes place. A favourable explanation for this effect is based upon complexation of the palladium species already σ-bonded to the norbornyl skeleton, with the π-cloud of the benzene ring (57). Support for such association is provided by the existence of a bisarene complex of palladium(II).[20]



(55) (56·5%) (56) (43·3%)



(57)

EXPERIMENTAL

Laporte Industries activated alumina type H and Grace silica were used in chromatography. Light petroleum used for eluant or for recrystallisation had b.p. 40—60° unless otherwise stated. A Pye 104 chromatograph was employed for all g.l.c. analysis (nitrogen carrier gas through glass columns 5 ft × 0·25 in). N.m.r. spectra were obtained with tetramethylsilane as internal standard and deuteriochloroform as solvent.

Olefins (1) and (2) were prepared by the addition of benzocyclobutene to cyclopentadiene [21] and the addition of

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[16] T. Koyana, *Bull. Chem. Soc. Japan*, 1970, **43**, 1439.

[17] T. Koyana, *Bull. Chem. Soc. Japan*, 1970, **43**, 3501.

[18] T. Koyana and O. Watanabe, *Bull. Chem. Soc. Japan*, 1971, **44**, 1378.

[19] M. Avram, I. Rogany, I. D. Dinulescu, F. Chiraleu, and C. D. Nenitzescu, *Rev. Roumaine Chim.*, 1970, **15**, 1207.

[20] R. S. Nyholm, 'Proceedings of the 8th International Conference on Co-ordination Chemistry,' Vienna, 1964, p. 149.

[21] M. P. Cava and M. J. Mitchell, *J. Amer. Chem. Soc.*, 1959, **81**, 5409.

benzyne to norbornadiene,[22] respectively, and (3) and (4) by reaction of acenaphthylene and cyclopentadiene.[9]

Reactions with Palladium Chloride–Cupric Chloride.—The general procedure was to heat the olefins (0·018 mol) with palladium chloride (0·086 g, 0·0048 mol), cupric chloride (4·29 g, 0·030 mol), and anhydrous sodium acetate (1·34 g, 0·017 mol) in freshly distilled glacial acetic acid (25 ml) at 80° for 72 h. After cooling and addition of water (200 ml), the products were extracted with ether (3 × 75 ml) and washed with sodium hydrogen carbonate solution. G.l.c. analysis of the crude products were made on a 5% diethylene glycol succinate column at 175° at 60 ml min^{-1} nitrogen flow.

TABLE 2

Physical data of products from reaction of (1)—(4) with palladium chloride and cupric chloride in acetic acid

Compound	M.p. (°C)	Analysis (%)	$\nu_{max.}$ (Nujol)/cm^{-1}	*m/e*
(5)	121—123	Found: C, 65·5; H, 4·9; Cl, 29·45. $C_{13}H_{12}Cl_2$ requires C, 65·3; H, 5·05; Cl, 29·55	940, 900, 755, 725, 680	167 (100%), 142 (70), 129 (70), 141 (63), 102 (56), 203 (42), 115 (42), 205 (14), 238 (9) (*M*), 240 (6), 242 (1)
(6)	136—138	Found: C, 68·7; H, 5·75; Cl, 13·55. $C_{15}H_{15}ClO_2$ requires C·68·6; H, 5·7; Cl, 13·5	1735, 1235, 1055, 760, 725	43 (100%), 142 (72), 167 (33), 129 (30), 141 (26), 202 (25), 91 (23), 77 (22), 155 (13), 227 (11), 128 (11), 115 (11), 262 (3) (*M*), 264 (1)
(7)	133·5—135	Found: C, 68·6; H, 5·75; Cl, 13·1. $C_{15}H_{15}ClO_2$ requires C 68·6; H 5·7; Cl, 13·5	1735, 1240, 1060, 760	167 (100%), 43 (48), 138 (36), 139 (33), 168 (24), 166 (24), 145 (24), 165 (21), 141 (20), 155 (18), 262 (15) (*M*), 264 (5)
(8)	152—153	Found: C, 65·2; H, 5·15. $C_{13}H_{12}Cl_2$ requires C, 65·3; H, 5·05	1265, 928, 908, 755, 745, 670	129 (100%), 167 (71), 142 (66), 163 (61), 141 (50), 128 (36), 165 (32), 115 (29), 102 (29), 92 (29), 75 (29), 238 (25) (*M*), 240 (18)
(9)	59·5—61·0	Found: C, 65·5; H, 5·35. $C_{13}H_{12}Cl_2$ requires C, 65·3; H, 5·05	1290, 1210, 935, 835, 800, 770, 742	142 (100%) 167 (70), 141 (50), 129 (40), 115 (32), 128 (30), 165(25), 203 (21), 102 (21), 238 (18) (*M*), 240 (12), 242 (2)
(10)	89—90	Found: C, 68·65; H, 5·75. $C_{15}H_{15}ClO_2$ requires C, 68·6; H, 5·7	1735, 1440, 1267, 1058, 735	167 (100%), 43 (59), 128 (30), 129 (25), 155 (23), 145 (15), 168 (14), 141 (13), 105 (12), 262 (11) (*M*), 264 (4)
(11)	192—194		1605, 925, 908, 780, 765, 705	153 (100%), 152 (92), 288 (44) (*M*), 217 (34), 154 (30), 290 (29), 65 (23), 15 (22), 165 (20), 101 (15)
(13)	172—174		1730, 1250, 1068, 830, 789	312 (100%), 152 (95), 153 (40), 217 (39), 314 (33), 313 (18), 216 (18), 165 (18), 202 (16), 43 (13)
(12)	Oil			152 (100%), 153 (70), 43 (38), 55 (36), 57 (34), 69 (32), 217 (30), 41 (28), 312 (12) (*M*), 165 (24)
(14)	185—187		1603, 1320, 915, 830, 783, 715	152 (100%), 153 (91), 57 (70), 288 (49) (*M*), 55 (49), 43 (49), 41 (42), 69 (40), 290 (33), 292 (6)
(15)	154—155		1312, 1280, 940, 830, 823, 790, 740	152 (100%), 153 (93), 288 (84) (*M*), 290 (54), 187 (30), 217 (27), 102 (21), 189 (18), 165 (18), 66 (18), 292 (9)
(16)	120—122		1725, 1603, 1235, 1065, 900, 835, 795, 710	57 (100%), 43 (95), 55 (90), 69 (70), 41 (63), 71 (59), 152 (32), 312 (23) (*M*), 217 (11), 314 (8)

The crude product was dissolved in benzene and chromatographed on neutral alumina (150 g). Elution was with light petroleum, mixtures of light petroleum and benzene, benzene, and benzene–diethyl ether mixtures, successively. In general, the *cis*-dichlorides were eluted with light petroleum, *trans*-dichlorides required benzene–light petroleum (1 : 9), and the chloroacetates benzene–light petroleum (1 : 1) or benzene–diethyl ether. The products were crystallised from light petroleum–diethyl ether mixtures and the physical data are summarised in Table 2. In all reactions the olefin was completely consumed and material balances were assessed by comparison of the total weight of crude product with the combined weights of the components purified by column chromatography. The products were demonstrated to be stable under the reaction and g.l.c. conditions and comparison of the weights of products isolated and percentages obtained by g.l.c. methods were similar. In a typical experiment, from (1) (3·0 g) was obtained 4·2 g of crude product which yielded (5) (1·63 g), (6) (0·25 g), and (7) (1·43 g) after column chromatography. Reactions with olefins (1)—(4) and cupric chloride were carried out in an identical manner.

Conversion of Chloroacetate (7) *into Chlorohydrin* (20).—Lithium aluminium hydride (0·1 g) was added to (7) (0·5 g) in dry diethyl ether (10 ml) and the mixture stirred at room temperature for 2 h. Sodium hydroxide solution (2N) was added dropwise until the precipitate coagulated. After drying and distillation of the ether, the crude solid (0·4 g) was chromatographed on silica and exo-5-*chloro*-7-*hydroxy*-exo-2,3-(o-*phenylene*)*norbornane* (20) (0·2 g) was obtained on elution with benzene, m.p. 102—103° (Found: C, 70·85; H, 5·95; Cl, 15·95. $C_{13}H_{13}ClO$ requires C, 70·9; H, 5·9; Cl, 15·9%), $\nu_{max.}$ (Nujol) 3200, 1360, 1310, 1180, 1120, 1080, 1040, 1040, and 750 cm^{-1}, *m/e* 129 (100%), 128 (74), 145 (50), 155 (41), 115 (39), 167 (36), 141 (30), 127 (21), 142 (20), 70 (20), 220 (10) (*M*), and 222 (3). The endo-*phenylene isomer* (22) was prepared in a similar manner, m.p. 116—117° (Found: C, 70·85; H, 6·0%), $\nu_{max.}$ (Nujol) 3300, 1305, 1265, 1110, 1075, 915, 765, and 740 cm^{-1}, *m/e* 128 (100%), 129 (88), 155 (66), 167 (56), 145 (56), 141 (50), 184, (44), 115 (44), 153 (38), 152 (34), 220 (9) (*M*), and 222 (3).

Dehydrochlorination of Compound (20).—A solution of

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[22] H. E. Simmonds, *J. Amer. Chem. Soc.*, 1961, **83**, 1657.

potassium t-butoxide (0·7 g) in dimethyl sulphoxide (3·75 ml) was added to a vigorously stirred solution of (20) (0·5 g) in dimethyl sulphoxide (1·25 ml). After 24 h, the solution was poured into water (25 ml) and acidified with 50% sulphuric acid. The mixture was extracted with diethyl ether and after drying ($MgSO_4$) the solvent was evaporated and the residual solid recrystallised from light petroleum–diethyl ether to give 7-*hydroxy*-exo-5,6-(o-*phenylene*)*norborn*-2-*ene* (21), m.p. 94·5—96·0° (Found: C, 84·75; H, 6·55. $C_{13}H_{12}O$ requires C, 84·8; H, 6·5%), $\nu_{max.}$ ($CHCl_3$) 3400, 2900, 1458, 1277, 1212, 1099, 1085, 1047, and 708 cm^{-1}; *m/e* 129 (100%), 156 (88), 154 (79), 142 (71), 165 (59), 116 (59), 184 (53) (*M*), 153 (47), 166 (41), 130 (41), and 103 (41).

Conversion of Compound (22) *into* (24).—Lithium wire (150 mg) was added to a solution of (22) (190 mg) and t-butyl alcohol (1·0 ml) in tetrahydrofuran (10 ml) under nitrogen and the mixture refluxed for 18 h. The solution was decanted through glass wool into water (200 ml) and the products extracted with diethyl ether. Evaporation of the dried solvent ($MgSO_4$) gave a crude solid (170 mg) comprising two products in the ratio 2 : 1. Platinum dioxide was added to a solution of the crude mixture (65 mg) in absolute alcohol and hydrogen passed into the solution for 2 h at room temperature, after which the catalyst was filtered off. Evaporation of the solvent afforded the *endo*-phenylenenorbornan-7-ol (24) (64 mg), m.p. 109—110°, $\nu_{max.}$ (Nujol) 3300, 1310, 1290, 1080, 1062, 1037, 760, and 732 cm^{-1}, *m/e* 129 (100%), 145 (70), 128 (60), 115 (31), 127 (23), 168 (22), 130 (22) 142 (20), 116 (15), and 186 (5) (*M*).

Oxidation of Alcohol (24).—The yellow complex (430 mg) formed from chromium trioxide (1·0 g) and pyridine (5 ml) at 0° [23] was added to a solution of (24) (50 mg) in dichloromethane (6·5 ml) and stirred for 21 h. After filtration the dichloromethane solution was washed, dried and evaporated to yield an oil, which was identical with a previously obtained sample of the 7-one (25),[24] $\nu_{max.}$ (Nujol) 1760, 1030, 1000, 760, and 745 cm^{-1}.

Preparation of Epoxides (28) *and* (33).—A solution of *m*-chloroperbenzoic acid (8·0 g) in chloroform (200 ml) was added to a solution of (1) or (2) (3·0 g) in chloroform (100 ml) over 30 min with stirring. The solution was left overnight and washed alternatively with 10% potassium hydroxide solution (2 × 100 ml) and water (2 × 100 ml). After drying, the solvent was removed to yield the epoxides which were recrystallised from light petroleum–diethyl ether: *endo*-phenylene isomer (28), m.p. 60·5—61·5°, $\nu_{max.}$ (Nujol) 2930, 1461, 1380, 962, 855, 758, and 734 cm^{-1}; *exo*-phenylene isomer (33), obtained as a clear oil, $\nu_{max.}$ (Nujol) 3010, 2950, 1460, 1378, 1280, 1200, 1000, 855, and 750 cm^{-1}.

Reactions of Epoxides with Hydrobromic Acid.—Compound (28) (0·5 g) was dissolved in diethyl ether (10 ml) and 48% hydrobromic acid (1 ml) added. The two-phase mixture was vigorously shaken at room temperature for 14·5 h before pouring into water. Extraction with diethyl ether and evaporation of the dried solvent yielded a pale yellow, viscous oil (0·67 g). G.l.c. analysis (diethylene glycol succinate 5%) at 175° revealed an 86% conversion into a mixture of two rearranged bromohydrins (29) and (30) which could not be separated and their structures were assigned from g.l.c.–mass spectral evidence: *exo*-5-bromo-isomer (29), *m/e* 129 (100%), 167 (75), 128 (68), 115 (57), 185 (43), 141 (43), 155 (33), 57 (29), 152 (25), 91 (25), 77 (25), 266 (3), and 264 (3) (*M*); *endo*-5-bromo-isomer (30), *m/e* 129 (100%), 167 (72), 128 (60), 115 (56), 141 (40), 185 (36), 155 (28), 152 (26), 127 (24), 77 (24), 266 (4), and 264 (4) (*M*). Relative g.l.c. retention times (29) : (30) = 1·00 : 1·40. Treatment of the mixture of isomers with potassium t-butoxide in dimethyl sulphoxide, as previously described produced the hydroxy-olefin (21).

A similar procedure was employed for treatment of compound (33) with hydrobromic acid and (28) and (33) with 39·6% hydrochloric acid: *exo*-5-bromo-isomer (34), m.p. 118—119°, $\nu_{max.}$ (Nujol) 1310, 1275, 1255, 1239, 1105, 1075, 915, 765, and 740 cm^{-1}, *m/e* 129 (100%), 167 (67), 128 (64), 185 (55), 57 (55), 115 (50), 43 (42), 141 (39), 155 (28), 107 (25), 266 (3), and 264 (3) (*M*); *endo*-5-bromo-isomer (35), m.p. 128—130°, $\nu_{max.}$ (Nujol), 1280, 1190, 1025, 985, 935, 765, and 740 cm^{-1}, *m/e* 57 (100%), 129 (67), 142 (50), 115 (30), 141 (27), 185 (25), 128 (20), 77 (14), 167 (13), 102 (13), 266 (4), and 264 (4) (*M*). From compound (33) and hydrochloric acid were obtained the chlorohydrins (22) and (36), m.p. 112—114°, $\nu_{max.}$ (Nujol), 3350, 1390, 1320, 1220, 1040, 1000, 950, 820, 770, and 750 cm^{-1}.

Solvolysis of Bromohydrin (29).—Treatment of compound (29) (80 mg) with 10% aqueous silver nitrate solution (10 ml) for 4 h at room temperature yielded an oil (70 mg) after extraction with diethyl ether and evaporation of the dried solvent. This was shown to be the *exo*-phenylene-5,7-diol, τ (CCl_4) 2·97 (4H, m, aromatic), 6·30 (1H, m, α-OH), 6·55 (3H, m, α-OH and hydroxy-groups), 7·00 (2H, s, benzylic), 7·83 (2H, m, bridgehead), and 8·12 (2H, m, geminal), $\nu_{max.}$ (Nujol) 3400, 2960, 1625, 1445, 1285, 1110, 1070, 870, and 755 cm^{-1}. Benzylic proton signals at τ 7·00, together with those for α-OH at 6·30 and 6·55 provide confirmation for the retained *exo*-phenylene configuration and the *exo*-arrangement of the 5-hydroxy-substituent. Similar treatment of compound (34) at 100° gave the *endo*-phenylene-5,7-diol (46), τ (CCl_4) 2·88 (4H, m, aromatic), 5·84 (3H, s, α-OH and hydroxy-groups), 6·46 (3H, m, benzylic and α-OH), 7·47 (2H, m, bridgehead), and 8·40 (2H, m, geminal), $\nu_{max.}$ (Nujol) 3400, 2950, 1630, 1360, 1220, 1095, 1060, and 750 cm^{-1}. Confirmation for the retained *endo*-phenylene stereochemistry is provided by benzylic proton signals at τ 6·46 whilst the α-OH proton at τ 6·46 indicates *exo*-orientation of this substituent.

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[3/1503 *Received*, 17*th July*, 1973]

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[23] R. Ratcliffe and R. Rodehorst, *J. Org. Chem.*, 1970, **35**, 4000.

[24] J. C. Salter, Ph.D. Thesis, University of Southampton, 1972.