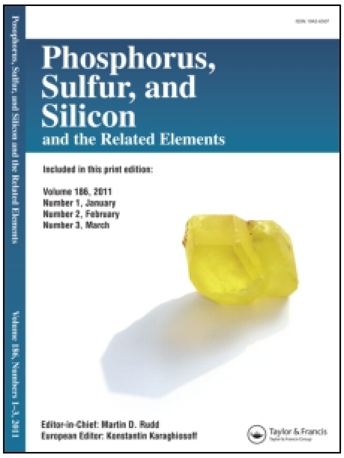

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REACTION OF ALKYL PHOSPHITES ON SOME DERIVATIVES OF MALONONITRILES

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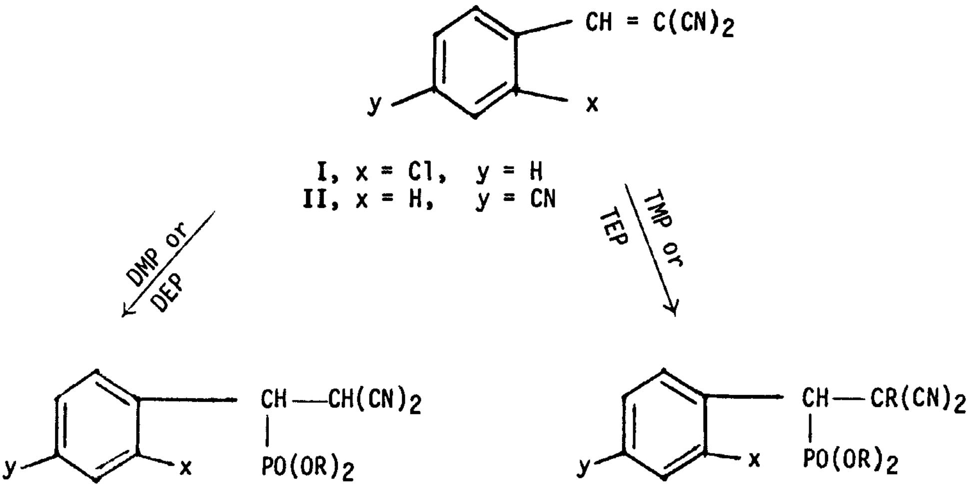
Alkyl phosphites add to carbon-carbon double bonds in malononitriles compounds **I** and **II** to give the corresponding phosphonates **IIIa,b**, **IVa,b**, **Va,b** and **VIa,b** respectively. Also, alkyl phosphites add to carbon-nitrogen double bonds in schiff bases **VII** and **VIII** to give the phosphonates **IX** and **X**. Structures of the new products were assigned and were consistent with analytical and spectroscopic measurements.

Key words: Malononitriles; Schiff bases; alkyl phosphites.

The interest shown recently in malononitriles compounds is largely due to the use of 2-chlorobenzylidenemalononitrile (CS) as the active component in numerous anti-personnel and riot control devices.[1–4] Exposure to particulate aerosols of the riot control agent (CS) causes irritation of the eyes and the mucosal surface of the respiratory tract.[5] A number of studies of the toxicity, pharmacology and bio-



I, x = Cl, y = H
II, x = H, y = CN

IIIa, x=Cl, y=H, R=CH_3
b, x=Cl, y=H, R=C_2H_5

Va, x=H, y=CN, R=CH_3
b, x=H, y=CN, R=C_2H_5

IVa, x=Cl, y=H, R=CH_3
b, x=Cl, y=H, R=C_2H_5

VIa, x=H, y=CN, R=CH_3
b, x=H, y=CN, R=C_2H_5

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TABLE I

Physical constants of analytical data of new compounds

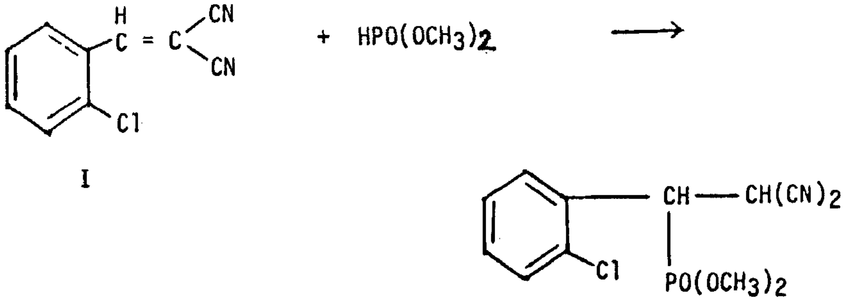
Compound	M.P. °C	Solvent of crystallization	Yield %	Formula mol. wt.	Elemental Analyses Calc./Found C	H	N	P	Cl
IIIa	73	Pet-ether 80–110	75	$C_{12}H_{12}N_2ClPO_3$	48.24	4.02	9.38	10.39	11.89
				298.5	48.49	4.11	9.30	10.27	11.72
IIIb	108	Ethyl acetate	72	$C_{14}H_{16}N_2ClPO_3$	51.46	4.90	8.58	9.50	10.87
				326.5	51.40	4.82	8.50	9.20	10.69
IVa	80	Ethyl acetate	66	$C_{13}H_{14}N_2ClPO_3$	49.92	4.48	8.96	9.92	11.36
				312.5	49.84	4.39	8.85	9.77	11.12
IVb	84	Pet-ether 80–110	70	$C_{16}H_{20}N_2ClPO_3$	54.16	5.64	7.90	8.75	10.01
				354.5	53.98	5.52	7.75	8.59	9.95
Va	95	Ethyl acetate	85	$C_{13}H_{12}N_3PO_3$	53.98	4.15	14.53	10.73	—
				289	54.01	4.20	14.35	10.80	—
Vb	105	Benzene	90	$C_{15}H_{16}N_3PO_3$	56.78	5.05	13.25	9.78	—
				317	56.82	5.21	13.05	9.67	—
VIa	130	Ethanol	72	$C_{14}H_{14}N_3PO_3$	55.45	4.62	13.86	10.23	—
				303	55.51	4.66	13.63	10.00	—
VIb	140	Ethanol	75	$C_{15}H_{20}N_3PO_3$	56.08	6.23	13.08	9.66	—
				321	56.24	6.30	13.00	9.70	—
IX	176	Ethanol	70	$C_{12}H_{17}N_5PO_3$	46.45	5.48	22.58	10.00	—
				310	46.29	5.53	22.32	10.24	—
X	180	Ethanol	65	$C_{15}H_{23}N_3PO_5$	50.56	6.45	11.80	8.71	—
				356	50.62	6.51	11.63	8.62	—

chemistry of CS aerosols have been reported.[6,7] Interesting pharmacological properties are exhibited by these compounds, which were taken as starting materials, to extend the work in this field.

Compounds, 2-chlorobenzylidenemalononitrile, **I**, and 4-cyanobenzylidenemalononitrile **II**, were allowed to react with dimethyl phosphite, DMP, diethyl phosphite, DEP, trimethyl phosphite, TMP and triethyl phosphite, TEP, in the absence of solvent at 100°C to give the phosphonate adducts **IIIa,b, IVa,b, Va,b** and **VIa,b,** respectively. The structures of the aforementioned compounds were confirmed by the elemental analyses (Table I), molecular weight determination (MS), I.R., ^{1}H-NMR and ^{31}P spectra.

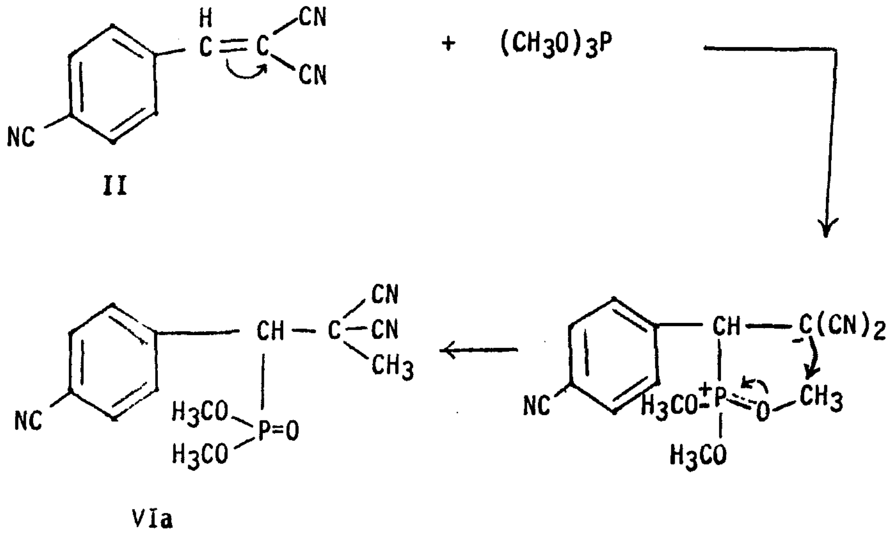
The mechanism of the reaction of DMP with I involved the addition of the phosphite radical to more electrophilic carbon atom of the double bond followed by hydrogen abstraction from the phosphite ester.[8–10]

We have found that the products can be to the assigned alkyl phosphonate



I

IIIa



" Scheme A "

structures **III, IV, V** and **VI**, since ^{31}P NMR measurements for these adducts showed positive chemical shifts (vs. 85% H_3PO_4) around δ 21 ppm. This confirms a structure with a phosphorus-to-carbon linkage.[11] The proton NMR spectra of adducts were also compatible with the assigned structures.

The elemental analysis of **IIIa** corresponded to $C_{12}H_{12}N_2PClO_3$. The IR spectrum (using KBr) revealed the presence of strong absorption bands at 2870 cm^{-1} (CH), 1250 cm^{-1} (P=O) and 1020 cm^{-1} (P—O—CH_3). The NMR spectrum showed signals at δ 4.7 ppm (2H, dd, CH—CH), δ 3.9 ppm (6H, d, OCH_3). The aromatic protons gave multiple at δ 7.3–7.8 ppm region (4H); in the ^{31}P-NMR spectrum there is singlet at δ 21.36 ppm. The MS spectrum showed m/e 298.5 (M^+).

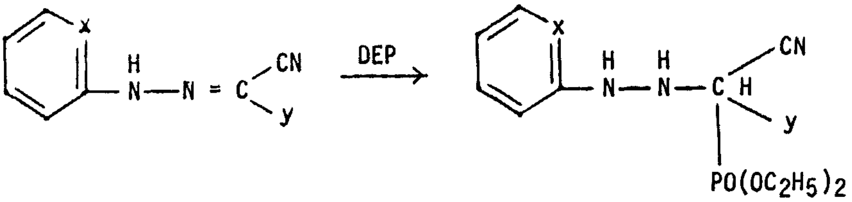
This compound **IIIa** regenerated the parent **I** when heated and when refluxed with alcoholic hydrochloric acid.

The mechanism of the reactions of TMP (or TEP) with compounds **I** and **II** is illustrated in Scheme "A".

Taking compound **VIa**, as an example, its elemental analyses corresponded to $C_{14}H_{14}N_3PO_3$. The IR spectrum (using KBr) was consistent to the proposed structure. It showed bands at 2850 cm^{-1} CH, 1425 cm^{-1} CH_3, 1250 cm^{-1} P=O and 1050 cm^{-1} $POCH_3$. The NMR showed signals at δ 4.3 ppm (1H, CH), δ 2.1 ppm (3H, CH_3), δ 3.8 ppm (6H, d, OCH_3), and the aromatic protons gave multiple at δ 7.8–8.1 ppm region (4H).

Also, we have found that the reaction of DEP with the Schiff bases **VII** and **VIII**, in the absence of solvent at 100°C gave the diethylphosphonate adducts **IX** and **X**, respectively.[12]

The mechanism involved the addition of the phosphite radical to the double bond followed by hydrogen abstraction from the phosphite ester.[12] The IR spectrum of compound **IX** (using KBr), as an example, was quite consistent with the assigned structure. It showed bands at 3400 cm^{-1} (—NH), at 2800 cm^{-1} (—CH), at 1250 cm^{-1} (P=O) and at 1050 cm^{-1} (P—O—C_2H_5). Its NMR spectra was also com-



VII, x=N, y=CN
VIII, x=H, y=CO_2Et

IX, x=N, y=CN
X, x=H, y=CO_2Et

patible with the assigned structure. It showed signals at δ 12.7 ppm (2H, NH—NH), at δ 4.1 ppm (1H, CH, d), at δ 3.6 ppm (4H, ethoxy CH_2, q), at δ 1.6 ppm (6H, ethoxy CH_3, t) and the aromatic protons (4H, multiplet) in the region δ 8.0–8.6 ppm. The MS spectrum showed m/e 310 (M^+).

EXPERIMENTAL

All melting points are uncorrected. The IR spectra were run on a Peckmann 4220 Infracord Model in KBr and expressed in cm^{-1} and ^{1}H-NMR spectra were measured in $CDCl_3$ or DMSO-d_6 and expressed in the δ-scale at 60 MHz or 90 MHz on a Varian instrument using TMS as an internal standard. The ^{31}P spectra were taken on a Varian CFT-20 (vs. 85% H_3PO_4). The mass spectra were performed at 70 eV a Varian MAT 112 Mass spectrometer. The dialkyl phosphites[13] were freshly distilled. Trialkyl[14] phosphites were purified by treatment with sodium ribbon followed by fractional distillation. The starting materials were freshly prepared and twice crystallized before use.

General procedure for the reactions of **I**, **II**, **VII** *and* **VIII** *with alkyl phosphites.* A mixture of 0.01 mole of the starting compound and 0.02 mole of alkyl phosphite was heated in absence of solvent on a steam bath for 8 hrs. The excess of alkyl phosphite was removed under vacuum, then the residue was washed several times with light petroleum and crystallized from the appropriate solvent to give the adducts **IIIa,b**, **IVa,b** **Va,b**, **VIa,b** **IX** and **X**. Percentage yields, physical and analytical data are given in Table I.

Degradation experiments of **IIIa**.

a) Thermolysis: The phosphonate adduct **IIIa**, taken as example, (0.8 g) was heated in a cold finger sublimator at 220°C (bath temperature) for about 30 minutes under reduced pressure (10 mm/Hg). The substance which sublimed was recrystallized from benzene to give I (0.38 g, yield 75%) (identified by m.p., mixed m.p. and comparative IR spectra with an authentic sample). DMP was detected in the receiver by the development of a violet color on addition of 3,5-dinitrobenzoic acid in the presence of an alkali.[15]

b) Action of hydrochloric acid: Adduct **IIIa** (0.2 g) was refluxed with alcoholic hydrochloric acid (5 ml of hydrochloric acid sp. gr. 1.18 and 15 ml ethanol) for 6 hrs. The reaction mixture was cooled and the precipitate which separated after neutralization with sodium bicarbonate was collected and crystallized from benzene to give I (0.11 g, yield 80%) (m.p., mixed m.p. and comparative IR spectra with authentic sample).

REFERENCES

1. K. Trouren-Trend and D. Crichton, Porton Memo., 1/57 (1957).
2. D. Crichton, M. A. P. Hogg, P. J. R. Bryant and G. J. Lewis, Porton Technical Paper, No. 65 (1958).
3. D. Crichton, Porton Technical Paper, No. 672 (1959).
4. P. J. Gutentag, J. Hart, E. J. Owens and C. L. Punte, CWLR, 2365 (1960).
5. L. Leadbeater, *Toxicology and Applied Pharmacology*, **25**, 101–110 (1973).

6. S. V. Sokolov and S. N. Borodulina, *Zh. Org. Khim.*, **2,** 1088 (1966); Chem. Abstr., **65,** 15302c (1966).
7. K. Tanaka et al., *Takeda Kenkyusho Nempo*, **22,** 192 (1963); *Chem. Abstr.*, **60,** 12008 h (1964).
8. J. Bougault, *Ann. Chim. Phys.*, **15,** 49 (1908).
9. N. H. Cromwell, P. L. Greges and K. E. Cook, *J. Am. Chem. Soc.*, **78,** 4412 (1956).
10. Z. Rappoport and S. Gertter, *J. Chem. Soc.*, 1360 (1964).
11. M. M. Crutchfield, O. H. Dungan, J. H. Letcher, V. Mark and J. R. van Wazer, ^{31}P Nuclear Magnetic Resonance, Interscience, New York, 1967, P. 227; F. Ramirez, *Pure and Appl. Chem.*, **9,** 337 (1964) and References Therein Cited.
12. T. S. Hafez and A. A. Fahmy, *Phosphorus and Sulfur*, Vol. 37, pp. 129–132 (1988).
13. P. W. Gan and R. L. Heider, U.S., 2, 692, 890 (1954), C.A. **49,** 1252 q (1955).
14. H. McCombie, B. C. Saunders and G. J. Stacey, *J. Chem. Soc.*, 380 (1945).
15. B. C. Saunders and B. P. Stark, *Tetrahedron*, **14,** 197 (1958).