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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 OXACYCLOOCTATRIENONE SYSTEM

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The treatment of chlorinated 2-oxabicyclo[4.2.0]oct-4-en-3-ones, 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 2-oxabicyclooctenones 14) 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 1a (1.0 mmol) with triethylamine (1.5 mmol) in ethanol (5 ml) under reflux for 15 h afforded a dehydrochlorinated product 2a, mp 130-132 °C, in 97% yield. In a similar treatment of a mixture of photoadducts, 1b and 1b', 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.

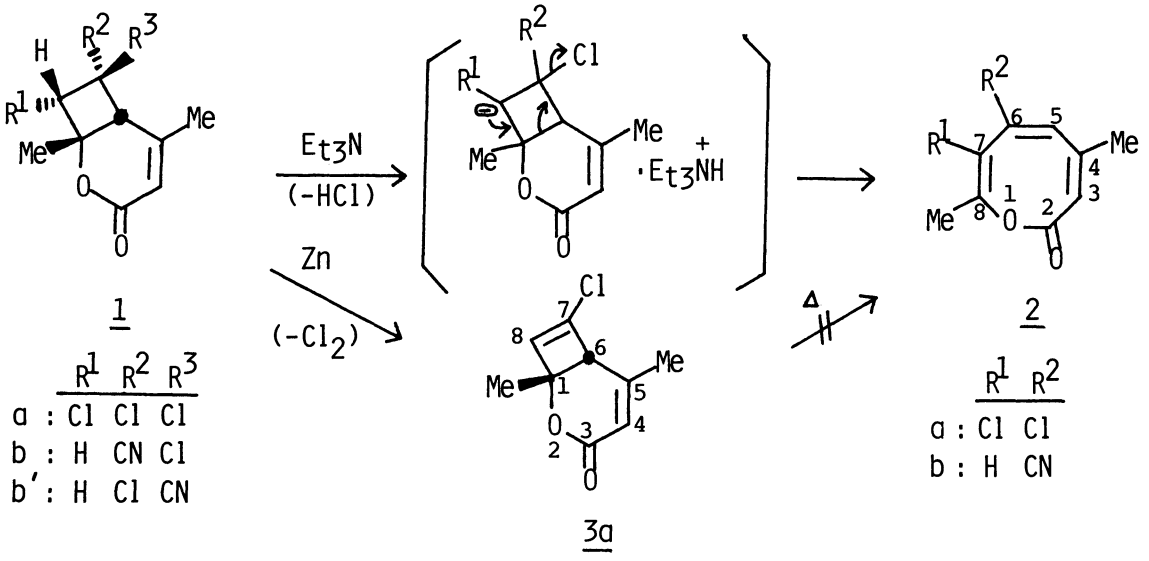
However, such dehydrochlorination of 1 did not occur in benzene. On the other hand, reduction of 1a with zinc dust in refluxing acetonitrile for 8 h gave the 2-oxabicyclo[4.2.0]octadienone 3 (mp 39-40 °C, 81%), which was stable in boiling ethanol.6)

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-

Table 1. Spectral data of 2H-oxocin-2-ones, 2a and 2b[a)]

	^{1}H-NMR (δ)			^{13}C-NMR (δ)							M^+
	3-H	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 or	161.1s	111.5d	113.5s	120.8d	154.4s	127.3s	218
2b	6.06 or	5.96	6.42	160.7s	154.4s	111.8d	113.1s	138.3d	138.3s	111.8d	175

a) 2a: IR (kBr) 1720 cm^{-1} (C=O); UV (MeOH) λmax (ε) 296 nm (5930); ^{1}H-NMR δ 2.13, 2.25 (methyls); ^{13}C-NMR δ 17.9, 19.3 (methyls). 2b: IR (KBr) 1720, 1740 cm^{-1} (C=O); UV (MeOH) λmax (ε) 293 nm (5790); ^{1}H-NMR δ 2.20, 2.30 (methyls); ^{13}C-NMR δ 18.4, 20.3 (methyls), 116.1 (CN). NMR spectra were measured in $CDCl_3$.



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., 36, 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 1a and a mixture of 1b and 1b' (4:1), respectively. The detailed results will be reported elsewhere.
5) All the compounds reported herein gave satisfactory elemental analyses.
6) 3a: IR (KBr) 1710 (C=O), 1655, 1585 cm^{-1} (C=C); ^{1}H-NMR ($CDCl_3$) δ 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, 3a was converted to 6-chloro-2-hydroxy-4-methylacetophenone. Details will be reported elsewhere.

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