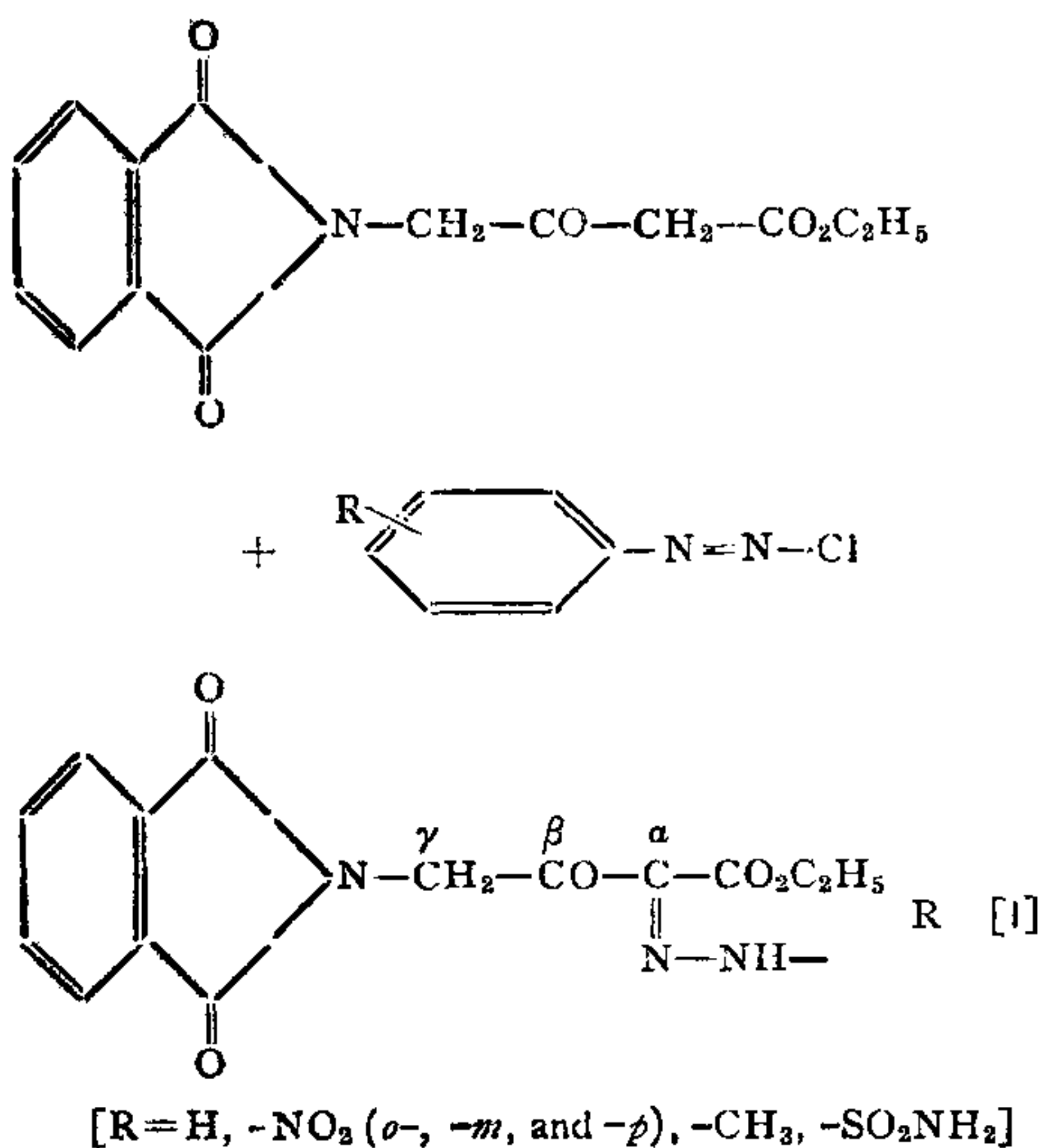


TABLE I

| Amines                              | Products formed<br>(mol. formula)                               | M.P.* | Colour      | Yield (%) | Elemental analyses (%) |      |          |     |          |      |
|-------------------------------------|---|-------|-------------|-----------|------------------------|------|----------|-----|----------|------|
|                                     |   |       |             |           | Carbon                 |      | Hydrogen |     | Nitrogen |      |
|                                     |   |       |             |           | F                      | C    | F        | C   | F        | C    |
| Aniline                             | C <sub>21</sub> H <sub>19</sub> O <sub>5</sub> N <sub>3</sub>   | 140°  | Yellow      | 66        | 63.2                   | 63.3 | 4.5      | 4.4 | 11.0     | 11.1 |
| <i>o</i> -Nitroaniline              | C <sub>20</sub> H <sub>16</sub> O <sub>7</sub> N <sub>3</sub>   | 205°  | Yellow      | 65        | 56.5                   | 56.6 | 3.6      | 3.7 | 13.1     | 13.2 |
| <i>m</i> -Nitroaniline              | C <sub>20</sub> H <sub>16</sub> O <sub>7</sub> N <sub>3</sub>   | 208°  | Pale yellow | 80        | 56.4                   | 56.6 | 3.4      | 3.7 | 13.0     | 13.2 |
| <i>p</i> -Nitroaniline              | C <sub>20</sub> H <sub>16</sub> O <sub>7</sub> N <sub>3</sub>   | 220°  | Yellow      | 70        | 56.5                   | 56.6 | 3.5      | 3.7 | 13.0     | 12.2 |
| <i>p</i> -Toluidine                 | C <sub>21</sub> H <sub>19</sub> O <sub>5</sub> N <sub>3</sub>   | 140°  | Red         | 40        | 63.9                   | 64.1 | 4.8      | 4.8 | 10.8     | 10.7 |
| <i>p</i> -Amino benzene-sulfonamide | C <sub>21</sub> H <sub>20</sub> O <sub>7</sub> N <sub>4</sub> S | 125°  | Light green | 60        | 53.1                   | 53.3 | 4.2      | 4.2 | 11.9     | 11.8 |

\* All melting points are uncorrected. F = Found ; C = Calculated.



surface of a cold, well-stirred solution of 3.1 g. (0.03 mol.) of aniline in 8 ml. of concentrated hydrochloric acid. The temperature of the solution was kept at 0–5° C. during addition. After ten minutes the solution was made alkaline to congo red by the addition of sodium acetate solution. The diazonium solution was added drop by drop with stirring to a cold solution of 9.1 g. (0.03 mol.) of phthalimido acetoacetic ester, 8.2 g. (0.1 mol.) of sodium acetate, 50 ml. of water and 250 ml. of acetone. The temperature was maintained below 10° during the addition. The mixture was stirred for a further thirty minutes at room temperature, then 100 ml. of water was added before the yellow solid was filtered. The yield of the solid obtained was found to be 8.0 g. (66%) and the melting point 140° C. The solid may be recrystallized by ethyl acetate.

Melting points and analytical data of the hydrazones prepared are listed in Table I.

The authors are thankful to Professor R. A. Srivastava for providing the necessary facilities.

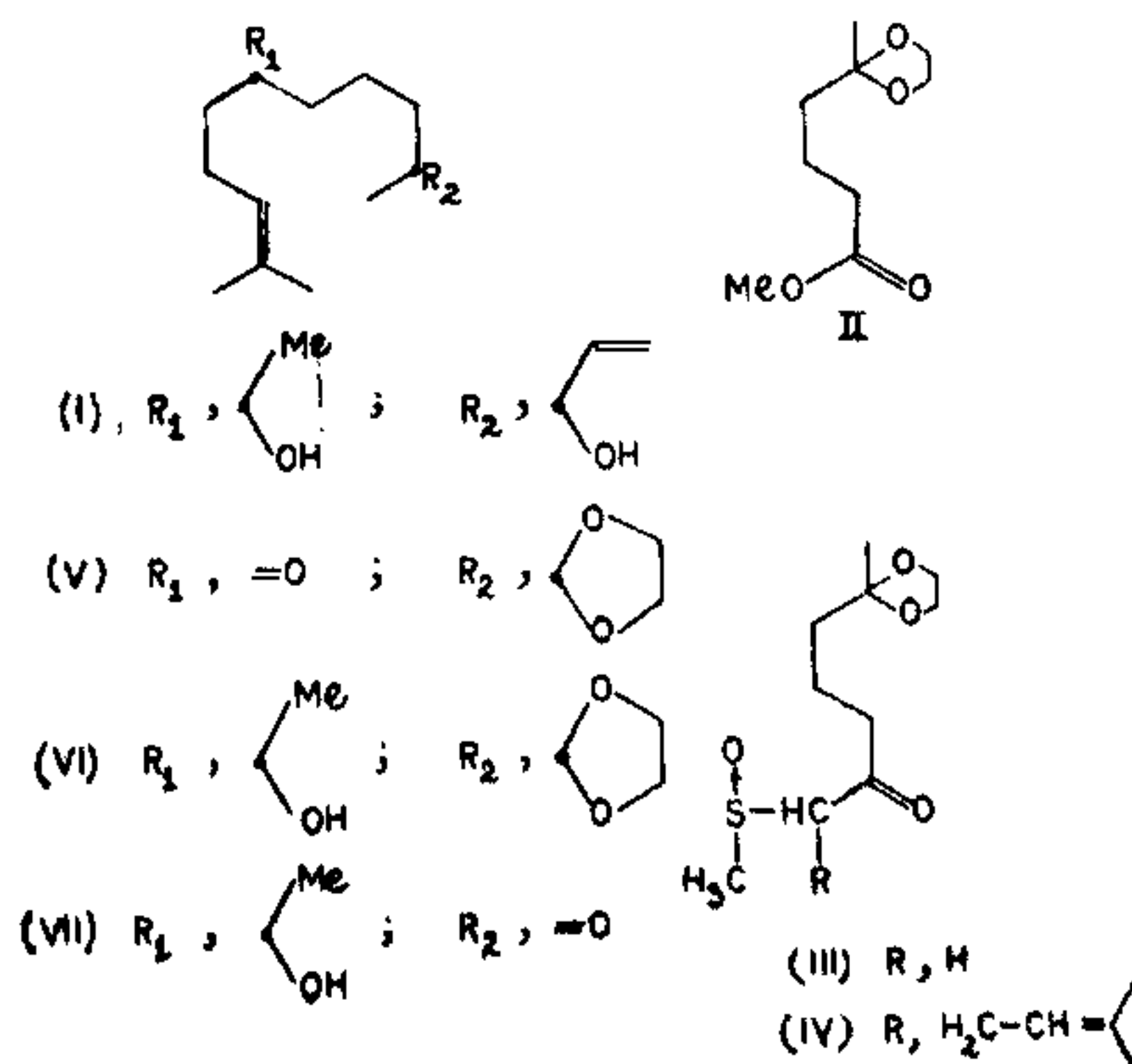
Chemical Laboratories,  
D.A.V. College,  
Kanpur, December 4, 1969.

R. K. SAKSENA,  
S. D. VERMA.

1. Wiley and Jarboe, *J. Am. Chem. Soc.*, 1955, 77, 403.
2. Bulow and Neber, *Ber.*, 1908, 45, 3732.
3. Goldberg and Kelly, *J. Chem. Soc.*, 1948, p. 1919.
4. Chattway and Ashworth, *Ibid.*, 1923, p. 475.

### A SYNTHESIS OF CAPPARAPIDIOL

As a part of our investigations towards the syntheses of terpenoids through  $\beta$ -keto-sulphoxide as the key intermediate, we report in the present communication a synthesis of structure (I) assigned to capparapidiol, a sesquiterpene diol isolated<sup>1</sup> from 'capparap' oil.



Methyl 5,5-ethylenedioxy-hexanoate (II) was prepared by ketalising<sup>2</sup> methyl 5-oxo-

hexanoate<sup>3</sup> with ethylene glycol in 50% yield (b.p. 105–107°/7–8 mm.). Reaction of (II) with methylsulphonyl carbanion<sup>4</sup> afforded  $\beta$ -ketosulphoxide (III) as a thick oil (b.p. 145–155°/0.5–1 mm.  $\nu_{\max}$ , 1705, 1040  $\text{cm}^{-1}$ ). Alkylation<sup>5</sup> of (III) with isoprene bromide in DMF and NaH followed by reductive cleavage<sup>6</sup> of sulphoxide group with Al (amalgam) in 10% aq. THF furnished ketal-ketone (IV) in 40% yield (b.p. 166–168°/10–13 mm.  $\nu_{\max}$ , 1715, 1060, 1040  $\text{cm}^{-1}$ ). Grignard reaction on (V) with methylmagnesium iodide secured the corresponding ketal alcohol (VI) in 63% yield (b.p. 150–152°/5–6 mm.  $\nu_{\max}$ , 3425, 1110, 1060–1040  $\text{cm}^{-1}$ ). Deketalisation<sup>7</sup> of ketal alcohol with aqueous acetone and PTS furnished keto alcohol (VII) ( $\nu_{\max}$ , 3425, 1705, 1100  $\text{cm}^{-1}$ ). Finally, compound (VII) was submitted to the excess of vinyl magnesium bromide in THF to give the diol (1) which showed comparable I.R. spectrum with that reported for capparapidiol.<sup>1</sup>

Wherever necessary the intermediates were chromatographed, fractionated under vacuum and then characterised by analytical and infrared spectral data. A full account of the paper will be published elsewhere when more compounds along these lines would be synthesised.

One of the authors (R. C. A.) is thankful to CSIR for the award of a Junior Research Fellowship.

Department of Chemistry,  
Panjab University,  
Chandigarh-14,  
December 19, 1969.

O. P. VIG.  
R. C. ANAND.  
K. L. MATTA.

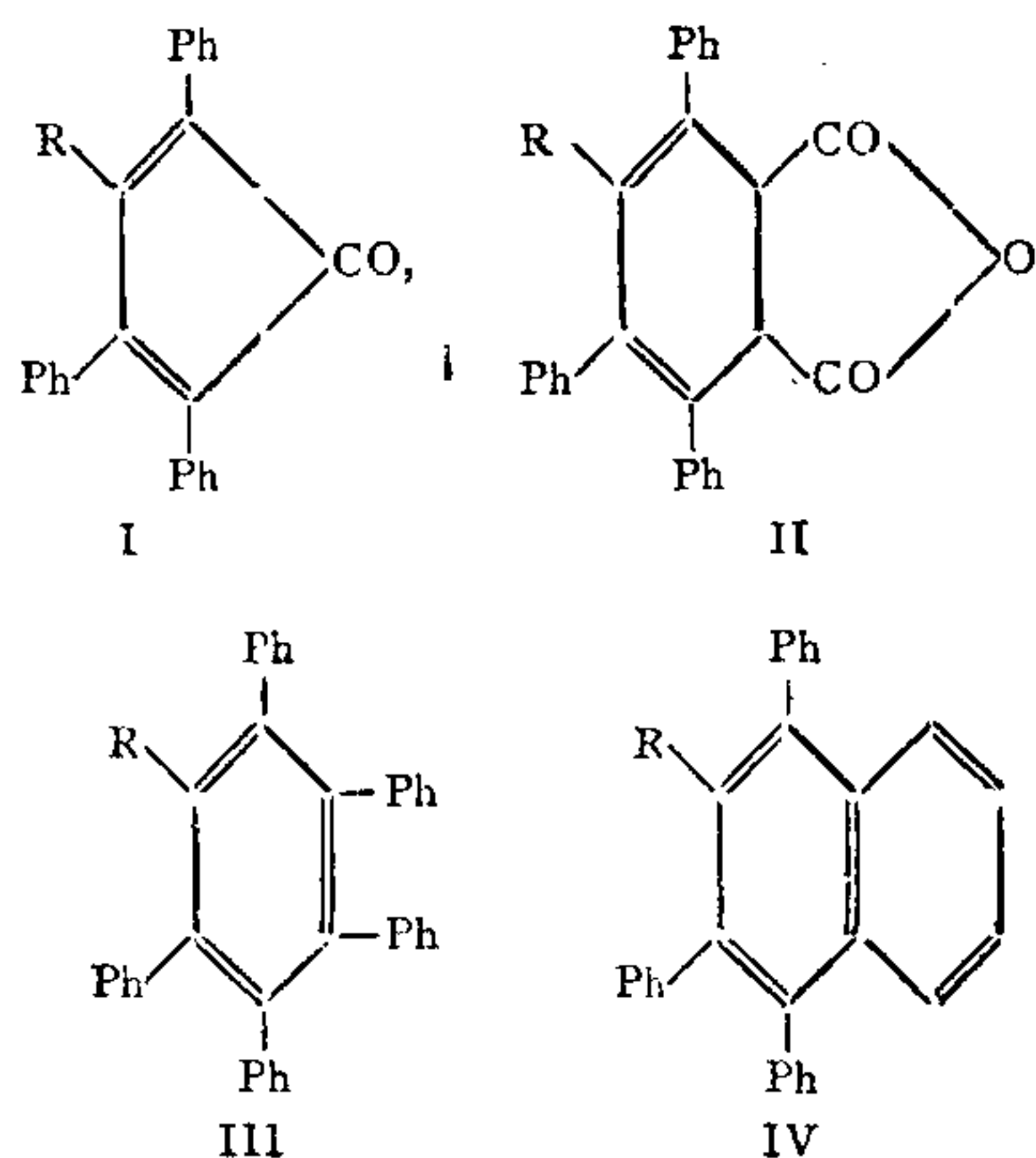
1. Castillo, J. B., Brooks, C. J. W. and Campbell, M. M., *Tetrahedron Letters*, 1966, p. 3731.
2. Salmi, *Fer.*, 1938, **71 B**, 1803.
3. Chong, R. and Clezy, P. S., *Austr. J. Chem.*, 1967, **20**, 123.
4. Corey, E. J. and Chaykovsky, M., *J. Am. Chem. Soc.*, 1965, **87**, 1345.
5. Gassman, P. G. and Richmond, G. D., *J. Org. Chem.*, 1966, **31**, 2355.
6. Corey, E. J. and Chaykovsky, M., *J. Am. Chem. Soc.*, 1964, **86**, 1641; 1966, **88**, 5498.
7. Johnson, W. S., Bass, J. D. and Williamson, K. L., *Tetrahedron*, 1963, **19**, 862.

### 'SYNTHESIS OF HYDRINDENE DERIVATIVES

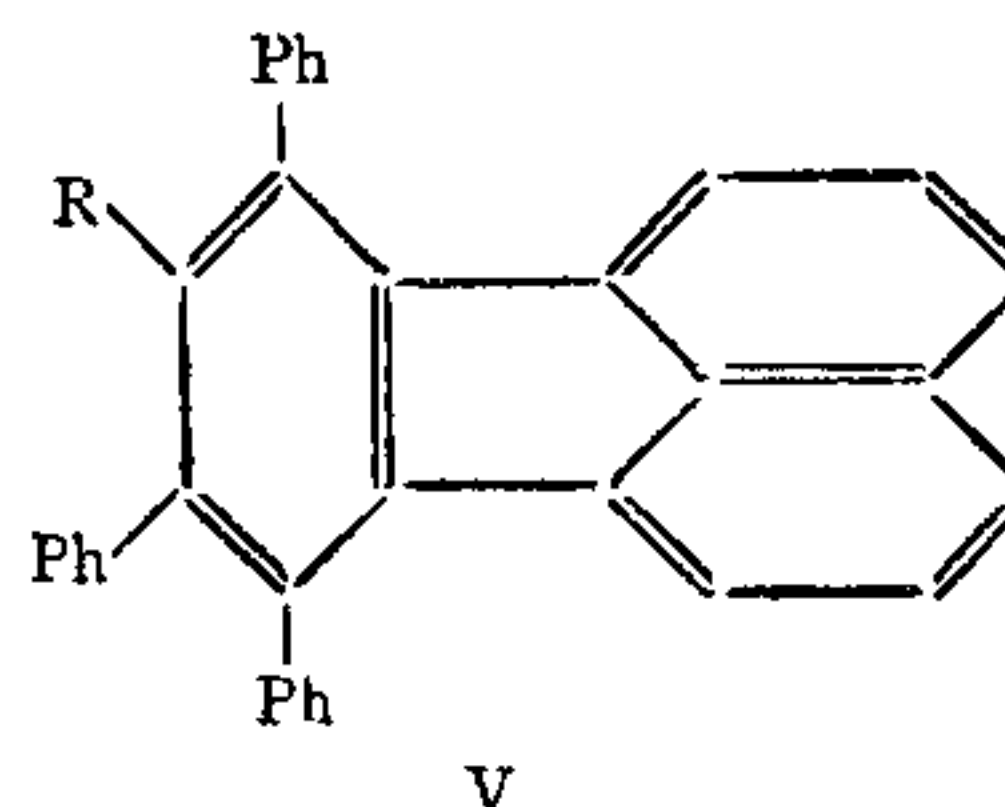
PHENYL acetyl chloride was condensed with Hydrindene in presence of anhydrous aluminium chloride in nitrobenzene to form 5-hydrindyl benzyl ketone, m.p. 111°, yield

47%. The ketone on oxidation with  $\text{SeO}_2$  gave the corresponding  $\alpha$ -diketone, m.p. 101°, yield 60%, which on treatment with alkaline  $\text{H}_2\text{O}_2$  gave hydrindene-5-carboxylic acid.

The diketone smoothly condensed with dibenzyl ketone in alcoholic KOH to form the cyclopentadienone derivative (I), m.p. 231°, yield 94%. The compound (I) is a very reactive diene and undergoes normal Diels-Alder reaction with (a) maleic anhydride to form (II), m.p. 217°, yield 60%, (b) with diphenyl acetylene to form (III), m.p. 305°, yield 80%, (c) with benzyne to form (IV), m.p. 175°, yield 70%, and (d) with acenaphthylene at high temperature to form (V), m.p. 148°, yield 60%.



and



where R = 5-Hydrindyl.

Microanalyses were done in Alfred Bernhardt's laboratory, W. Germany. Melting points are not corrected.

Organic Chem. Lab., A. J. BHATTACHARJEE,  
University of Burdwan, S. N. MANDAL,  
West Bengal (India), December 26, 1969.