Results and Discussion

The aqueous solution of the dye shows a maximum at 490 nm irrespective of the pH of the solution. The dye as such is not extracted in chloroform but the ion pair of the alkaloid cinchonine with the dye is extracted as pink coloured species, showing a maximum at 510 nm. Change in pH of the solution does not affect the maximum of the organic extract. Amongst the different halogenated extractants investigated for the extraction of the ion pair, chloroform was found to the best. The ion pair is extracted into the chloroform form pH range 1 to 7 the maximum extraction being at pH 6. The composition of the ion pair complex as found by continuous variation and molar ratio methods is 1:2 [Alkaloid (A): Dye (D)], suggesting an ion pair formation of the type $(A^{2+})(D^{-})_2$.

Beer's law is obeyed in the range of 8–450 μg. The molar absorptivity of the system at 510 nm is 16,000 lit. mol^{-1} cm^{-1}. The sensitivity expressed by Sandell's notation is 1 $\mu g/cm^2/0{\cdot}004$ abs. unit. A five fold excess of the dye is required for maximum colour development. About one minute of shaking is sufficient for complete extraction of the ion pair of the alkaloid. The following substances do not interfere even in ten fold excess: citric acid, sodium benzoate, sodium salicylate, acetyl salicylic acid (aspirin), sodium diethyl barbituric acid, sodium sacchharin, sacchharin, glucose and fructose.

Procedure

To a suitable aliquot of the alkaloid solution containing 0·025–0·1 mg of the alkaloid add 10 ml of buffer of pH 6 and 5 ml of 10^{-3} M aqueous solution of the dye. Shake for one minute with 15 ml of chloroform in a separatory funnel. Separate the chloroform layer and read its absorbance at 510 nm. Prepare the standards accordingly.

A set of analytical results obtained by following the above procedure are given in Table I. Each reported value is based on six determinations and the data show a precision of ± 1·5%. As is evident from the table, the method gives fairly accurate results.

TABLE I

Results of cinchonine determination by Solochrome Green V 150

Added (μg)	Found (μg) ($n = 6$)	Relative error (%)
50	49·6	−0·8
125	123·5	−1·2
200	200	0·0
275	278	+1·1
350	353·5	+1·0
400	406	+1·5

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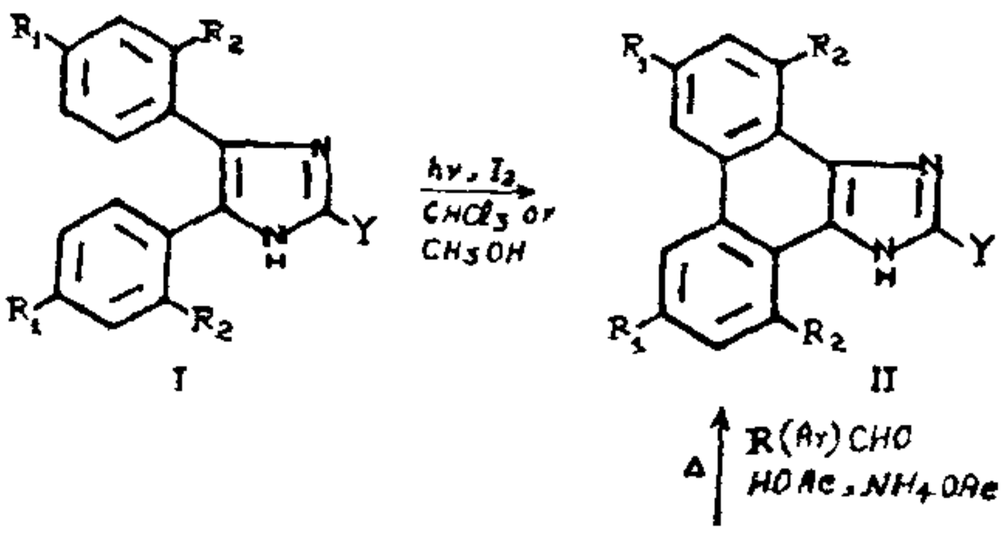
1. Celap, M. B., Janjic, T. J. and Jevtic, V. D., *Microchem. Ichnoanal. Acta*, 1963, p. 1043.
2. Petru Spacu and Cornelia Ianu, *Z. Anal. Chem.*, 1960, **174**, 87.
3. Palumbo, M. and Sacca, S., *Farmaco (Pavia) Ed. Prat.*, 1962, **17**, 65.
4. Linden, E. and Goran Schill, *Acta Pharma. Suec.*, 1967, p. 327.
5. Bose, P. C., Singh, R. K., Ray, G. K. and Mukerji, B., *J. Sci. Indian Res. India*, **D**. 21, 1962, p. 386.
6. Pankiewicz, *Farm. Pol.*, 1963, **19**, 234.
7. Nonclercq, M. and Nys, C., *J. Pharm. Belg.*, 1962, **17**, 241.
8. Laugel, P., *Compt. Rend.*, 1962, **255**, 692.
9. Schill, G., *Acta Pharm. Suec.*, 1965, **2**, 13.
10. Rama Rao, N. V. and Tandon, S. N., *Z. Anal. Chem.*, 1977, **286**, 255.
11. — and —, *Chem. Anal.*, 1977, **22**, 965.
12. — and —, *Presented at All India Chemical Convention of Chemists*, 1976.

PHOTOCHEMICAL AND THERMAL SYNTHESIS OF PHENANTHR [9, 10-*d*] IMIDAZOLES

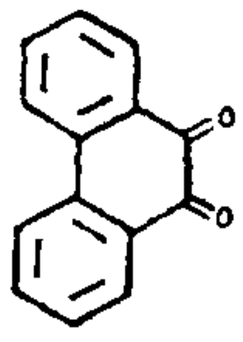
PHOTOCHEMICAL cyclodehydrogenation reaction of stilbene and its analogues represents a prominent route for the synthesis of a number of phenanthrene derivatives[1]. Recently this reaction has been used for the synthesis of phenanthro heterocyclics[2,3], and in some cases where some other chromophores are also present, selective cyclization of the stilbene chromophore has been found to occur[4,5]. This paper reports on the utility of the stilbene photodehydrocyclization in the synthesis of a number of phenanthr [9, 10–*d*] imidazoles. Thus the direct irradiation of 4, 5–diarylimidazoles (Ia–c) in suitable solvents in the presence of iodine or oxygen has been found to result in the oxidative cyclization at the stilbene chromophore to give phenanthr [9, 10–*d*] imidazoles (IIa–c).

The general method for the photoconversion of I to II is as follows: a 0·005M solution of I in chloroform (150 ml) containing iodine (15–20 mgs) was irradiated in a pyrex photochemical reactor by immersing a water-cooled Philips HPK 125 W high pressure

mercury-quartz lamp. During photolysis crystals got deposited on the sides of the reaction vessel. When the reaction was complete (as evidenced by tlc), the solvent was distilled off from the photolysate, and the residue crystallised from suitable solvents to give II.



a : $R_1 = R_2 = Y = H$
b : $R_1 = Cl$, $R_2 = Y = H$
c : $R_2 = Cl$, $R_1 = Y = H$
d : $R_1 = R_2 = H$, $Y = C_6H_5$
e : $R_1 = R_2 = H$, $Y = o\text{-}ClC_6H_4$
f : $R_1 = R_2 = H$, $Y = p\text{-}NO_2C_6H_4$
g : $R_1 = R_2 = H$, Y = furyl



III

In all the cases, products were found to be homogeneous to tlc. The identity of the compounds was established by elemental analysis, spectral data and by comparison with specimens prepared by an independent route starting from phenanthro–9, 10–quinone (III). The details of the photoreaction along with the yield and melting points of the compounds are given in Table I. 2, 4, 5–Triarylimidazoles (Id–g), on irradiation under the same conditions as above, decomposed completely and no crystalline products were isolated in these cases.

TABLE I

Photoconversion of 4, 5-diarylimidazoles into phenanthr [9, 10-d] imidazoles (II)

4, 5-Diaryl-imidazole (I)	Solvent	Irradiation time, hrs.	Yield of II	m.p. ° C
Ia : $R_1 = R_2 =$ Y = H	Chloroform	20	59%	299
Ib : $R_1 = Cl$, $R_2 = Y$ = H	Chloroform	25	61%	322
Ic : $R_2 = Cl$, $R_1 = Y = H$	Methanol	20	54%	231

The photoproducts (II) were also thermally prepared by the extension of the general imidazole synthesis[6], starting from phenanthrene–9, 10–quinone (III). The following procedure is typical of the thermal synthesis of these phenanthrimidazoles :

A mixture of phenanthraquinone (2·1 gm), hexamine (0·26 gm) and ammonium acetate (6 gm) in glacial acetic acid was heated under reflux for 1 hour. The resulting solution was added to water, basified and the resulting precipitate filtered, washed and dried; yield: 2·1 gm. Recrystallisation from pyridine afforded phenanthr [9, 10–*d*] imidazole (IIa) as light yellow needles, m.p. 299°; (Found C, 82·1; H, 4·6; $C_{15}H_{10}N_2$ required C, 82·5; H, 4·5). Admixture with the specimen obtained from the photoreaction did not depress the melting point.

Similar reaction of phenanthraquinone with other aldehydes resulted in the formation of the corresponding phenanthrimidazoles in identical yields. The results are given in Table II.

TABLE II

Thermal conversion of phenanthraquinone to phenanthr [9, 10-d] imidazoles (II)

Phenanthr [9, 10-*d*] imidazole (II)	Yield of II	m.p. ° C
II : Y = H, $R_1 = R_2 = H$	74%	299
II : $Y = C_6H_5$, $R_1 = R_2 = H$	80%	259
II : Y = *o*-ClC_6H_4, $R_1 = R_2 = H$	83%	225
II : Y = *p*-$CH_3C_6H_4$, $R_1 = R_2 = H$	77%	273
II : Y = *p*-$OCH_3C_6H_4$, $R_1 = R_2 = H$	75%	318

The photochemical conversion of I to II was also found to occur on exposure of the solution of I to sunlight. Irradiation of Ia-c employing aerial oxidation (instead of iodine) also afforded IIa-c; but the reaction was found to be slow in these cases. Irradiation of Ia in a deaerated condition (*i.e.* under nitrogen atmosphere) gave a different product. The structure of the compound and the reaction is under investigation.

Professor S. S. Moosath is thanked for encouragement, the University of Calicut for facilities and the C.S.I.R., New Delhi, for the award of a research fellowship to one of the authors (E. P.).

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May 25, 1978.

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1. Blackburn, E. V. and Timmons, C. J., *Chem. Soc. Rev.*, 1969, 23, 482.
2. Padwa, A. and Hartmann, R., *J. Am. Chem. Soc.*, 1966, 88, 3759.
3. Grimshaw, J. and Mannus, D., *J. C. S. Perkin I*, 1977, p. 2096.
4. Pillai, V. N. R. and Ravindran, M., *Ind. J. Chem.*, 1977, 15B, 1043.
5. Cooper, J. L. and Wasserman, H. H., *Chem. Comm.*, 1969, p. 200.
6. Davidson, D., Weiss, M. and Jelling, M., *J. Org. Chem.*, 1937, 2, 328.

HAND-AXE—A NEW DISCOVERY IN GHAGGAR-NALAGARH COMPLEX

THE Siwaliks probably bear the potentials of revealing the relics of early man in India. The discovery of the fossils of *Hyoselephas hydsudricus, Sus hysudricus, Merycopotamus dissimilis, Cervus, Sivatherium giganteum, Sivacobus palaeindicus, Bubalus platyceros, Proamphilios kashmiricus, Bucapra daviosii, Pentalophodon knetpuraliensis, Stegodon insignis, Stegodon bombifrons, Stegodon ganesa, Stegodon Katliensis, Archidiskodon planifrons, Elephas hysudricus, Hipparion antelopinum, Equus sivalensis, Rhinoceros palacindicus, Coelodonta platyrhinus, Potamochoerus palacindicus, Hippohyus tatroti, Hexaprotodon sivalensis, Camelus sivalensis, Leptobos falconeri, Hemibos acuticornis, Hemibos chaukiensis, Hemibos triquetricornis, Bos acutifrons,* Khan[1] and Nanda[5] have rendered the region all the more important from the viewpoint of lithic tools belonging to the pleistocene period. The valley of the Ghaggar which has its origin in the Siwalik hills was a cluster of fresh water marshy lakes at the foot of lower Siwalik ranges about two to three million years ago. This region around might have fairly thickly forested to rear big animals like buffalo, horse, giraffe, straight tusked elephant, rhinoceros, pigs, camels, hippopotamus, crocodile and tortoise. There seem to have occurred enormous rhythmic climate fluctuations caused by intense glaciation in higher Himalayan ranges resulting in the waning and waxing of these lakes, rendering the region unfavourable for those animals. The glaciations and pluviations gave rise to a series of terrace levels on the river banks. There can be recognised four prominent terrace levels at heights of about 55 m, 45 m, 20 m, and 6 m respectively on the right bank of the river Jhajra which belong to the Ghaggar river system above the present river bed. At places a fifth terrace level less than 5 m above the river bed, can also be identified which is not fully developed. Of these the terrace at 55 m is most extensive and at its upper limits is covered with colluviation cone deposits, above which the Siwalik beds appear. The occurrence of terraces at various heights is a clear evidence that the Ghaggar river was flowing in the past at each of these heights at different times. These terraces are mostly composed of river gravel and Boulder Conglomerate of the Siwalik formations.

During the periods when climate remained congenial, the readily available life sustaining elements like vegetation and animal life created a suitable habitat for early human settlements here. The early man preferred to camp on the terrace which was the most convenient flat surface. The raw material in the form of river pebbles was also at hand to design and fabricate the tools required for his hunting pursuits. For cutting the hunted animals, extracting flesh and removing their skins the early man employed stone tools like choppers and scrapers which have sharp edges suitable for such functions. These tools clearly indicate the earlier stage of human culture. As a result of various exploratory efforts, stone artefacts comprising mostly choppers, chopping tools, cores and flakes of pebbles and a few molars from conglomerate zone have been discovered from the Ghaggar valley.

Realizing the potentiality of the river valley, renewed efforts to discover newer tools were undertaken by the present author accompanied by Mr. Manmohan Sharma, a research scholar of the Kurukshetra University. The tools discovered during the present venture comprise scrapers on flakes, and flakes and cores. The material commonly employed was quartzite. Most interesting, however, is the discovery in this area of an Acheulian type pear-shaped quartzite hand-axe neatly trimmed all over by controlled flaking on both sides. The hand-axe is discovered from the most extensive upper terrace (Terrace I) at a distance of about 500 m due north of Kotla village (latitude 30° 45′ N and longitude 76° 54′ E) in Ghaggar valley of Ambala District.

The archaeological investigations conducted earlier by Prufer[6], Sen[7], Sharma[8], Sharma[9], Khatri[2] and Mohapatra[4] in the Sohan, Sirsa, Sutlej and Ghaggar valleys had discovered some Sohanian quartzite palaeoliths mainly choppers, scrapers, cores and flake cores and a few molars from conglomerate zone. Though hand-axes or their prototype were also stated to have been discovered, yet the existence of the true hand-axe remained controversial in the region. The present discovery of the true pear-shaped Acheulian quartzite hand-axe, however, dispels the general belief held by a majority of archaeologists that the Ghaggar-Nalagarh complex is devoid of hand-axes.

Archaeological explorations conducted earlier by the present writer[3] around Chandigarh and in the foot hills of the Siwaliks brought to light important ancient sites like Saketri, Karor, Nada, Badi Parachh, Chhoti Parachh and Hathnaur besides chalcolithic remains which yielded choppers, scrapers, cores, and flake cores. Further detailed work in this region might