($M^+$ - BuOCO - $CO_2$), 256 ($M^+$ - $CO_2$PNB), 249 ($M^+$ - $C_4H_8OCO$ - $CH_3CH_2CHCO_2H$), 156 ($M^+$ - $C_4H_8OCO$ - $CO_2$PNB), 138 ($C_8H_{12}NO^+$); the low-resolution mass spectrum shows a low-intensity molecular ion at $m/e$ 436.

A sample of **17a** was treated with diazomethane in ether to give the methyl ester **20a** (quantitative); high-resolution mass spectrum, calcd for $C_{17}H_{21}N_2O_6$ $m/e$ 349.1399, found $m/e$ 349.1405; $m/e$ 349 ($M^+$ - BuOCO), 249 ($M^+$ - $CH_3CH_2CHCO_2CH_3$ - $C_4H_8OCO$), 170 ($M^+$ - $CO_2$PNB - $C_4H_8OCO$); the low-resolution mass spectrum shows a molecular ion at $m/e$ 450.

***p*-Nitrobenzyl (±)-6-Ethylcarbapenam-3-carboxylates 25a and 25b.** 2-[1-(*tert*-butoxycarbonyl)-2-(*p*-nitrobenzyloxycarbonyl)-5-pyrrolidinyl]butanoic acid (**17a**; 140 mg, 0.32 mmol) was dissolved in 1 N HCl in EtOAc (4 mL) and stirred for 2.5 h at room temperature. The solvent was evaporated, and $CCl_4$ was added and evaporated again. The residue was washed with ether and dried to give the hydrochloride of 2-[2-(*p*-nitrobenzyloxycarbonyl)-5-pyrrolidinyl]butanoic acid (**22a**) as a solid (119 mg, quantitative). To a cold solution (0 °C) of the hydrochloride of **22a** (112 mg, 0.30 mmol) in dry $CH_2Cl_2$ (180 mL) were added pyridine (34 mg, 0.43 mmol) and 1-(3′-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (154 mg, 0.80 mmol). The reaction mixture was stirred at 0 °C under argon for 1 h and then for 22 h at room temperature, and it was then washed with ice-cold water (4 × 50 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue (silica gel, 0.04–0.063 mm; ether–hexane, 2:1) afforded the carbapenam **25a**: 39 mg (41%); IR ($CH_2Cl_2$) 1760, 1742, 1610, 1522 $cm^{-1}$; NMR (270 MHz, $CD_2Cl_2$) $\delta$ 0.95 (t, $J$ = 7.4 Hz, 8-$H_3$), 1.40–1.72 (m, 7-$H_2$), 1.74–1.96 (m, 1-$H_2$), 2.30 (m, 2-$H_2$), 3.13 (dddd, $J$ = 9, 8, 5, 1 Hz, 6-H), 3.78 (ddd, $J$ = 9, 6, 5 Hz, 5-H), 3.92 (dt, $J$ = 5, 1 Hz, 3-H), 5.21 and 5.28 (AB q, $J$ = 13.4 Hz, $CH_2$Ar), 7.58 and 8.22 (aB q, $J$ = 8.8 Hz, $C_6H_4NO_2$); high-resolution mass spectrum, calcd for $C_{16}H_{18}N_2O_5$ $m/e$ 318.1215, found $m/e$ 318.1211; $m/e$ 318 ($M^+$), 301 ($M^+$ - OH), 290 ($M^+$ - CO), 249 ($M^+$ - $CH_3CH_2C{=}C{=}O$), 182 ($M^+$ - PNB, 138 ($M^+$ - $CO_2$PNB), 137 ($CH_3C_6H_4NO_2^+$), 136 ($PNB^+$). Further elution with ether gave the dimer **26**: 10 mg (10%); IR ($CH_2Cl_2$) 1730, 1660 $cm^{-1}$; high-resolution mass spectrum, calcd for $C_{32}H_{36}N_4O_{10}$ $m/e$ 636.2431, found $m/e$ 636.2436; $m/e$ 636 ($M^+$), 607 ($M^+$ - Et), 456 ($M^+$ - $CO_2$PNB), 428 ($M^+$ - $CO_2$PNB -CO).

When a mixture of the two isomers **15a** and **15b** was subjected to the sequence of reactions described above for the conversion of **15a** into **25a**, a mixture of the *cis*-6-ethylcarbapenam **25a** and its trans isomer **25b** was obtained. This mixture exhibits the same IR and high-resolution mass spectra as pure **25a**. NMR of **25b**, obtained by substraction of the spectrum of **25a** from that of the mixture (270 MHz, $CD_2Cl_2$): $\delta$ 1.00 (t, $J$ = 7 Hz, 8-$H_3$), 1.30–1.75 (m, 7-$H_2$), 1.75–2.20 (m, 1-$H_2$), 2.25–2.39 (m, 2-$H_2$), 2.86 (ddd, $J$ = 8, 6, 2 Hz, 6-H), 3.46 (ddd, $J$ = 8, 5, 2 Hz, 5-H), 3.93 (t, $J$ = 5 Hz, 3-H), 5.22 and 5.30 (AB q, $J$ = 13.5 Hz, $CH_2$Ar), 7.58 and 8.21 (AB q, $J$ = 9 Hz, $C_6H_4NO_2$).

**Registry No.** (±)-**6**, 84911-17-1; (±)-**7**, 84927-07-1; (±)-**9**, 84911-19-3; (±)-**10**, 84911-20-6; **11**, 84911-22-8; (±)-**13a**, 84911-21-7; (±)-**13b**, 84984-88-3; (±)-**14a**, 84911-23-9; (±)-**14b**, 84984-89-4; (±)-**15a**, 84911-24-0; (±)-**15b**, 84984-90-7; (±)-**16a**, 84911-25-1; (±)-**16b**, 84984-91-8; (±)-**17a**, 84911-29-5; (±)-**18a**, 84911-27-3; (±)-**19a**, 84911-26-2; (±)-**20a**, 84911-30-8; (±)-**21a**, 84911-28-4; (±)-**22a**·HCl, 84911-31-9; (±)-**25a**, 84911-32-0; (±)-**25b**, 84984-92-9; **26**, 84911-33-1; ethyl (±)-pyroglutamate, 66183-71-9; ethyl (±)-2-bromo-3-oxobutyrate, 84911-18-2; diethyl 2-bromomalonate, 685-87-0.

# Reaction of Sydnones with Oxygen†

Masayuki Nakajima and Jean-Pierre Anselme*

*Department of Chemistry, University of Massachusetts at Boston, Harbor Campus, Boston, Massachusetts 02125*

*Received October 4, 1982*

The reaction of 3-benzyl- and 3-(*p*-chlorobenzyl)-4-phenylsydnones (**1a** and **1b**) and of 3-benzylsydnone (**1c**) with oxygen at room temperature in the dark is described. Possible rationalizations for the formation of the products obtained are suggested.

In the context of our study of the decarboxylations of α-nitrosamino acids,[1] some anhydro-α-nitrosamino acids[2] (sydnones[3]) were prepared. Sydnones, unsubstituted at the 4-position, are known to undergo electrophilic aromatic substitution.[3] Thus the conversion of α-nitrosamino acids to sydnones, followed by introduction of a substituent at the 4-position of the sydnone ring and regeneration of the α-nitrosamino acid, would constitute a means of obtaining *N*-nitrosamines[4] from glycines, via the decarboxylation of *N*-nitrosoglycines.[1,5]

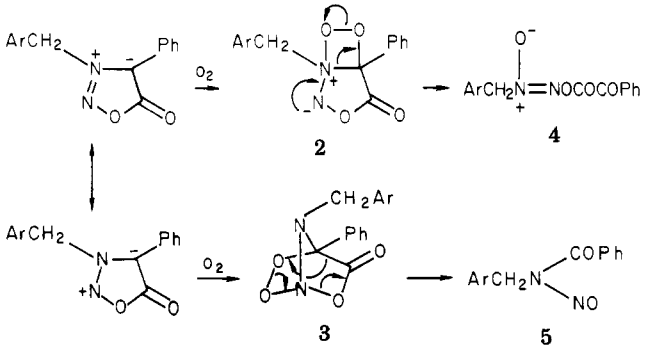
During the course of the recrystallization of 3-benzyl-4-phenylsydnone (**1a**), a benzene–ether solution of sydnone **1a** upon long standing deposited colorless crystals, identified as benzoic acid. This result was surprising in view of the fact that the chemistry of sydnones had been studied extensively and thus was believed to be understood rather well. Yet no precedent could be found in the literature with regard to the fact that sydnones may be sensitive to oxygen. Recently George and his co-workers[6] have reported the *photosensitized* oxidation of sydnones with *singlet* oxygen. Therefore it was decided to undertake the investigation of the reaction of sydnones with oxygen.

† Taken in part from the Ph.D. Thesis of M. Nakajima, University of Massachusetts, Sept 1982. This is the 10th article dealing with the chemistry of *N*-nitrosamines and related compounds. For the previous publication, see K. Kano, C. A. Kelly, and J.-P. Anselme, *Tetrahedron Lett.*, 1427 (1982).

(1) M. Nakajima and J.-P. Anselme, *Tetrahedron Lett.*, 4037 (1979).
(2) A. R. Katritzky, *Chem. Ind. (London)*, 521 (1955).
(3) (a) J. D. Earl and A. W. Mackney, *J. Chem. Soc.*, 899 (1935); (b) F. H. C. Stewart, *Chem. Rev.*, **64**, 129 (1964); (c) M. Ohta and H. Kato, "Nonbenzenoid Aromatics", J. P. Snyder, Ed., Academic Press, New York, 1969, Vol. 1, 117; (d) W. D. Ollis and C. A. Ramsden, "Advances in Heterocyclic Chemistry", A. R. Katritzky and A. J. Boulton, Eds., Academic Press, New York, 1976, Vol. 19, p 3.
(4) This would appear to be perhaps one true case of reverse *polarization* (also called umpolung) as the 4-position of the sydnone is the position that is flanked *both* by the nitrosamino and the carbonyl group of α-nitrosoamino acids.
(5) (a) M. Nakajima and J.-P. Anselme, unpublished results; (b) M. Nakamura, N. Baba, and Y. Wada, *J. Food Sci.*, **41**, 874 (1976); (c) K. R. Bharucha, C. K. Cross, and L. J. Rubin, *J. Agric. Food Chem.*, **27**, 63 (1973).
(6) V. Bhat, V. M. Dixit, R. G. Ungarker, A. M. Trozzolo, and M. V. George, *J. Org. Chem.*, **44**, 2957 (1979).

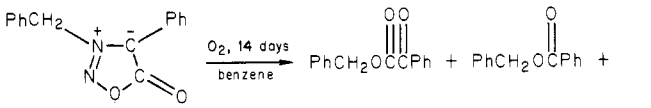
0022-3263/83/1948-1444$01.50/0 

Scheme I



## Results

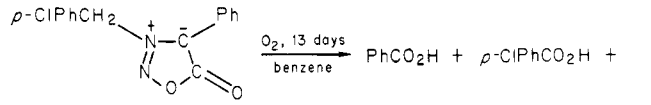
A solution of 3-benzyl-4-phenylsydnone (**1a**) in oxygen-saturated benzene was kept in the *dark* and protected from moisture. When the solution was allowed to stand for 2 weeks, the products generated from the oxidation



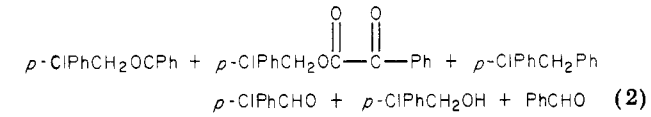
**1a**

$$PhCH_2Ph + PhCH_2OH + PhCHO + PhCO_2H \quad (1)$$

mixture were benzoic acid, benzyl benzoate, benzyl phenylglyoxylate, diphenylmethane, benzaldehyde, and benzyl alcohol; an unknown high-melting solid[7] was isolated in trace quantities. In order to demonstrate that oxygen is necessary for the reaction, a degassed benzene solution of the sydnone was kept in a sealed tube in the dark for the same period of time; unchanged sydnone was recovered in quantitative yield. It thus became essential to determine the source of benzoic acid that, in principle, might have arisen either from the *C*-phenyl portion or the *N*-benzyl portion of **1a**. 3-(*p*-Chlorobenzyl)-4-phenylsydnone (**1b**) was prepared and oxidized as described above. Although



**1b**



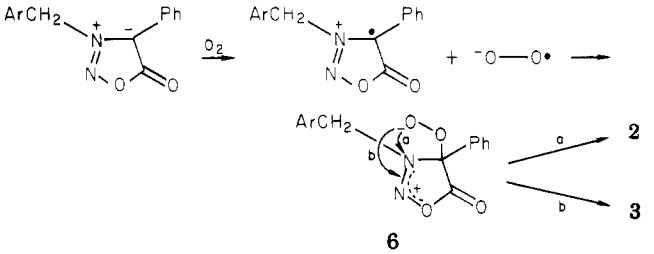
small quantities of *p*-chlorobenzoic acid could be characterized by TLC and IR, benzoic acid was isolated as the major acid; *p*-chlorobenzaldehyde and benzaldehyde were formed in substantial quantities. Other products were *p*-chlorobenzyl benzoate, *p*-chlorobenzyl phenylglyoxylate, and (*p*-chlorophenyl)phenylmethane. These results are comparable to those obtained from **1a**. In contrast to the recent report of the reaction of 3-phenylsydnone with singlet oxygen in which no isolatable products were obtained,[6] the oxidation of 3-benzylsydnone gave benzaldehyde, benzyl formate, and benzyl alcohol very cleanly.

## Discussion

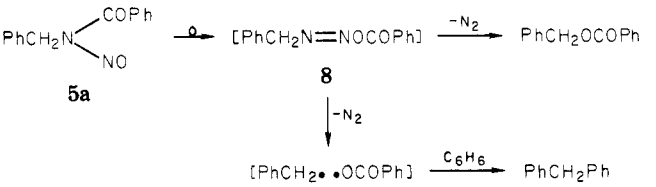
The formation of the esters may be rationalized in terms of two different modes of addition of oxygen to the sydnone ring, namely, 1,2-addition to the 3,4-bond and 1,3-addition across the 2,4-positions of the ring, giving **2** and **3**, respectively, as illustrated in Scheme I. These two

(7) It is believed to be a salt (ammonium?) of phenylglyoxylic acid.

Scheme II



Scheme III



intermediates could arise from an initial electron-transfer reaction of the sydnone with oxygen; recombination of the radical ion[8] with $\cdot O_2^-$ (Scheme II) would lead to the hydroxyperoxy zwitterion (**6**), which could then cyclize at the 2- or 3-position to give **2** and **3**, respectively. Collapse of **2** as depicted in Scheme I could then give *N'*-(phenylglyoxylyl)-*N*-benzyldiimide *N*-oxide (**4**), which by loss of nitrous oxide[10] would yield benzyl phenylglyoxylate. Indeed, the reaction of the sodium salt of *N*-nitroso-*N*-benzylhydroxylamine with phenylglyoxylyl chloride afforded benzyl phenylglyoxylate as the major product along with traces of benzaldehyde; similarly, benzoyl chloride gave benzyl benzoate.

The loss of carbon dioxide from cycloadduct **3** should result in the formation of the corresponding *N*-nitrosobenzamide **5**. Similar adducts have been postulated in the reaction of the other mesoinic systems with singlet oxygen[11] and of sydnones with benzaldehyde[12a] and tetracyanoethylene.[12b] The TLC detection of *N*-nitroso-*N*-benzylbenzamide (**5**, Ar = Ph) in a partially oxidized solution of **1a** supports this view. Homolytic dissociation of the diazotate ester **8** could afford benzoyl and benzyl radicals and further interaction of the latter radical with the solvent (benzene) would yield diphenylmethane. A benzene solution of **5** gave not only benzyl benzoate as the major product[13] but also traces of diphenylmethane upon long standing (Scheme III). George and his group[6] have isolated $\alpha,\beta$-dibenzoylphenylhydrazine, which was shown to arise from the reaction of diphenylnitrilimine with benzoic acid, in 25% yield from photooxidation of 3,4-diphenylsydnone with oxygen. As to the source of benzoic acid, George and his group proposed the decomposition of benzoyl phenyldiazotate, resulting from the rearrangement of *N*-nitroso-*N*-phenylbenzamide. This report made it necessary to test the mechanism from the *N*-nitrosamide **5** to benzoic acid not only under our reaction conditions but also under the sensitized oxygenation conditions.

(8) For references on captodative substitution or merostabilization, see W. E. McEwen, et al., *J. Org. Chem.*, **47**, 3098 (1982) and ref 35–39 therein.

(9) R. Lindner, *Justus Liebigs Ann. Chem.*, **275**, 133 (1893).

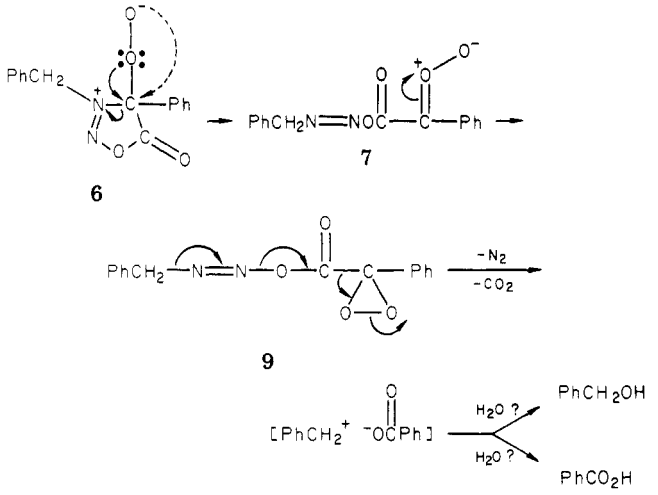
(10) E. H. White, M. J. Todd, T. J. Ryan, A. A. F. Sieber, R. E. Dickerson, and J. Bordner, *Tetrahedron Lett.*, 4467 (1970); E. H. White and D. W. Grisley, *J. Am. Chem. Soc.*, **83**, 1191 (1961); *J. Org. Chem.*, **29**, 2636 (1964).

(11) N. H. Toubro, B. Hansen, H. Harrit, A. Holm, and K. J. Potts, *Tetrahedron*, **35**, 229 (1979).

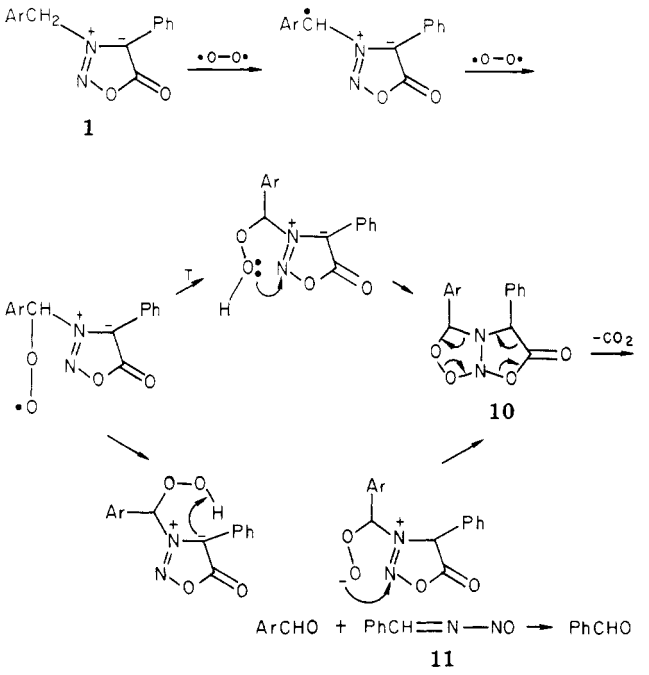
(12) (a) R. Huisgen, *Angew. Chem.*, **25**, 604 (1963); (b) H. C. Berk and J. E. Franz, *J. Org. Chem.*, **44**, 2395 (1979).

(13) E. H. White, *J. Am. Chem. Soc.*, **77**, 6014 (1955); E. H. White and C. A. Aufdermarsh, *ibid.*, **83**, 1174 (1961).

Scheme IV



Scheme V



As was stated earlier, benzoic acid was not isolated nor detected from a benzene solution of *N*-nitroso-*N*-benzylbenzamide (**5a**), which had been allowed to stand in the presence of oxygen for 2 weeks. Neither, could benzoic acid be detected under the sensitized oxygenation conditions;[6] only the denitrosated product *N*-benzylbenzamide could be isolated in good yield under those conditions. Denitrosation of a similar *N*-nitrosamide by photolysis in the presence of oxygen has been reported.[14] At this stage, a clear-cut mechanism for the formation of benzoic acid cannot be offered. It might be speculated that the intermediate that lead to **2** (Scheme II) could yield the unusual but not unprecedented[15] three-membered dioxirane intermediate **9** as illustrated in Scheme IV. This dioxirane intermediate **9**, which by loss of nitrogen and carbon dioxide and concurrent fission of the oxygen–oxygen bond of the dioxirane ring, would lead to the benzyl cation and benzoate anion. Water, perhaps from the solvent, could react with those two ions to afford benzyl alcohol and benzoic acid, respectively.

A possible rationale for the formation of benzaldehydes is depicted in Scheme V. Abstraction of a benzylic hydrogen with oxygen would generate the benzyl radical, which could then capture oxygen to form the peroxy radical. The hydroxyperoxide intermediate might cyclize to form the bicyclic intermediate **10**, which could then collapse, affording the corresponding aldehyde and *N*-nitrosobenzaldimine (**11**). Conversion of the latter compound to benzaldehyde has been described previously.[16] A control experiment which showed that benzaldehyde is partially oxidized to benzoic acid under the conditions of the reaction suggests that the aldehydes may also be the precursors of the benzoic acids.

Although the present study leaves many questions unanswered, it does demonstrate that sydnones may not be as stable as previously believed and that a rich harvest may still be reaped from further investigation of the chemistry of sydnones.

## Experimental Section

All melting and boiling points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Infracord, and NMR spectra were determined in $CCl_4$ or $CDCl_3$ on a R-24 Hitachi-Perkin-Elmer spectrometer using $Me_4Si$ as an internal standard.

***N*-Nitroso-*N*-benzylglycine.** A solution of sodium nitrite (22.0 g, 0.32 mol) in water (60 mL) was added to suspension of *N*-benzylglycine hydrochloride (54.7 g, 0.271 mol)[17] in water (200 mL) with an ice–water bath. The resulting mixture was stirred at 5 °C for 0.5 h and then stirred at room temperature for 1 h. The yellowish precipitate was collected and air-dried. Recrystallization from boiling water yielded 32 g (61%) of *N*-nitroso-*N*-benzylglycine; mp 142.5–143 °C (lit.[17] mp 148 °C).

***N*-Benzyl-α-phenylglycine.** A solution of benzylamine (21.4 g, 0.20 mol) in ether (50 mL) was added to a solution of α-bromophenylacetic acid (21.5 g, 0.10 mol) in ether (100 mL). The resulting mixture was heated to reflux overnight. The colorless precipitate was collected, and benzylamine hydrobromide was removed by washing the precipitate with hot water to leave 16.9 g (70%) of *N*-benzyl-α-phenylglycine as a colorless solid; mp 216–217 °C (lit.[18] mp 225–227 °C).

***N*-(*p*-Chlorobenzyl)-α-phenylglycine.** A mixture of (α-bromophenyl)acetic acid (21.5 g, 0.10 mol) and *p*-chlorobenzylamine (35.4 g, 0.20 mol) in ether (300 mL) was heated to reflux overnight. The colorless precipitate was collected and washed with water (200 mL) to leave *N*-(*p*-chlorobenzyl)-α-phenylglycine as a colorless solid (27.0 g, 98%); mp 193–195 °C dec. An analytical sample, mp 193–195 °C dec, was obtained by two recrystallizations from water. Anal. Calcd for $C_{15}H_{14}ClNO_2$: C, 65.34; H, 5.12; N, 5.08. Found: C, 65.10; H, 5.15; N, 4.99.

***N*-Nitroso-*N*-benzyl-α-phenylglycine.** A solution of sodium nitrite (9.0 g, 130 mmol) in water (10 mL) was added to a suspension of *N*-benzyl-α-phenylglycine (16.9 g, 70 mmol) in a mixture of water (200 mL) and acetic acid (120 mL) at −3 to −5 °C. The resulting mixture was stirred at −3 to −5 °C for an additional 0.5 h and then stirred at ambient temperature overnight. The mixture upon dilution with water (200 mL) yielded 4.81 g of a nearly colorless precipitate, which was collected and air-dried; mp 117–117.5 °C. The aqueous filtrate was extracted with ether (150 mL × 3), and the ethereal extract was washed with saturated aqueous sodium chloride solution thoroughly and dried over $MgSO_4$. Evaporation of ether left an oil (12 g), which solidified on standing. The colorless precipitate and the solidified residue were combined and recrystallized from benzene to yield yellowish crystals (10.2 g, 54%); mp 120–123 °C. Anal. Calcd for $C_{15}H_{14}N_2O_3$: C, 66.65; H, 5.22; N, 10.31. Found: C, 66.52, 66.55; H, 5.21, 5.28; N, 10.36, 10.35.

(14) Y. L. Chow, *ACS Symp. Ser.* **No. 101**, 13 (1978).
(15) R. E. Keay and G. A. Hamilton, *J. Am. Chem. Soc.*, **98**, 6578 (1976).
(16) (a) T. E. Stevens, *J. Org. Chem.*, **29**, 311 (1964); (b) C. J. Thoman and I. M. Hunsberger, *ibid.*, **33**, 2852 (1968); E. H. White, A. P. Wilson, J. P. Anhalt, R. J. Baumgarten, and J. I. Choca, *ibid.*, **47**, 2892 (1982).
(17) W. Baker, W. D. Ollis, and W. D. Poole, *J. Chem. Soc.*, 307 (1949).
(18) R. R. Fraser, G. Broussard, S. D. Potescu, J. J. Whiting, and Y. Y. Wigfield, *Can. J. Chem.*, **51**, 1109 (1973).

***N*-Nitroso-*N*-(*p*-chlorobenzyl)-α-phenylglycine.** A solution of sodium nitrite (10.0 g, 145 mmol) in water (50 mL) was added to a suspension of *N*-(*p*-chlorobenzyl)-α-phenylglycine (15.8 g, 57 mmol) in a mixture of water (200 mL) and acetic acid (200 mL) cooled in an ice–salt bath. The resulting mixture was stirred at 0–2 °C for 2 h and then stirred at room temperature overnight. The mixture was diluted with water (300 mL) and extracted with ether (100 mL × 3). The ethereal layer was washed with water thoroughly and dried over $MgSO_4$. Evaporation of ether left a solid residue, which was crystallized from ether–benzene–hexanes to yield *N*-nitroso-*N*-(*p*-chlorobenzyl)-α-phenylglycine (9.1 g, 52%); mp 118–119.5 °C. Anal. Calcd for $C_{15}H_{13}ClN_2O_3$: C, 59.12; H, 4.20; N, 9.20. Found: C, 59.20, 59.05; H, 4.41, 4.58; N, 9.19, 9.13.

**3-Benzylsydnone.** A mixture of *N*-nitroso-*N*-benzylglycine (5.0 g, 26 mmol) and acetic anhydride (30 mL) was stirred on a hot water bath for 5 h. The mixture was cooled to room temperature and poured slowly into a mixture of ice and water with vigorous stirring to give a yellowish solid (3.30 g, 72%), which was collected, washed with cold water, and air-dried; mp 66–67 °C (lit.[17] mp 69.5 °C).

**3-Benzyl-4-phenylsydnone.** A mixture of *N*-nitroso-*N*-benzyl-α-phenylglycine (5.4 g, 20 mmol) and acetic anhydride (20 mL) was heated on a boiling water bath for 1.5 h. The mixture was cooled to room temperature and poured into a mixture of crushed ice and water with vigorous stirring, giving a colorless precipitate (5.0 g, 99%), mp 97–98.5 °C, which was collected and air-dried. Recrystallization from an ether–benzene mixture afforded 3-benzyl-4-phenylsydnone as an analytical sample; mp 98–100 °C (lit.[19] mp 101–103 °C); $^1H$ NMR ($CDCl_3$) δ 5.40 (s, 2 H, $PhCH_2$), 7.00–7.30 (m and s, 10 H aromatic). Anal. Calcd for $C_{15}H_{12}N_2O_2$: C, 71.41; H, 4.80; N, 11.18. Found: C, 71.37, 71.44; H, 4.77, 4.89; N, 11.21, 11.22.

**3-(*p*-Chlorobenzyl)-4-phenylsydnone.** A mixture of *N*-nitroso-*N*-(*p*-chlorobenzyl)-α-phenylglycine (8.17 g, 26.8 mmol) and acetic anhydride (40 mL) was heated on a boiling water bath for 4 h. The mixture was cooled to room temperature and poured into a mixture of crushed ice–water with vigorous stirring to afford a colorless precipitate, mp 87–89 °C, which was collected and air-dried. Recrystallization from benzene–ether gave 3-(*p*-chlorobenzyl)-4-phenylsydnone (4.58 g, 60%): mp 92.5–94 °C dec; $^1H$ NMR ($CDCl_3$) δ 5.40 (s, 2 H, *p*-$ClPhCH_2$), 6.85–7.10 (d, d, and s, 9 H, aromatic). Anal. Calcd for $C_{15}H_{11}ClN_2O_2$: C, 62.83; H, 3.87; N, 9.77. Found: C, 62.99, 62.97; H, 4.01, 4.06; N, 9.66, 9.63.

**Reaction of 3-Benzyl-4-phenylsydnone with Oxygen.** Oxygen was passed through benzene for 15 min. 3-Benzyl-4-phenylsydnone (2.0 g, 7.9 mmol) was dissolved in oxygen-saturated benzene (30 mL). The solution was stirred at room temperature in a flask covered with aluminum foil and protected by a calcium sulfate tube for 14 days. *N*-nitroso-*N*-benzylbenzamide was identified by comparison of $R_f$ values on TLC plates (silica gel) after overnight stirring of the solution. Evaporation of benzene gave a residue (2.07 g), which was chromatographed on silica gel (mesh 60–200, 36 g). Elution with a mixture of benzene and hexanes (1:2 v/v) (125 mL) afforded diphenylmethane (21 mg, 1.6%), whose IR and NMR spectra were identical with those of an authentic sample. Further elution (100 mL) gave a mixture (538 mg) of benzaldehyde (3.4%), benzyl alcohol (3.4%), and benzyl benzoate (29%); the molar ratio of these compounds was estimated by NMR integration of benzyl and aldehydic hydrogens. Further elution with a mixture of benzene and hexanes (1:2–1:1 v/v) and with benzene (200 mL) gave benzyl phenylglyoxylate (151 mg, 8.3%), whose IR and NMR spectra were superimposable upon those of an authentic sample.[20] Continued elution with benzene (50 mL) and then with a mixture of benzene and ether (5:1 v/v) (50 mL) gave an unknown product (17 mg). Elution with a mixture of benzene and ether (5:1–2:1 v/v) (100 mL) afforded benzoic acid (520 mg, 54%), mp 110–115 °C, whose IR and NMR spectra were superimposable upon those of an authentic sample. Elution with ether (150 mL) and methanol (150 mL) gave a solid (26 mg), mp 197–200 °C, which was recrystallized from methanol to afford water-soluble crystals (100 mg), mp >250 °C. The NMR spectrum suggests it to be a salt of phenylglyoxylic acid.

***N*-Benzylhydroxylamine.** A mixture of *N*-benzylidene benzylamine *N*-oxide[21] (7.5 g) and concentrated hydrochloric acid (35 mL) was placed in a distillation flask. Steam was passed through the mixture until all the benzaldehyde had been removed. The aqueous solution was made alkaline with sodium bicarbonate and extracted with ether (60 mL × 3). The ethereal layer was dried over $MgSO_4$. Evaporation of ether afforded *N*-benzylhydroxylamine (3.47 g, 79%); mp 54–56 °C (lit.[22] mp 57 °C).

***N*-Nitroso-*N*-benzylhydroxylamine.** *N*-Benzylhydroxylamine (8.91 g) was treated with gaseous hydrogen chloride (10 g) in anhydrous ether (100 mL) at 15 °C to yield the hydrochloride salt (8.43 g); mp 105–107 °C dec. A solution of sodium nitrite (3.7 g) in water (30 mL) was added to a solution of *N*-benzylhydroxylamine hydrochloride (8.4 g) in water (250 mL) at 0–3 °C. A colorless solid precipitated immediately. The mixture was stirred for an additional 30 min. The precipitate was collected, treated with ice-cold water, and air-dried overnight to give *N*-nitroso-*N*-benzylhydroxylamine (6.1 g, 76%); mp 75–77 °C (lit.[23] mp 77–78 °C).

***N*-Nitroso-*N*-benzylhydroxylamine Sodium Salt.** A solution of *N*-nitroso-*N*-benzylhydroxylamine (6.10 g) in absolute ethanol (90 mL) was added to a solution of sodium ethoxide prepared from sodium hydride (1.0 g) and absolute ethanol (25 mL). The colorless solid was collected and treated with absolute ethanol to leave *N*-nitroso-*N*-benzylhydroxylamine sodium salt (5.78 g); mp 238–239 °C dec (lit.[9] mp 233–234 °C).

**Phenylglyoxylyl Chloride.** A solution of thionyl chloride (2.9 g, 24 mmol) and anhydrous ether (30 mL) was added to a mixture of phenylglyoxylic acid (3.0 g, 20 mmol) and pyridine (1.58 g) in anhydrous ether (25 mL) at room temperature. The resulting mixture was stirred at room temperature for 1.5 h. The ethereal solution was decanted and concentrated to leave a residual oil. Hexane (20 mL) was added to the residual oil and the solution evaporated again. The remaining hexanes and thionyl chloride were removed under reduced pressure (20 mmHg) to yield phenylglyoxylyl chloride. Owing to its instability, the crude material obtained was used for the next step without purification and delay.

**Reaction of *N*-Nitroso-*N*-benzylhydroxylamine Sodium Salt with Phenylglyoxylyl Chloride.** A solution of the crude material obtained above (1.5 g, 8.9 mmol) in acetonitrile (35 mL) was added to a suspension of *N*-nitroso-*N*-benzylhydroxylamine sodium salt (1.73 g, 9.9 mmol) in acetonitrile (25 mL) at 22–25 °C. Gas evolution was observed immediately after addition of the chloride was started. The resulting mixture was stirred at room temperature overnight. The mixture was poured into water (60 mL). Organic materials were extracted with ether (20 mL × 3). The ethereal layer was dried over $MgSO_4$. Evaporation of ether left a residual oil (1.8 g, 85%), whose IR and NMR spectra were consistent with those of benzyl phenylglyoxylate and of benzaldehyde (trace amounts).

***N*-Nitroso-*N*-benzylhydroxylamine Sodium Salt with Benzoyl Chloride.** A solution of benzoyl chloride (1.7 g, 12.6 mmol) in acetonitrile (30 mL) was added to a suspension of *N*-nitroso-*N*-benzylhydroxylamine sodium salt (1.79 g, 9.74 mmol) in acetonitrile (35 mL) at room temperature. Gas evolution was observed during the addition of the acid chloride. The resulting mixture was stirred at room temperature for 2 days. Inorganic materials were filtered, and the filtrate was concentrated to an oil that was dissolved in ether (60 mL). The ethereal solution was washed with dilute aqueous sodium hydroxide solution and dried over $MgSO_4$. Evaporation of the ether afforded benzyl benzoate (1.7 g, 82%), whose IR and NMR spectra were superimposable upon those of an authentic sample.

**Reaction of 3-(*p*-Chlorobenzyl)-4-phenylsydnone (1b) with Oxygen.** A solution of 3-(*p*-chlorobenzyl)-4-phenylsydnone (1.1 g, 3.7 mmol) in oxygen-saturated benzene (30 mL) was stirred for 13 days at room temperature as described previously.

(19) L. E. Kholodov and V. G. Yachunskii, *Dokl. Akad. Nauk SSSR*, **179**, 366 (1968); *Chem. Abstr.*, **69**, 106607 (1968).

(20) An authentic sample of benzyl phenylglyoxylate was prepared from the reaction of phenylglyoxylic acid with phenyldiazomethane in ether.

(21) M. Najima, K. Takeuchi, E. Fukui, and N. Tokura, *J. Chem. Soc., Perkin Trans. 1*, 2202 (1976).

(22) L. W. Jones and C. M. Sneed, *J. Am. Chem. Soc.*, **39**, 677 (1917).

(23) R. Behrend and E. Konig, *Justus Liebigs Ann. Chem.*, **263**, 217 (1891).

Evaporation of benzene left a residue (1.0 g), which was chromatographed on silica gel (mesh 60–200, 25 g). Elution with a mixture of benzene and hexanes (1:1 v/v) (80 mL) gave a fraction consisting mainly of (*p*-chlorophenyl)phenylmethane (36 mg, 6%)[24] along with unknown products. (*p*-Chlorophenyl)phenylmethane was identified by comparison of its IR and NMR spectra with those of an authentic sample. Continued elution (80 mL) afforded a mixture (0.53 g) of *p*-chlorobenzaldehyde, *p*-chlorobenzyl phenylglyoxylate, and *p*-chlorobenzyl benzoate. Upon evaporation, *p*-chlorobenzaldehyde was oxidized to *p*-chlorobenzoic acid (134 mg, 25%), mp 226–229 °C, which was separated from the mixture by extraction with aqueous sodium bicarbonate to leave a mixture of *p*-chlorobenzyl benzoate (15%) and *p*-chlorobenzyl phenylglyoxylate (9%). Further elution with a mixture of benzene and hexanes (1:1 v/v) (100 mL) gave *p*-chlorobenzyl alcohol (22 mg, 0.15 mmol), whose IR and NMR spectra were superimposable upon those of an authentic sample. Elution with the same mixture (40 mL) and then with ether (120 mL) gave a mixture of benzoic acid, *p*-chlorobenzyl alcohol, and 3-(*p*-chlorobenzyl)-4-phenylsydnone; benzoic acid (70 mg, 17%), mp 112–113 °C, was extracted from the fraction with aqueous sodium bicarbonate to leave a mixture (90 mg) of *p*-chlorobenzyl alcohol and 3-(*p*-chlorobenzyl)-4-phenylsydnone in a molar ratio of 1:2 estimated by NMR integration.

An authentic sample of *p*-chlorobenzyl phenylglyoxylate (2.4 g, 47%) was prepared from the reaction of *p*-chlorobenzyl chloride (3 g, 18.6 mmol) and sodium phenylglyoxylate (3.4 g, 20 mmol) in $Me_2SO$ under reflux; mp 54–55 °C. Anal. Calcd for $C_{15}H_{11}CO_3$: C, 65.58; H, 4.04. Found: C, 65.77; H, 4.11.

The reaction was repeated in an attempt to detect the presence of *p*-chlorobenzoic acid. A solution of 3-(*p*-chlorobenzyl)-4-phenylsydnone (1.51 g, 5.27 mmol) in oxygen-saturated benzene (40 mL) was stirred at room temperature for 14 days as previously described. The benzene solution was extracted with a saturated aqueous sodium bicarbonate solution (3 × 20 mL). The benzene layer was dried over anhydrous $MgSO_4$ and concentrated on a rotary evaporator to leave an oil (1.07 g), whose NMR spectrum suggested it to be a mixture of *p*-chlorobenzaldehyde (25%), benzaldehyde (11%), 3-(*p*-chlorobenzyl)-4-phenylsydnone (8%), *p*-chlorobenzyl phenylglyoxylate (30%), *p*-chlorobenzyl benzoate (25%), and *p*-chlorobenzyl alcohol (6%). The yields indicated were estimated by the NMR integration of the aldehydic and benzylic hydrogens. The aqueous sodium bicarbonate layer was acidified with concentrated aqueous hydrochloric acid and extracted three times with ether, and the combined ethereal extract was dried over $MgSO_4$. Evaporation of the ether left a residue (0.25 g), whose NMR spectrum indicated it to be mainly benzoic acid. Recrystallization of the residue from an ethanol–water mixture gave a small amount (approximately 10 mg) of *p*-chlorobenzoic acid, mp 200–205 °C, whose IR spectrum was identical with that of an authentic sample; the filtrate was concentrated in vacuo to yield a new solid, mp 95–105 °C, whose IR was superimposable upon that of benzoic acid. *p*-Chlorobenzoic acid could not be detected in the solid by comparison of $R_f$ values (silica gel).

**Reaction of 3-Benzylsydnone (1c) with Oxygen.** A solution of 3-phenylsydnone (1.72 g, 9.7 mmol) in oxygen-saturated benzene (30 mL) was stirred at room temperature for 3 weeks as described previously. Evaporation of benzene afforded a residual oil (1.3 g), which was chromatographed on silica gel (mesh 60–200, 30 g). Elution with benzene (150 mL) yielded a mixture (0.47 g) of benzaldehyde (11%) and benzyl formate (32%). Further elution with benzene (75 mL) gave an unknown product (8 mg). Continued elution with benzene (75 mL) and then with a mixture of ether and benzene (1:2 v/v) (20 mL) gave another unknown product (27 mg). Elution with a mixture of ether and benzene (1:1 v/v) (80 mL) afforded benzyl alcohol (0.32 g, 35%), whose IR and NMR spectra were superimposable upon those of an authentic sample. Further elution with the same solvent mixture (50 mL) and then with ether (50 mL) gave 3-benzylsydnone (203 mg, 11.9%), whose IR and NMR spectra were identical with those of an authentic sample.

**Benzyl Alcohol with Air.** A solution of benzyl alcohol (1.0 g) in benzene (20 mL) was stirred at room temperature vigorously in an open beaker for 15 days. Evaporation of benzene gave unchanged benzyl alcohol.

**Benzoylformic Acid in Oxygen-Saturated Benzene.** A solution of benzoylformic acid (2.12 g) in oxygen-saturated benzene (40 mL) was stirred at room temperature in a flask covered with aluminum foil and protected with a calcium sulfate drying tube for 16 days. Evaporation of benzene led to a quantitative recovery of benzoylformic acid; mp 63–66 °C.

***N*-Nitroso-*N*-benzylbenzamide in Oxygen-Saturated Benzene.** A solution of *N*-nitroso-*N*-benzylbenzamide (635 mg) in oxygen-saturated benzene (30 mL) was stirred at room temperature in a flask covered with aluminum foil and protected with a calcium sulfate drying tube for 14 days. Evaporation of benzene yielded a mixture (621 mg) of benzyl benzoate and *N*-nitroso-*N*-benzylbenzamide in 1:1 molar ratio estimated by an NMR integration of benzylic hydrogens.

**Photolysis of *N*-Nitroso-*N*-benzylbenzamide in Methanol.** A solution of *N*-nitroso-*N*-benzylbenzamide (652 mg, 2.7 mmol) and Rose Bengal (18 mg) in methanol (350 mL) was photolyzed under a stream of oxygen gas for 1 h, as described by George et al.[6] The methanolic solution was concentrated under reduced pressure to leave an oil (816 mg), which showed no detectable amount of benzoic acid present by comparison of $R_f$ values on TLC (silica gel, methylene chloride). The oil was dissolved in ether (40 mL), and the ethereal solution was washed with saturated aqueous sodium bicarbonate solution (25 mL × 2). The aqueous layer was separated and acidified with concentrated hydrochloric acid. Extraction of the acidified aqueous solution with ether (25 mL × 2), followed by concentration, gave a semisolid (66 mg) whose IR suggested it to be the free acid of Rose Bengal. The ethereal layer left after extraction with aqueous sodium bicarbonate solution was dried over $MgSO_4$. Evaporation of ether gave *N*-benzylbenzamide (400 mg, 70%), which solidified on standing. Recrystallization of crude benzamide from benzene–hexanes gave crystals; mp 101–103 °C (lit.[25] mp 105–106 °C).

**Acknowledgment.** A valuable and stimulating discussion with Professor Sir Derek H. R. Barton and the technical assistance of Mary Ann Rezendes are gratefully acknowledged.

**Registry No.** **1a**, 20067-23-6; **1b**, 85152-72-3; **1c**, 16844-42-1; *N*-benzylglycine hydrochloride, 7689-50-1; *N*-nitroso-*N*-benzylglycine, 6344-41-8; *N*-benzyl-α-phenylglycine, 1859-51-4; α-bromophenylacetic acid, 4870-65-9; benzylamine, 100-46-9; *p*-chlorobenzylamine, 104-86-9; *N*-(*p*-chlorobenzyl)-α-phenylglycine, 85152-73-4; *N*-nitroso-*N*-benzyl-α-phenylglycine, 49746-38-5; *N*-nitroso-*N*-(*p*-chlorobenzyl)-α-phenylglycine, 85152-74-5; *N*-benzylidenebenzylamine *N*-oxide, 3376-26-9; *N*-benzylhydroxylamine, 622-30-0; *N*-nitroso-*N*-benzylhydroxylamine, 28571-11-1; *N*-nitroso-*N*-benzylhydroxylamine sodium salt, 85166-50-3; phenylglyoxylyl chloride, 25726-04-9; phenylglyoxylic acid, 611-73-4; benzyl phenylglyoxylate, 62977-82-6; *p*-chlorobenzyl phenylglyoxylate, 85152-75-6; *p*-chlorobenzyl chloride, 104-83-6; sodium phenylglyoxylate, 43165-51-1; benzoyl chloride, 98-88-4.

(24) Bp 90–95 °C (0.75 mmHg) [lit. bp 147–148 °C (8 mmHg) [J. Bernstein, J. S. Ruth, and W. J. Miller, *J. Am. Chem. Soc.*, **70**, 2310 (1948)] by the Wolff–Kishner reduction of *p*-chlorobenzophenone.

(25) E. Beckmann, *Ber.*, **23**, 3331 (1890).