Formation and Dienophilic Reactions of Transient *C*-Nitrosocarbonyl Compounds

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Oxidation of benzohydroxamic acid with tetraethylammonium periodate in the presence of the conjugated diene thebaine (1) gave the cycloadduct 6β,14β-(*N*-benzoylepoxyimino)-6,14-dihydrothebaine (2; R = Ph), in high yield. The corresponding *N*-acetyl derivative (2; R = Me) was prepared similarly using acetohydroxamic acid. Likewise, 2-benzoyl- and 2-acetyl-3,6-dihydro-2*H*-1,2-oxazine (5; R = Ph) and (5; R = Me) were obtained from buta-1,3-diene, and the *N*-benzoyl and *N*-acetyl derivatives of 9,10-epoxyimino-9,10-dihydro-9,10-dimethylanthracene (6; R = PhCO) and (6; R = Ac) from 9,10-dimethylanthracene (DMA). These reactions are believed to involve the formation of nitrosocarbonylbenzene or nitrosocarbonylmethane, representatives of a new class of transient, reactive species. The cycloadduct (6; R = Ac) decomposed in benzene at 60 °C in the presence of thebaine (1) to give the thebaine adduct (2; R = Me) and DMA. First-order kinetics were observed for the release of DMA, consistent with slow dissociation of the adduct (6; R = Ac) followed by rapid capture of nitrosocarbonylmethane by thebaine. The related adduct (6; R = PhCO) behaved similarly. DMA adducts of the type (6) are valuable in studies on the reactions of nitrosocarbonyl compounds, especially with co-reactants sensitive to oxidation. Thus (6; R = Ac) and 1,3-diphenylisobenzofuran (7) reacted cleanly in benzene at 80 °C to give the *O*-acetyloxime (10) of 1,2-dibenzoylbenzene, possibly *via* the *N*-acetylnitrone (9) derived from the initially formed cycloadduct (8).

NITROSYL cyanide (O=N–C≡N) undergoes Diels–Alder reactions with conjugated dienes to form 2-cyano-3,6-dihydro-2*H*-1,2-oxazines.[1,2] It appears that the electron-withdrawing cyano-group enhances the dienophilic character of the *C*-nitroso-group while presenting minimal steric hindrance to cycloaddition. We considered [3] that compounds of the general class XC(=Y)NO, where Y may be an electronegative element O, N, or S, should also be reactive, electron-demanding dienophiles. We describe here the formation and reactions of *C*-nitrosocarbonyl compounds, the first members of this new class (X = C≤; Y = O) of transient species.[4]

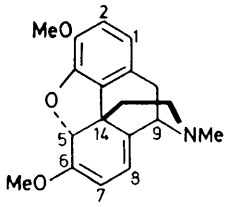
C-Nitrosocarbonyl compounds had been proposed several times prior to our studies as possible intermediates in organic reactions, *viz.* in the pyrolysis of mixtures of nitrite esters and aldehydes,[5] in the pyrolysis of azidoformates in dimethyl sulphoxide,[6] and in the oxidation of hydroxamic acids with sodium periodate, iodine, *N*-bromosuccinimide, or potassium ferricyanide [7] or with dicyclohexylcarbodi-imide and phosphoric acid.[8] In none of these studies were the proposed intermediate species, RCONO or ROCONO, observed directly and, in all cases, product formation involved cleavage of the relevant CO–N bond. Hydroxamic acids, RCONHOH or ROCONHOH, are readily prepared and may be oxidised under mild conditions with a wide variety of reagents.[9] We considered that nitrosocarbonyl compounds, if formed, might be trapped as cycloadducts when the oxidations were carried out in the presence of conjugated dienes. Tetraethylammonium periodate,[10] which is freely soluble in both water and organic solvents, was chosen as a convenient, mild oxidant. For initial experiments, the alkaloid thebaine (1) was selected as the conjugated diene since the spectroscopic and chemical properties of its adducts with *C*-nitroso-compounds were well understood.[1,11,12]

RESULTS AND DISCUSSION

Benzohydroxamic acid (2.3 mol equiv.) was added in portions to a stirred mixture of thebaine (1) (1 mol. equiv.) and tetraethylammonium periodate (1.45 mol. equiv.) in ethyl acetate and aqueous buffer (pH 6) at 0 °C. The major product (97%) was identified as the cycloadduct (2; R = Ph) from its spectroscopic properties and by hydrolysis with hot aqueous methanolic hydrogen chloride to give the known [12] compound (3; R = H). The yield of the adduct (2; R = Ph) was high (77%) even from equimolar amounts of thebaine, periodate, and benzohydroxamic acid, indicating a remarkably efficient capture of the putative intermediate, nitrosocarbonylbenzene, PhCONO. Similarly, thebaine was converted by acetohydroxamic acid and periodate into the corresponding adduct (2; R = Me). This was reduced with hydrogen and platinum oxide to give the 7,8-dihydro-derivative and was hydrolysed with acid catalysis to give the compound (3; R = Ac). The structure of the latter was established unambiguously by rearrangement with sodium methoxide to the phenol (4; R = H) which, upon acetylation, gave the known [12] diacetyl derivative (4; R = Ac). The formation of cycloadducts was also observed using buta-1,3-diene, the products (5; R = Ph or Me) being identified by comparison with samples prepared from 3,6-dihydro-2*H*-1,2-oxazine.[13]

The formation of cycloadducts of the type (2)/(5) does not necessarily imply the involvement of nitrosocarbonylbenzene or -methane as a discrete intermediate. Confirmatory evidence was obtained in the following way. We had shown [2] that the adduct (6; R = CN) of 9,10-dimethylanthracene (DMA) and nitrosyl cyanide dissociates smoothly, and reversibly, at 40 °C and that the liberated nitrosyl cyanide may be captured efficiently by conjugated dienes present in the reaction mixture. The

related adducts (6; R = PhCO) and (6; R = Ac) were therefore prepared by oxidation of benzo- and aceto-hydroxamic acid, respectively, with tetraethylammonium periodate in dichloromethane in the presence of DMA. Both these adducts were readily purified by



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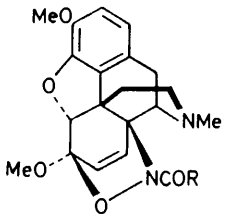

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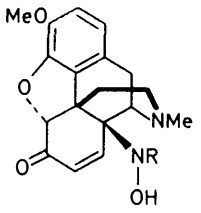

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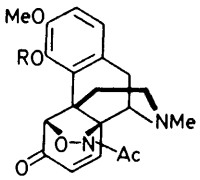

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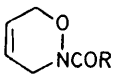

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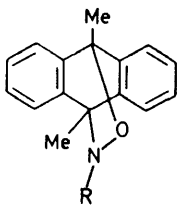
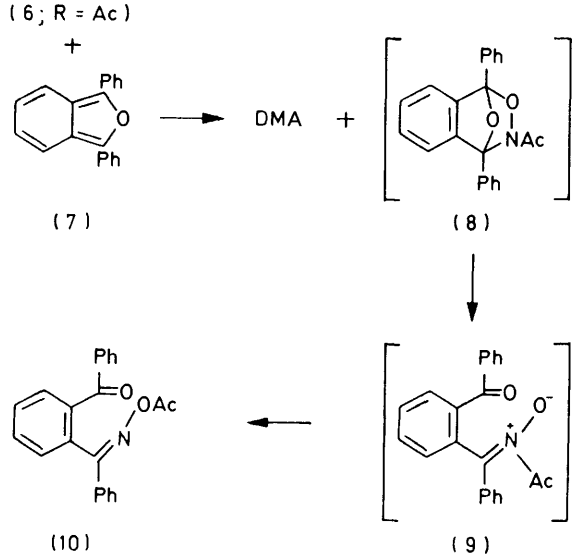


(6)

crystallisation and were stable without special precautions for extended periods. However, like (6; R = CN) [2] but unlike (2; R = Ph or Me), they did not show molecular ion peaks in their mass spectra and did show peaks attributable to DMA. The thermal transfer of nitrosocarbonylbenzene from (6; R = PhCO), and of nitrosocarbonylmethane from (6; R = Ac), to thebaine (1) was accomplished in refluxing benzene. The corresponding adducts (2) of thebaine were isolated from the reaction mixtures, after chromatographic separation from DMA, and shown to be identical with samples prepared by the foregoing, ' direct ' method. Insight into the mechanism of these transfer reactions was obtained by kinetic studies, in the manner described for the nitrosyl cyanide adduct (6; R = CN).[2] Thus, the adduct (6; R = Ac) (4 mM) and thebaine (1) (4 mM) were kept in benzene at 60 °C, the progress of reaction being monitored by the appearance of DMA (absorption at 385 nm). First-order kinetics were observed, $k = 4.4 \times 10^{-5}$ s^{-1}, and higher initial concentrations of thebaine (8 mM and 16 mM) did not significantly increase the rate of release of DMA, the rate constants (k) being 4.8×10^{-5} and 4.9×10^{-5} s^{-1}, respectively. These observations are consistent with a slow, reversible dissociation (rate constant k) of (6; R = Ac) followed by rapid and irreversible capture of nitrosocarbonylmethane by the reactive diene, thebaine (1). Similar results were obtained with (6; R = PhCO) (4 mM) and thebaine (1) at two initial concentrations (4 and 8 mM) in benzene at 60 °C; the first-order rate constants (k) for the appearance of DMA were 5.4×10^{-5} and 4.7×10^{-5} s^{-1}, respectively. Both the adducts

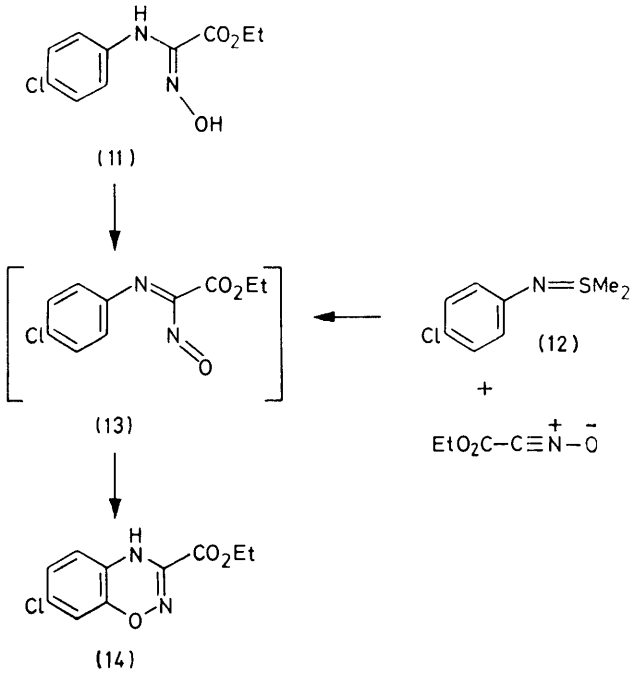


(6; R = Ac) and (6; R = PhCO) dissociated much more slowly than the nitrosyl cyanide adduct (6; R = CN), their dissociations rates at 60 °C being similar to that of (6; R = CN) at only 40 °C ($k = 6.8 \times 10^{-5}$ s^{-1}).[2] Also the adducts (6; R = Ac) and (6; R = PhCO), unlike (6; R = CN), decomposed slowly at 60 °C in benzene even in the absence of thebaine. This decomposition was kinetically complex, and was not studied in detail, but it presumably reflects the intrinsic thermal instability of nitrosocarbonyl compounds.

Dimethylanthracene adducts of the type (6) have proved to be valuable in studies on the reactions of nitrosocarbonyl compounds,[14] especially with co-reactants which are sensitive to the oxidising conditions used in the direct route from hydroxamic acids. This is illustrated here by the reaction of the adduct (6; R = Ac) with the readily oxidised 1,3-diphenylisobenzofuran (7) in refluxing benzene under nitrogen. The major product, apart from DMA, was identified as the *O*-acetyloxime (10) from its spectroscopic properties and hydrolysis to give the mono-oxime of 1,2-dibenzoylbenzene. No intermediates were detected in this reaction but it is likely that the cycloadduct (8) is first formed. If this were to rearrange to the *N*-acetylnitrone (9) then the formation of (10) would follow since it is known [15] that *N*-acylnitrones are transformed rapidly into the related *O*-acyloximes.

The foregoing observations provide strong circumstantial evidence for the formation and free, if fleeting existence of nitrosocarbonyl-arenes and -alkanes. Inde-

pendent studies [14,16] which have appeared since our original publication [4] lend support to the idea that nitrosocarbonyl compounds constitute a new class of transient, reactive intermediates. However, to date, they have evaded detection by direct physical methods. The same is true of a closely related class of *C*-nitroso-imines, discovered by Gilchrist, Rees *et al.*[17] For example,



oxidation of the amidoxime (11) with lead tetra-acetate or treatment of the sulphimide (12) with ethyl cyanoformate *N*-oxide gave the oxadiazine (14). However, when each experiment was repeated in the presence of thebaine (1) the intermediate (13) was trapped efficiently as a cycloadduct analogous to (2).

EXPERIMENTAL

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

Tetraethylammonium Periodate.—This was prepared by the published method.[10] **CAUTION.** Evaporation of the aqueous solution and extraction of the crude salt with hot t-butyl alcohol should be carried out behind a protective screen. Overheating of the salt may cause violent decomposition. In our hands, recrystallised tetraethylammonium periodate appears to be stable when stored and handled normally.

6β,14β-(N-*Benzoylepoxyimino*)-6,14-*dihydrothebaine* (2; R = Ph).—Thebaine (1) (500 mg) in ethyl acetate (25 ml) and tetraethylammonium periodate (750 mg) in aqueous 0.2M-sodium acetate (25 ml), adjusted to pH *ca.* 6 with hydrochloric acid, were stirred at 0 °C. Benzohydroxamic acid (500 mg) was added in small portions during 10 min. After 1 h, sodium disulphite was added in small portions until the solution had become pale yellow. The hydroiodide of (2; R = Ph) crystallised from the mixture and was collected, washed with water and ethyl acetate, and dried (yield 897 mg). The *cycloadduct* (2; R = Ph) *hydroiodide* had m.p. 207—209 °C (from MeOH–$CHCl_3$) (Found: C, 54.6; H, 4.7; N, 5.1. $C_{26}H_{27}IN_2O_5$ requires C, 54.4; H, 4.7; N, 4.9%). Treatment of a suspension of this salt in chloroform with saturated aqueous sodium hydrogen carbonate gave the *cycloadduct* (2; R = Ph), m.p. 168—170 °C (from benzene–light petroleum or ethyl acetate) (Found: C, 70.1; H, 5.6; N, 6.35. $C_{26}H_{26}N_2O_5$ requires C, 69.9; H, 5.9; N, 6.3%); $\nu_{max.}$ (KBr) 1 660 cm^{-1}; τ 2.12—2.72 (m, PhCO), 3.32 and 3.42 (ABq, *J* 8 Hz, 2-H and 1-H), 3.70 and 4.06 (ABq, *J* 9 Hz, 8-H and 7-H), 5.08 (d, *J* 7 Hz, 9-H), 5.40 (s, 5-H), 6.20 (s, 3-OMe), 7.04 (s, 6-OMe), and 7.52 (s, NMe); *m/z* 446. The yield of (2; R = Ph) from equimolar amounts of thebaine, tetraethylammonium periodate, and benzohydroxamic acid was 77%. Tetraethylammonium periodate may be replaced by sodium periodate in this preparation of (2; R = Ph) providing that the two-phase reaction mixture is stirred vigorously.

The cycloadduct (2; R = Ph) (500 mg) was hydrolysed in refluxing water (5 ml), methanol (5 ml), and concentrated hydrochloric acid (1 ml) for 1 h. The solution was concentrated under reduced pressure until crystals began to separate. After 1 h at room temperature filtration yielded 14-hydroxyaminocodeinone (3; R = H) hydrochloride (342 mg) which was identical spectroscopically with material prepared by an alternative method.[12]

6β,14β-(N-*Acetylepoxyimino*)-6,14-*dihydrothebaine* (2; R = Me).—The oxidation of acetohydroxamic acid with tetraethylammonium periodate or sodium periodate in the presence of thebaine was carried out as described above for benzohydroxamic acid. The reaction mixture was basified with aqueous sodium hydrogen carbonate and the ethyl acetate layer was separated. The aqueous layer was extracted with ethyl acetate and the combined ethyl acetate layers were washed with aqueous sodium thiosulphate then dried (Na_2SO_4) and evaporated. The *cycloadduct* (2; R = Me) (96%) had m.p. 192—194 °C (from benzene–light petroleum or ethyl acetate) (Found: C, 65.8; H, 6.1; N, 7.5. $C_{21}H_{24}N_2O_5$ requires C, 65.6; H, 6.3; N, 7.3%); $\nu_{max.}$ (KBr) 1 680 cm^{-1}; τ 3.36 and 3.46 (ABq, *J* 8 Hz, 2-H and 1-H), 3.90 and 4.00 (ABq, *J* 9 Hz, 8-H and 7-H), 5.22 (d, *J* 7 Hz, 9-H), 5.44 (s, 5-H), 6.22 (s, 3-OMe), 6.44 (s, 6-OMe), 7.55 (s, NMe), and 7.99 (s, Ac); *m/z* 384.

14β-(N-*Acetylhydroxyamino*)*codeinone* (3; R = Ac).—The cycloadduct (2; R = Me) (1 g) was dissolved in N-hydrochloric acid (5 ml) at room temperature then kept at 0 °C for 5 d to allow slow separation of the product. Filtration gave 14β-(N-*acetylhydroxyamino*)*codeinone hydrochloride hydrate* (547 mg), m.p. 206—208 °C (decomp.) (from EtOH) (Found: C, 56.8; H, 5.5; N, 6.45. $C_{20}H_{23}ClN_2O_5 \cdot H_2O$ requires C, 56.5; H, 5.9; N, 6.6%); $\nu_{max.}$ (KBr) 3 420, 1 680, and 1 655 cm^{-1}.

5β,14β-(N-*Acetylepoxyimino*)*thebainone* (4; R = H).—The foregoing hydrochloride (250 mg) in methanol (1 ml) was treated with sodium methoxide prepared from sodium (40 mg) in methanol (5 ml). After 10 min at room temperature the orange solution was evaporated and the residue, in water (7 ml), was treated with an excess of solid carbon dioxide to precipitate the phenol (4; R = H). The *phenol* (4; R = H) melted at 130—132 °C, resolidified at *ca.* 163—165 °C, and remelted at 219—220 °C (decomp.) (from MeOH–H_2O) (Found: C, 61.9; H, 6.3; N, 7.1. $C_{20}H_{22}N_2O_5 \cdot H_2O$ requires C, 61.85; H, 6.2; N, 7.2%); $\nu_{max.}$ (KBr) 3 350 and 1 670 cm^{-1}; τ 2.87 (d, *J* 10 Hz, 8-H), 3.34 (s, 1-H and 2-H),

4.02 (dd, *J* 10 and 2 Hz, 7-H), 4.06 (br s, OH, exchangeable with D_2O), 4.88 (d, *J* 2 Hz, 5-H), 5.73 (d, *J* 7 Hz, 9-H), 6.20 (s, OMe), 7.52 (s, NMe), and 7.88 (s, Ac). Acetylation of (4; R = H) with acetic anhydride in pyridine, in the usual way, gave (4; R = Ac), identical (m.p. and i.r. spectrum) with a sample prepared [12] from (3; R = H).

6β,14β-(N-*Acetylepoxyimino*)-6,7,8,14-*tetrahydrothebaine*. —The cycloadduct (2; R = Me) (192 mg) in ethanol (5 ml) was hydrogenated at ambient temperature and pressure using platinum oxide catalyst (20 mg). Chromatography of the reaction mixture on silica plates developed with chloroform–methanol (96 : 4) gave the cycloadduct (2; R = Me) (48 mg) and the corresponding *dihydro-derivative* (88 mg), m.p. 162—164 °C (from benzene–light petroleum) (Found: C, 65.5; H, 6.8; N, 7.4. $C_{21}H_{26}N_2O_5$ requires C, 65.3; H, 6.8; N, 7.25%); $\nu_{max.}$ (KBr) 1 665 cm^{-1}; τ 3.23 and 3.37 (ABq, *J* 8 Hz, 2-H and 1-H), 5.50 (br s, 5-H), 5.74 (d, *J* 7 Hz, 9-H), 6.14 (s, 3-OMe), 6.54 (s, 6-OMe), 7.60 (s, NMe), and 7.77 (s, Ac); *m/z* 386.

2-*Benzoyl*-3,6-*dihydro*-2H-1,2-*oxazine* (5; R = Ph) *and* 2-*acetyl*-3,6-*dihydro*-2H-1,2-*oxazine* (5; R = Me).—Benzohydroxamic acid (500 mg) was added in portions during 10 min, with stirring, to tetraethylammonium periodate (750 mg) and buta-1,3-diene (*ca.* 2 ml) in nitromethane (25 ml) at −10 °C. The mixture was kept at −10 °C for 20 min then at 5 °C for 30 min. Chloroform (25 ml) was added and the mixture washed successively with aqueous sodium hydrogen carbonate, aqueous sodium disulphite, and water, and then dried and evaporated. The residue was passed through a short column of alumina in chloroform, to remove *NO*-dibenzoylhydroxylamine. Evaporation of the chloroform gave the oily oxazine (5; R = Ph) (441 mg), identical (i.r. and ^1H n.m.r. spectra) with a sample prepared by benzoylation of the parent dihydro-oxazine [13] with benzoic anhydride. Similarly, buta-1,3-diene was converted into the oily oxazine (5; R = Me) with tetraethylammonium periodate and acetohydroxamic acid in dichloromethane. Again, the product was identified by comparison with a sample prepared from the parent [13] dihydro-oxazine with acetic anhydride in pyridine.

9,10-*Dimethylanthracene* (DMA) (with J. E. T. Corrie).—9,10-Bis(chloromethyl)anthracene [18] (20 g) was extracted (Soxhlet) into tetrahydrofuran (350 ml) containing lithium aluminium hydride (4.7 g). After 18 h, the mixture was cooled and treated cautiously with water then aqueous sodium hydroxide then diluted with ether (150 ml) and filtered. The filtrate yielded crude DMA, which crystallised from benzene–light petroleum (b.p. 60—80 °C) as yellow needles (10.8 g), m.p. 182—184 °C (lit.,[18] 180—181 °C). **CAUTION.** 9,10-Bis(chloromethyl)anthracene may cause skin irritation and should be handled with gloves and face-mask in a fume-cupboard.

9,10-(N-*Acetylepoxyimino*)-9,10-*dihydro*-9,10-*dimethylanthracene* (6; R = Ac) (with J. E. T. Corrie).—Acetohydroxamic acid (1.95 g) was added in portions with stirring during 10 min to 9,10-dimethylanthracene (DMA) (2.4 g) and tetraethylammonium periodate (3.0 g) in dichloromethane (150 ml) at 0—5 °C. The mixture was stirred for a further 10 min then tetraethylammonium periodate (1.5 g) was added, followed by acetohydroxamic acid (0.75 g) in portions during 10 min. After 1 h at 0—5 °C, water (100 ml) was added, followed by sufficient aqueous sodium disulphite to discharge the iodine colour. The organic layer was separated and washed with aqueous sodium hydrogen carbonate and then water, then dried and evaporated. The adduct (6; R = Ac) was obtainable directly at this stage by recrystallisation (as follows) of the residue. Better yields were obtained by chromatography on grade III neutral alumina (100 g). DMA was eluted with dichloromethane–light petroleum (b.p. 40—60 °C) (3 : 7) and the adduct (6; R = Ac) (1.6 g) with dichloromethane–light petroleum (b.p. 40—60 °C) (3 : 1). The *adduct* (6; R = Ac) had m.p. 133—136 °C (from ethyl acetate–light petroleum) (Found: C, 77.7; H, 6.2; N, 5.2. $C_{18}H_{17}NO_2$ requires C, 77.4; H, 6.1; N, 5.0%); $\nu_{max.}$ (KBr) 1 680 cm^{-1}; τ 2.62 (m, ArH), 7.26 (s, 9-Me), 7.77 (br s, Ac), and 8.17 (s, 10-Me); *m/z* 206 ($M^{+\bullet}$ −73).

9,10-(N-*Benzoylepoxyimino*)-9,10-*dihydro*-9,10-*dimethylanthracene* (6; R = PhCO) (with J. E. T. Corrie).—Benzohydroxamic acid (2.0 g) was added in portions to 9,10-dimethylanthracene (DMA) (2.0 g) and tetraethylammonium periodate (2.5 g) in dichloromethane (125 ml) at 0—5 °C, as in the foregoing preparation of (6; R = Ac). The mixture was worked up as before except that the crude residue containing DMA and (6; R = PhCO) was dissolved in ether and washed with aqueous sodium hydroxide to remove NO-dibenzoylhydroxylamine. The ethereal solution was washed with water and brine, dried, and evaporated. The residue was chromatographed on alumina, as before. The *adduct* (6; R = PhCO) (1.57 g) had m.p. 127—128 °C (from ethyl acetate–light petroleum) (Found: C, 81.1; H, 5.8; N, 4.0. $C_{23}H_{19}NO_2$ requires C, 80.9; H, 5.6; N, 4.1%); $\nu_{max.}$ (KBr) 1 665 cm^{-1}; τ 2.62 (m, ArH), 7.23 (s, 9-Me), and 7.97 (s, 10-Me); *m/z* 206 ($M^{+\bullet}$ −135).

Kinetic Studies on the Reaction of the Adducts (6) *with Thebaine*.—These were conducted as described [2] for the adduct of 9,10-dimethylanthracene and nitrosyl cyanide but at 60 °C rather than 40 °C. The results are given in the main text. The thermal transfer of nitrosocarbonylmethane from (6; R = Ac) and nitrosocarbonylbenzene from (6; R = PhCO) to thebaine (1) was accomplished in refluxing benzene. The thebaine adducts (2) were identified by comparison with samples prepared as described above.

Reaction of the Adduct (6; R = Ac) *with* 1,3-*Diphenylisobenzofuran* (7).—The adduct (6; R = Ac) (150 mg) and 1,3-diphenylisobenzofuran (7) (100 mg) were heated under reflux in benzene (5 ml) under oxygen-free, dry nitrogen for 30 min. The solvent was evaporated off and the residue chromatographed on silica plates developed with chloroform. Elution of a band at R_f 0.2 gave the *O*-acetyloxime (10) (119 mg), m.p. 107—110 °C (Found: M^+, 343.1202. $C_{22}H_{17}NO_3$ requires *M*, 343.1208). This product (50 mg) in methanol (3 ml) was treated with saturated aqueous sodium hydrogen carbonate (4 drops) at room temperature for 18 h. Chromatography of the product on silica plates gave 1,2-*dibenzoylbenzene mono-oxime* (23 mg), m.p. 127—129 °C (from MeOH) (Found: C, 79.8; H, 5.2; N, 4.5. $C_{20}H_{15}NO_2$ requires C, 79.7; H, 5.0; N, 4.65%); $\nu_{max.}$ (KBr) 3 200 cm^{-1}; *m/z* 301, 284, and 270. This product was shown (i.r. spectrum and mixed m.p.) to be identical with material prepared from 1,2-dibenzoylbenzene and hydroxylamine (1 mol. equiv.). The lack of i.r. carbonyl absorption suggests that this ' oxime ' may exist as the cyclic, hydroxyoxazine, tautomer. The mono-oxime, m.p. 150 °C, reported earlier [19] may have the alternative, oxime stereochemistry.

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