

In this case $b_{\text{opt}} = -B(\bar{X} + a) - \bar{Y}$. The two conditions on b , corresponding to (2.5) and (2.6), are that it lies between $-\bar{Y}$ and $-(D + \bar{Y})$, and 0 and $-(D + 2\bar{Y})$. As compared to the usual product estimator $\hat{Y}_p = N\bar{y}(\bar{x}/\bar{X})$, there will be a reduction in the absolute bias if and only if $|\bar{X} + a| > |\bar{X}|$. This will always hold when $\bar{X} \geq 0$ since $a > 0$. If $\bar{X} < 0$, it becomes necessary that $a > 2|\bar{X}|$.

ACKNOWLEDGEMENT

The authors wish to thank the referee for his very helpful comments on the first version of this paper.

21 February 1983; Revised 12 January 1984

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POLYCYCLIC AROMATIC COMPOUNDS: SYNTHESIS OF POLYCYCLICS CONTAINING ANTHRACENE, PHENANTHRENE AND FLUORENE NUCLEUS

S. MONDAL and A. J. BHATTACHARYA

Department of Chemistry, University of Burdwan, Burdwan 713 104, India.

ABSTRACT

A new series of polycyclic aromatic compounds with anthracene, phenanthrene and fluorene nucleus have been prepared. The method involves the Diel's-Alder cycloaddition of cyclopentadienones (I, II, III) with the dienophiles, e.g. 1-chloro-3,4-dihydronaphthylene (VI) and 5,6-dimethyl-1-chloro-3(H)-indene (V). The dienophiles V and VI are prepared from the corresponding cyclic ketone with phosphorus pentachloride.

INTRODUCTION

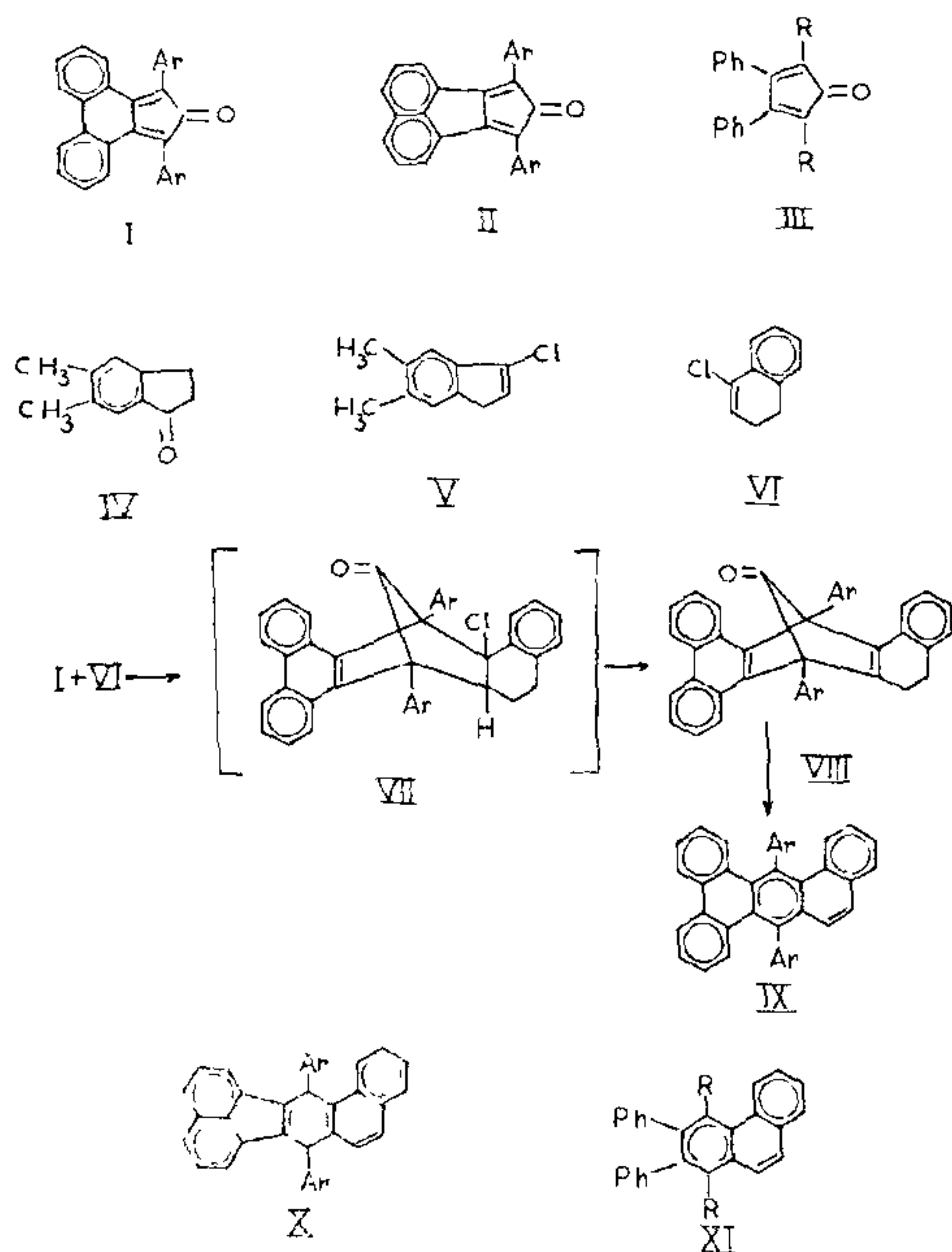
CARCINOGENIC activity found in certain polynuclear hydrocarbons with a certain degree of molecular complexity and chemical reactivity prompted us to devise a synthetic method for a new series of highly substituted aromatic hydrocarbons. 1:2, 3:4, 5:6-tribenzanthracene¹ and 1,2,3,4-tetramethylphenanthrene are feebly active. Replacing two methyl groups in the latter by a benzene ring leads to more active 1,2-dimethylchrysene. It is observed that substitution both on the phenanthrene and on anthracene nucleus plays an important role on their physiological activities.

In the present work, the chloro olefinic compounds, 1-chloro-3,4-dihydronaphthylene (VI) and 5,6-dimethyl-1-chloro-3(H)-indene (V) were synthesised and successfully used as dienophiles in the diene synthesis. A new series of 1,2,3,4-tetraarylphenanthrene and 9,10-diaryl-1:2, 3:4, 5:6-tribenzanthracene derivatives were synthesised in order to evaluate the effect of various aryl groups in the 1,2,3,4-position of phenanthrene nucleus and in the 9,10-position of tribenzanthracene nucleus.

MATERIALS AND METHODS

The method involves Diels-Alder cycloaddition reaction of various cyclopentadienones, viz 1,3-diaryl-2(H)-cyclopenta[1]-phenanthrene-2-one [Ia, Ar = Ph; Ib, Ar = *p*-CH₃C₆H₄; Ic, Ar = *p*-C₂H₅C₆H₄; Id, Ar = 3,4-(CH₃)₂C₆H₃], 2,5-diaryl-8(H)-oxo-cyclopent[a]-acenaphthylene (IIa, Ar = Ph; IIb, Ar = *p*-OCH₃C₆H₄) and 1,4-diaryl-2,3-diphenyl-cyclopentadienone (IIIa, Ar = Ph, IIIb, Ar = *p*-OCH₃C₆H₄) with 1-chloro-3,4-dihydronaphthylene (VI). It is believed that the reaction of the chloro compounds (V, VI) with cyclopentadienones follows the Alder-Endo rule². The cycloaddition reaction of cyclopentadienones with V and VI could follow two courses. However, in general, only one of these is actually realised. After preorientation of the reactants, the dienophile is added in such a way as to give the maximum concentration of π -bonds in the transition state. Maleic anhydride forms exclusively an *endo*-adduct with cyclopentadiene³. The formation of an *endo*-adduct is also found in the condensation of cyclopentadienones with *p*-benzoquinone⁴. The dienophile (VI) was conveniently prepared by the

action of phosphorus pentachloride on α -tetralone by the usual procedure. The dienone (Ia-e) when refluxed in tetralin with VI readily underwent aromatisation under the conditions of experiment to the hydrocarbons, 9,10-diaryl-1:2, 3:4, 5:6-tribenzanthracene (IXa-d) *via* the intermediate (VII) by the AE mechanism. The hydrocarbons (IXa-d) showed no alteration of melting point on dehydrogenation with chloranil in xylene. The carbonyl bridged adduct (VIII) could be easily isolated if the above condensations were carried out in boiling benzene. We isolated 7,8,9,10-tetrahydro-1:2, 3:4, 5:6-tribenz-9,10-diphenyl-9,10-endocarbonylanthracene (VIIIa) by the condensation of phenicyclone (Ia) with VI in benzene. The IR spectra of VIIIa showed a strong carbonyl absorption at 1760 cm^{-1} . However the carbonyl bridged adduct (VIIIa) gets readily converted into the aromatic hydrocarbon (IXa) at high temperature with the evolution of carbonmonoxide as well as hydrogen gas.

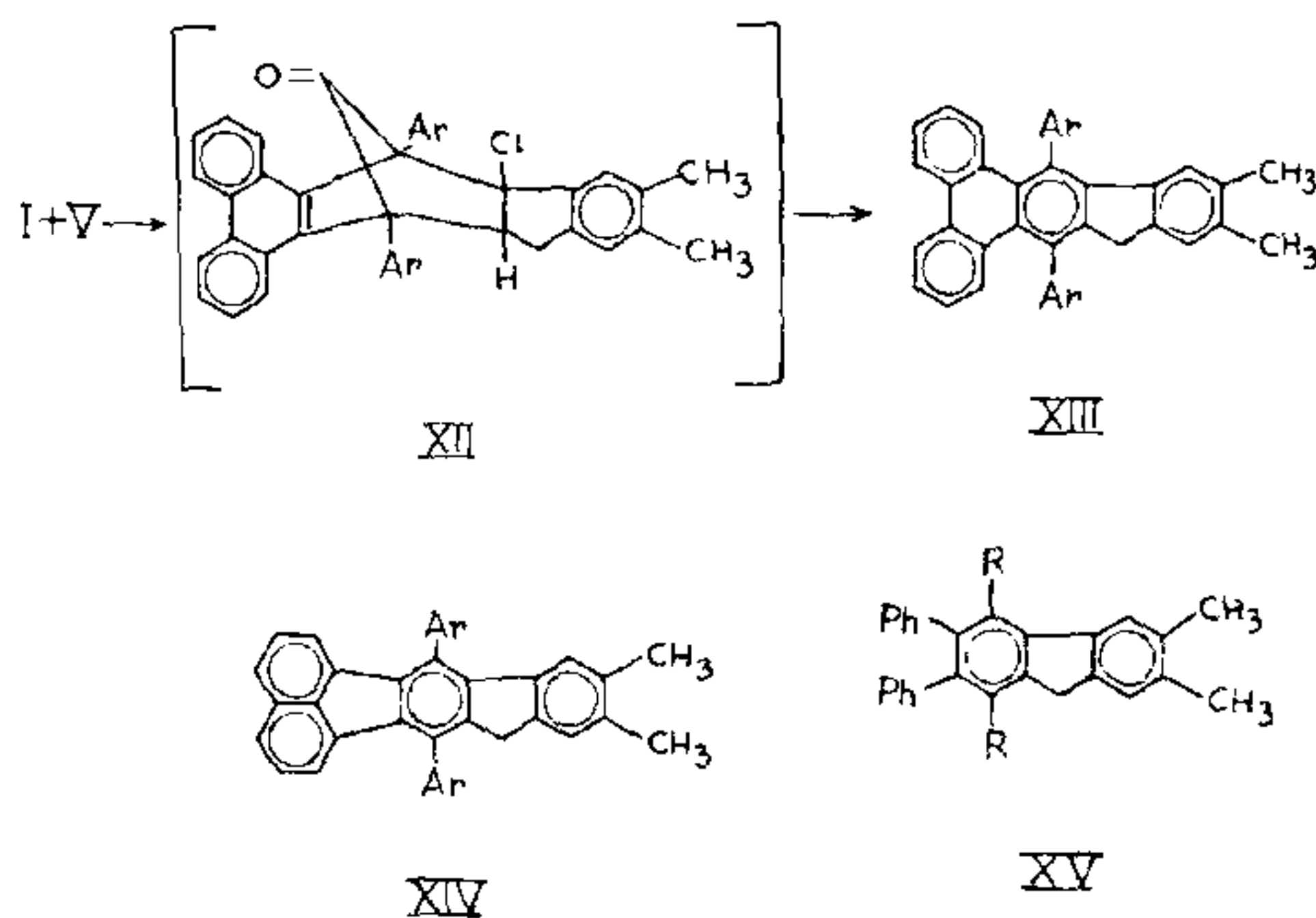


Scheme 1

Similarly, when IIa, b and IIIa, b were heated with VI in tetralin, 1,4-diaryl-2,3-(1',8'-naphthylene) phenanthrene (Xa, b) and 1,4-diaryl-2,3-diphenylphenanthrene (XIa, b) were obtained respectively with the simultaneous loss of carbonmonoxide and hydrogen

chloride gases. In both cases, no carbonyl bridged adducts could be isolated even if the reactions were carried out under cold conditions. The properties of IXa-d, Xa, b and XIa, b are given in table 1.

In the present work, we also report the synthesis of a new series of highly arylated fluorene derivatives by using 5,6-dimethyl-1-chloro-3(H)-indene (V) as a dienophile. The latter was conveniently prepared by the action of phosphorus pentachloride on 5,6-dimethyl-indan-1-one (IV) by the usual procedure. When V was heated with Ia, b, c, IIa, b and IIIa in xylene, 1,4-diaryl-6,7-dimethyl-2,3-biphenylfluorene (XIIIa, b, d) 1,4-diaryl-6,7-dimethyl-2,3-(1',8'-naphthylene) fluorene (XIVa, b) and 1,2,3,4-tetraphenyl-6,7-dimethylfluorene (XVa) respectively were obtained with the elimination of carbonmonoxide as well as hydrogen chloride. No carbonyl bridged adduct could be isolated in any case.



Scheme 2

1,4,6,7-Tetramethyl-2,3-biphenylfluorene (XVb, Ar is replaced by CH₃ group) was also prepared by the condensation of V with 2,5-dimethyl-3,4-diphenylcyclopentadienone in boiling xylene. IR spectra of XIIIa, b, d, XIVa, b and XVa, b showed the bands at $3100-2750\text{ cm}^{-1}$ ($\nu_{\text{C-H}}$); $900-675\text{ cm}^{-1}$ ($\nu_{\text{C-H}}$, out of plane), $1600-1450\text{ cm}^{-1}$ ($\nu_{\text{C-C}}$). Properties of all the fluorene derivatives are given in table 1.

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.

5,6-Dimethyl-1-chloro-3(H) indene (V) - 5,6-Dimethyl-indan-1-one (IV, 20 g) in dry benzene (75 ml) was added dropwise to a cooled solution of phos-

Table 1 Characterisation data of Anthracene (IXa-d), Phenanthrene (Xa, b, XIa, b) and Fluorene Derivatives (XIIIa, b, d, XIVa, b and XVa, b).

Compound	Ar	m.p. (°C)	Mol. formula
IXa	Ph	312	C ₃₈ H ₂₄
IXb	<i>p</i> -CH ₃ C ₆ H ₄	304	C ₄₀ H ₂₈
IXc	<i>p</i> -C ₂ H ₅ C ₆ H ₄	260	C ₄₂ H ₃₂
IXd	3,4-(CH ₃) ₂ C ₆ H ₃	293	C ₄₂ H ₃₂
Xa	Ph	240	C ₃₆ H ₂₂
Xb	<i>p</i> -OCH ₃ C ₆ H ₄	248	C ₃₈ H ₂₆ O ₂
XIa	Ph	220	C ₃₈ H ₂₆
XIb	<i>p</i> -OCH ₃ C ₆ H ₄	195	C ₄₀ H ₃₀ O ₂
XIIIa	Ph	201	C ₃₉ H ₂₈
XIIIb	<i>p</i> -CH ₃ C ₆ H ₄	303	C ₄₁ H ₃₂
XIIIc	3,4-(CH ₃) ₃ C ₆ H ₃	220	C ₄₃ H ₃₆
XIVa	Ph	80	C ₃₇ H ₂₆
XIVb	<i>p</i> -OCH ₃ C ₆ H ₄	160	C ₃₉ H ₃₀ O ₂
XVa	Ph	205	C ₃₉ H ₃₀
XVb	CH ₃	345	C ₂₉ H ₂₆

Compounds IXb-d and XIIIa, b, d were crystallised from benzene-ethanol, Xa, b; XIa, b and XIVa, b; XVa from benzene-pet. ether (40-60°), IXa from tetralin and XVb from xylene. All compounds were colourless except IXd, Xa, Xb, XIVa, XIVb and XVb which were yellow.

phorus pentachloride (100 g) in dry benzene (75 ml) (during 1 hr) with vigorous shaking. The mixture was stirred for further 3 hr and poured on to crushed ice. The product was extracted with ether, the ethereal solution washed with 5% aq. sodium carbonate, dried (Na₂SO₄) and the solvent removed. The residual liquid on distillation gave V, b.p. 109-10°/6 mm, yield 12 g (Found: Cl, 19.71 C₁₁H₁₁Cl requires Cl, 19.88%).

1-Chloro-3,4-dihydronaphthylene (VI)—This was prepared in a similar way from α -tetralone, b.p. 70°/6 mm (Found: Cl, 21.47 C₁₀H₉Cl requires Cl, 21.58%).

7,8,9,10-Tetrahydro-1:2, 3:4, 5:6-tribenz-9,10-diphenyl-9,10-endocarbonylanthracene (VII)—Phenicyclone (0.01 mol) was mixed with 1-chloro-3,4-dihydronaphthylene (VI, 0.01 mol) in dry benzene (80 ml) and kept at room temperature until the colour of the dienone was discharged (40 hr). The product (VIII) separated as colourless crystals was filtered, washed with benzene and crystallised from the same, m.p. 162 (Found: C, 91.61; H, 4.88 C₃₉H₂₆O required C, 91.76; H, 5.10%).

9,10-Diaryl-1:2, 3:4, 5:6-tribenzanthracene (IX)—Compounds I (0.01 mol) and VI (0.015 mol) were refluxed in tetralin (30 ml) until the colour of the solution was discharged (2-3 hr). During the reaction,

CO and HCl gas were evolved. The solvent was removed and the residue purified by column chromatography and crystallised from suitable solvents (table 1).

1,4-Diaryl-2,3-(1',8'-naphthylene) phenanthrene (X)—A mixture of II (0.01 mol) and VI (0.015) in tetralin (30 ml) was refluxed until the colour of the dienone was discharged (8-9 hr). The product was worked up as described from IX. All the compounds were yellow in colour (table 1).

1,4-Diaryl-2,3-diphenylphenanthrene (XI)—Condensation of the cyclopentadienone III (0.01 mol) and VI (0.015 mol) in tetralin (30 ml) was carried out as described for X to give the colourless hydrocarbons (XIII) (table 1).

1,4-Diaryl-6,7-dimethyl-2,3-biphenylene fluorene (XIII)—Compounds I (0.01 mol) and V (0.015 mol) were heated in xylene (25 ml) until the colour of the solution faded (4-5 hr). The solvent was removed by steam-distillation. The residue was filtered, washed with ethanol and chromatographed over neutral alumina using benzene as eluent. The product was finally crystallised from suitable solvents (table 1).

1,4-Diaryl-6,7-dimethyl-2,3-(1',8'-naphthylene) fluorene (XIV)—A mixture of II (0.01 mol) and V (0.015 mol) was heated in xylene (25 ml) until the colour of the dienone was discharged (5-6 hr). After completion of the reaction, the solvent was removed, the residue purified by column chromatography and finally crystallised from suitable solvents (table 1).

1,4,6,7-Tetramethyl-2,3-biphenylfluorene (XVb)—2,5-dimethyl-3,4-diphenylcyclopentadienone (0.01 mol) and V (0.015 mol) were refluxed in xylene (25 ml) until the colour of the solution faded (8 hr). The solution was cooled when the product separated as light yellow crystals. It was filtered, washed with a little xylene and finally crystallised from the same (table 1).

1,2,3,4-Tetraphenyl-2,3-dimethylfluorene (XVa)—This was prepared similar to that described for XIV by the condensation of III (0.01 mol) and V (0.015 mol) in xylene (25 ml). It was found to be colourless (table 1).

ACKNOWLEDGEMENT

SM expresses his grateful thanks to the Burdwan University for the award of a fellowship.

16 January 1984; Revised 26 March 1984

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A COMPARISON OF DIFFERENT THEORIES OF VISCOUS FLOW FOR BINARY LIQUID MIXTURES OF TOLUENE WITH CHLOROBENZENE, BENZYLALCOHOL AND N-HEXANOL AT DIFFERENT TEMPERATURES

A. P. SRIVASTVA and S. N. DUBEY

Department of Chemistry, National Degree College, Barhalganj, Gorakhpur 273 402, India.

ABSTRACT

The viscosity in binary liquid mixtures of toluene with chlorobenzene, benzyl alcohol and n-hexanol has been evaluated at 30, 40, 50 and 60°C by Naidu, Ubbelohde, Grunberg-Nissam and Katti-Chaudhuri's method and the result has been compared with the experimental values. The result has been discussed in terms of inter-molecular interaction. The agreement is better for toluene with non-associated liquids.

An attempt has been made to compare the relative merits of Naidu, Ubbelohde, Grunberg-Nissam and Katti-Chaudhuri's method for the theoretical evaluation of viscosity in binary liquid mixtures of toluene with chlorobenzene, benzyl alcohol and n-hexanol at 30°, 40°, 50° and 60°C, over the complete composition range, with the experimental value. Furthermore, the deviation of the theoretical value from the experimental results has been discussed in terms of intermolecular-interaction. The required experimental data for the comparison have been taken from the literature¹. Naidu² obtained the following relation for the theoretical value of viscosity for binary liquid mixture

$$\ln \eta_m = x_1^2 \ln \eta_1 + x_2^2 \ln \eta_2 + 2x_1 x_2 \ln \eta_{12} \quad (1)$$

where η_1 and η_2 are the viscosities of the pure liquid components whose mole fractions are x_1 and x_2 . η_m is the viscosity of the mixture and η_{12} is the viscosity at equimolar concentration. The value of η_{12} is obtained by the relation $\eta_{12} = 0.5 \eta_1 + 0.5 \eta_2$. Hind *et al*³ and Frankel⁶ used the following expressions for the viscosity of a liquid mixture, respectively,

$$\eta_m = x_1^2 \eta_1 + 2x_1 x_2 \eta_{12} + x_2^2 \eta_2 \quad (2)$$

$$\log \eta_m = x_1 \log \eta_1 + x_2 \log \eta_2 + 2x_1 x_2 \log \eta_{12} \quad (3)$$

The viscosity of a liquid mixture according to

Grunberg and Nissam⁴ and Katti-Chaudhuri⁵ is obtained by following two different equations, respectively;

$$\ln \eta_m = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d \quad (4)$$

and

$$\ln \eta_m(a) \cdot V_m = x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2 + x_1 x_2 \frac{W_{vis}}{RT} \quad (5)$$

where $W_{vis} = \frac{RT}{x_1 x_2} \ln \left[\frac{V_m}{V_1^{x_1} V_2^{x_2}} + x_1 x_2 d \right]$ (6)

In (4), d is the approximate measure of strength of interaction and in equations (5) and (6), V_1 , V_2 and V_m represent the molar volumes of the component 1, 2 and mixture, respectively. W_{vis} stands for interaction energy between the components at temperature T .

The experimental and theoretical values of viscosities obtained by different methods, for the title binaries, at different temperatures are listed in tables 1, 2 and 3, respectively. Table 1 indicates that at all the mole fractions and at all the temperatures studied, Naidu and Ubbelohde relations give values more comparable with the experimental values than Grunberg and Nissam and Katti-Chaudhuri's relations. For the systems toluene + benzyl alcohol and toluene + n-hexanol, only Frankel⁶, Ubbelohde and