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CYCLOAROMATIZATION OF α-OXOKETENE DITHIOACETALS AND β-OXODITHIOACETALS WITH BENZYL-,1-(NAPHTHYLMETHYL) AND 2-(NAPHTHYLMETHYL)MAGNESIUM HALIDES: SYNTHESIS OF CONDENSED POLYNUCLEAR AROMATIC HYDROCARBONS

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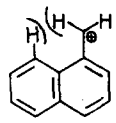
Abstract: *An efficient route for the synthesis of substituted naphthalenes, phenanthrenes and other polynuclear aromatic hydrocarbons has been developed. The methodology involves 1,2- (or sequential 1,4- and 1,2-) addition of either benzyl, 1-(naphthylmethyl) or 2-(naphthylmethyl) magnesium halides to α-oxoketene dithioacetals or β-oxodithioacetals followed by borontrifluoride etherate catalyzed cycloaromatization of the resulting carbinols.*

Construction of aromatic rings from acyclic precursors constitutes an important synthetic operation in organic chemistry[1]. As a part of this programme, we had reported a new approach for aromatic and heteroaromatic annelation of active methylene ketones via their α-oxoketene dithioacetals, through 1,2-addition of allyl[2,3] and azaallyl anions[4,5] followed by Lewis acid catalyzed cycloaromatization. However, the benzylmagnesium chloride underwent a sequential 1,4- followed by 1,2- addition to afford the corresponding benzyl substituted naphthalenes or their annelated derivatives 5a-e [6] (Scheme 1). In an effort to circumvent this sequential 1,4- and 1,2-addition, the corresponding β-oxodithioacetals 6,9 and 11 (Scheme 2 and 3) obtained by 1,4-reduction of 1-3 were considered appropriate to exclude the undesirable benzyl group in the naphthoannelated products. Similarly these studies were extended to the reaction of 1- and 2-(naphthylmethyl)magnesium halides with 1 to assess the possible *peri* interaction. In 1-(naphthylmethyl)magnesium halide the possible *peri* interaction might hinder the liberal delocalization of the negative charge over the ring and allow the preferred charge controlled 1,2-addition[7]. On the other hand, the corresponding 2-(naphthylmethyl)magnesium halide might simply follow sequential 1,4- followed by 1,2-addition in the absence of steric inhibition for the charge delocalization[7]. In their solvolytic studies, Dewar and Sampson[8] have shown that the methylene group in 1-(naphthylmethyl)cation cannot be coplanar with the ring without one of its hydrogen atoms overlapping too closely with the *peri*-hydrogen (A). The strain energy in these systems was calculated to be around 2.3 kcal/mole, which is enough to hinder the electronic interaction between ring and the methyl cation. However, in another study, Kronzer and Sandel[9] have investigated the structural features of 1- and 2-(naphthylmethyl)anions by ^{1}H NMR spectra and concluded that the methylene

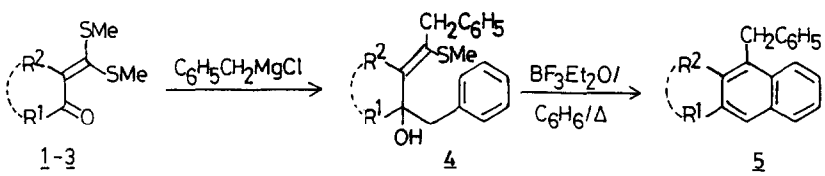


A

carbon is sp^2 hybridized and consequently the methylene hydrogens lie in or near the plane of ring. But the regioselectivity of these anions towards ambident electrophiles has not been investigated. Dewar argues that the strain energy of 2.3 kcal/mole calculated for naphthylmethyl and related systems using PMO method is correct, while the other methods of calculations which do not distinguish between α-naphthyl and β-naphthyl type systems are in error[8]. Our experiments corroborate Dewar's arguments and show that 1-(naphthylmethyl)magnesium chloride reacts with α-oxoketene dithioacetals in charge controlled 1,2-fashion, while the 2-(naphthylmethyl)magnesium bromide reacts with 1 in orbital controlled 1,4-fashion followed by 1,2-addition, with a few exceptions in each case. The initial carbinolacetals thus obtained in high yields, have been further cyclized in the presence of borontrifluoride etherate to the corresponding condensed aromatics. The method therefore provides a direct and efficient entry to polynuclear aromatic hydrocarbons from α-oxoketene dithioacetals. Our results are discussed in this paper.

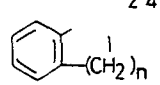
Results and Discussion

In our preliminary communication[6], we had reported the reaction of benzylmagnesium chloride with α-oxoketene dithioacetals 1-3 to afford the corresponding carbinolacetals 4 through sequential 1,4- followed by 1,2-addition (Scheme 1). These carbinolacetals were shown to undergo smooth cycloaromatization, when treated with borontrifluoride etherate to afford the corresponding benzyl substituted naphthalenes and their condensed aromatic systems 5a-e in high yields. To circumvent this 1,4-selectivity, the reaction of benzylmagnesium chloride with β-oxodithioacetals 6,9 and 11 was attempted. These β-oxodithioacetals were obtained by our recently reported procedure through 1,4-reduction of the respective dithioacetals with sodium borohydride in acetic acid[10]. Thus 6a reacted smoothly with benzylmagnesium chloride to afford the corresponding carbinolacetal 7a which underwent cycloaromatization in the presence of BF_3-etherate to afford 2-phenylnaphthalene (8a) in 90% yield. Similarly,



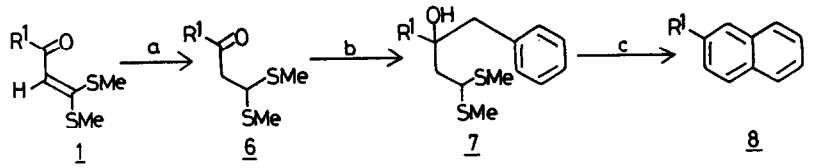
1-3 4 5

1, 4-5a, $R^1 = C_6H_5$; R^2 = H
1, 4-5b, R^1 = 2-naphthyl; R^2 = H
2b, 4-5c, $R^1 = R^2 = -(CH_2)_4-$

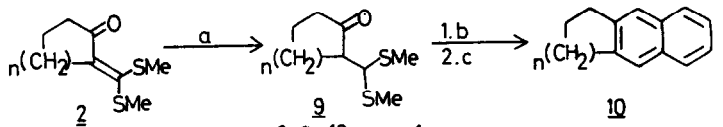
$R^1 = R^2$ = 

3a, 4-5d, n = 1
3b, 4-5e, n = 2

Scheme-1



1,6-8a, $R^1 = C_6H_5$
b, R^1 = 2-naphthyl
c, R^1 = Me

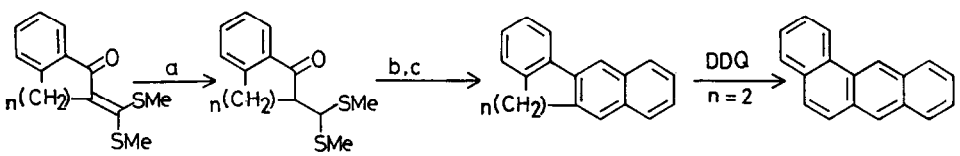


2,9-10a, n=1
b, n=2

a, $NaBH_4$/AcOH; b, $C_6H_5CH_2MgCl$, Et_2O/RT; c, $BF_3Et_2O/C_6H_6/\Delta$

Scheme-2

2,2'-binaphthyl (8b) and 2-methylnaphthalene (8c) were obtained in good yields (Scheme 2). The cyclic β-oxodithioacetals 9a-b similarly yielded the corresponding benz[*f*]indan (10a) and 1,2,3,4-tetrahydroanthracene (10b) under similar reaction conditions. The corresponding 11*H*-benzo[*b*]fluorene (12a) and 5,6-dihydrobenz[*a*]anthracene (12b) were similarly obtained from the respective β-oxodithioacetals 11a and 11b in good yields (Scheme 3). Dehydrogenation of 12b with DDQ afforded the known benz[*a*]anthracene (13) in 88% yield (Scheme 3) which was identical with the reported compound.



3a-b; 11a, n=1; b, n=2; 12a, n=1; b, n=2; 13

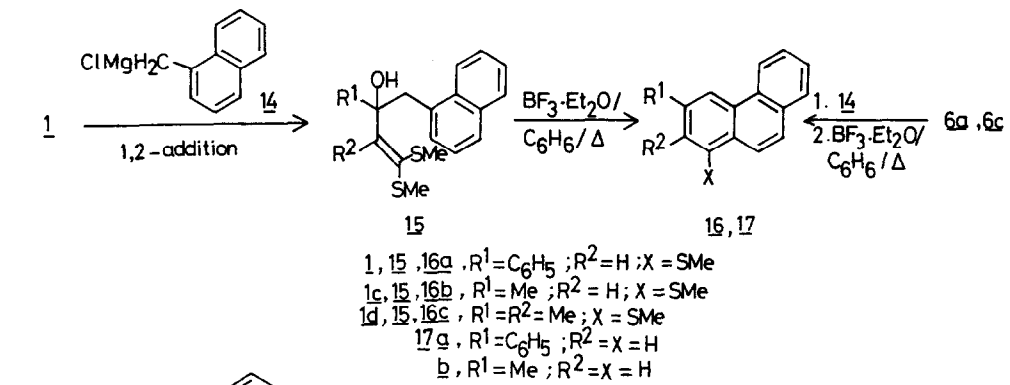
a, $NaBH_4$/AcOH; b, $C_6H_5CH_2MgCl/Et_2O$; c, $BF_3.Et_2O/C_6H_6/\Delta$

Scheme-3

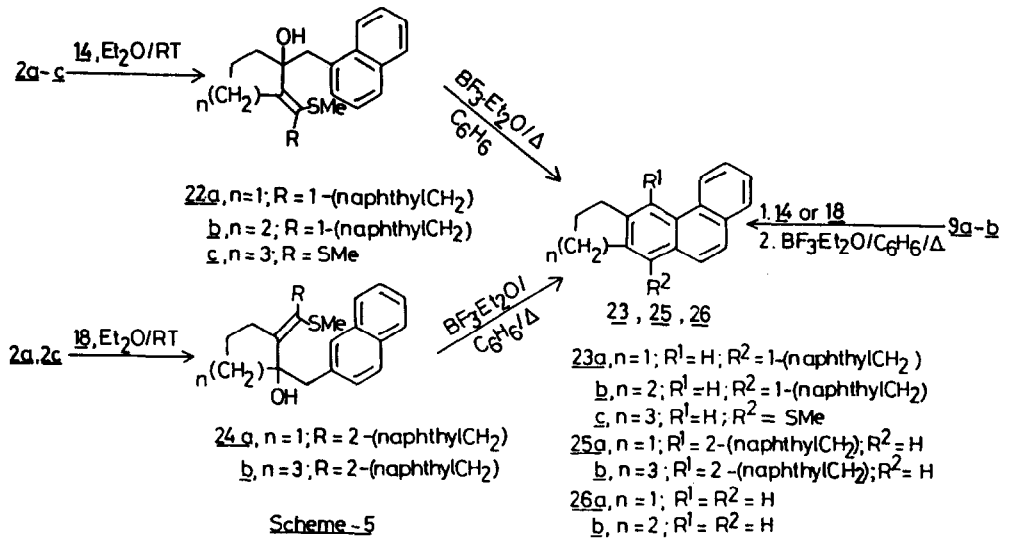
The reaction of 1- and 2-(naphthylmethyl)magnesium halides 14 and 18 with α-oxoketene dithioacetals was next investigated. Thus when 1a was reacted with 1-(naphthylmethyl)magnesium chloride 14, the corresponding carbinol-acetal 15a arising from exclusive 1,2-addition was obtained in 95% yield. Treatment of 15a with $BF_3.Et_2O$ in refluxing benzene gave the expected 1-(methylthio)-3-phenylphenanthrene (16a) in 74% yield (Scheme 4). The structure of 16a was fully established by analytical and spectral data followed by its conversion to the known 3-phenylphenanthrene (17a) by Raney Nickel desulphurization. Similarly, the 3-methyl-(16b) and 2,3-dimethyl-(16c) 1-methylthiophenanthrenes were obtained in 68-69% overall yields (Scheme 4). The phenanthrene 16b on desulphurization as described earlier

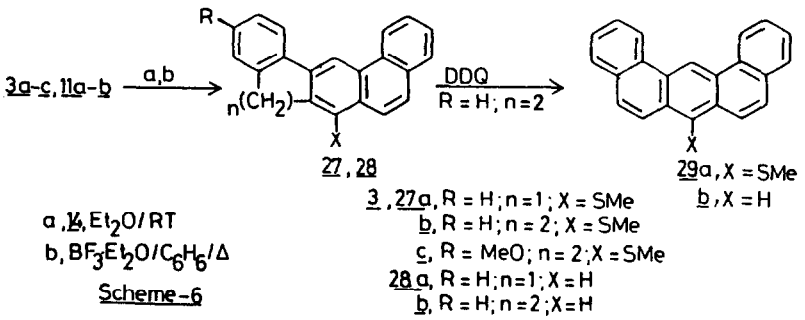
gave 3-methylphenanthrene (17b) in high yield. Also through the alternative route, phenanthrenes 17a and 17b could be directly obtained by reacting 14 with β-oxodithioacetals 6a and 6c under the described reaction conditions. However, the reactivity of 14 with the cyclic dithioacetals 2a-b differed from the aforementioned examples and displayed sequential 1,4- followed by 1,2-regioselectivity yielding the corresponding (1-naphthylmethyl)substituted 2,3-annelated phenanthrenes 23a-b in good yields (Scheme 5). Further attempts to a directed 1,2-addition under varying temperature conditions led only to the formation of carbinols 22. However, the desired cyclopenta[*b*]phenanthrene 26a and tetrahydrobenz[*a*]anthracene 26b were obtained by reacting 14 with the corresponding β-oxodithioacetals 9a and 9b respectively (Scheme 5). Interestingly, 14 reacted with dithioacetal 2c derived from cycloheptanone in the 1,2-fashion to afford the corresponding 7-methylthio-9,10,11,12-tetrahydro-8*H*-cyclohepta[*b*]phenanthrene (23c) (68%) after $BF_3.Et_2O$ catalyzed cycloaromatization of the resulting carbinol.

The addition of 14 with oxoketene dithioacetals 3a-c from indanone and α-tetralone also proceeded in 1,2- manner to afford the corresponding 2,3-annelated phenanthrenes 27a-c in good yields after cycloaromatization (Scheme 6). Raney Nickel dethiomethylation of 27a-b gave 28a-b respectively which were alternatively obtained by reacting 14 with the corresponding β-oxodithioacetals 11a-b (Scheme 6). Attempted dehydrogenation of 28b with DDQ to give the desired dibenz[*a,j*]anthracene 29b was not successful even after prolonged refluxing. However 29b was obtained by dehydrogenation of the corresponding methylthio derivative 27b with DDQ followed by Raney Nickel desulphurization of the resulting 29a (Scheme 6).



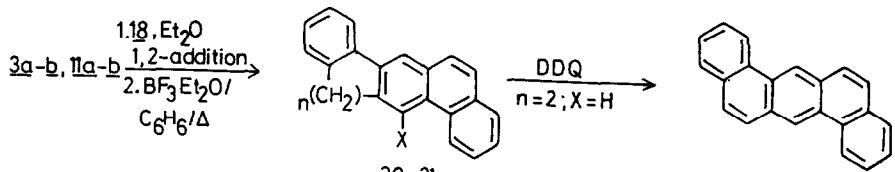
Scheme-4





The reaction of 2-(naphthylmethyl)magnesium bromide 18 with acyclic ketene dithioacetals 1a, 1c or the cyclic 2a, 2c followed the expected sequential 1,4- and 1,2-addition to afford the corresponding carbinolacetals 19a-b and 24a-b respectively (Scheme 4 and 5). These carbinolacetals underwent smooth cycloaromatization with $BF_3.Et_2O$ to the corresponding 4-(2-naphthylmethyl)-2-substituted 20a-b or 2,3-annelated 25a-b phenanthrenes in good yields (Scheme 4 and 5). Again, the problem of 1,4-addition was circumvented by reacting the respective β-oxodithioacetals 6a, 6c with 18 as described earlier to afford the corresponding 2-phenyl (21a) and 2-methyl (21b) phenanthrenes respectively in high yields (Scheme 4)[11].

The reactions of 2-(napthylmethyl)magnesium bromide 18, with 3a and 3b were the only exceptions which followed exclusive 1,2-addition pattern, to yield the corresponding carbinolacetals which underwent cycloaromatization to afford the respective indenophenanthrene 30a and dihydrodibenz[*a*,*h*]-anthracene 30b (Scheme 7).The Raney Nickel desulphurization of the products 30a-b afforded 31a-b respectively, which were also obtained by the reaction



30, 31

32

30a, n=1; X=SMe
b, n=2; X=SMe
31a, n=1; X=H
b, n=2; X=H

Scheme-7

sequence from 18 and 11a-b. The structure of 30b was further confirmed by its conversion to the known dibenz[*a,h*]anthracene 32 through dehydrogenation of 31b with DDQ.

In conclusion, a simple and efficient method for substituted and annelated naphthalene and phenanthrene derivatives has been developed with regiocontrol so that the desired substituents in the products could be incorporated both in the substrate molecule as well as in the Grignard reagents. The 1,4-selectivity can be easily circumvented by reacting benzyl or (naphthylmethyl)magnesium halides with the corresponding β-oxodithioacetals. The phenanthrene ring systems have been synthesized using multistep classical approaches in overall poor yields that do not enjoy prepartive advantages[12]. The present method appears to be of general application not only for regiospecifically substituted phenanthrenes but other important polycyclic hydrocarbons as exemplified by the synthesis of dibenz[*a,j*]anthracene (29b) as well as dibenz[*a,h*]anthracene (32). The only example of phenanthrene synthesis with similar strategy, which is recently described[13] in the literature, involves the reaction of 2-naphthylmethyl lithium with α-trimethylsilyloxymethylene cycloheptanone followed by its acid catalyzed cyclization. However, the generality of this reaction has not been investigated. The present method therefore fills the gap and provides a facile entry to 2,3-substituted phenanthrenes and condensed polynuclear hydrocarbons from easily accessible active methylene ketones.

Experimental Section

General: Melting points were determined on a Thomas Hoover melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 297 spectrophotometer. ^{1}H NMR spectra were measured at 90 MHz on a Varian EM-390 spectrometer in $CDCl_3$ or CCl_4 using TMS as internal standard. Mass spectra were obtained on a Jeol JMS-D-300 spectrometer. Elemental analysis were carried out on a Heraeus CHN-O-RPID instrument. All the starting α-oxoketene dithioacetals and β-oxodithioacetals were prepared according to the earlier reported procedures[10,14].

General Procedure for the Reaction of α-Oxoketene Dithioacetals or β-Oxodithioacetals with Benzyl, 1-(Naphthylmethyl) and 2-(Naphthylmethyl) magnesium halides

The reaction of oxoketene dithioacetal 1a with benzylmagnesium chloride is

representative. To an ice-cooled solution (0-5°C) of benzylmagnesium chloride [0.03 mol, prepared from magnesium turnings ((1.0g) and benzyl chloride (3.80g, 0.03 mol)] in dry ether (60 ml), 1a (3.40 g, 0.015 mol) in dry benzene (25 ml) was added dropwise (2-3 min.) under N_2 atmosphere. The reaction mixture was further stirred for 45 min. and the temperature was raised to room temperature. It was then decomposed by pouring over satd. aqueous NH_4Cl solution (50 ml), extracted with ether (2x50 ml) and the combined ether extracts were washed with water (50 ml), dried (Na_2SO_4) and evaporated to give the crude carbinol 4a which was used as such for cycloaromatization step. The reactions of oxoketene dithioacetals and β-oxodithioacetals with 1-(naphthylmethyl)-(14) and 2-(naphthylmethyl)-(18) magnesium halides were carried out in the similar manner except for the variation in molar quantities. Equimolar amount of Grignard reagent was used for 1,2-addition reaction, whereas two equivalents of either 14 or 18 was utilized for sequential 1,4- and 1,2-addition reactions.

General Procedure for $BF_3.Et_2O$ Cycloaromatization of Carbinols
Cycloaromatization of carbinol 4a is representative. To a solution of crude allylic carbinol 4a (0.015 mol),obtained from the reaction of 1a with benzylmagnesium chloride, in dry benzene (50 ml), borontrifluoride etherate (2 ml) was added and the reaction mixture was refluxed for 45 min. It was then cooled, poured into satd. $NaHCO_3$ solution (50 ml), extracted with chloroform (2x100 ml), washed with water (50 ml), dried (Na_2SO_4) and evaporated to give a viscous residue which on column chromatography over silica gel (hexane as eluent) afforded analytically pure **1-benzyl-3-phenylnaphthalene** (5a) as colourless crystals; 68%; m.p. 95-96°C; IR (KBr) 1495, 1448, 758, 700 cm^{-1}; δ_H (CCl_4) 3.92 (brs, 2H, $C_6H_5CH_2$); 6.65 (s, 1H, ArH); 7.01-7.71 (m, 15H, ArH); (Found: C, 93.62, H, 6.32. Calcd. for $C_{23}H_{18}$: C, 93.84; H, 6.16%); m/z 294 (M^+, 26%); 217 (25).

The spectral and analytical data of unknown and the known products (whose spectral data is not described earlier) thus obtained are given below.

4-Benzyl-2,2'-binaphthyl (5b); pale yellow crystals; 58%; m.p. 190-191°C, IR (KBr) 1495, 1445, 800, 718, 710 cm^{-1}; δ_H (CCl_4) 4.39 (s, 2H, $C_6H_5CH_2$); 6.42-6.61 (m, 2H, ArH); 7.01-8.06 (m, 16H, ArH); (Found: C, 94.33; H, 5.60. Calcd. for $C_{27}H_{20}$: C, 94.15; H, 5.85%); m/z 344 (M^+, 100%); 267 (22).

9-Benzyl-1,2,3,4-tetrahydroanthracene (5c); white crystals; 81%; m.p. 106°C; spectral and analytical data as described earlier[6].

10-Benzyl-11*H*-benzo[*b*]fluorene (5d); colourless crystals; 62%; m.p. 187-188°C; IR (KBr) 1496, 1448, 761, 730, 700 cm^{-1}; δ_H (CCl_4) 3.91 (s, 2H, CH_2); 4.50 (s, 2H, $C_6H_5CH_2$); 6.98-7.51 (m, 9H, ArH); 7.70-8.19 (m, 4H, ArH); 8.04 (s, 1H, H-5), (Found: C, 93.84; H, 5.73. Calcd. for $C_{24}H_{18}$: C, 94.08; H, 5.92); m/z 306 (M^+, 34%); 228 (12).

7-Benzyl-5,6-dihydrobenz[*a*]anthracene (5e); colourless crystals; 71%; m.p. 108°C; IR (KBr) 1488, 1008, 820, 698 cm^{-1}; δ_H (CCl_4) 3.00 (brs, 4H, CH_2); 4.49 (s, 2H, $C_6H_5CH_2$); 6.88-7.61 (m, 8H, ArH); 7.61-8.03 (m, 5H, ArH); 8.19 (s, 1H, H-12); (Found: C, 93.97; H, 6.51. Calcd. for $C_{25}H_{20}$: C, 93.71; H, 6.29%); m/z 320 (M^+,100%); 229 (62); 228 (73).

2-Phenylnaphthalene (8a); colourless crystals; 90%; m.p. 101-102°C (lit.[15] 103°C); IR (KBr) 1596, 1489, 1448, 855, 815, 716, 703, 682 cm^{-1}; (Found: C, 94.33; H, 6.15. Calcd. for $C_{16}H_{12}$: C, 94.07; H, 5.92%); m/z 204 (M^+, 100%).

2,2'-Binaphthyl (8b); colourless crystals (92%); m.p. 185-186°C (lit.[16] 187°C); IR (KBr) 1616, 1408, 900, 864, 825, 743 cm^{-1}; δ_H ($CDCl_3$) 7.40-7.72 (m, 4H, ArH); 7.80-8.11 (m, 8H, ArH); 8.11-8.51 (m, 2H, ArH); (Found: C, 94.71; H, 5.29. Calcd. for $C_{20}H_{14}$: C, 94.45; H, 5.55%).

2-Methylnaphthalene (8c); colourless crystals; 90%; m.p. 36-37°C (lit.[17] 37°C); IR (KBr) 1599, 819, 805, 745 cm^{-1}; δ_H (CCl_4) 2.40 (s, 3H, CH_3); 7.19-7.83 (m, 7H, ArH); (Found: C, 92.65; H, 6.87. Calcd. for $C_{11}H_{10}$: C, 92.91; H, 7.09%).

Benz[*f*]indan (10a); colourless crystals; 95%; m.p. 83-84°C (lit.[13,18] 84-85°C); IR, NMR data as described; (Found: C, 93.01; H, 7.38. Calcd. for $C_{13}H_{12}$: C, 92.81; H, 7.19%); m/z 168 (M^+, 100%).

1,2,3,4-Tetrahydroanthracene (10b); colourless crystals; 89%; m.p. 92-93°C (lit.[13] 92-94°C); IR and NMR data as reported; (Found: C, 92.51; H, 8.03. Calcd. for $C_{14}H_{14}$: C, 92.26; H, 7.74%); m/z 182 (M^+, 100%).

11*H*-Benzo[*b*]fluorene (12a); colourless crystals; 80%; m.p. 206-207°C (lit.[19a] 209°C); IR (KBr) 1619, 1568, 883, 726 cm^{-1}; δ_H ($CDCl_3$) 3.63 (s, 2H, CH_2); 7.44-7.78 (m, 5H, ArH); 7.90-8.19 (m, 3H, ArH); 8.31-8.49 (m, 2H, ArH); (Found: C, 94.68; H, 5.81 Calcd. for $C_{17}H_{12}$: C, 94.41; H, 5.59%).

5,6-Dihydrobenz[*a*]anthracene (12b); colourless crystals; 92%; m.p. 92-93°C; IR (KBr) 1510, 890, 808, 768, 740 cm^{-1}; δ_H ($CDCl_3$) 2.91 (brs, 4H, CH_2); 7.19-7.50 (m, 5H, ArH); 7.63 (s, 1H, H-7); 7.58-8.11 (m, 3H, ArH); 8.19 (s, 1H, H-12); (Found: C, 94.11; H, 5.89. Calcd. for $C_{18}H_{14}$: C, 93.87; H, 6.13%); m/z 230 (M^+, 50%).

1-(Methylthio)-3-phenylphenanthrene (16a); colourless crystals; 74%; m.p. 116-117°C; IR (KBr) 1590, 1398, 850, 801, 752, 730 cm^{-1}; δ_H ($CDCl_3$) 2.50 (s, 3H, SCH_3); 7.40-7.98 (m, 10H, ArH); 8.24 (d, J=8Hz, 1H, H-5); 8.73 (brs, 2H, H-2 and H-4); (Found: C, 84.24; H, 5.61. Calcd. for $C_{21}H_{16}S$: C, 83.96; H, 5.37%); m/z 300 (M^+, 100%), 285 (17); 252 (20).

3-Methyl-1-(methylthio)-phenanthrene (16b); colourless crystals; 69%; m.p. 79-80°C; IR (KBr) 1598, 1457, 1135, 903, 853, 832, 810, 732 cm^{-1}; δ_H ($CDCl_3$) 2.54 (s, 3H, CH_3); 2.62 (s, 3H, SCH_3); 7.29 (s, 1H, ArH); 7.45-7.90 (m, 5H, ArH); 8.36 (s, 1H, H-2); 8.61 (m, 1H, H-4); (Found: C, 80.76; H, 6.26. Calcd. for $C_{16}H_{14}S$: C, 80.63; H,5.92%); m/z 238 (M^+, 100%); 223 (26).

2,3-Dimethyl-1-(methylthio)-phenanthrene (16c); light yellow crystals; 68%; m.p. 92-93°C; IR (KBr) 1585, 1510, 1440 cm^{-1}; δ_H ($CDCl_3$) 2.42 (s, 3H, CH_3); 2.55 (s, 3H, CH_3); 2.61 (s, 3H, SCH_3); 7.42-7.80 (m, 3H, ArH); 7.63 (d, J=8Hz, 1H, ArH); 7.90 (d, J=8Hz, 1H, ArH); 8.32 (s, 1H, H-4); 8.55,(brd, J=8Hz, 1H, H-5); (Found: C, 81.12; H, 6.41. Calcd. for $C_{17}H_{16}S$: C, 80.90; H, 6.39%); m/z 252 (100%).

3-Phenylphenanthrene (17a) was obtained either by cycloaromatization of β-oxodithioacetal with 1-(naphthylmethylmagnesium)chloride **14** according to general procedure described (Method A) or by Raney Nickel dethiomethylation

of 16a (Method B) as described in the following section. A suspension of 16a (0.2g,0.0007 mol) and W-4 Raney Nickel (2.0g) in methanol (20 ml) was stirred at room temperature for 6 hr (monitored by T.L.C.). Raney Nickel was filtered, washed with hot methanol (3x10 ml) and the filtrate was concentrated under reduced pressure. The residue was diluted with $CHCl_3$ (30 ml), washed with water (2x25 ml), dried and evaporated to give crude 17a, which was purified by column chromatography over silica gel using hexane as eluent; colourless crystals; 89% (Method A); 85% (Method B); m.p. 71-72°C (lit.[20] 73°C); IR (KBr) 1613, 816, 757; 743 cm^{-1}; δ_H ($CDCl_3$) 7.19-8.95 (m, 11H, ArH); 8.12 (d, J=2.5Hz, 1H, H-4); 8.59-8.76 (m, 2H, ArH); (Found: C, 94.20; H, 5.76. Calcd. for $C_{20}H_{14}$: C, 94.45; H, 5.55%).

3-Methylphenanthrene (17b); colourless crystals; 82% (Method A); 85% (Method B); m.p. 62-63°C (lit.[19b] 64°C); IR (KBr) 1599, 819, 805, 745 cm^{-1}; NMR data as described[17]; (Found: C, 93.97; H, 6.56. Calcd. for $C_{15}H_{12}$: C, 93.71; H, 6.29%).

4-[2-(Naphthylmethyl)]-2-phenylphenanthrene (20a) ; colourless crystals; 71%; m.p. 149-150°C; IR(KBr) 1595, 882, 855, 810, 763, 740 cm^{-1}; δ_H ($CDCl_3$) 4.79 (s, 2H, CH_2); 7.28-8.28 (m, 17H, ArH); 8.15 (brs, 1H, ArH); 8.49 (s, 1H, ArH); 8.59 (brs, 1H, ArH); (Found: C, 94.57; H, 5.91. Calcd. for $C_{31}H_{22}$: C, 94.38; H, 5.62%); m/z 394 (M^+, 4%); 279 (20).

2-Methyl-4-[2-(naphthylmethyl)]phenanthrene (20b); colourless crystals; 72%; m.p. 122-123°C; IR (KBr) 1590, 860, 845, 800, 740, 700 cm^{-1}; δ_H ($CDCl_3$) 2.70 (s, 3H, CH_3); 4.25 (s, 2H, CH_2); 7.04-8.12 (m, 13H, ArH); 8.31 (s, 1H, ArH); 8.49 (s, 1H, ArH); (Found: C, 94.21; H, 6.32. Calcd. for $C_{26}H_{20}$: C, 93.94; H, 6.06%); m/z 332 (M^+, 100%); 317 (29).

2-Phenylphenanthrene (21a) was obtained by cycloaromatization of 6a with 18 (Method A); colourless crystals; 95%; m.p. 196-197°C (lit.[20], 198°C); IR(KBr) 1461, 891, 815, 757, 742, 712 cm^{-1}; δ_H ($CDCl_3$) 7.18-8.97 (m, 11H, ArH); 8.14 (d, J=2.5Hz, 1H, H-1); 8.60-8.70 (m, 2H, ArH); (Found: C, 94.36; H, 5.28 Calcd. for $C_{20}H_{14}$: C,94.45; H, 5.55%).

2-Methylphenanthrene (21b) was prepared by Method A; colourless crystals; 88%; m.p. 56-57°C (lit.[19b] 57-58°C);IR (KBr) 1600,820,804,745 cm^{-1} NMR data as described[17]; (Found: C,93.53;H,6.48. Calcd.for $C_{15}H_{12}$: C,93.71,H,6.29%).

9,10-Dihydro-8*H*-7-[1-(naphthylmethyl)]cyclopenta[*b*]phenanthrene (23a); colourless crystals; 58%; m.p. 141-142°C; IR (KBr) 1598, 1441, 1392, 820, 788, 760 cm^{-1}; δ_H ($CDCl_3$) 2.15 (quint, J=7Hz, 2H, CH_2); 2.98 (t, J=7Hz, 2H, CH_2); 3.25 (t, J=7Hz, 2H, CH_2); 4.91 (s, 2H, benzylic CH_2); 6.72 (d, J=8Hz, 1H, ArH); 7.23 (distorted t, J=8Hz, 2H, ArH); 7.43-8.30 (m, 9H, ArH); 8.45 (dd, J=8, 2.5Hz, 1H, ArH); 8.72 (s, 1H, H-10); 8.89 (d, J=8Hz, 1H, ArH); (Found: C, 93.70; H, 5.95. Calcd. for $C_{28}H_{22}$:C,93.81;H,6.19%); m/z 358 (M^+, 100%); 356 (30); 233 (96).

7-[1-(Naphthylmethyl)]-8,9,10,11-tetrahydrobenz[*a*]anthracene (23b); colourless crystals; 68%; m.p. 178°C; IR (KBr) 1596, 816, 792, 772, 762 cm^{-1}; δ_H ($CDCl_3$) 1.83 (brs, 4H, CH_2); 2.81 (brt, 2H, CH_2); 3.13 (brt, 2H, CH_2); 4.73 (s, 2H, benzylic CH_2); 6.58 (d, J=8Hz, 1H, ArH); 7.15 (distorted t, J= 8Hz, 2H, ArH); 7.30-8.05 (m, 18H, ArH); 8.38 (d, J=8Hz, 1H, ArH); 8.50 (s, 1H,

H-12); 8.78 (d, J=8Hz, 1H, ArH); (Found: C, 93.80; H, 6.74. Calcd. for $C_{29}H_{24}$: C, 93.51; H, 6.49%); m/z 372 (M^+, 100%); 244 (74).

7-(Methylthio)-9,10,11,12-tetrahydro-8*H*-cyclohepta[*b*]phenanthrene (23c); colourless crystals; 68%; m.p. 114-115°C; IR (KBr) 1588, 1465, 1440, 805, 746 cm^{-1}; δ_H ($CDCl_3$) 1.55-2.10 (m, 6H, CH_2); 2.68 (s, 3H, SCH_3); 3.05-3.55 (m, 4H, CH_2); 7.53-8.05 (m, 4H, ArH); 8.15 (d, J=8Hz, 1H, ArH); 8.58 (s, 1H, H-13); 8.80 (d, J=8Hz, 1H, ArH); (Found: C, 81.93; H, 7.01. Calcd. for $C_{20}H_{20}S$: C, 82.14; H, 6.89%); m/z 292 (M^+, 100%); 215 (62).

11-[2-(Naphthylmethyl)]-9,10-dihydro-8*H*-cyclopenta[*b*]phenanthrene (25a); colourless crystals; 56%; m.p. 142-143°C; IR (KBr) 1599, 900, 878, 815, 719 cm^{-1}; δ_H ($CDCl_3$) 2.08 (quint, J=8Hz,2H, CH_2);3.05 (t, 2H, CH_2); 3.15 (t, 2H, CH_2); 4.64 (s, 2H, benzylic CH_2); 7.02-8.02 (m, 12H, ArH); 8.30 (brs, 1H, ArH); 8.45 (brs, 1H, ArH); (Found: C, 93.66; H, 5.97. Calcd. for $C_{28}H_{22}$: C, 93.81; H, 6.19%); m/z 358 (M^+, 100%); 215 (22).

13-[2-(Naphthylmethyl)]-9,10,11,12-tetrahydro-8*H*-cyclohepta[*b*]phenanthrene (25b); colourless crystals; 68%; m.p. 151-152°C; IR (KBr) 1600, 880, 868, 845, 805 cm^{-1}; δ_H ($CDCl_3$) 1.32-1.88 (m, 6H, CH_2); 2.75-3.10 (m, 4H, CH_2); 4.70 (s, 2H, benzylic CH_2); 7.15-8.09 (m, 12H, ArH); 8.35 (s, 1H, ArH); 8.50 (s, 1H, ArH); (Found: C, 92.96; H, 7.02. Calcd. for $C_{30}H_{26}$: C, 93.22; H, 6.78%); m/z 388 (M^+, 100%).

9,10-Dihydro-8*H*-cyclopenta[*b*]phenanthrene (26a) was obtained from **9a** and **14** (or **18**) (Method A); colourless crystals; 86%; m.p. 133-134°C; IR (KBr) 1593, 811, 772, 747 cm^{-1}; δ_H ($CDCl_3$) 2.25 (quint, J=8Hz, 2H, CH_2); 3.09-3.40 (two overlapping t, 4H, CH_2); 7.45-7.98 (m, 6H, ArH); 8.51-8.75 (m, 2H, ArH); (Found: C, 93.79; H, 6.68. Calcd. for $C_{17}H_{14}$: C, 93.54; H, 6.46%); m/z 218 (M^+, 100%).

8,9,10,11-Tetrahydrobenz[*a*]anthracene (26b); obtained from **9b** and **14** (or **18**) (Method A); colourless crystals; 90%; m.p. 121-122°C; IR (KBr) 1600, 887, 747 cm^{-1}; δ_H (CCl_4) 1.74-2.19 (m, 4H, CH_2); 2.92 (brt, 2H, CH_2); 3.19 (brt, 2H, CH_2); 7.61-7.92 (m, 6H, ArH); 8.26-8.72 (m, 2H, ArH); (Found: C, 93.27; H, 7.20. Calcd. for $C_{18}H_{16}$: C, 93.06; H, 6.94%).

7-(Methylthio)-8*H*-indeno[2,1-*b*]phenanthrene (27a); colourless crystals; 66%; m.p. 145-146°C; IR (KBr) 1431, 1412, 1390, 819, 760, 740, 724 cm^{-1}; δ_H ($CDCl_3$) 2.51 (s, 3H, SCH_3); 4.30 (s, 2H, CH_2); 7.49-8.31 (m, 8H, ArH); 8.85-9.18 (m, 2H, ArH); 9.30 (s, 1H, H-13); (Found: C, 84.79; H, 5.34. Calcd. for $C_{22}H_{16}S$: C, 84.57; H, 5.16%); m/z 312 (M^+, 50%); 265 (100).

7-(Methylthio)-5,6-dihydrodibenz[*a*,*j*]anthracene (27b); colourless crystals; 67%; m.p. 85-86°C; IR (KBr) 1592, 833, 824, 753 cm^{-1}; δ_H ($CDCl_3$) 2.18 (s, 3H, SCH_3); 2.78 (brt, 2H, CH_2); 3.36 (brt, 2H, CH_2); 7.02-7.89 (m, 8H, ArH); 8.54 (brd, J=8Hz, 2H, ArH); 8.86 (s, 1H, H-14); (Found: C, 84.90; H, 5.32.Calcd. for $C_{23}H_{18}S$: C, 84.62; H, 5.56%); m/z 326 (M^+, 81%); 278 (100).

3-Methoxy-7-(methylthio)-5,6-dihydrodibenz[*a*,*j*]anthracene (27c); light yellow crystals; 74%; m.p. 144-145°C; IR (KBr) 1602, 1029, 842, 813, 742 cm^{-1}; δ_H ($CDCl_3$) 2.30 (s, 3H, SCH_3); 2.75-3.02 (distorted t, 2H, CH_2); 3.34-4.42 (distorted t, 2H, CH_2); 3.85 (s, 3H, OCH_3); 6.82 (brs, 1H, H-4);

6.95 (brd, J=8Hz, 1H, H-2); 7.54-8.08 (m, 5H, ArH); 8.65-8.89 (m, 2H, ArH); 9.02 (s, 1H, H-14); (Found: C, 80.61; H, 5.89. Calcd. for $C_{24}H_{20}OS$: C, 80.86; H, 5.66%); m/z 356 (M^+, 100%); 308 (65); 264 (75).

8H-Indeno[2,1-*b*]phenanthrene (28a); colourless crystals; 82% (Method A); 65% (Method B); m.p. 101-102°C; IR (KBr) 1590, 809, 801, 734 cm^{-1}; δ_H ($CDCl_3$) 4.02 (s, 2H, CH_2); 7.21-8.05 (m, 10H, ArH); 8.75 (brd, J=8Hz, 1H, ArH); 9.01 (s, 1H, H-13); (Found: C, 94.83; H, 5.54. Calcd. for $C_{21}H_{14}$: C, 94.70; H, 5.30%).

5,6-Dihydrodibenz[*a*,*j*]anthracene (28b); colourless crystals; 85% (Method A); 81% (Method B); m.p. 134-135°C; IR (KBr) 1597, 882, 764, 740 cm^{-1}; δ_H ($CDCl_3$) 3.00 (brs, 4H, CH_2); 7.18-8.00 (m, 9H, ArH); 8.09 (brd, J=8Hz, 1H, ArH); 8.64 (brd, J=8Hz, 1H, ArH); 9.11 (s, 1H, H-14); (Found: C, 94.47; H, 5.91. Calcd. for $C_{22}H_{16}$: C, 94.25; H, 5.75%).

13-(Methylthio)-12*H*-indeno[1,2-*b*]phenanthrene (30a), colourless crystals; 70%; m.p. 172-173°C; IR (KBr) 1600, 1467 cm^{-1}; δ_H ($CDCl_3$) 2.31 (s, 3H, SCH_3); 4.08 (s, 2H, CH_2); 7.28-8.13 (m, 8H, ArH); 8.50-8.81 (m, 2H, ArH); 8.91 (s, 1H, ArH); (Found: C, 84.31; H, 5.39. Calcd. for $C_{22}H_{16}S$: C, 84.57; H, 5.16%).

7-(Methylthio)-8,9-dihydro[*a*,*h*]anthracene (30b); colourless crystals; 53%; m.p. 93-94°C; IR (KBr) 1600, 1490 cm^{-1}; δ_H ($CDCl_3$) 2.18 (s, 3H, SCH_3); 2.58-2.98 (m, 2H, CH_2); 3.21-3.51 (m, 2H, CH_2); 7.09-8.22 (m, 10H, ArH); 9.09 (brs, 1H, ArH); (Found: C, 84.88; H, 5.79. Calcd. for $C_{23}H_{18}S$: C, 84.62; H, 5.56%); m/z 326 (M^+, 64%); 278 (100).

12*H*-Indeno[1,2-*b*]phenanthrene (31a); colourless crystals; 75% (Method A); 74% (Method B); m.p. 132-133°C; IR (KBr) 1612, 874, 811, 743 cm^{-1}; δ_H ($CDCl_3$) 3.82 (s, 2H, CH_2); 7.10 (d, J=8Hz, 2H, ArH); 7.50-8.22 (m, 9H, ArH); 8.90 (brs, 1H, ArH); (Found: C, 94.48; H, 5.07. Calcd. for $C_{21}H_{14}$: C, 94.70; H, 5.30%).

5,6-Dihydrodibenz[*a*,*h*]anthracene (31b); colourless crystals; 68% (Method A); 90% (Method B); m.p. 189-190°C; IR (KBr) 1603, 1433, 887, 775, 761, 732 cm^{-1}; δ_H ($CDCl_3$) 2.72-3.31 (m, 4H, CH_2); 7.23-8.12 (m, 9H, ArH); 8.28 (s, 1H, ArH); 8.63 (brs, 1H, ArH); 8.76 (brd, 1H, ArH); (Found: C, 94.48; H, 5.91. Calcd. for $C_{22}H_{16}$: C, 94.25; H, 5.75%); m/z 280 (M^+, 100%).

General Procedure for Dehydrogenation of 12b, 27b and 31b with DDQ Dehydrogenation of 12b is representative. A solution of 12b (0.1g, 0.0004 mol) and DDQ (0.1g, 0.0005 mol) in dioxane (20 ml) was refluxed for 24 hr under N_2 atmosphere. The precipitated hydroquinone was filtered off and the filtrate was concentrated under reduced pressure. The residue was purified by passing through a small silica gel column using hexane as eluent to give pure **Benz[*a*]anthracene (13)**; colourless crystals; 88%; m.p. 159-160°C (lit.[19c], 161-162°C); IR, NMR as described[21]; (Found: C, 94.93; H, 5.59. Calcd. for $C_{18}H_{12}$: C, 94.70; H, 5.30%).

7-(Methylthio)-dibenz[*a*,*j*]anthracene (29a); colourless crystals; 96%; m.p. 193-194°C; IR (KBr) 1512, 875, 822, 750, 745 cm^{-1}; δ_H ($CDCl_3$) 2.38 (s, 3H, SCH_3); 7.58-8.02 (m, 8H, ArH); 8.69-9.04 (m, 4H, ArH); 10.00 (s, 1H, H-14); (Found: C, 84.86; H, 4.70. Calcd. for $C_{23}H_{16}S$: C, 85.14; H, 4.97%).

Dibenz[*a*,*j*]anthracene (29b) 78%; m.p. 196-197°C (lit.[19d], 198°C); 1H NMR data[21]; (Found: C, 95.21; H, 5.31. Calcd. for $C_{22}H_{14}$: C, 94.93; H, 5.07%).

Dibenz[*a,h*]anthracene (32); colourless crystals; 72%; m.p. 264-265°C (lit.[19e], 269°C); IR (KBr) 1610, 1503 cm^{-1}; NMR data as described[21]; (Found: C, 95.17; H, 5.23. Calcd. for $C_{22}H_{14}$: C, 94.93; H, 5.07%).

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