

Reactions of Transient C-Nitrosocarbonyl Compounds with Dienes, Mono-olefins, and Nucleophiles

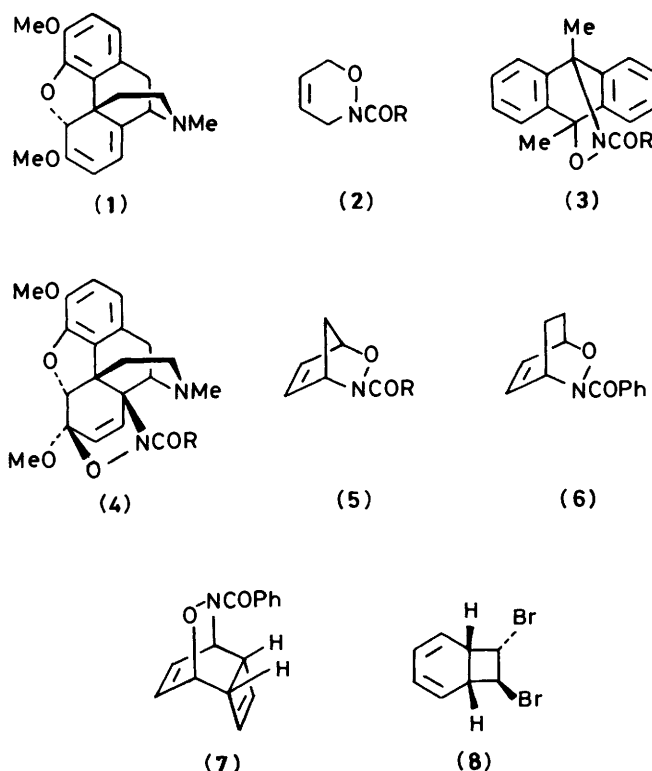
John E. T. Corrie, Gordon W. Kirby,* and John W. M. Mackinnon
 Department of Chemistry, University of Glasgow, Glasgow G12 8QQ

Nitrosocarbonylbenzene and nitrosocarbonylmethane, formed as transient intermediates by oxidation of benzo- and aceto-hydroxamic acid, respectively, with tetraethylammonium periodate, are trapped by cyclopentadiene to give the corresponding cycloadducts (5). The adduct (5; R = Ph) dissociates in solution at 80 °C to reform nitrosocarbonylbenzene, which reacts with thebaine (1) to give (4; R = Ph) and with triphenylphosphine to give phenyl isocyanate. Cycloadducts of nitrosocarbonylbenzene with cyclohexa-1,3-diene (6) and with cyclo-octatetraene (7) have also been prepared. The adduct (3; R = Ph) of nitrosocarbonylbenzene and 9,10-dimethylantracene, when heated with 1-allyl-3,4-methylenedioxybenzene, oct-1-ene, or 2,5-dimethylhexa-2,4-diene, gives the corresponding 'ene' reaction products of the olefins and nitrosocarbonylbenzene. When heated alone, the adduct (3; R = Ph) gives 9,10-dimethylantracene, benzoic anhydride, and nitrous oxide. Oxidation of 2,4,6-trimethylbenzohydroxamic acid in the presence of thebaine gives the adduct (4; R = 2,4,6-trimethylphenyl). However, 2,4,6-trimethylnitrosocarbonylbenzene is insufficiently stable to be isolated; in the absence of a diene it decomposes to give 2,4,6-trimethylbenzoic anhydride as the major product.

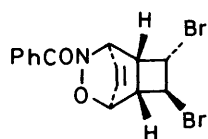
In an earlier paper¹ we concluded that oxidation of hydroxamic acids, RCONHOH, generates C-nitrosocarbonyl compounds, RCONO, representatives of a new class of transient dienophiles.² When the oxidations were carried out in the presence of the conjugated dienes, buta-1,3-diene, 9,10-dimethylantracene (DMA), or thebaine (1) the corresponding cycloadducts (2), (3), and (4) were produced in good yield. Further, we showed³ that nitrosocarbonyl compounds, released by thermal dissociation of the adducts (3), react rapidly with triphenylphosphine to give isocyanates and triphenylphosphine oxide. Here we describe a wider investigation of the chemistry of C-nitrosocarbonyl compounds including their reactions with various cyclic dienes, mono-olefins, and nucleophiles. A brief study of the decomposition of nitrosocarbonylbenzene in the absence of co-reactants is recorded.

As expected, oxidation of benzohydroxamic acid, in dichloromethane, with tetraethylammonium periodate in the presence of cyclopentadiene² or cyclohexa-1,3-diene gave the corresponding, crystalline adducts (5; R = Ph) and (6) in good yield. The cycloadduct (5; R = Me) of cyclopentadiene and nitrosocarbonylmethane was obtained similarly, although not in crystalline form. An attempt to trap nitrosocarbonylbenzene under these conditions with the unreactive diene,⁴ cyclo-octatetraene, gave no detectable amounts of cycloadduct. However, our alternative procedure was successful. Thus, the adduct (3; R = Ph) was heated for 6 h at 80 °C in benzene with an excess of cyclo-octatetraene to give, cleanly, DMA and the adduct (7). The same product was obtained more conveniently from the dibromide (8).⁵ Oxidation of benzohydroxamic acid with periodate in the presence of (8) gave a product which appeared to be a mixture of the diastereoisomers, (9a) and (9b). Treatment of this mixture with zinc dust in dimethyl sulphoxide⁶ then gave the adduct (7).

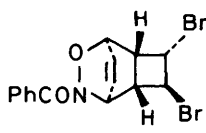
The thermal stability of the adduct (5; R = Ph) was studied to determine whether retro-Diels-Alder cleavage would occur under mild conditions. This was of interest since cyclopentadiene is more readily available than DMA and adducts of the type (5) might serve, like (3), as convenient precursors for nitrosocarbonyl compounds. Accordingly, equimolar amounts of (5; R = Ph) and thebaine (1) were heated in benzene at 60 °C, the course of reaction being monitored by t.l.c. After 6.5 h the mixture yielded (69%) the known¹ adduct (4;



R = Ph) of thebaine. Similarly, heating (5; R = Ph) at 80 °C in benzene with triphenylphosphine (1 mol equiv.) led to complete decomposition of (5; R = Ph) in 3 h with the formation of phenyl isocyanate.³ The preparative value of adducts of the type (5; R = R'O) will be illustrated in a later paper on the reactions of O-nitrosocarbonyl compounds (C-nitrosoformates).⁷ Dao *et al.*⁸ have independently studied the thermal decomposition of (5; R = Ph) and related cycloadducts. The adduct (5; R = Ph), when heated alone under reflux in benzene, decomposed to give a dark, complex mixture of products which was shown by n.m.r. spectroscopy to contain

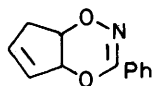


(9a)



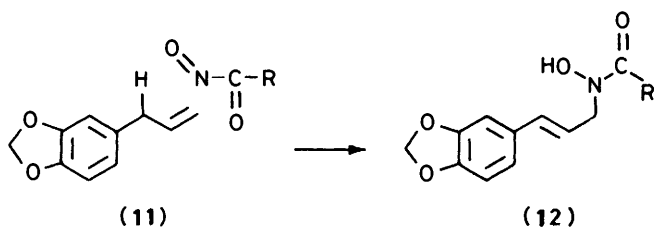
(9b)

substantial amounts of the isomeric dioxazine (10). More recently, Ranganathan *et al.*⁹ have reinvestigated the thermal decomposition of (5; R = Ph) and have identified several products in addition to (10).



(10)

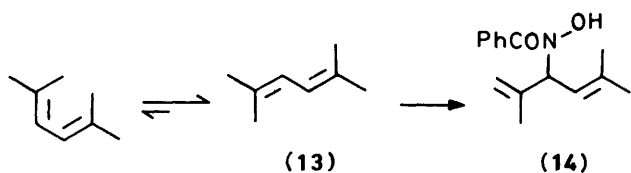
Nitrosoarenes are known to react with mono-olefins by an 'ene' process leading to allylic hydroxylamines.¹⁰ Similarly, when the DMA adduct (3; R = Ph) was heated with an excess of safrole (11) the 'ene' reaction product (12; R = Ph) was obtained in satisfactory (65%) yield. The structure (12; R = Ph) was confirmed by synthesis from *N*-(3,4-methylenedioxy-cinnamyl)hydroxylamine, which was obtained by reduction of the appropriate oxime with sodium cyanoborohydride. Similarly, the adduct (3; R = Me) and safrole gave (12; R = Me). In both these examples the 'ene' reaction is favoured by



(11)

(12)

movement of the double bond into conjugation with the benzene ring. Nevertheless, oct-1-ene also reacted with nitrosocarbonylbenzene, again generated from (3; R = Ph), to form the corresponding 'ene' product, although in diminished yield. Finally, 2,5-dimethylhexa-2,4-diene reacted, presumably through its predominant *s-trans* form (13), with (3; R = Ph) to give the hydroxamic acid (14). Keck *et al.*¹¹ have reported other examples of the intermolecular 'ene' reactions of nitrosocarbonyl compounds and have demonstrated the value of the related intramolecular reactions in natural product synthesis.



(13)

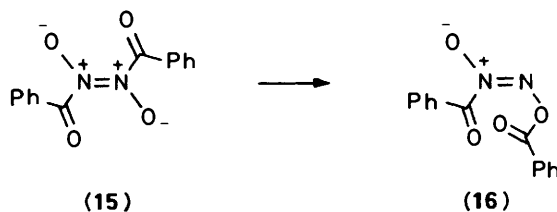
(14)

Finally, we shall consider briefly the fate of *C*-nitroso-carbonyl compounds when they are generated in the absence of dienes, mono-olefins, or phosphines. Two earlier studies reported the oxidation of benzohydroxamic acid with aqueous

periodic acid. In one¹² the major product was *O*-benzoylbenzohydroxamic acid (40%), PhCONHOCOPh, and in the other¹³ the products were *O*-benzoylbenzohydroxamic acid (25%) and benzoic acid (70%). Similarly, we find that oxidation of benzohydroxamic acid with tetraethylammonium periodate in dichloromethane, under our standard conditions, gives *O*-benzoylbenzohydroxamic acid (17%) and benzoic anhydride (25%). It appears therefore that benzohydroxamic acid is converted by oxidation into some electrophilic species able to benzoylate water or benzohydroxamic acid or to decompose to form benzoic anhydride. Further, when the adduct (3; R = Ph) was heated alone in benzene, benzoic anhydride was formed, along with DMA, in good (73%) yield. When this last experiment was conducted in an evacuated, sealed tube, nitrous oxide was detected by mass-spectrometry in the evolved gases. This suggests that nitrosocarbonylbenzene decomposes according to equation (1). However, the formation of *O*-

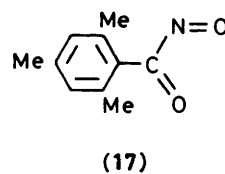


benzoylbenzohydroxamic acid, referred to above, cannot occur solely from the reaction of benzoic anhydride with benzohydroxamic acid. This was demonstrated by heating the adduct (3; R = Ph) in benzene with an excess of benzohydroxamic acid. *O*-Benzoylbenzohydroxamic acid was formed in a yield [83% based on (3; R = Ph)] greater than the maximum (50%) expected from the benzoic anhydride formed according to equation (1). The foregoing results are most simply accommodated by an ionic mechanism involving initial dimerisation of nitrosocarbonylbenzene. In the dimer [represented arbitrarily as the *trans* form (15)] both benzoyl groups are attached to nitrogen carrying a partial positive charge and, consequently, might be detached by a nucleophile giving, after proton transfer, hyponitrous acid, HON=NOH, a known¹⁴ source of nitrous oxide. Alternatively, the dimer might behave like an *N*-acylnitronium¹⁵ and rearrange to the *O*-benzoyl derivative (16), which could collapse to give benzoic anhydride and nitrous oxide. However, a radical chain process, initiated by homolysis of nitrosocarbonylbenzene to give a benzoyl radical and nitric oxide, cannot be excluded. The oxidation of 2,4,6-trimethylbenzohydroxamic acid was carried out in the hope that the *ortho* methyl groups would stabilise the derived nitrosocarbonyl compound (17) and allow its detection in solution or even isolation. Oxidation of this hydroxamic acid in the presence of thebaine (1), in the usual way, gave the expected adduct (4; R = 2,4,6-trimethylphenyl), thus indicating the transient formation of (17). However, oxidation in the absence of thebaine gave 2,4,6-trimethylbenzoic anhydride (48%) and,

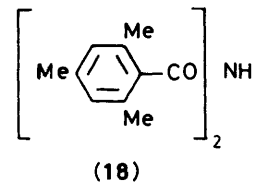


(15)

(16)



(17)



(18)

curiously, the imide (**18**) (4.6%), but at no stage of the oxidation was any blue or green colour observed that might have been attributed to a transient C-nitroso-compound.

Experimental

M.p.s were determined with a Kofler hot-stage apparatus. N.m.r. spectra were recorded at 60 MHz for deuteriochloroform solutions with tetramethylsilane as internal standard. I.r. spectra were recorded for KBr discs. Except where otherwise stated, light petroleum refers to the fraction b.p. 60–80 °C.

3-Benzoyl-2,3-oxazabicyclo[2.2.1]hept-5-ene (5; R = Ph).—Benzohydroxamic acid (2.0 g, 15 mmol) was added in portions with stirring during 15 min to freshly distilled cyclopentadiene (660 mg, 10 mmol) and tetraethylammonium periodate (2.50 g, 8 mmol) in dichloromethane (125 ml) at 0 °C. Stirring was continued for 45 min and the mixture was then washed successively with aqueous sodium thiosulphate, 10% aqueous sodium hydroxide, and brine. The dichloromethane solution was dried (MgSO₄) and evaporated to yield the adduct (**5; R = Ph**), which crystallised as prisms (1.50 g, 74%), m.p. 78–79 °C (from benzene–light petroleum) (lit.⁸ 73–75.5 °C) (Found: C, 71.4; H, 5.5; N, 6.9. Calc. for C₁₂H₁₁NO₂: C, 71.6; H, 5.5; N, 7.0%); ν_{\max} . 1 630 cm⁻¹; δ 1.78 (dm, J 9 Hz, 7-H), 2.10 (dm, J 9 Hz, 7-H), 5.26 (br s, 1- and 4-H), 6.35 (m, 5- and 6-H), and 7.1–7.8 (m, Ph); *m/z* 201.

3-Acetyl-2,3-oxazabicyclo[2.2.1]hept-5-ene (5; R = Me).—Prepared from acetohydroxamic acid and cyclopentadiene, according to the foregoing method, the adduct (**5; R = Me**) was obtained as an undistillable oil (70%). Chromatography on grade III, neutral alumina and elution with chloroform gave pure material; ν_{\max} . (thin film) 1 662 cm⁻¹; δ 2.00 (s, Me), 1.95 (m, CH₂), 5.29 (br s, 1- and 4-H), and 6.45 (m, 5- and 6-H); *m/z* 139.

3-Benzoyl-2,3-oxazabicyclo[2.2.2]oct-5-ene (6).—Prepared from benzohydroxamic acid and cyclohexa-1,3-diene following the method described for (**5; R = Ph**), the adduct (**6**) (84%) formed needles, m.p. 108–110 °C [from benzene–light petroleum (b.p. 40–60 °C)] (lit.¹⁶ 105–108 °C) (Found: C, 72.4; H, 6.0; N, 6.3. Calc. for C₁₃H₁₃NO₂: C, 72.6; H, 6.05; N, 6.5%); ν_{\max} . 1 640 cm⁻¹; δ 1.4–2.4 [m, (CH₂)₂], 4.74 (br s, CH), 5.10 (br s, CH), 6.52 (m, 5-H and 6-H), 7.1–7.8 (m, Ph); *m/z* 215.

10-Benzoyl-9,10-oxazatricyclo[4.2.2.0^{2,5}]deca-3,7-diene (7).—The adduct (**3; R = Ph**) (34 mg) and cyclo-octatetraene (0.1 ml) were heated in benzene at 80 °C under nitrogen for 6 h. Chromatography of the mixture on silica plates developed in chloroform gave the *cyclo-octatetraene adduct (7)* (14.5 mg, 61%), m.p. 114–116 °C [from benzene–light petroleum (b.p. 40–60 °C)] (Found: C, 75.4; H, 5.4; N, 5.5. C₁₅H₁₃NO₂ requires C, 75.3; H, 5.5; N, 5.85%); ν_{\max} . 1 645 cm⁻¹; δ 3.32 (m, 2- and 5-H), 4.90 (m, 1- or 6-H), 5.27 (m, 1- or 6-H), 6.01 (s, 3- and 4-H), 6.25 (m, 7- and 8-H), and 7.2–7.8 (m, Ph); *m/z* 239.

Alternatively, benzohydroxamic acid (200 mg, 1.5 mmol) was oxidised with tetraethylammonium periodate (250 mg) in the presence of cyclo-octatetraene dibromide (**8**)⁵ (264 mg, 1.0 mmol), as described from the preparation of (**5; R = Ph**), to give an oily mixture (381 mg, 92%) of the diastereoisomers (**9a**) and (**9b**), ν_{\max} . (liquid film) 1 640 cm⁻¹; *m/z* 399. This mixture (80 mg) in dry, redistilled dimethyl sulphoxide (2 ml) was stirred under nitrogen at room temperature with zinc powder⁶ (100 mg) for 20 h and then for 14 h after addition of more zinc powder (100 mg). The reaction mixture was diluted with water (100 ml), filtered, and the filtrate extracted with dichloromethane (3 × 25 ml). The extract was dried (MgSO₄) and evaporated. The

residue was chromatographed, as before, to give the adduct (**7**) (34 mg, 71%) having physical properties identical with those of a sample prepared using (**3; R = Ph**).

Retro-Diels–Alder Reactions of the Cyclopentadiene Adduct (5; R = Ph).—The adduct (**5; R = Ph**) (20 mg, 0.1 mmol) and thebaine (**1**) (31 mg, 0.1 mmol) were heated in benzene (5 ml) under nitrogen at 60 °C. The reaction was complete (t.l.c. control) in 6.5 h. Chromatography of the products on silica plates developed with chloroform gave the thebaine adduct (**4; R = Ph**) (31 mg, 69%), m.p. 170–172 °C (from benzene–light petroleum), identical with a sample prepared by the standard method.¹ Similarly, the adduct (**5; R = Ph**) (40.6 mg, 0.2 mmol) and triphenylphosphine (52.4 mg, 0.2 mmol) were heated in benzene at 80 °C. The i.r. spectra of aliquots were compared with those of the adduct (**5; R = Ph**) (1 650 cm⁻¹) and phenyl isocyanate (2 250 cm⁻¹). After 3 h the band at 1 650 cm⁻¹ had disappeared and that at 2 250 cm⁻¹ had increased to maximum intensity.

The 'Ene' Reaction of Nitrosocarbonylbenzene and 1-Allyl-3,4-methylenedioxybenzene.—The adduct (**3; R = Ph**) (200 mg) and 1-allyl-3,4-methylenedioxybenzene (9 ml) were heated at 85 °C for 1.5 h. The mixture was diluted with ether and extracted three times with 5% aqueous sodium hydroxide. The extracts were acidified with hydrochloric acid and extracted with ether. The ethereal extracts were washed with water, dried, and evaporated to give *N*-(3,4-methylenedioxy-cinnamyl)benzohydroxamic acid (**12; R = Ph**) (112 mg, 65%), m.p. 153–154 °C (from ethyl acetate–hexane) (Found: C, 68.6; H, 5.3. C₁₇H₁₅NO₄ requires C, 68.7; H, 5.1%); λ_{\max} . (EtOH) 265 (ε 18 100), 270 (18 100), and 307 nm (8 700); ν_{\max} . 3 200 and 1 605 cm⁻¹; δ 4.38 (d, J 5 Hz, CH₂N), 5.95 (s, OCH₂O), 6.08 (dt, J 16 and 5.5 Hz, CH₂CH=CHAr), 6.47 (d, J 16 Hz, CH₂CH=CHAr), 6.65–6.95 (3 H, m, ArH), 7.45–7.70 (m, Ph), and 8.6 (br s, OH, exchangeable with D₂O); *m/z* 297.

Synthesis of N-(3,4-Methylenedioxy-cinnamyl)benzohydroxamic Acid (12; R = Ph).—3,4-Methylenedioxy-cinnamaldehyde oxime¹⁷ (0.53 g) in methanol (50 ml) containing a trace of Methyl Orange indicator was treated¹⁸ with sodium cyanoborohydride (0.12 g) with stirring at room temperature. Methanolic hydrogen chloride was added periodically to maintain the solution at pH 3. Further quantities of sodium cyanoborohydride were added after 2 h (0.11 g) and 3 h (0.10 g). The mixture was evaporated and the residue dissolved in dilute hydrochloric acid. The solution was washed with ether then made alkaline with sodium hydroxide and extracted with ether. The extracts were washed with brine, dried (MgSO₄), and evaporated to afford *N*-(3,4-methylenedioxy-cinnamyl)-hydroxylamine (0.28 g) as an unstable solid. This was dissolved in ether and extracted into 0.5 M-hydrochloric acid (2 × 3 ml). The extracts were treated at room temperature with sodium hydrogen carbonate (0.62 g) and water (15 ml) followed by benzoyl chloride (0.25 ml). The resulting suspension was shaken for 0.5 h and the precipitate was collected, washed with water and a little ethanol, and dissolved in ether. The solution was extracted with aqueous sodium hydroxide and the extracts were neutralised and re-extracted with ether to afford the hydroxamic acid (**12; R = Ph**) (0.25 g), which was identical with the product from the foregoing 'ene' reaction.

The 'Ene' Reaction of Nitrosocarbonylmethane and 1-Allyl-3,4-methylenedioxybenzene.—The adduct (**3; R = Me**) (0.14 g) and 1-allyl-3,4-methylenedioxybenzene (7.5 ml) were heated at 85–90 °C for 2 h. The mixture was worked up as described for the experiment using (**3; R = Ph**) to give *N*-(3,4-methylenedioxy-cinnamyl)acetohydroxamic acid (**12; R = Me**) as plates, m.p. 116–117 °C (from ethyl acetate–light petroleum) (Found: C,

61.2; H, 5.9; N, 6.1. $C_{12}H_{13}NO_4$ requires C, 61.3; H, 5.6; N, 5.95%; ν_{\max} , 3 240 and 1 592 cm^{-1} ; δ 2.16 (s, Me), 4.34 (d, J 6 Hz, CH_2N), 5.92 (s, OCH_2O), 6.00 (dt, J 16 and 6 Hz, $CH_2CH=CHAr$), 6.48 (d, J 16 Hz, $CH_2CH=CHAr$), 6.65–6.95 (3 H, m, ArH), and 8.52 (br s, OH, exchangeable with D_2O); m/z 235.

The 'Ene' Reaction of Nitrosocarbonylbenzene and Oct-1-ene.—The adduct (**3**; R = Ph) (0.2 g) and oct-1-ene (9 ml) were heated in benzene (6 ml) at 80–90 °C for 2 h. Work-up of the product, as before, gave *N*-oct-2-enylbenzohydroxamic acid (74 mg) as a waxy solid which could not be crystallised (Found: m/z 247.1571. $C_{15}H_{21}NO_2$ requires M , 247.1572; ν_{\max} , 3 210, 1 610, and 1 600 cm^{-1} ; δ 0.90 (distorted t, Me), 1.1–1.6 [6 H, m, $(CH_2)_3$], 1.7–2.3 (m, allylic CH_2), 4.1–4.2 (m, NCH_2), 5.5–5.8 (2 H, m, vinyl H), 7.50 (br s, Ph), and 7.9 (br s, OH, exchangeable with D_2O).

The 'Ene' Reaction of Nitrosocarbonylbenzene and 2,5-Dimethylhexa-2,4-diene.—The adduct (**3**; R = Ph) (0.1 mmol) and 2,5-dimethylhexa-2,4-diene (0.2 mmol) were heated in benzene (2 ml) at 80 °C for 5 h. The mixture was chromatographed on silica plates, developed with chloroform, to give *N*-(2,5-dimethylhexa-1,4-dien-3-yl)benzohydroxamic acid (**14**) (23 mg, 94%), m.p. 58–60 °C (from benzene–light petroleum) (Found: m/z 245.1416. $C_{15}H_{19}NO_2$ requires M , 245.1416; ν_{\max} , 3 420 and 1 616 cm^{-1} ; δ 1.31 (s, Me), 1.76 (s, Me), 1.77 (s, Me), 4.95 (br s, CH_2), 5.09 (br d, J 9 Hz, vinyl H), 5.59 (br d, J 9 Hz, NCH), and 7.47 (br s, Ph).

Oxidation of Benzohydroxamic Acid.—Benzohydroxamic acid (300 mg) was added in portions with stirring to tetraethylammonium periodate (430 mg) in dichloromethane (28 ml) at 0 °C. After 1 h the solution was washed with aqueous sodium thiosulphate, aqueous sodium hydrogen carbonate, and brine, and was then dried ($MgSO_4$) and evaporated. The residue was chromatographed on silica plates developed with dichloromethane to afford benzoic anhydride (25%) and *O*-benzoylbenzohydroxamic acid (17%).

Thermal Decomposition of the Adduct (3; R = Ph).—The adduct (**3**; R = Ph) (60 mg) was heated under reflux overnight in benzene (10 ml). The solution was evaporated and the residue chromatographed on silica plates developed with dichloromethane–light petroleum (b.p. 40–60 °C) (1:1) to afford benzoic anhydride (15 mg). The experiment was repeated and the yield of benzoic anhydride (73%) was determined by g.l.c. (1%, OV1, 80 °C). In a third experiment, using a sealed, evacuated tube, the evolved gases were examined by mass spectrometry. Nitrous oxide (m/z 44) was detected (benzene vapour control).

The Reaction of Benzohydroxamic Acid with the Adduct (3; R = Ph).—The adduct (**3**; R = Ph) (34 mg) and benzohydroxamic acid (137 mg) were heated in benzene (2 ml) at 80 °C for 2 h. The mixture was diluted with ether and washed with aqueous ferric nitrate to remove benzohydroxamic acid. Chromatography of the product mixture on silica plates developed with chloroform–ethyl acetate (95:5) gave *O*-benzoylbenzohydroxamic acid (20 mg, 83%), m.p. 159–161 °C (from chloroform–light petroleum), undepressed upon admixture with reference material. In a separate experiment the evolved gases were shown, as before, to contain nitrous oxide.

6 β ,14 β -(*N*-2,4,6-Trimethylbenzoylperoxyimino)-6,14-dihydro-thebaine (**4**; R = 2,4,6-trimethylphenyl).—2,4,6-Trimethyl-

benzohydroxamic acid¹⁹ (240 mg) was added in portions during 10 min to thebaine (100 mg) in ethyl acetate (5 ml) and tetraethylammonium periodate (200 mg) in 0.2 M-acetate buffer (pH ca. 6) (5 ml) with vigorous stirring at 0 °C. After 1 h the layers were separated and the aqueous layer was made alkaline with sodium hydrogen carbonate, and extracted with ethyl acetate. The combined ethyl acetate solutions were washed with brine, dried, and evaporated. The residue was chromatographed on silica plates, developed with chloroform, to give the adduct (**4**; R = 2,4,6-trimethylphenyl) (127 mg), which crystallised only after prolonged storage. Recrystallisation gave needles, m.p. 188–190 °C (from benzene–light petroleum) (Found: C, 71.1; H, 6.9; N, 6.0. $C_{29}H_{32}N_2O_5$ requires C, 71.3; H, 6.6; N, 5.7%; ν_{\max} , 1 652 cm^{-1} ; δ 2.05 (s, ArMe), 2.21 (s, ArMe), 2.40 (s, ArMe), 2.50 (s, NMe), 3.08 (s, 6-OMe), 3.80 (s, 3-OMe), 4.50 (s, 5-H), 5.00 (d, J 7 Hz, 9-H), 6.05 and 6.25 (ABq, J 9 Hz, 7- and 8-H), and 6.5–6.9 (4 H, m, ArH); m/z 488.

Oxidation of 2,4,6-Trimethylbenzohydroxamic Acid.—2,4,6-Trimethylbenzohydroxamic acid (300 mg) was added in portions during 10 min to tetraethylammonium periodate (340 mg) in dichloromethane (21 ml) with stirring at 0 °C. After 1 h the mixture was washed with aqueous sodium thiosulphate, aqueous sodium hydrogen carbonate, and water and was dried and evaporated. The residue (200 mg) was chromatographed on silica plates to give 2,4,6-trimethylbenzoic anhydride (125 mg, 48%) and bis(2,4,6-trimethylbenzoyl)amine (**18**) (12 mg, 4.6%).

Acknowledgements

We thank the S.R.C. for financial support.

References

- G. W. Kirby and J. G. Sweeny, *J. Chem. Soc., Perkin Trans. 1*, 1981, 3250.
- G. W. Kirby, *Chem. Soc. Rev.*, 1977, 6, 1.
- J. E. T. Corrie, G. W. Kirby, and R. P. Sharma, *J. Chem. Soc., Perkin Trans. 1*, 1982, 1571.
- L. A. Paquette, *Tetrahedron*, 1975, 31, 2855.
- W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Annalen*, 1948, 560, 1.
- M. Oda, Y. Kayama, and Y. Kitahara, *Tetrahedron Lett.*, 1974, 23, 2019.
- Cf. G. W. Kirby, J. W. M. Mackinnon, and R. P. Sharma, *Tetrahedron Lett.*, 1977, 215.
- Le H. Dao, J. M. Dust, D. Mackay, and K. N. Watson, *Can. J. Chem.*, 1979, 57, 1712; see also G. Just and L. Cutrone, *ibid.*, 1976, 54, 867.
- D. Ranganathan, S. Ranganathan, and C. B. Rao, *Tetrahedron*, 1981, 37, 637.
- G. T. Knight and B. Pepper, *Tetrahedron*, 1971, 27, 6201; M. E. Cain, G. T. Knight, P. M. Lewis, and B. Saville, *Rubber J.*, 1968, 150, 10; M. E. Cain, G. T. Knight, and P. M. Lewis, *Chem. Ind. (London)*, 1970, 126.
- G. E. Keck, R. R. Webb, and J. B. Yates, *Tetrahedron*, 1981, 37, 4007; G. E. Keck and J. B. Yates, *J. Org. Chem.*, 1982, 47, 3590.
- T. F. Emery and J. B. Neiland, *J. Org. Chem.*, 1962, 27, 1075.
- J. E. Rowe and A. D. Ward, *Aust. J. Chem.*, 1968, 21, 2761.
- M. N. Hughes, *Q. Rev. Chem. Soc.*, 1968, 22, 1.
- S. A. Hussain, A. H. Sharma, M. J. Perkins, and D. Griller, *J. Chem. Soc., Chem. Commun.*, 1979, 289.
- G. E. Keck and S. A. Fleming, *Tetrahedron Lett.*, 1978, 4763.
- A. Quilico, *Gazz. Chim. Ital.*, 1928, 58, 317.
- R. F. Borch, M. D. Bernstein, and H. D. Durst, *J. Am. Chem. Soc.*, 1971, 93, 2897.
- C. Grundmann and H. D. Frommeld, *J. Org. Chem.*, 1966, 31, 157.

Received 23rd August 1984; Paper 4/1469