Formation and Thermal Cleavage Reactions of the Cycloadduct of 9,10-Dimethylanthracene and Nitrosyl Cyanide

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Nitrosyl cyanide and 9,10-dimethylanthracene (DMA) (2) reacted at -25 °C to form the crystalline cycloadduct, 9,10-dihydro-9,10-(*N*-cyanoepoxyimino)-9,10-dimethylanthracene (1). The adduct (1) decomposed in the presence of the conjugated diene thebaine (3), to form DMA (2) and the adduct (4) of nitrosyl cyanide and thebaine. First-order kinetics, $k = 6.9 \times 10^{-5} s^{-1}$, were observed for the release of DMA in benzene at 40 °C, consistent with slow dissociation of the adduct (1) followed by rapid capture of nitrosyl cyanide by thebaine. A similar first-order rate, $k = 6.8 \times 10^{-5} s^{-1}$, was observed for the reaction of the adduct (1) and triphenylphosphine (2 mol equiv.) under the same conditions, the products being DMA, triphenylphosphine oxide, and triphenylphosphine *N*-cyano-imide (5). The reactions of nitrosyl cyanide, generated thermally from the adduct (1), were studied with a range of dienes. The conjugated dienes, *N*-cyanomethyl-*N*-northebaine (3; NCH₂CN replacing NMe), *trans,trans*-1,4-diphenylbuta-1,3-diene (6; R = H), and ergosteryl acetate (11) all gave the expected cycloadducts (3,6-dihydro-2*H*-1,2-oxazines). Norbornadiene gave the tetracyclic adduct (10) arising from 1,4-conjugate addition of heractions of the adduct (1) with tetraphenylcyclopentadienone (14), 1,3-diphenyliso-indole (23), diazofluorene (24), and diphenyldiazomethane all took a more complex course leading in each case to the formation of an *N*-cyano-ketimine (alkylidene-cyanamide)

NITROSYL cyanide, formed from nitrosyl chloride and silver cyanide, reacts rapidly with various 1,3-dienes to yield cycloadducts.¹ When prepared in this way, gaseous nitrosyl cyanide contains impurities, for example nitrosyl chloride and nitrogen dioxide, which may react competitively with the dienes or lead to by-products by attack on the olefinic cycloadducts. We describe here ² an alternative, ' clean ' procedure for generating nitrosyl cyanide involving thermal cleavage of the adduct (1) prepared from impure nitrosyl cyanide and 9,10dimethylanthracene (DMA) (2).

RESULTS AND DISCUSSION

When a solution of DMA (2) in dichloromethane was added to nitrosyl cyanide, prepared in the usual way¹ from nitrosyl chloride and an excess of solid silver cyanide, at -25 °C, the green colour of the gas was rapidly discharged. Chromatography of the reaction mixture gave some unchanged DMA, a yellow byproduct, identified as 9-methyl-10-nitromethylanthracene,³ and the desired cycloadduct (1) (20-30%) yield), which was readily purified further by crystallisation. The ¹H n.m.r. spectrum of (1) showed two singlets, at τ 7.75 and 7.83, for the non-equivalent methyl groups [cf. τ 7.00 (s, Me) for DMA] and a broad signal, τ 2.65, for the protons on isolated benzene rings. Additionally, an i.r. band at 2 210 cm⁻¹ confirmed the presence of a cyano-group. Initially, the cycloadduct (1) appeared to be inconveniently stable to heat. It survived sublimation (140 °C, 0.5 mmHg) and, when refluxed in benzene, underwent only minor (ca. 10%) decomposition in 48 h. However, it became clear, as described in the sequel, that the dissociation of (1) into DMA (2) and nitrosyl cyanide takes place readily even at 40 °C and that the apparent thermal stability of (1) arises from the very high rate of recombination.

An equimolar solution of the adduct (1) and the reactive diene thebaine (3) in deuteriochloroform was kept at 35 °C, and examined at intervals by ¹H n.m.r. spectroscopy. The signals for (1) and (3) slowly decreased in intensity and were replaced by signals for DMA (2) and the cycloadduct (4), which had been prepared earlier ¹ from thebaine (3) and impure nitrosyl cyanide. The reaction was complete within 45 h and no significant



amounts of by-products were detected spectroscopically. In a preparative experiment, thebaine (3) and the adduct (1) were refluxed in benzene for 15 min. The products (2) and (4) were isolated and identified. Similarly, *N*cyanomethyl-*N*-northebaine reacted with (1) to give the corresponding thebaine derivative (4; NCH₂CN replacing NMe).¹ The thermal transfer of nitrosyl cyanide from DMA-ONCN (1) to thebaine (3) was then studied kinetically, the progress of the reaction being followed by the appearance of DMA (absorption at 385 nm). First-order kinetics were observed, $k = 6.8 \times 10^{-5}$ s⁻¹,

for the reaction of (1) (4 mm) and (3) (4 mm) in benzene at 40 °C. Higher initial concentrations (8 and 16 mm) of thebaine did not significantly alter the rate of formation of DMA, the observed rate constants being $k = 7.4 \times$ 10^{-5} and 6.5×10^{-5} s⁻¹, respectively. No detectable amount of DMA was liberated from (1) in the absence of thebaine under these conditions. These results are consistent with a slow, reversible dissociation (rate constant k) of DMA-ONCN (1) followed by rapid, irreversible capture of ONCN by thebaine (3). Confirmation of this interpretation was obtained using a different class of co-reactant. C-Nitroso-compounds are known⁴ to react rapidly with phosphines and phosphites to yield products derived, at least formally, from the corresponding nitrenes. Triphenylphosphine was expected, therefore, to react readily with nitrosyl cyanide to give the known⁵ phosphinimide (5) either via cyano-



nitrene (as in Scheme 1) or by direct attack of triphenylphosphine on the terminal nitrogen of the intermediate, dipolar adduct. In accord with this expectation, the adduct (1) and triphenylphosphine (2 mol. equiv.) reacted in benzene at 80 °C to yield a mixture of the phosphinimide (5), triphenylphosphine oxide, and DMA. The course of reaction was studied, as before, in benzene at 40 °C. First-order kinetics were observed for the formation of DMA, the rate constant, $k = 6.8 \times 10^{-5}$ s⁻¹, having a value close to that for the corresponding reaction of (1) with thebaine. Again, we conclude that the rate-determining step in the reaction sequence is the dissociation of DMA-ONCN (1) into its components. In an early experiment, trans.trans.1,4-diphenylbuta-1,3-diene (6; R = H) was treated with impure nitrosyl cyanide generated from nitrosyl chloride and silver cyanide in chloroform at -20 °C. A complex mixture of products was obtained which yielded the yellow nitrocompound (6; $R = NO_2$)⁶ and a colourless chlorocompound (7), which was identified spectroscopically and



by its conversion on alumina into (6; $R = NO_2$). Clearly, both these products must have arisen by reaction of the diphenylbutadiene (6; R = H) with impurities, for example NOCl, NO_2 , and possibly NO_2 Cl, in the crude nitrosyl cyanide.⁷ In contrast, treatment of the butadiene (6; R = H) with the adduct (1) in benzene at 80 °C gave the oily oxazine (8) (72%) and DMA as the only detectable products. Similarly, an initial attempt to demonstrate addition of nitrosyl cyanide to the homoconjugated diene, norbornadiene, was frustrated by impurities in the gaseous reagent. The only product isolated in a pure state was the dimeric chloro-nitrosocompound (9).⁸ However, the tetracyclic adduct (10) was obtained as a distillable oil when norbornadiene and the adduct (1) were refluxed in benzene for 48 h.

The chemistry of nitrosyl cyanide was explored further by heating the adduct (1), generally at 80 °C in benzene, with a wider range of reactive species. Ergosteryl acetate (11) gave a separable mixture of the adducts (12) and (13) arising, as expected, from the two modes of cycloaddition to ring B. The reaction with tetraphenylcyclopentadienone (14) proceeded cleanly to give the *N*cyanoimine (17) in high yield, presumably *via* the transient intermediates (15) and (16) (Scheme 2).⁹ The structure of (17) was confirmed by its hydrolysis to *cis*-dibenzoylstilbene. However, the adduct (1) reacted



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with 1,3-diphenylisobenzofuran (18) (1 mol. equiv.) in an unexpected manner. The major products, apart from DMA, were 1,2-dibenzoylbenzene (ca. 50%) and the related N-cyanoimine (19) (ca. 50%). It is likely that the bridged adduct (20) was formed first. Collapse of this could lead to the N-cyanonitrone (21) or the Ncyano-oxaziridine (22), either of which might be capable of transferring oxygen to (18) to yield the observed products. Alternatively, the adduct (20) might fragment to give 1,2-dibenzoylbenzene and cyanonitrene, the to give benzophenone (58%) and the corresponding cyanoimine ¹¹ (10%). The formation of mixtures of related ketones and cyanoimines recalls the outcome of the reaction of the isobenzofuran (18) with the adduct (1). However, intermediates in all these reactions remain elusive.

EXPERIMENTAL

General Methods.—M.p.s were determined with a Kofler hot-stage apparatus. Except where otherwise stated,



latter then reacting with (18) to yield (19). Curiously, treatment of the isoindole (23) with the adduct (1) also gave the cyano-imine (19) (66%), accompanied by a small amount of 1,2-dibenzoylbenzene. The fate of the N-methyl moiety of (23) remains obscure.

Consideration of the possible formation of an Ncyanonitrone (21) or N-cyano-oxaziridine (22) from the adduct (20) led us to explore an alternative route to compounds of this type. It is known ¹⁰ that diazocompounds and C-nitroso-compounds react readily to give nitrones. Diazofluorene (24) was selected first for n.m.r. spectra were obtained for deuteriochloroform solutions with tetramethylsilane as internal reference. T.l.c. separations were carried out on Merck silica F_{254} plates. Light petroleum refers to the fraction of b.p. 60–80 °C.

9,10-Dihydro-9,10-(N-cyanoepoxyimino)-9,10-dimethylanthracene (1).—Gaseous nitrosyl cyanide was generated, as before,¹ from dry silver cyanide (5 g) and nitrosyl chloride (1 ml). 9,10-Dimethylanthracene (DMA) (1 g) in dry dichloromethane (30 ml) was admitted to the reaction vessel maintained at -25 °C. The green colour of the nitrosyl cyanide was rapidly discharged. The reaction mixture was allowed to warm up to room temperature with stirring



our study on account of its stability in benzene at 80 °C. The adduct (1) and diazofluorene (24) were refluxed in benzene for 24 h to yield a complex mixture of products. Preparative t.l.c. gave fluorenone (50%), the corresponding cyanoimine (25) (11%), and unidentified polar material. Essentially the same result was obtained by treatment of diazofluorene (24) with impure, gaseous nitrosyl cyanide at -30 °C. Similarly, diphenyldiazomethane reacted with gaseous nitrosyl cyanide at -30 °C

and then filtered through Celite. The filtrate was evaporated and the residue was chromatographed on a silica column, eluting with benzene. The early fractions yielded a mixture of DMA (2) and 9-nitromethyl-10-methylanthracene. Crystallisation from benzene afforded 9-nitromethyl-10-methylanthracene (40 mg), m.p. 211—212 °C (lit.,³ m.p. 197—198 °C) (Found: C, 76.4; H. 5.2; N. 5.7. Calc. for C₁₆H₁₃NO₂: C, 76.5; H, 5.2; N, 5.6%); $\nu_{max.}$ (KBr) 1 545, 1 435, and 1 355 cm⁻¹; τ (AsBr₃) 1.45—2.45 (m, aryl-H), 3.53 (s, CH₂), and 6.83 (s, Me); *m/e* 251, 205, and 204.

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Later fractions gave the cycloadduct (1) (350 mg), m.p. 169—171 °C (from MeOH or benzene-light petroleum) (Found: C, 77.7; H, 5.5; N, 10.7. $C_{17}H_{14}N_2O$ requires C, 77.8; H, 5.4; N, 10.7%); ν_{max} . (KBr) 2 215, 1 465, and 1 387 cm⁻¹; τ 2.65 (m, aryl-H), 7.75 (s, Me), and 7.83 (s, Me); m/e 206 (M^+ – 56).

N-Cyanomethyl-N-northebaine (3; NCH₂CN replacing NMe) (with M. Heintzman).—N-Northebaine (150 mg) was treated in ethanol (7 ml) with 40% aqueous formaldehyde (75 μ l) with stirring for 10 min at room temperature. 2-Hydroxy-2-cyanopropane (84 mg) was added to the resulting milky solution, and the mixture was left overnight and then evaporated. Crystallisation of the residue gave N-cyanomethyl-N-northebaine (120 mg), m.p. 149 °C (from MeOH) (Found: C, 71.4; H, 5.9; N, 8.2. C₂₀H₂₀N₂O₃ requires C, 71.4; H, 6.0; N, 8.3%); ν_{max} (KBr), 1 678, 1 636, and 1 608 cm⁻¹; τ 3.41 (s, 1-H and 2-H), 4.43 (d, J 7 Hz, 8-H), 4.77 (s, 5-H), 4.99 (d, J 7 Hz, 7-H), 6.18 (s, 3-OMe), and 6.43 (s, 6-OMe and NCH₂CN).

Reaction of the Adduct (1) with N-Cyanomethyl-N-northebaine and Thebaine (3).—The adduct (1) (30 mg) and Ncyanomethyl-N-northebaine (3; NCH₂CN replacing NMe) (30 mg) were refluxed in benzene (2 ml) for 3 h under nitrogen. The mixture of products was separated on t.l.c. plates developed with chloroform-methanol (98:2) to afford the adduct (4; NCH₂CN replacing NMe) (25 mg), m.p. 185—186 °C (decomp.) (from MeOH-CHCl₃), which was identical (i.r. spectrum, mixed m.p.) with a sample prepared earlier.¹ Similarly, the adduct (1) and thebaine (3) gave the adduct (4). In this latter experiment, 9,10dimethylanthracene was isolated and identified (¹H n.m.r. spectrum).

Reaction of the Adduct (1) with Triphenylphosphine.— The adduct (1) (36 mg, 0.14 mmol) and triphenylphosphine (72 mg, 0.28 mmol) were refluxed in benzene (5 ml) for 2 h under nitrogen. Separation of the reaction mixture on t.l.c. plates developed with benzene gave a crystalline mixture (66 mg) of triphenylphosphine oxide and the imide (5). Fractional crystallisation from benzene–light petroleum gave triphenylphosphine N-cyanoimide (5) (24 mg, 58%), m.p. 192—196 °C (lit.,⁵ m.p. 193—195 °C); ν_{max} . (KBr) 2 170 cm⁻¹; τ 2.1—2.7 (m) (Found: M^+ , 302.0973. Calc. for C₁₉H₁₅N₂P: M, 302.0973).

Kinetic Studies on the Dissociation of the Adduct (1).---Solutions of the adduct (1) (4 mM) and thebaine (4, 8, or 16 mM) or triphenylphosphine (8 mM) in benzene were kept at 40 °C. Aliquots (0.1 ml) were removed periodically and diluted with hexane-ethanol (1:1) (2.0 ml). The release of DMA (2) from (1) was monitored during 6 h by measurement of the absorption at 358 nm. 'Infinity' readings were taken after 24 h. The results are given in the main text. As expected (see Scheme 1), the reaction of the adduct (1) (4 mM) and triphenylphosphine (4 mM) stopped after the release of only 50% of the DMA (2) from the adduct (1).

Reaction of trans, trans-1,4-Diphenylbuta-1,3-diene with Impure Nitrosyl Cyanide.—The butadiene (6; R = H) (1 g) in chloroform (30 ml) was added to nitrosyl cyanide, prepared in the usual way ¹ from silver cyanide (4.5 g) and nitrosyl chloride (1.0 ml), in chloroform (40 ml) at -20 °C. The reaction mixture was filtered through Celite and the filtrate was evaporated to yield an orange gum. Addition of methanol (8 ml) caused the separation of a white, crystalline solid (150 mg). Recrystallisation gave 3-chloro-4-nitro-1,4diphenylbut-1-ene (7), m.p. 161—163 °C (from EtOH) (Found: C, 66.7; H, 5.0; Cl, 12.2; N, 5.0. $C_{16}H_{14}ClNO_2$ requires C, 66.8; H, 4.9; Cl, 12.3; N, 4.9%); v_{max} (Nujol) 1 647, 1 550, and 1 360 cm⁻¹; τ 2.60 (m, Ph), 3.19 (d, J 15.4 Hz, 1-H), 3.72 (dd, J 15.4 and 8.2 Hz, 2-H), 4.36 (d, J 9.4 Hz, 4-H), and 4.69 (dd, J 9.4 and 8.2 Hz, 3-H). This chloro-compound (50 mg) was chromatographed on neutral grade III alumina. Elution with chloroform gave 1-nitro-1,4-diphenylbuta-1,3-diene (6; R = NO₂) (40 mg), m.p. 110 °C (from MeOH) (lit.,⁶ m.p. 111—112 °C); v_{max} (Nujol) 1 630, 1 503, and 1 315 cm⁻¹; τ 2.04 (d, J 11 Hz, 2-H), 2.40—2.90 (m, Ph), 2.89 (d, J 16 Hz, 4-H), and 3.38 (dd, J 16 and 11 Hz, 3-H).

Reaction of trans, trans-1,4-Diphenylbuta-1,3-diene with the Adduct (1).—The butadiene (6; R = H) (100 mg, 0.48 mmol) and the adduct (1) (100 mg, 0.38 mmol) were refluxed in benzene (2 ml) for 48 h. The reaction mixture was separated on t.l.c. plates developed with benzene. Elution of a band running just below the adduct (1) gave 2-cyano-3,6-dihydro-3,6-diphenyl-2H-1,2-oxazine (8) (72 mg) as an oil; $\nu_{max.}$ (film) 2 205, 1 495, and 1 450 cm⁻¹; τ 2.60 (s, Ph), 3.87 (br s, 4-H and 5-H), 4.30 (br t, 6-H), and 5.06 (br t, 3-H) (Found: M^+ , 262.11073. C₁₇H₁₄N₂O requires M, 262.11060).

Reaction of Norbornadiene with the Adduct (1).—The adduct (1) (100 mg) and bicyclo[2.2.1]hepta-2,5-diene (500 mg) were refluxed for 48 h in benzene under nitrogen. The products were separated by t.l.c., as described above. The oily *tetracyclic adduct* (10) (27 mg) was further purified by bulb-to-bulb distillation (120 °C, 0.5 mm Hg) (Found: C, 64.95; H, 5.5; N, 18.9. C₈H₈N₂O requires C, 64.85; H, 5.4; N, 18.9%); ν_{max} . (film) 2 100 cm⁻¹; τ 5.30 (1 H, m), 5.87 (1 H, m), 7.48 (1 H, m), 8.09 (2 H, br s), 8.25 (1 H, br m), and 8.41 (2 H, m); m/e 148.

Reaction of Ergosteryl Acetate (11) with the Adduct (1).-Ergosteryl acetate (11) (600 mg) and the adduct (1) (300 mg) were refluxed in benzene for 24 h. The reaction mixture was chromatographed on a silica column. Successive elution with benzene, to remove DMA (2), then chloroformmethanol (9:1) gave a mixture of the adducts (12) and (13)(387 mg). A portion (100 mg) of the mixture was separated on t.l.c. plates, developed four times with benzene, to afford the adduct A [(12) or (13)] (56 mg) (lower band), m.p. 171--173 °C (from MeOH) (Found: C, 75.1; H, 9.2; N, 5.65. $C_{31}H_{46}N_2O_3$ requires C, 75.3; H, 9.3; N, 5.7%); ν_{max} (KBr) 2 205 and 1 735 cm⁻¹; τ 3.56 and 3.77 (AB q, J 9 Hz, 6-H and 7-H), 4.83 (m, 22-H and 23-H), 5.00 (m, 3-H), and 7.98 (s, Ac); m/e 494 and 378: and the adduct B [(12) or (13)] (27) mg) (upper band), m.p. 144-145 °C (from MeOH-H₂O) (Found: C, 75.2; H, 9.5; N, 5.5%); v_{max.} (KBr) 2 205 and 1 735 cm⁻¹; τ 3.42 and 3.75 (AB q, J 9 Hz, 6-H and 7-H), 4.82 (m, 22-H and 23-H), 4.95 (m, 3-H), and 7.98 (s, Ac); m/e 438 and 378 (no M^+ peak).

Reaction of Tetraphenylcyclopentadienone with the Adduct (1).—Tetraphenylcyclopentadienone (150 mg) and the adduct (1) (75 mg) were refluxed in benzene (4 ml) for 18 h. Separation of the products by t.l.c. as before gave 4-cyano-imino-1,2,3,4-tetraphenylbut-2-en-1-one (17) (107 mg), m.p. 209—211 °C (from benzene-light petroleum) (Found: C, 84.3; H, 4.95; N, 6.8. C₂₉H₂₀N₃O requires C, 84.5; H, 4.85; N, 6.8%); ν_{max} (KBr) 2 190 and 1 660 cm⁻¹; m/e 412. Hydrolysis of (17) was effected by refluxing in ethanol-6N hydrochloric acid (1:1) for 15 min to afford cis-dibenzoyl-stilbene, which was identified by comparison (i.r. spectrum and mixed m.p.) with authentic material.

Reaction of 1,3-Diphenylisobenzofuran (18) with the

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Adduct (1).-1,3-Diphenylisobenzofuran (18) (40 mg) and the adduct (1) (40 mg) were refluxed in benzene for 14 h under dry, oxygen-free nitrogen. The products were separated on t.l.c. plates developed with ether-light petroleum (1:1) to give 1,2-dibenzoylbenzene (21 mg, 50%) and the cyanoimine (19) (22 mg, 48%), m.p. 133-134 °C (from benzene-light petroleum) (Found: C, 81.35; H, 4.6; N, $C_{21}H_{14}N_{2}O$ requires C, 81.3; H, 4.55; N, 9.0%); 9.2. $v_{\text{max.}}$ (KBr) 2 180 and 1 660 cm⁻¹; m/e 310, 270, and 233. Similar results were obtained for reactions in dichloromethane at room temperature (48 h) or at 40 $^\circ C$ (14 h) except that the yields of (19) were lower (30%). Hydrolysis of (19) in hot, ethanolic hydrochloric acid gave 1,2dibenzoylbenzene.

Reaction of 1,3-Diphenyl-2-methylisoindole (23) with the Adduct (1).-1,3-Diphenyl-2-methylisoindole (31 mg) and the adduct (1) (27 mg) were refluxed in dichloromethane for 15 h under dry, oxygen-free nitrogen. The products were separated by t.l.c. as before to give the cyanoimine (19) (21 mg, 66%).

Reaction of Diazofluorene (24) with the Adduct (1).-Diazofluorene (24) (300 mg) and the adduct (1) (273 mg) were refluxed in benzene for 24 h under dry, oxygen-free nitrogen. Partial separation of the reaction mixture was effected on t.l.c. plates developed in benzene to give, in order of decreasing $R_{\rm F}$, fraction A (170 mg) [mainly DMA (2)], fraction B (130 mg), and fraction C (250 mg). Fraction B was separated further on plates developed repeatedly with benzene-light petroleum (1:1) to afford fluorenone (92 mg) and 9-cyanoiminofluorene (25) [24 mg, 11% yield based on (1)], m.p. 134-137 °C (from MeOH) (Found: C, 82.2; H, 4.2; N, 13.95%; M^+ , 204.0684. $C_{14}H_8N_2$ requires C, 82.35; H, 3.9; N, 13.7%; M, 204.0687); ν_{max} (KBr) 2 185, 2 165, 1 622, and 1 588 cm⁻¹. Hydrolysis of (25) with hot ethanolic hydrochloric acid gave fluorenone.

Reaction of Diazofluorene with Gaseous Nitrosyl Cyanide.-Diazofluorene (24) (1.11 g) in dichloromethane (30 ml) was added to gaseous nitrosyl cyanide, generated as usual ¹ from silver cyanide (5 g) and nitrosyl chloride (1 ml), at -30 °C.

Layer chromatography of the reaction mixture, as before, gave fluorenone (570 mg) and 9-cyanoiminofluorene (25) (224 mg).

Reaction of Diphenyldiazomethane with Gaseous Nitrosyl Cyanide.—Diphenyldiazomethane (1.0 g) was treated with gaseous nitrosyl cyanide as described above for diazofluorene. Layer chromatography of the products gave benzophenone (545 mg) and cyanoiminodiphenylmethane (102 mg), m.p. 78-79 °C (from light petroleum) (lit.,¹¹ m.p. 81-83 °C) (Found: C, 81.7; H, 4.9; N, 13.4. Calc. for $C_{14}H_{10}N_2; \ C,\,81.55; \ H,\,4.85; \ N,\,13.6\%); \ \nu_{max.} \, (KBr) \ 2 \ 170,$ 1 595, and 1 582 cm⁻¹; m/e 206. Hydrolysis of this imine with hot ethanolic hydrochloric acid gave benzophenone.

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