Registry No.—**1A,** 742-01-8; **1B,** 6969-04-6; **1C,** 2755-71-7; **1D,** 2756-72-8; **1E,** 2515-62-0; **1F,** 19429-34-6; **1G,** 4035-38-5; **1H,** 5204-27-3; **1I,** 4035-37-4; **1J,** 20264-73-7; **1K,** 10252-46-7.

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(10) It was found that bubbling in oxygen through an open system was less efficient, requiring about 5 h to complete the reaction. Use of a slight positive pressure is expected to increase the dissolved oxygen content, thereby accelerating the oxidation reaction.

Deoxygenation of Amine *N*-Oxides or *C*-Nitroso Compounds by Dialkyl Sulfoxylates

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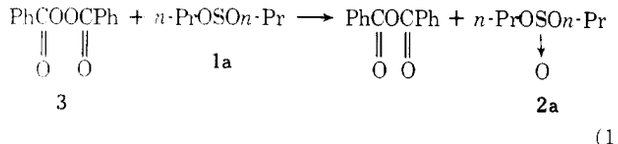
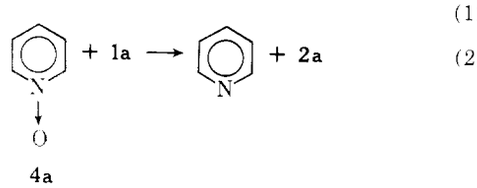
Deoxygenation reactions of a variety of organic compounds by trivalent phosphorus compounds are well known. For example, dibenzoyl peroxide,[1] pyridine *N*-oxide,[2] or nitrosobenzene[3] is deoxygenated by triphenyl phosphine or triethyl phosphite to give benzoic anhydride, pyridine, or azoxybenzene, respectively. Sulfoxylates (**1**) are readily oxidized,[4] yielding sulfites (**2**) upon exposure to air; nevertheless, little attention has been paid to the deoxygenation reactions by **1**. Thus it seemed reasonable that a similar deoxygenation reaction could be carried out by **1**. Di-*n*-propyl sulfoxylate (**1a**) and diethyl sulfoxylate (**1b**) were used in the present study; the former was more accessible and stable than the latter.

First, dibenzoyl peroxide (**3**) was allowed to react with **1a**. The reaction took place violently even at room temperature and benzoic anhydride and di-*n*-propyl sulfite (**2a**) were obtained in almost quantitative yields (eq 1). The result is in contrast to the reaction of dioxetane, a cyclic peroxide, and **1** which affords tetraalkoxysulfurane instead of oxirane.[5]

Pyridine *N*-oxide (**4a**) also reacted with **1a** at room temperature to give pyridine and **2a** in yields of 96 and 85%, respectively (eq 2). Similarly, 2-picoline *N*-oxide (**4b**), 3-picoline



(1)

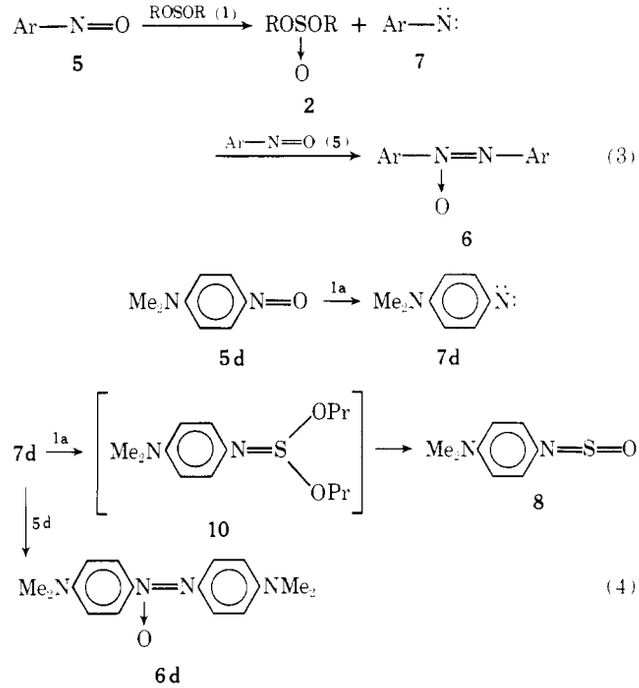


(2)

N-oxide (**4c**), or 4-picoline *N*-oxide (**4d**) reacts with **1a** at room temperature or in refluxing benzene to give amine and **2a** as shown in Table I. 4-Nitropyridine *N*-oxide (**4e**) did not react with **1a** under similar conditions, but, upon heating in the absence of solvent a vigorous exothermic reaction occurred with the evolution of nitric oxide. The only product isolated from the reaction mixture was di-*n*-propyl sulfite (**2a**). The deoxygenation of pyridine *N*-oxide (**4a**) or its homologues by triphenyl phosphine must be carried out under drastic conditions (heating above 200 °C).[2]

Reactions of *C*-nitroso compounds with sulfoxylates (**1**) gave a variety of products. When equimolar quantities of nitrosobenzene (**5a**) and **1a** or **1b** were refluxed in benzene or CCl_4, the solution gradually turned from green to reddish brown and azoxybenzene (**6a**) was obtained in 61–76% yields (eq 3). *p*-Nitrosotoluene (**5b**) or *o*-nitrosotoluene (**5c**) similarly reacted with **1a** to give 4,4′-dimethylazoxybenzene (**6b**) or 2,2′-dimethylazoxybenzene (**6c**). The sulfite (**2**) was not isolated in these cases but its formation was confirmed by an infrared spectrum.

In addition, we examined the reaction of **1a** and *p*-dimethylaminonitrosobenzene (**5d**) and found that *p*-dimethylamino-*N*-sulfinylaniline (**8**) was formed together with 4,4′-bis(dimethylamino)azoxybenzene (**6d**) and 4,4′-bis(dimethylamino)azobenzene (**9**). The mechanism of the formation of **8** is not obvious. Bunyan and Cadogan[3] proposed the mechanism of formation of **6** by assuming arylnitrene (**7**) to be a transient intermediate. Accordingly, the reaction presumably proceeds through the intermediate **10** generated by the attack of nitrene **7d** on **1a**.[6]

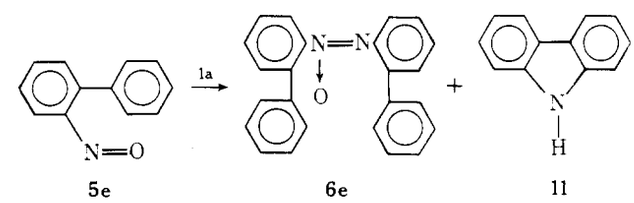


(3)

(4)

The path of the formation of **9** also cannot be elucidated. However, the dimerization of **7d** to give **9** is excluded as has been pointed out by Bunyan and Cadogan,[3] and our separate experiment confirmed that both the deoxygenation of **6d** to **9** by **1a** and the reaction of **8** with **5d** to form **9** did not occur under similar conditions.

o-Nitrosobiphenyl (**5e**) reacted with **1a** to give *o*-azoxybiphenyl (**6e**) (34%) and carbazole (**11**) (20%). In the case of the reaction with phosphine or phosphite, only **11** was obtained in high yield.[3]



(5)

Finally, reactions of sulfoxylates and other compounds such as sulfoxides, sulfones, aromatic nitro compounds, or *N*-nitroso compounds were examined. However, deoxygenation

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Table I

Amine *N*-oxide	Registry no.	Solvent	Reaction temp, °C	Time, h	Yield of product, % Amine	Yield of product, % Sulfite (**2a**)
(**4a**) Pyridine	694-59-7	$CHCl_3$	Room temp	3	96	85
(**4b**) 2-Picoline	931-19-1	Benzene	Reflux	1	78	75
(**4c**) 3-Picoline	1003-73-2	CH_2Cl_2	Room temp	2	94	72
(**4d**) 4-Picoline	1003-67-4	Benzene	Reflux	0.5	70	71
(**4e**) 4-Nitropyridine	1124-33-0	None	110–120	1	0	18

did not take place even by refluxing in benzene for a long time and the starting materials were recovered.

Experimental Section

IR spectra were measured with a Hitachi EPI-G2 spectrometer. NMR spectra were determined in CCl_4 or $CDCl_3$ solution with a JEOL JNM-PMX-60 spectrometer. Mass spectra were obtained on a Hitachi Double Focusing Mass Spectrometer RMU-7M at 70 eV. Di-*n*-propyl sulfoxylate (**1a**),[7] diethyl sulfoxylate (**1b**),[4] and *o*-nitrosobiphenyl (**5e**)[8] were prepared by the methods of the literature, respectively. All other reagents were obtained commercially.

Reaction of Dibenzoyl Peroxide (3) with 1a. A solution of 4.5 g (0.03 mol) of **1a** in 20 mL of benzene was added to a stirred solution of 7.3 g (0.03 mol) of **3** in 30 mL of benzene at room temperature during 1 h. The reaction is exothermic and proceeded violently unless controlled by addition of **1a**. The stirring was continued for an additional 1 h. The solvent was removed and the residue was distilled to give 3.8 g (77%) of di-*n*-propyl sulfite (**2a**),[9] bp 65 °C (6 mm). The oily residue was chromatographed on silica gel using ether–hexane (1:2) as eluent to give 6.7 g (99%) of benzoic anhydride, mp 40–42 °C. Di-*n*-propyl sulfite (**2a**) was identified by spectral data, IR (neat) ν(S→O) 1200 cm^{-1}; NMR (CCl_4) δ 3.90 (m, 2 H) 1.71 (m, 2 H) 0.99 (t, 3 H).

Reaction of Amine *N*-Oxides (4) with 1a. A solution of 4.5 g (0.03 mol) of **1a** in 20 mL of $CHCl_3$ was added to a stirred solution of 2.9 g (0.03 mol) of pyridine *N*-oxide (**4a**) in 30 mL of $CHCl_3$ at room temperature during 1 h. The stirring was continued for an additional 2 h. The solvent and pyridine were removed by evaporation and the residue was distilled to give 4.0 g (85%) of **2a**. Amount of pyridine was estimated as its hydrochloride, 3.3 g (96%). Similarly, 2-picoline *N*-oxide (**4b**), 3-picoline *N*-oxide (**4c**), or 4-picoline *N*-oxide (**4d**) was allowed to react with **1a** and 2-picoline (bp 56–58 °C (50 mm)), 3-picoline (bp 62–65 °C (24 mm)), or 4-picoline (bp 65 °C (29 mm)) and **2a** were obtained by fractional distillation. 4-Nitropyridine *N*-oxide (**4e**) (5.6 g 0.04 mol) and **1a** (6 g 0.04 mol) were heated at 110–120 °C for 1 h; the mass turned to dark brown with evolution of nitric oxide. Di-*n*-propyl sulfite (**2a**) (1.2 g) was obtained by distillation of the reaction mixture.

Reaction of Nitrosobenzene (5a), *p*-Nitrosotoluene (5b), or *o*-Nitrosotoluene (5c) with Sulfoxylate (1). A solution of 1.6 g (0.015 mol) of **5a** and 2.3 g (0.015 mol) of **1a** in 25 mL of benzene was refluxed under nitrogen atmosphere. The green solution turned reddish brown gradually. After 10 h, the solvent was removed and the residue was chromatographed on alumina using hexane–benzene (1:1) as eluent to give 0.9 g (61%) of azoxybenzene (**6a**) as yellow crystals: mp 33–36 °C; IR (neat) ν(N→O) 1475 cm^{-1}. Similarly, **6a** was obtained in 76% yield by the reaction of **1b** and **5a** in CCl_4 solution. *p*-Nitrosotoluene (**5b**) or *o*-nitrosotoluene (**5c**) was allowed to react with **1a** under similar conditions and 4,4′-dimethylazoxybenzene (**6b**) (48%) [mp 70 °C; IR (KBr) ν(N→O) 1465 cm^{-1}] or 2,2′-dimethylazoxybenzene (**6c**) (56%) [mp 58 °C; IR (KBr) ν(N→O) 1475 cm^{-1}] was obtained by column chromatography on silica gel using hexane–benzene (3:2) as eluent.

Reaction of *p*-Dimethylaminonitrosobenzene (5d) with 1a. A solution of 2.0 g (0.0133 mol) of **5d** and 4.0 g (0.0266 mol) of **1a** in 20 mL of benzene was refluxed for 20 h under nitrogen atmosphere. The solvent was removed and the residue was chromatographed on silica gel using benzene as eluent to give 1.1 g (45%) of *p*-dimethylamino-*N*-sulfinylaniline[10] (**8**) as red crystals: mp 72 °C (lit. 72 °C); IR (nujol) ν(S→O) 1140 cm^{-1}; NMR (CCl_4) δ 7.78 (d, 2 H) 6.52 (d, 2 H) 3.06 (s, 6 H). Further elution with chloroform gave 0.2 g of 4,4′-bis(dimethylamino)azobenzene (**9**) as reddish brown crystals [mp 270–273 °C (lit.[3] 271–273 °C); NMR ($CDCl_3$) δ 7.83 (d, 4 H) 6.78 (d, 4 H) 3.10 (s, 12 H)] and 0.25 g of 4,4′-bis(dimethylamino)azoxybenzene (**6d**) as reddish orange crystals [mp 245–246 °C (lit.[3] 257–259 °C); IR (KBr) ν(N→O) 1455 cm^{-1}; NMR ($CDCl_3$) δ 8.30 (d, 2 H) 8.17 (d, 2 H) 6.77 (d, 2 H) 6.72 (d, 2 H) 3.10 (s, 12 H)].

Reaction of *o*-Nitrosobiphenyl (5e) with 1a. A solution of 1.8 g (0.01 mol) of **5e** and 1.5 g (0.01 mol) of **1a** in 25 mL of toluene was refluxed for 10 h under nitrogen atmosphere. The solvent was removed and the residue was chromatographed on silica gel using benzene–hexane (2:1) as eluent to give 0.33 g (20%) of carbazole as colorless plates [mp 242 °C (lit. 245 °C); IR (KBr) ν(N–H) 3410 cm^{-1}] and 0.60 g (34%) of *o*-azoxybiphenyl (**6e**) as light yellow crystals [mp 157 °C (lit. 157–158 °C); IR (KBr) ν(N→O) 1450 cm^{-1}; mass *m/e* 350 (M^+), 349 ($M^+ - H$), 334 ($M^+ - O$), 333, 184, 168, 167, 166, 153, 152].

Registry No.—**1a,** 3359-70-4; **2a,** 623-98-3; **3,** 94-36-0; **5a,** 586-96-9; **5b,** 623-11-0; **5c,** 611-23-4; **5d,** 138-89-6; **5e,** 21711-71-7; **6a,** 495-48-7; **6b,** 955-98-6; **6c,** 956-31-0; **6d,** 794-95-6; **6e,** 7334-103; **8,** 13066-26-7; **9,** 6257-64-3; 2-picoline, 109-06-8; 3-picoline, 108-99-6; 4-picoline, 108-89-4.

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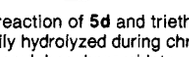
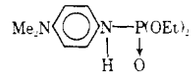
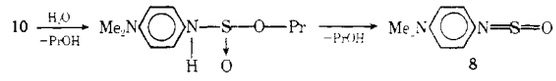
(6) Bunyan and Cadogan[3] reported that triethyl *N*-*p*-dimethylaminophenylphosphorimidate,



was obtained by the reaction of **5d** and triethyl phosphite and this phosphorimidate was readily hydrolyzed during chromatography to give diethyl *N*-*p*-dimethylaminophenylphosphoramidate



Presumably, the labile intermediate **10** is likewise hydrolyzed during chromatographic separation to form the aminosulfinate, which decomposes into **8** and *n*-propyl alcohol.



Aminosulfinates, RNHS(O)OR′, are known as very unstable compounds which decompose into *N*-sulfinylamines and alcohols immediately. G. Zinner, *Chem. Ber.*, **91,** 966 (1958).
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Structure of Tirotundin[1]

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Tirotundin, the main sesquiterpene lactone of *Tithonia rotundifolia* (Mill.) Blake, was assigned[2] the gross structure and stereochemistry depicted in formula **1a** (R = H), although formula **2** could not be excluded with certainty. Because of this ambiguity and because the substance exhibited some anti-

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