

Gas chromatographic measurements were made on a Netel model 'Omega' instrument equipped with a dual flame ionization detector (FID) and a single pen recorder with an input of 1 mv. A glass column pre-treated with KOH, 2 meters in length with outer diameter of 1/4 inch and packed with 10% FFAP + 2% KOH on chromosorb W-HP, 80/100 mesh was used. The oven temperature was maintained at 210°C. The temperature of the detector and injection port were adjusted to 230°C and 300°C respectively. Nitrogen was used as a carrier gas at a flow rate of 45 ml/min and the FID was used with flow rates of hydrogen and air maintained at 30 ml/min and 300 ml/min respectively. The chart speed was 0.5 cm/min. The retention time of 1-naphthylamine under these conditions was 20 minutes and that of 2-naphthylamine 23 minutes (figure 1).

**Preparation of solutions:** Stock solutions of 1-naphthylamine (250 mg) and 2-naphthylamine (100 mg) were prepared in benzene (5 ml). Standard mixtures of 2-naphthylamine in 1-naphthylamine were prepared to give a series of standard solutions in the range of 0.1% to 0.5%. The sample (250 mg) was dissolved in benzene (5 ml) and this solution was used for injection.

**Procedure:** Standard solutions (0.6 µl) were injected sequentially and a calibration curve was prepared. A plot of peak heights against concentrations gave a straight line in the range 0.1-0.5% of 2-naphthylamine. The sample was treated in the same manner as the standards and the peak height was extrapolated to give the 2-naphthylamine content. Results obtained on various samples are as shown in table I.

TABLE I

*2-Naphthylamine content in 1-naphthylamine*

Sample	I	II	III
Amount of 2-naphthylamine estimated in sample	0.58%	1.10%	2.03%
Number of observations	10	10	10
Standard deviation	0.06	0.04	0.07
Per cent recovery after standard addition	101.90	100.58	101.87

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### STUDIES IN THE REARRANGEMENT OF SPIRANES: SYNTHESIS OF 1',2',3',4'-TETRAHYDRO SPIRO [2,3,4-TRIMETHYL CYCLOPENTANE-1,2'-NAPHTHALENE] AND ITS REARRANGEMENT ON CATALYTIC DEHYDROGENATION

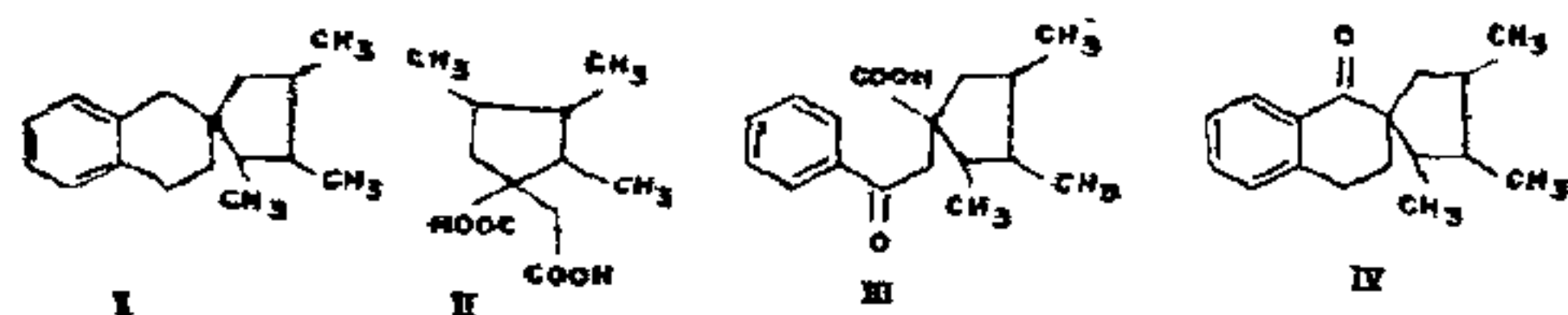
D. N. CHATTERJEE AND BHARATI CHAKRABORTY  
Department of Chemistry, Presidency College,  
Calcutta 700 073, India.

SPIRANES of the type 1',2',3',4'-Tetrahydrospiro cyclopentane-1,2'-naphthalene are known to undergo rearrangement on dehydrogenation with 10% Pd-C catalyst<sup>1</sup>. Recently we synthesised a substituted spirane of the above type<sup>2</sup> and observed that it underwent smooth ring transformation on catalytic dehydrogenation without any loss of carbon atom giving substituted phenanthrene. We now report the synthesis of highly substituted spirane, 1',2',3',4'-tetrahydrospiro-[2,3,4-trimethyl cyclopentane-1,2'-naphthalene] (I) with a view to studying its rearrangement on dehydrogenation.

The hydrocarbon (I) was synthesised starting from 2,3,4-trimethyl cyclopentane prepared from crotonic acid by addition of potassium iodide in phosphoric acid solution followed by coupling of the

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resulting  $\beta$ -iodo butyric acid in the presence of copper powder<sup>3</sup>. The resulting  $\beta\gamma$ -dimethyl adipic acid through esterification, Dieckmann cyclisation followed by alkylation in acetone solution in the presence of anhydrous  $K_2CO_3$  and subsequent hydrolysis afforded 2,3,4-trimethyl cyclopentanone b.p. 170-175°, semi carbazone m.p. 175°. Condensation of this ketone with ethyl cyano acetate followed by addition of KCN in aqueous alcoholic solution and subsequent hydrolysis of the dicyano ester by 6N HCl furnished 2,3,4-trimethyl cyclopentane-1-carboxy-1-acetic acid (II) m.p. 153°, anhydride b.p. 153°/3 mm, anilic acid m.p. 176° in 85% overall yield.



The anhydride of the acid (II) on Friedel-Crafts condensation with benzene in the presence of  $AlCl_3$  gave  $\alpha\alpha$ -(2,3,4-trimethyl cyclopentane)- $\beta$ -benzoyl propionic acid (III) m.p. 118°, D.N.P. derivative m.p. 207° which on catalytic reduction in a Paar apparatus at 60° in ethanolic solution furnished  $\alpha\alpha$ -(2,3,4-trimethyl cyclopentane)- $\gamma$ -phenyl butyric acid, b.p. 180°/0.8 mm. This was cyclised in quantitative yield by PPA to 3',4'-dihydro spiro-[2,3,4-trimethyl cyclopentane 1,2'-(1'-H)-naphthalene]-1'-one (IV), b.p. 140°/1 mm (carbonyl stretching at  $5.95\mu$ ), which on Clemmensen reduction gave the desired spirane (I) b.p. 120-122°/1 mm.

The hydrocarbon underwent smooth rearrangement on heating with 10% Pd-C catalyst at 330° by fission of the spiro cyclopentane away from the substituents followed by angular cyclisation and dehydrogenation yielding 1,2,3-trimethyl phenanthrene<sup>4</sup>, m.p. 63°, picrate m.p. 185°. T.N.B. complex m.p. 198°.

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4. Louis F. Fieser and William H. Daudt, *J. Am. Chem. Soc.*, 1941, 63, 782.

## A NOTE ON THE NEWLY DISCOVERED COLUMBITE-TANTALITE, BERYL AND CASSITERITE BEARING PEGMATITES IN KATEKALYAN AREA, BASTAR DISTRICT, MADHYA PRADESH

P. V. RAMESH BABU AND T. M. RAMACHAR  
Atomic Minerals Division, Department of Atomic Energy, Begumpet, Hyderabad 500 016, India.

OCCURRENCE of columbite-tantalite, beryl and cassiterite in the pegmatites of Tongpal valley of south Bastar has come to limelight in recent years. The general trend of the pegmatite belt in this area is NW-SE. Intensive surveys carried out around Katekalyan, helped in not only establishing the north western continuity of the pegmatite belt, but also in proving that the pegmatites in this region are richer in columbite-tantalite and beryl than in the south eastern region. Katekalyan village ( $18^\circ 48' 10''$ ;  $81^\circ 37' 50''$ ) is located about 20 km north-west of Tongpal in top-sheet No. 65F/9. The area is approachable by fair weather roads from Darbha and Dantewara.

The rock units exposed in the area are andalusite schist, quartz-muscovite schist and quartzite belonging to the Bengal group of metasediments (Archean) intruded by basic sills. These are later intruded by granite, pegmatite, quartz vein and basic dykes. Kurnool(?) sedimentaries (upper pre-cambrian) comprising of conglomerate, quartzite, ferruginous shale and limestone unconformably overlie these rocks.

Columbite-tantalite, beryl and cassiterite bearing pegmatites have been discovered near Parcheli, Katekalyan, Metapal, Bodenar and Jamair. These pegmatites are emplaced along fractures in basic rock near its contact with quartz-muscovite schist or granite. In general the pegmatites are lensoid and sheet like bodies varying from 10 m to 150 m in length and 1 m to 20 m in width.

The rare metal bearing pegmatites in this area are mostly of asymmetrically zoned type with prominent quartz core, perthite and quartz-perthite, muscovite intergrowth zones. Replacement zones with cleavelandite and interlocked green muscovite replacing perthite are noticed in some pegmatites. Samples of columbite-tantalite from the above pegmatites have analysed from 31.4% to 51.42%  $Ta_2O_5$ , 11.1% to 44.0%  $Nb_2O_5$  and less than 0.1% to 9.27%  $SnO_2$ . Beryl samples from these pegmatites have analysed up to 9.2%  $BeO$ . The cassiterite occurring in a pegmatite analyses 86.3%  $SnO_2$ , 2.8%  $Ta_2O_5$  and 1.3%  $Nb_2O_5$ .

The studies so far carried out in Bastar-Koraput pegmatite belt indicate that incidence of cassiterite is more than that of columbite-tantalite in pegmatites