RING-EXPANSION OF 7-CHLORO-2-OXABICYCLO[4.2.0]OCT-4-EN-3-ONES TO 2H-OXOCIN-2-ONES WITH BASE. FORMATION OF A NEW OXACYCLOOCTA-TRIENONE SYSTEM

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The treatment of chlorinated 2-oxabicyclo[4.2.0]oct-4-en-3ones, which are photoadducts between 4,6-dimethyl-2-pyrone and chloroethylenes, with a base gives new 2H-oxocin-2-ones in good yields. This provides the first example for preparation of a monocyclic oxacyclooctatrienone system.

Little attention has been paid to a ring-expansion reaction of oxabicyclo-[4.2.0]octane ring systems. An attempt to convert photoadducts between 2,6-dimethyl-4-pyrone and acetylenes to the oxacyclooctatrienone ring system was unsuccessful,¹⁾ although pyrolysis of a 3-chlorocoumarin photodimer at 290 °C gave a low yield of an oxacyclooctatrienone with the elimination of hydrogen chloride.²⁾ Thus, monocyclic oxacyclooctatrienones have not been prepared up to date. We have recently³⁾ reported the sensitized photoaddition reaction of 4,6-dimethyl-2-pyrone with ethylenes to produce the 2-oxabicyclo[4.2.0]oct-4-en-3-ones as major products.

In this communication we report a ring-expansion reaction of chlorinated 2oxabicyclooctenones $\underline{1}^{4}$ leading to the formation of 2H-oxocin-2-ones: this provides the first example for the preparation of a monocyclic oxacyclooctatrienone system.

The reaction of photoadduct <u>la</u> (1.0 mmol) with triethylamine (1.5 mmol) in ethanol (5 ml) under reflux for 15 h afforded a dehydrochlorinated product <u>2a</u>, mp 130-132 °C, in 97% yield. In a similar treatment of a mixture of photoadducts, <u>lb</u> and <u>lb</u>', with 2 equivalents of triethylamine, an 89% yield of the dehydrochlorinated compound 2b, mp 63-64 °C, was obtained as the sole product.

Both 1 H- and 13 C-NMR spectra as well as other spectral data (Table 1) $^{5)}$ indicate that both dehydrochlorinated products have the 2H-oxocin-2-one structure, that is, 2a is 6,7-dichloro-4,8-dimethyl-2H-oxocin-2-one, and 2b 6-cyano-4,8-dimethyl-2H-oxocin-2-one.

However, such dehydrochlorination of <u>1</u> did not occur in benzene. On the other hand, reduction of <u>1a</u> with zinc dust in refluxing acetonitrile for 8 h gave the 2-oxabicyclo[4.2.0]octadienone <u>3</u> (mp 39-40 °C, 81%), which was stable in boiling ethanol.⁶)

On the basis of the above facts, the pathway for the formation of 2 can be illustrated as shown in Scheme 1. The elimination of a proton from 1 with tri-

	¹ H-NMR (δ)			¹³ C-NMR (δ)							м+
	3-н	7 - H	5 - H	2-C	8-C	3-C	4-C	5-C	6-C	7-C	(m/e)
2a	6.05		6.60	161.2s d	or 161.1s	111.5d	113.5s	120.8d	154.4s	127.3s	218

Table 1. Spectral data of 2H-oxocin-2-ones, 2a and 2b^{a)}

a) <u>2a</u>: IR (kBr) 1720 cm⁻¹ (C=O); UV (MeOH) λmax (ε) 296 nm (5930); ¹H-NMR δ 2.13, 2.25 (methyls); ¹³C-NMR δ 17.9, 19.3 (methyls). <u>2b</u>: IR (KBr) 1720, 1740 cm⁻¹ (C=O); UV (MeOH) λmax (ε) 293 nm (5790); ¹H-NMR δ 2.20, 2.30 (methyls); ¹³C-NMR δ 18.4, 20.3 (methyls), 116.1 (CN). NMR spectra were measured in CDCl₃.

154.4s 111.8d 113.1s 138.3d 138.3s 111.8d 175



Scheme 1.

ethylamine generates an anion intermediate which is stabilized in ethanol. This is followed by the elimination of a chloride ion with a concurrent ring-expansion.

References

- 1) J. W. Hanifin and E. Cohen, J. Org. Chem., <u>36</u>, 910 (1971).
- 2) J. W. Hanifin and E. Cohen, J. Org. Chem., 33, 2811 (1968).
- 3) T. Shimo, K. Somekawa, and S. Kumamoto, Nippon Kagaku Kaishi, 1983, 394.
- 4) Sensitized photoaddition reaction of 4,6-dimethyl-2-pyrone with trichloroethylene and 2-chloroacrylonitrile gave <u>la</u> and a mixture of <u>lb</u> and <u>lb'</u> (4:1), respectively. The detailed results will be reported elsewhere.
- 5) All the compounds reported herein gave satisfactory elemental analyses.
- 6) <u>3a</u>: IR (KBr) 1710 (C=O), 1655, 1585 cm⁻¹ (C=C); ¹H-NMR (CDCl₃) & 1.64 (s, 1-Me), 2.06 (bs, 5-Me), 3.31 (s, 6-H), 5.82 (bs, 4-H), 6.15 (s, 8-H); MS m/e 149 (M⁺ Cl). When heated in refluxing toluene for 80 h, <u>3a</u> was converted to 6-chloro-2-hydroxy-4-methylacetophenone. Details will be reported elsewhere.

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6.06 or 5.96 6.42 160.7s