The Chemistry of N-Nitrosoketimines[1]

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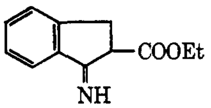
The reaction of nine ketimines with nitrosyl chloride in cold carbon tetrachloride produced brightly colored N-nitrosoketimines of varying stability, which decomposed *via* a first-order mechanism to the corresponding ketones and nitrogen. Stability toward such decomposition is enhanced by the presence of bulky substituents on the ketimine carbon atom, and, in the case of the N-nitrosobenzophenonimines, by the presence of electron-withdrawing substituents on the benzene rings. The reaction of four N-nitrosoketimines with triethyloxonium fluoroborate produced the corresponding 1,1-disubstituted propylene oxides, whose structure was proved by chemical and spectral evidence. A notable contribution of a 1,4-dipolar structure to the ground state of the N-nitrosoketimines is consistent with observed chemical and spectral properties.

N-Nitrosoketimines (**1**) were desired as starting materials for a projected synthesis of certain sydnones. The present work was initiated by preparing nine ketimines (**2a**–**i**) from the appropriate nitriles (**3**) and Grignard reagents (**4**).[2] Of these, seven (**2c**–**i**) were 2,4′- or 4,4′-disubstituted benzophenonimines and two (**2a**, **b**) were alkyl *o*-tolyl ketimines. The three 2,4′-disubstituted benzophenonimines (**2g**–**i**) were notably more stable toward hydrolysis than their respective 4,4′ isomers (**2c**, **d**, **f**) or benzophenonimine itself (**2e**). Our observations substantiate earlier work by Pickard,[3,4] who showed that, though electronic factors may exert some influence, stability toward hydrolysis increases with increasing bulk of the groups attached to the ketimine carbon atom.

Until recently, the rather extensive literature on ketimines contained only two references[5] to their nitrosation, and our work casts doubt on the authenticity of the products reported. Though Mitchell and Thorpe[5a] proposed structure **6** for the product of the attempted nitrosation of 1-imino-2-carboethoxyhydrindene (**5**),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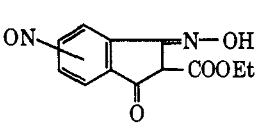
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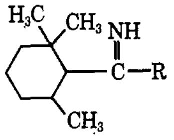
7a, R = C_6H_5
b, R = CH_3

Beilstein[6] reports it only as a "compound derived from 1-iminohydrindene-2-carboethoxy." Lochte, *et al.*,[5b] attempted the nitrosation of two ketimines (**7a**, **b**), but the products obtained gave combustion analyses which offered questionable support for the proposed N-nitroso structure.

When 4,4′-dimethoxybenzophenonimine (**2c**) and the 4,4′-dimethyl analog (**2d**) were treated with nitrous fumes[5b] at room temperature, we obtained products which gave positive Liebermann tests; however, their combustion analyses indicated the presence of two more atoms of oxygen per molecule than expected for the N-nitrosoketimines. Isolation of 4,4′-dimethoxy- and 4,4′-dimethylbenzophenone in excellent yields on acid hydrolysis of these products proved that ring nitrosation had not occurred. The virtual identity of the nmr spectra of these two products with those of the hydrochloride salts of **2c** and **2d** showed them to be the nitrate salts of **2c** and **2d**.

It was interesting to note that Thorpe's analysis of **6** also indicated the presence of two more atoms of oxygen per molecule than was expected.[5a] This leads us to suggest that Mitchell and Thorpe[5a] and also Lochte, *et al.*,[5b] probably had obtained nitrate salts of the respective ketimines rather than N-nitroso derivatives. Their own combustion analyses support this suggestion.

Our ketimines (**2**) were successfully nitrosated by treatment with nitrosyl chloride in cold carbon tetrachloride. Initially, the presence of **1h** in the cold solution was surmised by the appearance of an intense blue color on mixing the reagents; both the color and the product were lost during attempts at isolation at room temperature, and an excellent yield of 2,4′-dimethylbenzophenone resulted.[7] The isolation of the N-nitrosoketimines finally was accomplished by the method of Paskovich,[8] who with Zimmerman[9] had independently synthesized three very stable, highly hindered N-nitrosoketimines by the action of dinitrogen tetroxide on the ketimines. These were neither purified nor characterized, but were immediately reduced to the corresponding diazoalkanes.

The seven diaryl N-nitrosoketimines (**1c**–**i**) are deep blue or purple in color and differ widely in stability. Though the color was produced on addition of nitrosyl chloride to the ketimine in each case, some products (**1c**, **d**, **g**) were so unstable that they decomposed during attempted isolation. Those which could be isolated (**1e**, **f**, **h**, **i**) decomposed more or less slowly at room temperature. The two highly hindered alkyl aryl N-nitrosoketimines (**1a**, **b**) are raspberry-red oils which took 6 to 8 weeks to decompose at room temperature. One

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[1] From the Ph.D. Dissertation of C. J. Thoman, University of Massachusetts, 1966. Partial support of this work by a research grant (CA-05478) from the National Cancer Institute of the National Institutes of Health, and by a University of Massachusetts Research Grant (FR-J11-65) is gratefully acknowledged.

[2] P. L. Pickard and T. L. Tolbert, *J. Org. Chem.*, **26**, 4886 (1961).

[3] P. L. Pickard and D. J. Vaughan, *J. Amer. Chem. Soc.*, **72**, 876 (1950).

[4] (a) P. L. Pickard and D. J. Vaughan, *ibid.*, **72**, 5017 (1950); (b) P. L. Pickard and C. W. Young, *ibid.*, **73**, 42 (1951); (c) P. L. Pickard and E. F. Engles, *ibid.*, **74**, 4607 (1952); (d) P. L. Pickard and E. F. Engles, *ibid.*, **75**, 2148 (1953); (e) P. L. Pickard and S. H. Jenkins, Jr., *ibid.*, **75**, 5899 (1953).

[5] (a) A. D. Mitchell and J. F. Thorpe, *J. Chem. Soc.*, **97**, 2261 (1910); (b) H. L. Lochte, J. Horeczy, P. L. Pickard and, A. D. Barton, *J. Amer. Chem. Soc.*, **70**, 2012 (1948); (c) Nitrososydnonimines [H. Kato, M. Hashimoto, and M. Ohta, *Nippon Kagaku Zasshi*, **78**, 707 (1957); P. Brookes and J. Walker, *J. Chem. Soc.*, 4409 (1957)] and nitrosoiminothiazolinones [H. Beyer and H. Drews, *Chem. Ber.*, **87**, 1500 (1954)] are not "true" nitrosoketimines.

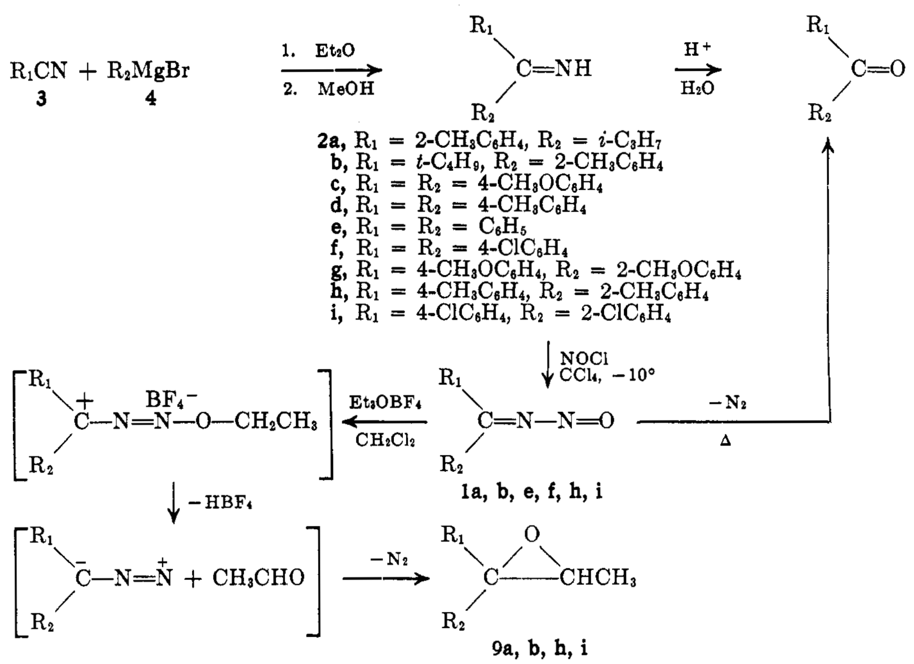
[6] F. K. Beilstein, "Handbuch der organischen Chemie," IVth ed, under $C_{12}H_{10}N_2O_5$ in the General Formelregister, **29** II, p 1237; *cf.* **10** I, pp 345, 346.

[7] E. Robson and J. M. Tedder, *Proc. Chem. Soc.* (London), 13 and 344 (1963), reported similar behavior when diacetylenic mercury compounds were nitrosated with nitrosyl chloride at −78°.

[8] D. H. Paskovich, University of Ottawa, private communication, 1963.

[9] H. Zimmerman and D. H. Paskovich, *J. Amer. Chem. Soc.*, **86**, 2149 (1964).

SCHEME I

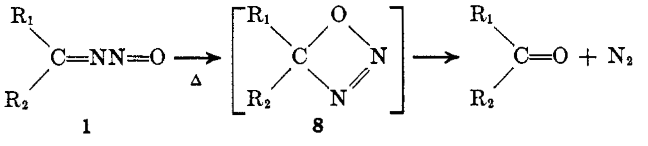


of the products of these decompositions was always the ketone.

This tendency of the N-nitrosoketimines to decompose to the corresponding ketones parallels the propensity of the parent ketimines toward hydrolysis, which in some cases is effected merely by atmospheric moisture. In each case, resistance to decomposition is enhanced by the presence of bulky R groups. It was surprising, then, to discover that a given N-nitrosoketimine is transformed to the corresponding ketone as readily in the absence of, as in the presence of, moisture (*e.g.*, under nitrogen, both in the solid state and in a dry solvent; at reduced pressure; and on a column of silica gel during attempted chromatography). Furthermore, when highly stable **1b** was allowed to stand at room temperature in water for several days, it was recovered virtually unchanged (nmr spectrum), while heating a carbon tetrachloride solution of the same compound on a steam bath caused total decomposition to the ketone within 30 min. This is not to deny that hydrolysis may be a competing reaction, especially for the less stable **1**.

That the above decomposition is not hydrolysis was further indicated by a kinetic study; appropriate plots of nitrogene volution *vs.* time indicated that the reaction is first order.

That nitrogen gas is the other product of this decomposition was proved by infrared and mass spectrometry. In view of the first-order kinetics, the thermally initiated decomposition of the N-nitrosoketimines would seem to involve an intra- rather than an intermolecular transition state (**8**).



If the nitroso oxygen atom is nucleophilic, an N-nitrosoketimine might be expected—by analogy with sulfoxides[10] and amine oxides[11]—to oxidize appropriate halides to aldehydes or ketones with the simultaneous formation of the corresponding disubstituted diazomethane. Numerous attempts to react N-nitrosoketimines with a variety of halides produced either unchanged starting materials or the ketone, the latter being formed by loss of nitrogen from the nitroso compound. However, reaction of **1b** with triethyloxonium fluoroborate produced an epoxide (**9b**), presumably by combination of the intermediate diazomethane (or the carbene derived from it) with transiently formed acetaldehyde[12] (see Scheme I).

The reaction was repeated with the other five N-nitrosoketimines (**1a**, **e**, **f**, **h**, **i**) that had been isolated. The two least stable of them (**1e**, **f**) yielded the corresponding benzophenones, owing to decomposition of the starting material. That the products (**9a**, **h**, **i**) obtained from the others were the corresponding epoxides was indicated by their combustion analyses, spectral properties, and chemical behavior, and was substantiated for one of them (**9i**) by the independent synthesis shown in Scheme II. Surprisingly, the final product of this synthesis was not the epoxide but one of the ketones (**10** or **11**). This ketone, a pale yellow oil, formed a 2,4-dinitrophenylhydrazone but did not give a positive iodoform reaction. The same yellow 2,4-dinitrophenylhydrazone slowly deposited when epoxide **9i** was allowed to stand for several days at room temperature in an acidic aqueous ethanolic solution of 2,4-dinitrophenylhydrazine.

The infrared spectrum of the above pale yellow oil had a strong carbonyl band at 1721 cm^{-1}; slow vacuum distillation of epoxide **9i** caused the appearance of this same band at 1719 cm^{-1}. The nmr spectrum showed

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(10) N. Kornblum, *et al.*, *ibid.*, **79**, 6562 (1957); H. R. Nace and J. J. Monagle, *J. Org. Chem.*, **24**, 1792 (1959); I. M. Hunsberger and J. M. Tien, *Chem. Ind.* (London), 88 (1959).

(11) L. J. Fliedner, M.S. Thesis, Fordham University, New York, N. Y., 1960; A. Javellana, M.S. Thesis, Fordham University, New York, N. Y., 1959.

(12) Attempts to identify acetaldehyde in the reaction mixture proved fruitless.

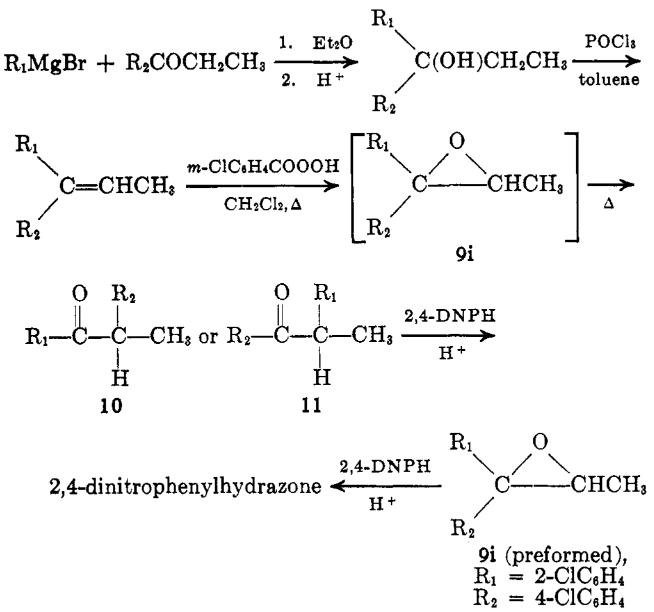
TABLE I

KETIMINES

Compd	Bp (mm) or mp, °C	Lit. bp (mm) or mp, °C	Yield, %	Nmr[a] (δ) N–H	ArH[b]	ArCH$_3$
2a	59–63 (0.4)	86–87 (5)[3]	6.2	. . .	7.23 (4.0)	2.30 (2.4)[c]
2b[d]	234–235 (755)	235 (740)[3]	77	8.80 (?)	6.73 (4.0)	1.98 (3.0)[e]
2c[f,g]	131–132	129–130[14]	54	. . .	7.27 (8.0)[h]	
2d[i]	65–67	67–69,[j] 81[4a]	50	9.20 (0.5)	7.44 (8.0)	2.38 (6.0)
2e	135–138 (4)	127 (3.5)[2]	68	. . .	7.32	
2f[k]	55–57	59.5–60.5[j]	80	9.52 (0.7)	7.21 (8.0)	
2g[l,m]	64–67		87	8.95 (0.6)	7.19 (8.0)[n]	
2h	134–137 (2.5)	138–140 (2)[4a]	54	8.92 (0.8)	7.01 (8.0)	1.95 (3.0) 1.78 (3.0)
2i[o]	163–164 (0.8)		57	9.52 (0.7)	7.25 (8.0)	

[a] Nmr values were measured in parts per million (ppm) downfield from TMS as an internal standard; intensities (in parentheses) relative to phenyl H; CCl$_4$ solvent. [b] The approximate center of complex absorption for the diaryl compounds is listed. [c] Alkyl CH$_3$ absorption is at 1.43 (5.7); the isopropyl methyne absorption is at 2.31 (0.8). [d] Prepared from *t*-BuCl (rather than *t*-BuBr). [e] Alkyl CH$_3$ absorption is at 1.02 (9.0). [f] Calcd for $C_{15}H_{15}NO_2$: C, 74.66; H, 6.27; N, 5.81. Found: C. 74.06, 74.24; H, 6.05, 5.94; N, 5.27, 5.35. [g] Reaction with NOCl (green color on mixing) gave 4,4′-dimethoxybenzophenone (89% yield). [h] Aromatic OCH$_3$ absorption is at 3.85 (3.0), 3.82 (3.0). [i] Reaction with NOCl (blue color on mixing) gave 4,4′-dimethylbenzophenone (62% yield). [j] E. J. Grubbs, J. D. McCullough, B. H. Weber, and J. R. Maley, *J. Org. Chem.*, **31**, 1098 (1966). [k] Calcd for $C_{13}H_9NCl_2$: C, 62.42; H, 3.63; N, 5.60; Cl, 28.35. Found: C, 62.61; H, 3.60; N, 5.51; Cl, 28.50. [l] Calcd for $C_{15}H_{15}NO_2$: C, 74.66; H, 6.27; N, 5.81. Found. C, 74.20; H, 6.36; N, 5.68. [m] Reaction with NOCl (blue color on mixing) gave 2,4′-dimethoxybenzophenone (59% yield). [n] Aromatic OCH$_3$ absorption is at 3.72 (3.0), 3.62 (3.0). [o] Calcd for $C_{13}H_9NCl_2$: C, 62.42; H, 3.63; N, 5.60; Cl, 28.35. Found: C, 62.61; H, 3.60; N, 5.51; Cl, 28.50.

SCHEME II



no indication of an aldehydic hydrogen, but it did contain a quartet–doublet pairing at 3.42 and 1.12 ppm, indicating the presence of a >CH–CH$_3$ group in the molecule.

Apparently, the conditions of the epoxidation were severe enough to open the transiently formed epoxide (**9i**), the resulting intermediate then stabilizing itself by migration of one of the aryl groups (probably 4-ClC$_6$H$_4$) to form **10** or **11**. No attempt was made to further identify this product.

Pertinent data on the infrared and nmr spectra of the ketimines, N-nitrosoketimines, and 1,1-disubstituted propylene oxides are collected in Tables I, II, and III, respectively. Pickard and Polly[13] studied the infrared spectra of 15 dialkyl, alkyl aryl, and diaryl ketimines and reported the presence of N–H stretching absorption between 3247 and 3205 cm^{-1}, and of C=N stretching absorption between 1653 and 1603 cm^{-1}. They compared the latter to the stretching absorption of the corresponding ketones, which lies between 1718 and 1661 cm^{-1}. For **2c**, Williams and his coworkers[14] found these two absorptions at 3257 and 1646 cm^{-1}, respectively.

Our ketimines showed N–H stretching absorption between 3257 and 3215 cm^{-1} and C=N stretching absorption between 1623 and 1603 cm^{-1}, whereas the C=O stretching absorption of our corresponding ketones occurred between 1689 and 1647 cm^{-1}. Further comparison of the infrared spectra of our ketimines with those of the corresponding ketones revealed that only the ketimines exhibit a strong absorption near 1350 cm^{-1} (range of 1372–1340 cm^{-1}); this band may be distinctive of the ketimines (probably C=NH bending). The assignment of this band to the Ar$_2$C=N grouping[14] cannot be reconciled with the fact that the absorption also appears in the spectra of our alkyl aryl ketimines.

Roberts[15] found N–H bands of three N^{14}-labeled ketimines to be about 9 ppm downfield from tetramethylsilane. In carbon tetrachloride, this peak broadened to a bump, which at times proved difficult to detect at room temperature; in other solvents, notably carbon disulfide, it sharpened, especially at low temperatures. The nmr spectra of our ketimines confirm the position of this N–H absorption and the difficulty in detecting it. Its extreme breadth tends to cause low integration values.

From a study of the infrared spectra of N-nitrososydnonimines, Hashimoto[16] concluded that they exist to a great extent in a 1,3-dipolar form and assigned bands at 1680–1665 and 1555 cm^{-1} to C=N$^+$ and $^+$N=N, respectively. Bellamy[17] indicates the existence of two absorptions distinctive of N—O$^-$ between 1310 and 1250 cm^{-1}; our N-nitrosoketimines consistently exhibited a strong band toward the upper end of

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(13) P. L. Pickard and G. W. Polly, *J. Amer. Chem. Soc.*, **76**, 5169 (1954).

(14) H. B. Williams, P. E. Koenig, G. Huddleston, T. Couvillon, and W. Castille, *J. Org. Chem.*, **28**, 463 (1963).

(15) J. B. Lambert, W. L. Oliver, and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 5085 (1965).

(16) M. Hashimoto, Ph.D. Thesis, Tokyo Institute of Technology, Tokyo, Japan, 1960.

(17) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1960, p 308.

TABLE II

N-NITROSOKETIMINES

Compd	Mp, °C[a]	Color	Yield, %	Principal ir[b] bands (1700–1000 cm^{-1})	Nmr[c] (δ) ArH[d]	Nmr[c] (δ) ArCH$_3$	Nmr[c] (δ) AlkCH$_3$
1a	Oil[e]	Red	51	1695, 1608, 1580, 1484, 1466, 1319	7.00 (4.0)	2.17 (2.4)	1.22 (6.2)[f]
1b	Oil[e]	Red	83	1698, 1610, 1580, 1481, 1466, 1321	6.88 (4.0)	2.17 (3.2)	1.23 (9.8)
1e[g]	50–53	Blue	25	1669, 1603, 1570, 1493, 1451, 1321	7.55		
1f[h]	61–63	Blue	41	1660, ——, 1587, 1497, 1485, 1312			
1h[i,j]	43[k]	Purple	68	1668, 1610, 1570, 1498, 1488, 1316	7.27 (8.0)	2.38 (3.0) 2.12 (2.5)	
1i[i,l]	69–71	Purple	76	1669, 1600, 1575, 1515, 1477, 1311			

[a] All samples melted with decomposition. [b] Spectra were determined in CCl_4 with a Beckman IR-5. [c] Nmr values were measured in parts per million (ppm) downfield from TMS as an internal standard; intensities (in parentheses) relative to phenyl H; CCl_4 solvent. [d] The approximate center of complex absorption for the diaryl compounds is listed. [e] An analytically pure sample was not obtained. [f] The isopropyl methyne absorption is at 2.27 (0.8). [g] Reaction with Et_3OBF_4 gave benzophenone (66% yield). [h] Reaction with Et_3OBF_4 gave 4,4′-dichlorobenzophenone (48% yield). [i] Mailed (air freight) for combustion analysis packed in Dry Ice. [j] Calcd for $C_{15}H_{14}N_2O$: C, 75.60; H, 5.92; N, 11.76. Found: C, 75.54, 75.62; H, 6.14, 6.30; N, 11.01, 11.24. [k] See ref 8. [l] Calcd for $C_{13}H_8N_2OCl_2$: C, 55.94; H, 2.89; N, 10.04; Cl, 25.41. Found: C, 55.76, 55.77; H, 3.15, 3.28; N, 9.68, 9.81; Cl, 25.22, 25.11.

TABLE III

1,1-DISUBSTITUTED PROPYLENE OXIDES

Compd	Bp (mm), °C	Yield, %	Formula	Calcd, % C	Calcd, % H	Found, % C	Found, % H	Ir,[a] cm^{-1} Epoxy methyne stretch	Ir,[a] cm^{-1} Epoxide bend	Nmr[b] (δ) ArH[c]	Nmr[b] (δ) ArCH$_3$	Nmr[b] (δ) Oxide H	Nmr[b] (δ) Oxide CH$_3$
9a	77–78 (2.0)[d]	26						3236	1252	6.96 (4.0)	2.13 (2.7)[e]	3.45 (1.2)	1.17 (3.0)
9b	58–60 (0.5)	69	$C_{14}H_{20}O$	82.30	9.87	82.17, 82.34	9.78, 9.90	3226	1251	6.88 (4.0)	2.05 (3.1)[f]	2.87 (0.8)	1.12 (3.2)
9h	129–131 (0.8)	61	$C_{17}H_{18}O$	85.67	7.61	85.47	7.23	3236	1268	7.20 (8.0)	2.28 (3.6), 2.23 (1.9)	3.37 (0.9)	2.00 (2.8)
9i	172–173 (2.6)	40	$C_{15}H_{12}OCl_2$[g]	64.53	4.33	64.43	4.50	3247	1261	7.18 (8.0)		3.19 (0.9)	1.12 (3.0)

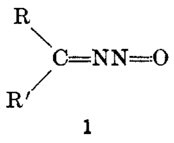
[a] Spectra determined with a Beckman IR-5; CCl_4 solvent for **9a** and **9b**; **9h** and **9i** neat. [b] Nmr spectra were measured in parts per million (ppm) downfield from TMS as an internal standard; intensities (in parentheses) relative to phenyl H. [c] The approximate center of complex absorption for the diaryl compounds is listed. [d] Not analytically pure. [e] The isopropyl methyne absorption is at 2.27 (0.9); the alkyl CH_3 absorption is at 1.17 (6.0). [f] The alkyl CH_3 absorption is at 1.15 (8.1). [g] Calcd: Cl, 25.40. Found: Cl, 25.27.

this region. Their most distinctive absorptions, however, are the pairs of strong bands at 1515–1451 cm^{-1}. Both the infrared and nmr spectra of our N-nitrosoketimines exhibited no absorption in the N—H region.

All the 1,1-disubstituted propylene oxides exhibited a sharp, weak band in the infrared at 3226–3247 cm^{-1}, which may be ascribed to the epoxy methyne hydrogen. Normal methyne absorption (where the other three bonds are all to carbon) is found at about 2960 cm^{-1}, and this would be expected if the product were the isomeric disubstituted acetone. The most distinctive epoxide absorption[18] also is present at 1251–1268 cm^{-1}.

The nmr spectra of these epoxides all contain two distinctive related absorptions: a quartet at 3.45–2.87 and a doublet at 2.00–1.12 ppm, of relative intensities 1:3. These cannot be explained on the basis of the product being either the isomeric 1,1-disubstituted acetone or the isomeric 2,2-disubstituted propionaldehyde. Furthermore, no aldehyde absorption was evident in the nmr spectrum.[19]

Three of the possible structures contributing to the resonance of N-nitrosoketimines are shown below. None of the physical measurements essential for the determination of their true structure has yet been made. Still, some evidence is provided by their chemical properties and physical characteristics.



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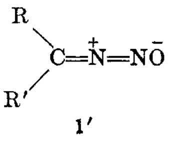

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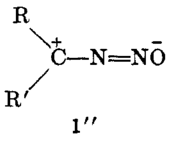

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The individual N-nitrosoketimines vary widely in stability. Within the two series of N-nitroso-4,4′- and 2,4′-disubstituted benzophenonimines (**1c–f** and **1g–i**), stability is increased by electron-withdrawing substituents and lowered by electron-donating ones, as is the case with corresponding diazonium salts.[20] Steric considerations, however, seem to be of even greater importance. **1h** can be isolated while **1d** (its (4,4′ analog) cannot, and **1i** treated with triethyloxonium fluoroborate forms an epoxide while **1f** decomposes under the same conditions to the corresponding ketone. The two highly hindered alkyl aryl N-nitrosoketimines (**1a, b**) are the most stable of those studied.

While chemical properties indicate only the structure of the transition state, the fact that intramolecular decomposition of unhindered N-nitrosoketimines occurs at room temperature, or even below, is consistent with a low activation energy and a substantial contribution of the 1,4-dipolar structure (**1″**) to the ground state. Also, the presence of bulky R groups around the ketimine carbon atom would be expected to impede the formation of the postulated four-membered cyclic intermediate (**8**) by attack of the nucleophilic nitroso oxygen atom. The nucleophilic nature of this oxygen atom also is shown by the reaction with triethyloxonium fluoroborate.

A characteristic property of the N-nitrosoketimines is their intense color, and this prompted the recording of their ultraviolet–visible absorption spectra (Table IV). The low extinction coefficients of all peaks in the visible region led us to suspect that the deep colors of the N-nitrosoketimines might be due to a surface phe-

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(18) See ref 17, pp 118, 119.

(19) Further chemical evidence that excludes these isomeric carbonyl compounds includes the failure of the product to form a 2,4-dinitrophenylhydrazone under ordinary conditions or to give the iodoform test.

(20) Z. E. Jolles in "The Chemistry of Carbon Compounds," Vol. IIIa, E. H. Rodd, Ed., Elsevier, New York, N. Y., 1954, p 266. *Cf.* also C. C. Snow, *Ind. Eng. Chem.*, **24**, 1420 (1932).

TABLE IV

ULTRAVIOLET–VISIBLE ABSORPTION SPECTRA OF N-NITROSOKETIMINES

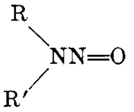
Compd	Solvent	λ, mμ (log ε)
1a	CCl_4	254, 268, 273, 284, 500, 518
b	EtOH	226, 268, 275, 284, 502, 518
f	CCl_4	256 (3.993), 265 (4.001), 306 (3.943), 522 (2.033), 596 (2.033)
h	EtOH	259 (4.009), 312 (3.925), 494 (1.380), 520 (1.518)
i	EtOH	258 (3.596), 310 (3.721), 523 (2.079), 585 (2.033)

nomenon, though the intense colors of their solutions suggested otherwise.

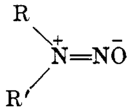
The ordinary nitrosochromophore causes a blue or green color in the monomeric state corresponding to distinctive bands at 300 and 665 mμ; such bands are absent in the spectra of **1** (Table IV). The azo chromophore also produces intense colors, the wavelength of the absorption bands varying with the amount of conjugated unsaturation. Dialyl compounds **1** are blue or purple in color, indicating a high degree of conjugation. The less conjugated alkyl aryl **1** are red, revealing the expected hypsochromic effect.

Although both **1′** and **1″** contain the azo chromophore, the failure of the N-nitrosoketimines to undergo attempted 1,3-dipolar cycloadditions with ketene, ketene diethyl acetal, and dimethyl acetylenedicarboxylate is consistent with a low contribution of **1′** to the transition state of the molecule.

The 1,3-dipolar structure of the nitrosamines (**12′**), originally proposed on the basis of spectral evidence,[21] is consistent with the synthesis and isolation of a host of nitrosimmonium salts.[22] A major contribution of **1″** to the transition state, and probably to the ground state, of the N-nitrosoketimines would be directly analogous. Unfortunately, the nmr method, which worked so well in determining the structure of **12**, is incapable of distinguishing the relative contributions of **1**, **1′**, and **1″**. Structure **1″** emphasizes that N-nitrosoketimines usefully may be regarded as N-oxides of disubstituted diazomethanes.



12



12′

Experimental Section[23]

General Synthesis of Ketimines (2).—A Grignard reagent was prepared by slowly adding about 0.4 mol of the appropriate halide in 100 ml of anhydrous ether to magnesium turnings (10 g, 0.41 g-atom) in 25 ml of anhydrous ether. The dark solution was allowed to stand for several hours until cool. In those reactions in which steric hindrance was a factor, dry toluene (150 ml) was added and the ether was distilled until the temperature had reached 100°; a light solid usually appeared in the toluene solution. The appropriate nitrile (about 0.36 mol) in 50 ml of solvent (or enough to effect solution) was added dropwise, and the resulting suspension refluxed for about 2 days. To the cooled suspension, anhydrous methanol (90 ml) was added with efficient stirring and the stirring continued for an additional 2 hr under gentle reflux. The hot suspension was filtered with suction and the solid, white methoxymagnesium halide was washed several times with anhydrous ether. Removal of the solvent from the filtrate at reduced pressure afforded the crude ketimine, from which the pure product was obtained by recrystallization or vacuum distillation. Data on the individual ketimines are found in Table I.

Nitrate Salt of 4,4′-Dimethoxybenzophenonimine.—4,4′-Dimethoxybenzophenonimine (**2c**) (0.5 g, 2 mmol) was suspended in 25 ml of petroleum ether (bp 30–60°) and nitrous fumes were introduced. A deep blue color developed immediately, but was replaced after about 3 hr by a clear brown solution containing a light yellow powder. Filtration followed by washing with petroleum ether left 0.54 g (85%) of a solid which gave a strong Liebermann test. Several recrystallizations from chloroform–petroleum ether afforded the analytical sample, mp 178–180° with sweating from 140°.

Anal. Calcd for $C_{15}H_{14}N_2O_5$: C, 59.21; H, 5.30; N, 9.21. Found: C, 59.17, 59.33; H, 5.30, 5.33; N, 9.02, 9.14.

Nitrate Salt of 4,4′-Dimethylbenzophenonimine.—The crude yield of this compound, prepared as above from 4,4′-dimethylbenzophenonimine (**2d**), was 1.3 g (99%). Several recrystallizations from chloroform–petroleum ether produced the analytical sample, mp 190–192° with sweating from 150°.

Anal. Calcd for $C_{15}H_{16}N_2O_3$: C, 66.14; H, 5.92; N, 10.29. Found: C, 66.68; H, 6.01; N, 9.91, 9.72.

Hydrolysis of 4,4′-Dimethoxybenzophenonimine (2c).—A suspension of **2c** (0.50 g, 1.66 mmol) in 20 ml of 6 *N* hydrochloric acid was refluxed for 24 hr. The solution was cooled, filtered, and the gray solid (mp 145–147°) washed with ether. The yellow filtrate was extracted three times with ether, and the combined extracts were dried and evaporated to give 0.09 g of 4,4′-dimethoxybenzophenone as white needles, mp 142–144° (lit.[24] mp 143–144°). Total yield was 0.44 g (86%).

Hydrolysis of the Nitrate Salt of 2c.—A similar hydrolysis of the nitrate salt of **2c** gave 0.32 g of a product that melted over a wide range. Fractional crystallization from cyclohexane gave very thin, colorless needles, mp 108–110°, and clusters of colorless rods, mp 137–139°. The infrared spectrum of the latter was identical with that of 4,4′-dimethoxybenzophenone[25] (lit.[24] mp 143–144°).

Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.83; O, 19.81. Found: C, 74.65; H, 5.68; O, 19.67.

The infrared spectrum of the colorless needles was similar to, but not identical with, the spectrum of 4,4′-dimethoxybenzophenone. No mention of a lower melting form of this ketone was found in the literature. These needles were also analyzed.

Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.83; O, 19.81. Found: C, 74.79; H, 5.34; O, 19.87.

Hydrolysis of 4,4′-Dimethylbenzophenonimine (2d).—A similar hydrolysis of **2d** gave the corresponding ketone as white needles, mp 95–96° (lit.[25] mp 92–95°), whose infrared spectrum agreed with that in the literature.[25]

General Synthesis of N-Nitrosoketimines (1).—A suspension of sodium acetate (14.8 g, 0.145 mol) in 40 ml of dry carbon tetrachloride was cooled to below −10° (internal temperature) in a Dry Ice–acetone bath. Nitrosyl chloride (4.00 g, 60 mmol) was added with stirring, followed by a solution of the ketimine (**2**) (40 mmol) in 10 (more, if necessary) ml of dry carbon tetrachloride cooled to −10°, the internal temperature being kept at or below −10°. Addition of the ketimine caused the immediate appearance of a dark color. The mixture was stirred for 20 min at −10° and quickly washed with 200 ml of ice-cold 10% potassium bicarbonate, followed by 200 ml of ice-water. The dried (anhydrous magnesium sulfate) solution was evaporated under reduced pressure and the resultant, deeply colored oil was dis-

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(21) C. R. Looney, W. D. Phillips, and E. L. Reilly, *J. Amer. Chem. Soc.*, **79**, 6163 (1957); G. J. Karabatsos and R. A. Taller, *ibid.*, **86**, 4373 (1964).

(22) S. Hünig, L. Geldern, and E. Lücke, *Rev. Chim.* (Bucharest), **7**, 935 (1962); *Angew. Chem.*, **75**, 476 (1963); A. Schmidpeter, *Tetrahedron Lett.*, 1421 (1963); *Chem. Ber.*, **96**, 3275 (1963); D. Klamann and W. Koser, *Angew. Chem.*, **75**, 1104 (1963).

(23) All melting points, which are uncorrected, were determined with a Kofler hot stage, except those (so designated) taken in sealed capillaries, which were determined with a Hershberg-type apparatus. Combustion analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Infrared spectra were obtained with a Beckman IR-5 or a Perkin-Elmer Model 21 spectrophotometer. Ultraviolet and visible spectra were obtained with a Cary Model 14 recording spectrophotometer. Nuclear magnetic resonance spectra were determined with a Varian A-60 high-resolution spectrometer. The mass spectrograph was determined with a Hitashi Perkin-Elmer Model RMU-6A mass spectrophotometer.

(24) K. Auwers, *Ann. Chem.*, **356**, 127 (1907).

(25) N. Lozach and G. Guillouzo, *Bull. Soc. Chim. Fr.*, [5] **24**, 1221 (1957).

solved in 10 ml of anhydrous ether and cooled to −78° in Dry Ice. If a solid separated, it was recrystallized from petroleum ether by dissolution at 0° followed by cooling in Dry Ice to −78°. Data on the individual **1**, including combustion analyses, are found in Table II. No way was found to purify the two red oils (**1a, b**), since they decomposed to the corresponding ketones on attempted vacuum distillation and on attempted chromatography on silica gel.

Kinetic Study of the Decomposition of N-Nitrosoketimines (1).—N-Nitroso-2,4′-dimethylbenzophenonimine (**1h**) (0.50 g, 2.1 mmol) was dissolved in 25 ml of cyclohexane at 23°; the gas evolved (N_2) was allowed to displace water from a gas measuring tube. A sample of the data collected was subjected to analysis for both first- and second-order kinetics. The linearity of the first-order curve and the constancy of the first-order rate constant and of the resultant first-order half-life (4.75 hr) all indicate a first-order mechanism for the decomposition.

General Synthesis of 1,1-Disubstituted Propylene Oxides (9).—Twenty milliliters of an ethylene chloride solution containing 1.17 mmol of triethyloxonium fluoroborate[26] per milliliter (4.45 g, 23.4 mmol) was cooled to 5° in a three-neck flask fitted with a reflux condenser, a dropping funnel, and an inlet tube for maintaining a nitrogen atmosphere, and treated dropwise with a solution of the N-nitrosoketimine (**1**) (16.8 mmol) in 10 ml of ethylene chloride. The resulting deeply colored solution was stirred at 0–5° for 1 hr and then allowed to warm slowly to room temperature. Gas evolution occurred during this warming, followed by a gradual change of the deep red or blue color to bright orange. After evolution of gas had ceased, the solvent was removed under reduced pressure and the residual orange-red oil was dissolved in 20 ml of anhydrous ether and washed twice with 5% sodium bicarbonate and twice with water. Evaporation of the dried (anhydrous magnesium sulfate) ether solution under reduced pressure and vacuum distillation of the resulting oil afforded the 1,1-disubstituted propylene oxide (**9**) as a colorless or pale yellow oil. Data on **9**, including combustion analyses, are found in Table III.

Similar reactions of triethyloxonium fluoroborate with **1e** and **1f** produced only the corresponding ketones.

1-(2-Chlorophenyl)-1-(4-chlorophenyl)-1-propanol.—A Grignard reagent was prepared from magnesium turnings (2.75 g, 0.113 g-atom) in 10 ml of anhydrous ether and 2-bromochlorobenzene (21.00 g, 0.1097 mol) in 90 ml of anhydrous ether. After the dark solution was stirred for 2 hr under gentle reflux, a solution of 4-chloropropiophenone (16.86 g, 0.1000 mol) in 30 ml of anhydrous ether was added dropwise, and the resulting suspension was refluxed overnight, cooled in an ice bath, and treated with 50 ml of 20% sulfuric acid and 70 g of ice. The ether solution was separated, the aqueous layer was extracted twice with 20-ml portions of ether, the combined ether extracts were dried over anhydrous magnesium sulfate, and the ether was removed under reduced pressure to give a crude orange-brown oil, vacuum distillation of which afforded 17.8 g (63.4%) of a colorless oil, bp 138–140° (30 mm). Its infrared and nmr spectra coincided with expectations.

1-(2-Chlorophenyl)-1-(4-chlorophenyl)propene.—1-(2-Chlorophenyl)-1-(4-chlorophenyl)-1-propanol (17.80 g, 63.3 mmol) was refluxed overnight in a solution of 5 ml of phosphorus oxychloride in 25 ml of toluene. The solution was cooled and poured with stirring into 50 g of ice. After the ice had melted, the toluene was separated and the aqueous fraction was extracted three times with 10-ml portions of ether. The combined organic fractions were washed three times with 15-ml portions of 5% sodium bicarbonate and twice with 15-ml portions of water and dried over magnesium sulfate, and the solvents were removed at reduced pressure. Vacuum distillation of the deep orange oil yielded 10.9 g (65.5%) of a pale yellow oil, bp 132–134° (0.35 mm).

Anal. Calcd for $C_{15}H_{12}Cl_2$: C, 68.46; H, 4.60; Cl, 26.94. Found: C, 68.33, 68.57; H, 4.43, 4.37; Cl, 27.21, 27.08.

1-(2-Chlorophenyl)-2-(4-chlorophenyl)-1-propanone (10) or 1-(4-Chlorophenyl)-2-(2-chlorophenyl)-1-propanone (11).—A solution of *m*-chloroperbenzoic acid (4.47 g, 22.0 mmol) in 60 ml of methylene chloride was added dropwise to a solution of 1-(2-chlorophenyl)-1-(4-chlorophenyl)propene (4.20 g, 16.0 mmol) in 10 ml of methylene chloride, and the mixture was refluxed for 18 hr. After cooling, the excess per acid was decomposed by stirring with 25 ml of 10% aqueous sodium sulfite until no iodine was liberated from a sample on addition of a solution of potassium iodide in 95% ethanol. The methylene chloride layer was separated and washed twice with 15 ml of 5% aqueous sodium bicarbonate and twice with water and dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. Vacuum distillation afforded 4.05 g (90.5%) of **10** or **11** as a yellow oil, bp 146–148° (0.35 mm).

Anal. Calcd for $C_{15}H_{12}OCl_2$: C, 64.53; H, 4.33; Cl, 25.40. Found: C, 64.43; H, 4.50; Cl, 25.27.

The yellow 2,4-dinitrophenylhydrazone of this oil, mp 156–158°, also was analyzed.

Anal. Calcd for $C_{21}H_{16}Cl_2N_4O_4$: C, 54.92; H, 3.51; N, 12.20; Cl, 15.44. Found: C, 54.79; H, 3.81; N, 12.11; Cl, 15.40.

Registry No.—**1a**, 16620-65-8; **1b**, 16620-66-9; **1e**, 16620-67-0; **1f**, 16620-68-1; **1h**, 16620-69-2; **1i**, 16620-70-5; **2a**, 16620-71-6; **2b**, 16620-72-7; **2c**, 5291-48-5; **2c** nitrate salt, 16620-74-9; **2d**, 16620-75-0; **2d** nitrate salt, 16620-76-1; **2e**, 1013-88-3; **2f**, 5526-10-3; **2g**, 16621-07-1; **2h**, 16621-08-2; **2i**, 16621-09-3; **9a**, 16621-10-6; **9b**, 16621-11-7; **9h**, 16621-12-8; **9i**, 16621-13-9; 1-(2-chlorophenyl)-1-(4-chlorophenyl)-1-propanol, 16621-14-0; 1-(2-chlorophenyl)-1-(4-chlorophenyl)propene, 16621-15-1.

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[26] H. Meerwein, *Org. Syn.*, **46**, 113 (1966).