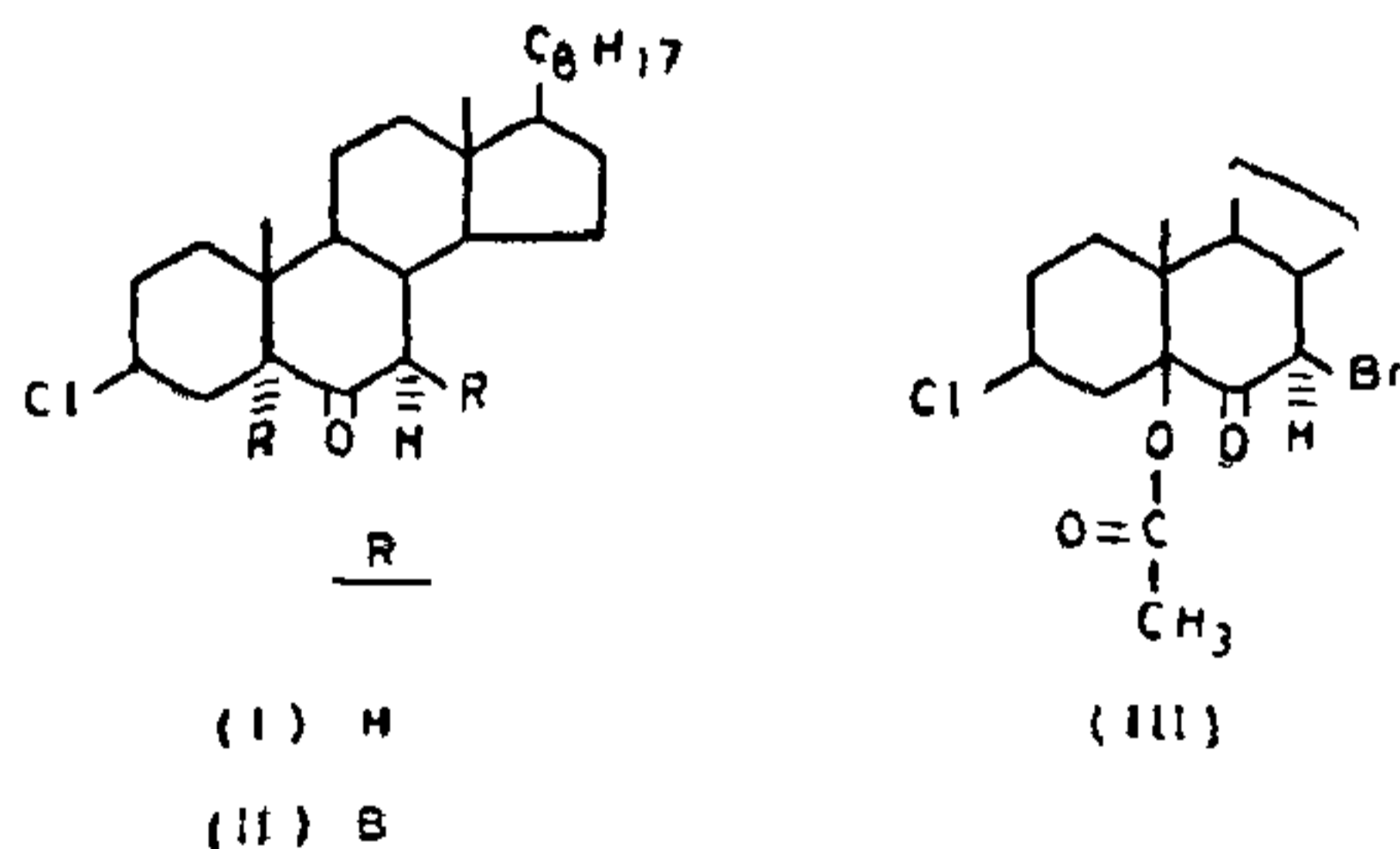


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### STEREOCHEMICAL STUDY OF $\alpha$ -BROMOKETONE: ACETOLYSIS OF

#### 3 $\beta$ -CHLORO-5, 7 $\beta$ -DIBROMO-5 $\alpha$ -CHOLESTAN-6-ONE (II) WITH SODIUM ACETATE-ALCOHOL

DURING the course of our study on bromination of steroidal ketones and subsequent reactions of  $\alpha$ -bromoketones, we subjected II obtained from bromination of 3 $\beta$ -chloro-5 $\alpha$ -cholestan-6-one (I) ( $\text{Br}_2$ -HBr at room temperature) to acetolysis using  $\text{CH}_3\text{COONa}$ - $\text{C}_2\text{H}_5\text{OH}$  and obtained 3 $\beta$ -chloro-5-acetoxy, 7 $\beta$ -bromo-5 $\beta$ -cholestan-6-one (III), the structures and stereochemistry of which are discussed.

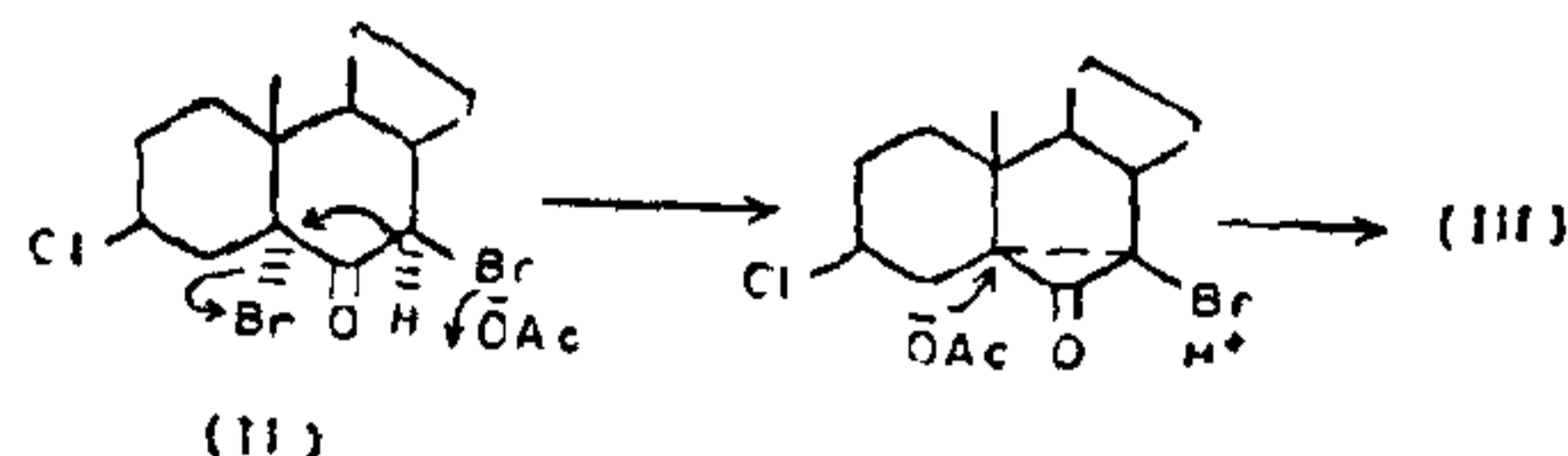


The acetoxy ketone (III) analysed for  $\text{C}_{29}\text{H}_{46}\text{BrO}_3\text{Cl}$  and gave a positive Beilstein test for halogens. The i.r. spectrum of III exhibited bands at 1745 ( $-\text{CO}-\text{O}-$ ), 1730 ( $>\text{C}=\text{O}$ ), 1237 ( $-\text{C}-\text{O}-$ ), 735 ( $\text{C}-\text{Cl}$ ),  $652\text{ cm}^{-1}$  ( $\text{C}-\text{Br}$ ). The n.m.r. spectrum gave signals at  $\delta$  4.46 d ( $\text{C}_7$ - $\alpha\text{H}$ ;  $J$   $\text{C}_7$ - $\alpha\text{H}$ ,  $\text{C}_8$ - $\beta\text{H}$  = 9 Hz; axial), 3.84 br ( $\text{C}_3$ - $\alpha\text{H}$ ;  $W_{\frac{1}{2}} = 12$  Hz; equatorial), 2.4s ( $\text{C}_5$ - $\text{O}-\text{CO}-\text{CH}_3$ ), 0.90, 0.80 and 0.68 ( $\text{C}_{10}$ - $\text{CH}_3$ ,  $\text{C}_{13}$ - $\text{CH}_3$  and other methyl protons).

It is reported that on inversion of configuration at C5 from 5 $\alpha$  to 5 $\beta$ , the C3- $\alpha$  proton changes from axial to equatorial. This stereochemical change during the acetolysis is revealed by i.r. and n.m.r. spectra of (II) and (III). C3- $\alpha$  proton in (III) is subjected to two equatorial and two axial vicinal couplings. This combination of splitting results in a broad signal at  $\delta$  3.84 with half band width = 12 Hz. This supports

equatorial orientation for C3- $\alpha\text{H}$  and implies cis A/B ring function. For axial C3- $\alpha$  proton,  $W_{\frac{1}{2}}$  is reported 22 Hz as in (II)<sup>1</sup>. The axial configuration of C3-C<sub>4</sub> in (III) was further substantiated by an i.r. band at  $735\text{ cm}^{-1}$  for C-Cl band<sup>2</sup>.

A tentative mechanism for the formation of (III) can be suggested as follows:



#### Experimental

Melting points are uncorrected. i.r. spectra were recorded with a Perkin-Elmer 237 spectrophotometer in Nujol. n.m.r. spectra were run in  $\text{CDCl}_3$  with Varian A100 MHz instrument with TMS as the internal standard (s, singlet; d, doublet; br, broad;  $W_{\frac{1}{2}}$ , half band width).

#### 3 $\beta$ -Chloro-5, 7 $\beta$ -dibromo-5 $\alpha$ -cholestan-6-one (II)

To a solution of 3 $\beta$ -chloro-5 $\alpha$ -cholestan-6-one (I) (4.0 g, m.p.  $128^\circ$ ) in ether (30 ml) at room temperature was added a solution of bromine in acetic acid (40 ml, 5%) which was completed over a period of half an hour. The reaction mixture (catalysed by a few drops of hydrobromic acid) was allowed to stand at room temperature for 3 days. The solid material thus obtained was filtered and air-dried. Rectification from pet. ether afforded the bromoketone (II), m.p.  $174-75^\circ$  (Found C, 55.95; H, 7.45.  $\text{C}_{27}\text{H}_{43}\text{OClBr}_2$  required C, 56.05; H, 7.44%) (positive Beilstein test);  $\nu_{\text{max}}$  (Nujol) 1725 ( $>\text{C}=\text{O}$ ), 758 ( $\text{C}-\text{Cl}$ ), 736 and  $655\text{ cm}^{-1}$  ( $\text{C}-\text{Br}$ ); n.m.r. ( $\text{CDCl}_3$ );  $\delta$  5.35 (d,  $\text{C}_7$ - $\alpha\text{H}$ ,  $J = 9$  Hz, axial), 4.39 (br,  $\text{C}_3$ - $\alpha\text{H}$ ,  $W_{\frac{1}{2}} = 22$  Hz, axial) 1.1 (s,  $\text{C}_{10}$ - $\text{CH}_3$ ), 0.72 (s,  $\text{C}_{13}$ - $\text{CH}_3$ ), 0.95 and 0.84 (other methyl protons).

#### 3 $\beta$ -Chloro-5-acetoxy, 7 $\beta$ -bromo-5 $\beta$ -cholestan-6-one (III)

A mixture of bromoketone (II) (1.0 g), sodium acetate trihydrate (4.0 g) in ethanol (75 ml) was heated under reflux for 4 hrs. The solvent was removed by distillation under reduced pressure and residue poured into ice-cold water and extracted with ether. The ethereal solution was washed with water and dried over anhydrous sodium sulphate. Evaporation of ether provided an oil which was chromatographed over silica gel (20.0 g). Elution with pet. ether-ether (6:1) furnished a solid which was recrystallized from pet. ether (590 mg), m.p.  $155^\circ$  (Found C, 62.38; H, 8.19.  $\text{C}_{29}\text{H}_{46}\text{ClBrO}_3$  requires C, 62.47; H, 8.25%).

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#### ALLYLIC OXIDATION OF (+)-CAR-3-ENE

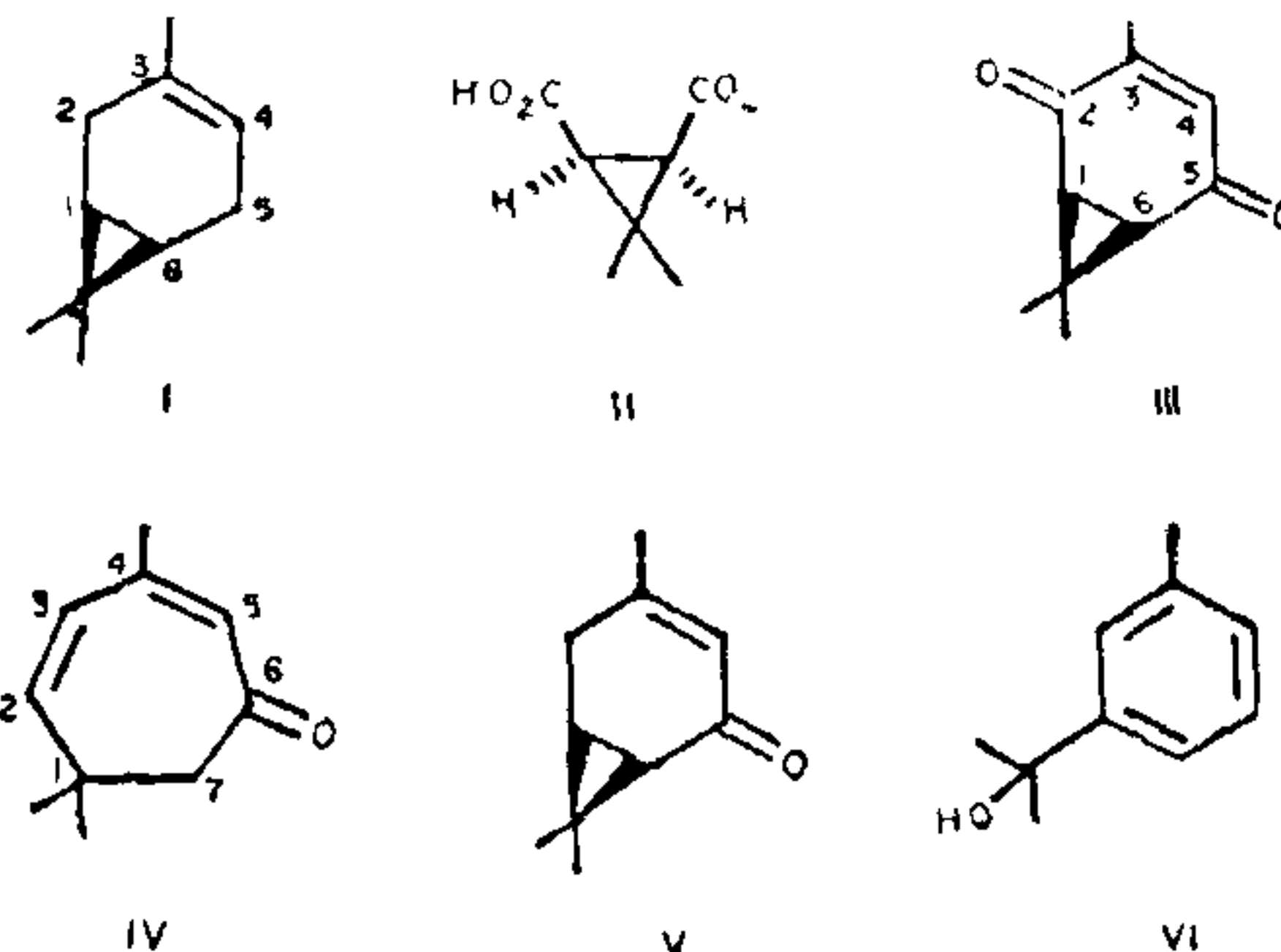
THE oxidation of (+)-car-3-ene (I) by oxidising agents like potassium permanganate<sup>1</sup> in acetone, chromic acid<sup>2</sup> in acetone and pyridine, has been reported to give a complex mixture of compounds consisting of acids and neutral compounds. In these methods the neutral oxidation products were obtained in about 10–15% yield and have been separated into their constituents by employing column chromatography, fractionation and preparative GLC techniques.

In our attempts to convert (I) into *cis* caronic acid (II), we were interested in a suitable method of converting (I) into the intermediate diketone (III), so that the latter could be oxidised to (II) by the known procedure<sup>3</sup>. The formation of (III) has been reported only in the oxidation of (I) by potassium permanganate<sup>1</sup>.

With a view to obtaining the diketone (III), (I) was subjected to allylic oxidation using sodium dichromate-acetic acid<sup>4</sup> (48 hrs, at room temperature, 1.5 moles of Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) to give the oxidation product, which was chromatographed on alumina (Gr. II, 1:20) and eluted with pet. ether, pet. ether + benzene (1:1), benzene, chloroform and acetone. The fraction eluted with pet. ether (70% of the total oxidation product) chiefly consists of unchanged (I) along with rearranged hydrocarbons, according to IR spectrum and comparative GLC.

The fraction eluted with pet. ether-benzene (TLC, 5-spots) being in small quantity was not investigated. Some of the fractions eluted with benzene gave a liquid ketone (TLC, 1 spot, 95% pure by GLC) which was further purified by distillation [b.p. 140–145° (bath)/4 mm] and identified as 1, 1, 4-trimethyl, 2, 4-diene-6-one (IV) as per elemental analysis and spec-

tral data; C<sub>10</sub>H<sub>14</sub>O, M<sup>+</sup> 150, IR bands: 1650 (>C=O of completely conjugated dienone); 1610 (conj -HC=CH- and >C=CH), 1,380, 1,365 cm<sup>-1</sup> (gem dimethyl); NMR (CCl<sub>4</sub>) signals at τ: 8.92 (6H, s, gem dimethyl at C<sub>1</sub>); 8.0 (3H, s, C<sub>4</sub>-vinyl CH<sub>3</sub>); 7.5 (2H, s, C<sub>7</sub>-CH<sub>2</sub> adjacent to >C=O); 3.95 (1H, d, J = 13.2 Hz, C<sub>2</sub>-olefinic proton); 4.32 (1H, d, J = 13.2 Hz, C<sub>3</sub>-olefinic proton) and 4.10 (1H, s, olefinic proton at C<sub>6</sub>); UV λ<sub>max</sub> 298 mμ, ε<sub>max</sub> 5500;



2:4 DNP C<sub>16</sub>H<sub>18</sub>O<sub>4</sub>N<sub>4</sub>, m.p. 173–175° (Lit.<sup>2</sup> records for 2:4 DNP of IV, m.p. 175–176°). As reported<sup>2</sup> earlier, ketone (IV) might have been formed by acid rearrangement of the ketone (V), also expected to be formed from (I) in the reaction. The tail fractions eluted with benzene (TLC, single spot) on crystallisation from ethanol gave a solid, C<sub>10</sub>H<sub>12</sub>O<sub>2</sub> m.p. 95–96°, identified as car-3-ene 2, 5-dione (III) by physical constants and spectral data. IR bands at 1650 (conj. >C=O), 1613, 858 cm<sup>-1</sup> (conj. -CH=C-); NMR (CCl<sub>4</sub>) signals at τ: 8.63, 8.67 (6H, s, gem dimethyl on cyclopropane); 8.07 (3H, s, C<sub>3</sub>-vinyl CH<sub>3</sub>); 7.8 (2H, s, cyclopropyl protons at C<sub>1</sub> and C<sub>6</sub>) and at 3.6 (1H, br s, olefinic proton at C<sub>4</sub>); UV λ<sub>max</sub> 227 mμ, ε<sub>max</sub> 8800; 241 mμ, ε<sub>max</sub> 10420; dioxime C<sub>10</sub>H<sub>14</sub>O<sub>2</sub>N<sub>2</sub>, m.p. 182–3° (Lit.<sup>3</sup> records for dioxime of III, m.p. 185°).

The fractions eluted with chloroform were purified by chromatography over alumina and the tail fractions distilled to give a liquid alcohol C<sub>10</sub>H<sub>14</sub>O, M<sup>+</sup> 150 identified as *m*-cymenol (VI) by spectral data: IR bands 3400 (OH), 4 bands at 1961, 1887, 1792, 1754 (all weak bands) (meta disubstituted benzene<sup>5</sup>), 1605, 1587 cm<sup>-1</sup> (aromatic); NMR (CCl<sub>4</sub>) signals at τ: 8.5 (6H, s, methyls of hydroxy isopropyl); 7.65 (3H, s, CH<sub>3</sub>-aromatic); 7.27 (s, 1H, exchangeable with D<sub>2</sub>O, OH-proton); 3.04 and 2.67 (4H, m, aromatic protons).

The major oxidation product was found to be *m*-cymenol (VI) while ketones (III) and (IV) were obtained in about 2.5% yield each.