Nitrosyl Cyanide: a Possible Intermediate in the Formation of *N*-Cyano-1,2-oxazines from Conjugated Dienes

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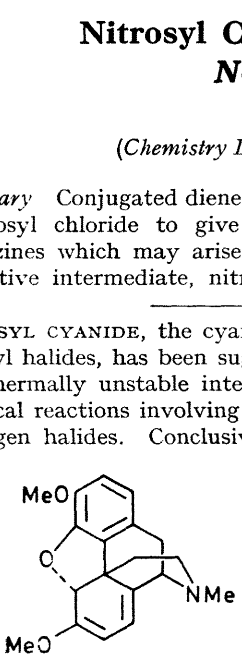
Summary Conjugated dienes react with silver cyanide and nitrosyl chloride to give *N*-cyano-3,6-dihydro-2*H*-1,2-oxazines which may arise from cycloaddition with the reactive intermediate, nitrosyl cyanide.

NITROSYL CYANIDE, the cyanogen analogue of the familiar nitrosyl halides, has been suggested[1] as a photochemically and thermally unstable intermediate in gas-phase photochemical reactions involving nitric oxide and cyanogen or cyanogen halides. Conclusive evidence for the existence and structure of nitrosyl cyanide and information on its reactions with other molecules are apparently still lacking. Since *C*-nitroso-compounds form 1,4-adducts with conjugated dienes,[2] including the alkaloid thebaine[3] (1), nitrosyl cyanide, generated for example from silver cyanide and nitrosyl chloride, might in principle be trapped in this way.



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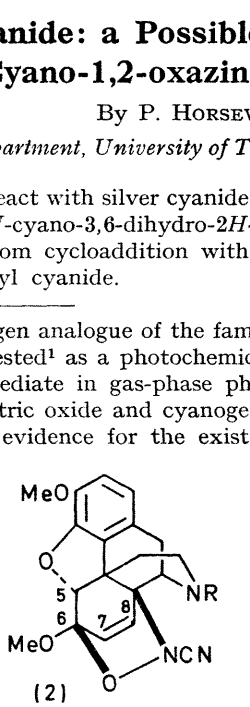

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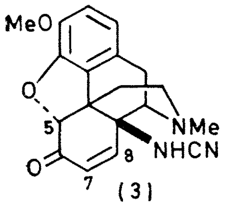

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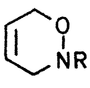

(4)

Nitrosyl chloride was added to a stirred suspension of dry silver cyanide (2 molar equiv.) in chloroform–ethanol (99:1) at −20°. After *ca.* 3 min. thebaine (0·25—0·50 molar equiv.) was added in the same solvent and the reaction mixture allowed to warm up to room temperature. Chromatography of the product gave thebaine (11—46% yield in several experiments), and the adduct (2; R = Me) (52—11%), m.p. 149—150° (decomp.). The same adduct was formed when nitrosyl chloride and silver cyanide were allowed to react at −20° (a green vapour formed above the reaction mixture) and thebaine was then added in dichloromethane. The n.m.r. spectrum of (2; R = Me) showed signals, τ ($CDCl_3$) 3·66 (q, *J* 9 and *ca.* 1 Hz, 7-H), 4·00 (d. *J* 9 Hz, 8-H), and 5·47 (d, *J ca.* 1 Hz, 5-H), expected[3] for a 1,4-adduct of thebaine. The presence of an *N*-cyano-group was shown by the i.r. absorption, ν_{max} (Nujol) 2205 cm^{-1}, and hydrolysis to the corresponding urea after prolonged contact with neutral alumina (grade III). The cyclic nature of the adduct was proved by hydrogenation in methanol with platinum oxide to yield, presumably *via* a hemiacetal intermediate, the cyanamide (3), ν_{max} ($CHCl_3$) 3220, 2215, and 1695 cm^{-1}, τ ($CDCl_3$) 3·42 and 3·70 (AB q, *J* 10·3 Hz, 8-H and 7-H), 4·88 (broad s, NH), and 5·04 (s, 5-H). Unlike the adducts of thebaine and nitrosoarenes,[3] the adduct (2; R = Me) did not dissociate detectably in solution over prolonged periods at room temperature. Passage of butadiene into a solution of "nitrosyl cyanide" in dichloromethane at −20° gave the analogous product (4; R = CN) as a liquid, purified by molecular distillation

(50°, 0·5 mm Hg), ν_{max} (liquid film) 2215 cm^{-1}, τ ($CDCl_3$) 4·03, 5·45, and 6·02 (all 2-proton multiplets). The olefinic band (τ 4·03) was resolved at 220 MHz into an AB quartet (*J* 11·7 Hz), each component showing further multiplet splitting. High-resolution mass spectrometry confirmed the molecular formula, $C_5H_6N_2O$ (fragment ions, $C_4H_4N_2$, C_4H_6, and C_3H_3, with metastable peaks for $C_5H_6N_2O \rightarrow C_4H_4N_2$ and $C_4H_6 \rightarrow C_3H_3$). The same compound was obtained from the known[4] oxazine (4; R = H) by treatment with cyanogen bromide in ether.

Thebaine or the adduct (2; R = Me) reacted with an excess of silver cyanide–nitrosyl chloride to form (typically 40% yield) the cyanomethyl derivative (2; R = CH_2CN), m.p. 184—185° (decomp.), ν_{max} (Nujol) 2245 (weak) and 2215 cm^{-1}. The n.m.r. spectrum closely resembled that of the precursor (2; R = Me) except that the *N*-methyl signal was replaced by a methylene quartet, τ 6·20 and 6·35 (*J* 11 Hz). The compound was converted (as above) into the corresponding urea and, with sodium methoxide in methanol into the corresponding *O*-methylisourea. This unusual cyanation of an *N*-methyl group may be general since *N*-methylmorpholine was converted,[5] under the same conditions, into *N*-cyanomethylmorpholine identical with material prepared[6] from morpholine by the action of formaldehyde bisulphite complex and acetone cyanohydrin.

The observed conversion of conjugated dienes into *N*-cyano-3,6-dihydro-2*H*-1,2-oxazines is considered good evidence, though not complete proof, for the formation of nitrosyl cyanide, ONCN, from silver cyanide and nitrosyl chloride. Attempts are being made to isolate this powerfully electrophilic species which we believe may have significant life-time at room temperature.

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