

DDQ OXIDATION OF SOME ERYTHRINAN ENONES AND DIENONES:

SYNTHESES OF (±)-ERYTHARBINE AND (±)-CRYSTAMIDINE¹

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Abstract——DDQ oxidation of 3,8-dioxoerythrinan-1(6)-ene **1** in dioxane gave the ring C/D oxidized product, the dienone **2**, while that of 3,8-dioxoerythrinan-1-ene **4** gave the ring B dehydrogenated product **5**. The either product was convertible to the same trienone **3** on further oxidation in different solvents. The trienone **3a** and **3b** were transformed by a conventional procedure to the highly dehydrogenated oxo-erythrinan alkaloids, erytharbine **8a** and crystamidine **8b**, respectively.

During our synthetic work on erythrinan alkaloids,¹ we have observed interesting solvent and structure dependence on DDQ oxidation of some erythrinan enones and dienones.

The enone-a **1a**¹, when heated with an excess of DDQ (7 eq.) in dioxane at 110°C for 5 h, gave the dienone **2a**², mp 193-195°C, in 29% yield. On the other hand, it gave the trienone **3a**, gum³, as a major product together with minute amount of the dienone **2a** on a similar oxidation in benzene (130°C, 3 h). In the latter solvent, it was difficult to isolate the dienone **2a**, since the trienone **3a** was always formed predominantly even when the starting material remained in the reaction mixture.

In contrast, the isomeric enone-b **4a**¹, on a similar treatment with DDQ either in dioxane or benzene (110°C, 1.5 h), suffered the oxidation at different position to give the isomeric dienone **5a**³, mp 243-247°C, in 59% yield with recovery of

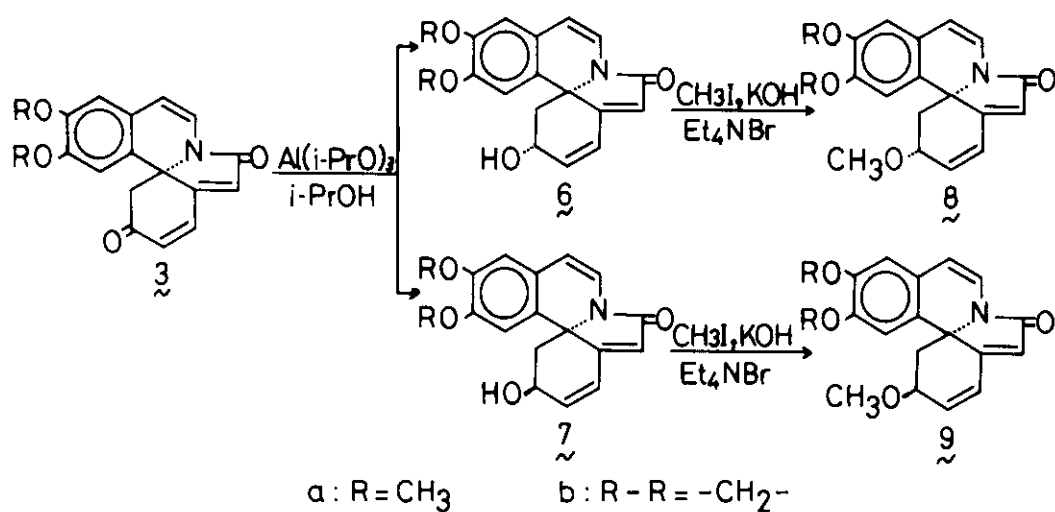


Chart 2

Table I. ¹H-NMR Chemical Shifts of The Aromatic and Olefinic Protons

Compd.	Ar-H	C ₁ -H	C ₂ -H	C ₇ -H ^a	C ₁₀ -H ^b	C ₁₁ -H ^b
1a	6.30, 6.56	6.06 (m)	----	----	----	----
4a	6.58, 6.64	7.04 (dd 10,5)	6.29 (dd 10,2)	----	----	----
2a	6.64, 6.84	7.75 (dd 10,1)	6.40 (d 10)	6.35	----	----
2b	6.65, 6.77	7.76 (dd 10,1)	6.37 (d 10)	6.39	----	----
3a	6.60, 6.74	7.85 (dd 10,1)	6.37 (d 10)	6.46	6.90	6.16
3b	6.66, 6.71	7.83 (dd 10,1)	6.36 (d 10)	6.46	6.90	6.13
5a	6.62, 6.66	7.20 (dd 10,5)	6.29 (d 10)	----	6.85	6.02
6a	6.67, 6.76	6.32 (d 10)	6.98 (dd 10,2)	6.09	6.91	6.16
6b	6.68, 6.71	6.29 (d 10)	6.91 (dd 10,2)	6.07	6.88	6.10
7a	6.77, 6.88	6.97 (d 10)	6.32 (dd 10,5)	6.04	6.88	6.13
7b	6.72, 6.88	6.93 (d 10)	6.28 (dd 10,5)	6.02	6.85	6.08
8a	6.66, 6.75	6.32 (d 10)	6.95 (dd 10,2)	6.07	6.90	6.14
8b	6.69, 6.72	6.31 (d 10)	6.91 (dd 10,2)	6.06	6.89	6.10
9a	6.65, 6.87	6.95 (d 10)	6.30 (dd 10,5)	6.00	6.82	6.09
9b	6.64, 6.87	6.94 (d 10)	6.28 (dd 10,5)	6.01	6.82	6.07

a): singlet. b): doublet, J=7 Hz.

total syntheses of these natural alkaloids.

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3. Unless otherwise stated, IR spectra were taken in CHCl_3 (cm^{-1}), UV in EtOH [λ_{max} nm(log ϵ)], and NMR in CDCl_3 (δ).
3a: 309 (M^+); IR: 1710, 1690; UV: 246 (4.13), 277 (4.15).
3b: IR (Nujol): 1700, 1670; UV: 246 (4.28), 276 (4.31), 418 (3.22).
5a: 311 (M^+); IR (KBr): 1710, 1690; UV: 230 (4.39), 319 (4.04).
6a: mp 257-259°C; IR: 1690; UV: 267 (4.47), 360 (3.34).
6b: mp 219-220°C; IR (Nujol): 1650; UV: 228 (4.35), 265 (4.38), 360 (3.44).
7a: gum; IR: 1690. 7b: gum; IR: 1680.
8a: gum; IR: 1685; UV: 225 (4.32), 266 (4.32), 355 (3.25).
8b: gum; IR: 1680; UV: 228 (4.28), 264 (4.29), 357 (3.35).
9a: gum; IR: 1690; UV: 230 (4.27), 255 (4.11), 370 (2.90).
9b: gum; IR: 1690; UV: 225 (4.37), 255 (4.24), 368 (3.28).
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