

**POLYCYCLIC AROMATIC COMPOUNDS: A NEW SYNTHESIS OF POLYARYLATED BENZOFLUORANTHENE DERIVATIVES BY [4 + 2]-CYCLOADDITION REACTION**

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**ABSTRACT**

A large number of polycyclic aromatic compounds containing benzofluoranthene nucleus (IV–XI) have been prepared by cyclo-addition reaction of 1,3-di-(3',4')-O-xylylcyclopent-[a]-aceanthrylen-2(H)-one(III) with various dienophiles containing a reactive ethylenic or acetylenic bond. The dienone (III) has been prepared from aceanthraquinone (I) and 3,4,3',4'-tetramethyldibenzyl ketone (II).

**INTRODUCTION**

**I**N the present communication, we report that synthesis of a new series of highly substituted benzofluoranthene derivatives to determine whether the substituents in various positions of fluoranthene system would increase its chemical reactivity and molecular complexity which are the important factors from the stand point of physiological activities.

In the literature, we found that synthesis of some isomeric benzofluoranthene derivatives<sup>1-6</sup> by multi-steps reaction and the overall yields in all the cases were not good. We have prepared some 1,2-benzofluoranthene derivatives by a simple Diel's Alder cyclo-addition reaction of a new reactive diene, viz 1,3-di-(3',4')-O-xylylcyclopent-[a]-aceanthrylene-2(H)-one (III) with various dienophiles, viz maleic anhydride, chloromaleic anhydride, bicyclo-[2.2.1]-hepta-2,5-diene, diphenylacetylene, benzyne, acenaphthylene, 1-chloroacenaphthylene and 6-methyl-1-chloro-3(H)-indene.

**MATERIALS AND METHODS**

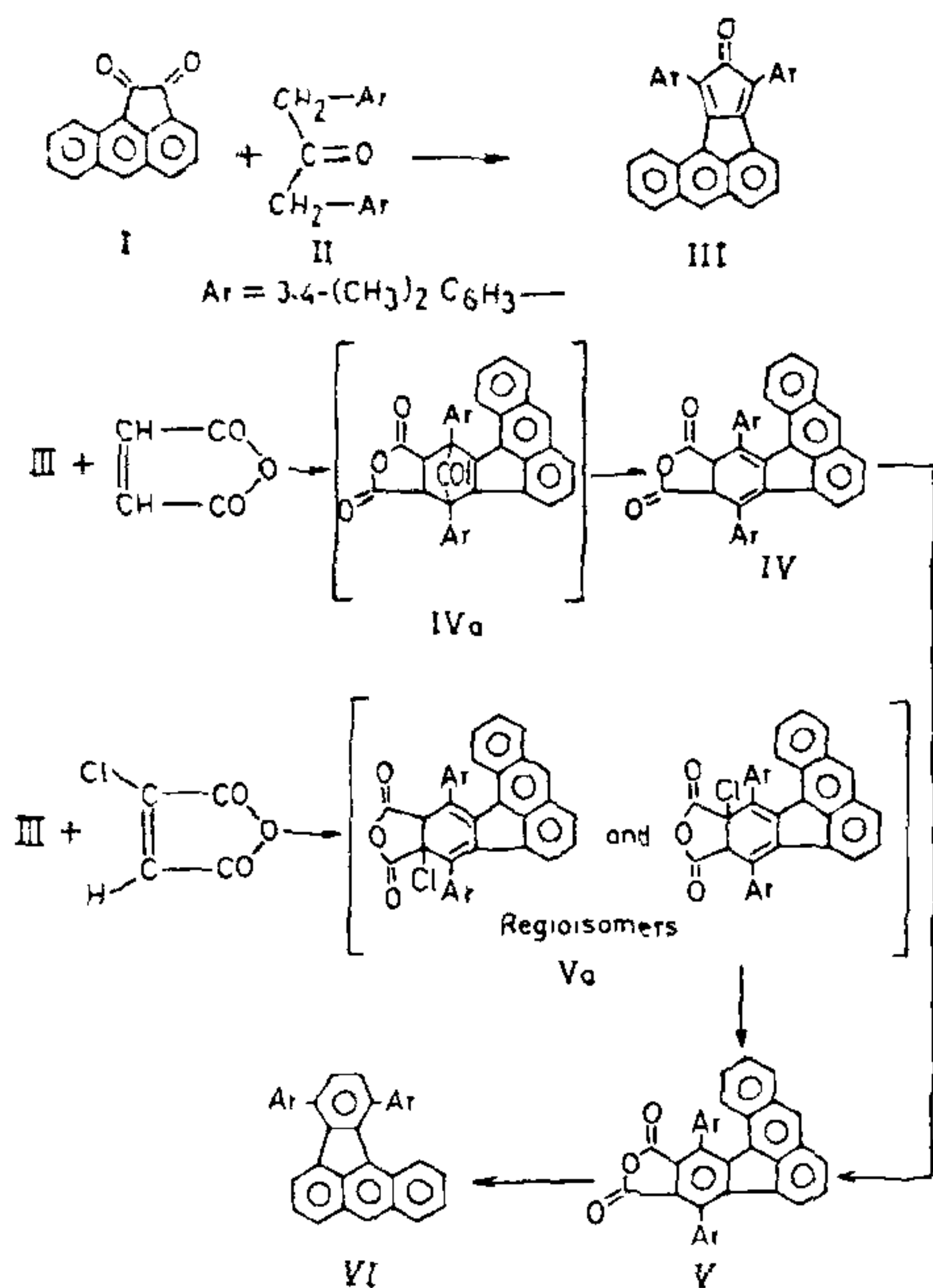
Base catalysed condensation of aceanthraquinone (I)<sup>7</sup> with 3,4,3',4'-tetramethyldibenzyl ketone (II) on a water-bath in an alcoholic medium gave the diene, 1,3-di-(3',4')-O-xylylcyclopent-[a]-aceanthrylen-2(H)-one (III) in good yield (65%). The IR spectrum of III showed a strong absorption at 1700 cm<sup>-1</sup> indicating the presence of an  $\alpha,\beta$ -unsaturated carbonyl group and the UV spectrum in benzene exhibited the  $\lambda_{max}$  at 280 nm ( $\epsilon = 33250$ ) due to C=C chromophore and at 435 nm ( $\epsilon = 6625$ ) due to C=O chromophore.

The dienone (III) when heated under controlled conditions with maleic anhydride in xylene, formed directly the dicarbonyl compound, 9a,12a-dihydro-

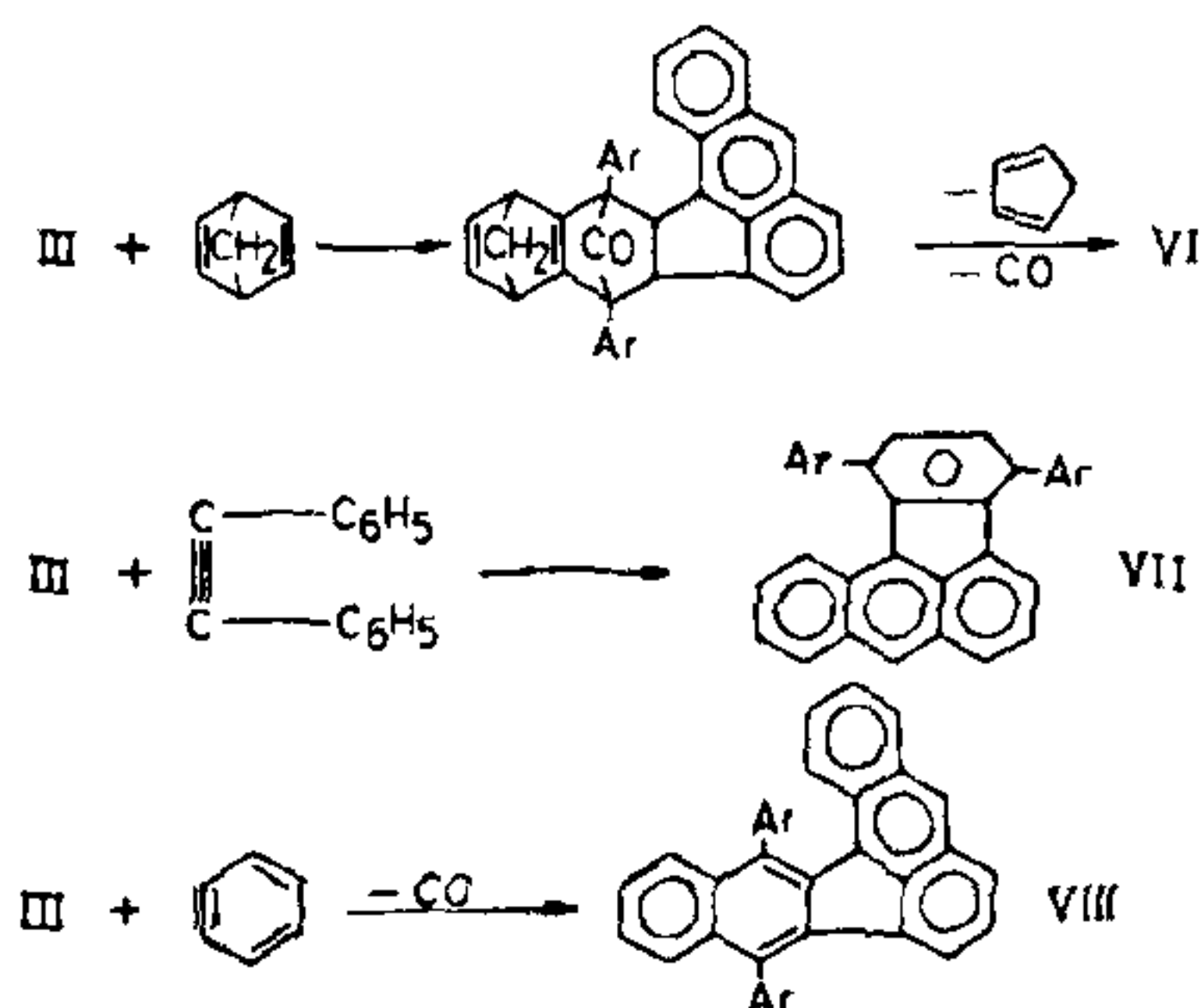
9, 13-di (3,4)-O-xylylaceanthrylene-[1, 2-f]-isobenzofuran-10,12-diene (IV). The intermediate carbonyl-bridged adduct, 9,9a,12a,13-tetrahydro-9,13-carbonyl-9, 13-di-(3', 4')-O-xylylaceanthryleno-[1, 2-f]-isobenzofuran-10,12-dione (IVa) could not be isolated even if the above condensation was carried out at a lower temperature (58–60°C). The dicarbonyl compound (IV), on dehydrogenation with chloranil gave, 9, 13-di-(3', 4')-O-xylylaceanthryleno-[1, 2-f]-isobenzofuran-10,12-dione (V). If (V) could also be obtained directly by the condensation of III with chloromaleic anhydride in bromobenzene. On decarboxylation with soda lime, V afforded the hydrocarbon, 1,4-di-(3',4')-O-xylylbenz[a]-aceanthrylene (VI) (scheme 1). The dienone (III) when refluxed in xylene with excess of bicyclo-[2.2.1]-hepta-2,5-diene, gave the same hydrocarbon (VI) alongwith some cyclopentadiene with the evolution of carbonmonoxide. Cyclopentadiene was isolated as maleic anhydride adduct (scheme 2).

Diphenylacetylene also underwent cycloaddition reaction with the dienone (III) in gently boiling tetralin forming directly 2,3-diphenyl-1,4-di-(3',4')-O-xylylbenz-[a]-aceanthrylene (VII) (scheme 2). 9,14-di-(3',4')-O-xylynaphth-[2,3-a]-aceanthrylene (VIII) was prepared by trapping benzyne, produced *in situ* by aprotic diazotization of anthrahilic acid<sup>8</sup>, with the dienone (III). During the course of reaction, carbonmonoxide was evolved and the colour changed from black to orange (scheme 2).

The dienone (III) when heated with acenaphthylene in xylene formed 9a,15b-dihydro-9,15-di-(3',4')-O-xylylfluoranthene-[9,8-a]-aceanthrylene (IX) alongwith 9,16-di-(3',4')-O-xylylfluoranthene-[9,8-a]-aceanthrylene (IX) due to thermal dehydrogenation of IX. The heterogeneous mixture (IX, X) was heated with chloranil in xylene to give the hydrocarbon (X). This (X) could also be obtained directly by heating a



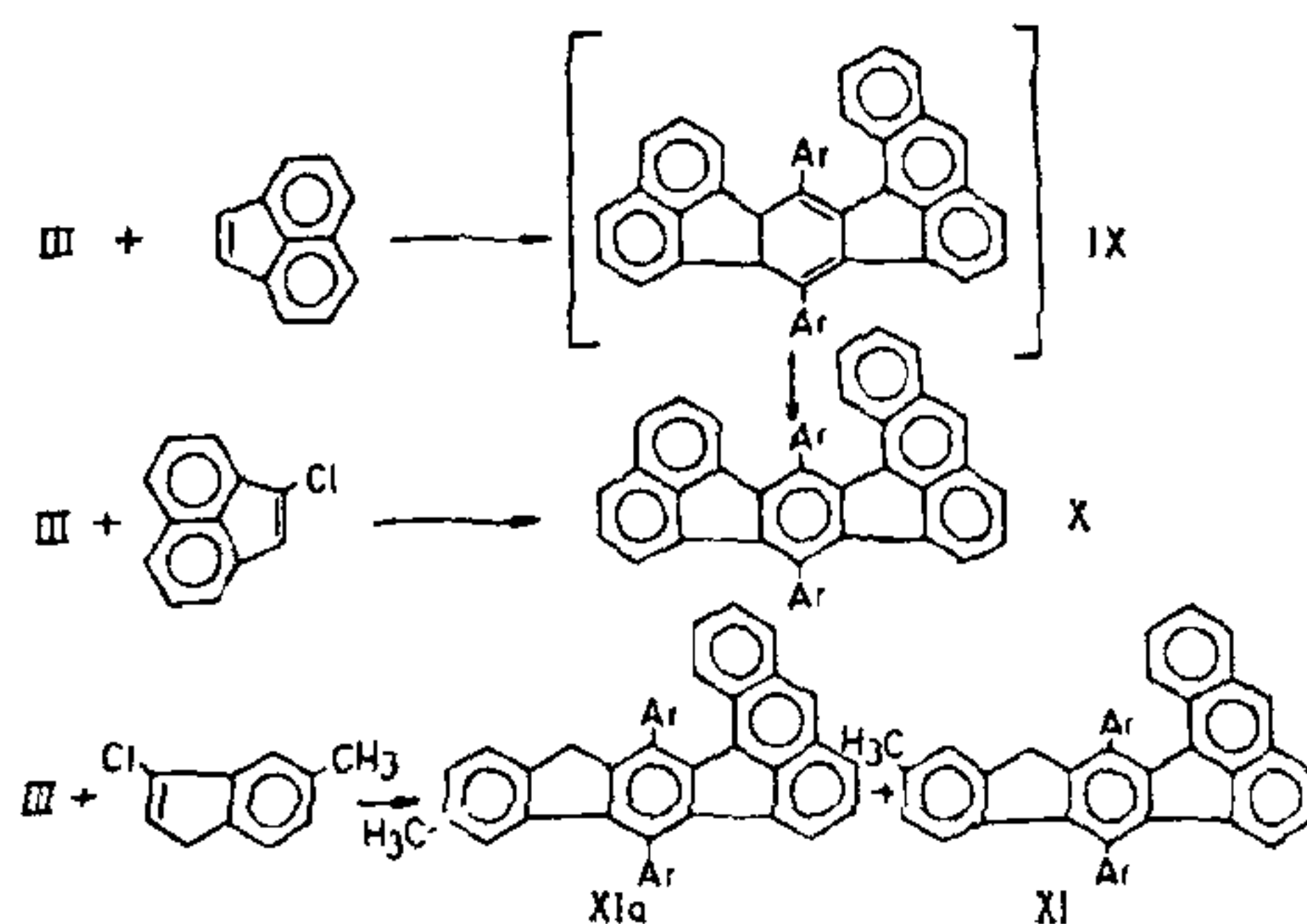
Scheme 1



Scheme 2

mixture of the dienone (III) and 1-chloroacenaphthylene in xylene until the colour of the dienone was discharged. During the course of the reaction carbon-monoxide and hydrogen chloride gases were evolved (scheme 3).

6-Methyl-1-chloro-3(H) indene was also successfully used as a dienophile and when condensed with the dienone (III) in xylene afforded 13-methyl-9,15-di-(3',4')-O-xylyl-10 (H)-fluoreno-[3, 2-a]-aceanthrylene



Scheme 3

(XI) together with isomeric 11-methyl-9,15-di-(3,4)-O-xylyl-14(H)-fluoreno-[2,3-a]-aceanthrylene (XIa) (scheme 3). Typical polynuclear compound VIII has been checked through its H<sup>1</sup> NMR. ( $\delta$  scale) spectra analysis. The NMR spectrum of compound VIII (C<sub>40</sub>H<sub>30</sub>) showed signals at 6.9–7.6 (18H, m, aromatic), 2.2 [6H, d, two-CH<sub>3</sub>(ortho)], 2.45 and 2.33 [6H, s, two-CH<sub>3</sub>(P)].

## EXPERIMENTAL PROCEDURE

All the melting points reported are uncorrected.

1, 3-Di-(3', 4')-O-xylylcyclopenta-[a]-aceanthrylene-2(H)-one (III). To a refluxing solution of aceanthraquinone (I, 0.01 mol) and 3,4,3',4'-tetramethyldibenzyl ketone (II, 0.015 mol) in abs. methanol (100 ml) was added methanolic caustic potash solution (10%) slowly with shaking when a reddish black coloration developed. After refluxing for 30 min the product separated as shining black crystals. The solution was cooled, washed with methanol and crystallised from benzene. Yield (28 g) 65%, m.p. 220° (Found: C, 90.79; H, 5.44 C<sub>35</sub>H<sub>26</sub>O required C, 90.90; H, 5.62%).

9a, 12a-Dihydro-9, 13-di-(3', 4')-O-xylylaceanthrylene-[1,2-f]-isobenzofuran-10,12-dione (IV). A mixture of III (0.01 mol) and maleic anhydride (0.015 mol) was refluxed in xylene (30 ml) until the colour of the dienone was discharged (6 hr). The solvent was removed by steam-distillation and the crude product was crystallised from benzene as yellow crystals, yield (4.52 g) 85%, m.p. 212° (Found: C, 85.53; H, 5.20 C<sub>38</sub>H<sub>28</sub>O<sub>3</sub> required C, 85.71; H, 5.26%).

9, 13-Di-(3', 4')-O-xylylaceanthrylene-[1, 2-f]-isobenzofuran-10,12-dione(V): Method (A). The adduct (IV, 2 g) was heated with chloranil (1.2 g) in xylene



(25 ml) for 16 hr. The reaction mixture was cooled, diluted with an equal volume of ether and filtered. The filtrate was washed with aq. NaOH (5%) and then with water and dried ( $\text{Na}_2\text{SO}_4$ ). The solvent was removed and the product was purified by column chromatography using benzene as eluent. On evaporation of the solvent and subsequent crystallisation from benzene-pet. ether (40–60°), V was obtained as orange crystals, yield (1.5 g) (63%), m.p. 360° (Found: C, 85.95; H, 4.80  $\text{C}_{38}\text{H}_{26}\text{O}_3$  required C, 86.03; H, 4.90\*).

**Method (B).** A mixture of III (0.01 mol) and chloromaleic anhydride (0.012 mol) was refluxed in bromobenzene (25 ml) until the colour of the solution was discharged (6 hr). The solvent was removed by steam-distillation and the product worked up as above to give V, yield (4.27 g) 80%, m.p. remained undepressed when mixed with the sample of V obtained by the method A.

**1,4-Di-(3',4')-O-xyllylbenz-[a]-aceanthrylene (VI):**

**Method (A).** V (2 g) and soda lime (10 g) were heated in a sublimation tube at 350–400°/1mm until no further material sublimed (8 hr). The sublimate was extracted with benzene and chromatographed over neutral alumina. Evaporation of the solvent and subsequent crystallisation from benzene-pet. ether (40–60°) yielded orange crystals, yield (7 g) 40%, m.p. 210–212°C (Found: C, 93.94; H, 5.87  $\text{C}_{36}\text{H}_{28}$  required C, 93.91; H, 6.08%).

**Method (B).** The dienone (III, 2 g) was heated with bicyclo-[2.2.1]-hepta-2,5-diene (2 ml) in dry xylene (30 ml). Nitrogen was passed through the above boiling mixture to carry the cyclopentadiene produced. The cyclopentadiene so produced was reacted with maleic anhydride (0.5 g) in ether (15 ml). At the end of the reaction, the colour of the xylene solution was discharged. The solvent was removed by steam-distillation, the residue filtered; washed with pet. ether (40–60°) and finally crystallised from benzene-pet. ether (40–60°) as orange crystals, yield (1.7 g) 85%, m.p. undepressed when mixed with the sample of VI obtained by the method A. The ethereal solution was evaporated until the crystals began to separate out. These were filtered, m.p. 163–64°, undepressed on admixture of bicyclo-[2.2.1]-hept-5-ene-2,3-dicarboxylic anhydride prepared by the addition of cyclopentadiene to maleic anhydride at 10°.

**2, 3-Diphenyl-1, 4-di-(3', 4')-O-xyllylbenz-[a]-aceanthrylene (VII).** The dienone (III, 4.34 g) and diphenylacetylene (3.56 g) were heated under reflux in tetralin (30 ml) until the colour of the solution was

discharged (6–7 hr). The solvent was removed by steam-distillation, the residue filtered, washed with pet. ether (40–60°) and purified by passing through a column of neutral alumina using benzene as eluent. The hydrocarbon (VII) was finally crystallised from benzene-petroleum (40–60°) as light yellow crystals, yield (3 g) 50%, m.p. 269° (Found: C, 94.02; H, 5.89  $\text{C}_{48}\text{H}_{36}$  required C, 94.11; H, 5.88%).

**9, 14-Di-(3', 4')-O-xyllynaphth-[2, 3]-aceanthrylene (VIII).** A solution of anthranilic acid (0.72 g) in acetone (60 ml) was added dropwise over 2–3 hr to a refluxing mixture of III (2 g) and isoamyl nitrite (1.2 g) in chloroform (120 ml). Towards the end of the reaction, the colour changed from black to orange. The solvents were removed and the resultant oil was dissolved in benzene and passed through a short column of neutral alumina; a light yellow solution was rapidly eluted. Evaporation of benzene, gave VIII which was finally crystallised from benzene-petroleum ether (40–60°) as light orange crystals, yield (1.4 g), 62.7%, m.p. 339° (Found: C, 93.94; H, 5.70  $\text{C}_{40}\text{H}_{30}$  required C, 94.11; H, 5.88%).

**9, 16-Di-(3', 4')-O-xyllylfluoranthene-{9, 8-a}-aceanthrylene (X): Method (A).** A mixture of III (2 g) and acenaphthylene (1.08 g) was refluxed in xylene (25 ml) for 10 hr. The solvent was removed by steam-distillation, the residue filtered, washed with petroleum (40–60°) and on crystallization with benzene-petroleum (40–60°) gave no sharp melting compound. The residue (1.5 g) was heated with chloranil (1.2 g) in xylene (25 ml) for 16 hr. The solution was cooled, the solvent removed by steam-distillation and the product (X) was worked up as described for V and finally crystallised from benzene-petroleum (40–60°) as deep orange crystals, yield (1.2 g) 48.9%, m.p. 352° (Found: C, 94.41; H, 5.29  $\text{C}_{46}\text{H}_{32}$  required C, 94.52; H, 5.47%).

**Method (B).** The dienone (III, 4.34 g) was mixed with 1-chloroacenaphthylene (2 g) in dry xylene (30 ml) and refluxed until the colour of the dienone was discharged (5–6 hr). The solvent was removed and the product was purified by column chromatography using benzene as eluent. Evaporation of solvent and subsequent crystallisation from benzene-petroleum (40–60°) gave X, yield (4.2 g) 80%, identical (m.p.) with the sample obtained by method A.

**13-Methyl-9,15-di-(3',4')-O-xyllyl-10(II)-fluoreno-[3,2-a]-aceanthrylene (XI) and II-methyl-9,15-di-(3',4')-O-xyllyl-14(II)-fluoreno-[2,3-a]-aceanthrylene (XIa).** A mixture of III (0.01 mol) and 6-methyl-1-chloro-3(II) indene (0.015 mol) was heated in xylene (25 ml) until

the colour of the dienone was discharged (4–5 hr). The solvent was removed and the product worked up as described for X. The compound (XI, XIa) was finally crystallised from benzene-petroleum (40–60°), yield (1.4 g) 25%, m p. 265–70° and gave satisfactory C, H analysis.

#### ACKNOWLEDGEMENT

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## NEWS

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### GENE THERAPY: EXAGGERATED HOPES?

... "Last fall when activist Jeremy Rifkin tried to convince the Natl. Insts. of Health [NIH] to ban all interspecies gene transfers, the loudest protests came, surprisingly, not from the scientific community but from members of the public who knew someone suffering from genetic disease. . . . J. Michael and Christina L Downard of Athens, Ohio, wrote: 'As parents of two daughters afflicted with metachromatic leukodystrophy (MLD), we are only too aware of the possible consequences of any interruption in this work. . . . The Downard's letter was accompanied by more than 250 other letters. . . . More troubling to many observers today than exaggerated fears of gene therapy are exaggerated hopes. (NIH's Recombinant-DNA Advisory Committee [RAC] members were amazed, for example, by the number of letters they received on behalf of the Downard family's

two children with MLD. Yet MLD is not a disease likely to be treatable by gene therapy anytime in the foreseeable future. This disease acts on its victim's brain, and researchers have not come close to figuring out how to get transplanted genes to move from bone marrow cells to brain cells. So far these researchers have resisted any public pressure to bring gene therapy out of the laboratory before it is ready. 'I think investigators have been very responsible in allowing the guideline formulation process to go forward,' says LeRoy Walters [Georgetown U. and RAC]."

[(Laura Tangley in *Bio Science* 35(1): 8-10, Jan. 85. Reproduced with permission from Press Digest, *Current Contents*®, No. 8, February 25, 1985, p. 12.) (Published by the Institute for Scientific Information®, Philadelphia, PA, USA.)]

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