# Medium-sized Cyclophanes. Part XVI.[1] Substitution *versus* Transannular Reaction of [2.2]Metacyclophanes with Benzoyl Peroxide and Cupric Chloride. Importance of a Cation Radical Intermediate in the Transannular Dehydrogenation

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Two types of reactions occur when [2.2]metacyclophane (1) was treated with benzoyl peroxide (BPO) and cupric chloride in acetonitrile; one is nuclear substitution giving the 4-benzoate and the 8-cyanomethyl derivatives, each formed by a radical attack *via* a cyclohexadienyl intermediate, and the other is transannular dehydrogenation to give pyrene and hydropyrenes. The latter reaction occurs with BPO alone or with other metal halides. Transannular dehydrogenation is favoured for alkyl derivatives of (1). No nuclear substitution occurs with the 5,13-dimethyl derivative (12a). Relative rates of dehydrogenation induced by cupric chloride are 1, 160, 120, and 40 for (1), (12a), the diethyl derivative (12b), and the tetramethyl derivative (19), respectively. These rates are related to ionization potentials and the stability of an intermediate. The importance of a cation radical intermediate formed by an one-electron transfer process is advanced.

UNDER a variety of conditions, [2.2]metacyclophane (1) undergoes transannular reactions.[2] Two types of reaction have been recognized, dehydrogenation to give 4,5,9,10-tetrahydropyrene (2), and cycloisomerization to give 1,2,3,3a,4,5-hexahydropyrene (3).

(1)   (2)   (3)   (4)
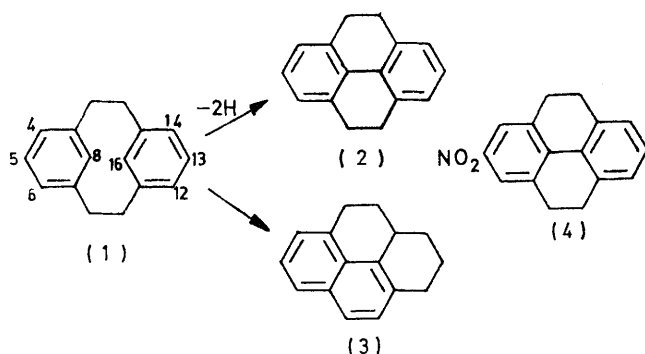
Photolytic[3] and electrophilic[4] reactions gave compound (2) as the initial product and this was further dehydrogenated or substituted. For example nitration gave (4) *via* (2).[4a,b,d] Generation of an anion radical by reduction of (1) with alkali metal also gave (2).[5]

On the other hand, compound (1) gave (3) on treatment with iodine.[6] Though less effective aluminium chloride [7a,†] and sulphuric acid † also gave (3). With cupric chloride or ferric chloride, however, compound (2) but not (3) was formed.[8]

† With aluminium chloride, compound (1) gave octahydro-, m.p. 76—77°, and decahydro-pyrenes, m.p. 53·5—54·5°, as well as compounds (2), (3), and (6). By treatment with concentrated sulphuric acid, compound (1) produced (2), (3), (6), and octahydropyrene.

‡ Other examples are dehydrogenation of compound (1) over palladium–charcoal gave (6),[7a] while hydrogenation gave perhydropyrene.[7b]

Owing to these ready transannular reactions,‡ substitution without transannular bonding has never been realized, although the method would appear to be the one of choice to make substituted derivatives of (1). In fact, compared with the analogous paracyclophane, only a small number of derivatives of compound (1) are known. Unsymmetrically substituted derivatives have been especially difficult to prepare [9] and require special synthetic techniques.[10-13]

In this paper we describe the successful introduction of 4- as well as 8-substituents into compound (1) by the use of a free-radical reaction.[8a] We also discuss the mechanism of the transannular reactions, and present evidence on the importance of an electron-transfer process for the transannular dehydrogenation step.

RESULTS AND DISCUSSION

Nuclear Substitution.—The benzylic positions of compound (1) are known to be extremely inert to chemical transformations, since benzylic stabilization of a radical or cation is not possible because of the unfavourably rigid molecular geometry.[14] Utilizing this

1 Part XV, T. Sato and K. Uno, *J.C.S. Perkin I*, 1973, 895.

2 (a) R. W. Griffin, jun., *Chem. Rev.*, 1963, **63**, 45; (b) T. Sato, *Nippon Kagaku Zasshi*, 1971, **92**, 277; (c) F. Vögtle and P. Neumann, *Angew. Chem. Internat. Edn.*, 1972, **11**, 73.

3 (a) T. Sato, E. Yamada, Y. Okamura, T. Amada, and K. Hata, *Bull. Chem. Soc. Japan*, 1965, **38**, 1049; (b) T. Sato, S. Akabori, S. Muto, and K. Hata, *Tetrahedron*, 1968, **24**, 5557; (c) T. Sato, M. Wakabayashi, S. Hayashi, and K. Hata, *Bull. Chem. Soc. Japan*, 1969, **42**, 773; (d) T. Sato, K. Nishiyama, S. Shimada, and K. Hata, *ibid.*, 1971, **44**, 2858; (e) S. Hayashi and T. Sato, *ibid.*, 1972, **45**, 2360.

4 (a) N. L. Allinger, M. A. DaRooge, and R. B. Hermann, *J. Amer. Chem. Soc.*, 1961, **83**, 1947; (b) M. Fujimoto, T. Sato, and K. Hata, *Bull. Chem. Soc. Japan*, 1967, **40**, 600; (c) T. Sato, M. Wakabayashi, Y. Okamura, T. Amada, and K. Hata, *ibid.*, 1967, **40**, 2363; (d) N. L. Allinger, B. J. Gordon, H.-E. Hu, and R. A. Ford, *J. Org. Chem.*, 1967, **32**, 2272; (e) R. W. Griffin, jun., and R. A. Coburn, *ibid.*, p. 3956.

5 W. B. Martin and F. Gerson, *J. Amer. Chem. Soc.*, 1969, **91**, 1883; H. Kowata, M. Hoshino, and M. Koizumi, Abstracts, 24th Annual Meeting of the Chemical Society of Japan, Osaka, 1971.

6 T. Sato, K. Nishiyama, and A. Murai, *J.C.S. Chem. Comm.*, 1972, 163; T. Sato and K. Nishiyama, *J. Org. Chem.*, 1972, **37**, 3254.

7 (a) W. Baker, J. F. W. McOmie, and J. M. Norman, *J. Chem. Soc.*, 1951, 1114; (b) E. Larger and H. Lehner, *Tetrahedron Letters*, 1973, 1143.

8 Preliminary account, T. Sato and K. Nishiyama, *J.C.S. Chem. Comm.*, 1973, 220.

9 V. Boekelheide, C. Ramey, E. Sturm, T. Miyasaka, and B. A. Hess, jun., *J. Org. Chem.*, 1969, **34**, 1956.

10 H. E. Zimmerman and G. Jones II, *J. Amer. Chem. Soc.*, 1970, **92**, 2735.

11 R. H. Mitchell and V. Boekelheide, *J. Amer. Chem. Soc.*, 1970, **92**, 3510.

12 E. Langer and H. Lehner, *Tetrahedron*, 1973, **29**, 375.

13 V. Boekelheide, I. D. Reingold, and M. Tuttle, *J.C.S. Chem. Comm.*, 1973, 406.

14 B. H. Smith, ' Bridged Aromatic Compounds,' Academic Press, New York, 1964, p. 267.

lack of reactivity and the lowered positional selectivity of the aromatic nuclei towards radical attack we examined the reactions of (I) with benzoyl peroxide (BPO) and cupric chloride.

When a mixture of compound (1), BPO (3 equiv.), and cupric chloride (ca. 0·2 equiv.) in acetonitrile was warmed at 80° for 42 h, five products were formed. Fractions eluting rapidly upon chromatography on neutral alumina eluting with hexane–benzene contained (2) (4·5%), 4,5-dihydropyrene (5) (5·8%), and pyrene (6) (1·6%), each confirmed by comparison with the authentic material. On further elution with benzene, 4-benzoyloxy[2.2]metacyclophane (7a) (5·2%) and 8-cyanomethyl[2.2]metacyclophane (8) (1·6%) were isolated. Representative experiments are summarized in Table 1.
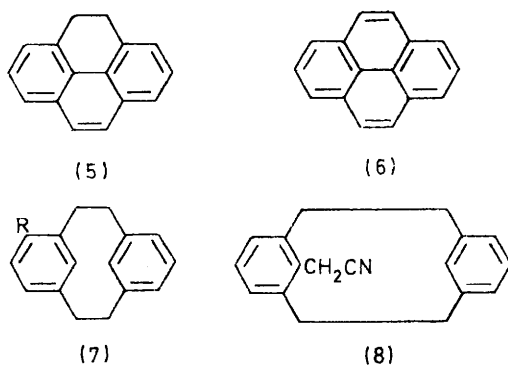
is indicated by the appearance of two types of inner aryl proton signals at δ 4·2—4·3 (d, J 2 Hz) and 4·4—4·6 (t, J 2 Hz).

Table 2 summarizes chemical shifts for the inner aryl proton. 16-H, the inner aryl proton of the unsubstituted side, should appear as a triplet due to *meta*-coupling, whereas 8-H should appear as a doublet. While the chemical shifts of 8-H are similar to that of compound (1) and almost constant, those of 16-H depend on the substituent in the benzene ring opposite. This indicates that the inner aryl proton extends into the ring current of the benzene ring opposite.

The unusual cyanomethyl derivative (8) showed resonances at δ 3·83 (1H) and 1·68 (2H), respectively. On irradiating the aryl protons at 716 Hz (100 MHz) the former signal became a sharp singlet and thus was

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TABLE 1

Yields of reaction products from compound (1) with BPO and/or CuCl$_2$ [a]

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Compound (1) (mmol)	BPO (mmol)	CuCl$_2$ (mmol)	MeCN (ml)	Products (%)				
				(2)	(5)	(6)	(7a)	(8)
0·30	0·55		3·0	13·2	5·1	Trace	8·1	
0·31 [b]	0·57	0·30	3·0	21·4	6·2		8·4	
0·31 [b]	0·59	0·30	3·0	12·5	5·4		12·8	
0·36	0·58		3·0	1·0	1·0	Trace		
0·30		0·30	3·0	20·1	Trace			
3·1 [c]	9·9	ca. 0·6	25	4·5	5·8	1·6	5·2	1·6

[a] Reactions carried out at 80° for 20 h under vacuum (see Experimental section). Product analyses were performed by g.l.c. [b] Sodium hydrogen carbonate added, [(1)]/[NaHCO$_3$] = 1·8. [c] The reaction was carried out at 80° for 42 h in air and products separated by column chromatography.

The benzoate (7a) was obtained as a viscous oil, 1730 cm^{-1} (C=O), m/e 328 (M^+). On alkaline hydrolysis (7a) gave 4-hydroxy[2.2]metacyclophane (7c), which was converted to the methyl ether (7d), m.p. 80—81°. With p-chlorobenzoyl peroxide the corresponding p-chlorobenzoate (7b), $v_{max.}$ 1740 cm^{-1}, m/e 362, was obtained, also as a viscous oil.

The ^{1}H n.m.r. spectra of compounds (7) determined in CDCl$_3$ showed bridging methylene protons as two sets of

assigned to 16-H. The 2H signal was assigned to CH$_2$CN. The signal is shifted to higher field by almost

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TABLE 2

Chemical shifts of 8- and 16-H in CDCl$_3$

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Compound	8-H	16-H
(1)	4·25 (t)	4·25 (t)
(7a)	4·30 (d)	4·60 (t)
(7b)	4·29 (d)	4·55 (t)
(7c)	4·20 (d)	4·42 (t)
(7d)	4·23 (d)	4·36 (t)

1·8 p.p.m. again due to the diamagnetic ring current effect (cf. PhCH_2CN, δ 3·44). Addition of [^{2}H$_{27}$]Eu(fod)$_3$ caused a general downfield shift, which was largest for CH$_2$CN (Δv CH$_2$CN/ArH ca. 5). The fact that all the external aryl protons shifted to low field by a similar magnitude indicated that CH$_2$CN was introduced into the central part of the molecule, namely the 8- but not the 4- or 5-positions.

Dehydrogenation and substitution reactions could be differentiated by selecting the reaction conditions. When cupric chloride was absent neither benzoate (7a) nor nitrile (8) was formed and only a small amount of compound (2) was obtained. Aeration appeared to be necessary for the formation of compound (8) since the deaerated mixture containing cupric chloride did not produce (8). Addition of sodium hydrogen carbonate increased the yield of benzoate (7a) but decreased pyrene formation. Cupric chloride alone was found to dehydrogenate compound (1) to (2) in 20% yield.

Benzoate formation can be explained by attack of a

(5)

(6)

(7)

(8)

a; R = BzO
b; R = p-ClC$_6$H$_4$CO$_2$
c; R = HO
d; R = MeO

multiplets at δ 1·5—3·5. Unequivocal evidence for the cyclophane structure and the position of the substituent

benzoyloxyl radical generated from BPO. The reaction is favoured when hydrogen abstraction from a hexadienyl radical is facilitated by an oxidant such as $CuCl_2$,[15] I_2,[16] or O_2.[17] In our case, oxygen was less effective. Iodine appeared to be the best choice,[18,19] but it caused ready cycloisomerization.[6] According to Kovacic[15] hydrogen abstraction from a cyclohexadienyl radical proceeds most effectively when the ratio of cupric chloride to substrate is 1 : 60. Hashimoto[20] has established the following order for the efficiency of metal halides as oxidants during benzoyloxylation: $CuCl_2 \gg CrCl_2 > MnCl_2 > FeCl_3$, $CoCl_2$, $NiCl_2$. Accordingly, we selected cupric chloride as the oxidant and used a limited amount of the salt to improve the yield of substituted products.

Neither the 5- nor the 8-substituted isomer could be detected in the reaction mixture in spite of careful examination by g.l.c. which could identify <1% of material if present. This can be understood by considering the partial rate factors when m-xylene is introduced into the reaction mixture,[21] from which the reactivity of the 5-position of (1) can be estimated as ca. 1/30 that of the 4-position. The absence of the 8-benzoate is reasonable on steric grounds.

Attack at C-5 can lead to benzoyloxytetrahydropyrene (9a) via the transannular benzoate (10a) followed by

(9)

a; R = BzO
b; R = Ph
c; R = HO

(10)

a; R = BzO
b; R = Ph
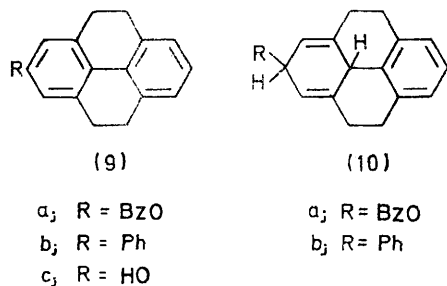
dehydrogenation. The absence of (9a) was proved by comparison with an authentic sample. There is no participation by a phenyl radical in the BPO reaction. With phenylazotriphenylmethane (PAT) in acetonitrile dehydrogenation did not occur nor were phenylation products formed. A possible transannular product is 2-phenyltetrahydropyrene (9b), the absence of which was proved by comparison with authentic material.

The formation of the cyanomethyl compound (8) is somewhat surprising since the 8-position is the least accessible site of the molecule. This can be explained by substitution involving a cyanomethyl radical generated from acetonitrile by hydrogen abstraction.[22] Compound (8) was also formed, though in a low yield, when compound (1) and PAT in acetonitrile were heated

in oxygen. The reaction in the absence of air, however, did not produce (8).

The reaction occurs because (i) the cyanomethyl radical is a highly electrophilic, small, and linear species not subject to steric overcrowding, (ii) the strain energy in the cyclophane structure (13 kcal mol⁻¹)[23] is largely released in a cyclohexadienyl radical intermediate (11), and (iii) attack by an electrophilic species is expected to be assisted by a transannular electronic interaction.

CH₂CN
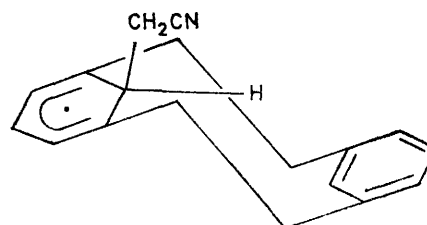
(11)

Transannular Dehydrogenation.—When 5,13-dimethyl-[2.2]metacyclophane (12a) was used as the substrate no

(12)

a; R = Me
b; R = Et

(13)

a; R = Me
b; R = Et

(14)

(15)

(16)

(17)

(18)

(19)
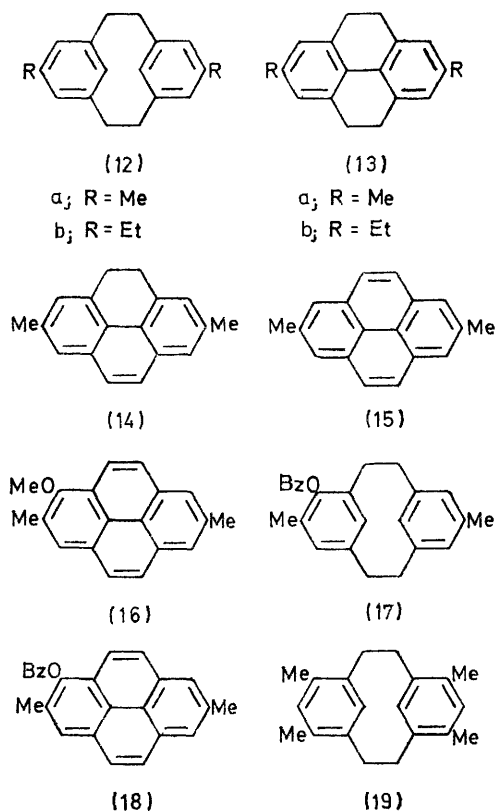
nuclear-substituted products preserving the cyclophane structure were formed but only pyrene derivatives were produced. From the reaction of compound (12a), BPO

[15] M. E. Kurz and P. Kovacic, J. Amer. Chem. Soc., 1967, 89, 4940.

[16] A. Perret and R. Perrot, Helv. Chim. Acta, 1945, 28, 558.

[17] T. Nakata, K. Tokumaru, and O. Simamura, Tetrahedron Letters, 1967, 3303.

[18] M. E. Kurz and P. Kovacic, J. Org. Chem., 1968, 33, 1950.

[19] P. Kovacic, C. G. Reid, and M. J. Brittain, J. Org. Chem., 1970, 35, 2152.

[20] S. Hashimoto, W. Koike, and Y. Matsuda, Kogyo Kagaku Zasshi, 1969, 72, 2277.

[21] P. Kovacic, C. G. Reid, and M. E. Kurz, J. Org. Chem., 1969, 34, 3302.

[22] R. F. Bridger and G. A. Russell, J. Amer. Chem. Soc., 1963, 85, 3754.

[23] C.-F. Shieh, D. McNally, and R. H. Boyd, Tetrahedron, 1969, 25, 3653.

(3·3 equiv.), and cupric chloride (*ca.* 0·5 equiv.) in aceto-nitrile at 80° for 42 h, 2,7-dimethyl-4,5,9,10-tetrahydro-pyrene (13a), 2,7-dimethyl-4,5-dihydropyrene (14), 2,7-dimethylpyrene (15), and a viscous, oily material which showed $v_{max.}$ 1730 cm^{-1} were obtained. Hydrolysis of the latter followed by methylation gave colourless crystals, which n.m.r. and mass spectral and analytical data showed to be 1-methoxy-2,7-dimethylpyrene (16). The oily material is thus 1-benzoyloxy-2,7-dimethylpyrene (18), which can be formed either by benzoyloxylation followed by dehydrogenation [(12a) —→ (17) —→ (18), path a] or by step-wise dehydrogenation followed by benzoyloxylation [(12a) —→ (13a) —→ (14) —→ (15) —→ (18), path b].

To choose between these two possibilities, the reaction of (12a) with BPO and/or cupric chloride was examined (Table 3). Unlike compound (1), which gave only a

found effect. Rate enhancement occurs with reagents having higher electron affinity. Dehydrogenation is possible only with electrophilic radical sources such as BPO, substituted BPO, and di-isopropyl peroxydicarb-onate (IPP),[21] but not with di-t-butyl peroxide, azobis-isobutyronitrile, and PAT.[3d]

These facts suggest the importance of an electron-transfer process for the transannular reaction. An electron transfer gives an equilibrium mixture of ion pairs (20). A cation radical (20a) is formed initially which then enters into equilibration with the trans-annular form (20b). It is also probable that electron transfer gives (20b) in a concerted manner. Hydrogen abstraction from (20b) gives (2) *via* (21).

The importance of (20a and b) was confirmed by the solvent effects summarized in Table 5. The solvents selected have low reactivity toward radical hydrogen

TABLE 3

Yields of reaction products from compound (12a) [a]

Compound (12a) (mmol)	BPO(mmol)	CuCl$_2$ (mmol)	FeCl$_3$ (mmol)	Products (%)		
				(13a)	(14)	(15)
0·31	0·60			3·0	6·9	7·5
0·31	0·61	0·30		24·0	39·0	4·2
0·32		0·31		39·7	5·2	Trace
0·31			0·33	26·4	1·7	

[a] The degassed reaction mixture was heated at 80° for 20 h in acetonitrile (3 ml).

small amount of (2) by reaction with BPO (without an added oxidant), compound (12a) gave a total of 12% of (13a), (14), and (15). Similarly metal salts such as cupric chloride or ferric chloride gave a higher yield of pyrenes compared with compound (1) (Tables 1 and 3). The ready dehydrogenation of dimethyl derivative (12a) and the absence of intermediates such as 1-benzoyloxy-2,7-dimethyl-4,5,9,10-tetrahydro- and -4,5-dihydro-pyrenes, suggest that the reaction proceeds by path b. Pyrene is known to be attacked by radicals at the 1-position.[24]

The presence of a methyl group enhances the rate of transannular dehydrogenation for both the BPO and cupric chloride reactions. The relative rates obtained from competitive experiments using CuCl$_2$ for compounds (1), (12a and b), and (19) are shown in Table 4. Alkyl derivatives generally, especially 6,13-isomers, enhance the rate.

TABLE 4

Relative reactivity of transannular dehydrogenation and ionization potentials

	Relative rate	I.P./eV	Benzenoid compound	I.P./eV
(1)	1	8·41 [a]	*m*-Xylene	8·71
(12a)	160	8·26	Mesitylene	8·57
(12b)	120	8·20		
(19)	40	8·14 [a]	Durene	8·45

[a] See ref. 25. Other values were similarly calculated from charge-transfer complex data.

Metal salt and BPO reactions share common features. The position and nature of an alkyl group have a pro-

[24] R. O. C. Norman, G. A. Thompson, and W. A. Waters, *J. Chem. Soc.*, 1958, 175.

abstraction.[22] The yield of pyrenes was found to be dependent on the solvent polarity. For both (1) and
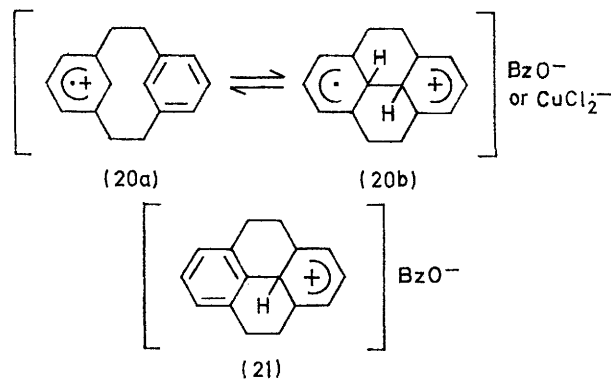
(19) yields increased with higher solvent polarity which stabilizes the ion pair. For compound (12a), however, solvent polarity had little effect on pyrene formation.

The electron-transfer process can be related to the ionization potential of the substrates. As shown in Table 4 the ionization potentials calculated by the Rose–Drago equation [25] are appreciably lower than those for the corresponding methylbenzenes. This must be due to transannular effects and the unique geometrical features of cyclophane molecules and will enhance the electron-transfer process. The alkyl derivatives (12a and b) and (19) are dehydrogenated faster than the parent compound (1). Noteworthy is the large enhancement for the 5,13-dialkyl cases (Table 4). This can be ex-

[25] S. Hayashi and T. Sato, *Nippon Kagaku Zasshi*, 1970, **91**, 950.

plained by an additional factor involving a transannular resonance structure (22), in which cationic and radical centres are stabilized by the methyl group. Such

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TABLE 5

Solvent effects

</div>

Solvent	$\frac{[(1)]/}{[BPO]}$	(2)	(5)	(6)	$\frac{[(1)]/}{M}$
MeCN	0·52	1·0	1·0	Trace	0·1
MeNO$_2$	0·54	2·3	1·6	Trace	0·1
MeCO$_2$H	0·53	Trace	Trace	0	0·1
MeCO$_2$Me	0·53	Trace	Trace	0	0·1

	$\frac{[(12a)]/}{[BPO]}$	(13a)	(14)	(15)	$\frac{[(12a)]/}{M}$
MeCN	0·52	3·0	6·9	7·5	0·1
MeNO$_2$	0·51	12·1	5·2	2·3	0·1
MeCO$_2$H	0·52	3·9	6·8	4·2	0·1
MeCO$_2$Me	0·52	3·2	7·4	3·2	0·1

	[(19)]/[BPO]	Tetrahydro-(19)	Dihydro-(19)	[(19)]/M
MeNO$_2$	0·51	3·7	1·9	0·05
MeCO$_2$H	0·49	Trace	Trace	0·05
MeCO$_2$Me	0·50	Trace	Trace	0·05

stabilization cannot be expected for compounds (1) and (19). The somewhat decreased reactivity of the ethyl homologue (12b) (0·75 that of the dimethyl compound) is the result of loss of hyperconjugation.

(22)
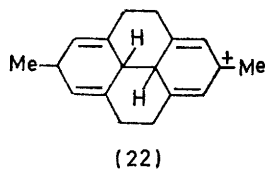
Recently Norman and his co-workers [26] have shown intermolecular aryl coupling through a cation radical intermediate. A more closely related case to ours is intramolecular cyclization induced by electron transfer.[27]

It is probable that the electron-transfer process formulated above might be responsible for the formation of (2) from (1) by an electrophilic reaction.[4] However, whether the reaction with nitronium ion proceeds via electron transfer has not been conclusively settled by a preliminary e.s.r. study.*

EXPERIMENTAL

Methods.—[1]H N.m.r. spectra were obtained on Varian XL-100 or Hitachi R-20B spectrometers using CDCl$_3$ or CS$_2$ solution with tetramethylsilane as internal standard. Mass spectra were obtained with a Hitachi RMU-6E mass spectrometer, ionization current 70 eV. I.r. spectra were recorded on a Hitachi EPI-G2 spectrometer. G.l.c. analyses were performed on a Hitachi K-53 equipped with a flame

* Two alternative routes are conceived for the formation of compound (2) from (1). Elimination of benzoic acid from the transannular benzoate (10a) will afford (2). Dehydrogenation rather than elimination, however, is favoured for (10a), and especially for (10b). In neither case were the substituted tetrahydropyrenes (9a and b) detected. If direct abstraction of hydrogen from C-8 is responsible for transannular dehydrogenation, not only BPO and IPP but also other radical species must be effective. All evidence points to the electron-transfer mechanism and involvement of the ion pair.

ionization detector using 3 mm × 1 m or 2 m stainless steel columns packed with SE-30 or Apiezon grease L both on Daichrom A. M.p.s are uncorrected.

Materials.—Compound (1) was prepared as previously [4b] and was purified by sublimation followed by column chromatography and recrystallization from ethanol, m.p. 132—133°. Compound (12a) was prepared according to the reported procedure,[3b] m.p. 148—149°. The diethyl derivative (12b) was prepared from (12a) by dibromination with N-bromosuccinimide followed by reaction with methylmagnesium iodide. After chromatography on alumina, the product was recrystallized from methanol as plates, m.p. 75—76°, m/e 264 (M^+), δ 1·25 (6H, t) and 2·65 (4H, q) (Found: C, 91·2; H, 9·2. C$_{20}$H$_{24}$ requires C, 90·85; H, 9·15%). The tetramethyl derivative (19) was prepared by the reported method,[3b] m.p. 205—206°.

Commercial hydropyrenes (2), m.p. 137—138°, and (5), m.p. 131—132°, were purified by column chromatography and recrystallization from ethanol, the purity being checked by g.l.c. (>99%). Commercial benzoyl peroxide was purified by crystallization from chloroform–methanol. Anhydrous cupric chloride obtained by drying over P$_2$O$_5$ was employed.

2-Phenyl-4,5,9,10-tetrahydropyrene (9b).—Following Allinger's method [4a,d] the nitrotetrahydropyrene (4) was prepared by nitration of compound (2). Reduction with Pd–C, followed by acetylation and nitrosation gave 2-(N-nitrosoacetylamino)-4,5,9,10-tetrahydropyrene, which was decomposed in benzene. Column chromatographic purification (hexane–benzene) followed by recrystallization from ethanol gave plates, m.p. 126—126·5°, v$_{max}$ (KBr) 870, 765, 755, 725, and 692 cm^{-1}, m/e 282 (M^+), δ 2·81 (8H, s), 6·85 (3H, s), and 7·0—7·3 (7H, m) (Found: C, 93·6; H, 6·35. C$_{22}$H$_{18}$ requires C, 93·6; H, 6·4%).

2-Benzoyloxy-4,5,9,10-tetrahydropyrene (9a).—2-Hydroxy-4,5,9,10-tetrahydropyrene (9c), obtained by diazotization followed by hydrolysis of 2-amino-4,5,9,10-tetrahydropyrene, was treated with benzoyl chloride and pyridine in benzene. A benzene extract was chromatographed on silica gel, eluting with hexane–benzene. Recrystallization from hexane gave needles, m.p. 162—163°, v$_{max}$ (KBr) 1730, 890, 790, and 710 cm^{-1}, m/e 326 (M^+), δ 2·85 (8H, s) and 6·9—8·3 (10H, m) (Found: C, 84·25; H, 5·55. C$_{23}$H$_{18}$O$_2$ requires C, 84·65; H, 5·55%).

Reaction of Compound (1) with BPO and Cupric Chloride.— (a) In air. A mixture of compound (1) (645 mg, 3·1 mmol), BPO (2·4 g, 9·9 mmol), and CuCl$_2$ (135 mg, 1 mmol) in acetonitrile (25 ml) was stirred for 42 h at 80°. After extraction with benzene, the solution was washed with aqueous NaHCO$_3$ and water, dried, concentrated, and passed through alumina. Elution with hexane–benzene gave (1) and pyrenes which were identified by comparison with authentic materials. Further elution with benzene gave 4-benzoyloxy- (7a) and 8-cyanoethyl[2.2]metacyclophane (8): (7a), oil, v$_{max}$ 1730 cm^{-1}, m/e 328 (M^+); (8), needles, m.p. 181—182°, v$_{max}$ (KBr) 2350 cm^{-1}, m/e 247 (M^+) (Found: C, 87·4; H, 6·95. C$_{18}$H$_{17}$N requires C, 87·4; H, 6·95%).

Similar reaction using p-chlorobenzoyl peroxide produced

[26] D. R. Harvey and R. O. C. Norman, J. Chem. Soc., 1964, 4860; R. A. McClelland, R. O. C. Norman, and C. B. Thomas, J.C.S. Perkin I, 1972, 562; R. O. C. Norman, C. B. Thomas, and J. S. Willson, ibid., 1973, 325.

[27] L. J. Kricka and A. Ledwith, J.C.S. Perkin I, 1973, 294; L. L. Miller, F. R. Stermitz, and J. R. Falck, J. Amer. Chem. Soc., 1973, 95, 2651.

compound (7b), $\nu_{max.}$ 1740 cm^{-1}, m/e 362 (M^+), among other products.

(b) *Under vacuum.* A reaction tube containing compound (1) (62 mg, 0·30 mmol), BPO (138 mg, 0·57 mmol), CuCl$_2$ (40 mg, 0·30 mmol), and acetonitrile (3 ml) was evacuated by repeated freeze–thaw cycles. The tube was heated at 80° for 20 h. The work-up was as before. Several examples are summarized in Table 1. The reactions of compounds (12a and b) and (19) were carried out in the same way.

Solvent effects were studied in the same way (Table 5).

Kinetics.—In competitive experiments using cupric chloride, relative rates were calculated from the Ingold–Show equation.[28] The relative rates did not vary when the ratio of the substrates were changed.

Preparations of Authentic Samples.—2,7-Dimethyl-4,5,9,10-tetrahydropyrene (13a) was identified by comparison with an authentic sample formed by irradiation of (12a) in the presence of iodine.[3a] 2,7-Dimethylpyrene (15),

m.p. 229—230°, was prepared by dehydrogenation of 2,7-di-methyl-1,2,3,3a,4,5-hexahydropyrene [6] over Pd–C. An authentic specimen of 2,7-diethyl-4,5,9,10-tetrahydropyrene (13b), m.p. 145—146°, was prepared by photo-dehydrogenation of (12b) in the presence of iodine.[3] Similarly 1,3,6,8-tetramethyl-4,5,9,10-tetrahydropyrene, m.p. 196—197°, was prepared by photolysis of (19).[3]

4-Methoxy[2.2]metacyclophane (7d).—Hydrolysis of compound (7a) in alkaline aqueous ethanol gave (7c) as a paste, $\nu_{max.}$ (KBr) 3500 cm^{-1}, m/e 224 (M^+).

Compound (7c) was then treated with dimethyl sulphate without being purified. The *methyl ether* (7d) was obtained by column chromatography (hexane) and recrystallized from methanol, plates, m.p. 80—81°, $\nu_{max.}$ (KBr) 2850 and 1250 cm^{-1}, m/e 238 (M^+) (Found: C, 85·35; H, 7·85. C$_{17}$H$_{18}$O requires C, 85·7; H, 7·6%).

[28] C. K. Ingold and F. R. Show, *J. Chem. Soc.,* 1927, 2918.