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REARRANGEMENTS OF BICYCLIC-δ-HYDROXY-α,β-ENONES—IV[1]

BASE CATALYSED REARRANGEMENTS OF SOME BICYCLIC-α-SUBSTITUTED-δ-HYDROXY-α,β-ENONES

S. SWAMINATHAN, K. G. SRINIVASAN and P. S. VENKATARAMANI
Department of Organic Chemistry, University of Madras, Madras-25, India

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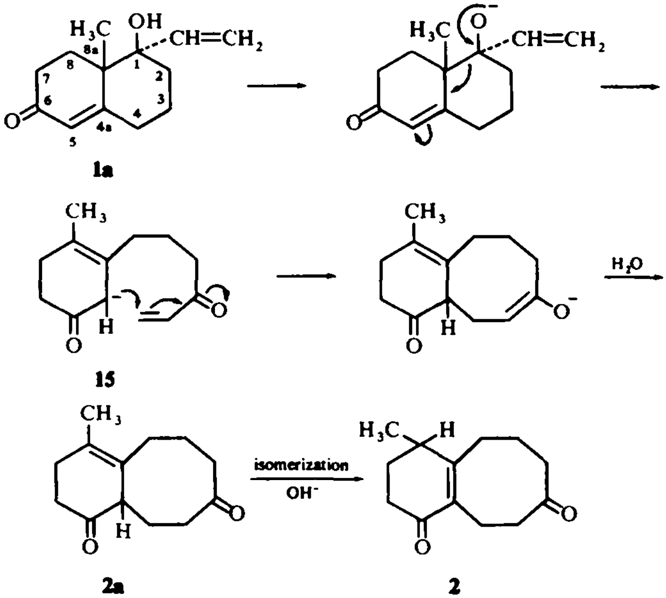
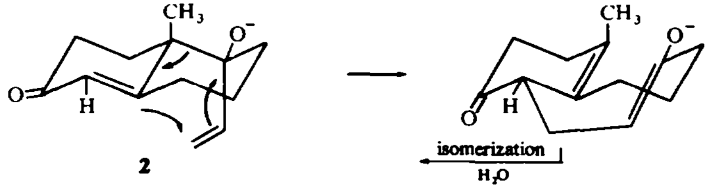
Abstract—The hydroxy enones **5a, 5b, 5c, 4d, 4a** and **4b** rearrange when treated with aqueous alkali to the diones **6a, 6b, 8** and **13** and acids **9** and **12** respectively. The diones **2** and **6a** are also formed by thermal rearrangement of enones **1a** and **5a**.

THE base catalysed rearrangement of the hydroxy enone **1a** to the dione **2** has recently been confirmed.[1]

The mechanism[2] for this rearrangement is as follows:

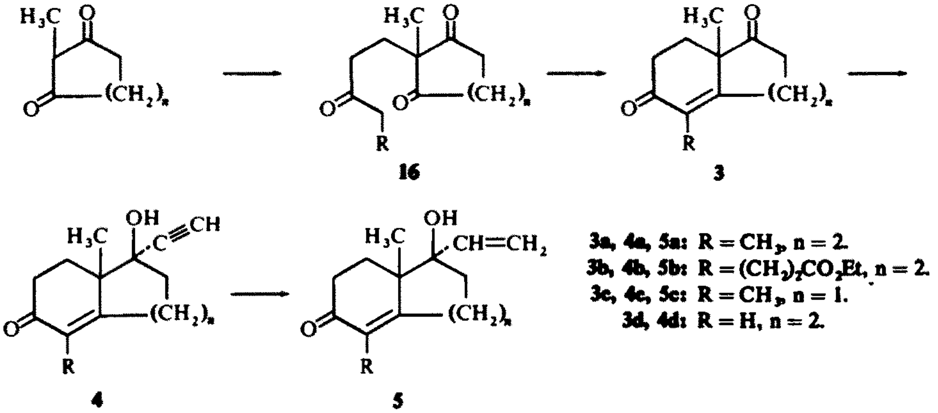


A concerted mechanism may also be envisaged as follows:



On present evidence it is not clear which mechanism is operative.* The olefinic C_5 is a key atom involved in the formation of a new C—C bond as well as in the equilibration of the primary rearrangement product **2a** to the final α,β-conjugated product **2**; the present work was undertaken to determine if the C_5 substituted derivatives of **1a** (and analogues) would undergo the rearrangement.

The compounds selected for study were the hydroxy enones **5a**, **5b**, **4a**, **4b**, **5c** and **4c**. The octalin derivatives **5a** and **4a** reported[4] as well as other compounds specified above were obtained by syntheses patterned on the highly successful route to the hydroxy enone **1a**.



3a, 4a, 5a: $R = CH_3$, $n = 2$.
3b, 4b, 5b: $R = (CH_2)_2CO_2Et$, $n = 2$.
3c, 4c, 5c: $R = CH_3$, $n = 1$.
3d, 4d: $R = H$, $n = 2$.

Ethynylations of the known dione **3b**,[5] furnished in 49% yield the ethynyl carbinol **4b**, selectively reduced to the vinyl carbinol **5b**. The carbinols **5a** and **4a** were obtained as reported.[4] Base catalysed additions of 2-methylcyclopentane-1,3-dione to ethylvinylketone furnished the expected Michael adduct which was dehydrated with *p*-toluenesulphonic acid to furnish the liquid dione **3c** in 66% yield. This was converted into the crystalline carbinols **4c** and **5c**. The acetylenic and vinyl carbinols have the expected spectral absorptions. The *cis* orientation of the —OH group in these compounds with respect to the angular Me group is assumed by analogy to the course of ethynylation of the dione **3d**. In these ethynylation reactions, there was no evidence of formation of the *trans*-hydroxy epimers.

When treated with methanolic potassium hydroxide the crystalline carbinol **5a** gave an isomeric liquid in 60% yield. The IR spectrum of the product showed strong CO absorption at 5·85 μ, but no absorption for —OH. The NMR spectrum confirmed the absence of —OH proton and also showed that vinyl protons were absent. There were

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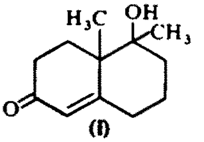
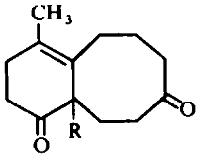
* Photochemical and base catalysed rearrangements of the related hydroxyenone (I) have been reported by Gravel and Gauthier.[3] They have isolated several intermediates that may be expected on the basis of the stepwise mechanism.



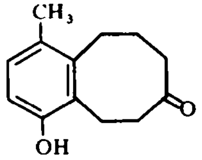
(I)

In the case of octalenone (I), however, the concerted mechanism cannot operate and the isolation of the said intermediates cannot be interpreted in favour of either mechanism in the *present* case.

singlet Me absorptions at τ 8·93 and 8·3 which may be assigned to a tertiary Me and a Me attached to a vinyl carbon respectively. Based on the rearrangement of **1a** to the dione **2**, the structure (**6a**) for the product is consistent with the NMR and IR absorptions. The observed UV absorption at 226 mμ (ε, 3149) is also in accord with absorptions reported for some related β,γ-unsaturated carbonyl compounds.* The structure was confirmed by dehydrogenation under relatively drastic condition to the known phenol **7**.



6a: R = CH_3
6b: R = $(CH_2)_2 \cdot CO_2H$



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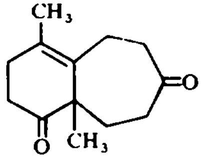
Likewise, the hydroxy enone **5b** when treated with alkali gave a crystalline acid with properties in complete accord with structure **6b**. The observed UV absorption was again at 224 mμ (ε, 4245) as for **6a**. The crystalline indane derivative **5c** also underwent the expected rearrangement to furnish a liquid product having light absorption properties consistent with structure **8**.



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Unlike the dione **6a**, the rearranged products **6b** and **8** resisted dehydrogenation even under drastic conditions.

The reaction of the acetylenic precursors **4a**, **4b** and **4c** with base was next studied. The carbinol **4a** when treated with alkali furnished a crystalline acid $C_{14}H_{20}O_3$ and very little neutral product. The IR spectrum indicated the absence of C≡CH group and the presence of two unconjugated CO groups. The NMR spectrum indicated the presence of two vinyl Me groups, one vinyl proton and one acidic proton. These data can be accommodated by structures **9** or **10**.

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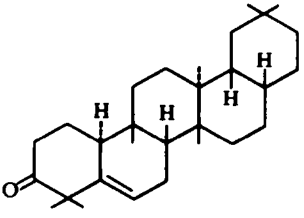
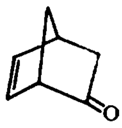
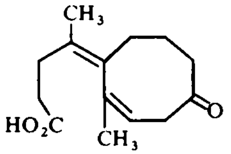
* Δ³-cyclohexenone absorbs at 217 mμ (ε, 2500) whereas the ketones (I) and (II) have λ_{max} 216 mμ (ε, 5600) and λ_{max} 210 mμ (ε, 3000) respectively.[6]



(I)



(II)



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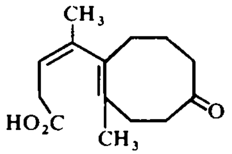

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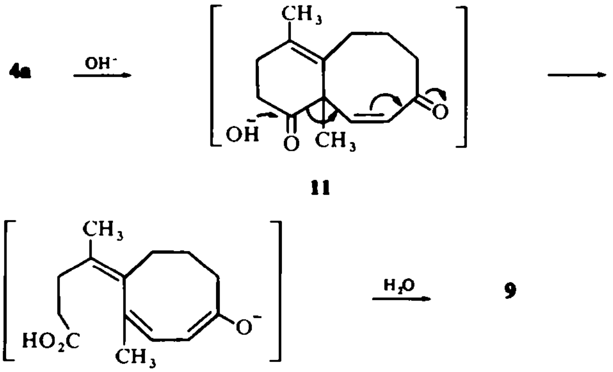
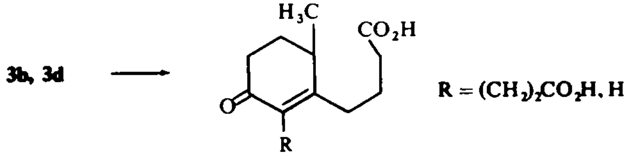
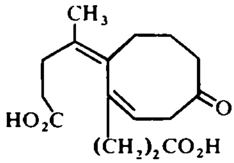
The observed UV absorption at 220 mμ (ε, 4688) seems anomalous and is at variance with values that may be predicted from Woodward's rules for either of the two structures. It is not certain, however, whether these rules are valid for systems where the diene chromophore is part of medium sized rings* as in structures **9** and **10**. Attempts to effect a Diels–Alder addition with maleic anhydride under mild conditions were unsuccessful, indicating that structure **9** is perhaps to be preferred. The formation of acid **9** may be visualised as follows:



The primary product of rearrangement **11**, is a vinylogous β-diketone of the type **3d** and **3b** which are known to undergo ready cleavage as indicated with alkali.[8]



The reaction of the carbinol **4b** with base furnished a dibasic acid $C_{16}H_{22}O_5$ which may be similarly formulated as **12** on the basis of its spectral absorptions. The



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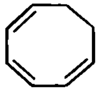
* For example,[7] the diene (i) and the triene (ii) are reported to have λ_{max} 230 mμ (ε, 4169) and λ_{max} 265 mμ (ε, 3350)—values different from those that may be expected from application of Woodward's rules.

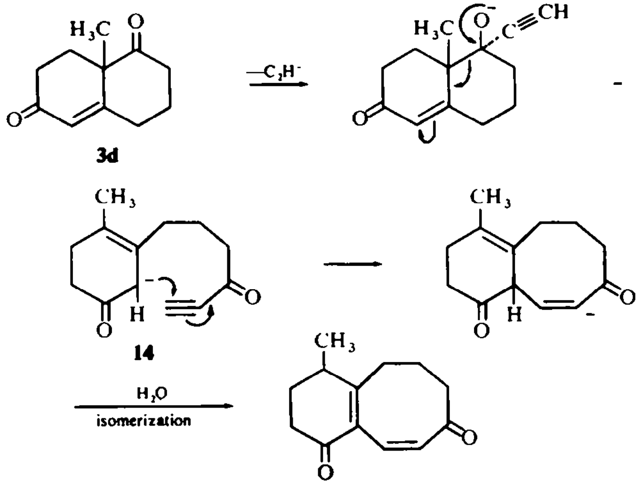
(i)



(ii)

carbinol **4c** gave a crude acidic liquid which resisted attempts at purification and characterization.

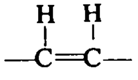
It has been reported earlier[9-11] that the conditions of formation of the acetylenic carbinol **4d** are quite critical. Prolonged treatment of 8a-methyl-Δ^{4a}-octalin-1,6-dione (**3d**) with sodium acetylide has been reported to furnish instead of the crystalline carbinol **4d**, an isomeric liquid product. It seemed possible that this liquid might have structure **13** based on the rearrangement of the enone **1a** to the dione **2**.



3d

14

13

A liquid product could indeed be obtained as reported. TLC analysis showed it to be a mixture of at least 4 components one of which could be obtained as a pure liquid in ca. 25% yield after chromatographic purification. It was isomeric with the carbinol **4d** and showed conjugated CO absorption at 6·0 μ and no —OH or —C≡CH absorption. It furnished a mono 2,4-DNP derivative whose IR absorptions confirmed the presence of *two α,β enone* units in the molecule. The UV maximum of the 2,4-DNP derivative was as expected though it cannot be inferred from this absorption alone whether a conjugated dienone or an enone moiety is present in the parent ketone. The UV absorption ($\lambda_{\max}^{\mathrm{EtOH}}$ 221, 255–65 mμ, ε, 3599 and 2034 respectively) may be considered anomalous but data for similar cyclooctadienones are not available in the literature* for a proper comparison to be made. The NMR absorption, however, confirmed the presence of $>$CH—CH$_3$ and  $-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-$ groups and there is no doubt that one of the products of the prolonged reaction of the dione **3d** with lithium acetylide is indeed the ring enlarged dione **13**—a fact also confirmed by its controlled reduction to the dione **2** in good yield. That the conversion of **3d** to **13** really involves the ethynylation reaction was also verified by treatment of the alcohol **4d** with lithium acetylide under the same conditions, when the dione **13** could again be isolated in ca. 27% yield. As stated earlier, the dione **13** is only one of several products formed in the above reaction. It is not surprising that the rearrangement of the acetylenic carbinol **4d** is more complicated than the corresponding vinyl carbinol **1a**, since the acetylenic ketone intermediate involved (species 14 protonated) may be expected *per se* to be

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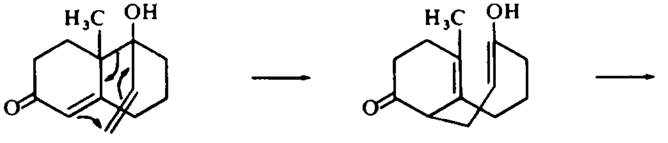
* See footnote on page 000.

more reactive than the vinyl ketone intermediate (species 15 protonated). In fact, the treatment of the carbinol **4d** with aqueous methanolic alkali at room temperature furnished a crude mixture—partly polymeric—of at least five components one of which was the dione **13** as indicated by TLC.

The dione **2** has also been obtained previously from the enone **1a** and its C_1 epimer by rearrangement with acids.[2] This rearrangement, it is now found, can be brought about by simply refluxing **1a** in a high boiling solvent like ethylene glycol or diethylene glycol in the absence of any catalyst. This thermal rearrangement gave exclusively the dione **2** as revealed by TLC, in the case of the homologous compound **5a**, a mixture of products was formed of which one was identified as the enedione **6a**. It is not, perhaps, surprising that these bicyclic enones should undergo such thermal rearrangements since a diallyl moiety is present in their structure and may be expected to facilitate a Cope rearrangement as indicated. The inference is obvious that rearrangements (or ring enlargements) of the type **1a** to **2** may, perhaps, be effected with similar systems under thermal conditions whether or not functional groups are present at C_1 and C_6; the presence of such groups would appear to be necessary for acid or base catalysed rearrangements. Further work is planned to verify this and other obvious inferences based on an ionic mechanism or Cope type mechanism.



2

EXPERIMENTAL

1,6-*Dioxo*-5,8a-*dimethyl*-1,2,3,4,6,7,8,8a-*octahydronaphthalene* (**3a**). This was prepared as described,[12] except that for the cyclization of **16** ($R = CH_3$), pyrrolidine in refluxing benzene was used instead of piperidine phosphate. m.p. 46–47°. $\lambda_{max}^{CHCl_3}$ 5·88, 6·05 and 6·25 μ; λ_{max}^{EtOH} 245 mμ (ε, 13,680) lit[12] 252·5 mμ (ε, 12,390); NMR ($CDCl_3$) (τ_{ppm}): 8·6 (3H, $-\overset{|}{\underset{|}{\mathrm{C}}}-\mathrm{C}\underline{\mathrm{H}}_3$) 8·2 (3H, $=\overset{|}{\mathrm{C}}-\mathrm{CH}_3$), 7·1–8·1 (10H, methylenes).

1α-*Ethynyl*-1β-*hydroxy*-6-*oxo*-5,8a-*dimethyl*-1,2,3,4,6,7,8,8a-*octahydronphthalene* (**4a**). This was also prepared as reported,[4] m.p. 142–143·4° (EtOAc–light petroleum); λ_{max}^{KBr} 3·09, 4·76, 6·06 and 6·25 μ; NMR ($CDCl_3$) (τ_{ppm}): 8·72 (3H, $-\overset{|}{\underset{|}{\mathrm{C}}}-\mathrm{C}\underline{\mathrm{H}}_3$) 8·2 (3H, $=\overset{|}{\mathrm{C}}-\mathrm{C}\underline{\mathrm{H}}_3$), 7·5–8·2 (11H, methylenes and —$\mathrm{C}\equiv\mathrm{C}\underline{\mathrm{H}}$), 7·3 (1H, —OH).

1α-*Vinyl*-1β-*hydroxy*-6-*oxo*-5,8a-*dimethyl*-1,2,3,4,6,7,8,8a-*octahydronaphthalene* (**5a**)[4]. Hydrogenation of **4a**, in presence of Pd/$CaCO_3$ furnished **5a**, m.p. 99–100° (ether–light petroleum); λ_{max}^{KBr} 6·06 and 6·25 μ; NMR ($CDCl_3$) (τ_{ppm}): 8·65 (3H, $-\overset{|}{\underset{|}{\mathrm{C}}}-\mathrm{C}\underline{\mathrm{H}}_3$) 8·18 (3H, $=\overset{|}{\mathrm{C}}-\mathrm{C}\underline{\mathrm{H}}_3$), 7·3–8·1 (11H, methylenes and —OH), 3·62–4·97 (3H, $\underline{\mathrm{H}}\mathrm{C}=\mathrm{C}\underline{\mathrm{H}}_2$).

1α-*Ethynyl*-1β-*hydroxy*-5-(2′-*carbethoxy ethyl*)-6-*oxo*-8a-*methyl*-1,2,3,4,6,7,8,8a-*octahydronaphthalene* (**4b**). The carbinol **4b** was prepared by reacting **3b**[5] (14 g) with lithium acetylide (prepared from Li, 0·7 g) in liquid ammonia at −78° and working up the reaction mixture after 20 min., yield: 7·5 g, m.p. 72–74° (ether–light petroleum). (Found: C, 71·4, H, 8·3; $C_{18}H_{24}O_4$ requires: C, 71·0, H, 8·0%); $\lambda_{max}^{CHCl_3}$ 2·80, 3·04, 5·8, 6·025 and 6·25 μ; λ_{max}^{EtOH} 247 mμ (ε, 15,560); NMR ($CDCl_3$) (τ_{ppm}): 8·72 (3H, $-\overset{|}{\underset{|}{\mathrm{C}}}-\mathrm{C}\underline{\mathrm{H}}_3$), 8·67–8·9 (3H, $-OCH_2C\underline{H}_3$), 6·75–8·07 (16H, methylenes, $-C{\equiv}CH$, and $-OH$), 5·7–6·04 (2H, $-OC\underline{H}_2CH_3$).

1α-Vinyl-1β-hydroxy-5-(2.1-carbethoxyethyl)-6-oxo-8a-methyl-1,2,3,4,6,7,8,8a-actahydronaphthalene (**5b**). The carbinol **4b** (1·52 g) was hydrogenated to **5b** (1·45 g) monohydrate. m.p. 67·5–69° from moist ether-light petroleum. (Found: C, 67·0, H, 8·9; $C_{18}H_{26}O_4 \cdot H_2O$ requires: C, 66·6, H, 8·7%); $\lambda_{max}^{CHCl_3}$ 2·80, 5·825, 6·025 and 6·26 μ; λ_{max}^{EtOH} 250 mμ (ε, 14,570); NMR ($CDCl_3$) (τ_{ppm}): 8·62–8·84 (3H, $-OCH_2C\underline{H}_3$), 8·62 (3H, $-\overset{|}{\underset{|}{C}}-CH_3$), 7·08–8·3 (14H, methylenes), 5·7–6·03 (2H, $-OC\underline{H}_2CH_3$), 3·6–4·9 (3H, $\overset{|}{\underline{H}C}{=}C\underline{H}_2$).

The vinyl carbinol loses water of crystallization and turns to a liquid when dried *in vacuo* or over a desiccator. b.p. 180–181°/0·55 mm.

1,5-Dioxo-4,7a-dimethyl-2,3,5,6,7,7a-hexahydroindene (**3c**). A mixture of 2-methylcyclopentant-1,3-dione (12 g), MeOH (50 ml) and ethyl vinyl ketone (16 g) was refluxed for 5 hr. The trione obtained was distilled, b.p. 106°/0·6 mm. This trione (10 g) in dry benzene (50 ml) was refluxed with *p*-toluenesulphonic acid (250 mg) for 2 hr and yielded the dione **3c** (6 g), b.p. 104°/0·4 mm; $\lambda_{max}^{CHCl_3}$ 5·75, 6·02 and 6·075 μ; λ_{max}^{EtOH} 250 mμ (ε, 12330); NMR ($CDCl_3$) (τ_{ppm}): 8·68 (3H, $-\overset{|}{\underset{|}{C}}-C\underline{H}_3$), 8·2 (3H, $=\overset{|}{C}-C\underline{H}_3$) 7·1–8·17 (8H, methylenes). The dione was characterized as its dioxime, m.p. 236° from EtOH. (Found: C, 63·4, H, 7·6. $C_{11}H_{16}N_2O_2$ requires: C, 63·5, H, 7·6%).

1α-Ethnyl-1β-hydroxy-5-oxo-4,7a-dimethyl-2,3,5,6,7,7a-hexahydroindene (**4c**). The carbinol **4c** was prepared by reacting **3c** (7 g) with lithium acetylide (prepared from 3 g Li) in liquid ammonia at −33°, yield: 4 g, m.p. 136–137° from ether–light petroleum. (Found: C, 75·9, H, 8·0. $C_{13}H_{16}O_2$ requires: C, 76·4, H, 7·8%); $\lambda_{max}^{CHCl_3}$ 2·77, 3·02, 6·02 and 6·1 μ; λ_{max}^{EtOH} 250 mμ (ε, 14,720); NMR ($CDCl_3$) (τ_{ppm}): 8·77 (3H, $-\overset{|}{\underset{|}{C}}-C\underline{H}_3$), 8·33 (3H, $=\overset{|}{C}-C\underline{H}_3$), 7·2–8·25 (9H, methylenes and $-C{\equiv}CH$), 7·08 (1H, $-OH$).

1α-Vinyl-1β-hydroxy-5-oxo-4,7a-dimethyl-2,3,5,6,7,7a-hexahydroindene (**5c**). The carbinol **4c** (1·5 g) was catalytically hydrogenated to **5c** (0·8 g), m.p. 101–101·5° from ether–light petroleum. (Found: C, 75·2; H, 9·2. $C_{13}H_{18}O_2$ requires: C, 75·7; H, 8·7%); λ_{max}^{KBr} 2·9 and 6·1 μ; λ_{max}^{EtOH} 252 mμ (ε, 15,040); NMR ($CDCl_3$) (τ_{ppm}): 8·7 (3H, $-\overset{|}{\underset{|}{C}}-CH_3$), 8·33 (3H, $=\overset{|}{C}-CH_3$), 7·37–8·18 (9H, methylenes and $-OH$), 3·94–5·0 (3H, $-CH{=}CH_2$).

Rearrangements of enones (**5a**), (**5b**) *and* (**5c**). A mixture of **5a** (1 g), MeOH (10 ml) and KOH aq (5·6%, 15 ml) was refluxed on a water bath for 1 hr. MeOH was completely removed and the residue was taken up in ether, washed with water, dried and solvent removed. The resulting yellow liquid, was adsorbed on a column of alumina and eluted with 10% ether–light petroleum to yield **6a** (0·6 g) found homogeneous by TLC; λ_{max}^{CH2Cl2} 5·85 μ, λ_{max}^{EtOH} 226 mμ (ε, 3,149); NMR (CCl_4) (τ_{ppm}); 8·9 (3H, $-\overset{|}{\underset{|}{C}}-C\underline{H}_3$), 8·3 (3H, $=C-C\underline{H}_3$), 7·3–8·2 (14H, methylenes). This liquid gave a dioxime. m.p. 168·6–169·2° from EtOAc. (Found: C, 67·4; H, 9·2; N, 10·9. $C_{14}H_{22}N_2O_2$ requires: C, 67·2; H, 8·9; N, 11·2%).

Similar treatment of **5b** (1·1 g) with 4% KOH aq (10 ml) furnished little neutral product. The aqueous layer was acidified with conc HCl and then extracted with ether to obtain **6b** as a colourless crystalline solid, yield: 0·3 g, m.p. 116·8–117·8° ether–light petroleum. (Found: C, 69·2, H, 8·2. $C_{16}H_{22}O_4$ requires: C, 69·0, H, 8·0%); $\lambda_{max}^{CHCl_3}$ 5·85, 5·9 (sh) μ; λ_{max}^{EtOH} 224 mμ (ε, 4,245); NMR ($CDCl_3$) (τ_{ppm}): 8·28 (3H, $=\overset{|}{C}-C\underline{H}_3$), 7·4–8·14 (18H, methylenes), minus 0·5 (1H, $-COOH$).

Similarly, **5c** (1·5 g) in MeOH (15 ml) reacted with 5% KOH aq (25 ml) and furnished a neutral liquid which on chromatographic purification gave **8** (0·6 g); $\lambda_{max}^{CHCl_3}$ 5·88 μ; λ_{max}^{EtOH} 220 mμ (ε, 1,990); NMR ($CDCl_3$) (τ_{ppm}): 8·75 (3H, $-\overset{|}{\underset{|}{C}}-CH_3$), 8·24 (3H, $=\overset{|}{C}-C\underline{H}_3$), 7·25–8·17 (12H, methylenes). The liquid was characterized as its dioxime m.p. 171·5–172° from EtOAc. (Found: C, 66·1, H, 8·8, N, 11·6. $C_{13}H_{20}N_2O_2$ requires: C, 66·1, H, 8·5, N, 11·9%).

Aromatization of the dione (**6a**). The dione **6a** (1 g) was heated with Pd/C (5%, 0·1 g) at 290° for 30 min, the mixture cooled and diluted with ether. The ether soln furnished a crude phenolic liquid (0·3 g) when extracted with NaOH aq. This liquid was adsorbed on a column of silica gel and eluted with 5% ether–light petroleum to obtain a solid (60 mg) m.p. 148–149°, identified as **7** by mixed m.p., TLC, and IR absorptions.

Rearrangements of carbinols (**4a**) *and* (**4b**). A soln of **4a** (1 g) in MeOH was mixed with a soln of 4% KOH aq (10 ml) and left overnight. The mixture was refluxed for 2 hr and worked up as for **6b** to furnish **9** (0·45 g), m.p. 74–75° from (EtOAc–light petroleum). (Found: C, 70·8, H, 8·5. $C_{14}H_{20}O_3$ requires: C, 71·2, H, 8·5%); λ_{max}^{KBr} 5·85 and 5·92 μ; λ_{max}^{EtOH} 220 mμ (ε, 4,688): NMR ($CDCl_3$) (τ_{ppm}): 8·54 (3H, $^{-}\ ^{-}C-C\underline{H}_3$), 8·23 (3H, $=\overset{|}{C}-C\underline{H}_3$), 7·0–8·17 (12H, methylenes), 4·4–4·7 (1$\underline{H}$, $=\overset{|}{C}H$), 1·5–0·0 (1H, —COOH) N.E. Found 234. Calc. 236.

The carbinol **4b** (1·1 g) was treated with 4% KOH aq (10 ml) similarly to furnish the diacid **12** as a colourless solid (0·64 g), m.p. 142–143° from EtOAc. (Found: C, 65·3, H, 7·8. $C_{16}H_{22}O_5$ requires: C, 65·3, H, 7·5%); $\lambda_{max}^{CHCl_3}$ 5·88 μ. λ_{max}^{EtOH} sh. at 215 mμ (unaffected by H^+) (ε, 5.653); NMR (DMSO) (τ_{ppm}): 8·45 (3H, $=\overset{|}{C}-C\underline{H}_3$), 7·77–8·25 (16H, methylenes), 4·4–4·7 (1H, $=\overset{|}{C}H$), 1·7 (2H, 2—COOH): N.E. Found: 147. Calc. 147.

Attempted dehydrogenation and decarboxylation of **12** did not give any useful material.

Prolonged reaction between lithium acetylide and dione (**3d**)*. To a suspension of lithium acetylide in liquid NH_3 (prepared from 1 g Li) cooled by dry ice–EtOH mixture, the dione **3d** (12 g) in ether (30 ml) was added. After stirring for 30 min at dry ice temp, it was allowed to stand overnight. The residue was decomposed with sat NH_4Cl aq and extracted with ether, extract washed with water, dried and solvent removed to get a dark viscous liquid (10 g). A portion of this liquid (3 g) was adsorbed on a column of alumina and eluted with 10% ether–light petroluem to get the dienedione (**13**) (1 g) as a liquid. The same dione (**13**) could be obtained as one of the products when sodium acetylide was used. (Found: C, 76·5, H, 8·2. $C_{13}H_{16}O_2$ requires: C, 76·4, H, 7·9%); $\lambda_{max}^{thin\ film}$ 6·06 and 6·25 μ, λ_{max}^{EtOH} 221 mμ (ε, 3599), 255–265 mμ (ε, 2034); NMR (CCl_4) (τ_{ppm}) 8·7 (3H, $-\overset{|}{C}H-C\underline{H}_3$), 7–8·25 (11H, methine and methylene protons), 3·1–4·1 (2H, $-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-$). The dione **13** gave a mono 2,4-DNP m.p. 198·5–199·2° from EtOAc–light petroleum. (Found: C, 59·3, H, 6·1, N, 14·5. $C_{19}H_{20}N_4O_5$ requires: C, 59·1, H, 5·8, N, 14·5%); $\lambda_{max}^{CHCl_3}$ 6·0, 6·18 and 6·27 μ; λ_{max}^{EtOH} 382 mμ (ε, 21,380); NMR ($CDCl_3$) (τ_{ppm}): 8·68 (3H, (CH—C$\underline{H}_3$), 7·17–8·17 (11H, methine and methylene protons), 3·17–3·7 (2H, $-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-$), 1·5–2·0 and 0·85 (3H, ar. protons) minus 1·4 (1H, $-\overset{|}{N}H$).

The carbinol **4d** when treated with Li or sodium acetylide under the same conditions also furnished **13** in ca. 27% yield.

Hydrogenation of the dione **13** *to* **2**. A soln of **13** (1·13 g) in EtOH (70 ml) was hydrogenated in the presence of Pd/$BaCO_3$ (10%, 0·1 g) until one mole equiv H_2 was absorbed. Usual work up furnished **2** (0·5 g), m.p. and mixed m.p. 58–59°.

Thermal rearrangement of vinyl carbinol (**1a**). The carbinol **1a** (2 g) was heated under reflux in diethylene glycol (5 ml) for 6 hr. The mixture was diluted with water and extracted with ether. The organic layer was washed once with water, dried and concentrated to furnish a liquid (2 g) which was chromatographed over alumina. Elution with ether–light petroleum (1 : 1) gave 1·2 g of a liquid found identical with **2** (IR, TLC and m.p. of the dioxime).

When the reaction was carried out in ethylene glycol soln and followed by TLC the dione **2** appeared after 1 hr but the reaction was still incomplete after 15 hr.

Thermal rearrangement of vinyl carbinol (**5a**). The carbinol **5a** (1 g) was refluxed for 3 hr in ethylene

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* Preliminary studies of this reaction were first carried out by Dr. S. K. Sankarappa.

glycol (15 ml) and then concentrated *in vacuo*. The residue was diluted with water and extracted with ether. The ether extract furnished a liquid (0·7 g). TLC analysis indicated it to be a mixture, with **6a** as one of the components. The liquid was adsorbed on a column of silica gel and eluted with 5% ether–light petroleum to get **6a** (50 mg) identical (TLC and IR) with that obtained by the base catalysed isomerization of **5a**.

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REFERENCES

[1] Part III. J. P. John, K. G. Srinivasan, P. S. Venkataramani and S. Swaminathan, *Tetrahedron* **25** (13), 2661 (1969).
[2] S. Swaminathan, R. K. Natarajan, S. Ramachandran, and S. K. Sankarappa, *J.Org.Chem.* **31**, 656 (1966).
[3] D. Gravel and J. Gauthier, *Tetrahedron Letters* 2320 (1968)
[4] V. F. Kucherov, I. A. Gurvich, and T. V. Ilukhina, *J.Gen.Chem., USSR* 748 (1961).
[5] P. Wieland, H. Ueberwasser, G. Anner, and K. Mischer, *Helv.Chim.Acta* **36**, 376 (1953).
[6] H. Labharat and G. Waginere, *Ibid.* **42**, 2219 (1959).
[7] A. C. Cope, C. L. Stevens, and F. A. Hochstein, *J.Am.Chem.Soc.* **72**, 2510 (1950).
[8] N. L. Wendler, H. L. Slates, and M. Tischler, *Ibid.*, **73**, 3816 (1951).
[9] I. N. Nazarov and I. A. Gurvich, *J.Gen.Chem., USSR* 956 (1955).
[10] S. Swaminathan and M. S. Newman, *Tetrahedron* **2**, 88 (1958).
[11] C. A. Friedman and R. Robinson, *Chem. & Ind.* 777, 1117 (1951).
[12] V. F. Kucherov and I. A. Gurvich, *J.Gen.Chem., USSR* 731 (1961).