were determined by titrating the chloride ion with standardized silver nitrate (0.0100 N) solution to a Mohr visual end point.

Anal. Calcd for $C_{13}H_8O_2P_2Cl_{10}$ (equiv wt): 61.27. Found: 61 ± 0.5 (average and average deviation for four determinations).

Gravimetric analysis for the per cent of xanthone in the complex was carried out by hydrolyzing the samples (160–200 mg) at room temperature for 24 hr. The xanthone was collected on weighed filter paper and dried in a drying pistol for 24 hr by using continuous vacuum without applying heat. Phosphorus pentoxide was the desiccant used in the drying pistol. Three samples were run varying in weight from 168 to 200 mg.

Anal. Calcd for xanthone (wt %): 32.02. Found: 34.3 ± 2.3 (average and average deviation for three determinations).

A large scale reaction was run in methylene chloride to check for any phosphoryl chloride. A 10-g (0.051 mol) sample of xanthone was added to 100 ml of methylene chloride containing 10.6 g (0.051 mol) of phosphorus pentachloride. The solution was rotary evaporated, and the distillate was checked by vpc for phosphoryl chloride. None was present.

Thioxanthone PCl_4^+-PCl_6^-.—The same procedures as described above for xanthone were followed with thioxanthone. Thioxanthone (Aldrich Chemical Co.) was recrystallized once from toluene, mp 208–209°. The quantities used were 10 g (0.047 mol) of thioxanthone, 41.8 g (0.071 mol) of phosphorus pentachloride, and 22.2 g (0.145 mol) of phosphoryl chloride in 100 ml of dry toluene. During the 3-hr reflux period, a bright red precipitate formed. Gas chromatographic analysis revealed no change in the phosphoryl chloride concentration. Similar results were observed when 8.6 g (0.0405 mol) of thioxanthone and 8.4 g (0.0405 mol) of phosphorus pentachloride in 200 ml of dry methylene chloride were stirred for 20 hr at room temperature. Again, no phosphoryl chloride was generated.

The pure ionic complex was generated by mixing a solution of 1.72 g (0.0081 mol) of thioxanthone in 100 ml of methylene chloride with a 100-ml solution of 1.65 g (0.0081 mol) of phosphorus pentachloride. The solution was filtered after 24 hr, washed with methylene chloride, and dried, mp 231–232° dec. Sample sizes for the chloride ion titration varied from 2 to 3 mg and for the gravimetric analysis from 150 to 300 mg.

Anal. Calcd for $C_{13}H_8OSP_2Cl_{10}$ (equiv wt): 62.87. Found: 63 ± 0.0 (average and average deviation for three determinations).

Anal. Calcd for thioxanthone (wt %): 33.67. Found: 35.4 ± 1.5 (average and average deviation for two determinations).

Both of the ionic complexes were extremely hygroscopic. Several unsuccessful attempts were made to obtain carbon, hydrogen, and phosphorus analyses. However, the analytical laboratory was not able to weigh the samples without hydrolysis occurring.

Vpc Analysis.—Standard solutions of phosphoryl chloride in toluene were prepared and analyzed on a Beckman GC-2A gas chromatograph equipped with a thermal conductivity detector and Honeywell 1-mV recorder. The packing contained a 60–60 mesh diatomaceous earth (Gas Pack PA) coated with 15% DC-710 silicon fluid. Isothermal determinations were made at 100° for toluene and 130° for methylene chloride.

Registry No.—Ia, 26219-78-3; Ib, 26219-79-4.

Oxidation of Mercaptans with Diethyl Azodicarboxylate and Trivalent Phosphorus Compounds

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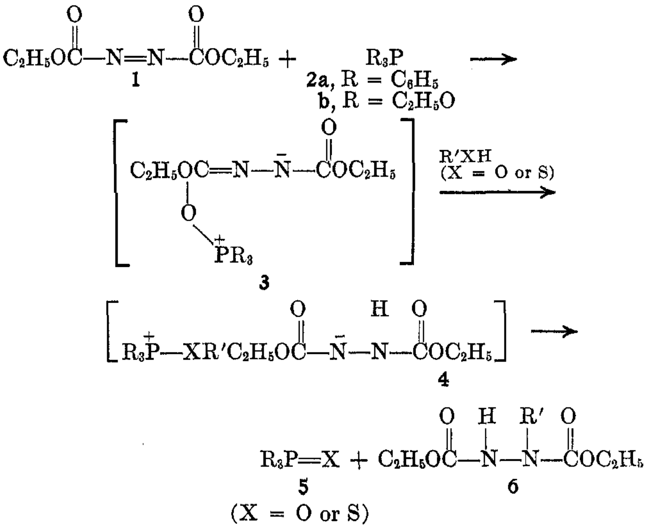
Received July 10, 1968

Schenck, *et al.*,[1] and Cookson, *et al.*,[2] have reported photochemical dehydrogenation with diethyl azodicarboxylate (**1**). Recently, Yoneda, *et al.*,[3] have successfully used **1** in a nonphotochemical hydrogen abstracting oxidation of hydrogen donors such as alcohols, mercaptans, or amines. They have found that the reaction of mercaptans with **1** giving disulfides and diethyl hydrazodicarboxylate (**7**) proceeded under a mild condition; either **1** and the mercaptans were kept without solvent in the dark at room temperature for 1–3 days or the mercaptans and **1** were refluxed in an anhydrous solvent for 0.5–10 hr.

We have investigated the oxidation of trivalent phosphorus compounds (**2**) using **1** and an alcohol such as benzyl or allyl alcohol and obtained corresponding diethyl N-alkyl hydrazodicarboxylates (**6**) and phosphates or phosphine oxides (**5**, X = O).[4] The reaction was explained by assuming the formation of an imidoyl phosphonium salt (**3**),[5] followed by the nucleophilic attack of the alcohol giving an alkoxy phosphonium salt (**4**). Since aldehydes and diethyl hydrazodicarboxylate were not produced, the formation of **3** may be faster than the hydrogen abstracting reaction of the alcohol with **1**.



In this paper, the possibility that the reaction of mercaptans with **1** and triphenylphosphine (**2a**) could yield **6** and triphenylphosphine sulfide (**5**, R = C_6H_5–; X = S) was investigated. Contrary to our expectation, di-n-propyl disulfide and **7** were formed when **1** and **2a** were treated with an equimolar amount of n-propyl mercaptan at room temperature. Triphenyl-

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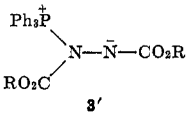
(1) G. O. Schenck and H. Formaneck, *Angew. Chem.*, **70**, 505 (1958).

(2) R. C. Cookson, I. D. R. Stevens, and D. T. Watt, *Chem. Commun.*, 259 (1965).

(3) F. Yoneda, K. Suzuki, and Y. Nitta, *J. Amer. Chem. Soc.*, **88**, 2328 (1966); F. Yoneda, K. Suzuki, and Y. Nitta, *J. Org. Chem.*, **32**, 727 (1967).

(4) O. Mitsunobu, M. Yamada, and T. Mukaiyama, *Bull. Chem. Soc. Jap.*, **40**, 935 (1967).

(5) (a) V. A. Ginsburg, M. N. Vasil'eva, S. S. Dubov, and A. Ya. Yakubovich, *Zh. Obshch. Khim.*, **30**, 2854 (1960); *Chem. Abstr.*, **55**, 17477 (1961). (b) Morrison[6] and Brunn and Huisgen[7] have proposed that the betaine has structure **3′** rather than **3**.



3′

(6) D. C. Morrison, *J. Org. Chem.*, **23**, 1072 (1968).

(7) E. Brunn and R. Huisgen, *Angew. Chem. Int. Ed. Engl.*, **8**, 513 (1969).

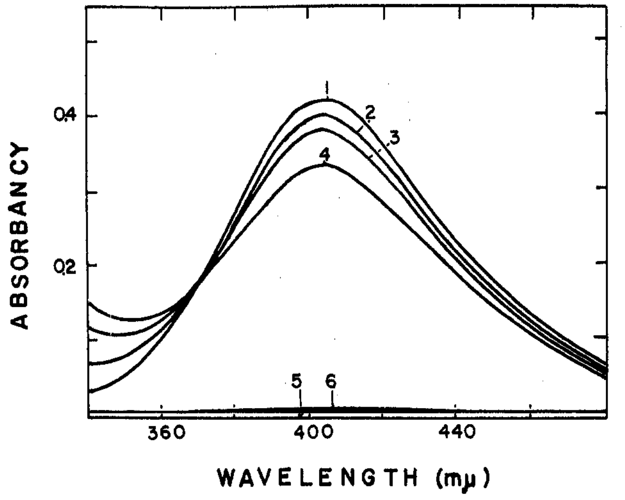


Figure 1.—Perturbation of the 405-mμ diethyl azodicarboxylate band by triphenylphosphine.

	Concentration[a]	
	Diethyl azodicarboxylate	Triphenylphosphine
1	1.012×10^{-2} *M*	0
2	1.012×10^{-2} *M*	1.014×10^{-3} *M*
3	1.012×10^{-2} *M*	2.028×10^{-3} *M*
4	1.012×10^{-2} *M*	4.056×10^{-3} *M*
5	0	1.014×10^{-3} *M*
6[b]	1.0×10^{-3} *M*	1.0×10^{-3} *M*

[a] THF is used as solvent. [b] In the presence of *n*-dodecyl mercaptan (2.0×10^{-3} *M*).

phosphine was recovered and neither triphenylphosphine sulfide nor **6** was obtained. Then, 2 mol of a mercaptan was allowed to react with **1** and **2a** in tetrahydrofuran (THF) at room temperature. The orange-red of the solution disappeared immediately and then the reaction mixture was stirred for 2 hr at room temperature. The completion of the reaction was confirmed by thin layer chromatography. The corresponding disulfides and **7** were produced in essentially quantitative yields while **2a** was recovered unchanged. The reaction was also accelerated in the dark. The use of triethyl phosphite in the place of triphenylphosphine gave the corresponding disulfide in a good yield. The results are summarized in Table I. As shown in Table I, the change in mole ratio of triphenylphosphine–mercaptan does not affect the yield of the disulfide. From these results, the trivalent phosphorus compounds appear to accelerate the reaction and improve yields.

The present oxidation reaction could not be explained by the intermediate of **3** or **3′**. The energies of the molecular orbitals of **1** have been examined by Hückel MO calculation,[8,8] and it is known that **1** possesses an unusual vacant bonding orbital. Earlier papers[9,10] show that **1** is a strong electron acceptor. On the other hand, trivalent phosphorus compounds or amines are known as electron donors. **1** might be expected to combine readily with trivalent phosphorus compounds to initially form adducts or charge transfer complexes which then convert to **3**, radical or radical ions.[11]

Table I

Oxidation of Mercaptans by Means of Diethyl Azodicarboxylate and Trivalent Phosphorus Compounds at Room Temperature for 2 Hr

R′SHR′	R_3PR	Mol ratio of R_3P:R′SH	Yield, %	R′S–SR′[a] mp, °C (bp, °C)
n-C_3H_7–	C_6H_5–	0.50	75	(192–194)
n-$C_{12}H_{25}$–	C_6H_5–	0.50	89[b]	34
		0.50	81[c]	
		0.50	95[d]	
		0.25	97	
		0.01	98	
		0	...[e]	
	C_2H_5O–	0.05	92	
$C_6H_5CH_2$–	C_6H_5–	0.50	97	68–69
	C_2H_5O–	0.50	89	
C_6H_5–	C_6H_5–	0.05	96	60

[a] The products were identified by lit.[14] boiling point or melting point, mixed examination by authentic sample [T. J. Wallace, *J. Amer. Chem. Soc.*, **86**, 2018 (1964)], or infrared spectra. [b] The mercaptan was added several minutes after an adduct was formed from **1** and **2** at room temperature. [c] An adduct was formed from **1** and **2** at 0° and then allowed to stand for 1 hr at 0°. Then the mercaptan was added to the solution. [d] Even if these reactions were performed in the dark, the yields of products were almost unchanged. [e] It was confirmed by thin layer chromatography that only a trace of the corresponding disulfide was formed.

The absorption spectra obtained for the THF solutions of **1** and triphenylphosphine are shown in Figure 1. It shows that the free **1** band at 405 mμ diminishes intensity and new absorption appears at a shorter wavelength upon adding triphenylphosphine to the solution. It seems reasonable to attribute this newly appearing absorption to charge transfer bands arising from **1**–**2a** complex. Because of the strong absorption due to **2a**, it was not possible to follow this new band to its maximum which must lie at a shorter wavelength.

A solution of **1** was mixed with a solution of **2a** at 0° and a pale yellow solution was obtained and allowed to set aside for 1 hr at 0°. When *n*-dodecyl mercaptan was added to the solution, it was immediately decolored and di-*n*-dodecyl disulfide was obtained in an 81% yield. On the other hand, the orange-red color of **1** changed to deep red when **1** and **2a** were brought together in THF solution at room temperature. Addition of *n*-dodecyl mercaptan caused immediate discoloration and the disulfide was obtained in an 89% yield. The yields of the disulfide in both cases were lower than that of the general procedure in which **1** was added to the solution of **2a** and mercaptans. These results suggest that the charge transfer complex formation may be the key step of the reaction and that this adduct may be converted slowly to inactive species in the absence of mercaptans. The deep coloration may be explained by radical or radical ions, to which the adduct converts at room temperature and at high concentration, that is, the reaction conditions. Further investigation were not performed in connection with radical species.

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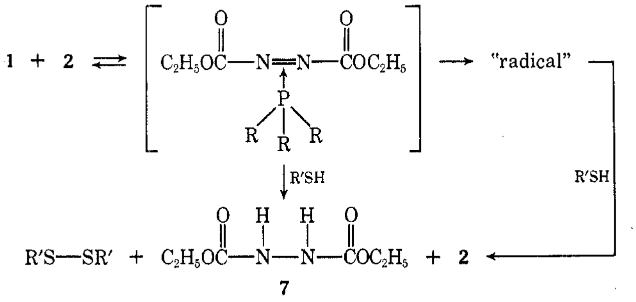
(8) A. Zweig and A. K. Hoffman, *J. Amer. Chem. Soc.*, **85**, 2736 (1963).

(9) R. Stolle, *Chem. Ber.*, **45**, 273 (1912).

(10) R. Huisgen and Jakob, *Justus Liebigs Ann. Chem.*, **590**, 37 (1954).

(11) E. A. Lucken, F. Ramirez, V. P. Catto, D. Rhum, and S. Dershowitz, *Tetrahedron*, **22**, 637 (1967). In this report, they found that a charge transfer complex may be formed by the reaction of chloranil with trivalent phosphorus compounds to give radical ions.

Although the mechanism of the oxidation reaction is still not completely elucidated, the reaction can be represented by he following scheme.



In order to extend the reaction, amines, which might become electron donors, were used in the place of trivalent phosphorus compounds in the above reactions. This investigation will be reported in a next paper.

Experimental Section

Reagents.—Diethyl azodicarboxylate was prepared by the procedure of Rabjohn.[12] The other reagents were purchased from Wako Pure Chemical Industries, Ltd., and purified in general methods. Thin layer chromatography was carried out on Wakogel B-O and was developed with *n*-hexane. For column chromatography Wakogel C-300 (silica gel) or alumina (300 mesh) was used. The silica gel and the alumina were activated by heating at 120° for 2 hr. Sulfur-containing compounds were detected by a spray of *ca.* 0.5% w/v 2,6-dibromo-*p*-benzoquinone-4-chloroimine in cyclohexane[13] or with iodine vapor.

General Procedure of the Oxidation of Mercaptans with Diethyl Azodicarboxylate and Triphenylphosphine.—A solution of diethyl azodicarboxylate (5×10^{-3} mol) in 5 ml of THF was added dropwise to a solution of triphenylphosphine (5×10^{-3} mol) and a mercaptan (1×10^{-2} mol) in 5 ml of THF with vigorous stirring. After 2 hr at 25°, the THF was removed. The residue was washed with 10 ml of dry ether to give diethyl hydrazodicarboxylate as white needles: 0.83–0.78 g; mp 129–131°, undepressed on admixture with an authentic sample.[12] Each disulfide was isolated from the filtrate and purified by the following procedures.

A. Di-*n*-propyl Disulfide.—After removal of the ether, di-*n*-propyl disulfide was obtained by distillation at reduced pressure, bp 72° (14 mm) (75%). Redistillation gave an analytical sample, bp 192–194°, n^{20}_{D} 1.4977. (lit.[14] bp 194°, n^{20}_{D} 1.4980).

Anal. Calcd for $C_6H_{14}S_2$: C, 47.94; H, 9.34. Found: C, 48.23; H, 9.20.

From the residue of the distillation, triphenylphosphine was isolated and was recrystallized from ethanol, 1.16 g (88.5%), mp 79°.

B. Di-*n*-dodecyl Disulfide.—The mother liquid was completely evaporated under reduced pressure and the residue was separated into di-*n*-dodecyl disulfide (1.90 g, 95%, mp 34°), the recovered mercaptan (trace), and triphenylphosphine (1.22 g, 93.2%, mp 76–77.5°) by silica gel column chromatography (3.0 × 40 cm; eluate, *n*-hexane).

When the mole ratio of the mercaptan–triphenylphosphine was changed, the products were also purified by the same procedure. The yields of the disulfide are summarized in Table I.

When *n*-dodecyl mercaptan was allowed to react with **1** in the presence of triethyl phosphite for 2 hr at room temperature in the dark, nearly quantitative yields of di-*n*-dodecyl disulfide and **3** were obtained by the same procedure described above (Table I).

C. Dibenzyl Disulfide.—Ethanol–ether (1:1) was added to the residue resulting from removal of ether. Dibenzyl disulfide was obtained by filtration and purified by recrystallization from ethanol, 1.19 g (97%), mp 68–69°. The filtrate was evaporated to give triphenylphosphine which was recrystallized from ethanol, 1.19 g (91%), mp 72–74°.

D. Diphenyl Disulfide.—Diphenyl disulfide (1.08 g, 96%, mp 60°) and triphenylphosphine (0.13 g, 99.5%, mp 70–74°) were separated by alumina column chromatography (3.0 × 40 cm; eluate, benzene) and purified by recrystallization from ethanol.

Spectra.—Absorption spectra were recorded on Hitachi recording spectrometer EPS-3T type with quartz cell of optical path 1.0 cm. A solution of diethyl azodicarboxylate was mixed with a solution of triphenylphosphine at 0°, and then the mixed solution was allowed to warm to room temperature. All measurements were performed at room temperature.

Registry No.—**1,** 1972-28-7; **2a,** 603-35-0; **2b,** 122-52-1; *n*-propyl mercaptan, 107-03-9; *n*-dodecyl mercaptan, 112-55-0; benzyl mercaptan, 100-53-8; phenyl mercaptan, 108-98-5.

Acknowledgment.—We are pleased to acknowledge helpful discussions wirh Drs. I. Ichikizaki and T. Hoshi.

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[12] N. Rabjohn, "Organic Syntheses," Coll. Vol. III, Wiley, New York, N. Y., 1955, p 375.

[13] J. R. S. Edmundson, *J. Chem. Soc.*, 1635 (1967).

[14] E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. III, Chemical Publishing Co., New York, N. Y., 1960, pp 396–399.

Nitration Studies. XVII. Conversion of Carboxylic Acid Derivatives to Nitroalkanes

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Received March 2, 1970

Acetyl nitrate has been known for some time as a dangerously explosive compound.[3] Its decomposition under controlled conditions seems not to have been studied previously. We have found that when diluted it undergoes smooth thermolysis to give carbon dioxide and nitromethane (eq 1). In the same way higher acyl nitrates give the corresponding nitro alkanes containing one less carbon atom. This new synthesis provides a ready preparation for nitroalkanes of various types in yields which compare favorably with or exceed those of other methods (see Table I).

$$CH_3CO_2NO_2 \xrightarrow[\text{solvent}]{290°} CH_3NO_2 + CO_2 \qquad (1)$$

Acyl nitrates may be prepared by a number of different methods. Fortunately they need not be isolated for purposes of this synthesis, but may be used in the presence of an excess of one reactant or an added solvent. We have employed the following methods of preparation (eq 2–6). Each method offers certain advantages and disadvantages relative to the others. Thus, for example, method E can be used when the corresponding acid anhydride is not readily available

$$\text{A.}\quad (RCO)_2O + N_2O_4 \longrightarrow RCO_2NO_2 + RCO_2NO \qquad (2)$$

$$\text{B.}\quad (RCO)_2O + HNO_3 \longrightarrow RCO_2NO_2 + RCO_2H \qquad (3)$$

$$\text{C.}\quad (RCO)_2O + N_2O_5 \longrightarrow 2RCO_2NO_2 \qquad (4)$$

$$\text{D.}\quad (RCO)_2O_2 + N_2O_4 \longrightarrow 2RCO_2NO_2 \qquad (5)$$

$$\text{E.}\quad RCOCl + AgNO_3 \longrightarrow RCO_2NO_2 + AgCl\downarrow \qquad (6)$$

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[1] To whom correspondence should be addressed.

[2] Commercial Solvents Corporation Research Assistant, 1968–1969.

[3] (a) W. Konig, *Angew. Chem.*, **67**, 157 (1955); (b) J. Dunbar and J. Colzia, *C. R. Acad. Sci.*, *Ser. C*, 1114 (1968); (c) T. A. Brown and J. A. C. Watt, *Chem. Brit.*, **3**, 504 (1967); (d) F. E. Francis, *J. Chem. Soc.*, **89**, 1 (1906).