Nitrosocarbonyl Compounds as Intermediates in the Oxidative Cleavage of Hydroxamic Acids

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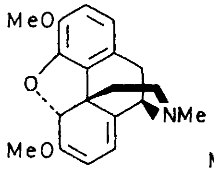
Summary Periodate oxidation of hydroxamic acids in the presence of conjugated dienes gives, in good yield, *N*-acyl-3,6-dihydro-2*H*-1,2-oxazines derived, presumably, from nitrosocarbonyl intermediates.

Nitrosocarbonyl-alkanes and -arenes, RCONO (**1**), have been proposed as transient intermediates in the oxidative cleavage of hydroxamic acids,[1,2] RCONHOH (**2**), and the pyrolysis of alkyl nitrites in the presence of aldehydes.[2] No direct evidence for the existence of the species (**1**) appears to be available; characteristic decomposition products are acyl derivatives formed, apparently, from attack by nucleophiles at the carbonyl group. The powerful dienophilic character of nitrosyl cyanide[3] suggested that *C*-nitrosocarbonyl compounds, though short-lived, might be trapped efficiently by conjugated dienes. We find that this is so.



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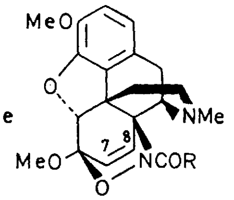

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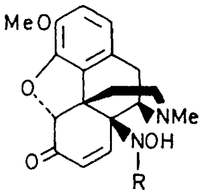

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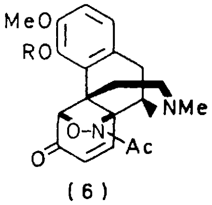

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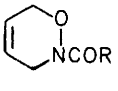

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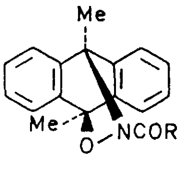

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Addition of benzohydroxamic acid (**2**; R=Ph) (2·3 mol. equiv.) to a stirred mixture of thebaine (**3**) (1·0 mol. equiv.) in ethyl acetate and tetraethylammonium periodate[4] (1·45 mol. equiv.) in aqueous acetic acid–sodium acetate (pH *ca.* 6) at 0 °C gave the adduct (**4**; R = Ph), isolated as the hydriodide (97% yield). Hydrolysis with refluxing aqueous methanolic hydrogen chloride gave 14-hydroxyaminocodeinone (**5**; R = H), obtained earlier[5] from the reaction of thebaine hydrochloride with 1-chloronitrosocyclohexane in aqueous ethanol. Similarly, thebaine was converted, with acetohydroxamic acid (**2**; R = Me) and periodate, into the adduct (**4**; R = Me) (96%). Acid-catalysed hydrolysis at 0 °C gave the enone (**5**; R = Ac) which, upon treatment with sodium methoxide in methanol, cyclised to the phenol (**6**; R = H). Acetylation then gave the acetate (**6**; R = Ac) obtainable[5] similarly from (**5**; R = H) by cyclisation and acetylation. Catalytic (PtO_2) hydrogenation of the adduct (**4**; R = Me) gave the corresponding 7,8-dihydro-derivative. Treatment of butadiene with benzohydroxamic acid in nitromethane, or acetohydroxamic acid in dichloromethane, and tetraethylammonium periodate yielded the known[6] *N*-acyloxazines (**7**; R = Ph or Me).

Compelling evidence for the free existence of nitrosocarbonylmethane and nitrosocarbonylbenzene was obtained as follows. The crystalline adducts (**8**; R = Me or Ph) were prepared (*ca.* 50% yield) from 9,10-dimethylanthracene in the usual way. Both were stable at ambient temperatures. However, treatment of thebaine (**3**) with each adduct (**8**) in hot benzene caused intermolecular transfer of RCONO to yield the corresponding thebaine adducts (**4**) and 9,10-dimethylanthracene.

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