

## POLYCYCLIC AROMATIC COMPOUNDS: A NEW SYNTHESIS OF HIGHLY ARYLATED QUINONES BY DIELS-ALDER REACTION

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### ABSTRACT

A large number of polycyclic aromatic quinones have been prepared. The synthesis involves Diels-Alder reaction of various cyclopentadienones (I, II) with benzoquinone and naphthaquinone. The monoadduct when used as dienophile condenses with I, affording a new series of quinones (XV).

### INTRODUCTION

OKAHARA AND MURATA<sup>1</sup> prepared 2-methyl-1:4-naphthaquinone by the condensation of 2-methylbenzoquinone with butadiene. Bailey and Modoff reported the synthesis of 6,13-diketooctadecahydro-pentacene using 1,2-dimethylene cyclohexane and benzoquinone. Arbusow *et al*<sup>3</sup> obtained tetraphenyltetra-benzophentacenequinone by condensing two molecules of phenicyclone with benzoquinone. In the present communication we report a new series of aromatic quinones bearing anthracene, tetracene and pentacene nucleus utilising the dienophilic character of benzo and naphthaquinone on various cyclopentadienones.

### MATERIALS AND METHODS

The synthetic method involved (4+2)-cyclo-addition of various reactive cyclopentadienones, viz 1,3-diaryl-2H-cyclopenta[1]-phenanthrene-2-ones<sup>4,5</sup> (Ia-d) and 2,5-dimethyl-3,4-diphenyl cyclopentadienone (IIa) with benzoquinone and naphthaquinone.

Cyclopentadienones (I) readily formed the carbonyl bridged adducts 9,10,4a,10a-tetrahydro-9,10-diaryl-9,10-endocarbonyl-5:6, 7:8-dibenzanthracene-1,4-quinone (III) in good yield when refluxed with benzoquinone in benzene. The adducts (III) when boiled in nitrobenzene, afforded 9,10-diaryl-5:6, 7:8-dibenzanthracene-1,4-quinones (V) with the elimination of carbon monoxide gas. It was also observed that when the adduct (III) refluxed in xylene, formed the intermediate dihydro compound, 4a,10a-dihydro-9,10-diaryl-9,10-endocarbonyl-5:6, 7:8-dibenzanthracene-1,4-quinone [VI] by selective abstraction of hydrogen from III. The compounds (VI) were unstable and on further heating in tetralin gave V.

The quinone 9,10-diaryl-5:6, 7:8-dibenzanthracene-1,4-quinone (V) on reduction with lithium alum-

inum hydride boiling tetrahydrofuran gives the corresponding hydrocarbon 9,10-diaryl-5:6, 7:8-dibenzanthracene (VII)<sup>6</sup>.

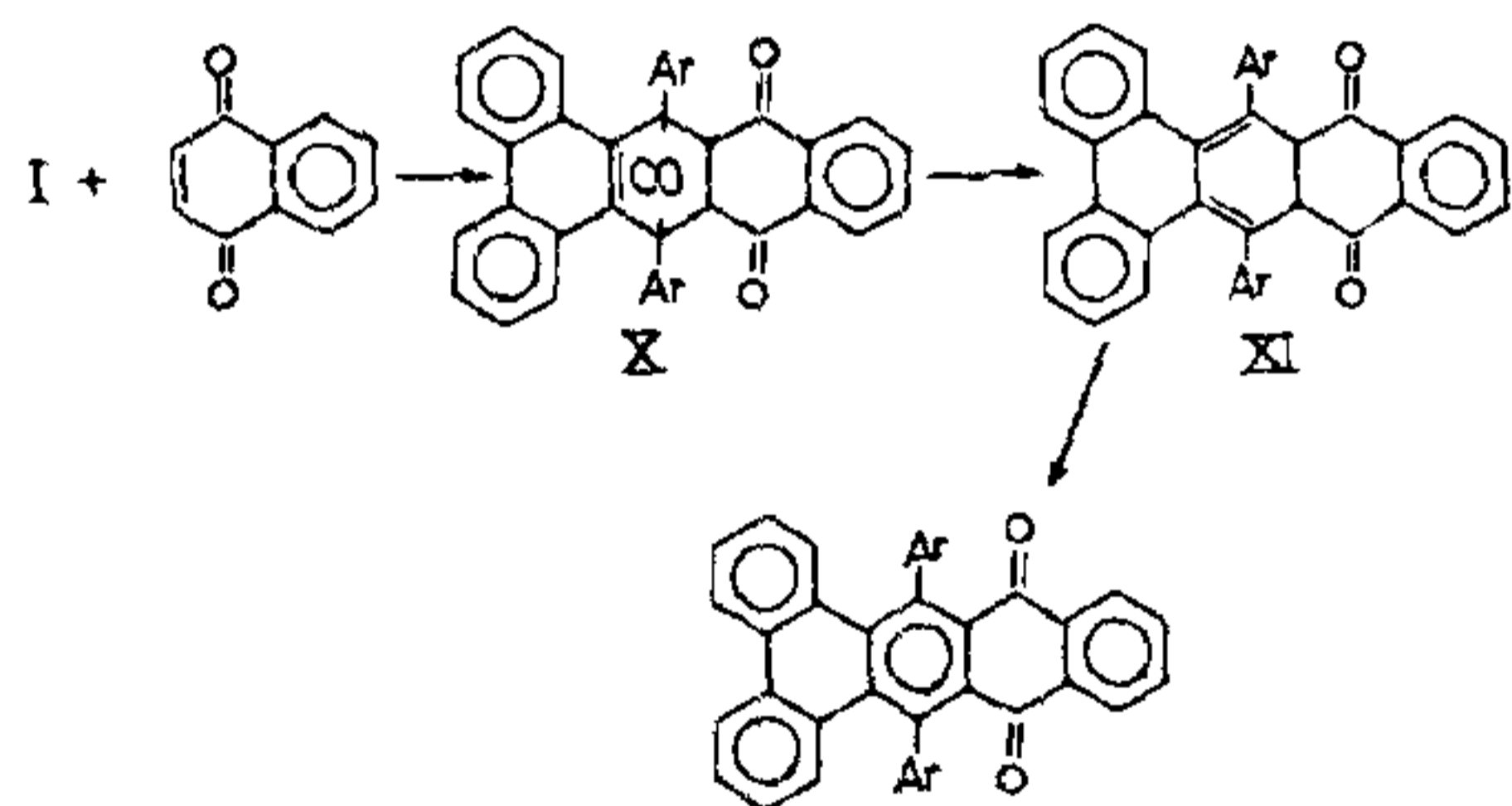
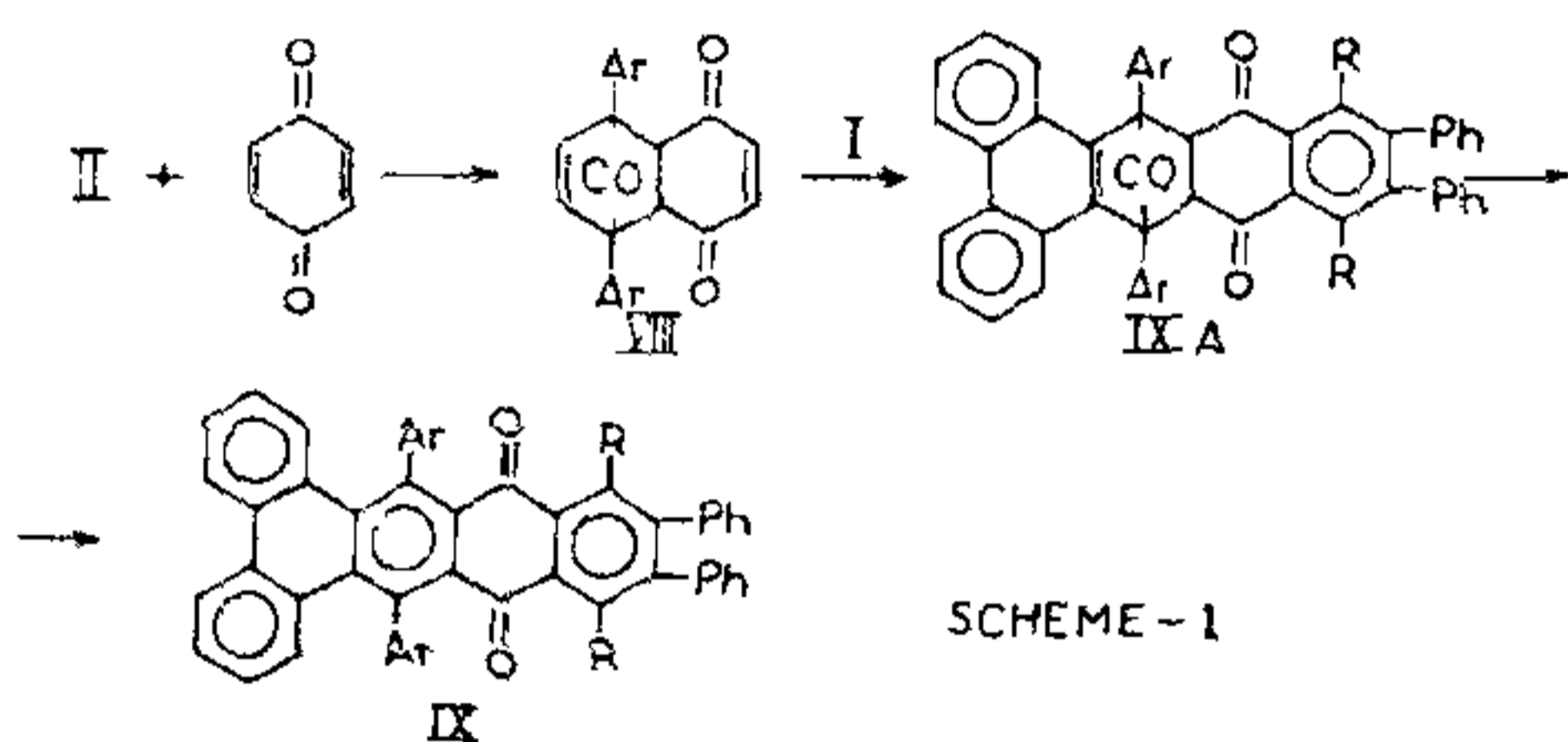
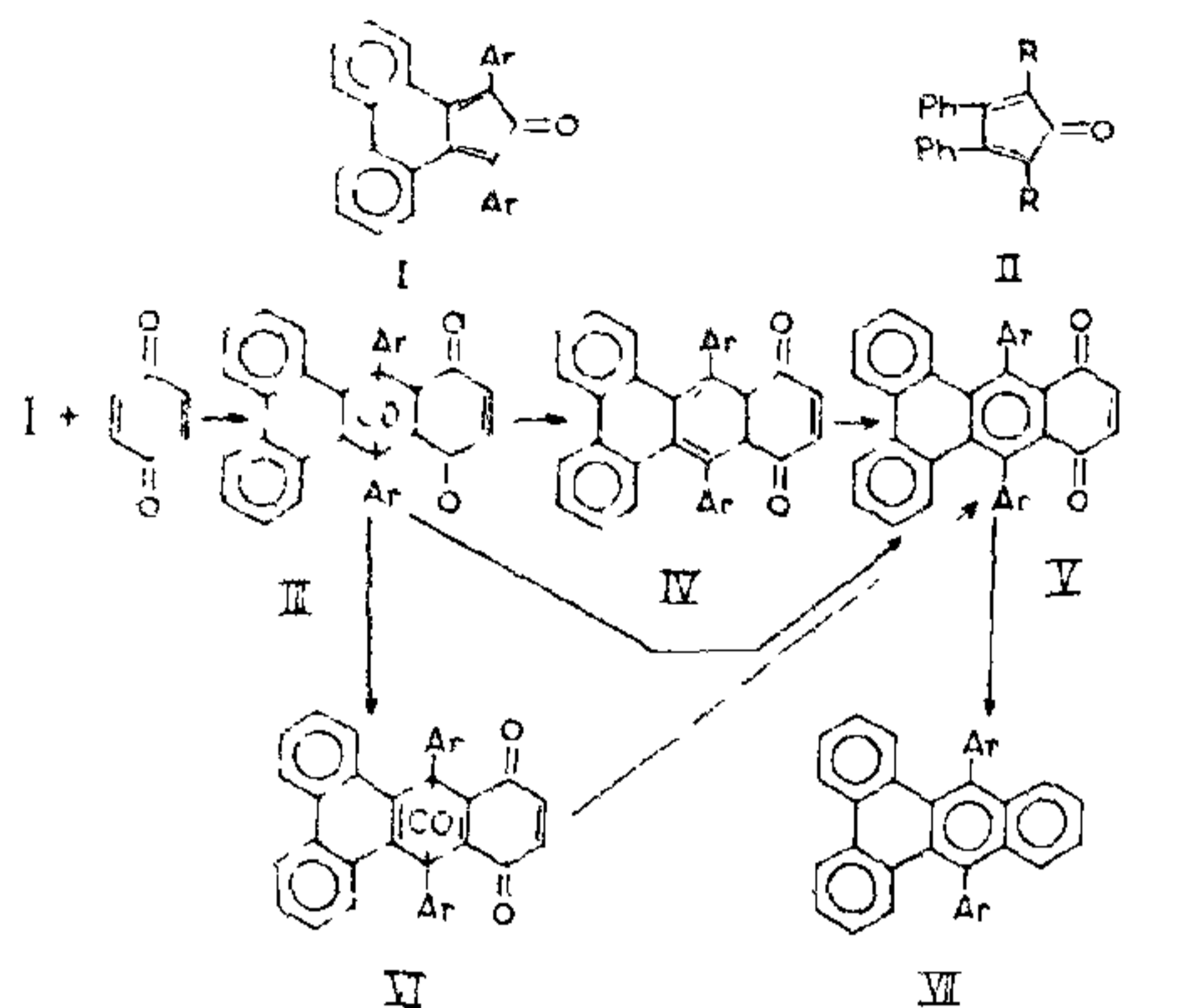
Tetracyclone does not react with benzoquinone. But when the phenyl group in the 2,5-position of tetracyclone was replaced by methyl group, it increased the reactivity of cyclopentadienone and readily condensed with benzoquinone in benzene to give the carbonyl bridged compounds 5,8,4a,8a-tetrahydro-6,7-diphenyl-5,8-dimethyl-5,8-endo-carbonyl naphthalene-1,4-quinone (VIII, R = CH<sub>3</sub>).

The monoadduct (VIII) could be successfully used as dienophile and when treated with III in xylene readily formed the compound, 5a,11a,6,11-tetrahydro-1,4-dimethyl-2,3-diphenyl-6,11-diaryl-6,11-endo-carbonyl-7:8, 9:10-dibenzotetracene-5,12-quinone (IXA). The adduct (IXA) when boiled in nitrobenzene formed 1,4-dimethyl-2,3-diphenyl-6,11-diaryl-7:8, 9:10-dibenzotetracene-5,12-quinone (IX) (scheme 1).

Naphthaquinone could also be successfully used as dienophile and when condensed with I in benzene, formed the carbonyl bridged compound, 5a,11a,6,11-tetrahydro-6,11-diaryl-6,11-endocarbonyl-7:8, 9,10-dibenzanthracene-5:12-quinone (X).

The adduct (X) when refluxed in xylene probably formed the intermediate dihydro compound, 5a,11a-dihydro-6,11-diaryl-7:8, 9:10-dibenzotetracene-5:12-quinone (XI) which when boiled in tetralin, formed the compound, 6,11-diaryl-7:8, 9:10-dibenzotetracene-5:12-quinone (XII) (Scheme 2).

The monoadduct (III) had also been successfully used as dienophile and when condensed with the dienone (I) in benzene, formed the carbonyl bridged compound 5,14,7,12,6a,7a,11a,12a-octahydro-5,14,7,12-tetraphenyl-5:14, 7:12-diendocarbonyl-1:2, 3:4, 8:9, 10:11-tetrabenzpentacene-6,13-quinone (XIII). The adduct (XIII) when heated with chloranil in xylene formed probably the carbonyl-bridged adduct 5,14,7,12-tetrahydro-5,14,7,12-tetraphenyl-5:14, 7:12-

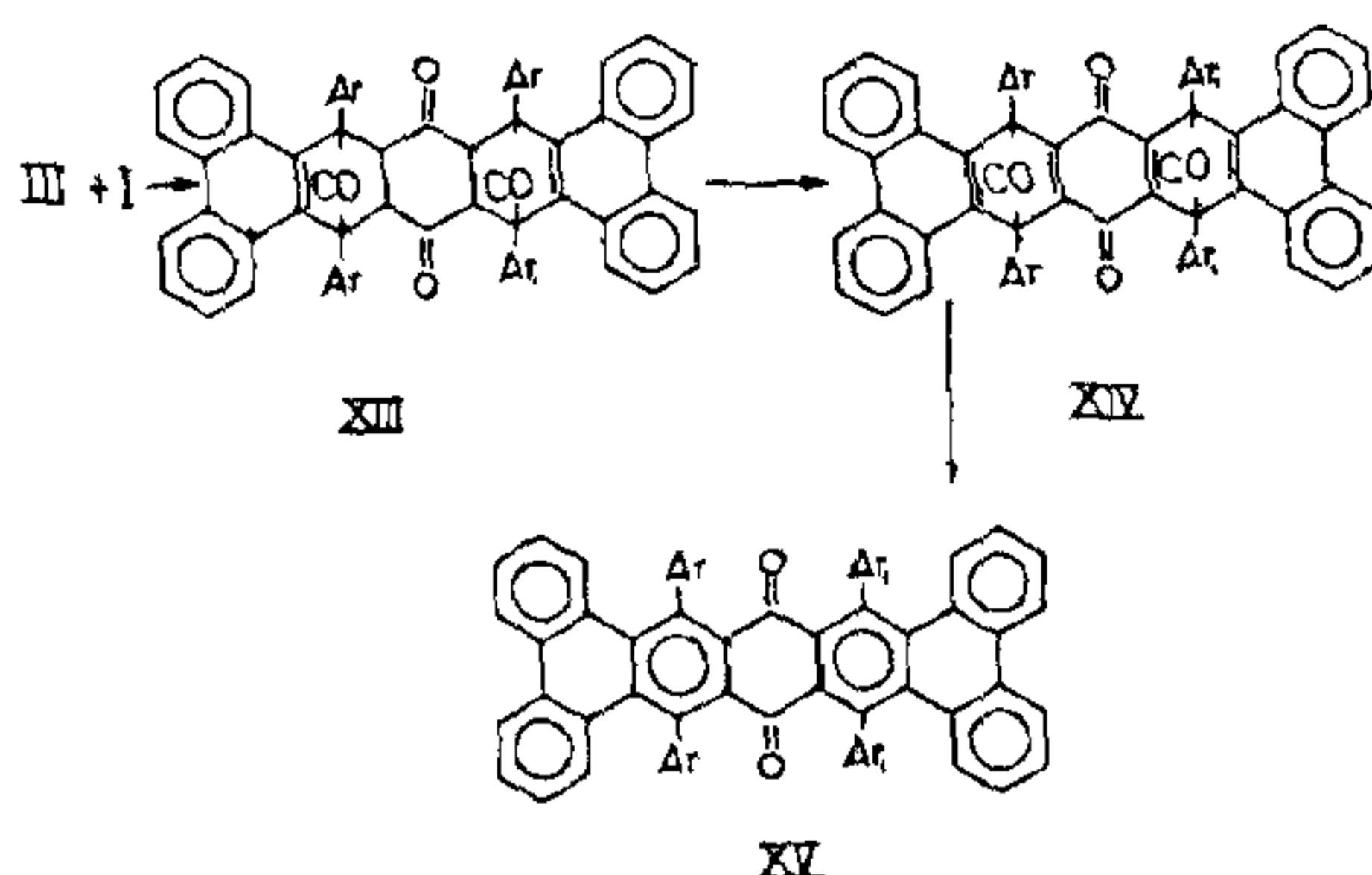


SCHEME-2

XII

diendocarbonyl-1:2, 3:4, 8:9, 10:11-tetrabenzpenta-cene-6,13-quinone (XIV). The adduct (XIV) when refluxed in tetralin, readily formed the aromatic quinones 5,14,7,12-tetraphenyl-1:2, 3:4, 8:9, 10:11-tetra-benzpenta-cene-6,13-quinone (XV) (Scheme 3).

IR spectra of compounds III, VIII, IXa, X, XIII and XIV show absorption in the region 1790, 1770, 1780, 1750, 1800 and 1790  $\text{cm}^{-1}$  respectively. The above absorptions are the characteristic of endo-carbonyl group which are present in the compounds. IR spectra



of compound (V) showed the absorption at 1750  $\text{cm}^{-1}$  and in the region 1300–2800 (C–H), 790–650 (C–H out of plane) and 1600–1450  $\text{cm}^{-1}$  (C–C). The other IR absorption bands of compounds X, III and XIV in the region 1660, 1670–1680 and 1710  $\text{cm}^{-1}$  respectively correspond to carbonyl absorptions due to quinones.

The structures of the typical polynuclear compounds IIIc, III d, Vd, XII, XIIIc have been checked through analysis of their  $^1\text{H}$  NMR ( $\delta$ -scale) spectra. The NMR spectrum of IIIc showed signals at 3.85 (6H, S, two- $\text{OCH}_3$  group), 4.55 (2H, S, 4a, 10a), 7.1 (2H, S, 2, 3), 7.1–8.1 (16H, m, aromatic). III d showed signals at 2.1 and 2.15 (12H, nearly doublet, 4- $\text{CH}_3$ ), 4.7 (2H, S, 4a, 10a), 6.75 (2H, S, 2, 3), 7.1–8.7 (14H, m, aromatic). Vd showed signals at 2.1 (6H, S, 2-Me(P)), 2.15 (6H, S, 2-Me(m)), 6.9–8.8 (16H, m, aromatic). XII showed signals at 2.1 (6H, S, 2- $\text{CH}_3$ (P)), 2.15 (6H, S, 2- $\text{CH}_3$ (m)), 7.0–8.9 (18H, m, aromatic). XIIIc showed signals at 2.3 (24H, S (nearly doublet), 8- $\text{CH}_3$ ), 4.5 (4H, S, 6a, 7a, 11a, 12a), 7.0–8.7 (28H, m, aromatic). The numbers of aliphatic and aromatic compounds found in this way are all in conformity with the structures assigned to the compounds synthesised.

## EXPERIMENTAL PROCEDURE

All the melting points reported are uncorrected. All compounds described in the table gave C and H analyses within  $\pm 0.3\%$  error.

*9, 10, 4a, 10a-Tetrahydro-9, 10-Di-aryl-9, 10-endo-carbonyl-5:6, 7:8-dibenzanthracene-1, 4-quinone (III)* – A mixture of i (0.01 mol) and benzoquinone (0.015 mol) was refluxed in dry benzene (50 ml) on a water bath until the colour of the dienone was discharged (10–12 hr). The solvent was removed and the residue chromatographed on an alumina column (50 g) prepared in benzene and eluted successively with



dry benzene. The product was crystallised from benzene-ethanol. The yield varied from 78–88 based on cyclopentadienone (I) used (table 1).

9, 10-Dihydro-9, 10-diaryl-9, 10-endocarbonyl-5:6, 7:8-dibenzanthracene-1,4-quinone (VI) – Compound (III, 0.01 mol) was refluxed with equimolecular amount of chloranil (1.5 g) in xylene (24 ml) for 12 hr. The solvent was removed by steam distillation, the residue filtered, washed with ethanol and recrystallised from benzene, yield 80–85% (table 1). 9,10-Diaryl-5:6, 7:8-dibenzanthracene-1,4-quinone (V).

Method A – (III, 0.01 mol) was refluxed in nitrobenzene (30 ml) for 10 hr. The solvent was removed by steam distillation, the product filtered, washed with ethanol, chromatographed over neutral alumina using benzene as eluant and finally crystallised from benzene-ethanol, yield 70–80% (table 1).

9,10-Diaryl-5:6, 7:8-dibenzanthracene (VII) – Quinone V (0.003 mol) was extracted (soxhlet) into a solution of lithium aluminium hydride (1 g) in boiling tetrahydrofuran (150 ml) for 10 hr. The excess hydride was decomposed with moist ether, and dilute hydrochloric acid added, the direct ethereal layer yielded

yellow solid. All the compounds crystallised from acetone-methanol. Yield varies from 60–70% (table 1).

5,8,4a,8a-Tetrahydro-6, 7-diphenyl-5, 8-dimethyl-5, 8-endo-carbonulnaphthalene-1, 4-quinone (VIII,  $R = CH_3$ ) – A mixture of II (0.01 mol) and benzoquinone (0.005 mol) was refluxed in dry benzene (50 ml) until the colour of the dienone faded (10 hr). The solvent was removed and the product was worked up as described for III. The compound (VIII) was crystallised from benzene-ethanol as light yellow crystals, m.p. 215°, yield – 86% (Found: C, 81.41; H, 5.30.  $C_{25}H_{20}O_3$ , requires C, 81.52; H, 5.43%).

5a,11a,6,11-Tetrahydro-1, 4-dimethyl-2, 3-diphenyl-6, 11-diaryl-6, 11-endocarbonyl-7:8, 9:10-dibenzotetracene-5, 12-quinone (IXA) – A mixture of VIII (0.01 mol) and I (0.01 mol) was refluxed in dry benzene (50 ml) until the colour of the dienone was discharged (18 hr). The solvent was removed and the product was finally crystallised from benzene. Compound IXA (Ar = ph): m.p. 247°, IXA (Ar = p- $CH_3C_6H_4$ ) m.p. 278°. Both the compounds gave satisfactory C, H analysis.

1,4-Dimethyl-2,3-diphenyl-6,11-diaryl-7:8, 9:10-dibenzotetracene-5,12-quinone (IX) – Compound (IXA,

Table 1. Characterisation Data of Dibenzanthracenaquinone, Dibenzanthracene and Tetrabenzpentacene-6,13-Quinone Derivatives.

Compound	Ar	Ar <sub>1</sub>	m.p. (°C)	Mo. formula
IIIa	ph	—	195	C <sub>35</sub> H <sub>22</sub> O <sub>3</sub>
IIIb	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	—	295	C <sub>37</sub> H <sub>26</sub> O <sub>3</sub>
IIIc	p-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	—	255	C <sub>37</sub> H <sub>26</sub> O <sub>5</sub>
III d	3',4'-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	—	255	C <sub>39</sub> H <sub>30</sub> O <sub>3</sub>
Va	ph	—	305	C <sub>34</sub> H <sub>20</sub> O <sub>2</sub>
Vb	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	—	290	C <sub>36</sub> H <sub>24</sub> O <sub>2</sub>
Vc	p-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	—	278	C <sub>36</sub> H <sub>24</sub> O <sub>4</sub>
Vd	3',4'-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	—	280	C <sub>38</sub> H <sub>28</sub> O <sub>2</sub>
VIa	ph	—	315	C <sub>35</sub> H <sub>20</sub> O <sub>3</sub>
VI d	3',4'-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	—	290	C <sub>39</sub> H <sub>28</sub> O <sub>3</sub>
VIIa	ph	—	274	C <sub>34</sub> H <sub>22</sub>
VIIb	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	—	268	C <sub>36</sub> H <sub>26</sub>
VIIc	p-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	—	196	C <sub>36</sub> H <sub>26</sub> O <sub>2</sub>
VII d	3',4'-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	—	230	C <sub>38</sub> H <sub>30</sub>
XIIIa	ph	3',4'-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	270	C <sub>68</sub> H <sub>48</sub> O <sub>4</sub>
XIIIb	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	360	C <sub>68</sub> H <sub>48</sub> O <sub>4</sub>
XIIIc	3',4'-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	3',4'-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	272	C <sub>72</sub> H <sub>56</sub> O <sub>4</sub>
XVa	ph	3',4'-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	261	C <sub>66</sub> H <sub>44</sub> O <sub>2</sub>
XVb	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	175	C <sub>66</sub> H <sub>44</sub> O <sub>2</sub>
XVc	3',4'-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	3',4'-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	257	C <sub>70</sub> H <sub>52</sub> O <sub>2</sub>

All the compounds (VIa, d), (XIIIa–c) and (XVa–c) were crystallised from benzene except the compounds (IIIa–d), (Va–d) which are crystallised from benzene-ethanol and (VIIa–d) crystallised from acetone-methanol.

0.01 mol) was refluxed in nitrobenzene (30 ml) for 12 hr. The solvent was removed by steam distillation and the product was worked up as described for V and crystallised from benzene. Compound IXa (Ar = ph): m.p. 316°, IXb (Ar = p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>); m.p. 305°. Both the compounds gave satisfactory C, H analyses.

*5a,11a,6,11-Tetrahydro-6,11-diaryl-6,11-endocarbo-nyl-7:8, 9:10-dibenzotetracene-5:12-quinone* [(X, Ar = 3',4'-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)]—A mixture of Id (Ar = 3',4'-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 0.01 mol) and naphthaquinone (0.01 mol) was refluxed in benzene (40 ml) until the colour of the dienone was discharged (6 hr). The product was worked up in the usual manner and finally crystallised from benzene as orange crystals, m.p. 170°, yield 80% (Found: C, 86.46; H, 5.22 C<sub>43</sub>H<sub>32</sub>O<sub>3</sub> requires C, 86.57, H, 5.36%).

*6,11-Diaryl-6:8, 9:10-dibenzotetracene-5,12-quinone* [(XII, Ar = 3',4'-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)]—Compound (XII, 0.01 mol) was refluxed in nitrobenzene (30 ml) for 10 hr. The solvent was removed and the product was worked up in the usual manner and finally crystallised from benzene, m.p. 291°, yield 78% (Found C, 88.87; H, 5.24. C<sub>42</sub>H<sub>30</sub>O<sub>2</sub> requires C, 89.94; H, 5.30%).

*5,14,7,12,6a,7a,11a,12a-Octahydro-5,14,7,12-tetra-phenyl-5:14, 7:12-diendocarbonyl-1:2:3:4, 8:9, 10:11-tetrabenzepentacene-6,13-quinone* (XIII)—A mixture of I (0.01 mol) and III (0.01 mol) in dry benzene (60 ml) was refluxed until the colour of the dienone was discharged (10 hr). The product was

worked up as described for III and finally crystallised from benzene, yield 70–80% (table 1).

*5,14,7,12-Tetraphenyl-1:2, 3:4,8:9, 10:11-tetrabenz-pentacene-6,13-quinone* (XV)—Compound (XIII, 0.01 mol) was refluxed with chloranil (1.5 g) in xylene (25 ml) for 12 hr. The solvent was removed by steam-distillation, the residue filtered, washed with ethanol and refluxed with tetralin (30 ml) 12 hr. The product was worked up as described for V and crystallised from benzene, yield 70–80% (table 1).

#### ACKNOWLEDGEMENT

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## ANNOUNCEMENT

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### NATIONAL BOTANICAL RESEARCH INSTITUTE, LUCKNOW—NEW DIRECTOR

Dr P. V. Sane, a well-known plant physiologist and biochemist has been recently appointed Director of the National Botanical Research Institute, Lucknow, Winner of 1981 Shanti Swarup Bhatnagar Prize in Biological Sciences, Dr Sane's main research interest lies in the field of Biochemistry of Photosynthesis. He has published over seventy original research papers

and several review articles, besides contributing chapters for books.

He headed the Agricultural Biochemistry Section and Biology and Agriculture Division of the Bhabha Atomic Research Centre, Bombay. He joined the National Botanical Research Institute, Lucknow as its Deputy Director in June 1983.