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Studies in the Cycloproparene Series: Reactions with Radicals

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Abstract

The behaviour of 1*H*-cyclopropabenzene (1) and 1*H*-cyclopropa[*b*]naphthalene (23) towards a variety of radicals results in opening of the three-membered ring to give *ortho*-substituted benzyl and 2-methylnaphthalene derivatives, e.g. (13) and (28), respectively. Ring expansion into the cycloheptatriene manifold by way of addition to the bridge bond and norcaradiene formation have not been observed. Analogous reactions with the methylidenecyclopropa[*b*]naphthalenes (33) and (34) lead to much decomposition, and provide little evidence for the C 1 cycloproparenyl radicals (35) and (36).

In the 30 years since Anet and Anet[1] recorded the first authenticated synthesis of a cyclopropparene derivative, many facets of this intriguing class of compounds have been examined[2] and the ring system has been found attractive for a variety of synthetic purposes.[3,4] However, many fundamental features associated with the ring system remain to be explored. Thus the 1*H*-cycloproparenyl radical has yet to be detected[5] despite the fact that the corresponding anion is well known and easily

[1] Anet, R., and Anet, F. A. L., *J. Am. Chem. Soc.*, 1964, **86**, 525.
[2] Halton, B., 'Cycloproparenes' in 'The Chemistry of the Cyclopropyl Group' Part 3 (John Wiley: Chichester 1995, in press).
[3] Halton, B., Kay, A. J., McNichols, A. T., Stang, P. J., Boese, R., Haumann, T., Apeloig, Y., and Maulitz, A. H., *Tetrahedron Lett.*, 1993, **34**, 6151.
[4] Halton, B., Cooney, M. J., and Wong, H., *J. Am. Chem. Soc.*, 1994, **116**, 11574; McNichols, A. T., Stang, P. J., Halton, B., and Kay, A. J., *Tetrahedron Lett.*, 1993, **34**, 3131; Kagabu, S., Saito, K., Watanabe, H., Takahashi, K., and Wada, K., *Bull. Chem. Soc. Jpn*, 1991, **64**, 106; Neidlein, R., and Krämer, B., *Chem. Ber.*, 1991, **124**, 353; Neidlein, R., Constantinescu, T., and Kohl, M., *Phosphorus, Sulfur Silicon Relat. Elem.*, 1991, **59**, 165; Neidlein, R., and Kohl, M., *Helv. Chim. Acta*, 1990, **73**, 1497; Neidlein, R., Krämer, B., and Krieger, C., *Z. Naturforsch., Teil B*, 1990, **45**, 1577; Mynott, R., Neidlein, R., Schwager, H., and Wilke, G., *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 367; Schwager, H., Reactions of Cyclopropabenzenes with Nickel(0) Complexes—Synthesis of Nickelabenzocyclobutenes and Methanobridged Annulenes, Ph.D. Thesis, University of Bochum, 1986.
[5] Ingold, K. U., 1985, personal communication.

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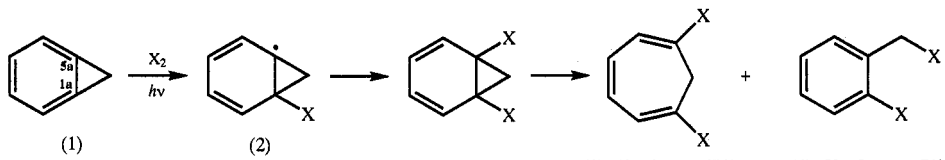
available,[2,6,7] and the cation equivalent formed upon ionization of appropriate 1-halo derivatives.[8] While we have yet to obtain the essential experimental evidence to substantiate unequivocally the existence of a C 1 1*H*-cyclopropabenzenyl radical, we provide here an account of the behaviour of 1*H*-cyclopropabenzene* (1), 1*H*-cyclopropa[*b*]naphthalene (23) and the methylidenecyclopropa[*b*]naphthalene derivatives (33) and (34) towards a variety of radical reagents.



Scheme 1

The interaction of cyclopropabenzenes with radical species has not previously been subjected to detailed examination. However, Okazaki and his coworkers[9] have found that (1) reacts with iodine and thiocyanogen under photochemical conditions to give 1,6-disubstituted cycloheptatrienes (3) and (5), respectively, as the major products of reaction (Scheme 1). The formation of these compounds is explicable in terms of radical addition ($I^{\bullet}$ or $SCN^{\bullet}$) to C 1a of (1) to give a norcaradienyl radical (2) whose capture is followed by facile electrocyclic ring-opening to (3)/(5). When the reactions are performed in the dark the *o*-substituted benzyl derivatives (4) and (6) predominate (Scheme 1),[9,10] and electrophilic addition with opening of the three-membered ring is presumed to be involved.[11,12] To the best of our knowledge, these reactions provide the only reported examples of interaction between a cyclopropabenzene and a radical species. As a consequence we have exposed the cyclopropabenzene hydrocarbons (1) and (23) to a variety of radical reagents, and also attempted to generate a C 1 cyclopropabenzenyl radical from similar reactions with the alkylidene derivatives (33) and (34).

* IUPAC and the Chemical Abstracts Service are unanimous in naming (1) as bicyclo[4.1.0]hepta-1,3,5-triene whereas with (23) cyclopropa fusion nomenclature applies. For the convenience of comparison with (23), the ring system (1) is named in the text as 1*H*-cyclopropabenzene.

[6] Eaborn, C., Eidenschink, R., Harris, S. J., and Walton, D. M. R., *J. Organomet. Chem.*, 1977, **124**, C27; Eaborn, C., and Stamper, J. G., *J. Organomet. Chem.*, 1980, **192**, 155.

[7] Halton, B., and Stang, P. J., *Acc. Chem. Res.*, 1987, **20**, 443.

[8] Halton, B., Hugel, H. M., Kelly, D. P., Müller, P., and Burger, U., *J. Chem. Soc., Perkin Trans. 2*, 1976, 258; Müller, P., and Thi, H. C. N., *Isr. J. Chem.*, 1981, **21**, 135; Müller, P., and Rodriguez, D., *Helv. Chim. Acta*, 1986, **69**, 1546.

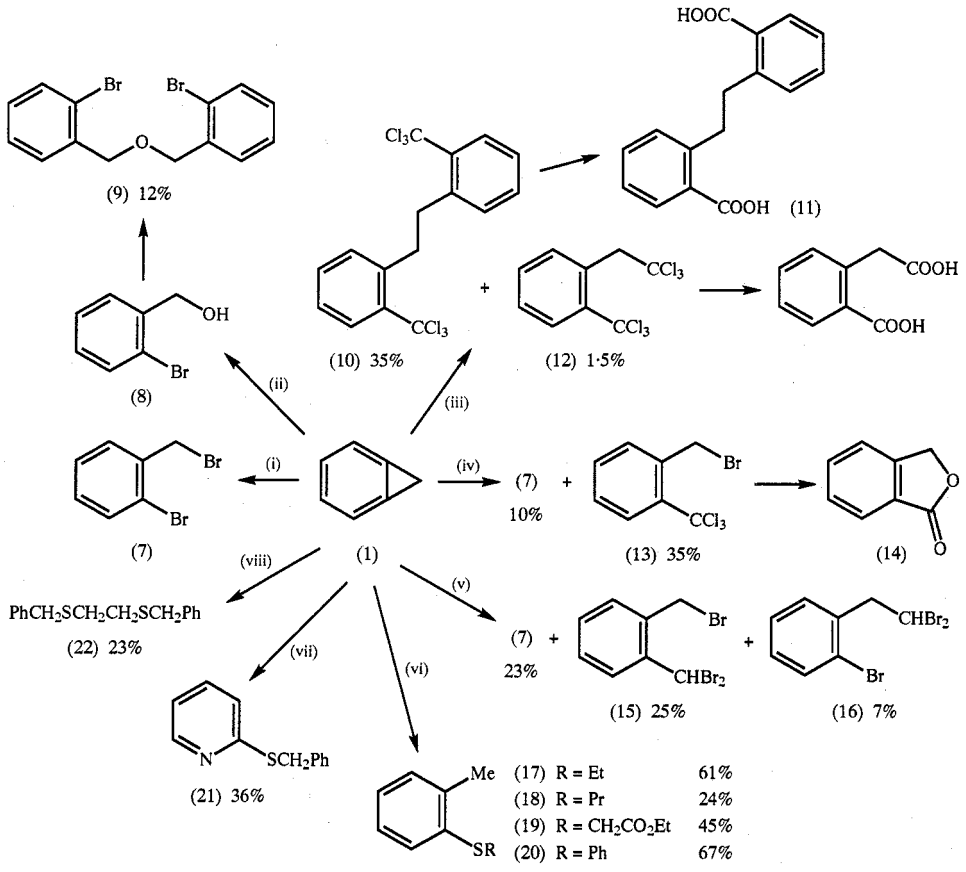
[9] Okazaki, R., O-oka, M., Tokitoh, N., and Inamoto, N., *J. Org. Chem.*, 1985, **50**, 180; Okazaki, R., O-oka, M., Tokitoh, N., Shishido, Y., and Inamoto, N., *Angew, Chem., Int. Ed. Engl.*, 1981, **20**, 799.

[10] Vogel, E., Grimme, W., and Korte, S., *Tetrahedron Lett.*, 1965, 3625.

[11] Bee, L. K., Garratt, P. J., and Mansuri, M. M., *J. Am. Chem. Soc.*, 1980, **102**, 7076.

[12] Billups, W. E., Chow, W. Y., and Smith, C. V., *J. Am. Chem. Soc.*, 1979, **96**, 1979; Billups, W. E., and Rodin, W. A., *J. Org. Chem.*, 1988, **53**, 1312; Christen, D., Ph.D. Thesis, University of Heidelberg, 1986; Neidlein, R., and Christen, D., *Helv. Chim. Acta*, 1986, **69**, 1623; Neidlein, R., Christen, D., Poignée, V., Boese, R., Bläser, D., Gieren, A., Ruiz-Perez, C., and Hübner, Th., *Angew, Chem., Int. Ed. Engl.*, 1988, **27**, 294.

The behaviour of the volatile and highly odoriferous cyclopropabenzene (1) with a range of reagents in the presence of radical initiators (or under other conditions conducive to radical generation) is depicted in Scheme 2. While the reactions have proved difficult to monitor, bromination of (1) with *N*-bromosuccinimide in dichloromethane at 40°C leads to *o*-bromobenzyl bromide (7) but in a meagre 16% yield. This compares well with its behaviour in aqueous *N*-bromosuccinimide where electrophilic addition (Br_2/H_2O) may be activated by ultrasound and leads to ether (9) albeit in 12% yield, probably by way of *o*-bromobenzyl alcohol (8). With the halocarbons $BrCCl_3$, CCl_4 and $CHBr_3$ and dibenzoyl peroxide, benzyl derivatives (7), (10), (12), (13), (15), and (16) are formed (Scheme 2). In each case the major product stems from capture of radical at C 1a and opening of the three-membered ring in a radical chain reaction. For example, bromotrichloromethane, with its weak C–Br bond[13] gives the trichloromethyl radical that provides (13) as the major product of reaction. Distinction between



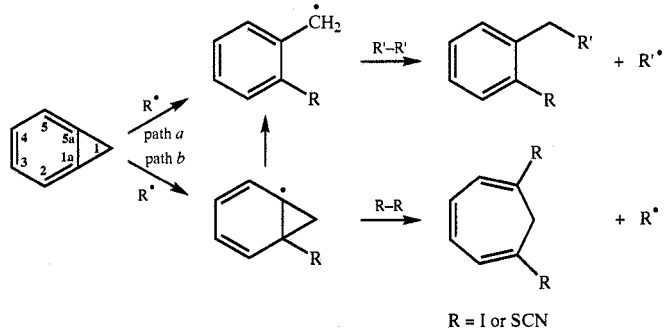
Scheme 2. (i) *N*-Bromosuccinimide; (ii) *N*-bromosuccinimide/H_2O/ultrasound; (iii) CCl_4/$(PhCO_2)_2$/reflux; (iv) $BrCCl_3/(PhCO_2)_2$/heat; (v) $CHBr_3/(PhCO_2)_2$/heat; (vi) RSH/$h\nu$; (vii) 2-$HSC_5H_4N/h\nu$; (viii) $HSCH_2CH_2SH/h\nu$.

[13] Walling, C., and Huyser, E., *Org. React.*, 1963, **13**, 604.

this and the alternative isomer with the substituent locations reversed, viz. 2-(2′-bromophenyl)-1,1,1-trichloroethane, was achieved by hydrolysis to the known[14] lactone (14) (Experimental). Especially notable, however, is the coupling to give diarylethane (10) in preference to the α,o-disubstituted toluene (12). Here dimerization of the benzylic radical with chain termination is clearly preferred and compatible with the quantity of initiator required; whether diffusion phenomena or steric congestion created by incorporation of a second trichloromethyl radical are involved is not known. Diarylethane (10) was unambiguously identified by hydrolysis to the known[15] diacid (11), and the minor product (12) confirmed by conversion into homophthalic acid[14,16] (Experimental). Although the appearance of α,o-dibromotoluene (7) in the reactions of (1) with $BrCCl_3$ and $CHBr_3$ is unusual, radical bromination by such reagents is not without precedent. Vasin *et al.* and Christl and his group have showed[17] that it is two bromine atoms that add across the bridge bond of tricyclo[4.1.0.$0^{2,7}$]heptane on reaction with $BrCCl_3$ and CBr_4, sometimes as the dominant process, cf. (15) and (7) in 25 and 23% yield, respectively (Scheme 2).

Under photochemical conditions, aliphatic and aromatic sulfanyl radical formation is followed by highly regioselective incorporation at C 1a of (1) with the formation of the *o*-substituted toluenes (17)–(20). An exception is recorded for pyridine-2-thiol but as this thiol has enhanced acidity (the ring nitrogen stabilizes negative charge on the sulfur atom) it is electrophilic addition that leads to the benzyl derivative (21). Ethane-1,2-dithiol was also examined in the hope that the second thiol moiety might provide for intramolecular trapping of the initially formed norcaradienyl radical. However, photolysis in the presence of (1) surprisingly gives the 2 : 1 coupled product (22) that might arise from initial electrophilic addition of proton.[11]

The outcomes of the various radical reactions recorded above are consistent with a marked preference for radical attack at C 1a of (1). Nonetheless, they



Scheme 3

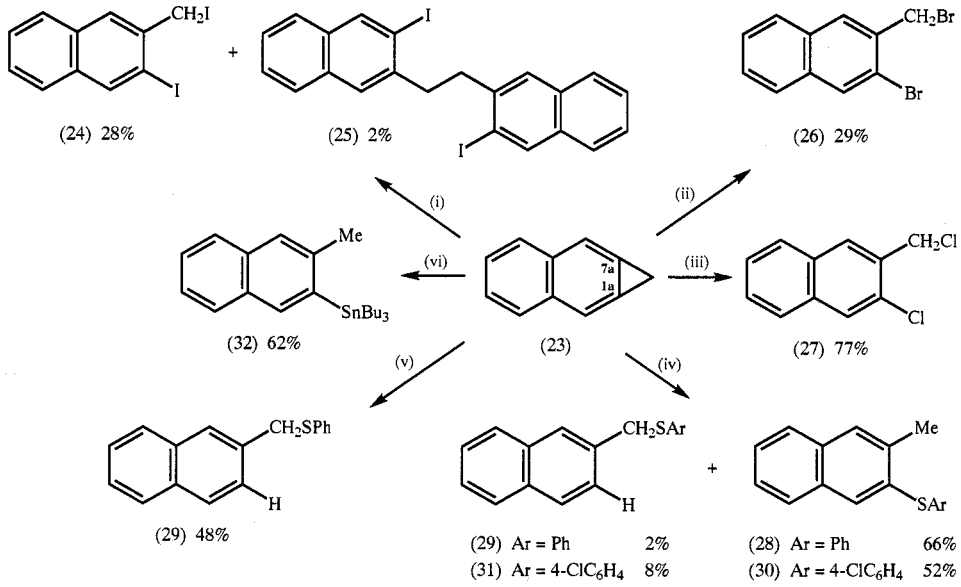
[14] Pouchert, C. J., 'The Aldrich Library of Infrared Spectra' (Aldrich Chemical Co. Inc.: Milwaukee 1970); Pouchert, C. J., and Campbell, J. R., 'The Aldrich Library of NMR Spectra' (Aldrich Chemical Co. Inc.: Milwaukee 1974).

[15] Thoshiro, M., Sumada, T., and Fukata, G., *Heterocycles*, 1981, **14**, 657.

[16] 'Dictionary of Organic Compounds' 4th Edn (Eyre & Spottiswoode: London 1965).

[17] Vasin, V. A., Bolusheva, I. Yu., Surmina, L. S., Buevich, A. V., Sergeev, N. M., Tanaseichuk, B. S., and Zefirov, N. S., *Zh. Org. Khim.*, 1990, **26**, 1501; Christl, M., in 'Advances in Strain in Organic Chemistry' (Ed. B. Halton) Vol. 4, pp. 163–224 (JAI: Greenwich, U.S.A., 1995).

do not allow for a distinction to be made between capture by the strained three-membered ring σ-bond or capture by the the π-framework (paths *a* and *b*, respectively, Scheme 3). In our view the former requires specific activation, e.g. with silver(I),[11] and the latter appears the more plausible. The absence of cycloheptatriene derivatives from the various product mixtures recorded herein clearly demonstrates that any π-addition at C 1a has to be followed by facile opening of the three-membered ring to a benzyl radical since capture to give a norcaradiene is not observed. Thus the rates of reaction of the norcaradienyl radical (2) with I_2 and $(SCN)_2$ to give (3) and (5), respectively, as major products (Scheme 1)[9] must be notably faster than those with the substrates employed in this study.

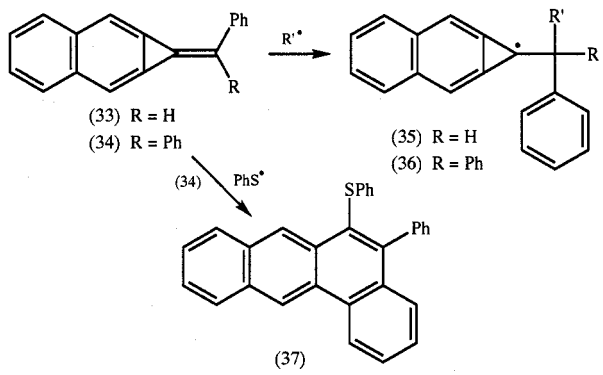


Scheme 4. (i) $I_2/h\nu$; (ii) *N*-bromosuccinimide/azobisisobutyronitrile/heat; (iii) SO_2Cl_2/azobisisobutyronitrile/heat; (iv) ArSH/$h\nu$; (v) PhSH/$AgNO_3$/dark; (vi) Bu_3SnH/azobisisobutyronitrile/heat.

Analogous reactions to those recorded above have been performed with 1*H*-cyclopropa[*b*]naphthalene (23), and the outcomes are depicted in Scheme 4. The results follow a series of control experiments which show that (23) is returned unchanged in high yields when subjected to the conditions of the various experiments in the absence of the essential radical source (Experimental). Addition to the bridge bond of (23) to give a benzo-fused cycloheptatriene is less likely than norcaradiene formation from (1) because of the high-energy *ortho*-quinodimethane intermediate that is required. Indeed, the products from photoreaction of iodine with (23) are naphthalene derivatives, and 2-iodo-3-(iodomethyl)naphthalene (24) predominates (Scheme 4). Radical bromination and chlorination of (23) leads to (26) and (27), respectively, but in the presence of an excess of the reagent further substitution at the 3-methyl centre can take place to give α,α,o-trihalogenated products (Experimental). The opposing regioselectivities associated with

radical and electrophilic addition are nicely demonstrated by the behaviour of (23) with benzenethiol. In the dark, both with and without silver(I) catalysis, the 2-naphthyl derivative (29) is formed while under photochemical conditions diaryl thioether (28) ensues. Finally, it is noteworthy that nuclear stannylation may be effected in good yield by reaction of (23) with tributyltin hydride in the presence of azobisisobutyronitrile as initiator; (32) is formed in 62% yield.

The reactions described thus far are unambiguous in showing that the simple cycloproparene hydrocarbons respond to radical attack by opening the three-membered ring, but they do not support the removal of a C1 hydrogen atom with formation of a cycloproparenyl radical at C1. In our view the stable C1 alkylidene derivatives[3,7,18] offer potential for the generation of such a reactive species, e.g. (35)/(36), by way of radical addition to the exocyclic centre. The readily available[19] phenyl- and diphenyl-methylidenecyclopropanaphthalenes (33) and (34) were chosen as representative substrates for this study. Control experiments have shown that these compounds are essentially stable to the various reaction conditions employed, as unchanged starting materials are returned in high yield (Experimental).



Scheme 5

The behaviour of olefins (33)/(34) towards *N*-bromosuccinimide, SO_2Cl_2, and PhSH with concomitant irradiation has been to provide complex, and often unstable, multicomponent product mixtures that have generally proved impossible to separate. Bromination of (33) resulted in the isolation of starting material but only in 24% yield. In comparison, the chlorination of (33) did provide some evidence for the addition of two chlorine atoms, as a crystalline mixture of products was obtained and for which the mass spectrum displayed a molecular ion cluster at *m/z* 298–302 ($C_{18}H_{12}Cl_2$). In our hands this mixture has proved impossible to separate. Reactions of (33) with benzenethiol have led only to the isolation and characterization of diphenyl disulfide (53%). In comparison, the analogous reaction with (34) gave 22% of starting material, 13% of diphenyl disulfide, and a new compound isolated in 11% yield that corresponds to the formal replacement of one hydrogen atom of (34) by a PhS moiety. The

[18] McNichols, A. T., Stang, P. J., Addington, D. M., and Halton, B., *Tetrahedron Lett.*, 1994, **35**, 437; Halton, B., *Pure Appl. Chem.*, 1990, **62**, 541.
[19] Halton, B., Randall, C. J., Gainsford, G. J., and Stang, P. J., *J. Am. Chem. Soc.*, 1986, **108**, 5949.

compound is tentatively proposed as 5-phenyl-6-phenylsulfanylbenz[*a*]anthracene (37) ($C_{30}H_{20}S$) (Scheme 5) from molecular ions at *m/z* 412 and 414 (100:11), and the appearance of bay region protons at 8·90, 9·15 and 9·24 ppm in the ^1H n.m.r. spectrum. Pathways exist for the formation of (37) by way of the C1 cycloproparenyl radical (36), but we have been unable to gain the necessary evidence to substantiate its involvement. The diphenylmethylidene compound (34) with SO_2Cl_2 provided a red crystalline monochlorinated product albeit in 4% yield. Molecular ions (3:1) at *m/z* 338 and 340 for $C_{24}H_{15}Cl$ signify the incorporation of one chlorine and the loss of one hydrogen atom. While a benz[*a*]anthracene analogue of (37) may seem logical, the proton signal most downfield in the ^1H n.m.r. spectrum resonates at 8·28 ppm, and this may rule out a comparable aromatic with bay region protons;[20] the structure of the compound remains unknown. Attempted stannylation of (33) and (34) akin to that of (23) resulted in the consumption of starting materials and the formation of inseparable multicomponent product mixtures. The complexities and instabilities of the products from radical reactions with (33) and (34) have prevented us from gaining definitive evidence for the intervention of the C1 species (35) and (36), respectively.

Experimental

Melting points were determined by using a Reichert hot-stage or Büchi melting point apparatus and are uncorrected. Microanalyses were performed at the University of Heidelberg and the Microanalytical Facility, Otago University, Dunedin. N.m.r. spectra were recorded for (D)chloroform solutions with tetramethylsilane as internal standard, Varian Associates FT80A and Bruker AC300 and WM250 instruments being used; the presence of a detailed assignment follows from two-dimensional COSY experiments. Electron impact mass spectra were recorded with either a Hewlett Packard HP5995 or a Varian Associates 311A instrument. Infrared spectra were recorded for KBr films by employing Biorad FTS7 and FTS40, and Perkin Elmer 325 spectrophotometers. Column, radial and and preparative layer chromatographies were performed with silica as the adsorbent, while thin-layer chromatagraphic analysis employed u.v.-active silica or alumina plates. Photolyses were performed with a Hanovia medium-pressure mercury lamp or a Hanau TQ150 immersion lamp.

(*a*) Reaction of Bicyclo[4.1.0]hepta-1,3,5-triene (1) with *N*-Bromosuccinimide

(i) *Under Anhydrous Conditions*

To a solution of (1)[21] (300 mg, 3·3 mmol) in dichloromethane (50 ml) was added *N*-bromosuccinimide (600 mg, 3·5 mmol), and the mixture stirred at 40°C for 8 h. Preparative t.l.c. (silica gel, hexane elution) afforded 1-bromo-2-(bromomethyl)benzene (7) as a yellow oil (130 mg, 16%) that crystallized at low temperature (hexane), m.p. 30°C (lit.[16] 31°C; b.p. 120–130°C/13 mmHg).

(ii) *In Aqueous Media*

To a suspension of *N*-bromosuccinimide (1·7 g, 8·8 mmol) in water (20 ml) was added (1) (900 mg, 10·0 mmol), and the mixture was subjected to ultrasonic irradiation for 30 min at a temperature that did not exceed 50°C. The suspension was extracted with ether; the extract was dried ($MgSO_4$) and concentrated in vacuum to an oil. Column chromatography

[20] Pretsch, E., Seibl, J., Simon, W., and Clerk, T., 'Tables of Spectral Data for Structural Determination of Organic Compounds' (Springer: Berlin 1983).
[21] Neidlein, R., and Poignée, V., *Chem. Ber.*, 1988, **121**, 1199.

(kieselgel 60; dichloromethane/pentane, 1:2) afforded bis(2-bromophenylmethyl) ether[22] (9) (200 mg, 12%) as colourless crystals (hexane), m.p. 61°C (lit.[22] not given). ^{1}H n.m.r. δ 4·73, s, 2×CH_2; 7·18, dt, ^3J 7·5, ^4J 2·0 Hz, 2H; 7·33, dt, ^3J 7·5, ^4J 1·5 Hz, 2H; 7·52–7·60, m, 4H.

(b) Reaction of Bicyclo[4.1.0]hepta-1,3,5-triene (1) with Tetrachloromethane

To a solution of dibenzoyl peroxide (4·84 g, 20 mmol) in tetrachloromethane (30 ml) under reflux was slowly added over 2 h a solution of (1) (900 mg, 10 mmol) in the same reagent solvent (20 ml). The solution was refluxed for a further 24 h, cooled and concentrated in vacuum to an oil. Flash chromatography gave two fractions A and B.

Fraction A (hexane) was concentrated to *c.* 8 ml and cooled to −10°C whereupon *1,2-bis[2′-(trichloromethyl)phenyl]ethane* (10) (725 mg, 35%) was obtained as colourless crystals, m.p. 158°C (Found: C, 46·0; H, 3·0. $C_{16}H_{12}Cl_6$ requires C, 46·1; H, 2·9%). Its identity was confirmed by hydrolysis to the corresponding dicarboxylic acid (11) (see below). ^{1}H n.m.r. of (10) δ 3·56, s, 2×CH_2; 7·27, td, ^3J 7·5, ^4J 1·9 Hz, 2×H5′; 7·46, td, ^3J 7·5, ^4J 1·9 Hz, 2×H4′; 7·57, dd ^3J 7·5, ^4J 1·4 Hz, 2×H6′; 8·10, dd, ^3J 7·5, ^4J 1·4 Hz, 2×H3′. ^{13}C n.m.r. δ 34·88, 2×CH_2; 97·91, 2×CCl_3; 125·75, 125·90, 130·90, 132·27 (all 2×CH); 140·28, 140·59 (both 2×q). ν_{max} 3070, 3030, 2940, 1600, 1575, 1480, 1180, 880, 795, 760, 748, 725 cm^{-1}. Mass spectrum *m/z* (relative abundance) 416 (0·6%; M+2), 381 (2·5), 345 (4·4), 307 (18), 172 (64), 136 (70), 101 (100).

Fraction B (dichloromethane) gave an oil that was subjected to preparative t.l.c. With pentane elution the major fraction provided a further portion of (10) as an oil identical in all respects that above; sublimation at 120°C/0·5 mmHg gave shiny crystals of (10), m.p. 158°C. The minor fraction was isolated as a colourless oil and identified as *1,1,1-trichloro-2-[2′-(trichloromethyl)phenyl]ethane* (12) (50 mg, 1·5%) (Found: $M^{+\bullet}$, 323·8600. $C_9H_6{}^{35}Cl_6$ requires $M^{+\bullet}$, 323·8601). Its identity was confirmed by hydrolysis to homophthalic acid (see below). ^{1}H n.m.r. of (12) δ 4·80, s, CH_2; 7·42, td, ^3J 9, ^4J 1·6 Hz, 1H; 7·51, td, ^3J 9, ^4J 1·6 Hz, 1H; 8·19, dd, ^3J 9, ^4J 1·6 Hz, 2H. ν_{max} (film) 3080, 2920, 1600, 1580, 1480, 1180, 870, 800, 740, 710 cm^{-1}. Mass spectrum *m/z* (relative intensity) 328, 326, 324 (3, 2, 0·4%; M); 292 (19), 256 (29), 208 (36), 126 (72), 92 (60), 75 (100).

Hydrolysis of hexachloride (10) to 2,2′-(ethane-1,2-diyl)bisbenzoic acid (11). Diarylethane (10) (400 mg, 1 mmol) was subjected to hydrolysis with 98% sulfuric acid (10 ml) by heating to 100°C for 5 min. The black solution was poured into water (100 ml), and the acid obtained by conventional methods. Sublimation of the resultant powder at 120°C/0·5 mmHg gave the known[15] diacid (11) as a white powder (40 mg, 15%), m.p. 228°C (dec.) (lit.[15] 230°C).

Hydrolysis of monoarylethane (12) to homophthalic acid. The hexachloride (12) (50 mg, 0·15 mmol) was subjected to hydrolysis as described for (10) above to give homophthalic acid (12 mg, 45%). Recrystallization (water) gave a sample with m.p. 184°C (lit.[14] 183–186°C, lit.[16] 180–181°C).

(c) Reaction of Bicyclo[4.1.0]hepta-1,3,5-triene (1) with Bromotrichloromethane

A solution of dibenzoyl peroxide (100 mg, 0·4 mmol) in bromotrichloromethane (35 ml) was heated to 80°C, and a solution of (10) (3 g, 33 mmol) in the same solvent (15 ml) added dropwise over 1 h. The resultant solution was concentrated in vacuum to an oil that was further purified by filtration through silica (hexane) to give an oil (5·5 ml). Fractional microdistillation (Vigreaux column, 10 cm) provided 1-bromo-2-(bromomethyl)benzene (7) (750 mg, 10%) as the forerun. Data were identical with those from the compound identified in Section (*a*)(i) above.

The main fraction from distillation was obtained as a pale yellow oil which would not crystallize. It was identified as *1-bromomethyl-2-(trichloromethyl)benzene* (13) (2·9 g, 35%), b.p. 123–125°C/1 mmHg (Found: $M^{+\bullet}$, 285·8718. $C_8H_6{}^{79}Br^{35}Cl_3$ requires $M^{+\bullet}$, 285·8718). Its identity was confirmed by hydrolysis to lactone (14) (see below). ^{1}H n.m.r. for (13) δ 5·03, s, CH_2; 7·34, td, ^3J 8·2, ^4J 1·5 Hz, 1H; 7·46, td, ^3J 8·2, ^4J 1·5 Hz, 1H; 7·69, dd, ^3J 8·2, ^4J 1·5 Hz, 1H; 8·03, dd, ^3J 8·2, ^4J 1·5 Hz, 1H. ^{13}C n.m.r. δ 30·3, CH_2; 96·6, CCl_3;

[22] Berndt, A. F., Corey, E. R., and Glick, M. D., *Acta Crystallogr., Sect. B*, 1981, **37**, 1294.

125·7, 127·9, 131·2, 134·7 (all CH); 136·0, 140·4 (both q). ν_{max} 3078, 1600, 1578, 1480, 1450, 1205, 890, 800, 710 cm^{-1}. Mass spectrum *m/z* (relative intensity) 288, 286 (4·2, 2·1%; M); 251 (26, M – Cl), 207 (91, M – Br), 172 (100, M – BrCl), 137 (94), 102 (76), 75 (67).

Hydrolysis of bromo trichloride (13) to phthalide (14). 1-Bromomethyl-2-(trichloromethyl)-benzene (13) (800 mg, 2·8 mmol) was heated to 100°C in sulfuric acid (98%) for 5 min. The black viscous liquid was poured into water (100 ml). Conventional workup afforded isobenzofuran-1(3*H*)-one (phthalide) (14) as a white powder that was sublimed at 100°C/0·5 mmHg (190 mg, 51%), m.p. 73°C (lit.[14] 73°C).

(d) Reaction of Bicyclo[4.1.0]hepta-1,3,5-triene (1) with Tribromomethane

A mixture of dibenzoyl peroxide (150 mg, 0·06 mmol) and (1) (250 mg, 2·7 mmol) in tribromomethane (15 ml) was heated at 80°C for 1 h. After cooling and diluting with hexane, the solution was filtered through silica, and concentrated to a yellow oil (900 mg). Preparative t.l.c. (pentane) at −25°C afforded three fractions A–C that were extracted (dichloromethane) to yield oils.

Fraction A was identified as 1-bromo-2-(bromomethyl)benzene (7) (153 mg, 23%) by comparison with the material obtained in Section (*a*)(i) above. Fraction B, a colourless oil, was identified as *1,1-dibromo-2-(2′-bromophenyl)ethane* (16) (18 mg, 7%) (Found: C, 28·1; H, 2·2. $C_8H_7Br_3$ requires C, 28·0; H, 2·1%). ^1H n.m.r. δ 3·84, d, ^3J 7·5 Hz, CH_2; 5·95, t, ^3J 7·5 Hz, $CHBr_2$; 7·15–7·25, m, 3H; 7·56, d, ^3J 9·4 Hz, H6′. ν_{max} 3060, 2930, 1570, 1470, 1440, 1030, 750, 670 cm^{-1}. Mass spectrum *m/z* (relative intensity) 346, 344, 342 (17, 54, 21%; M); 263 (65), 171 (99), 169 (100).

Fraction C, the major component, crystallized from hexane to provide 1-(bromomethyl)-2-(dibromomethyl)benzene (15) (60 mg, 25%) as white needles, m.p. 40°C (lit.[23] 40–41°C). ^1H n.m.r. δ 4·58, s, CH_2; 7·11, s, $CHBr_2$; 7·20–7·33, m, 2H; 7·42, td, ^3J 8·0, ^4J 2·2 Hz, 1H; 7·94, d, ^3J 8·0 Hz, 1H. ν_{max} 3070, 3040, 1458, 1230, 1148, 768, 752 cm^{-1}.

(e) Reactions of Bicyclo[4.1.0]hepta-1,3,5-triene (1) with Aliphatic Thiols

General Procedure

A solution of (1) (450 mg, 5 mmol) and the relevant thiol (6 mmol) in hexane (150 ml) was irradiated with an ultraviolet immersion lamp for 2 h. The solvent was removed and the yellowish brown residue chromatographed (dichloromethane/hexane, 2:1) to purify and separate the products.

Specific Products

(A) *From ethanethiol.* 2-(Ethylsulfanyl)-1-methylbenzene (17) (460 mg, 60%), b.p. 80°C/4 mmHg (lit.[24] 61·8°C/1·6 mmHg). ^1H n.m.r. δ 1·13, t, ^3J 9 Hz, CH_3; 2·23, s, CH_3; 2·73, q, ^3J 9 Hz, CH_2; 6·8–7·5, m, 4H.

(B) *From Propane-1-thiol.* 1-Methyl-2-(propan-1′-ylsulfanyl)benzene (18) (240 mg, 29%), b.p. 83°C/2 mmHg (lit.[25] 68·2°C/1·1 mmHg). ^1H n.m.r. δ 1·13, t, ^3J 7 Hz, CH_3; 1·69, sextet, CH_2; 2·36, s, CH_3; 2·87, t, ^3J 7 Hz, CH_2; 7·08–7·24, m, 4H.

(C) *From ethyl 2-sulfanylethanoate.* Ethyl 2-[(2′-methylphenyl)sulfanyl]ethanoate (19) (480 mg, 45%), b.p. 115°C/1·2 mmHg (lit.[26] 180°C/32 mmHg). ^1H n.m.r. δ 1·22, t, ^3J 7 Hz, CH_3; 2·38, s, CH_3; 3·49, s, SCH_2CO, 4·12, q, ^3J 7 Hz, CH_2OCO; 7·00–7·33, m, 4H.

(D) *From ethane-1,2-dithiol.* By employing (1) (400 mg, 4·5 mmol) and ethane-1,2-dithiol (470 mg, 5 mmol) under the same reaction conditions, 1,6-diphenyl-2,5-dithiahexane (22) (280 mg, 23%) was isolated as crystals (hexane), m.p. 38°C (lit.[27] 38°C). ^1H n.m.r. δ 2·53, s, 4H, SCH_2CH_2S; 3·62, s, 4H, 2×$ArCH_2S$; 7·20, s, 10H.

[23] Halford, I. O., and Weissmann, B., *J. Org. Chem.*, 1953, **18**, 30.
[24] Gasparic, J., Vecera, M., and Jurecek, M., *Collect. Czech. Chem. Commun.*, 1959, **24**, 1839.
[25] Profft, E., *Chem. Tech. (Leipzig)*, 1953, 239.
[26] Soper, Q. F., Whitehead, C. W., Behrens, O. K., Corse, J. J., and Jones, R. G., *J. Am. Chem. Soc.*, 1948, **70**, 2849.
[27] Mathias, S., *Bol. Fac. Filos., Cienc. Let., Univ. Sao Paulo 15, Quim.*, No. 1, 75; personal communication to R. Neidlein.

(f) Reaction of Bicyclo[4.1.0]hepta-1,3,5-triene (1) with Benzenethiol

A solution of (1) (200 mg, 2·2 mmol) and benzenethiol (300 mg, 2·7 mmol) in hexane (150 ml) was irradiated at 20°C for 1 h. Removal of the solvent left a yellow-brown oil that was purified by chromatography (dichloromethane/hexane, 1:1) to provide 1-methyl-2-(phenylsulfanyl)benzene (20) (300 mg, 67%) as a colourless oil, b.p. 120°C/1·5 mmHg (lit.[28] 164°C/12 mmHg). ^{1}H n.m.r. δ 2·25, s, CH_3; 7·0–7·4, m, 9H.

(g) Reaction of Bicyclo[4.1.0]hepta-1,3,5-triene (1) with 2-Sulfanylpyridine

A solution of (1) (400 mg, 4·4 mmol) and 2-sulfanylpyridine (500 mg, 4·5 mmol) in dichloromethane (150 ml) was irradiated for 4 h. The solution was concentrated and the residue purified (column chromatography; dichloromethane/hexane, 1:1) to provide 2-(benzylsulfanyl)pyridine (21) (320 mg, 36%) as crystals (hexane), m.p. 27–28°C (lit.[29] 28·5–29·5°C). ^{1}H n.m.r. δ 4·38, s, CH_2; 6·73–7·43, m, 8H; 8·30–8·43, m, 1H.

(h) Reaction of 1*H*-Cyclopropa[*b*]naphthalene (23) with Iodine

The reaction was performed with a modification to the method described by Okazaki *et al.* for cyclopropabenzene.[9] Thus a degassed solution of (23)[30] (209 mg, 1·49 mmol) in heptane (20 ml) was maintained at 0°C (circulating methanol from a cryogenic bath) in a quartz vessel, and irradiated while a degassed solution of iodine (396 mg, 1·36 mmol) in heptane (68 ml) was added over 2 h. Irradiation was continued for 2 h during which time the solution was allowed to warm to room temperature. Without exposure to light, the colourless solution was washed ($Na_2S_2O_3$, 5% aq.; 75 ml); the organic phase was separated, dried ($MgSO_4$), and concentrated in vacuum to a brown oil which gave two components A and B by radial chromatography (light petroleum).

Component A provided *2-iodo-3-(iodomethyl)naphthalene* (24) (152 mg, 28%) as yellow crystals (hexane), m.p. 119·5–121·0°C (Found: C, 33·7; H, 1·7%; $M^{+\bullet}$, 393·8717. $C_{11}H_8I_2$ requires C, 33·5; H, 2·0%; $M^{+\bullet}$, 393·8716). ^{1}H n.m.r. δ 4·73, s, CH_2; 7·45–7·51, m, H6/7; 7·67–7·76, m, H5/8; 7·96, s, H4; 8·36, s, H1. ^{13}C n.m.r. δ 12·7, CH_2; 96·4, C2; 126·5/127·7, C5/8; 127·0/127·2, C6/7; 128·4, C4; 133·1/134·3, C4a/8a; 137·7. C3; 139·7, C1. ν_{max} 3047, 1580, 1489, 1419, 1319, 1270, 1151, 1126, 972, 955, 884, 824, 752, 718, 556, 475 cm^{-1}. Mass spectrum *m/z* (relative intensity) 394 (3·2%, M), 267 (74, M − I), 140 (88, M − 2I), 139 (100%, M − I − HI).

Component B was a pale yellow solid proposed as 1,2-di(3′-iodo-2′-naphthyl)ethane (25) (12 mg, 2%). ^{1}H n.m.r. δ 3·24, s, 2×CH_2; 7·43–7·50, m, 4H; 7·70–7·75, m, 6H; 8·43; s, H1′/H4′. ^{13}C n.m.r. δ 41·4, 2×CH_2; 98·8, C3′; 126·1/126·6, C6′/7′; 126·4, C1′; 127·4/127·5, C5′/8′; 133·1/133·6, C4a′/8a′; 138·8, C4′; 140·1, C2′. Mass spectrum *m/z* (relative intensity) 534 (4·0%, M), 280 (26, M − 2I), 267 (28, M − 2I − Me), 139 (100, M − 2I − $C_{11}H_9$).

Irradiation of substrate (23) alone under the same reaction conditions resulted in an 85% recovery of unchanged material.

(i) Reaction of 1*H*-Cyclopropa[*b*]naphthalene (23) with *N*-Bromosuccinimide

(i) *With One Molar Equivalent of* N-*Bromosuccinimide*

A mixture of (23) (200 mg, 1·43 mmol), *N*-bromosuccinimide (254 mg, 1·43 mmol) and a catalytic amount of azobisisobutyronitrile (25 mg) in tetrachloromethane (10 ml) was degassed for 5 min (oxygen-free nitrogen), and then refluxed for 23 h at *c.* 80°C at which time succinimide was observed to be floating on the solvent. The solution was cooled, filtered through a plug of glass wool, and concentrated in vacuum to a brown residue. Column chromatography (light petroleum) afforded unchanged 1*H*-cyclopropa[*b*]naphthalene (23) (42·6 mg, 21%) as white needles (light petroleum), m.p. 86–88°C (lit.[30] 86–87°C), and

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[29] Jones, R. A., and Katritzky, A. R., *J. Chem. Soc.*, 1958, 3610.
[30] Billups, W. E., and Chow, W. Y., *J. Am. Chem. Soc.*, 1973, **95**, 4099.

2-bromo-3-(bromomethyl)naphthalene (26) (50 mg, 12%) as white crystals (hexane), m.p. 110·0–111·5°C (lit.[31] 111–112°C). ^{1}H n.m.r. δ 4·78, s, CH_2; 7·47–7·53, m, H 6/7; 7·70–7·80, m, H 5/8; 7·93, s, H 1; 8·20, s, H 4. ^{13}C n.m.r. δ 34·0, CH_3; 121·4, C 2; 126·7/127·9, C 5/8; 126·9/127·6, C 6/7; 130·5, C 1; 132·1, C 4; 132·3, C 4a/8a; 134·2, C 3. ν_{max} 3053, 2976, 1590, 1490, 1425, 1323, 1209, 1128, 989, 880, 865, 751, 694, 584, 477 cm^{-1}. Mass spectrum *m/z* (relative intensity) 302, 300, 298, (6·5, 14·3, 7·0%; M); 221, 219 (100, 98; M – Br); 140 (83, M – 2Br), 139 (95, M – Br – HBr).

(ii) *With Two and Four Molar Equivalents of* N-*Bromosuccinimide*

The same procedure as above but with 2 mol. equiv. of *N*-bromosuccinimide afforded (26) (112·1 mg, 26%) identical to the sample in (i) above as the sole compound isolated. However, with 4 mol. equiv. of *N*-bromosuccinimide two compounds were isolated. The first was identified as *2-bromo-3-(dibromomethyl)naphthalene* (4·4 mg, 1%) as white needles (hexane), m.p. 116·5–118·0°C (Found: C, 35·1; H, 1·7, Br, 63·4%; $M^{+\bullet}$, 375·8098. $C_{11}H_7{}^{79}Br_3$ requires C, 34·9; H, 1·9; Br, 63·3%; $M^{+\bullet}$, 375·8098). ^{1}H n.m.r. δ 7·21, s, $CHBr_2$; 7·51–7·58, m, H 6/7; 7·74–7·67, m, H 8; 7·88–7·92, m, H 5; 8·04, s, H 1; 8·53, s, H 4. ^{13}C n.m.r. δ 40·1, $CHBr_2$; 117·2, C 2; 126·6, C 8; 127·2, C 7; 128·3, C 6; 128·4, C 5; 131·1, C 4; 131·5, C 1; 132·4, C 4a; 134·6, C 8a; 137·3, C 3. ν_{max} 3045, 3014, 1585, 1490, 1431, 1350, 1325, 1257, 1194, 1148, 1133, 988, 955, 895, 885, 756, 699, 596, 474 cm^{-1}. Mass spectrum *m/z* (relative intensity) 382, 380, 378, 376 (0·8, 2·3, 2·4, 0·9%; M); 301, 299, 297 (17, 34, 19; M – Br); 219, 217 (2·1, 2·0; M – Br – HBr); 139 (100, M – 3Br). The second component was (26) (124·0 mg, 29%) identical to the sample in (i) above.

(iii) *At Room Temperature in the Absence of Azobisisobutyronitrile and Light*

The same procedure but in the absence of azobisisobutyronitrile and for 23 h at room temperature in the dark returned unchanged (23) (89%) as white needles, m.p. and mixed m.p. 86–88°C.

(iv) *With Azobisisobutyronitrile Under Reflux*

A solution of (23) with a catalytic amount of azobisisobutyronitrile in refluxing tetrachloromethane, but in the *absence* of *N*-bromosuccinimide, returned unchanged (23) (83% recovery) as white needles.

(j) Reaction of 1*H*-Cyclopropa[*b*]naphthalene (23) with Sulfuryl Chloride

(i) *With One Molar Equivalent of Sulfuryl Chloride*

A solution of (23) (210 mg, 1·50 mmol) in dry benzene (20 ml) with a catalytic amount of azobisisobutyronitrile (25 mg) was degassed for 5 min, and freshly distilled sulfuryl chloride (120 μl, 1·40 mmol) added via syringe. The solution was refluxed at 80°C for 3 h, cooled, and concentrated in vacuum to a yellow residue. Column chromatography (light petroleum) afforded *2-chloro-3-(chloromethyl)naphthalene* (27) (243 mg, 77%) as colourless crystals (hexane), m.p. 90–91°C (Found: C, 62·8; H, 3·6; Cl, 33·8. $C_{11}H_8Cl_2$ requires C, 62·6, H, 3·8, Cl, 33·6%). ^{1}H n.m.r. δ 4·86, s, CH_2; 7·46–7·55, m, H 6/7; 7·74–7·79, m, H 8; 7·81–7·84, m, H 5; 7·90, s, H 1, 7·95, s, H 4. ^{13}C n.m.r. δ 44·2, CH_2; 126·7, C 7; 126·8, C 8; 127·5, C 6; 127·9, C 5; 128·2, C 1; 130·3, C 4; 131·3, C 3; 131·9, C 4a; 132·7, C 2; 133·9, C 8a. ν_{max} 3058, 2972, 1626, 1588, 1569, 1490, 1454, 1326, 1263, 1236, 1175, 1130, 1009, 956, 930, 878, 846, 798, 753, 721, 647, 601, 478 cm^{-1}. Mass spectrum *m/z* (relative intensity) 214, 212, 210 (2·2, 13·5, 22·1%; M); 177, 175, (33, 100·0; M – Cl); 139 (45, M – Cl – HCl).

(ii) *With Two and Four Molar Equivalents of Sulfuryl Chloride*

The same procedure was used as above but with 2 and 4 mol. equiv. of sulfuryl chloride. The 2 mol. equiv. of SO_2Cl_2 led to *2-chloro-3-(dichloromethyl)naphthalene* (89·9 mg, 25%) as white needles (hexane, −10°C), m.p. 73·5–74·0°C (Found: C, 54·0; H, 2·9; Cl, 43·0. $C_{11}H_7Cl_3$ requires C, 53·8; H, 2·9; Cl, 43·3%). ^{1}H n.m.r. δ 7·27, s, 1H, $CHCl_2$; 7·51–7·58,

[31] Staab, H. A., Wehinger, E., and Thorwart, W., *Chem. Ber.*, 1972, **105**, 2290.

m, H6/7; 7·75–7·85, m, H5; 7·88–7·92, m, H8; 7·88, overlapping s, H1; 8·44, s, H4. ^{13}C n.m.r. δ 68·5, $CHCl_2$; 126·7, C5; 127·05, C6; 128·1, C1; 128·3, C7; 128·5, C8; 129·0, C4; 131·8, C3; 134·2, C2; 135·0, C4a/8a. ν_{max} 3058, 3014, 1627, 1590, 1494, 1448, 1434, 1328, 1277, 1215, 1158, 1134, 1012, 956, 898, 878, 846, 808, 788, 751, 735, 718, 650, 627, 600, 529, 504, 474 cm^{-1}. Mass spectrum *m/z* (relative intensity) 250, 248, 246, 244 (0·3, 2·8, 9·3, 8·9%; M); 213, 211, 209 (11, 64·0, 100·0; M – Cl); 175, 173 (8, 20; M – Cl – HCl); 139 (62, M – 3Cl). The second component was 2-choloro-3-(chloromethyl)naphthalene (27) (123·4 mg, 40%) identical to the sample in (i) above.

With 4 mol. equiv. of reagent, 2-chloro-3-(dichloromethyl)naphthalene (108·6 mg, 30%) and 2-chloro-3-(chloromethyl)naphthalene (27) (123·4 mg, 40%) were isolated and identical to the samples described in (i) and (ii) above.

(iii) *With Sulfuryl Chloride at Room Temperature and in the Dark*

Subjection of (23) to SO_2Cl_2 under the same conditions but at ambient temperature and in the dark for 20 h returned starting material (79% recovery).

(k) Reactions of 1*H*-Cyclopropa[*b*]naphthalene (23) with Arenethiols

General Procedure

To a quartz double-necked round-bottomed flask equipped with a condenser was added (23) (210 mg, 1·50 mmol) in dry benzene (5 ml). The solution was degassed for 5 min, and then irradiated with a 125 W broad-spectrum medium-pressure lamp located 12 cm from the reaction vessel. The thiol (*c.* 1·44 mmol) was added via syringe, and the reaction monitored by t.l.c.; starting material was consumed after 1 h. The product mixture was removed, concentrated in vacuum, and the residue subjected to column chromatography. In the absence of thiol, substrate (23) was recovered unchanged in 84% yield when irradiated under these conditions.

Specific Products

(A) *From benzenethiol (147 µl, 1·43 mmol).* Elution of the column (dichloromethane/light petroleum, 4:1) afforded unchanged starting material (23) (6 mg, 3%) and two other products identified as (28) and (29). *2-Methyl-3-(phenylsulfanyl)naphthalene* (28) (258 mg, 66%) was obtained as white needles (hexane), m.p. 67·5–68·5°C (Found: C, 81·5; H, 5·8; S, 12·9. $C_{17}H_{14}S$ requires C, 81·6; H, 5·6; S, 12·8%). ^1H n.m.r. δ 2·49, s, CH_3; 7·17–7·30, m, 5H; 7·37–7·46, m, H6/7; 7·66–7·75, m, H1/5/8; 7·69, overlapping s, H1; 7·81, s, H4. ^{13}C n.m.r. δ 20·7, CH_3; 125·6/126·4, C6/7; 126·5, C*p*; 127·0, 127·2, C5/8; 128·7, C1; 129·2, C*m*/*m*′; 129·8, C*o*/*o*′; 132·21, C4; 132·48/132·80, C2/3; 133·2, C*ipso*. ν_{max} 3054, 3025, 2975, 2950, 1579, 1476, 1027, 948, 883, 742, 688, 476 cm^{-1}. Mass spectrum *m/z* (relative intensity) 254, 252, 250 (0·01, 6·2, 100·0%; M); 217 (20, M – SH); 173, 171 (4·5, 26; M – H – Ph); 141 (23, M – PhS). 2-(Phenylsulfanylmethyl)naphthalene[32] (29) (8·6 mg, 2%) was obtained as white crystals (hexane), m.p. 99·5–100·5°C (Found: C, 81·7; H, 5·8; S, 12·9. Calc. for $C_{17}H_{14}S$: C, 81·6; H, 5·6; S, 12·8%). ^1H n.m.r. δ 4·27, s, CH_2S; 7·14–7·25, m, 3H; 7·31–7·34, m, 2H; 7·41–7·48, m, 3H; 7·72–7·81, m, 3H; 7·67, s, H1. ^{13}C n.m.r. δ 39·5, CH_2S; 125·8/126·1, C6/7; 126·5, C*p*; 127·0, C3; 127·4, C1; 127·4/127·7, C5/8; 128·3, C4; 128·9, C*m*/*m*′; 130·1, C*o*/*o*′; 132·6, C2; 133·3/135·0, C4a/8a; 136·3, C*ipso*. ν_{max} 3048, 2917, 1438, 1362, 969, 897, 865, 832, 774, 755, 738, 724, 688, 484 cm^{-1}. Mass spectrum *m/z* (relative intensity) 252, 250 (0·9, 15·2%; M); 141 (100, M – PhS).

(B) *From benzenethiol in the dark.* The reaction was performed as above but without irradiation and with the reaction mixture in a flask wrapped in aluminium foil. Stirring at ambient temperature resulted in consumption of starting material after 1 h. The reaction mixture was concentrated in vacuum in the dark to a yellow oil that upon chromatography afforded two components identified as the disubstituted naphthalene (28) (24 mg, 6%), m.p. 67·5–68·5°C, and substituted methyl isomer (29) (86 mg, 23%), m.p. 99·5–100·5°C. The samples were identical to those isolated in (A) above.

[32] Ho, K. M., Lam, C. H., and Luh, T.-Y., *J. Org. Chem.*, 1989, **54**, 4474.

(c) *In the dark with silver(I) catalysis.* To the degassed solution of (23) in dry benzene was added silver nitrate (71 mg, 0·04 mmol), and the flask wrapped in aluminium foil. Benzenethiol (150 μl, 1·46 mmol) was added via a syringe and the reaction mixture was stirred for 5 h in the dark. Column chromatography (light petroleum) afforded 2-(phenylsulfanylmethyl)naphthalene (29) (177 mg, 48%) as colourless crystals (hexane), m.p. 99·5–100·5°C, identical to the sample in (A) above.

(D) *From 4-chlorobenzenethiol (213 mg, 1·47 mmol) in degassed benzene (5 ml).* Elution of the column (light petroleum) afforded two components identified as (30) and (31). *3-(4′-Chlorophenylsulfanyl)-2-methylnaphthalene* (30) (216 mg, 52%) was obtained as white needles (hexane), m.p. 72–73°C (Found: C, 71·5; H, 4·3%; $M^{+\bullet}$, 284·0427. $C_{17}H_{13}{}^{35}ClS$ requires C, 71·7; H, 4·6%; $M^{+\bullet}$, 284·0426. ^{1}H n.m.r. δ 2·47, s, CH_3; 7·12–7·16, m, H2′/6′; 7·21–7·26, m, H3′/5′; 7·39–7·47, m, H6/7, overlapping s, H1; 7·71–7·76, m, H5/8; 7·84, s, H4. ^{13}C n.m.r. δ 20·7, CH_3; 125·8/126·6, C6/7; 127·0/127·2, C5/8; 128·9, C1; 129·3, C3′/5′; 130·6, C2′/6′; 132·0, C2; 132·4, C1′; 132·5/133·6, C4a/8a; 132·8, C4; 135·0, C4′; 137·8, C3. ν_{max} 3054, 2976, 2919, 1489, 1476, 1451, 1390, 1092, 1010, 881, 815, 746 cm^{-1}. Mass spectrum *m/z* (relative intensity) 286, 284 (12, 31%; M); 171 (20, M − Cl − PhH), 141 (85, M − SC_6H_4Cl). *2-[(4′-Chlorophenylsulfanyl)methyl]naphthalene* (31) (34·4 mg, 8%) was obtained as white crystals (hexane), m.p. 103·0–104·5°C (Found: C, 71·6; H, 4·6; S, 11·4. $C_{17}H_{13}ClS$ requires C, 71·7; H, 4·6; S, 11·3%). ^{1}H n.m.r. δ 4·23, s, CH_2; 7·17–7·25, m, 4H; 7·42–7·48, m, 3H; 7·73–7·82, m, 3H. ^{13}C n.m.r. δ 39·8, CH_2; 126·0/126·3, C6/7; 126·9, C3; 127·5, C1; 127·69/127·71, C5/8; 128·4, C4; 129·0, C3′/5′; 131·7, C2′/6′; 132·7/134·6, C1′/4′; 132·6, C2; 133·3/134·6, C4a/8a. ν_{max} 3056, 2913, 1477, 1390, 1099, 832, 813, 488 cm^{-1}. Mass spectrum *m/z* (relative intensity) 288, 286, 284 (0·1, 1·9, 4·9%; M); 141 (100, M − SC_6H_4Cl).

(l) Reaction of 1*H*-Cyclopropa[*b*]naphthalene (23) with Tributyltin Hydride

To a solution of (23) (203 mg, 1·45 mmol) and azobisisobutyronitrile (25 mg) in degassed dry benzene (20 ml) was added via syringe freshly distilled tributyltin hydride (384 μl, 1·43 mmol). The solution was refluxed at *c.* 80°C for 5 h, then concentrated in vacuum, and the yellow oil purified by radial chromatography (light petroleum) to give *2-methyl-3-(tributylstannyl)naphthalene* (32) (381 mg, 62%) as clear oil (Found: C, 64·0; H, 8·5. $C_{23}H_{36}Sn$ requires C, 63·9; H, 8·4%). ^{1}H n.m.r. δ 0·89, t, ^3J 7·3 Hz, 3×CH_3; 1·11–1·17, m, 3×CH_2; 1·29–1·41, sextet, ^3J 7·2 Hz, 3×CH_2; 1·51–1·61, m, 3×CH_2; 2·54, s, CH_3; 7·36–7·43, m, H6/7; 7·58–7·62, m, H1; 7·69–7·77, m, H5/8; 7·85, s, H4. ^{13}C n.m.r. δ 10·3, $SnCH_2$; 13·7, $\mathbf{C}H_3CH_2$; 25·2, Ar$\mathbf{C}H_3$; 27·4, $SnCH_2\mathbf{C}H_2$; 29·2, $CH_3\mathbf{C}H_2$; 124·9/125·9, C6/7; 126·7, C1; 127·1/127·3, C5/8; 131·3, C3; 133·7, C2; 136·7, C4; 141·4/141·5; C4a/8a. ν_{max} 3051, 2955, 2924, 2871, 2853, 1584, 1464, 1455, 1376, 872, 744, 666, 475 cm^{-1}. Mass spectrum *m/z* (relative intensity) 432 (0·02%, M); 379, 377, 375, 373, 371, 369 (1·0, 1·0, 6·4, 4·8, 2·7, 0·1; M − Bu); 323, 321, 319, 317, 315 (0·5, 0·5, 3·5, 2·8, 1·6; M − Bu − BuH); 265, 263, 261, 259, 257, 255 (2·7, 11·7, 15·9, 10·7, 4·1, 0·8; M − 3Bu); 141 (40, M − $SnBu_3$).*

(m) 1-(Phenylmethylidene)-1*H*-cyclopropa[*b*]naphthalene (33)

This compound was prepared by a modification of the literature method.[19] Thus, to a stirred solution of 1,1-bis(trimethylsilyl)-1*H*-cyclopropa[*b*]naphthalene (510 mg, 1·8 mmol) in anhydrous tetrahydrofuran (40 ml) at −70°C, under oxygen-free nitrogen, was added by syringe benzaldehyde (258 μl, 2·5 mmol). A suspension of potassium t-butoxide (270 mg, 2·4 mmol) in the same solvent (20 ml) was added slowly over 15 min. The solution was stirred for a further 30 min at −70°C, then warmed to −40°C and stirred at this temperature for 1·5 h followed by warming to room temperature over 1·5 h. Water was added and the aqueous mixture extracted with dichloromethane (3×50 ml). The combined organic extracts were washed with NaCl solution (saturated), dried ($MgSO_4$) and concentrated in vacuum to a yellow oil. Column chromatography (light petroleum) and crystallization (light petroleum) afforded

* Thermal reactions employing hexabutylditin in place of azobisisobutyronitrile as radical initiator afford stannylnaphthalene (32) in higher (75%) yield.

1-phenylmethylidene-1*H*-cyclopropa[*b*]naphthalene (33) (318 mg, 78%) as yellow crystals, m.p. 158–161°C (dec.) (lit.[19] yield 68%, m.p. 114–117°C) (Found: C, 94·5; H, 5·2. Calc. for $C_{18}H_{12}$: C, 94·7; H, 5·3%). Spectral data were in agreement with those previously reported.[19]

(n) Radical additions to 1-Phenylmethylidene-1*H*-cyclopropa[*b*]naphthalene (33)

(i) *With* N-*Bromosuccinimide*

Compound (33) (201 mg, 0·88 mmol), *N*-bromosuccinimide (156 mg, 0·88 mmol) and a catalytic amount of azobisisobutyronitrile (25 mg) were refluxed in tetrachloromethane (12 ml) for 48 h at *c.* 80°C as described for (23) above. Conventional workup provided a multicomponent product mixture. Radial chromatography (ethyl acetate/light petroleum, 1:20) provided unchanged (33) (49 mg, 24%) as the sole isolable product, m.p. and mixed m.p. 157–159°C.

(ii) *With Sulfuryl Chloride*

Reaction of (33) (103 mg, 0·45 mmol) with freshly distilled sulfuryl chloride (36 μl, 0·45 mmol) in the presence of a catalytic amount of azobisisobutyronitrile (15 mg) in refluxing benzene (20 ml) as described for (23) above for 5 h showed little consumption of starting material (t.l.c.). A further equal aliquot of sulfuryl chloride was added and the solution refluxed for a further 20 h; t.l.c. showed that (33) had been consumed. Attempted separation of the product mixture by radial chromatography was unsuccessful. Recrystallization (hexane) afforded a mixture of pale yellow crystalline compounds (36·2 mg, 27%, based upon $C_{18}H_{12}Cl_2$). Mass spectrum *m/z* (relative intensity) 302, 300, 298, (1·0, 6·6, 10·8%; M); 264, 262, (9·7, 21·6; M – HCl); 228 (93·6, M – 2Cl), 226 (45·5, M – 2HCl). All attempts to provide a pure sample resulted in decomposition.

(iii) *With Tributyltin Hydride*

Under the thermal conditions described for (23) above, the alkylidene compound (33) (51·9 mg, 0·23 mmol) with an equimolar amount of tributyltin hydride and a catalytic quantity of azobisisobutyronitrile (10 mg) gave a complex mixture of *c.* 11 products that resisted all attempts of separation. Under photochemical conditions (33) was recovered unchanged (68%).

(iv) *With Benzenethiol*

Reaction of (33) with benzenethiol under the conditions described for (23) afforded (as the only characterizable product) diphenyl disulfide (53%) as white needles (ethanol), m.p. 60–61°C (lit.[33] 60°C). ^{1}H n.m.r. δ 7·21–7·57, m, 10H. Mass spectrum *m/z* (relative intensity) 220, 218 (1·5, 15·7%; M); 187, 185 (0·3, 5·0; M – HS); 154 (9·0, M – 2S), 109 (100, M – PhS). Treatment of (33) with benzenethiol in the dark resulted in a 69% recovery of starting material; no other products were isolated.

(o) Radical Additions to 1-(Diphenylmethylidene)-1*H*-cyclopropa[*b*]naphthalene (34)

(i) *With Sulfuryl Chloride*

Compound (34)[19] (203 mg, 0·67 mmol) and a catalytic amount of azobisisobutyronitrile (25 mg) in dry benzene (20 ml) was reacted with sulfuryl chloride (54 μl, 0·67 mmol) as described above for (23). After 5 h of reflux, t.l.c. indicated little consumption of (34), and a second equal aliquot of sulfuryl chloride was added. After a further 20 h of reflux, starting material was consumed, and the solution was cooled and concentrated in vacuum to a yellow oil. Radial chromatography (dichloromethane/light petroleum, 1:10) afforded red crystals (hexane), m.p. 176–177°C (10 mg, 4% based upon $C_{24}H_{15}Cl$), tentatively assigned as 6-chloro-5-phenylbenz[*a*]anthracene. ^{1}H n.m.r. δ 7·29, s, 1H; 7·35–7·40, m, 1H; 7·42–7·47, m, 5H; 7·48–7·52, m, 4H+1H; 7·79–7·82, m, 1H; 8·19–8·24, m, 1H; 8·28, s, 1H. ^{13}C n.m.r. δ 119·3; 120·6; 124·8; 127·2; 128·2; 128·3; 129·8; 130·4, 131·0, 132·5, 133·74 (all CH); 127·4 (2×CH); 132·0, 133·67, 134·0, 134·2, 137·1, 138·2, 138·3, 143·2 (all q).

[33] Krafft, F., and Vorster, W., *Ber. Dtsch. Chem. Ges.*, 1893, **26**, 2831.

Mass spectrum *m/z* (relative intensity) 340, 338 (15, 46%; M); 302 (45, M – HCl), 300 (28, M – 2H – HCl), 224 (4, M – PhH – HCl), 151 (88), 150 (100).

^{1}H n.m.r. analysis of the slower moving components recovered from the radial chromatography plate (152 mg) showed the material had changed from the crude reaction mixture.

(ii) *With Benzenethiol*

Treatment of (34) (101 mg, 0·33 mmol) with benzenethiol (34 μl, 0·33 mmol) with simultaneous irradiation as described for (23) above gave a yellowish brown oil. Column chromatography (ethyl acetate/light petroleum, 1:20) afforded diphenyl disulfide[33] (9·4 mg, 13%), m.p. and mixed m.p. 57–59°C, identical to the sample described in Section (*n*)(iv) above. Unchanged (34) (22 mg, 22%), m.p. and mixed m.p. 108–111°C, was obtained and a new compound proposed as 5-phenyl-6-phenylsulfanylbenz[*a*]anthracene (37) (14·4 mg, 11% based upon $C_{30}H_{20}S$) as yellow crystals (hexane), m.p. 132–135°C. ^{1}H n.m.r. δ 7·00, s, 5H; 7·23–8·20, M, 17H; 8·85/8·95, d, 1H; 9·15, s, 1H; 9·24, s, 1H. Mass spectrum *m/z* (relative intensity) 414, 412 (5·8, 53·6%; M); 379 (13, M – HS); 336, 334 (4, 25; M – PhH); 302 (27, M – PhSH). Irradiation of (34) alone resulted in a 67% recovery of starting material as the only characterizable component.

(ii) *With Tributyltin Hydride*

The diphenylmethylidene compound (34) (201 mg, 0·66 mmol) was reacted with tributyltin hydride (178 μl, 0·66 mmol) in the presence of a catalytic amount of azobisisobutyronitrile (25 mg) as described for (23) above. Although starting material was consumed in less than 2 h, the complex product mixture resisted separation and characterization.

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