

## Preparation and Chemical Behaviour of *exo*-Methylene Compounds: Isoelectronic Compounds of 5-Methylenecyclohexa-1,3-diene

Akira Sugimoto,\* Junzo Yamano, Masahiro Yasueda, and Shigeo Yoneda

Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Mozu-Umemachi, Sakai, 591, Japan

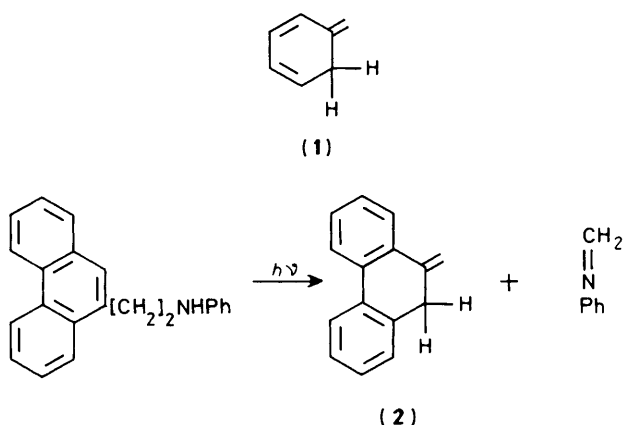
Some *exo*-methylene compounds such as 9-methylene-9,10-dihydrophenanthrene (**2**) were photolytically prepared and their chemical behaviour was investigated. Treatment of (**2**) with acid ( $\text{CF}_3\text{CO}_2\text{H}$ ) or base ( $^-\text{O}^+\text{Bu}^t$ ) led to the formation of 9-methylphenanthrene, with bromine to 9-bromomethylphenanthrene. Reaction with dimethyl acetylenedicarboxylate did not give Diels–Alder adduct but gave an ene adduct. Treatment with ethenetetracarbonitrile also gave an ene adduct. Reaction with carbene or carbenoids gave 9,10-dihydrophenanthrene-9-spirocyclopropanes. Reaction with ethenetetracarbonitrile was examined for other *exo*-methylene compounds, 1-methylene-1,2-dihydronaphthalene and 2-methylene-2,3-dihydrobenzo[*b*]thiophene. The aromatisation may be responsible for the reactions of these *exo*-methylene compounds except for the reaction with carbenes.

Since the synthesis of 5-methylenecyclohexa-1,3-diene (**1**), which is a double bond isomer of toluene, was reported by Bailey and Baylouny,<sup>1</sup> some papers related to the formation of compound (**1**) or its benzologues have been published.<sup>2</sup> Owing to the driving force for aromatisation, however, it is not easy to investigate the chemical properties of these compounds, *i.e.* the chemical characteristics of the *exo*-methylene double bond.<sup>3</sup> We have previously reported the isolation of 9-methylene-9,10-dihydrophenanthrene (**2**), which is a benzologue of compound (**1**), from the photolytic reaction mixture of 9-(2-anilinoethyl)phenanthrene.<sup>4</sup> This *exo*-methylene compound (**2**) shows

*exo*-methylene compounds and detailed studies on their chemical characteristics.

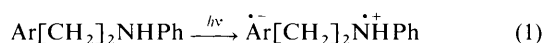
### Results and Discussion

*Preparation of *exo*-Methylene Compounds.*—Photolyses were carried out on benzene solutions of aniline derivatives which were synthesized by the reduction of the corresponding anilide with  $\text{LiAlH}_4$ . Photolysis of 1-(2-anilinoethyl)naphthalene gave 1-methylene-1,2-dihydronaphthalene (**13**) contaminated with its stable isomer, 1-methylnaphthalene. The chemical structures of compound (**13**) and its methyl isomer were identified by comparing the spectroscopic data with those reported in the literature.<sup>2c</sup> Similarly, 2-methylene-2,3-dihydrobenzo[*b*]thiophene (**14**) was obtained by the photolysis of the corresponding anilinoethyl derivative. The spectroscopic and elemental analysis data were consistent with the assigned structure (**14**). In particular, the  $^1\text{H}$  n.m.r. signals of the photoproduct at  $\delta$  4.11–4.13 (m) were assigned to those due to methylene protons of the ring and those at 5.12–5.15 (m) and 5.21–5.24 (m) to *exo*-methylene protons. As for the 2-naphthyl *exo*-methylene compound, its dimer, 2-[2-(2-naphthyl)ethyl]-1,2-dihydronaphthalene, was isolated and this has been reported already.<sup>5</sup> The formation mechanism of the *exo*-methylene compounds is as yet obscure. In our previous paper, however, we suggested that the intramolecular reaction of the phenanthrene moiety with the anilino group was a photo-induced electron-transfer.<sup>4b</sup> If the electron-transfer reaction is really induced in this case, the formation of *exo*-methylene compounds can be reasonably explained by the following sequential equations (1)–(3).



considerable thermal stability (half-life *ca.* 3 days in refluxing chloroform; see Experimental section) and consequently may serve as a good candidate for the elucidation of the chemical properties of the *exo*-methylene double bond.†

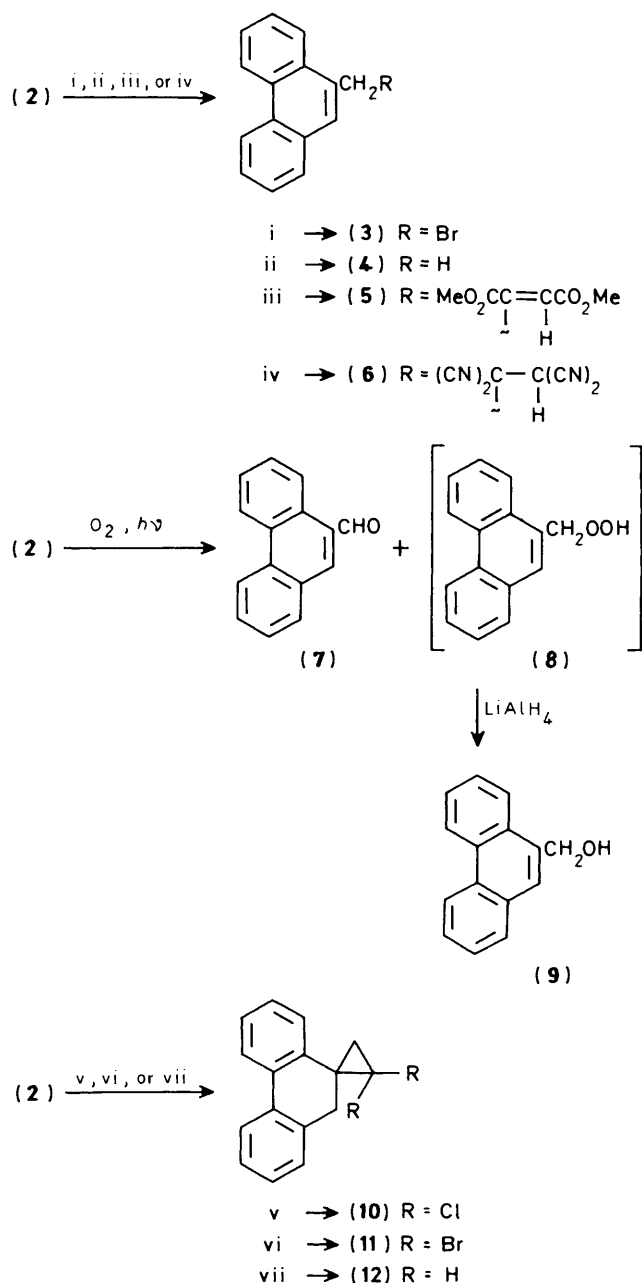
On the other hand, the present photolytic procedure was applicable to the preparation of the isoelectronic system of compound (**1**). This paper is concerned with the preparation of



The intermediate 1,4-biradical may behave in a similar manner to the Norrish II-type photochemical reaction of 'carbonyl compounds' having a  $\gamma$ -hydrogen.<sup>6</sup>

*Reactions.*—All the reactions of compound (**2**) examined here were summarised in Scheme 1. Reaction products were

† Simple Hückel calculations predict the stabilisation of compound (**2**) by aromatisation: ignoring  $\text{CH}_3$  or  $\text{CH}_2$  groups, the difference in energy between compound (**2**) and phenanthrene was 0.63  $\beta$ . Similarly, the difference between compound (**1**) and benzene was 1.01  $\beta$ , and that between 1-methylene-1,2-dihydronaphthalene and naphthalene was 0.82  $\beta$ .<sup>2c</sup>



**Scheme 1.** Reagents: i,  $\text{Br}_2\text{-CCl}_4$ ; ii,  $\text{CF}_3\text{CO}_2\text{H}$ ,  $\text{KOBu}^t$ ,  $\text{NaOMe}$ , or  $\text{I}_2$ ; iii, DMAD; iv, TCNE; v,  $\text{CHCl}_3\text{-NaOH}$ ; vi,  $\text{CHBr}_3\text{-NaOH}$ ; vii,  $\text{CH}_2\text{I}_2\text{-Zn}$

identified by comparing their spectroscopic data with those of authentic compounds. As for new compounds, spectroscopic data and elemental analyses confirmed the assigned structures.

**Reaction with cations and anions.** As expected from the chemical structure, compound (2) readily undergoes aromatisation on treatment with cationic or anionic reagents at room temperature. Thus, electrophilic reagents such as bromine led to aromatisation in preference to the usual reaction, addition to the double bond. Although the alternative reaction consisting of addition of bromine followed by elimination of hydrogen bromide may be possible, we have observed no evidence for the transient existence of an addition product, *i.e.* 9-bromo-9-bromomethyl-9,10-dihydrophenanthrene. In the presence of a large excess of bromine, compound (2) quantitatively gave 9-bromomethylphenanthrene (3),<sup>7</sup> whereas with an excess of (2)

the reaction led to the formation of 9-methylphenanthrene (4).<sup>8</sup> These results may be explained in terms of aromatisation by the electrophiles, *i.e.* bromine and the acid produced by the reaction of compound (2) with bromine. Treatment with acid (trifluoroacetic acid) at room temperature changed compound (2) into isomer (4) quantitatively. Similarly, addition of a solution of compound (2) in carbon tetrachloride to a solution of iodine gave isomer (4). On the other hand, compound (2) also isomerised to (4) on treatment with a base such as potassium *t*-butoxide or sodium methoxide in ether. These results demonstrated that aromatisation in preference to addition or substitution reactions is one of the characteristics of compound (2), although sterically hindered phenanthrenes, *i.e.* 1,4,5,8,9,10-hexamethyl- and decamethyl-phenanthrene, were reported to isomerise to *exo*-methylene-type compounds on treatment with acid.<sup>9</sup> Other *exo*-methylene compounds (13) and (14) changed to their respective aromatic isomers on treatment with acid at room temperature.

**Ene and related reactions.**<sup>10</sup> Dimethyl (9-phenanthrylmethyl)-maleate (5) was obtained by the reaction of compound (2) with dimethyl acetylenedicarboxylate (DMAD) under benzene reflux conditions. The ester (5) is not a Diels-Alder adduct but an ene adduct. The *Z*-structure of product (5) was inferred from a comparison of the i.r. spectrum with those of dimethyl fumarate and dimethyl maleate<sup>11</sup> and from the n.m.r. chemical shift of the olefinic proton:  $\delta$ -values of olefinic protons of dimethyl citraconate (*Z*-structure) and dimethyl mesaconate (*E*-structure) are reported to be 5.75 and 6.69, respectively.<sup>11</sup> The  $\delta$ -value of the corresponding proton of compound (5) was 5.49, suggesting the *Z*-structure. The formation of the ene adduct is reasonably explained in terms of an ene reaction with aromatisation stabilisation, while the formation of Diels-Alder adduct needs some energy due to de-aromatisation. Treatment of compound (2) with ethenetetracarbonitrile (TCNE) also led to formation of an ene adduct, 3-(9-phenanthryl)propane-1,1,2,2-tetracarbonitrile (6). Similarly, in the presence of Rose Bengal, compound (2) reacted with oxygen upon irradiation to give hydroperoxide (8) accompanied by 9-formylphenanthrene (7)<sup>12</sup> and (9-phenanthryl)methanol (9).<sup>7</sup> The aldehyde (7) may be formed by fission of the O-O bond of (8) followed by hydrogen transfer to OH radical. Peroxide (8) gave a positive peroxide test with potassium iodide solution and was identified by the formation of alcohol (9) on reaction with  $\text{LiAlH}_4$ . These results demonstrated that compound (2) is subject to ene reaction with aromatisation as illustrated in Scheme 2.

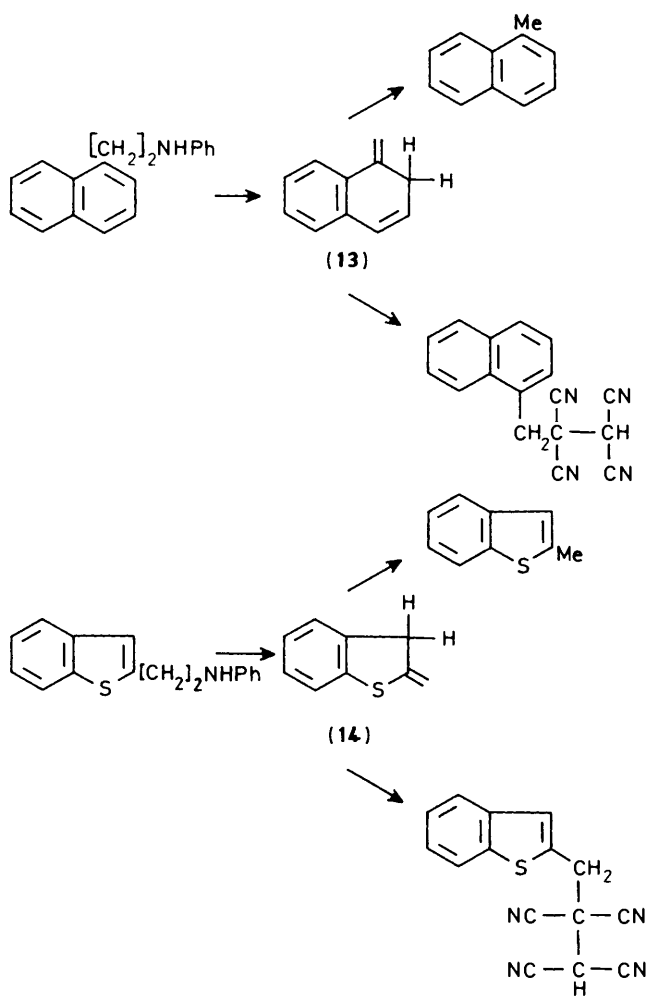


**Scheme 2.**

On the other hand, olefins such as styrene, maleic anhydride, and fumaronitrile were unreactive to the *exo*-methylene compound (2) under similar conditions. This result suggested the dependence of the present ene reaction on the electron affinity of the enophile. More information on this reaction, however, is necessary before the mechanism can be elucidated.

Other *exo*-methylene compounds (13) and (14) also underwent the ene reaction with TCNE to give tetracyano compounds (Scheme 3).

**Reaction with carbenes or carbenoid reagents.** These reactions resulted in the formation of spirocyclopropanes. In the presence of hexadecyltrimethylammonium bromide (CTAB), treatment of compound (2) with chloroform and aqueous base gave 2',2'-



dichloro-9,10-dihydrophenanthrene-9-spirocyclopropane (**10**) in good yield. The chemical structure of product (**10**) was identified on the basis of the following observations: (i) the  $^1\text{H}$  n.m.r. spectrum contained two AB-type quartet signals; the one at higher field ( $\delta$  1.73 and 2.31) corresponded to the signals due to the hydrogen atoms of the  $\text{CH}_2$  group in the dichlorocyclopropyl ring and the one at lower field ( $\delta$  2.92 and 3.49) to those

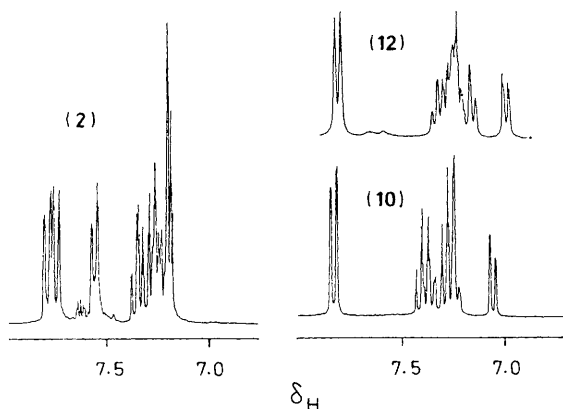


Figure.  $^1\text{H}$  N.m.r. spectra (aromatic regions) of compounds (**2**), (**10**), and (**12**)

in the dihydrophenanthrene ring; (ii) the upfield shift of one aromatic proton of compound (**10**), due to the anisotropy of the cyclopropane ring, is well known.<sup>13</sup> As shown in the Figure, both compound (**10**) and 9,10-dihydrophenanthrene-9-spirocyclopropane (**12**) (*vide infra*) showed doublets at  $\delta$  ca. 7.0, while compound (**2**) showed no signal in this region. The chemical shifts of the other aromatic protons of compounds (**10**) and (**12**) are similar to those of the aromatic protons of compound (**2**); (iii) other spectroscopic data (n.m.r., i.r., and mass) and elemental analysis were consistent with the assigned structure (**10**). In this reaction, trace amounts of 1,1-dichloro-1a-methyl-1a,9b-dihydro-1H-cyclopropa[b]phenanthrene\* were obtained from (**4**), while the product from carbene insertion to the C(10)–H bond was not detected by n.m.r. spectroscopy.† Similarly, reaction with dibromocarbene resulted in the formation of 2',2'-dibromo-9,10-dihydrophenanthrene-9-spirocyclopropane (**11**) in moderate yield. The chemical structure of product (**11**) was assigned in the same manner as in the case of the dichloro derivative.

On the other hand, reaction with Simmons–Smith reagent led to a mixture of spiro compound (**12**) (**24**), (**4**) (**29**), and 9-(2-iodoethyl)phenanthrene (5%). This iodide was identified by comparison of the spectroscopic data with those of the iodide which was prepared by a different method.

These results led to the conclusion that the *exo*-methylene double bond of compound (**2**) undergoes the usual addition reaction with carbene (in preference to aromatisation) or carbenoids (competition with aromatisation).

### Experimental

M.p.s were determined with a Yanaco micro-melting point apparatus (MP-500) and are uncorrected.  $^1\text{H}$  N.m.r. spectra were recorded on a Hitachi R-24A spectrometer (60 MHz) and/or JNM-GX270 spectrometer (270 MHz) with tetramethylsilane as internal standard. Mass spectra were obtained on a Shimadzu-LKB 9000 gas chromatograph–mass spectrometer. I.r. spectra were recorded on a Hitachi 215 i.r. spectrophotometer.

*Photolysis of 1-(2-Anilinoethyl)naphthalene.*—A solution of 1-(2-anilinoethyl)naphthalene (653 mg, 264 mmol) in benzene (500 ml) was bubbled with argon for 1 h and irradiated for 5 h. The solvent was evaporated off and the residue was chromatographed on silica gel with benzene–hexane (1:1). The first eluate gave a mixture of 1-methylnaphthalene and 1-methylene-1,2-dihydronaphthalene (**13**) as an oil [178 mg; purity 65%; contained (**13**) (0.81 mmol); yield 31%];  $\delta_{\text{H}}$ (270 MHz;  $\text{CDCl}_3$ ), 3.25 (2 H, m,  $=\text{CCH}_2\text{C}=\text{C}$ ), 5.01 (1 H, m,  $=\text{CHH}$ ), 5.36 (1 H, m,  $=\text{CHH}$ ), 5.99 (1 H, dt,  $J$  9.8, 4.0 Hz,  $\text{ArC}=\text{CH}$ ), 6.39 (1 H, dt,  $J$  9.8, 2.1 Hz,  $\text{ArCH}=\text{C}$ ), and 7.00–7.53 (4 H, m,  $\text{ArH}$ ). The second eluate contained unchanged 1-(2-anilinoethyl)naphthalene (155 mg, 24% recovery).

*Preparation and Photolysis of 2-(2-Anilinoethyl)benzo[b]thiophene.*—2-Benzo[b]thienylacetic acid (0.85 g, 4.42 mmol) ‡ was converted into the corresponding anilide by a

\* This compound was identified by comparison of its n.m.r. spectrum with that of the compound prepared from 9-methylphenanthrene: see Experimental section.

† Insertion into the C–H bond seems to be observed only with reactive carbenes: W. Kirmse, *Carbene Chemistry* 2nd edn., Academic Press, New York, 1971, p. 225.

‡ 2-Benzo[b]thienylacetic acid (m.p. 135–139 °C) was used as starting material: N. P. Kefford and J. M. Kelso [*Aust. J. Biol. Sci.*, 1957, **10**, 80 (*Chem. Abstr.*, 1957, **51**, 9066g)] reported the m.p. of this compound to be 141 °C.

standard method *via* the acid chloride; (*N*-2-benzo[*b*]thienyl-acetyl)aniline (0.84 g, 71%), m.p. 155–156 °C;  $\nu_{\max}$ (KBr) 3 250 (NH) and 1 660  $\text{cm}^{-1}$  (C=O). To a solution of this anilide (0.84 g, 3.15 mmol) in tetrahydrofuran–ether (1:1, 100 ml) was added  $\text{LiAlH}_4$  (1.0 g, 21 mmol) and the mixture was refluxed for 5 h. After treatment with aqueous ammonium chloride, the reaction mixture was extracted with ether. The extract was dried ( $\text{Na}_2\text{SO}_4$ ) and the solvent was evaporated off. The residue was chromatographed on silica gel with benzene to give 2-(2-anilinoethyl)benzo[*b*]thiophene (0.34 g, 42%), m.p. 81.5–82 °C (from benzene–hexane, 1:3) (Found: C, 76.0; H, 5.8; N, 5.6.  $\text{C}_{16}\text{H}_{15}\text{NS}$  requires C, 75.9; H, 6.0; N, 5.5%;  $\nu_{\max}$ (KBr) 3 400  $\text{cm}^{-1}$  (NH);  $\delta_{\text{H}}$ (270 MHz;  $\text{CDCl}_3$ ) 3.19 (2 H, t, *J* 6.4 Hz,  $\text{CH}_2$ ), 3.51 (2 H, t, *J* 6.4 Hz,  $\text{CH}_2$ ), and 6.61–6.75 (3 H, m), 7.07–7.35 (5 H, m), and 7.66–7.79 (2 H, m) (10 × ArH); *m/z* 273 ( $M^+$ , 14%), 148 (10), and 106 (100).

A degassed solution\* of 2-(2-anilinoethyl)benzo[*b*]thiophene (328 mg, 1.29 mmol) in benzene (80 ml) (in four tubes) was irradiated for 15 h. The solvent was removed by evaporation and the residue was chromatographed on silica gel with benzene–hexane (1:2). The first eluate yielded an oil which was a mixture of 2-methylbenzo[*b*]thiophene † and 2-methylene-2,3-dihydrobenzo[*b*]thiophene (14) [39 mg, purity 88%; contained (14) (0.23 mmol)] (Found: C, 72.7; H, 5.3.  $\text{C}_9\text{H}_8\text{S}$  requires C, 72.9; H, 5.4%;  $\delta_{\text{H}}$ (270 MHz;  $\text{CDCl}_3$ ) 4.12–4.14 (2 H, m, 3- $\text{H}_2$ ), 5.12–5.15 (1 H, m), 5.21–5.24 (1 H, m) (together = $\text{CH}_2$ ), and 7.00–7.15 (4 H, m, ArH). The second eluate contained unchanged 2-(2-anilinoethyl)benzo[*b*]thiophene (161 mg, 49% recovery).

**Reactions of Compound (2).**—As the *exo*-methylene compound gradually changed into the methyl isomer, the reactions were carried out without separation of the two isomers. Starting material (2) was contaminated with 4–15% of its isomer (4). Yields are based on the amount of pure compound (2) at the start of the reaction.

**Thermal stability of compound (2).** A  $\text{CDCl}_3$  (0.9 ml) solution of compound (2) [26 mg, purity 91%; contained (2) (0.12 mmol)] in an n.m.r. sample tube was heated in refluxing benzene. The ratio (2):(4) was checked by the integral intensity of the n.m.r. signals at  $\delta_{\text{H}}$  3.70 [for  $\text{CH}_2$  of (2)] and 2.73 [for  $\text{CH}_3$  of (4)]. After heating for 3 days, the ratio was *ca.* 1:1.

**Reaction with bromine.** (a) A solution of compound (2) [34 mg, purity 90%; contained (2) (0.16 mmol)] in carbon tetrachloride (10 ml) was added to a solution of bromine (3.9 g) in carbon tetrachloride (10 ml). After the solution had been stirred for a few min, the solvent was evaporated off. The residue was chromatographed on silica gel with benzene–hexane (1:2) to yield 9-(bromomethyl)phenanthrene (3) (42 mg, 87%), m.p. 118.5–119.5 °C (lit.,<sup>7</sup> 118.5–119 °C);  $\delta_{\text{H}}$ (270 MHz;  $\text{CDCl}_3$ ) 4.99 (2 H, s,  $\text{CH}_2$ ) and 7.58–8.22 (7 H, m) and 8.62–8.73 (2 H, m) (together 9 ArH); *m/z* 270 ( $M^+$ , 9%) and 191 (100,  $M^+$  – Br).

(b) A drop of bromine was added to a solution of compound (2) [29 mg, purity 85%; contained (2) (0.13 mmol)] in carbon tetrachloride (0.4 ml). After the solution had been shaken for a few min, the solvent was evaporated off. The residue was chromatographed on silica gel with hexane to give compound (4) (27 mg, 93%).

**Reaction with trifluoroacetic acid.** A drop of trifluoroacetic

acid was added to a solution of compound (2) [36 mg, purity 85%; contained (2) (0.16 mmol)] in carbon tetrachloride (0.4 ml). After being shaken for a few min the solution was evaporated under reduced pressure and the residue was chromatographed on silica gel with hexane to give compound (4) (36 mg) quantitatively; m.p. 92–93 °C (lit.,<sup>8</sup> 90–91 °C).

**Reaction with iodine.** A solution of compound (2) [39 mg, contained pure (2) (0.20 mmol); 96% purity] in carbon tetrachloride (10 ml) was added to a solution of iodine (242 mg, excess) in the same solvent (13 ml). After being stirred for a few min the solution was evaporated under reduced pressure to give compound (4)<sup>8</sup> quantitatively (39 mg) (identified spectroscopically).

**Reaction with potassium *t*-butoxide.** Potassium *t*-butoxide (20 mg, 0.18 mmol) was added to a solution of compound (2) [31 mg, purity 91%; contained (2) (0.18 mmol)] in anhydrous ether (10 ml). After being stirred for 1 h at room temperature the reaction mixture was poured into water and extracted with ether. The extract was dried ( $\text{MgSO}_4$ ) and evaporated. The residue was compound (4) (26 mg, 84%).

**Reaction with sodium methoxide.** A solution of compound (2) [30 mg, purity 90%; contained (2) (0.14 mmol)] in ether (10 ml) was added to a methanolic solution (3 ml) of sodium methoxide [prepared from Na (144 mg)]. After being stirred for 2 days at room temperature the mixture was poured into water and extracted with ether. The extract was dried and evaporated and the residue was chromatographed on silica gel with benzene–hexane (1:1) to give a mixture of isomers (2) and (4) [23 mg; (2) 15% and (4) 85% on the basis of n.m.r. analysis].

**Reaction with DMAD.** A solution of compound (2) [47 mg, purity 87% contained (2) (0.21 mmol)] and DMAD (116 mg, 0.82 mmol) in benzene (10 ml) was refluxed for 1 day. After cooling, the solution was concentrated almost to dryness and the residue was separated by chromatography on silica gel with benzene–hexane (1:1) to give a mixture of isomers (2) and (4) [20 mg; (2):(4) 54:46]. The second eluate contained unchanged DMAD (96 mg), and the third contained dimethyl-(9-phenanthrylmethyl)maleate (5) (37 mg, 52%), m.p. 117–118 °C (from hexane) (Found: C, 75.2; H, 5.3.  $\text{C}_{21}\text{H}_{18}\text{O}_4$  requires C, 75.4; H, 5.4%;  $\nu_{\max}$ (KBr) 1 720 (C=O) and 1 655  $\text{cm}^{-1}$  (C=C);  $\delta_{\text{H}}$ (270 MHz;  $\text{CDCl}_3$ ) 3.62 (3 H, s, Me), 3.86 (3 H, s, Me), 4.15 (2 H, d, *J* 1.8 Hz,  $\text{CH}_2$ ), 5.49 (1 H, t, *J* 1.8 Hz, =CH), and 7.60–7.97 (7 H, m) and 8.66–8.76 (2 H, m) (together 9 ArH); *m/z* 334 ( $M^+$ , 47%), 303 ( $M^+$  –  $\text{OCH}_3$ , 4), 302 (4), 274 (40), 260 (17), and 215 (100).

**Reaction with TCNE.** A solution of compound (2) (88 mg, purity 91%; contained (2) (0.42 mmol)] and TCNE (55 mg, 0.43 mmol) in benzene (20 ml) was stirred at room temperature for 2 days. Evaporation of solvent gave 3-(9-phenanthryl)propane-1,1,2,2-tetracarbonitrile (6) (119 mg, 89%), m.p. 160–163 °C [from benzene–hexane (1:1)] (Found: C, 78.8; H, 3.5; N, 17.6.  $\text{C}_{21}\text{H}_{12}\text{N}_4$  requires C, 78.7; H, 3.8; N, 17.5%;  $\nu_{\max}$ (KBr) 2 250  $\text{cm}^{-1}$  (CN);  $\delta_{\text{H}}$ (270 MHz;  $\text{CDCl}_3$ ) 4.16 (2 H, s,  $\text{CH}_2$ ), 4.49 (1 H, s, CH), and 7.65–8.19 (7 H, m) and 8.71–8.84 (2 H, m) (together 9 ArH); *m/z* 293 ( $M^+$  – HCN, 100%) and 191 (55).

**Reaction with singlet oxygen.** Under oxygen bubbling, a *t*-butyl alcohol solution (20 ml) of Rose Bengal (7 mg) and compound (2) [57 mg, purity 89%; pure (2) (0.26 mmol)] in a Pyrex tube was irradiated with a tungsten lamp (100 W) for 1 day at room temperature. After irradiation, the solvent was evaporated off under reduced pressure and the residue was chromatographed on silica gel with benzene–hexane (1:1). The first eluate gave isomer (4) (8 mg) and the second eluate yielded aldehyde (7) (13 mg, 24%), m.p. 101–102 °C (lit.,<sup>12</sup> 99–100 °C). Successive elution with benzene yielded (9-phenanthryl)-methyl hydroperoxide (8) (7 mg, 12%), m.p. 108–111 °C (decomp.);  $\nu_{\max}$ (KBr) 3 320  $\text{cm}^{-1}$  (OOH);  $\delta_{\text{H}}$ (270 MHz;  $\text{CDCl}_3$ ) 5.53 (2 H, s,  $\text{ArCH}_2$ ), and 7.61–8.20 (7 H, m), and

\* By a freeze–pump–thaw method. Details are in the Experimental section of ref. 4b.

† Authentic 2-methylbenzo[*b*]thiophene was prepared by the reaction of benzo[*b*]thiophene with butyl-lithium followed by reaction with methyl iodide; m.p. 51.5–52.5 °C (from ethanol); picrate, m.p. 108.5–109.5 °C (lit., m.p. 51.5–52 °C; and picrate, m.p. 108–109 °C; D. A. Shirley and M. D. Cameron, *J. Am. Chem. Soc.*, 1952, **74**, 664).

8.67—8.76 (2 H, m) (together 9 ArH) and then the alcohol (**9**) (16 mg, 30%), m.p. 151—152 °C (lit.,<sup>7</sup> 149 °C).

**Reduction of hydroperoxide (8).** An excess of LiAlH<sub>4</sub> was added to a solution of hydroperoxide (**8**) (10 mg, 0.04 mmol) in ether (4 ml) and the mixture was stirred overnight at room temperature, acidified, and extracted with ether. Alcohol (**9**) was obtained in quantitative yield (9 mg, 0.04 mmol), m.p. 151—152 °C.<sup>7</sup>

**Reaction of compound (13) with TCNE.** A solution of compound (**13**) (95 mg), contaminated with 1-methylnaphthalene; pure (**13**) (0.11 mmol) and TCNE (103 mg, 0.80 mmol) in benzene (25 ml) was stirred for 41 h at room temperature. After the solvent had been removed by evaporation, the residue was treated with a small amount of chloroform. Undissolved TCNE was removed by filtration and the filtrate was evaporated. Chromatography of the residue on silica gel with benzene gave 3-(1-naphthyl)propane-1,1,2,2-tetracarbonitrile (75 mg, 54%), m.p. 132—135 °C (reprecipitated from CHCl<sub>3</sub> by hexane) (Found: C, 75.7; H, 3.5; N, 20.75. C<sub>17</sub>H<sub>10</sub>N<sub>4</sub> requires C, 75.5; H, 3.7; N, 20.7%; v<sub>max</sub>(KBr) 2 250 cm<sup>-1</sup> (CN); δ<sub>H</sub>(270 MHz; CDCl<sub>3</sub>) 4.09 (2 H, s, CH<sub>2</sub>), 4.42 (1 H, s, CH), and 7.56—8.13 (7 H, m, ArH); δ<sub>C</sub>(68 MHz; CDCl<sub>3</sub>) 31.5, 37.0, 40.7, 107.4, 110.5, 122.6, 124.8, 125.5, 127.0, 127.7, 129.5, 129.9, 131.3, 131.6, and 134.3; m/z 243 (M<sup>+</sup> - HCN, 100%), 216 (M<sup>+</sup> - 2HCN, 23), 215 (39), 178 (24), and 141 (36). 1-Methylnaphthalene (19 mg) was recovered from the first eluate from the column.

**Reaction of compound (14) with TCNE.** A solution of compound (**14**) [39 mg, purity 88%; contained (**14**) (0.23 mmol)] and TCNE (45 mg, 0.35 mmol) in benzene (17 ml) was stirred at room temperature for 12 h. By a similar procedure to that in the case of compound (**13**), 3-(2-benzo[b]thienyl)propane-1,1,2,2-tetracarbonitrile was obtained (23 mg, 36%), m.p. 126—128 °C (decomp.) (reprecipitated from benzene by hexane) (Found: C, 65.4; H, 2.7; N, 20.2. C<sub>15</sub>H<sub>8</sub>N<sub>4</sub>S requires C, 65.2; H, 2.9; N, 20.3%; v<sub>max</sub>(KBr) 2 250 cm<sup>-1</sup> (CN); δ<sub>H</sub>(270 MHz; CDCl<sub>3</sub>) 3.94 (2 H, s, CH<sub>2</sub>), 4.32 [1 H, s, CH(CN)<sub>2</sub>], and 7.43—7.88 (5 H, m, ArH); m/z 249 (M<sup>+</sup> - HCN, 100%), 222 (M<sup>+</sup> - 2HCN, 22), and 147 (44).

**Reaction of compound (2) with dichlorocarbene.** A solution of compound (**2**) [96 mg, purity 92%; contained (**2**) (0.46 mmol)] in chloroform (9 ml) was added to a mixture of CTAB (40 mg, 0.11 mmol), aqueous sodium hydroxide (30 g; 33% w/w), and chloroform (2 ml). After being heated at 45 °C for 2 h, the reaction mixture was poured into ice-water, acidified with hydrochloric acid, and extracted with ether. The extract was washed with water, dried, and evaporated. Chromatography on silica gel with hexane yielded 2',2'-dichloro-9,10-dihydrophenanthrene-9-spirocyclopropane (**10**) (115 mg, 91%), m.p. 138—139 °C (from hexane) (Found: C, 69.6; H, 4.2. C<sub>16</sub>H<sub>12</sub>Cl<sub>2</sub> requires C, 69.8; H, 4.4%; δ<sub>H</sub>(270 MHz; CDCl<sub>3</sub>) 1.73 and 2.31 (2 H, q, J 7.9 Hz, cyclopropane), 2.92 and 3.49 (2 H, q, J 15.9 Hz, ArCH<sub>2</sub>), and 7.04—7.43 (6 H, m) and 7.81—7.84 (2 H, m) (together 8 ArH); δ<sub>C</sub>(68 MHz; CDCl<sub>3</sub>) 28.2, 34.6, 37.3, 65.0, 124.1, 124.3, 125.7, 127.1, 127.6, 128.0, 128.1, 128.3, 133.7, 134.3, 134.6, and 136.3; m/z 274 (M<sup>+</sup>, 3%), 239 (2, M<sup>+</sup> - Cl, 2), 203 (10), 202 (12), and 178 (100%).

**Reaction of compound (4) with dichlorocarbene.** By a similar procedure to that above, reaction of compound (**4**) (96 mg, 0.50 mmol) with dichlorocarbene gave 1,1-dichloro-1a-methyl-1a,9b-dihydro-1H-cyclopropa[b]phenanthrene (132 mg, 96%), m.p. 81—82.5 °C (from EtOH) (Found: C, 69.8; H, 4.4. C<sub>16</sub>H<sub>12</sub>Cl<sub>2</sub> requires C, 69.8; H, 4.4%; v<sub>max</sub>(KBr) 1 495, 1 450, 910, 760, and 720 cm<sup>-1</sup>; δ<sub>H</sub>(270 MHz; CDCl<sub>3</sub>) 1.94 (3 H, s, Me), 2.93 (1 H, s, ArCH), and 7.24—7.62 (6 H, m), and 7.98—8.01 (2 H, m) (together 8 ArH); m/z 274 (M<sup>+</sup>, 32%), 259 (M<sup>+</sup> - CH<sub>3</sub>, 54), and 239 (M<sup>+</sup> - Cl, 100).

**Reaction of compound (2) with dibromocarbene.** Except for the

addition of ethanol, the reaction procedure was similar to that carried out in the case of the dichloro derivative. A mixture of compound (**2**) [89 mg, contained 13% of (**4**); pure (**2**) 0.40 mmol] bromoform (25 g, 99 mmol), CTAB (40 mg, 0.11 mmol), ethanol (2 ml), and aqueous sodium hydroxide (30 g; 33% w/w) was stirred at 45 °C for 4 h. The first eluate from column chromatography of the reaction mixture on silica gel with hexane yielded compound (**4**) (18 mg). The second eluate yielded 2',2'-dibromo-9,10-dihydrophenanthrene-9-spirocyclopropane (**11**) (104 mg, 71%), m.p. 112—113 °C (from hexane) (Found: C, 53.1; H, 3.25. C<sub>16</sub>H<sub>12</sub>Br<sub>2</sub> requires C, 52.8; H, 3.3%; δ<sub>H</sub>(270 MHz; CDCl<sub>3</sub>) 1.94 and 2.50 (2 H, q, J 8.5 Hz, cyclopropane), 2.98 and 3.52 (2 H, q, J 15.9 Hz, ArCH<sub>2</sub>), and 7.04—7.44 (6 H, m) and 7.28—7.87 (2 H, m) (together 8 ArH); δ<sub>C</sub>(68 MHz; CDCl<sub>3</sub>) 30.0, 33.8, 35.1, 39.2, 124.0, 124.3, 126.1, 126.9, 127.6, 127.9, 128.3, 128.5, 134.3, 134.5, 134.9, and 136.2; m/z 362 (M<sup>+</sup>, 0.7%), 283 (M<sup>+</sup> - Br, 3), 203 (19), 202 (18), and 178 (100).

**Reaction of compound (2) with Simmons-Smith reagent.** A mixture of Zn-Cu couple (200 mg), methylene di-iodide (318 mg, 1.19 mmol), iodine (10 mg), and compound (**2**) (207 mg, 1.00 mmol calc. on 93% purity) in ether (30 ml) was refluxed under nitrogen for 48 h. After cooling, the mixture was filtered and the filtrate was washed successively with aqueous ammonium chloride and aqueous sodium hydrogen carbonate, dried, and evaporated to dryness. Separation by t.l.c. gave compound (**4**), 9,10-dihydrophenanthrene-9-spirocyclopropane (**12**) (50 mg, 24%), m.p. 54—56 °C (Found: C, 93.4; H, 6.9. C<sub>16</sub>H<sub>14</sub> requires C, 93.2; H, 6.8%; δ<sub>H</sub>(270 MHz; CDCl<sub>3</sub>) 0.78—0.98 (4 H, m, cyclopropane), 2.76 (2 H, s, CH<sub>2</sub>), and 6.97—7.81 (8 H, m, ArH); δ<sub>C</sub>(68 MHz; CDCl<sub>3</sub>) 13.7, 19.0, 39.4, 122.3, 123.86, 123.90, 126.3, 127.0, 127.4, 127.8, 127.9, 134.5, 135.5, 136.3, and 140.8; m/z 206 (M<sup>+</sup>, 38%) and 178 (100), and 9-(2-iodoethyl)phenanthrene (16 mg, 5%), m.p. 86—90 °C, which was identified spectroscopically.

**9-(2-Iodoethyl)phenanthrene.**—A mixture of 9-(2-chloroethyl)phenanthrene\* (1.79 g, 7.44 mmol), sodium iodide (5.76 g, 38.4 mmol), and butan-2-one (130 ml) was refluxed for 14 h. After the mixture had cooled, the precipitate was filtered off and the filtrate was evaporated. The residue was dissolved in benzene, and the solution was treated with aqueous sodium hydrogen sulphite, washed with water, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated to give 9-(2-iodoethyl)phenanthrene (1.73 g, 70%), m.p. 95—97 °C (from hexane) (Found: C, 58.0; H, 3.8. C<sub>16</sub>H<sub>13</sub>I requires C, 57.85; H, 3.9%; δ<sub>H</sub>(270 MHz; CDCl<sub>3</sub>) 3.50—3.56 (2 H, m, CH<sub>2</sub>), 3.67—3.73 (2 H, m, CH<sub>2</sub>), and 7.58—8.04 (7 H, m), and 8.64—8.77 (2 H, m) (together 9 ArH); m/z 332 (M<sup>+</sup>, 27%) and 205 (M<sup>+</sup> - I, 100).

\* 9-(2-Chloroethyl)phenanthrene (m.p. 81—82 °C) was prepared from 9-phenanthrylacetic acid by reduction with LiAlH<sub>4</sub> followed by treatment with thionyl chloride (lit., m.p. 82—84 °C; E. Bergmann and O. Blum-Bergmann, *J. Am. Chem. Soc.*, 1936, **58**, 1678).

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