TABLE I

SEPARATION OF TERTIARY PHOSPHINE MIXTURES ON ALUMINA

Mixture, g	1st recovery, g	2nd recovery, g
2.37 $(C_6H_5)_3P$[a]	2.0[a]	...
2.0 $(C_6H_5)_3PO$[b]	...	2.0[b]
2.0 $(C_6H_5)_3P$[a]	2.0[a]	...
2.0 $(C_6H_5)_3PS$[c]	...	2.0[c]

[a] Mp 80–82.5°. [b] Mp 154–156°. [c] Mp 160–161°.

(3-Bromophenyl)phenylphosphinic Acid.—To 0.1 mole of *n*-butyllithium in hexane at −68° was slowly added 23.6 g (0.01 mole) of *m*-dibromobenzene dissolved in 80 ml of tetrahydrofuran. The reaction was carried out in a Morton flask fitted with an external cooling jacket through which extended a bottom take-off with a stopcock which was in turn attached to a second reaction flask, also cooled to −68°. The system was pressure equalized and under a dry nitrogen atmosphere at all times. After 10 min of stirring, the white slurry was dropped into a slight excess of N,N-dimethylphenylphosphonamidic chloride dissolved in tetrahydrofuran. After warming to ambient temperature and a 15-min reflux period, the solvents were removed at reduced pressure. The residual material was heated with 50 ml of concentrated hydrochloric acid on a steam bath. The resulting white solid was recrystallized from isopropyl alcohol and water to yield 22.6 g (0.0761 mole, 76% yield) of (3-bromophenyl)phenylphosphinic acid melting at 163–164° (lit.[16] mp 161–162°) and having a neutralization equivalent of 298 (theory 297.1).

***p*-Phenylenebis(phenylphosphinic Acid) (IVa).**—Under an atmosphere of nitrogen and in the same two-flask reaction apparatus described above in the synthesis of (3-bromophenyl) phenylphosphinic acid, 4.8 g (0.02 mole) of *p*-dibromobenzene in 25 ml of tetrahydrofuran, and 0.08 mole (100% excess) of *n*-butyllithium were reacted at −70°. After 1 hr at −70°, the mixture was allowed to warm to room temperature before being dropped into a solution of 8.1 g (0.04 mole) of N,N-dimethylphenylphosphonamidic chloride and 50 ml of tetrahydrofuran. After the reaction mixture was then warmed to ambient temperature and the solvents were removed at reduced pressure, the residue was digested on a steam bath with concentrated hydrochloric acid for 18 hr. The solids were dissolved in sodium hydroxide solution, treated with Norit A, reacidified, and then digested with methanol. The resulting white, methanol-insoluble powder (4 g), melting above 315°, was identified as the desired *p*-phenylenebis(phenylphosphinic acid) (IVa).

Anal. Calcd for $C_{15}H_{16}O_4P_2$: C, 60.34; H, 4.50; P, 17.3; neut equiv, 179. Found: C, 60.19; H, 4.82; P, 17.3; neut equiv, 183.

Additionally, some experiments also yielded (4-bromophenyl)-phenylphosphinic acid as a methanol-soluble product melting at 174–176° (lit.[17] mp, 174.5°) in yields to 15%.

Anal. Calcd for $C_{12}H_{10}BrO_2P$: C, 48.51; H, 3.39; Br, 26.90; neut equiv, 297. Found: C, 48.75; H, 3.45; Br, 26.6; neut equiv, 289.

4,4′-Biphenylenebis(phenylphosphinic acid) (IVb).—Following the same general procedure as described above for the other phosphinic acids, 25 g (0.08 mole) of 4,4′-dibromobiphenyl dissolved in 200 ml of tetrahydrofuran was treated with 2 equiv of *n*-butyllithium in hexane at or below −65°. Subsequent reaction with 2 equiv of either N,N-dimethyl- or N,N-diethylphenylphosphonamidic chloride in 75–100 ml of tetrahydrofuran at the same low temperature, followed by removal of the solvents and acid hydrolysis, gave yields of 4,4′-biphenylenebis(phenylphosphinic acid) (IVb) of 30–40%. This acid was more soluble in organic solvents than the *p*-phenylene homolog IVa and could be recrystallized from isopropyl alcohol–water mixture to give beautiful, featherlike crystals, mp 213–215°C.

Anal. Calcd for $C_{24}H_{20}O_4P_2$: C, 66.36; H, 4.64; P, 14.4; neut equiv, 217. Found: C, 66.84; H, 4.94; P, 14.1; neut equiv, 217.

Registry No.—Ia, 4129-44-6; bis(benzylphosphonium chloride) salt of Ia, 10211-97-9; Ib, 1179-06-2; Ic, 1179-05-1; Id, 10211-98-0; bis oxide of Id, 10211-99-1; bis(benzylphosphonium chloride) salt of Id, 10212-00-7; IIIa, 734-59-8; oxide of IIIa, 5525-40-6; IIIb, 10212-03-0; oxide of IIIb, 10212-04-1; IVa, 10212-05-2; IVb, 10212-06-3; V, 10212-07-4; tris oxide of V, 10212-08-5; tris(tertiary phosphine) sulfide of V, 10212-09-6; VI, 10212-10-9; VII, 10212-11-0; disulfide of VII, 10235-66-2; triphenylphosphine, 603-35-0; $(C_6H_5)_3PO$, 791-28-6; $(C_6H_5)_3PS$, 3878-45-3.

Acknowledgments.—This investigation was supported by the Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, under Contracts AF 33(657)-11129 and 33(615)-3570. We wish to thank Messrs. Karl Sterner and William Birch for the elemental analyses and Messrs. G. David Homer and Robert J. Mitchell for their laboratory assistance.

(16) J. M. Denham and R. K. Ingham, *J. Org. Chem.*, **23**, 1298 (1958).

(17) W. C. Davies and F. G. Mann, *J. Chem. Soc.*, 276 (1944).

Aromatic Nitrile Oxides[1]

M. S. CHANG AND J. U. LOWE, JR.

Research and Development Department, Naval Ordnance Station, Indian Head, Maryland

Received November 22, 1966

The synthesis of 12 new isoxazolines and oxadiazoles has been achieved in a study of the reactions of 1- or 2-methyl-5-vinyltetrazole and 1- or 2-methyl-5-cyanotetrazole with nitrobenzonitrile oxides. Infrared and nmr spectral data of the compounds are consistent with proposed structures.

Aromatic nitrile oxides are labile compounds formed by the action of dilute alkali on hydroxamoyl chlorides which dimerize readily to furoxans.[2] The rate of the dimerization depends upon the nature of the substituent on the aromatic ring. The greater the electron-donor character of the substituent group the faster the dimerization occurs. Recently Grundmann and Dean[3,4] showed that aromatic nitrile oxides can be stabilized with sterically hindered groups. This encouraged us to study the isomers of nitrobenzonitrile oxide with 1- or 2-methyl-5-vinyltetrazole (MVT) and 1- or 2-methyl-5-cyanotetrazole (MCT) to ascertain the influence of the electrical nature of the nitro group and the effect of its position on the addition reaction.

(1) This work was supported by the Foundational Research Program of the Naval Ordnance Systems Command.

(2) R. Huisgen, *Angew. Chem.*, **75**, 751 (1963).

(3) C. Grundmann and J. M. Dean, *ibid.*, **76**, 682 (1964).

(4) C. Grundmann and J. M. Dean, *J. Org. Chem.*, **30**, 2809 (1965).

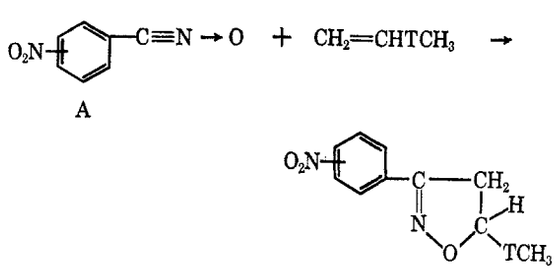
TABLE I
REACTION PRODUCTS FROM AROMATIC NITRILE OXIDES

Compd	Formula	Yield, %	Mp, °C	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
3-(*m*-Nitrophenyl)-5-(1-methyltetrazoyl)isoxazoline (I)	$C_{11}H_{10}O_3N_6$	75	104–105	48.17	3.68	30.65	48.15	3.64	30.53
3-(*p*-Nitrophenyl)-5-(1-methyltetrazoyl)isoxazoline (II)	$C_{11}H_{10}O_3N_6$	70	187–188	48.17	3.68	30.65	48.38	3.69	30.88
3-(*o*-Nitrophenyl)-5-(1-methyltetrazoyl)isoxazoline (III)	$C_{11}H_{10}O_3N_6$	39	99–100	48.17	3.68	30.65	48.29	3.87	30.69
3-(*m*-Nitrophenyl)-5-(2-methyltetrazoyl)isoxazoline (IV)	$C_{11}H_{10}O_3N_6$	69	77–78	48.17	3.68	30.65	48.26	3.59	31.01
3-(*p*-Nitrophenyl)-5-(2-methyltetrazoyl)isoxazoline (V)	$C_{11}H_{10}O_3N_6$	72	145–146	48.17	3.68	30.65	48.28	3.58	30.92
3-(*o*-Nitrophenyl)-5-(2-methyltetrazoyl)isoxazoline (VI)	$C_{11}H_{10}O_3N_6$	10	57–58	48.17	3.68	30.65	48.48	3.57	30.92
3-(*m*-Nitrophenyl)-5-(1-methyltetrazoyl)oxadiazole (VII)	$C_{10}H_7O_3N_7$	35	178–179	43.95	2.56	35.89	43.70	2.86	36.03
3-(*p*-Nitrophenyl)-5-(1-methyltetrazoyl)oxadiazole (VIII)	$C_{10}H_7O_3N_7$	37	200–201	43.95	2.56	35.89	43.90	2.89	36.14
3-(*m*-Nitrophenyl)-5-(2-methyltetrazoyl)oxadiazole (IX)	$C_{10}H_7O_3N_7$	31	134–135	43.95	2.56	35.89	43.99	2.79	36.04
3-(*p*-Nitrophenyl)-5-(2-methyltetrazoyl)oxadiazole (X)	$C_{10}H_7O_3N_7$	29	209–210	43.95	2.56	35.89	44.21	2.68	36.19
3-(2,4-Dinitrophenyl)-5-(1-methyltetrazoyl)isoxazoline (XI)	$C_{11}H_9O_5N_7$	85	165–166	41.37	2.82	30.72	41.66	3.14	30.70
3-(2,4-Dinitrophenyl)-5-(2-methyltetrazoyl)isoxazoline (XII)	$C_{11}H_9O_5N_7$	12	95–96	41.37	2.82	30.72	41.04	2.88	30.41

Since the Hammett[5] σ constants for *m*-nitro (+0.71) and *p*-nitro (+0.78) substituents are similar, one would predict that *m*-nitrobenzonitrile oxide and *p*-nitrobenzonitrile oxide should react with MVT or MCT in a similar manner. Indeed, the experimental results supported this view. The addition products of MVT or MCT gave the corresponding isoxazolines (dihydroisoxazoles) or oxadiazoles, respectively. (See eq 1–3.) The structures were supported by elemental analysis (Table I) and infrared and nmr spectral data.

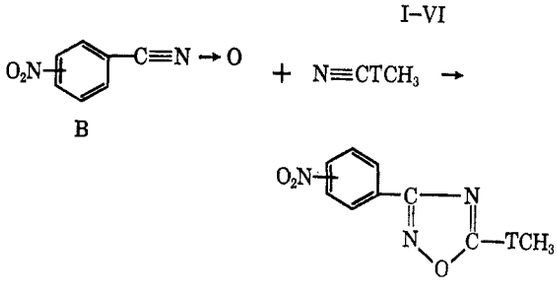
Leandri and Pallotti[6] reported that the addition of an aromatic nitrile oxide to an aryl nitrile is clearly hindered by *ortho*-substituted or electron-releasing *para*-substituted aryl nitrile. The reaction is favored, however, by aryl nitrile with electron-attracting *para* substituents. The influence of ring substitution on the reactivity of the aromatic nitrile oxide was not mentioned by earlier investigators. The addition reaction of *p*- and *m*-nitrobenzonitrile oxide with 1- or 2-methyl-5-cyanotetrazole proceeded smoothly to give the corresponding oxadiazole which indicated that the methyl group was not large enough to hinder the reaction. However, all attempts to isolate oxadiazoles from the reaction of MCT with *o*-nitro- or 2,4-dinitrobenzonitrile oxide were abortive. Thus, it is indicated that the presence of an *ortho* substituent on the aryl nitrile (A) or the aryl nitrile oxide (B) inhibits the addition reaction between A and B. However, the role of the reactivity of reactants A and B can not be overlooked.

In the addition reaction of 1-methyl-5-vinyltetrazole with *o*-nitrobenzonitrile oxide, the instantaneous formation of isoxazoline prevented the undesired side reaction. On the other hand, 2-MVT did not react so rapidly as 1-MVT; thus, a higher temperature



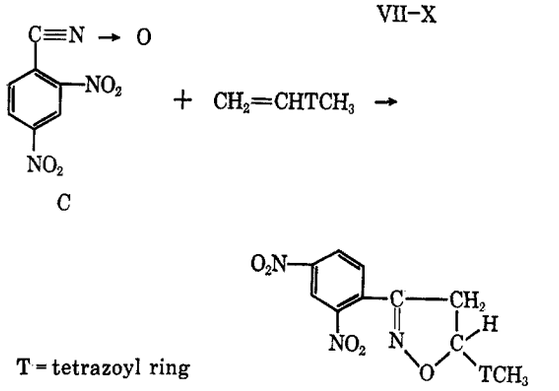
(1)

I–VI



(2)

VII–X



(3)

T = tetrazoyl ring

was required for the addition reaction. At the higher temperature several competitive reactions can occur: for example, dimerization of the nitrile oxide to a furoxan,[2] intramolecular reaction of *o*-nitro group with the nitrile oxide, and rearrangement of the nitrile

(5) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p 221.

(6) G. Leandri and M. Pallotti, *Ann. Chim.* (Rome), **47**, 376 (1957); *cf. Chem. Abstr.*, **51**, 15502c (1957).

oxide to an isocyanate[4] which leads to complex mixtures which were difficult to separate and purify. At lower temperature and longer reaction time, however, a small amount of isoxazoline was isolated and identified.

The introduction of the second nitro group stabilizes the nitrile oxide. The addition reaction with 1-MVT occurred immediately and the yield of XI was nearly quantitative. The lower yield of the 3-(2,4-dinitrophenyl)-5 (2-methyltetrazoyl)isoxazoline (XII) can be explained by lower reactivity of the 2-MVT. The failure of the addition reaction with 1-MCT and 2-MCT might be attributed to the steric effect as well as lower reactivity of MCT.

The infrared spectra of isoxazolines (N—O band at 1300–1380 cm^{-1}, C=N band at 1600–1635 cm^{-1}) and oxadiazoles (C—O band at 1030–1035 cm^{-1}) are consistent with infrared data reported in the literature.[7]

The CH_2 and CH bands could not be rigorously assigned. However, further support for the assigned structure of these compounds was obtained from nmr spectra.

The chemical shifts of the resonance lines in the range δ 3.97 to 4.17 and 6.02 to 6.17 are assigned, respectively, to the methylene and methine protons of the isoxazoline ring. The area of the methylene resonance to that of the methine resonance is in the ratio 2:1. These protons seem to approximate an ABX pattern from which the following coupling constants and chemical shift were estimated: $|J_{AB}| \sim 17.0$, $|J_{AX}| \sim 5.4$, $|J_{BX}| \sim 11.6$ cps; $\nu_0\delta_{AB} \sim 26.3$ ppm.

The chemical shift of the 1-methyl and 2-methyl resonances of the tetrazole ring occurred at δ 4.24–4.26 and 4.35–4.41, respectively. These values are in agreement with reported chemical shifts for methyl substituted tetrazoles.[8]

(7) M. Milone and E. Borello, *Gazz. Chim. Ital.*, **81**, 677 (1951); *cf. Chem. Abstr.*, **46**, 2402 (1952).

(8) (a) F. J. Pisacane and M. J. Cziesla, 151st National Meeting of the American Chemical Society, Abstracts, Organic Division, Pittsburgh, Pa., 1966, Abstracts, p K 95; (b) J. H. Markgraf, W. T. Bachmann, and D. P. Hollis, *J. Org. Chem.*, **30**, 3472 (1965).

Experimental Section[9]

General Procedure for I, II, and III.—A solution of nitrobenzhydroxyamoyl chloride (0.01 mole) in 120 ml of ether was extracted with a cold 5% aqueous sodium carbonate solution (13 ml, 0.01 mole) in a separatory funnel and the ether layer containing nitrobenzonitrile oxide was then removed, washed with a small quantity of water, dried over anhydrous calcium chloride for about 2 min, and treated with 1-MVT (0.009 mole).[10] A reaction developed almost immediately at the end of which the reaction mixture was set aside for about 2 hr at room temperature. Removal of the solvent under diminished pressure afforded an oily product which was treated with a small quantity of methanol and left in the refrigerator overnight. The solid that separated was filtered, washed with a little ice-cold methanol, and recrystallized from methanol or benzene.

General Procedure for IV and V.—The procedure was similar to that above, except that benzene was used instead of ether and 2-MVT was used instead of 1-MVT. The mixture was refluxed for 4–6 hr then allowed to stand at room temperature for 24 hr. Removal of the solvent under diminished pressure afforded an oily product which was treated similarly as above.

In the case of *o*-nitrobenzonitrile oxide the reaction mixture was stored at room temperature for 1 week, then worked up as above.

General Procedure for Oxadiazole.—A solution of nitrobenzhydroxamoyl chloride (0.01 mole) in 150 ml of ether was extracted with a cold 5% aqueous sodium carbonate solution (13 ml, 0.01 mole) in a separatory funnel and the ether layer containing nitrobenzonitrile oxide was then removed, washed with a small quantity of water, dried over anhydrous calcium chloride for about 2 min, and treated with 1- or 2-MCT.[11] The reaction mixture was allowed to stand at room temperature with occasional shaking for 2–5 days. Removal of the solvent under diminished pressure afforded an oily product which was treated with a small quantity of ethanol. The solid that separated was filtered, washed with ethanol, and repeatedly recrystallized from ethanol.

In the case of the *o*-nitrobenzonitrile oxide or 2,4-dinitrobenzonitrile oxide, the reaction conditions were varied but only oily, reddish tarlike materials were obtained.

Registry No.—I, 10221-26-8; II, 10221-27-9; III, 10221-28-0; IV, 10221-29-1; V, 10221-30-4; VI, 10221-31-5; VII, 10239-66-4; VIII, 10221-32-6; IX, 10221-33-7; X, 10221-34-8; XI, 10221-35-9; XII, 10221-36-0.

(9) All melting points are uncorrected.

(10) W. G. Finnegan, R. A. Henry, and S. Skolink, U. S. Patent 3004959 (1961); *cf. Chem. Abstr.*, **56**, 15518c (1962).

(11) E. Oliveri-Mandala and T. Passalacqua, *Gazz. Chim. Ital.*, **43**, 468 (1913).

Preparation of Unsymmetrical Dithiooxamides[1a]

BERNARD J. HASKE,[1b] MARGARET E. MATTHEWS, JOHN A. CONKLING, AND HERMAN P. PERZANOWSKI

Department of Chemistry, Washington College, Chestertown, Maryland 21620

Received October 28, 1966

A series of unsymmetrical aryl-substituted dithiooxamides were synthesized by thionation of the corresponding oxygen analogs with phosphorus pentasulfide. The ultraviolet absorption spectra of several monothiooxamides isolated have been reported and structural assignments made on the basis of these spectra. A number of alkyl-substituted dithiooxamides were synthesized by means of a new one-step reaction between the sodium salt of dithiooxamide and an aliphatic amine.

A widespread interest has recently been shown in the chemistry of dithiooxamide (rubeanic acid) and its derivatives. Hurd[2] has reviewed the literature of dithiooxamide and its derivatives; applications as metal deactivators in petroleum products, vulcanization accelerators, bacteriostatic agents, plant growth regulators, spirit duplication, photoconductolithography, and analytical reagents have been reported. More recently, publications have appeared on the possible application of these compounds in thermography[3] and as semiconductors.[4]

The majority of the dithiooxamide derivatives previously reported are N,N′ symmetrically substituted compounds, although a small number of unsymmetrical

(1) (a) A portion of this work was carried out at Wheeling College, Wheeling, W. Va. (b) To whom communications should be addressed.

(2) R. N. Hurd, "Review of Scientific and Patent Literature on Dithiooxamide: Its Substituted Derivatives and Their Metal Complexes," Mallinckrodt Chemical Works, St. Louis, Mo., 1963.

(3) Xerox Corp., British Patent 1,029,997 (May 18, 1966).

(4) M. J. S. Dewar and A. M. Talati, *J. Am. Chem. Soc.*, **86**, 1592 (1964).