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REACTION OF ALKOXYCARBONYLNITRENES WITH DIMETHYL SULPHOXIDE; FORMATION OF TRANSIENT NITROSOFORMATES

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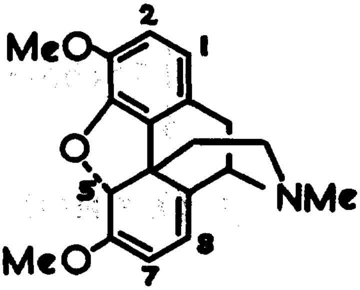
C-Nitrosocarbonyl-compounds, XCONO (X = alkyl or aryl), have been implicated[1] as transient intermediates in the oxidation of hydroxamic acids, XCONHOH. Characteristically, they may be trapped by conjugated dienes, for example, 9,10-dimethylanthracene (DMA) or thebaine 1, to give the corresponding cyclo-adducts 2 or 3.



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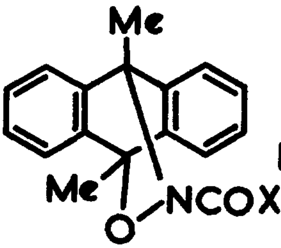

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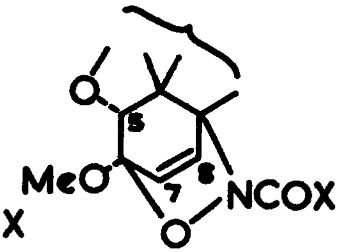

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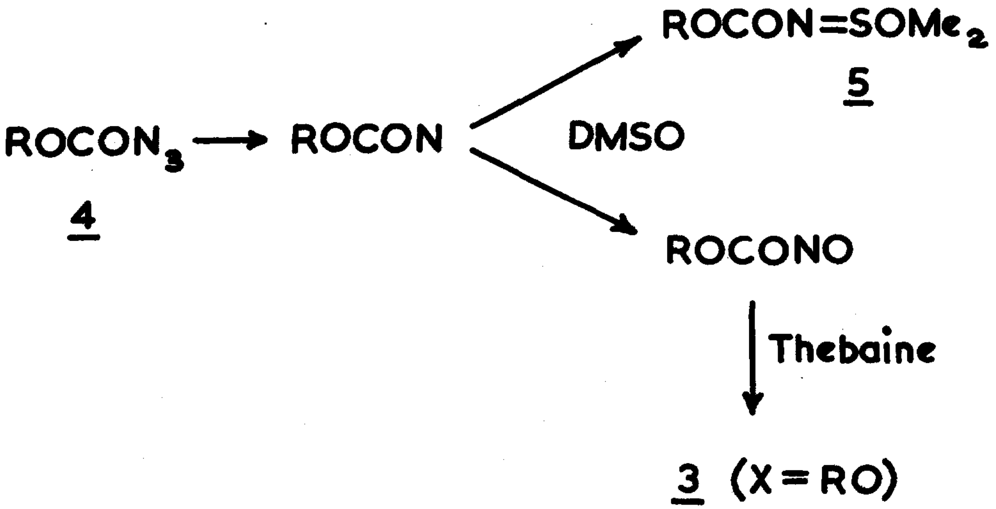
Prosser et al.[2] studied the thermal decomposition of octadecyl azidoformate in dimethyl sulphoxide (DMSO) at 120° and postulated the following reaction scheme to account for the formation of Me_2S, CO_2, and NO.

$$\mathrm{ROCON_3} \longrightarrow \mathrm{ROCON} + \mathrm{N_2}$$

$$\mathrm{ROCON} + \mathrm{Me_2SO} \longrightarrow \mathrm{ROCONO} + \mathrm{Me_2S}$$

$$\mathrm{ROCONO} \longrightarrow \mathrm{R^{\bullet}} + \mathrm{CO_2} + \mathrm{NO}$$

However, no direct evidence for the intermediacy of a nitrosoformate, ROCONO, was obtained. We reasoned that nitrosoformates, though short-lived, should behave, like the C-nitrosocarbonyl-compounds,[1] as powerful dienophiles and be susceptible to capture by conjugated dienes. We now report that this is so.



Benzyl azidoformate[3] 4 (R = $PhCH_2$) was heated in DMSO at 130° for 2 hours to give the sulphoximine[4] 5 (R = $PhCH_2$) (50-60%), m.p. 100-101°, ν_{max} (KBr) 1655 cm^{-1}, τ ($CDCl_3$) 2.63 (5H, broad s), 4.85 (2H, s), and 6.70 (6H, s). Benzaldehyde was identified as a by-product (15%) from this reaction. In contrast, decomposition of 4 (R = $PhCH_2$) (1.8 mmol) in DMSO in the presence of thebaine 1 (0.32 mmol) gave, along with 5 (R = $PhCH_2$) and benzaldehyde, the cyclo-adduct 3 (X = $PhCH_2O$), m.p. 104-106°, which was isolated in 66% yield (based on thebaine) by p.l.c. The structure of 3 (X = $PhCH_2O$) was deduced from the spectroscopic data, ν_{max} (KBr) 1716 cm^{-1}, τ ($CDCl_3$) 2.69 (5H, broad s, Ph), 3.37 and 3.39 (2H, q, *J* = 8 Hz, H-2 and H-1), 3.98 (2H, broad s, H-7 and H-8), 4.93 and 4.99 (2H, q, *J* = 12 Hz, Ph$\underline{CH_2}$), 5.43 (1H, s, H-5), 6.20 (3H, s, MeO), 6.51 (3H, s, MeO), and 7.56 (3H, s, MeN), and the following, alternative synthesis.

N-Benzyloxycarbonylhydroxylamine[5] (1.5 mmol) was added in portions with stirring to thebaine (1 mmol) and tetraethylammonium periodate[6] (0.8 mmol) in dichloromethane at 0°. After 1 hour the adduct 3 (X = $PhCH_2O$) was isolated in 76% yield (based on thebaine). Similarly, oxidation of the hydroxamic acid in the presence of DMA afforded the corresponding adduct 2 (X = $PhCH_2O$) (72%), m.p. 132-135°, ν_{max} (KBr) 1698 cm^{-1}, τ 2.45-3.10 (13H, m. aromatic H), 5.02 (2H, s, CH_2), 7.40 (3H, s, CH_3), and 7.75 (3H, s, CH_3). The adducts 2 and 3 are those expected[1] to arise from capture of benzyl nitrosoformate formed by oxidation of the hydroxamic acid. Evidence for the free existence of $PhCH_2OCONO$ was obtained as follows. When equimolar amounts of 1 and 2 (X = $PhCH_2O$) were heated in benzene under reflux, essentially quantitative formation of 3 (X = $PhCH_2O$) was observed with liberation of DMA. Release of DMA from 2 (X = $PhCH_2O$) (1 equiv.) was followed (absorption at 358 nm) kinetically in benzene at 60° in the presence of thebaine (1 or 2 equiv.). First-order kinetics were observed with $k = 4.3 \times 10^{-4} s^{-1}$. This implies rate-determining dissociation of 2 (X = $PhCH_2O$) to give DMA and $PhCH_2OCONO$ followed by rapid capture of the latter by thebaine.

Analogous transformations were carried out with t-butyl azidoformate 4 (R = Bu^t). Decomposition alone in DMSO at 115° gave the sulphoximine 5 (R = Bu^t) (58%), m.p. 72-74°, ν_{max} (KBr) 1660 cm^{-1}, τ ($CDCl_3$) 6.76 (6H, s) and 8.56 (9H, s). Decomposition of 4 (R = Bu^t) (2.5 mmol) in DMSO in the presence of thebaine (0.5 mmol) gave 5 (R = Bu^t) (51% based on 4) and the adduct[7] 3 (X = Bu^tO) (84% based on 1), ν_{max} (film) 1710 cm^{-1}, τ ($CDCl_3$) 3.30 and 3.44 (2H, q, J = 8 Hz, H-2 and H-1), 3.89 and 4.03 (2H, q, J = 8.5 Hz, H-7 and H-8), 5.48 (1H, s, H-5), 6.20 (3H, s, MeO), 6.41 (3H, s, MeO), 7.54 (3H, s, MeN), and 8.57 (9H, s, Me_3C). Again, the same adduct 3 (X = Bu^tO) was obtained (74% yield based on thebaine) when N-t-butoxycarbonylhydroxylamine[8] was oxidised with periodate in the presence of thebaine. The structure of 3 (X = Bu^tO) was confirmed by degradation. Treatment with methanolic hydrogen chloride at room temperature followed by dilution of the reaction mixture with ether gave 14-hydroxyaminocodeinone hydrochloride identical with material obtained earlier.[1]

The foregoing experiments, taken together, indicate that alkyl nitrosoformates are capable of independent existence and are formed during the decomposition of alkyl azidoformates in DMSO. Presumably, the intermediate nitrene, ROCON, attacks the solvent competitively either on sulphur to give a sulphoximine 5 (major pathway) or on oxygen to give ROCONO (minor pathway). We have verified that sulphoximine formation is essentially irreversible under the standard reaction conditions since heating 5 (R = $PhCH_2$) with thebaine 1 in DMSO at 130° for 2 hours have no detectable amounts of 3 (X = $PhCH_2O$).

Acknowledgement.

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