Registry No. $Fe(I)_3$ (X = H), 89710-86-1; $Co(I)_2$ (X = H), 89710-87-2; $Ni(I)_2$ (X = H), 54975-66-5; $Cu(I)_2$ (X = H), 14323-76-3; $Co(I)_2$ (X = NO_2), 89710-88-3; $Ni(I)_2$ (X = NO_2), 54975-67-6; $Cu(I)_2$ (X = NO_2), 54975-64-3; $Co(I)_2$ (X = Me), 89710-89-4; $Ni(I)_2$ (X = Me), 89710-90-7; $Cu(I)_2$ (X = Me), 89710-91-8; $Co(I)_2$ (X = Br), 89710-92-9; $Ni(I)_2$ (X = Br), 89710-93-0; $Cu(I)_2$ (X = Br), 89710-94-1; $Co(I)_2$ (X = CO_2H), 89710-95-2; $Ni(I)_2$ (X = CO_2H), 89710-96-3; $Cu(I)_2$ (X = CO_2H), 89710-97-4; $Cu(I)_2$ (X = OMe), 16527-48-3; $Cu(I)_2$ (X = Cl), 89710-98-5.

Literature Cited

(1) Shibata, S.; Gota, K.; Kamata, E. *Anal. Chim. Acta* **1971**, *55*, 234.
(2) Kaiser, A.; Longmann, A.; Zeller, P. *Experientia* **1964**, *20*, 503.
(3) Foth, B. *Cancer Res*. **1972**, *32*, 804.
(4) Masoud, M. S.; Salem, T. M.; Elhenawi, M., presented at the 18th International Conference on Coordination Chemistry, Sao Paulo, Brazil, July 18-23, 1977.
(5) Masoud, M. S.; Kaddah, A. M.; Khalil, A. M.; Tawfik, N. I. *Indian J. Chem. Sect. A* **1979**, *17*, 502.
(6) Masoud, M. S.; Osman, M. M.; Salem, T. M.; Khalil, E. A., presented at the 20th International Conference on Coordination Chemistry, Calcutta, India, Dec 10-14, 1979.
(7) Masoud, M. S.; Elzawawy, F. *Talanta* **1980**, *27*, 766.
(8) Masoud, M. S., presented at the 5th International Symposium on Solute-Solute-Solvent Interaction, Florence, Italy, June 2-6, 1980.
(9) Masoud, M. S.; Salem, T. M.; Elhenawi, M. *Synth. React. Inorg. Met.-Org. Chem.* **1981**, *11*, 577.
(10) Masoud, M. S.; Osman, M. M.; Salem, T. M.; Khalil, E. A. *Indian J. Chem., Sect. A* **1981**, *20*, 584.
(11) Masoud, M. S.; Salem, T. M.; Elhenawi, M. A. *Indian J. Chem., Sect. A* **1981**, *20*, 297.
(12) Masoud, M. S.; Abou Ali, S. A.; Ali, G. Y.; El-Dessouky, M. A. presented at the 22nd International Conference on Coordination Chemistry, Budapest, Hungary July 23-27, 1982.
(13) Masoud, M. S. "Proceedings of the 8th International Symposium on Solute-Solute-Solvent Interactions, Tokyo, Japan, July 5, 1982", 1p-19, p 38.
(14) Masoud, M. S.; Salem, T. M. "Proceedings of the 6th International Symposium on Solute-Solute-Solvent Interactions, Tokyo, Japan, July 9, 1982", 5p-34, p 226.
(15) Goher, M. S.; Masoud, M. S.; Heiba, A. M. *Pol. J. Chem.* **1983**, 1445.
(16) Masoud, M. S.; Abou Ali, S. A.; Ali, G. Y.; El-Dessouky, M. A. *J. Chem. Eng. Data* **1983**, *28*, 297.
(17) Vogel, A. I. "A Text Book of Practical Organic Chemistry", 3rd ed.; Longmans: London, 1962.
(18) Hathaway, B. J. "Essays in Chemistry"; Bradley, J. N., Gillard, R. D., Eds.; Academic Press: New York, 1971; p 61.
(19) Kneubuhl, F. K. *J. Chem. Phys.* **1960**, *33*, 1074.
(20) Smith, D. W. *J. Chem. Soc. A* **1970**, 3108.
(21) Procter, J. M.; Hathaway, B. J.; Nicholls, P. *J. Chem. Soc. A* **1968**, 1678.
(22) Chandra, S.; Pandeya, K. B.; Singh, R. P. *Indian J. Chem.* **1981**, *58*, 1097.
(23) Hathaway, B. J.; Billing, D. E. *Coord. Chem. Rev.* **1970**, *5*, 143.
(24) Wilson, R. B.; Wasson, J. R.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1978**, *17*, 641.
(25) Krishnamoorthy, G.; Prabhanda, B. S. *J. Phys. Chem.* **1980**, *84*, 637.
(26) Beedijk, J. *Trans. Met. Chem.* **1981**, *6*, 195.
(27) McGravey, B. R. *J. Phys. Chem.* **1967**, *71*, 51.
(28) Das, M.; Livingstone, S. E. *Aust. J. Chem.* **1974**, *27*, 53, 749, 1177, 2109, 2115.
(29) Bowie, J. H.; Lewis, G. E.f Cooks, R. G. *J. Chem. Soc. B* **1970**, 821.
(30) McLafferty, F. W. "Mass Spectrometry of Organic Ions"; Academic Press: New York, 1963; p 337.

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Derivatives of *p*-Cumenylphosphorodichloridate and -dichloridothioate[†]

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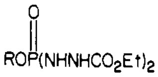
The title compounds were converted into 17 derivatives and the physical and spectral properties of these new compounds are reported.

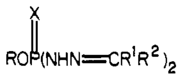
β-Phenyl-*p*-cumenylphosphorobis(hydrazide) and the bis(hydrazino)thioate (*1*) were characterized by reaction with ethyl chloroformate and carbonyl compounds to give the ethyl carbazate (I) and the hydrazones (IIa-e), respectively. The dichloridates were converted to the morpholinochloridates (IIIa,b), hydrazides (IVa,b), and hydrazones (Va-g). The structures of these compounds were confirmed by the analytical data, which were submitted for review, and by the spectral data (Table I).

In the IR spectra, the NH and P═O stretching absorptions generally appeared within the accepted ranges (*2*); however, in the ethyl carbazate (I), the value of the P═O absorption frequency was unexpectedly high. The frequency of the P-O-C stretching vibration is considerably lower than normally reported (*2b*). The P═S absorption is reported (*3*) to give two bands



$RO\overset{O}{\overset{\|}{P}}(NHNHCO_2Et)_2$

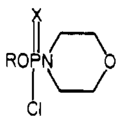
I



$RO\overset{X}{\overset{\|}{P}}(NHN{=}CR^1R^2)_2$

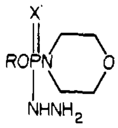
II

	X	R^1	R^2
a	O	H	C_6H_5
b	O	H	p-$CH_3OC_6H_4$
c	S	H	C_6H_5
d	S	H	p-$NO_2C_6H_4$
e	S	H	p-$CH_3OC_6H_4$



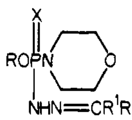
III

	X
a	O
b	S



IV

	X
a	O
b	S



V

	X	R^1	R^2
a	O	CH_3	CH_3
b	O	H	p-$NO_2C_6H_4$
c	O	H	p-$CH_3OC_6H_4$
d	O		$-(CH_2)_5-$
e	S	CH_3	CH_3
f	S	H	p-$NO_2C_6H_4$
g	S	H	p-$CH_3OC_6H_4$

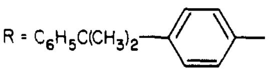


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Table I. Physical and Spectral Data

compd	mp, °C	yield, %	MS M^+ m/e	IR ν, cm^{-1}			^1H NMR δ
				NH	P=O (P=S)	P—O—C	
I	178–180	55	464	3300	1300 [1720 (C=O)]	1010	7.90 (s, NHCO, 2 H), 7.35–7.05 (m, ArH, 9 H), 6.10 (d, J_{PNH} = 32 Hz, PONH, 2 H), 4.10 (q, CH_2CH_3, 4 H), 1.65 (s, $C(CH_3)_2$, 6 H), 1.20 (t, CH_2CH_3, 6 H)
IIa	124–125	65	496	3140	1210	1010	7.85 (d, J_{PNH} = 28 Hz, NH, 2 H), 7.30–6.50 (m, ArH, CH=N, 19 H), 2.78 (s, OCH_3, 6 H), 1.65 (s, $C(CH_3)_2$, 6 H)
IIb	106	89	456	3160	1245	1005	
IIc	88–89	80	512	3210	(735)	1000	
IId	218–219	75	602	3200	(740)	1005	
IIe	132	88	572	3210	(730)	1000	
IIIa	oil (1.5575)[a]	83	379		1280	1005	
IIIb	oil (1.5875)[a]	89	395		(740)	1000	
IVa	80–81	98	375	3320 3220	1230	1010	
IVb	oil	74	391	3300 3200	(740)	1005	
Va	86	73	415	3200	1230	1010	7.25–7.10 (m, ArH, 9 H), 6.25 (d, J_{PNH} = 26 Hz, NH, 1 H), 3.65–3.20 (m, morpholine, 8 H), 1.80 (s, $C(CH_3)_2$, 6 H), 1.65 (d, $N=C(CH_3)_2$, 6 H)
Vb	70–72	85	508	3120	1230	1010	8.20 (d, J_{PNH} = 27 Hz, NH, 1 H), 7.65 (s, N=CH, 1 H), 7.50–6.85 (m, ArH, 13 H), 3.65–3.35 (m, morpholine, 8 H), 1.65 (s, CH_3, 6 H)
Vc	128–129	95	477	3120	1230	1010	
Vd	106	83	455	3160	1230	1005	
Ve	108–109	90	431	3210	(740)	1000	
Vf	160–161	85		3200	(740) [1580, 1380 (NO_2)]	1000	
Vg	139–140	88	509	3280	(740)	1010	8.00 (d, J_{PNH} = 25 Hz, NH, 1 H), 7.55–6.70 (m, ArH, CH=N, 14 H), 3.70–3.30 (m, morpholine, 8 H), 2.85 (s, OCH_3, 3 H), 1.68 (s, $C(CH_3)_2$, 6 H)

[a] n^{20}_D in parentheses.

in the regions 837–790 and 714–690 cm^{-1}, but we only observed the lower frequency vibration, in agreement with previous studies (*1*). The NMR spectra were consistent with the assigned structures; the value (ca. 30 Hz) for the coupling constant (J_{PNH}) between the phosphorus atom and the proton of the hydrazino group agrees with previous results (*4*, *5*). All the compounds showed the molecular ions (M^+) in the mass spectra, except compound Vf in which the highest fragment ion (*m/e* 447) corresponded to $M^+ - C_6H_5$.

Experimental Section

Melting points (Table I) were obtained with a Gallenkamp hot-stage apparatus and are uncorrected. IR spectra were recorded as Nujol mulls with a Unicam SP 1000 spectrometer. NMR spectra were obtained with a Varian HA 80 spectrometer in $CDCl_3$. Mass spectra were determined with a VG micromass 16F spectrometer at 70 eV. *p*-Cumenylphenylphosphorobis(hydrazide) and the bis(hydrazino)thioate were prepared from *p*-cumenylphenol, as previously described (*1*). The bis(hydrazones) (IIa–e) were obtained by boiling the hydrazide in benzene (30 mL) for 2 h. The cold suspension was filtered and the hydrazones were recrystallized from ethanol.

Preparation of the Amidic Chloride IIIa and the Amidic Chloridothioate IIIb. To a stirred solution of β-phenyl-*p*-cumenylphosphorodichloridate or -dichlorothioate (0.05 mol) in benzene (50 mol) was added dropwise morpholine (0.10 mol) in benzene (50 mL). After 24 h, the precipitate of morpholine hydrochloride was removed and the filtrate evaporated in vacuo to give the chloridates.

The compounds (IIIa,b, 0.01 mol) were reacted with hydrazine (0.02 mol) is acetonitrile (50 mL) for 6 h to give the hydrazides (IVa,b). These, by condensation with carbonyl compounds (0.1 mol), as described above, gave the hydrazones (Va–g).

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Registry No. I, 90585-36-7; IIa, 90585-37-8; IIb, 90585-38-9; IIc, 90585-39-0; IId, 90585-40-3; IIe, 90585-41-4; IIIa, 90585-42-5; IIIb, 90585-43-6; IVa, 90585-44-7; IVb, 90585-45-8; Va, 90585-46-9; Vb, 90585-47-0; Vc, 90585-48-1; Vd, 90585-49-2; Ve, 90585-50-5; Vf, 90585-51-6; Vg, 90585-52-7; β-phenyl-*p*-cumenylphosphorodichloridate, 52891-47-1; β-phenyl-*p*-cumenylphosphorodichlorothioate, 52891-48-2.

Literature Cited

(1) Cremlyn, R. J. W.; David, J.; Kishore, N. *Aust. J. Chem.* **1974**, *27*, 1065–74.
(2) (a) Bellamy, L. J. "The Infrared Spectra of Complex Molecules", 2nd ed.; Methuen: London, 1958; pp 203–6. (b) *Ibid.*, pp 311–5.
(3) Bellamy, L. J. "Advances in Infrared Group Frequencies"; Methuen: London, 1968; pp 210–2.
(4) El-Deek, M. *J. Chem. Eng. Data* **1979**, *24*, 76–7.
(5) Cremlyn, R. J. W.; Dewhurst, B. B.; Wakeford, D. H. *J. Chem. Soc. C* **1971**, 3011–7.

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