148. The Synthesis of Damascenone and β-Damascone and The Possible Mechanism of Their Formation from Carotenoids[1])

by **Sachihiko Isoe, Shigeo Katsumura** and **Takeo Sakan**

Department of Chemistry, Faculty of Science, Osaka City University
Sumiyoshi-ku, Osaka 558, Japan

(15. III. 73)

Summary. A brief synthesis of damascenone (**5**) from the acetylenic diol **2** and also that of β-damascone (**8**) from β-ionol, resembling the biogenetic synthesis, are described. A possible mechanism for the formation of damascenone from neoxanthin is proposed.

In recent years the isolation of damascenone (**5**) and β-damascone (**8**) [1] from several plants has stimulated considerable interest because of their powerful and pleasant fragrance. Our own interest in this field has been concerned with the metabolism of carotenoids [2].

We report herein a brief synthesis[2]) and a possible biogenesis of damascenone and β-damascone.

Reaction of the ketone **1** (derived from 2,2,6-trimethylcyclohexanone by bromination followed by dehydrobromination with dimethyl sulfoxide in the presence of sodium hydrogen carbonate [4]) with the lithium derivative of but-3-yn-2-ol in liquid ammonia yielded the *diol* **2**, m.p. 123–124.5° [IR. (Nujol): 3240, 1150, 1095, 1020, 840 cm^{-1}; NMR. (CD_3COCD_3): 1.00 (3 H, *s*), 1.05 (3 H, *s*), 1.37 (3 H, *d*, J = 6 Hz), 1.82 (3 H, *d*, J = 1.5 Hz), 3.0 (1 H, OH), 4.0 (1 H, OH), 4.43 (1 H, *q*, J = 6 Hz), 5.36 (1 H, *m*) ppm]. Treatment of diol **2** with 80% formic acid at room temperature for 30 min. gave a mixture from which were isolated the *hydroxyformate* **3** [UV. (λ_{max}, EtOH): 234 nm; IR. (liq.): 3400, 2200, 1720, 1175 cm^{-1}; NMR. ($CDCl_3$): 1.08 (3 H, *s*), 1.17 (3 H, *s*), 1.50 (3 H, *d*, J = 6 Hz), 1.85 (3 H, *s*), 4.7 (1 H, *q*, J = 6 Hz), 5.4 (1 H, *m*), 8.13 (1 H, *s*) ppm] and the *ketoformate* **4** [UV. (λ_{max}, EtOH): 280 nm; IR. (liq.): 2200, 1720, 1678, 1175 cm^{-1}; NMR. ($CDCl_3$): 1.13 (3 H, *s*), 1.20 (3 H, *s*), 1.94 (3 H, *s*), 2.40 (3 H, *s*), 5.4 (1 H, *m*), 8.22 (1 H, *s*) ppm].

On the other hand refluxing of diol **2** with the same acid for 30 min. yielded *damascenone* (**5**) [UV. (λ_{max}, EtOH): 228, 263, 310 nm; IR. (liq.): 3060, 1675, 1645, 1615, 970 cm^{-1}; NMR. ($CDCl_3$): 1.05 (6 H, *s*), 1.66 (3 H, *s*), 1.93 (3 H, $d \times d$, J = 1.3 Hz, J' = 6.5 Hz), 2.1 (2 H, *d*, J = 2 Hz), 5.8 (1 H, *m*), 6.1 (1 H, *m*), 6.74 (1 H, *m*) ppm; MS.: 190 (M^+)] and the *spiro-keto-ether* **6** [IR. (liq.): 1755, 1100, 1055 cm^{-1}; NMR. ($CDCl_3$): 0.90 (3 H, *s*), 1.03 (3 H, *s*), 1.28 (3 H, *d*, J = 7 Hz), 1.70 (3 H, *d*, J = 1.5 Hz), 2.36, 2.72 (2 H, *AB-q*, J = 19 Hz), 4.17 (1 H, $d \times q$, J = 7 Hz), 5.45 (1 H, *m*) ppm; MS.: 208 (M^+)]. Spectroscopic data of the damascenone thus obtained were identical in all respects with those of natural damascenone.

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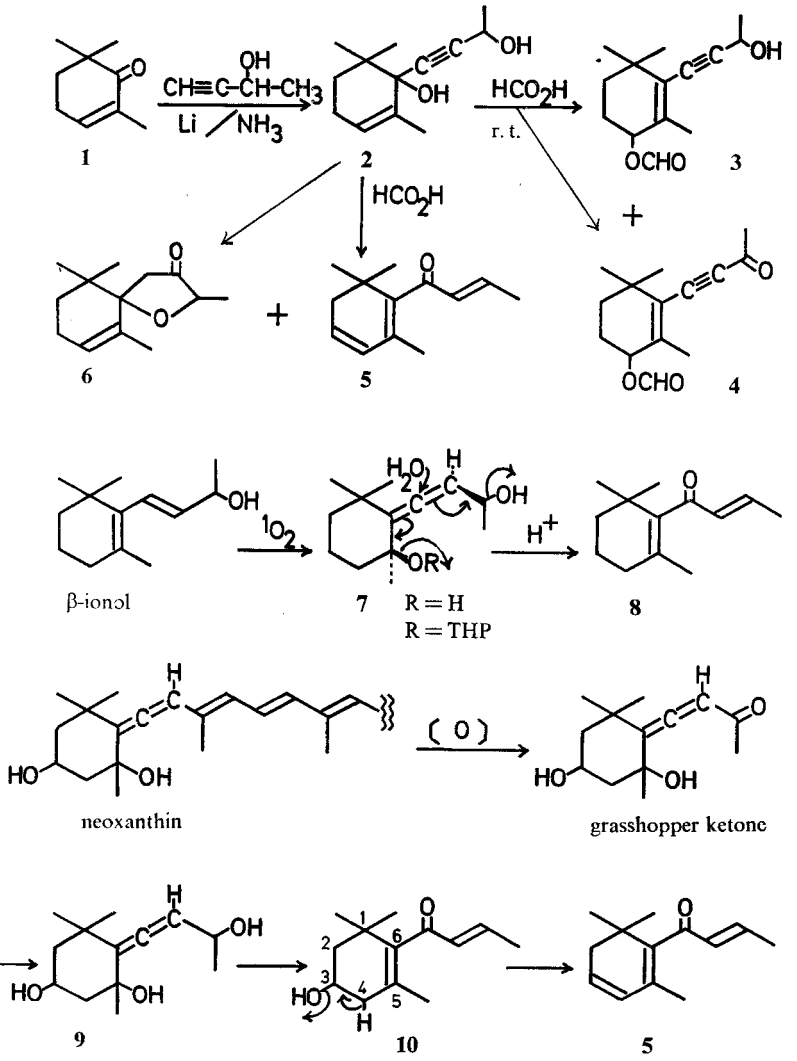
[1]) Part of this paper was presented at the 24th annual meeting of the Chemical Society of Japan, Osaka, April 1971, Abstract papers, page 1767.

[2]) Several attempts [3] have been made to synthesize damascenone and β-damascone.

β-Damascone was synthesized from β-ionol rather a process more nearly allied to a biogenetic route. We have already demonstrated that singlet oxygen oxidation of β-ionol yields the *allenic diol* **7** [5], m.p. 124–126° [IR. (Nujol): 3300, 1955 cm^{-1}; NMR. ($CDCl_3$): 1.04 (3 H, *s*), 1.24 (3 H, *s*), 1.31 (3 H, *d*, $J = 7$ Hz), 1.34 (3 H, *s*),



4.42 (1 H, *m*, $J = 7$ Hz), 5.48 (1 H, $d \times d$, $J = 7$ Hz, $J' = 5$ Hz) ppm]. Treatment of **7** with 80% acetic acid at room temperature for one hour furnished *β-damascone* (**8**) [UV. (λ_{max}, EtOH): 225 nm; IR. (liq.): 1680, 1650, 1620, 980 cm^{-1}; NMR. ($CDCl_3$): 1.00 (6 H, *s*), 1.50 (3 H, *s*), 1.92 (3 H, $d \times d$, $J = 6.5$ Hz, $J' = 1$ Hz), 6.0 (1 H, $d \times q$, $J = 16$ Hz, $J' = 1$ Hz), 6.6 (1 H, $d \times q$, $J = 16$ Hz, $J' = 6.5$ Hz) ppm; MS.: 192 (M^+)] in 35% yield. The same result was obtained starting from the allenic diol with opposite

stereochemistry[3]). A much better yield resulted by treatment of the tetrahydropyranyl ether of allenic diol **7** (prepared from the tetrahydropyranyl ether of 2-hydroxy-2,6,6-trimethyl-cyclohexanone by reaction with the lithium derivative of but-3-yn-2-ol followed by reduction with lithium aluminium hydride) with the same acid yielded β-damascone (yield: 78%).

This facile transformation of allenic diol to β-damascone strongly suggests that natural damascenone is derived from allenic carotenoids (*e.g.* neoxanthin) through grasshopper ketone [6], allenic triol **9** and 3-hydroxy-β-damascone (**10**), and that β-damascone may be derived from deoxy-neoxanthin, which it is hoped to isolate in the near future.

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[3]) Prepared from 4-(2,6,6-trimethylcyclohex-1-enyl)-but-3-yn-2-ol acetate by epoxidation followed by lithium aluminium hydride reduction; NMR. ($CDCl_3$): 1.04(3H, *s*), 1.20(3H, *s*), 1.27(3H, *d*, J = 7Hz), 1.34(3H, *s*), 4,36(1H, *q*, J = 7 Hz), 5,46(1H, *d* × *d*, J = 7Hz, J' = 5Hz) ppm; IR. (liq.): 3350, 1955 cm^{-1}.

149. Homopolar- and Heteropolar Bond Dissociation Energies and Heats of Formation of Radicals and Ions in the Gas Phase. I. Data on Organic Molecules

by **Kurt W. Egger** and **Alan T. Cocks**[1])

Monsanto Research S.A., Eggbühlstrasse 36, 8050 Zürich, Switzerland

(22. II. 73)

Summary. The literature data on heteropolar and homopolar 2-center bond dissociation energies in organic molecules in the gas phase and the corresponding heats of formation of radicals and ions have been critically evaluated. Data for more than 500 bonds are represented in tabular form together with the pertinent literature references.

Selected electron affinities and π-bond dissociation energies have also been incorporated. The follow-up paper will discuss some empirical general aspects of these data particularly regarding the effect of structure on the bond dissociation energies.

[1]) Post doctoral Research associate, present address: Department of Chemical Engineering, University College, London, WC1E, 7JE.