H_2–Pd–$BaSO_4$, after filtration and solvent removal, 0.84 g (3.8 mmol) of **33**: mp 121–122° (from benzene–*n*-hexane); mol wt 224; ir (KBr): 3310, 3250 cm^{-1} (NH); 1700 cm^{-1} (C=O); 1508 cm^{-1} (amide II); nmr ($CDCl_3$): 2.86 (s, 4 H); 3.46 (b, 1 H); 5.83 (q) J = 7 cps, 6.1 (m, 4 H); 7.08 (m, 4 H); 8.75 (t, 3 H), J = 7 cps.

Anal. Calcd for $C_{12}H_{16}N_2O_2$ (220.3): C, 65.43; H, 7.32; N, 12.72. Found: C, 65.42; H, 7.24; N, 12.75.

Synthesis[80] of Ethyl 3-(2-Indanyl)carbazate (33).—Addition of 0.5 ml of glacial acetic to a solution of 5.0 g (38 mmol) of 2-indanone[81] and 4.3 g (41 mmol) of ethyl carbazate (purum Fluka) in 75 ml of ethanol (95%) at 50° gave the precipitation of 6.0 g (28 mmol) of 2-indanone-N-carbethoxyhydrazone (**34**) in 5 min: mp 176–177° (from benzene–acetone–*n*-hexane), lit.[80] mp 168–169.5°; mol wt (acetone) 215; ir (KBr): 3200, 3120 cm^{-1} (NH); 1700, 1655 cm^{-1} (C=O, C=N); nmr ($CDCl_3$): 2.0 (b, 1 H); 2.79 (s, 4 H); 5.70 (q, 2 H), J = 7 cps; 6.25 (m, 4 H); 8.67 (t, 3 H), J = 7 cps.

Anal. Calcd for $C_{12}H_{14}N_2O_2$ (218.3): C, 66.04; H, 6.47; N, 12.84. Found: C, 65.83; H, 6.47; N, 12.57.

Compound **34** (1.0 g, 4.6 mmol) in 75 ml of ethanol and 25 ml of glacial acetic acid was shaken with H_2–Pt–charcoal for 3.5 hr. Filtration, solvent removal *in vacuo*, and recrystallization of the remaining product from benzene–*n*-hexane afforded 0.38 g (1.7 mmol) of **33**: mp 121–122°, lit.[80] mp 120–120.5°; mol wt 227.

Anal. Calcd for $C_{12}H_{16}N_2O_2$ (220.3): C, 65.43; H, 7.32; N, 12.72. Found: C, 65.10; H, 7.07; N, 12.78.

Compound **33**, synthesized following this procedure, was identical with the product from the catalytic hydrogenation of **32** according to ir, nmr, and mixture melting point.

Kinetic Measurements.—Absorption spectroscopy (uv) at 24400–24700 cm^{-1} (DEAD) and 18400 cm^{-1} (PTD) was used to monitor the concentrations of DEAD and PTD in all the kinetic runs. The measurements were carried out with a Zeiss spectrophotometer PMQ II in 1-cm water-jacketted cells. Temperature was controlled to ±0.1° with a Haake ultrathermostat. The following initial concentrations were used in various solvents (Table V): system DEAD–indene, 2×10^{-2} *M* DEAD–1.4 *M* indene; system DEAD–ethyl vinyl ether, 2×10^{-2} *M* DEAD–1.4 *M* ethyl vinyl ether; system PTD–indene, 7×10^{-3} *M* PTD–7×10^{-3} *M* indene. All runs were at least duplicated.

Standard equations and graphic methods were applied to determine the orders of reaction, rate constants, and activation parameters. The maximum error observed for the rate constants was ± 7%; it was only exceeded for PTD + indene in acetonitrile (±16%).

(80) G. P. Marshall, P. A. McCrea, and J. P. Revell, British Patent 1,019,363; *Chem. Abstr.*, **64**, 12620c (1966).

(81) J. E. Horan and R. W. Schiessler, *Org. Syn.*, **41**, 53 (1961).

Registry No.—**5**, 23358-00-1; **6**, 23358-01-2; **7**, 23358-02-3; **8**, 23358-03-4; **9**, 23358-04-5; **10**, 23358-05-6; **11**, 23358-06-7; **12**, 23358-07-8; **12-D_1**, 23358-08-9; **13**, 23358-09-0; **14**, 23358-10-3; **15**, 23358-11-4; **16**, 23358-12-5; **19**, 23358-13-6; **20**, 23358-14-7; **21**, 23358-15-8; **23**, 23358-16-9; **24**, 23358-17-0; **27**, 23358-18-1; **28**, 23358-19-2; **29**, 23358-20-5; **30a**, 23358-21-6; **30b**, 23358-22-7; **31**, 23358-23-8; **32**, 23358-24-9; **33**, 5156-54-7; **34**, 5168-61-6; **36**, 23358-27-2; **37**, 23358-28-3; *cis*-DEAD, 4143-60-6; *trans*-DEAD, 4143-61-7; indene, 95-13-6; ethyl vinyl ether, 109-92-2; PTD, 4233-33-4; DMAD, 2446-84-6.

Acknowledgment.—The authors are grateful to Dr. G. Schomburg, F. Weeke, and H. Behlau for their support with preparative glpc, and to Dr. E. G. Hoffmann for helpful discussion of ir data. D. V. White is indebted to the Max-Planck-Gesellschaft for a predoctoral fellowship, and to Boston College for a University Travel Grant.

3,4-Disubstituted and Fused 1,2,5-Thiadiazole N-Oxides

KURT PILGRAM

Biological Sciences Research Center, Shell Development Company, Modesto, California 95352

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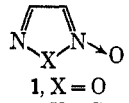
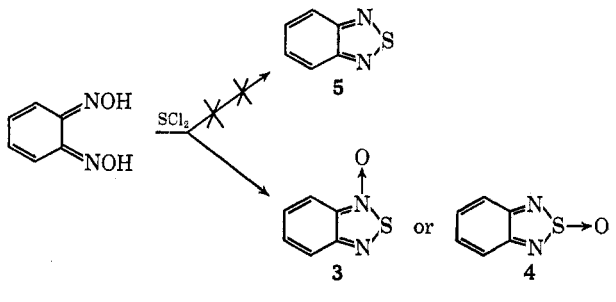
Acyclic and cyclic compounds containing the α-dioxime grouping are converted into mixtures of 3,4-disubstituted and fused 1,2,5-thiadiazoles and the corresponding N-oxides by reaction with sulfur dichloride.

Although furoxans (**1**) have been known for a long time, the corresponding 1,2,5-thiadiazole N-oxides (**2**) have not been definitely recognized. The reaction of



1, X = O
2, X = S

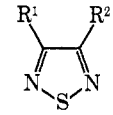
o-benzoquinone dioxime with sulfur dichloride has been reported,[1] but the structure of the reaction product was not determined unequivocally; the structures that were proposed are that of an N-oxide (**3**) and S-oxide (**4**); formation of 2,1,3-benzothiadiazole (**5**) was not observed.



5

3 **4**

Previous investigations of the action of sulfur monochloride and sulfur dichloride on aliphatic compounds containing an NCCN grouping also involved oximes and α-dioximes. α-Isonitrosocyanoacetamide and α-isonitrosophenylacetonitrile were converted into 3-cyano-4-hydroxy-1,2,5-thiadiazole[2] (**6**) and 3-chloro-4-phenyl-1,2,5-thiadiazole,[3] (**7**), respectively, while glyoxime and



6, R^1 = CN; R^2 = OH
7, R^1 = Cl; R^2 = C_6H_5
8, R^1 = R^2 = H and/or Cl
9, R^1 = R^2 = CH_3

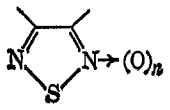
(1) V. G. Pesin, A. M. Khaletsky, and Chou-Chin, *J. Gen. Chem. USSR*, **28**, No. 7, 2131 (1958).

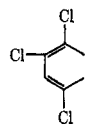
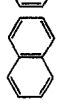
(2) J. M. Ross and W. C. Smith, *J. Amer. Chem. Soc.*, **86**, 2861 (1964).

(3) L. M. Weinstock, P. Davis, B. Handelsmann, and R. Tull, *J. Org. Chem.* **32**, 2823 (1967).

TABLE I

3,4-DISUBSTITUTED AND FUSED 1,2,5-THIADIAZOLES AND N-OXIDES



Compound	Group attached to basic structure	Method[a]	n	Yield, %	Mp or bp, °C	Analyses, % Nitrogen Calcd	Nitrogen Found	Sulfur Calcd	Sulfur Found	$\nu_{N\rightarrow O}$, cm^{-1}
5		A	0	38.1	43–44	20.6	20.9	23.5	23.2	
3			1	34.6	78–80	18.4	17.8	21.1	20.7	1365
10		C	0	22.7	163–164	11.9	11.8	13.6	13.2	
11			1	2.8	204–208	11.1	11.1	12.7	12.9	1375
13		A	0	7.3	123–124	11.7	11.8	13.4	13.2	
14			1	3.4	144–147	10.9	10.5	12.5	12.3	1370
15		B	0	67	65 (40 mm)	18.1	18.5	20.7	20.5	
16		C	0	5.7	83–84	11.8	11.8	13.4	13.1	
17			1	4.7	124	11.0	10.8	12.9	12.4	1360
18		C	0	23.0	132–133	13.3	13.2	15.3	15.8	
		B	0	81.9						

[a] (A) SCl_2 in benzene at 25°; (B) SCl_2 in DMF at 20–25°; (C) S_2Cl_2 in DMF at 5–25°.

dimethylglyoxime were converted into the 1,2,5-thiadiazoles **8**[3] and **9**;[3] formation of oxides analogous to **3** and **4** was not observed in these reactions.

Pesin's[1] report of an inability to distinguish between structures **3** and **4** and the failure of Ross and Smith,[2] and of Weinstock, *et al.*,[3] to observe formation of N-oxides or S-oxides in the reaction of acyclic oximes and α-dioximes with sulfur monochloride and sulfur dichloride prompted us to investigate the reaction of several aliphatic and aromatic α-dioximes with these reagents and determine the structures of the reaction products.

Results and Discussion

To elucidate the structure of the reaction product from *o*-benzoquinone dioxime and sulfur dichloride as that of **3** and **4**, it was decided to repeat Pesin's experiment. When *o*-benzoquinone dioxime[4] was allowed to react with sulfur dichloride in benzene at 25°, a 1:1 mixture of two products was obtained. Analytical, physical, and spectral data of the compound melting at 43–44° (see Table I) were in agreement with those of 2,1,3-benzothiadiazole (**5**). The compound that melted at 78–80° (lit.[1] mp 81–83°) has been assigned the N-oxide structure as shown in formula **3** rather than the S-oxide (**4**) structure. This assignment is based on its infrared spectrum which is consistent only with structure **3**. For example, the characteristic S → O stretching vibration of a sulfoxide[5] (*i.e.*, **4**) which occurs usually near 1050 cm^{-1} is absent, whereas a strong band at 1365 cm^{-1} indicates the presence of an heterocyclic N-oxide group. Support for this assignment comes from the infrared spectra of fused aromatic N-oxides:[6] the N → O stretching vibration of quinoxaline N-oxide which is isoelectronic with **3** has been assigned to the 1370-cm^{-1} band.[7]

9,10-Phenanthrenequinone dioxime[11] underwent reaction with excess sulfur monochloride at 25° in dimethylformamide (2 hr) to give a mixture of phenanthro[9,10-*c*]-1,2,5-thiadiazole (**10**) and the corresponding N-oxide (**11**). The structure of **10** was proven by independent, unequivocal synthesis from 9,10-diaminophenanthrene and thionyl chloride in the presence of triethylamine as scavenger for hydrogen chloride. The structure of **11** was indicated by the N–O band (ν 1375 cm^{-1}). To obtain additional support for the structure of **11** it was decided to prepare its only other positional isomer, namely the known[12] S-oxide (**12**) and establish their nonidentity. Reaction of phenanthrene-9,10-bis(trimethylsilyl)imine[12] with thionyl chloride afforded **12**, melting at 234–237° (lit.[12] mp 234.5–237°). Compounds **11** and **12** were not identical as shown by the differences in melting points. Consistent with the structure of **12** the infrared spectrum gave characteristic sulfoxide absorption at 1130 cm^{-1}, which is not present in **11**. The fact that **12** could readily be

(4) (a) Th. Zincke and P. Schwarz, *Justus Liebigs Ann. Chem.*, **307**, 28 (1899); (b) L. G. Green and F. W. Rowe, *J. Chem. Soc.*, 2452 (1912).

(5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1954, Chapter 22, p 288.

(6) G. R. Clemo and A. F. Daglish, *J. Chem. Soc.*, 1481 (1950).

(7) The relatively high value of $\nu_{N\rightarrow O}$ 1370 cm^{-1} is not surprising since the $^+N-O^-$ band in heterocyclic N-oxides such as those of pyridine[8a,9] and pyrazine[8b,10] is found in the 1319–1230-cm^{-1} region, pyrazine N-oxide having its $\nu_{N\rightarrow O}$ stretching band at 1318 cm^{-1}, which is some 54 cm^{-1} higher than in pyridine N-oxide; in general, the band rises with increasing electron-acceptor properties of the substituent.[9]

(8) (a) H. Shindo, *Chem. Pharm. Bull. Jap.*, **6**, 117 (1958), and **7**, 791 (1951); (b) *ibid.*, **8**, 33 (1960).

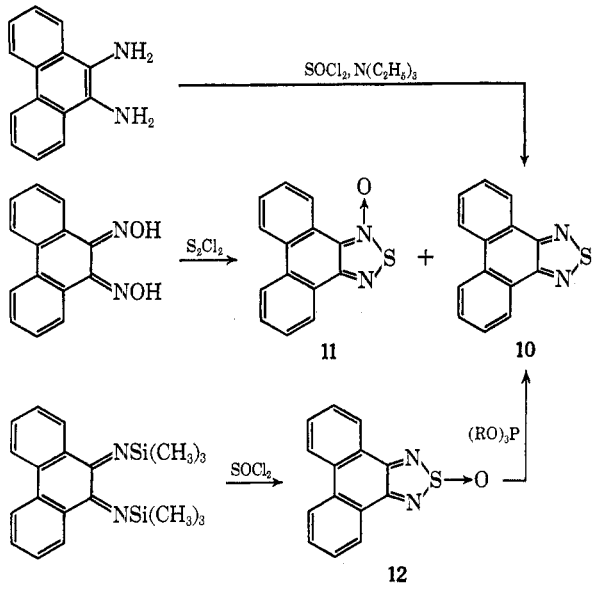
(9) A. R. Katritzky, J. A. T. Boulton, and N. A. Coats, *J. Chem. Soc.*, 3680 (1959).

(10) B. Klein and J. Berkowitz, *J. Amer. Chem. Soc.*, **81**, 5160 (1959).

(11) J. Schmidt and A. Soll, *Ber.* **40**, 2459 (1907).

(12) G. Tuchtenhagen and K. Rühlmann, *Justus Liebigs Ann. Chem.* **711**, 174 (1968).

reduced to the parent thiadiazole **10** under such mild conditions as warming a solution in excess triethyl phosphite at 60° for about 5 min is in marked contrast to the behavior of N-oxide **11** which underwent extensive decomposition under the same conditions; starting material (**11**) or reduced product (**10**) were not detectable in the dark reaction mixture.



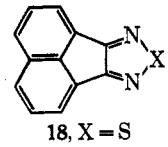
12

Reaction of 3,4,6-trichloro-*o*-benzoquinone dioxime with sulfur dichloride at 25° in benzene yielded two products in the approximate ratio of 2:1. The major component was identified as 4,5,7-trichloro-2,1,3-benzothiadiazole (**13**) by comparison of its physical and spectral data with those of an authentic sample prepared by the procedure reported by Van Daalen, *et al.*[13] The minor product was found to be 4,5(or 6),-7-trichloro-2,1,3-benzothiadiazole 1-oxide (**14**) by elemental analysis and its infrared spectrum (**14**, $\nu_{N\rightarrow O}$, 1370 cm^{-1}).

No reaction was observed between dichloroglyoxime[14] and sulfur dichloride in benzene at 25° after 2 hr. However, the reaction proceeded smoothly in dimethylformamide and was complete at 25–30° within 2 hr. Tlc indicated one major component along with one minor impurity. Purification by column chromatography afforded 67% 3,4-dichloro-1,2,5-thiadiazole (**15**) which was identical with the product obtained from cyanogen and sulfur dichloride according to the procedure of Vest.[15] The second (minor) component, presumably 3,4-dichloro-1,2,5-thiadiazole N-oxide, did not emerge from the column and therefore was not identified.

The reaction of diphenylglyoxime[16] with sulfur monochloride occurred also in dimethylformamide at 5° and gave 3,4-diphenyl-1,2,5-thiadiazole (**16**) and 3,4-diphenyl-1,2,5-thiadiazole N-oxide (**17**) in the approximate proportion of 1:1. Compound **16** was identical with the product obtained from 1,2-diphenylethane and tetrasulfur tetranitride (S_4N_4) according to the procedure of Bertini and Pino.[17] The structure of **17** follows from the value of $\nu_{N\rightarrow O}$ 1360 cm^{-1} and the absence of S → O, C=O, and OH stretching vibrations in the infrared spectrum. The H′ nmr spectrum has only a multiplet in the expected range of δ 7.7–8.7 ppm (phenyl H).

Reaction of acenaphthoquinone dioxime with sulfur monochloride or sulfur dichloride in dimethylformamide afforded acenaphtho[1,2-*c*]-1,2,5-thiadiazole (**18**); formation of the corresponding N-oxide was not observed. The ease of formation of **18** (23% with S_2Cl_2 and 82% with SCl_2) and its thermal stability are surprising in view of the structural similarity to the corresponding furazan analog **19** which is unknown. Attempts to prepare **19** by deoxygenation of the corresponding furoxan, which is prone to decompose violently at its melting point, have failed;[18] deoxygenation with trialkyl phosphites, which have proved to be efficient reagents for the reduction of furoxans to furazans,[19] gave instead naphthalene-1,8-dicarbonitrile.[18] Fusion of a furoxan or furazan nucleus to another five-membered ring apparently gives rise to an unfavorably strained situation,[20] whereas introduction of a larger sulfur atom in place of oxygen reduces ring strain.



18, X = S
19, X = O

The assignment of the 1,2,5-thiadiazole (D) and 1,2,5-thiadiazole N-oxide (C) structure to the products of these reactions allows the suggestion of a common reaction path for at least the early stages of all ring closure reactions involving α-dioximes and sulfur monochloride or sulfur dichloride. The formation of C and D has been rationalized according to Scheme I. It is plausible, for example, that the first step in all reactions is nucleophilic attack of nitrogen on the polarizable sulfur chloride to give A. The existence of compounds containing the chlorothio (ClS) group is well documented and, in several instances, compounds containing the chlorodithio (ClSS) group have been isolated.[21] Chlorodithio compounds as intermediates have also been postulated in the reaction of aliphatic amides[22] [to give bis(amido) sulfides and in the Herz reaction[23]]. Scheme I illustrates two possible routes to C and D. In the first (path a), nucleophilic attack of the nitrogen of the oxime group in A on the chlorothio group would

(13) J. J. Van Daalen, J. Daams, H. Koopmann, and A. Tempel, *Rec. Trav. Chim. Pays-Res.*, **86**, 1159 (1967); H. Koopmann, J. J. Van Daalen, and J. Daams, *Weed Res.* **7**, 200 (1967).

(14) (a) G. Ponzio and F. Baldracco, *Gazz. Chim. Ital.* **60**, 429 (1930); (b) H. E. Ungnade, G. Fritz, and L. W. Kissinger, *Tetrahedron*, **19**, *Suppl.* **1**, 245 (1963).

(15) R. D. Vest, U. S. Patent 3,115,497 (1963); *Chem. Abstr.*, **60**, 5512d (1964).

(16) K. v. Auwers and V. Meyer, *Ber.*, **22**, 547 (1889).

(17) V. Bertini and P. Pino, *Angew. Chem.* **77**, 262 (1965); *Angew. Chem., Int. Ed. Engl.*, **4**, 239 (1965).

(18) A. U. Rahman and A. J. Boulton, *Chem. Commun.*, 73 (1968).

(19) (a) C. Grundmann, *Ber.*, **97**, 575 (1964); (b) A. S. Bailey and J. M. Evans, *Chem. Ind.* (London), 1424 (1964); (c) T. Mukijama, N. Nambu, and M. Okamoto, *J. Org. Chem.*, **27**, 3651 (1962).

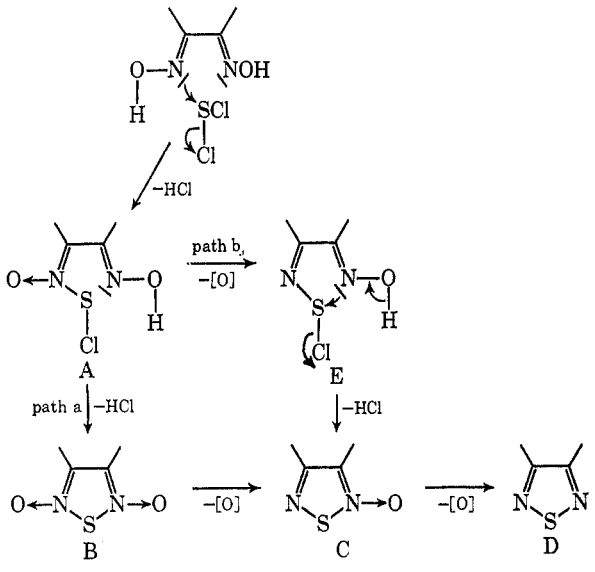
(20) H. J. Boyer in "Heterocylic Compounds," R. C. Elderfield, Ed., J. Wiley & Sons, Inc., New York, N. Y., 1961, p 462. The referee suggested that the stability difference between **18** and **19** may reflect a difference in aromaticity and not steric strain.

(21) Z. S. Ariyan and L. A. Wiles, *J. Chem. Soc.*, 4510 (1961); 1725 (1962).

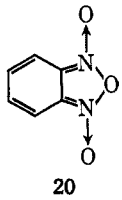
(22) P. Hope and L. A. Wiles, *ibid.*, 5679 (1964).

(23) P. Hope and L. A. Wiles, *Chem. Ind.* (London), 32 (1966).

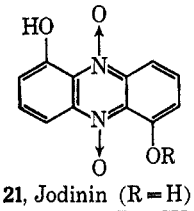
SCHEME I



lead to the di-N-oxide[24] (B) which is subsequently reduced to give C and, eventually, D. The second route (path b) would involve formation of the hypothetical intermediate E by loss of oxygen from A followed by nucleophilic attack of the nitrogen of the oxime group on sulfur of the chlorothio group to give the N-oxide C directly. If sulfur monochloride is employed in these reactions, the chlorodithio intermediates analogous to A and E are cleaved at the sulfur–sulfur bond during the ring clusure. Although at the present time we are unable to make a choice between these two mechanisms, we do favor path a. A possible explanation for the inability to detect the hypothetical B may be its inherent instability. For example, benzofurazan N,N-dioxide (**20**) has been shown to be unstable with respect to ring opening.[25] Another plausible explanation may be that the hypothetical B is easily reduced by any S^{+1} or S^{+2} source present in the reaction mixture before and after hydrolysis. The high oxidizing power of phenazine N,N-dioxides, such as the broad-spectrum antibiotics Jodinin[6] (**21**) and Myxin[26,27] (**22**), we regard as additional supporting evidence for path a.



20



21, Jodinin (R = H)
22, Myxin (R = CH_3)

Experimental Section

General.—Melting points were determined with a Thomas–Hoover capillary apparatus and are uncorrected. Infrared spectra were measured with a Perkin-Elmer Model 21 spectrometer. Nuclear magnetic resonance spectra were obtained on a Varian A-60 spectrometer.

α-Dioximes.—*o*-Benzoquinone dioxime prepared in 36.4% yield from benzofuroxan and hydroxylamine crystallized from aqueous ethanol and had mp 154° dec, lit.[4] mp 144° dec.

3,4,6-Trichloro-*o*-benzoquinone was prepared from 2,4,5-trichloroaniline *via* 2,4,5-trichloro-6-nitroaniline and 4,5,7-trichlorobenzofuroxan (47%, mp 104–105°) in 46% yield and melted at 193° dec.

Dichloroglyoxime from glyoxime by chlorination in 10% HCl at 0° had mp 198–199° dec, lit.[4] mp 198–199° dec.

The product obtained from benzil and hydroxylamine was *anti*-diphenylglyoxime, mp 244–246°, lit.[16] mp 244°.

9,10-Phenanthrenequinone dioxime from 9,10-phenanthrenequinone and hydroxylamine crystallized from methanol in 62.5% yield, mp 200–201°, lit.[11] mp 202°.

Acenaphthoquinone dioxime was prepared from acenaphthoquinone and hydroxylamine hydrochloric acid salt in refluxing ethanol (8 hr) and melted at 232°.

Anal. Calcd for $C_{12}H_8N_2O_2$:N, 13.2. Found: N, 12.9.

Reaction of *o*-Benzoquinone Dioxime with Sulfur Dichloride. Preparation of 2,1,3-Benzothiadiazole (5) and 2,1,3-Benzothiadiazole N-Oxide (3).—An adaptation of the procedure of Pesin, *et al.*,[1] was employed. A solution of 5 ml of sulfur dichloride in 25 ml of dry benzene was added dropwise at 25° and with constant stirring to a suspension of 5.0 g of *o*-benzoquinone dioxime in 100 ml of dry benzene. During the course of the mildly exothermic reaction, the dioxime dissolved. After 2 hr, the mixture was filtered and the filtrate was evaporated to dryness to give 4 g of product; tlc indicated two compounds. Separation was accomplished by column chromatography on deactivated silica gel[28] using hexane–ethyl acetate–tetrahydrofuran (40:8:2). The first fraction which emerged from the column was 2,1,3-benzothiadiazole(**5**), 1.88 g (38.1%), mp 43–44° (from hexane).

Anal. Calcd for $C_6H_4N_2S$: N, 20.6; S, 23.5. Found: N, 20.9; S, 23.2.

The second component (**3**) was obtained as yellow crystalline solid: mp 78–80°; 1.90 g (34.6%); ir spectrum: intense band at 1365 cm^{-1} (N→O); nmr spectrum, multiplet at δ 7.4 ppm (aromatic H).

Anal. Calcd for $C_6H_4N_2OS$: N, 18.4; S, 21.1. Found: N, 18.7; S, 20.8.

Reaction of 9,10-Phenanthrenequinone Dioxime with Sulfur Monochloride. Preparation of Phenanthro[9,10-*c*]-1,2,5-thiadiazole (10) and Phenanthro[9,10-*c*]-1,2,5-thiadiazole 2-Oxide (11).—A mixture of 10.0 g (0.042 mol) of phenanthrenequinone dioxime, 8 g (0.059 mol) of sulfur monochloride, and 20 ml of dimethylformamide was stirred for 2 hr at room temperature. The reaction mixture was poured into water and filtered. The crude mixture was separated by column chromatography over deactivated silica gel using a mixture of hexane–ethyl acetate–tetrahydrofuran (40:8:2) to give 2.07 g (22.7%) of **10** melting at 163–164°.

Anal. Calcd for $C_{14}H_8N_2S$: N, 11.9; S, 13.6. Found: N, 11.8; S, 12.9.

The fraction containing **11** was recrystallized from ethanol (5 times) to give 0.3 g (2.8%) of yellow brown solid, **11**: mp 204–208°; ir (KBr) 1375 cm^{-1} (N→O).

Anal. Calcd for $C_{14}H_8N_2OS$: N, 11.1; S, 12.7. Found: N, 11.1; S, 12.9.

Reaction of Phenanthro[9,10-*c*]-1,2,5-thiadiazole 1-Oxide (12) with Triethyl Phosphite.—A solution of 1.0 g (4 mmol) of **12** in 20 ml of triethyl phosphite was heated at 60° for 5 min. When the reaction mixture was allowed to cool to room temperature a brown solid melting at 158–159° crystallized out. Recrystallization from ethanol afforded 0.5 g (53%) of **10** as light brown solid, 163–164°. A mixture melting point with an authentic sample of **10** obtained from 9,10-diaminophenanthrene and thionyl chloride showed no depression.

Anal. Calcd for $C_{14}H_8N_2S$: N, 11.9; S, 13.6. Found: N, 11.9; S, 13.1.

Reaction of 3,4,5-Trichloro-*o*-benzoquinone Dioxime with Sulfur Dichlorodide. Preparation of 4,5,7-Trichloro-2,1,3-benzothiadiazole (13) and 4,5(or 6),7-Trichloro-2,1,3-benzothiadiazole 1-Oxide (14).—To a slurry of 11.1 g (0.046 mol) of 3,4,6-trichloro-*o*-benzoquinone dioxime in 100 ml of benzene was added in 15 min a solution of 5 ml (8.1 g, 0.79 mol) of sulfur dichloride

(24) The dioxide formulation was chosen for B to emphasize the symmetry of this type of molecule. Mallory, Schneller, and Wood[25] point out that a dioxide analogous to B would presumably be a resonance hybrid.

(25) F. B. Mallory, K. E. Schneller, and C. S. Wood, *J. Org. Chem.* **26**, 3312 (1961).

(26) O. E. Edwards and D. C. Gillespie, *Tetrahedron Lett.*, No. 40, 4867 (1966).

(27) M. Weigele and W. Leimgruber, *ibid.*, No. 8, 715 (1967).

(28) Deactivated by passing a stream of air through a layer of silica gel (Grace, grade 950, mesh size 60–200) for 12 hr.

in 25 ml of benzene. Stirring was continued for an additional 4 hr. The reaction mixture was poured over ice–water, extracted with 400 ml of ether and dried ($MgSO_4$). Evaporation of ether afforded a mixture of **13** and **14** which was separated by column chromatography over silica gel using the solvent mixture hexane–tetrahydrofuran–ethyl acetate (18:1:1). The first compound emerging from the column was identified as **13**, mp 123–124°, 0.8 g (7.3%).

Anal. Calcd for $C_6HCl_3N_2S$: N, 11.7; Cl, 44.5; S, 13.4. Found: N, 11.8; Cl, 44.4; S, 13.2.

The second fraction consisted of the N-oxide **14**: mp 144–147°; 0.4 g (3.4%); ir (KBr) 1370 cm^{-1} (N→O).

Anal. Calcd for $C_6HCl_3N_2OS$: N, 10.9; S, 12.5. Found: N, 10.5; S, 12.3.

Reaction of Diphenylglyoxime with Sulfur Monochloride. Preparation of 3,4-Diphenyl-1,2,5-thiadiazole (16) and 3,5-Diphenyl-1,2,5-thiadiazole N-Oxide (17).—Diphenylglyoxime, 30.0 g (0.125 mol), was added to a mixture of 32 ml (0.4 mol) of sulfur monochloride in 64 ml of dimethylformamide at 25°. The temperature of the reaction was maintained by external cooling with the aid of an ice bath. After 2 hr, the reaction mixture was poured onto 300 g of ice water and the precipitate was filtered and dried. Thin layer chromatography indicated the presence of three compounds in addition to large amounts of sulfur. The crude mixture was resolved by column chromatography on deactivated silica gel[28] using the solvent mixture hexane–tetrahydrofuran (9:1). Sulfur which emerged first from the column was discarded. After removal of the solvent, the second fraction was recrystallized from hexane to give 1.7 g (5.7%) of **16**: colorless, crystalline solid; mp 83–84°; nmr multiplet near 7.6 ppm (phenyl H).

Anal. Calcd for $C_{14}H_{10}N_2S$: N, 11.75; S, 13.45. Found: N, 11.8; S, 13.1.

The third fraction was recrystallized from hexane and afforded 1.5 g (4.7%) of **17**: colorless crystalline solid; mp 124°; ir (KBr pellet): 1360 cm^{-1} (N→O).

Anal. Calcd for $C_{14}H_{10}N_2OS$: N, 11.0; S, 12.9. Found: N, 10.8; S, 12.4.

A fourth compound, possibly the corresponding di-N-oxide, did not emerge from the column and therefore was not identified.

Preparation of Acenaphtho[1,2-*c*]-1,2,5-thiadiazole (18) from Acenaphthoquinone Dioxime. With Sulfur Dichloride.—Sulfur dichloride (20 ml, 32.4 g, 0.315 mol) was added dropwise with stirring at 25° to a solution of acenaphthoquinone dioxime (10.6 g, 0.05 mol) in dimethylformamide (150 ml). After 2.5 hr, the mixture was poured over ice–water and filtered. The solid was dissolved in methylene chloride, charcoaled, and dried ($MgSO_4$). Evaporation to dryness afforded a dark residual solid which was extracted with 500 ml of boiling hexane. This solution was concentrated to 150 ml and cooled to give 8.6 g (81.9%) of **18** as white solid melting at 132–133°. The nmr spectrum shows complex lines near 7.8 ppm (aromatic H).

Anal. Calcd for $C_{12}H_6N_2S$: N, 13.3; S, 15.3. Found: N, 13.2; S, 15.8.

With Sulfur Monochloride.—The reaction of acenaphthoquinone dioxime (10.6 g, 0.05 mol) with sulfur monochloride (25 ml, 42.5 g, 0.315 mol) which was carried out under the same reaction conditions (see above) afforded **18** in 23% yield with recovery of about 18% of acenaphthoquinone dioxime.

Registry No.—**3**, 23431-06-3; **5**, 273-13-2; **10**, 1143-73-3; **11**, 23431-09-6; **13**, 1982-55-4; **14**, 23431-11-0; **15**, 5728-20-1; **16**, 4057-61-8; **17**, 23431-14-3; **18**, 437-40-1; 3,4,6-trichloro-*o*-benzoquinone, 23431-16-5; acenaphthoquinone dioxime, 1932-08-7.

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Notes

Reactions of Trihalopropionitriles with Trialkyl Phosphite. A Convenient Synthesis of 2-Haloacrylonitriles

K. C. PANDE AND G. TRAMPE

Development Division, Chemicals and Plastics Group, Borg Warner Corporation, Washington, West Virginia 26181

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Vicinal dihalides react with trialkyl phosphites to yield either of two products, depending on the structure of the dihalide. In the absence of electron-withdrawing groups on the carbon atoms bearing the halogen atoms, phosphonate esters are formed (eq 1).[1]

$$(RO)_3P + BrCH_2CH_2Br \longrightarrow (RO)_2P(=O)CH_2CH_2Br + RBr \quad (1)$$

If, however, both halogen atoms are on carbon atoms bearing electron-withdrawing groups, dehalogenation occurs (eq 2), giving a high yield of olefin.[2]

$$C_6H_5C(=O)CHBrCHBrC(=O)C_6H_5 + (RO)_3P \longrightarrow C_6H_5C(=O)CH{=}CHC(=O)C_6H_5 + (RO)_2P(=O)Br + RBr \quad (2)$$

In the presence of an electron-withdrawing group on only one carbon atom, the usual course of reaction with trialkyl phosphites is formation of a phosphonate ester, as illustrated by the reaction of 2,3-dichloropropionitrile with triethyl phosphite (eq 3).[3]

$$ClCH_2CHClCN + (EtO)_3P \longrightarrow ClCH_2CH(CN)P(=O)(OEt)_2 + EtCl \quad (3)$$

However, styrene dibromide has been found to undergo dehalogenation when allowed to react with triethyl phosphite to give styrene in 50% yield.[4]

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