Intramolecular Conversion of *N*-Nitroso Ketimines into Ketones and Nitrogen. 1,2,3-Oxadiazetines as Analogues of Dioxetanes

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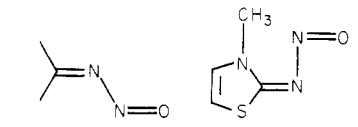
N-Nitrosobenzophenone imine and *N*-nitrosocamphorimine have been prepared by the nitrosation of the corresponding imines with nitrosyl chloride or dinitrogen tetraoxide. *N*-Nitrosobenzophenone imine decomposes by first-order kinetics to yield benzophenone and nitrogen; the activation parameters are $\Delta H^{\ddagger}_{25}$ = 18.7 kcal/mol and $\Delta S^{\ddagger}_{25}$ = −11 eu. The reaction is not affected appreciably by small amounts of water, and the use of $H_2{}^{18}O$ has shown that the oxygen atom of the nitroso imine is retained in the benzophenone. The kinetic information, entropy of activation, and lack of water incorporation indicate that the ketone-forming reaction is an intramolecular one. A proposed intermediate in this decomposition bears a resemblance to the dioxetanes, which are known to yield excited states on decomposition. However, we were unable to detect excited states from the decomposition of either *N*-nitrosobenzophenone imine or the nitroso imine of *N*-methylacridone.

The chemistry of the *N*-nitroso imines (1) has been slow in developing, largely because of their instability; until quite recently, only nitroso imines of heterocyclic systems (**2**)[1] or those with special stabilizing features (**3**)[2] had been obtained in a pure form.



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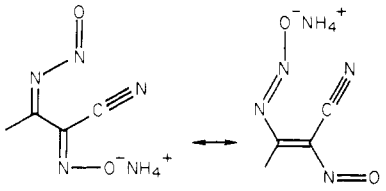

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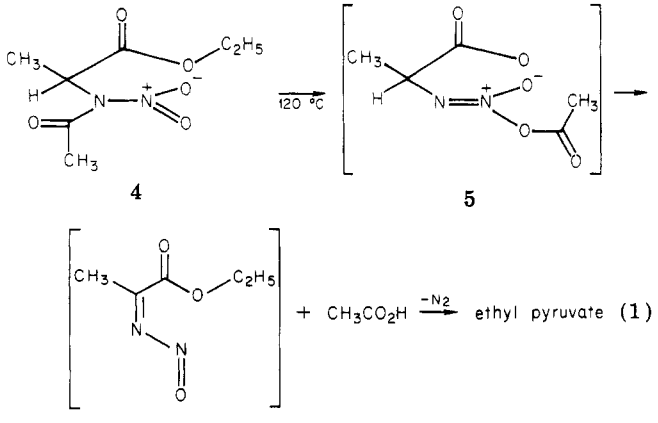
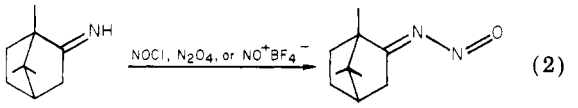
Our first attempts to prepare acyclic nitroso imines utilized an elimination reaction as the key step. The model for this approach was the pyrolysis of *N*-nitroso amides of the amino acid esters; the pyrolysis of ethyl *N*-nitroso-*N*-acetylalaninate, e.g., yields ethyl α-diazopropionate.[3] Pyrolysis of the *N*-nitro amide analogues (eq 1), however, did not yield the desired products; the reaction



4 **5** **6**

(1)

did lead to ketones (e.g., ethyl pyruvate from **4**), suggesting that nitroso imines had been formed as reaction intermediates.[4] At that time we also nitrosated various imines directly (eq 2), but the products, e.g., nitrosocamphorimine (**7**), were not obtained in a pure form.[5]



(2)

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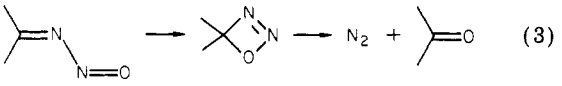
In the same year Zimmerman and Paskovich[6] described the preparation of two nitroso imines by means of reaction 2, but the nitroso imines were characterized only by their reduction to the corresponding diazoalkanes. Subsequently, Thoman and Hunsberger[7] reported the preparation of several nitroso imines, also by means of reaction 2; the compounds were characterized, and one of them, *N*-nitroso-2,4′-dichlorobenzophenone imine, was obtained analytically pure. Recently, metal salts of imines have also been nitrosated,[8] as have amidines[9] and guanidines.[10]

N-Nitroso ketimines are thermally unstable compounds, the decomposition giving, usually, the corresponding ketones and nitrogen. The decomposition, in the case of *N*-nitroso-2,4′-dimethylbenzophenone imine (not fully purified), followed first-order kinetics with a half-life of 4.75 h in cyclohexane at 23 °C.[7,11] On the basis of the observation of first-order kinetics, the authors proposed a cyclic mechanism for the reaction (eq 3). Although this



(3)

mechanism has been accepted by later workers,[8,10b] it seemed to us that an alternative mechanism for the decomposition had to be considered, namely, a chain reaction with water as the carrier molecule (eq 4). The present

(1) Näf, E. *Justus Liebigs Ann. Chem.* **1891**, *265*, 116.
(2) Lubin, *J. Chem. Ber.* **1904**, *37*, 3467; *J. Prakt. Chem.* **1906**, *74*, 529.
(3) White, E. H.; Baumgarten, R. J. *J. Org. Chem.* **1964**, *29*, 2070.
(4) White, E. H.; Baumgarten, R. J. *J. Org. Chem.* **1964**, *29*, 3636.
(5) Baumgarten, R. J. *Ph.D. Thesis*, The Johns Hopkins University, Baltimore, MD, 1962. Impure alkyl nitroso imines were also reported by Lochte, H. L.; Horeczy, J.; Pickard, P. L.; Barton, A. D. *J. Am. Chem. Soc.* **1948**, *70*, 2012-2015.
(6) Zimmerman, H. E., Paskovich, D. H. *J. Am. Chem. Soc.* **1964**, *86*, 2149-2160.
(7) Thoman, C. J.; Hunsberger, I. M. *J. Org. Chem.* **1968**, *33*, 2852-2857.
(8) Jappy, J.; Preston, P. N. *Tetrahedron Lett.* **1970**, 1157-1160.
(9) Vis, J. H.; Meinke, P. *J. Heterocycl. Chem.* **1970**, *7*, 1417-1419.
(10) (a) Akiba, K.; Matsunami, S.; Eguchi, C.; Inamoto, N. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 935-937. (b) Akiba, K.; Inamoto, N. *Heterocycles* **1977**, *7*, 1131-1162. (c) A related nitrosoguanidine was reported by R. Muller *J. Prakt. Chem.* **1897**, *56*, 483.
(11) The rate curve, which appears in the Ph.D. Thesis of C. J. Thoman (University of Massachusetts, 1966) shows some curvature, and it is there stated that the "solid nitrosoimine" was decomposed; first-order kinetics have also been observed for the thermal decomposition of the *N*-nitrosoguanidines.[10a,b]

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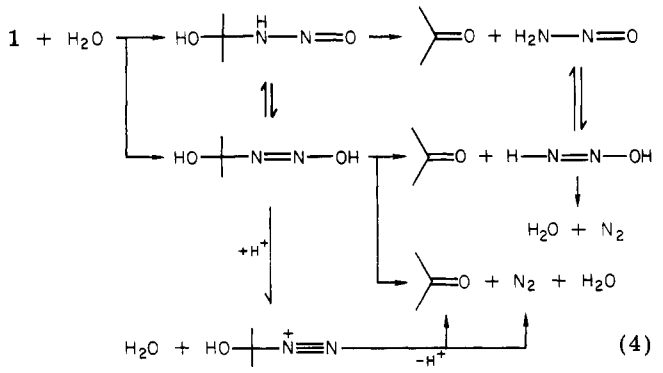


(4)

paper describes our synthesis of *N*-nitrosobenzophenone imine, the kinetics and activation parameters of its decomposition, an oxygen-18 tracer study of the decomposition, and our attempts to determine whether the ketone product of the reaction is formed in an excited state.

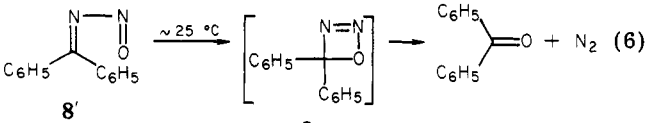
Results and Discussion

N-Nitrosobenzophenone imine (8) was prepared by the nitrosation of benzophenone imine. It could be prepared in an analytically pure form provided that reaction systems were kept dry and purification methods were carried out at low temperatures.

$$(C_6H_5)_2C{=}NH \xrightarrow[\text{or } N_2O_4]{NOCl} (C_6H_5)_2C{=}N{-}N{=}O \qquad (5)$$

8

Nitroso imine 8 decomposes readily at 25 °C to yield nitrogen and benzophenone, in accord with the results of Thoman and Hunsberger[7] for the decomposition of analogues. The cyclic reaction mechanism proposed by these authors is given in eq 6, along with the structure of a probable reaction intermediate, 1,2,3-oxadiazetine (9).



(6)

8′ 9

The ultraviolet absorption spectra of spent reaction mixtures were identical with that of benzophenone; on the basis of the absorbance at 252 nm, a yield of 93% of the ketone was calculated for the reaction (GLC analysis indicated a yield of 86%).

The decomposition of nitroso imine 8 was monitored at 593 nm, the center of its long-wavelength absorption band. Impure samples in acetonitrile decomposed via first-order kinetics up to approximately 25% decomposition; the rate at that point then decreased rather abruptly to a new value (still first order).

Pure *N*-nitrosobenzophenone imine, on the other hand, decomposed by strictly first-order kinetics for up to approximately 5 half-lives (Figure 1 illustrates the first 2 half-lives). This good first-order rate dependence and the negligible effect of dilution (10×) on the rate constant eliminated bimolecular modes of decomposition from consideration. The decomposition rates (Table I) in THF, chloroform, and acetonitrile show no pronounced solvent dependence (see following discussion for the reaction in alcohols), and oxygen appears to have no effect on the reaction.

The addition of moderate amounts of water to acetonitrile solutions of 8 led to only a small increase in the decomposition rates (Table I and Figure 1), suggesting that the chain reaction outlined in eq 4 was not a major reaction pathway. This lack of a water effect is consistent, however,

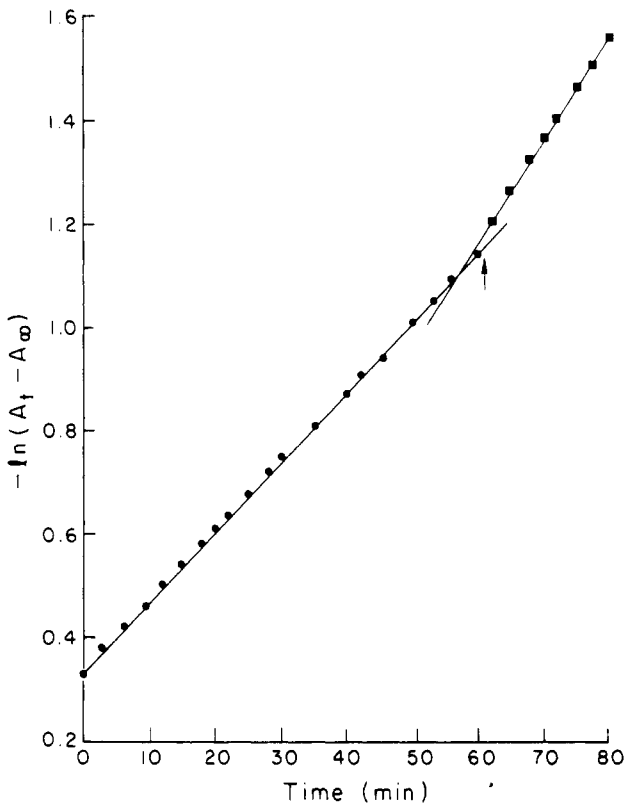
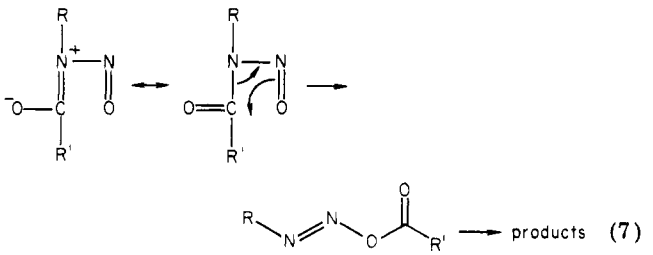


Figure 1. Rate of decomposition of *N*-nitrosobenzophenone imine (8) in acetonitrile at 17.4 °C; concentration, 0.02 M. At the arrow, 5% water (v/v) was added. For the dry system, $k = 2.2 \times 10^{-4}$ s^{-1} and for the wet, $k = 3.0 \times 10^{-4}$ s^{-1}.

with the operation of the cyclic decomposition mode outlined in eq 6. Also consistent with this pathway is the observation of a negative entropy of activation for the reaction (activation parameters for the reaction in acetonitrile were calculated from the rate data (Table I): $\Delta H^{\ddagger}_{25} = 18.7$ kcal/mol; $\Delta S^{\ddagger}_{25} = -11$ eu). The entropy of activation found is similar to that reported for other four-center reactions, e.g., the rearrangement (eq 7) of the *N*-nitroso amides[12] (compare to eq 6; the first step in both reactions is the rate-determining one). Similar entropies of activation have also been reported for the related decomposition of several *N*-nitro amides.[13]

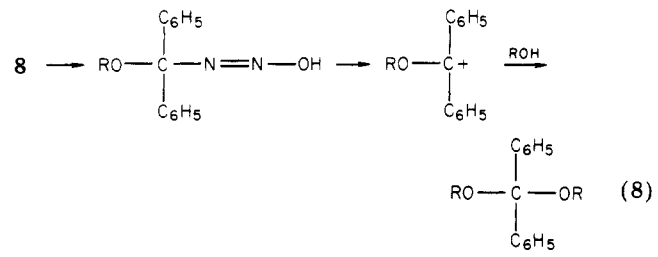


(7)

The high decomposition rates found for the reactions in methanol and ethanol (Table I) appear to result, in part, from the utilization of an alternative reaction mode involving direct participation by the solvent (eq 8). The formation of ketals in these reactions (80% in methanol and 50% in ethanol) provides support for this pathway.

To determine definitively whether chain reaction 4 was involved in the nitroso imine decomposition, we carried out the reaction in acetonitrile containing 0.1–0.4% $H_2{}^{18}O$ (molar ratios of H_2O relative to 8 = 6 to 23). Mass spec-

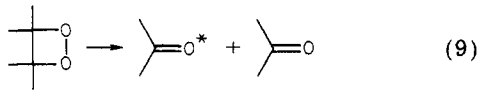
(12) Huisgen, R.; Reimlinger, H. *Justus Liebigs Ann. Chem.* **1956**, *599*, 161–182.
(13) White, E. H.; Dolak, L. A. *J. Am. Chem. Soc.* **1966**, *88*, 3790.



(8)

trometric analysis of the benzophenone formed showed that a majority of it was not labeled; only approximately 12% of the benzophenone contained ^{18}O in the run with 0.1% $H_2{}^{18}O$ [the 12% is a sum of incorporation via mechanism 5 and oxygen exchange of the benzophenone (~3%)]. Thus, the ^{18}O results, kinetic order, the negative entropy of activation, and the negligible effect of moderate amounts of water on the reaction rate all support the view that the nitroso imines decompose by a cyclic mechanism in nonreacting solvents (eq 6). In water-rich media, though, it is highly probable that a direct involvement of water would occur (eq 4) in a reaction similar to that observed with alcohol solvents.

The intermediate proposed for the decomposition in nonreacting solvents, **9**, bears a resemblance to the dioxetane class of compounds (**10**) in structure as well as in the formation of carbonyl-containing products.[14] Since dioxetanes yield excited states of ketones (or aldehydes) on decomposition (eq 9),[14] it was of interest to search for such



(9)

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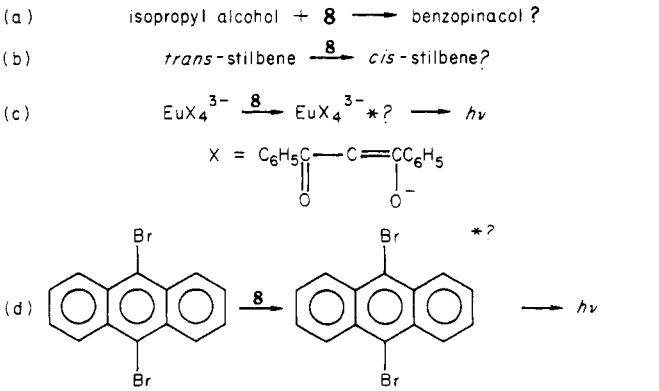
excited states in the decomposition of *N*-nitrosobenzophenone imine (**8**). Simple dioxetanes yield largely triplet states on decomposition[14] and since, in any case, the excited singlet state of benzophenone undergoes a rapid and essentially quantitative intersystem crossing to yield triplet benzophenone,[15] we conducted several searches (in essentially oxygen-free systems) for triplet benzophenone from the decomposition of nitroso imine **8**:



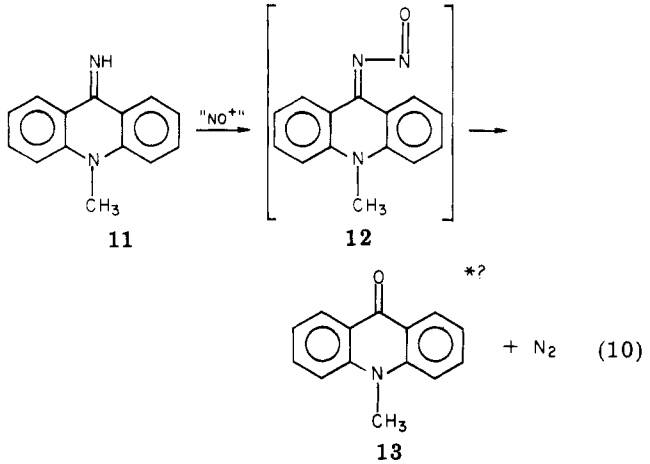
Transformations a–c are known to occur with triplet benzophenone,[15-17] and process d has been observed with triplet acetone as as the energy source.[18] In runs a–d with decomposing nitroso imine **8**, however, no indication of the formation of excited states was found.

Table I. Decomposition Rates of *N*-Nitrosobenzophenone Imine (**8**)

solv[a] and addends	temp, °C	rate × 10^4, s^{-1}
A. Solvent Effect		
CH_3CN	23.6	2.2
CH_3CN	25	3.6, 3.7, 3.5
C_2H_5OH		10.5
CH_3OH		45.0, 43.4
THF[b]	29.2	1.6
$CHCl_3$		9.7
B. Added Reagents		
CH_3CN/H_2O (96/4)[c]	17.4	2.6
CH_3CN/H_2O (99.5/0.5)[c]	23.6	3.0
CH_3CN/H_2O (99.5/0.5)[c]	25.0	4.2
CH_3CN (argon)		3.5
CH_3CN (O_2)		3.5
THF[b]/H_2O (96/4)[c]	29.2	2.2
CH_3CN/H_2O (96/4)[c]		10.2, 9.4
C. Temperature Effect		
CH_3CN	17.4	1.8, 2.2, 1.8
	29.3	6.6
	36.5	14.7, 15.0
	47.8	39.8

[a] Air saturated unless noted; concentration, 0.01 M. [b] Tetrahydrofuran. [c] Volume/volume; the water was added to dry solutions of **8** after ca. 2 half-lives.

Lastly, the conversion shown in eq 10 was carried out,



(10)

since the high fluorescence efficiency of *N*-methylacridone (**13**)[19] serves as a sensitive probe for excited singlet states; in fact, *N*-methylacridone is the light emitter in several chemiluminescent reactions.[20] However, with respect to the conversion outlined in eq 10, no light emission was detected.

Nitrosocamphorimine (7). The nitrosation of camphorimine with nitrosyl chloride gave essentially pure nitroso imine **7**; attempted nitrosation with dinitrogen tetraoxide,[21] however, led to *N*-nitrocamphorimine and

(14) White, E. H.; Harding, M. J. C. *Photochem. Photobiol.* **1965**, *4*, 1129; Kopecky, K. R.; Mumford, C. *Can. J. Chem.* **1969**, *47*, 709. White, E. H.; Wiecko, J.; Roswell, D. F. *J. Am. Chem. Soc.* **1969**, *91*, 5194. White, E. H.; Wildes, P. D.; Wiecko, J.; Doshan, H.; Wei, C. C. *Ibid.* **1973**, *95*, 7050. Horn, K. A.; Koo, J.-Y.; Schmidt, S. P.; Schuster, G. B. *Mol. Photochem.* **1978**, *9*, 1.

(15) Hammond, G. S.; Moore, W. M. *J. Am. Chem. Soc.* **1959**, *81*, 6334. Moore, W. M.; Hammond, G. S.; Foss, R. P. *J. Chem. Phys.* **1960**, *32*, 1594. Backstrom, H. L. J.; Sandros, K. *Acta Chem. Scand.* **1960**, *14*, 48. Moore, W. M.; Hammond, G. S.; Foss, R. P. *J. Am. Chem. Soc.* **1961**, *83*, 2789. Hammond, G. S.; Baker, W. P.; Moore, W. M. *Ibid.* **1961**, *83*, 2795.

(16) Herkstroeter, W. G.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 4769.

(17) El-Sayed, M. A.; Bhaumik, M. L. *J. Chem. Phys.* **1963**, *39*, 2391. Bhaumik, M. L.; El-Sayed, M. A. *J. Phys. Chem.* **1965**, *69*, 275. Bhaumik, M. L.; Nugent, L. J. *J. Chem. Phys.* **1965**, *43*, 1680.

(18) Turro, N. J. et. al. *J. Am. Chem. Soc.* **1974**, *96*, 1627–1629.

(19) Lee, C.; Singer, L. A. *J. Am. Chem. Soc.* **1980**, *102*, 3823–3829.

(20) Rauhut, M. M.; Sheehan, D.; Clarke, R. A.; Roberts, B. G.; Semsel, A. M. *J. Org. Chem.* **1965**, *30*, 3587–3592. McCapra, F.; Richardson, D. G. *Tetrahedron Lett.* **1964**, 3167. Rapaport, E.; Cass, M. W.; White, E. H. *J. Am. Chem. Soc.* **1972**, *94*, 3160–3167.

(21) White, E. H.; Feldman, W. R. *J. Am. Chem. Soc.* **1957**, *79*, 5832.

several other compounds as byproducts. Methylene chloride solutions of 7 were decolorized within seconds by anhydrous hydrogen chloride to yield nitrosyl chloride and camphorimine hydrochloride. Preliminary studies of the thermal decomposition of nitrosocamphorimine in carbon tetrachloride at 77 °C showed that the principal products were camphor and *N*-nitrocamphorimine; the same products, along with a small amount of camphorazine, were formed in a decomposition carried out directly on solid 7. *N*-Nitrocamphorimine may be a disproportionation product of *N*-nitrosocamphorimine.[22] The other expected product, diazocamphane, may be the source of the camphorazine observed, since azines are common products from the thermal decomposition of diazoalkanes. A diazoalkane has, in fact, been isolated from an elimination reaction similar to that outlined in eq 1.[4] Byproducts in the thermal decomposition of *N*-nitroso imines at moderately high temperatures have been noted before;[8] possibly, they are produced by free-radical reactions.

Experimental Section

Spectra were recorded with a Perkin-Elmer 599B IR spectrophotometer, a JEOL JNM-100 nuclear magnetic resonance spectrometer (tetramethylsilane used as internal standard), and a Varian Techtron 635 UV–vis spectrophotometer. A Varian Aerograph Series 1800 gas chromatograph was used for analytical separations. Melting points are uncorrected.

Benzophenone Imine. The procedure described by Pickard and Tolbert[23] was followed. GLC analysis of the distilled product showed that the imine was free of the parent ketone: IR (CCl_4) 3260, 1603, 1365 cm^{-1}. In other runs, up to 15% benzophenone was present.

***N*-Nitrosobenzophenone Imine (8). Method A.** Compound 8 was prepared by a slight modification of the general procedure of Thoman and Hunsberger.[7] Benzophenone imine (3.48 g, 19.2 mmol) in 10 mL of methylene chloride was added over a 5-min period to a stirred solution (at −20 °C) of nitrosyl chloride (1.9 g, 29 mmol) in 25 mL of methylene chloride containing potassium acetate (8.3 g, 84 mmol). The mixture was stirred for 45 min, and then rapidly washed with cold 10% potassium bicarbonate (100 mL) and with water (100 mL). The organic solution was dried ($MgSO_4$) and filtered. Evaporation of the solvent at −50 °C (under vacuum) left a blue crystalline solid, which was recrystallized from ether at −50 °C.

Anal. Calcd for $C_{13}H_{10}N_2O$: C, 74.27; H, 4.79. Found: C, 74.06; H, 4.83.

Method B. Benzophenone imine (1.0 g, 5.5 mmol; contained ca. 15% of benzophenone) in 5 mL of methylene chloride was added dropwise to a solution of dinitrogen tetraoxide (10.9 mmol) in 5 mL of methylene chloride mixed with sodium acetate (2.4 g, 29.3 mmol) at −70 °C under an argon atmosphere. The blue reaction mixture was warmed to −20 °C and stirred for a further 15 min. The slurry was quickly washed at 0 °C with water, saturated aqueous sodium carbonate solution, and finally with water. The blue organic phase was dried over Drierite for 5 min at 0 °C and filtered, and the solvent was removed at −10 °C (0.2 mmHg). The resultant deep-blue oily solid was dissolved in ether (5 mL) at 0 °C, and the solution was cooled overnight with dry ice. Cuboid crystals were obtained in greater than 50% yield upon removal of the mother liquor with a pipet. Two further low-temperature recrystallizations from a mixture of ether and pentane (50:50, v/v) gave chunky blue crystals: mp 52–52.5 °C (lit.[7] 50–53 °C); IR (CCl_4) 1662 (w), 1498 (s), 1445 (m), 702 (s) cm^{-1}; NMR ($CDCl_3$) δ 7.58 (m); UV–vis (CH_3CN) λ_{max} 595 nm (log ϵ 1.88), 304 (4.02), 258 (3.92). Thoman and Hunsberger[7] reported IR (CCl_4) 1669, 1600, 1575, 1515, 1477, 1311 cm^{-1} and UV λ_{max} 585 nm (log ϵ 2.033), 523 (2.079), 310 (3.721), 258 (3.596) for *N*-nitroso-2,4′-dichlorobenzophenone imine in ethanol and NMR (CCl_4) δ 7.55 for an impure sample of 8. The product was stored under argon at dry ice temperature and samples were removed under a blanket of argon.

***N*-Nitroso-2-camphanimine (7).** 2-Camphanimine (3.99 g, 26.4 mmol), prepared by the method of Heuben and Pfankuch,[24] was dissolved in 30 mL of hexane containing sodium acetate (130 mmol) and magnesium sulfate (130 mmol). The mixture was stirred at −20 °C and treated dropwise with nitrosyl chloride (25 mmol) in hexane (15 mL) over 2 min. The reaction mixture was stirred for 15 min at −10 to 0 °C, after which excess nitrosyl chloride was removed in vacuo, and the solids were filtered and washed with hexane. Evaporation of the filtrate gave 3.95 g (21.9 mmol, 84%) of purple crystalline nitroso imine 7. Sublimation at 0.1 mm and 0 °C followed by recrystallization from pentane at −20 °C gave a purple solid: mp 57–60 dec.

Anal. Calcd for $C_{10}H_{16}N_2O$: C, 66.63; H, 8.95; N, 15.54. Found: C, 66.04; H, 8.62; N, 16.33.

Decomposition of *N*-Nitrosobenzophenone Imine (8) in Acetonitrile (Estimation of Yield of Benzophenone). A solution of *N*-nitrosobenzophenone imine (0.99 mmol) in 100 mL of acetonitrile was decomposed at room temperature in the dark. After 48 h, this solution was diluted by a factor of 250 and the UV spectrum was measured. The spectrum obtained was identical with that of benzophenone. On the basis of the absorbance at 252 nm, a yield of 93% of benzophenone was calculated; a yield of 87% was calculated for a second run from the absorption at 340 nm. The extinction coefficient for sublimed benzophenone in acetonitrile was determined to be 1.77×10^4 mol^{-1} cm^{-1} at 252 nm (lit.[25] 1.80×10^4 at 253 nm in EtOH).

Kinetic Methods. a. Solvents. Chloroform was distilled from phosphorus pentoxide. Acetonitrile was Burdick and Jackson HPLC grade distilled from phosphorus pentoxide. Tetrahydrofuran was distilled from lithium aluminum hydride and methanol was distilled from magnesium methoxide. Ethanol, Pharmco 200° proof, was used as obtained. All distillations were through Vigreaux columns.

b. Procedure. All reactions were followed spectrophotometrically at 593 nm, using a thermostated cell compartment. The temperature fluctuation was less than 0.05 °C. Two 1-cm silica cells, equipped with Teflon stoppers, were used for each run. The cells, containing 1 mL of the appropriate solvent, were equilibrated in the cell compartment before the substrate (ca. 2.0 mg) was added as a solid to the sample cell, which was quickly shaken. The reaction was monitored for 10 half-lives, about 30 points being recorded for each reaction. The first-order rate constants were evaluated by using a "least-squares" regression routine. Correlation coefficients were never lower than 0.999, showing that good first-order kinetics were followed.

Decomposition of *N*-Nitrosobenzophenone Imine (8) in Methanol. *N*-Nitrosobenzophenone imine (90.8 mg, 43 mmol) was dissolved in dry methanol (75 mL). After 1 h in the dark at room temperature the solvent was removed on a rotary evaporator. Final traces of solvent were removed at 10^{-2} torr leave a slightly yellow solid (98.0 mg). The IR (KBr) and NMR ($CDCl_3$) spectra were indicative of a mixture of benzophenone (ca. 20%) and benzophenone dimethyl ketal (ca. 80%). GLC analysis of the reaction mixture (150 ft MBMA, 35 psi of N_2, 200 °C) showed one major (ca. 75%) and two minor (ca. 15% each) peaks. One of the minor peaks cochromatographed with benzophenone. The product was recrystallized twice from heptane and sublimed (80 °C, 0.2 mmHg) to give a white solid: mp 106–107 °C (lit.[26] mp 106.5–107 °C for benzophenone dimethyl ketal); IR (KBr) 2725, 1490, 1453, 1208, 1065, 997, 779, 752, 704 cm^{-1}; NMR ($CDCl_3$) δ 3.1 (6 H, s), 7.2–7.6 (10 H, m).

N-Nitrosobenzophenone imine was also decomposed in ethanol following the procedure described using methanol. GLC analysis of the reaction mixture (5 ft × $^1/_8$ in. 3% SE30, 35 psi of N_2, 130 °C) showed two peaks of equal size. One of the peaks cochromatographed with benzophenone.

Control Experiment for Ketal Formation from 8 in Methanol. Sublimed benzophenone (50 mg) was dissolved in 50 mL of methanol, and the solution was left in darkness for 1

(22) An example of a related oxygen atom transfer was reported by Olofson, R. A.; Michelman, J. S. *J. Am. Chem. Soc.* **1964**, *86*, 1863–1865.
(23) Pickard, P. L.; Tolbert, T. L. *J. Org. Chem.* **1961**, *26*, 4886.
(24) Houben, J.; Pfankuch, E. *Chem. Ber.* **1927**, *60*, 586.
(25) Rekker, R. F.; Nauta, W. *Recl. Trav. Chim. Pays-Bas* **1961**, *80*, 747.
(26) Mackenzie, J. E. *J. Chem. Soc.* **1896**, *69*, 985–993.

Table II. Mass Spectral Data[a]

m/e	% of base peak: run a (control)[b]	run b[b]	run c[c]
180	0.69		3.88
181	9.87	7.11	12.08
182	100	100	100
183	14.26	15.34	16.83
184	1.66	2.78	3.36

[a] Only weak peaks were observed with an m/e ratio >184. Benzophenone ($C_{13}H_{10}O$) was found to have a P + 2 peak intensity of 1.33% that of the base peak. The control showed 3% incorporation of ^{18}O [(1.66 - 1.33)(100)/11.71] and run b showed a total incorporation of 12% [(2.78 - 1.33)(100)/11.71]. [b] 0.1% H_2O in CH_3CN. [c] 0.4% H_2O in CH_3CN.

h. The solvent was removed on a rotary evaporator. Analysis of the residue by GLC (150 ft MBMA, 55 psi, 195 °C) showed only benzophenone to be present.

Labeling Studies. All operations were carried out in a glovebox under an argon atmosphere. Three solutions of nitroso imine and benzophenone were prepared in acetonitrile containing 11.71% ^{18}O enriched H_2O.

a. Run a (Control): 43.3 mg (0.24 mmol) of sublimed benzophenone in a mixture of 25 μL of $H_2{}^{18}O$ (1.4 mmol; 0.1% by volume) and 25 mL of acetonitrile.

b. Run b: 50 mg (0.24 mmol) of *N*-nitrosobenzophenone imine in 25 mL of acetonitrile and 25 μL of $H_2{}^{18}O$ as in part a. One milliliter of this solution was transferred to a UV cell, and the reaction was monitored at 593 nm. First-order kinetics were obtained ($k = 3.7 \times 10^{-4}$ s^{-1} at 23.8 °C).

c. Run c: 50 mg (0.24 mmol) of *N*-nitrosobenzophenone imine in a mixture of 100 μL of $H_2{}^{18}O$ (5.6 mmol; 0.4% by volume) and 25 mL of acetonitrile.

All three solutions were allowed to stand for 5 h (10 half-lives) in darkness. The residues obtained upon removal of the solvent in vacuo were used for mass spectrometric analysis. These were done at the Baker Laboratory, Department of Chemistry, Cornell University, Ithaca, NY. The results are shown in Table II.

Decomposition of *N*-Nitrosobenzophenone Imine (8) in the Presence of *trans*-Stilbene. A solution containing the nitroso ketimine (ca. 0.4 mmol) and *trans*-stilbene (ca. 0.4 mmol, containing 0.6% *cis*-stilbene) in benzene (10 mL) was degassed by four freeze–pump–thaw cycles at 10^{-3} torr and then sealed off in a glass tube. After 12 h at room temperature in darkness, the solution was concentrated and chromatographed on silica gel, using hexane as eluent. GLC analysis of the stilbene fraction on a 5% QF-1 column at 130 °C showed 0.5% *cis*-stilbene. GLC analysis of the crude reaction mixture showed mainly *trans*-stilbene and benzophenone. In addition to *cis*-stilbene, only two other peaks (<1%) were detected. IR confirmed that benzophenone was the major product. A repeat experiment using ca. 0.07 mol of *N*-nitrosobenzophenone imine gave the same result.

Decomposition of *N*-Nitrosobenzophenone Imine (8) in 2-Propanol. The nitroso imine (ca. 100 mg) was dissolved in 3 mL of 2-propanol containing one drop of acetic acid/75 mL. The solution was degassed by four freeze–pump–thaw cycles at 10^{-3} torr and sealed off in a glass tube. After decomposition (loss of blue color), TLC on silica gel indicated that no benzopinacol was present.

Decomposition of *N*-Nitrosobenzophenone Imine (8) in the Presence of Tetraethylammonium Tetrakis(1,3-diphenyl-1,3-propanedionato)europate (III). Nitrogen was bubbled through a solution of nitroso imine (ca. 20 mg) and the europium complex[17] (10 mg) in benzene (1 mL). The solution was heated to reflux in a dark room to effect decomposition of 8; no light was observed with dark-adapted eyes.

Decomposition of *N*-Nitrosobenzophenone Imine (8) in the Presence of Dibromoanthracene. A 3×10^{-3} M solution of nitroso imine 8 in toluene containing 9,10-dibromoanthracene (4.4×10^{-4} M) was degassed by pumping at 10^{-2} torr for 10 min. The container was filled with dry nitrogen and then placed in an oil bath at 190 °C. Observation of the contents with dark-adapted eyes led to no light detection.

Search for Light Emission in the Nitrosation of 9-Imino-10-methylacridan (11). Compound 11 was prepared in 38% yield from 9-aminoacridine by the method of Albert and Ritchie,[27] except that it was sublimed at 130 °C (0.2 torr): mp 138–140 °C (lit.[27] mp 134–136 °C); IR (KBr) 1605, 1590, 1495, 1470, 751 cm^{-1}; UV (CH_2Cl_2) λ_{max} 402 nm (log ε 3.97), 379 (3.90), 313 sh (3.63), 292 (3.96); NMR ($CDCl_3$) δ 3.7 (s, 3 H), 7.0–8.4 (m, 9 H).

Anal. Calcd for $C_{14}H_{12}N_2$: C, 80.74 H, 5.81; N, 13.45. Found: C, 80.82; H, 5.86; N, 13.60.

Imine 11 (100 mg, 0.48 mmol) was added as a fine powder to a stirred mixture of anhydrous sodium acetate (0.5 g, 6.1 mmol) and N_2O_4 (1 mL of a 4 M solution in CH_2Cl_2; 4 mmol) in a total of 3 mL of CH_2Cl_2 at −60 °C under an argon atmosphere. After the mixture was warmed at −20 °C, TLC on alumina showed the presence of only *N*-methylacridone (13). The above operations were carried out in a dark room; no light emission was detected with eyes that had been dark-adapted for 10 min. The reaction mixture was washed with water; the UV spectrum of the CH_2Cl_2 solution was identical with that of *N*-methylacridone.

No light was detected also when the above reaction was carried out with a N_2O_4/imine ratio of 0.5, or with $NO^+BF_4^-$ in a ratio of 0.6. In the latter case, TLC of the reaction mixture on alumina with 1/1 pyridine–toluene as the eluent showed the presence of both the imine 11 and *N*-methylacridone (13).

Reactions of *N*-Nitrosocamphorimine (7). Treatment of compound 7 (0.2 g) in 5 mL of methylene chloride with anhydrous hydrogen chloride for 30 s lead to an immediate loss of the purple color of 7. The infrared spectrum contained a peak at 2220 cm^{-1} for nitrosyl chloride and characteristic peaks for benzophenone imine hydrochloride. Evaporation of the solvent led to essentially pure imine hydrochloride (97% yield). Treatment of the imine hydrochloride in methylene chloride with ammonia led to a 71% yield of the imine, mp 90–95 °C. Recrystallization from cold ethanol led to the pure imine (43%), mp 96–98 °C (lit.[28] mp 98 °C).

A sample of nitroso imine 7 (6 g, 33 mmol) in 60 mL of CCl_4 was refluxed for 30 min, during which time the color changed to emerald green. An insoluble material which formed (0.24 g, 1.3 mmol, 4%) proved to be benzophenone imine hydrochloride). The IR spectrum of the solution showed the presence of camphor and *N*-nitrocamphorimine; major bands were also noted at 1695 and 1665 cm^{-1}. Evaporation of the solvent and distillation of the product yielded 4.1 g of a blue oil, GLC analysis of which identified camphor and *N*-nitrocamphorimine in the ratio of 1/2 as the principal products.

A sample of nitroso imine 7 (3.8 g, 21 mmol) sealed in a glass tube at 0.1 torr was allowed to decompose in the solid state at 25–30° until the color became a light yellow-green (2.5 days). Infrared spectra indicated the absence of nitrous oxide and the presence of camphor and *N*-nitrocamphorimine. Distillation of the product yielded 1.8 g of an oil, GLC analysis of which indicated that it contained 1.2 g (7.9 mmol, 38%) of camphor and 0.6 g (3.1 mmol, 15%) of *N*-nitrocamphorimine. The nonvolatile residue was extracted with hot hexane; the product obtained on cooling was recrystallized from ethanol/H_2O to give 42 mg (0.14 mmol, 0.7%) of camphorazine, mp 185–186 °C (lit.[29] mp 185–186 °C).

Camphor azine, prepared for comparison purposes, was synthesized from camphor hydrazone as described by Kishner.[29] *N*-Nitrocamphorimine was prepared from camphor oxime,[30] mp 42–43 °C (lit.[30] mp 43 °C).

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Registry No. 7, 81815-30-7; 8, 16620-67-0; 11, 5291-44-1; benzophenone imine, 1013-88-3; 2-camphanimine, 6791-26-0; benzophenone imine hydrochloride, 5319-67-5; camphor, 76-22-2; *N*-nitrocamphorimine, 31180-79-7; camphor azine, 47180-21-2.

(27) Albert, A.; Ritchie, B. *J. Chem. Soc.* **1943**, 458.
(28) Mahla, F.; Tiemann, F. *Chem. Ber.* **1900**, *33*, 1929.
(29) Kishner, N. *Chem. Zentralbl.* **1911**, *2*, 363.
(30) Angeli, A. *Gazz Chim. Ital.* **1896**, *2611*, 32. Hantzsch, A.; Dollfus, F. *Chem. Ber.* **1902**, *35*, 260.