

acid was heated to $\sim 60-70^\circ\text{C}$ and then treated portionwise with bromine (0.01 mol) for 15 min. The mixture was stirred further for 3 h and poured into ice water. The solid separated was filtered and crystallized from a proper solvent to give **8**.

Registry No. 1, 84587-35-9; **2a**, 89936-35-6; **2b**, 89936-36-7; **3a**, 89936-37-8; **3b**, 89936-38-9; **3c**, 89936-39-0; **3d**, 89936-40-3; **3e**, 89958-42-9; **4**, 89936-41-4; **5a**, 89936-42-5; **5b**, 89936-43-6; **5c**, 89958-43-0; **6**, 89936-44-7; **7a**, 89936-45-8; **7b**, 89936-46-9; **7c**, 89936-47-0; **8**, 89936-48-1; NH_2NH_2 , 302-01-2; $\text{C}_6\text{H}_5\text{NHNH}_2$, 100-63-0; $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$, 100-46-9; $p\text{-CH}_3\text{OC}_6\text{H}_4\text{NH}_2$, 104-94-9; $\text{CH}_3\text{CONHNH}_2$, 1068-57-1; $\text{C}_6\text{H}_5\text{CONHNH}_2$, 613-94-5; $o\text{-HOC}_6\text{H}_4\text{CONHNH}_2$, 936-02-7; NaN_3 , 26628-22-8; $p\text{-CH}_3\text{C}_6\text{H}_4\text{NH}_2$, 106-49-0.

Literature Cited

- (1) Curran, M. V. *J. Med. Chem.* **1974**, *17*, 273.
- (2) Nannini, G.; Blasoli, G.; Perrone, E.; Forgiione, A.; Buttinoni, A.; Ferrari, M. *Eur. J. Med. Chem.-Chim. Ther.* **1979**, *14*, 53.

- (3) Mohamed, M. M.; El-Hashash, M. A.; Islam, I.; Abo-Baker, O. A. *Rev. Roum. Chim.* **1982**, *27*, 865.
- (4) El-Hashash, M. A.; Hassan, M. A.; Sayed, M. A. *Pak. J. Sci. Ind. Res.* **1977**, *20*, 336.
- (5) El-Hashash, M. A.; El-Kady, M. Y.; Mohamed, M. M. *Indian J. Chem.* **1979**, *18*, 136.
- (6) Albright, J. D.; Moran, D. B.; Wright, W. B.; Collins, J. B.; Beer, B.; Lippa, A. S.; Greenblat, E. N. *J. Med. Chem.* **1981**, *24*, 592.
- (7) Leclerc, G.; Wermuth, G. G. *Bull. Soc. Chim. Fr.* **1971**, 1752.
- (8) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds", 4th ed.; Wiley: New York, 1981; pp 123-30.
- (9) Bellamy, L. G. "The Infrared Spectra of Complex Molecules", 2nd ed.; Wiley: New York, 1966; pp 96, 115, 205-63.
- (10) Reference 9, p 179.
- (11) Schwarz, J. C. P. "Physical Methods in Organic Chemistry", 1st ed.; Robert Cunningham and Sons: London, 1964; pp 68, 113.
- (12) Reference 11, p 113.
- (13) Dyer, J. R. "Application of Absorption Spectroscopy of Organic Compounds"; Prentice-Hall: Englewood Cliffs, NJ, 1965; p 33.

Received for review October 13, 1983. Accepted January 16, 1984.

Electron Spin Resonance and Mass Spectra of Substituted Azo Cresol Complexes

Mamdouh S. Masoud* and Mohyl M. El-Essawi

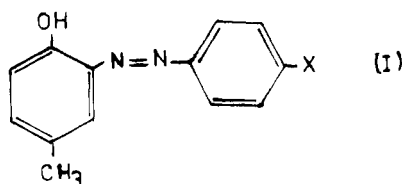
Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt

Transition-metal complexes of substituted azo cresol compounds were prepared. The structures and the mode of bonding were investigated on the basis of mass spectra for all systems and electron spin resonance for the copper complexes. The electronic characters of substituents on the data are discussed. The copper complexes give anisotropic ESR spectra with axial symmetry in tetragonal geometry for orbitally nondegenerate ground states.

The interesting azo family compounds continue to find applications in analytical chemistry (1). This type of compound is of biological importance from antifungal and antibacterial activities (2). The azo group is involved in a number of important biological reactions such as inhibition of DNA, RNA, and protein syntheses, carcinogenesis, and nitrogen fixation (3). In our laboratory (4-16), we studied the azo ligands with different functional groups from the point of view of their ability to be complexed with many metals. As part of a continuing study of the interesting behavior of such compounds, we have undertaken the title investigation of this manuscript.

Experimental Section

The ligands (I) were prepared by the usual method of dia-



zotization of *p*-cresol (17).

Table I. Electron Spin Resonance Data for *p*-Cresol Azo Complexes

substituent	g_{\parallel}	g_{\perp}	$\langle g \rangle$	G
OCH_3	2.300	2.058	2.139	5.17
CH_3	2.330	2.065	2.153	5.89
NO_2	2.260	2.070	2.133	3.71
COOH	2.322	2.074	2.156	4.35
Br		2.135		
Cl	2.28	2.076	2.147	3.68

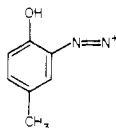
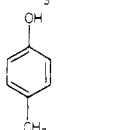
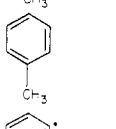
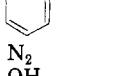
A general method was applied for the synthesis of cobalt, nickel, and copper complexes. An ammoniacal alcoholic solution of the metal salt (10 mmol) was mixed with the corresponding ligand (20 mmol) dissolved in ethanol. The mixture was refluxed for about 20 min and then allowed to cool, giving a precipitate of the required complex. The complexes were filtered and washed several times with ethanol and dried in a desiccator over P_2O_5 . The elemental analysis typified the presence of 1:2 complexes, with cobalt(II), nickel(II), and copper(II) salts and 1:3 iron(III) complexes (6, 10).

The ESR spectra of the copper complexes were recorded with E12 (X band) and E15 (Q band) instruments from Varian Associates. 2,2-Diphenyl-1-picrylhydrazide (DPPH, $g = 2.003$) was used as an external standard. The mass-spectrometric measurements were measured with CH4 and CH7 instruments from MAT-Bremen Co., West Germany. The physical measurements were done at the Chemistry Department, Marburg University, West Germany.

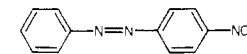
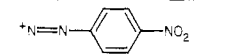
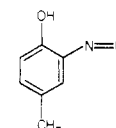
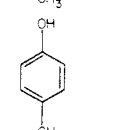
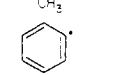
Results and Discussion

Electron Spin Resonance of Copper Complexes. The X-band spectra of the polycrystalline copper complexes (Figure 1) at room temperature are typical of those for axial symmetry

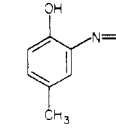
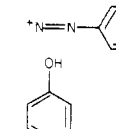
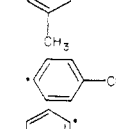
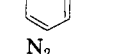
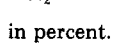
Table II. Major Fragmentation Pattern of (Phenylazo)-*p*-cresol (HL) and Its Metal Chelates^a

fragment	HL	FeL ₃	CoL ₂	NiL ₂	CuL ₂
HL	55.93	84.04	100.00	87.35	82.16
	23.98	35.38	40.51	40.56	29.45
	100.00	100.00	97.71	100.00	100.00
	1.88	2.71	2.64	2.56	2.47
	60.03	91.12		87.56	78.12
N ₂	2.47	2.11	1.98	2.19	2.08
OH	9.90	16.9	20.60	37.33	22.69

^a All values in percent.Table III. Major Fragmentation Pattern of [(*p*-Nitrophenyl)azo]-*p*-cresol (HL) and Its Metal Chelates^a

fragment	HL	CoL ₂	NiL ₂	CuL ₂
ML ₂			60.25	4.93
MH ₂ L			26.33	16.13
ML			73.27	38.78
L	39.61		44.44	40.76
		11.24	6.58	83.08
	3.64		1.95	1.05
	48.88	2.89	53.07	47.70
	100.00	10.38	100.00	100.00
	20.95	5.17	22.60	24.86
C ₆ H ₅	7.57	7.30	9.76	17.49
N ₂	3.94	80.6	19.69	34.88

^a All values in percent.Table IV. Major Fragmentation Pattern of [(*p*-Methylphenyl)azo]-*p*-cresol (HL) Ligand and Its Metal Chelates^a

fragment	HL	CoL ₂	NiL ₂	CuL ₂
HL	74.59	98.17	86.51	88.51
ML ₂		2.43	1.99	2.71
	22.41	38.13	23.57	30.87
	15.10	24.76	16.57	20.84
	67.83	99.49	68.57	97.48
	100.00	100.00	100.00	100.00
	13.94	27.39	16.76	21.17
N ₂	38.13	7.16	9.04	27.02

^a All values in percent.

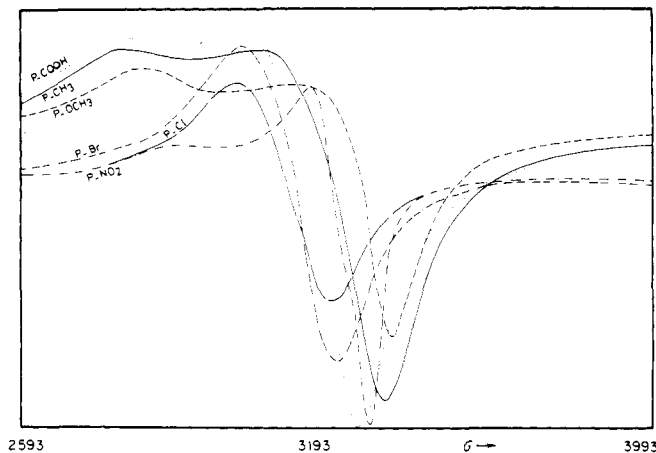
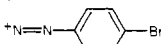
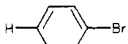
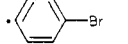
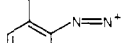
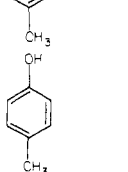



Figure 1. Electron spin resonance spectra of copper(II)-substituted azo cresol complexes.

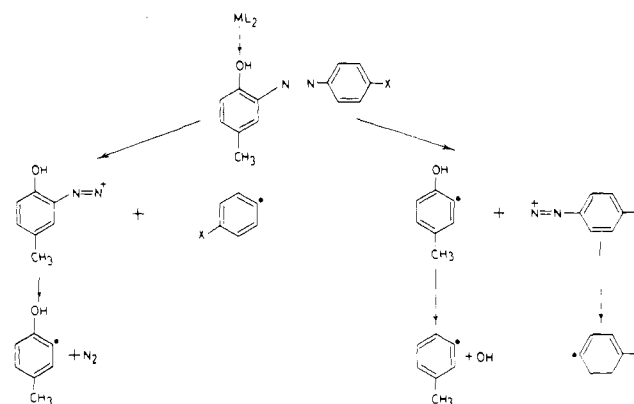
Table V. Major Fragmentation Pattern of [(*p*-Bromophenyl)azo]-*p*-cresol (HL) and Its Metal Chelates^a

fragment	HL	CoL ₂	NiL ₂	CuL ₂
HL	43.70	30.72	37.49	100.00
ML ₂		3.54	100.00	3.22
ML			21.11	
	8.28	5.36		98.04
	22.94	17.87	25.97	100.00
	22.89	17.97	28.00	100.00
	48.73	34.76	45.82	100.00
	100.00	83.71	87.45	100.00
	21.96	21.12	21.14	100.00
N ₂	10.51	18.21	31.80	52.19
OH		100.00		

^a All values in percent.

(18). All show anisotropic ESR spectra with two g values, g_{\parallel} and g_{\perp} (Table I), where $g_{\parallel} > g_{\perp}$. This is characteristic of tetragonal Cu(II) complexes with $d_{x^2-y^2}$ ground states (19) with stronger interaction along the Z axis accompanied by an increase in the value of g_{\parallel} with an increase in the length of the bond in the XY plane to decrease of both in-plane covalency and the energy of the $d_{x^2-y^2}$ transition (20). In axial symmetry, $G = g_{\parallel} - 2/g_{\perp} - 2$. If G is >4 , exchange interaction is negligible, while if G is <4 , considerable exchange interaction in the complex occurs (21, 22). The $\langle g \rangle$ value is evaluated as follows: $\langle g \rangle = 1/3 (g_{\parallel} + 2g_{\perp})$. $\langle g \rangle$ ranges from 2.133 to 2.156, in agreement with an orbitally nondegenerate ground state (23). The ESR data of the bromo complex give one broad signal with Δ value from peak to peak of 670.5 G (Figure 1). The data are due to dipolar broadening and enhanced spin-lattice relaxation of the bromide ion (24, 25). The electron-

Scheme I



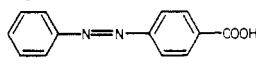
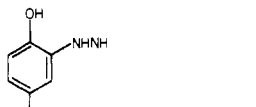
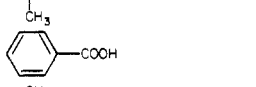



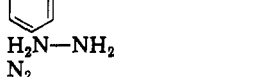
donating substituents lead to a negligible exchange interaction; the reverse is valid for the electron-attracting substituents. The slight increase in G for the copper carboxy compound is probably due to its existence in an associated form through intramolecular hydrogen bonding. In the past, it was customary to consider the covalent bonding between ligand orbitals and metal d orbitals while calculating the ligand hyperfine structure in transition-metal complexes (26). The ESR of copper(II) complexes suggests the involvement of metal $4s$ orbitals in the contribution to the isotropic part of the metal hyperfine constant (27). This suggests a polarization mechanism on the ligand involving the $4s$ bonding orbitals which results in a negative $4s$ spin density on the metal to lead to an increase in the hyperfine constant with increased covalent transfer of spin to the ligand from the metal d orbitals (28).

Mass-Spectral Studies. The data are listed in Tables II-VII. None of the (phenylazo)-*p*-cresol complexes show a peak due to the molecular ions, probably due to the existence of a high degree of polymerization or presumably due to thermal degradation in the mass spectrometer (28, 29). Two pathways are followed for fragmentation, one for the free ligand and the other for those containing metals (see Scheme I). The data indicate weak bonding between C and N atoms with a cleavage of the C-N bond to give m/e 77 and 105 due to C_6H_5 and $C_6H_5-N=N$ radicals, respectively. All the azobenzenes show skeletal-rearrangement ions in their mass spectra (29) where their genesis occurs by ionization of a double bond in the aromatic ring to furnish electron-deficient centers which are available for the attack of the incipient radical (30).

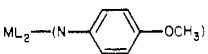
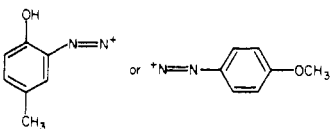
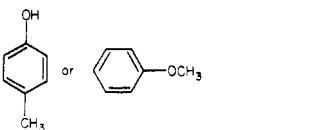

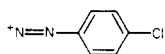

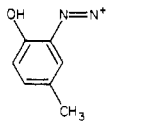
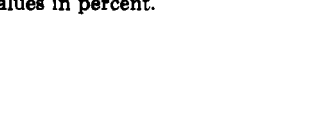
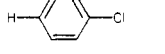
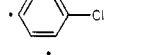

The Ni(II) and Cu(II) complexes of the *p*-NO₂ derivative show a peak due to the molecular ion while those of Co(II) do not have a fragment for the molecular ion. The latter is probably due to thermal degradation in the spectrometer or a higher degree of polymerization. The Ni(II) and Cu(II) complexes are subjected to thermal degradation by losing one ligand molecule and picking up 2H⁺ which are then lost in the next step, followed by losing the metal ion. After this step, the fragmentation patterns of the *p*-NO₂ systems proceed in a similar fashion, depending on breaking the C-N bonds.

All the bis *p*-methyl complexes derived from Co(II), Ni(II), and Cu(II) gave a molecular ion. (1) The Ni(II) and Cu(II) *p*-NO₂ complexes have fragments with m/e 302 and 306, respectively, due to the possible existence of hydrazo species. (2) The *p*-Br system gave two fragments with m/e 181 and 182, probably due to an isotopic effect. (3) The *p*-Cl compound gave two fragments with m/e 414 and 416. These fragments are due to the formation of another complex compound and also a new fragment by losing *p*-hydroxytoluene, respectively. The m/e 417 is given to the CuL₂ after losing the *p*-chloroazo fragment of a species composed of 1 mol of the free ligand

Table VI. Major Fragmentation Pattern of [*p*-Carboxyphenyl]azo]-*p*-cresol (H₂L) and Its Metal Chelates^a

fragment	HL	Co(HL) ₂	Ni(HL) ₂	Cu(HL) ₂
H ₂ L	46.82		1.00	3.14
H ₂ L-(COOH)				61.51
		33.22		3.52
	36.07	4.07	2.87	30.49
	20.27	6.64	10.67	5.45
	100.00	11.67	15.82	94.14
		18.21	10.38	2.32
	1.26		15.16	10.45
	20.04	15.56	8.39	96.56
H ₂ N-NH ₂				23.25
N ₂	17.87	99.16	100.00	43.04

^a All values in percent.Table VII. Major Fragmentation Pattern of [*p*-Methoxyphenyl]azo]-*p*-cresol (HL) and Its Copper(II) Chelate and of [*p*-chlorophenyl]azo]-*p*-cresol (HL') and Its Copper(II) Chelate^a

fragment	HL	CuL ₂	fragment (HL') system	HL'	CuL ₂ '
		12.32	ML ₂		7.47
HL	60.09	100.00	<i>m/e</i> 416		
	36.05	96.34	<i>m/e</i> 414	19.65	95.24
	100.00	100.00	HL		
	11.15	25.10		44.37	17.61
	26.53	51.89		13.22	48.22
				32.21	18.43
				100.00	64.90
				7.05	23.30
OCH ₃	2.91	3.51	N ₂	7.29	15.31
N ₂	25.78	17.75			

^a All values in percent.

complexed with Cu(II) in the presence of 1 mol of *p*-hydroxytoluene radical (*m/e* 107). The total fragments illustrated the existence of 1 mol of the free ligand coordinated to Cu(II), that attached to a species of the form C₆H₅-N=N⁺ (*m/e*

105). This is a good criterion for the existence of two complexes with stoichiometry 1:1 and 1:2. (4) The *p*-carboxy compound gave a fragment due to benzoquinone, assuming that the phenolic part of the molecule is subjected to oxidation.

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 = NO₂), 89710-88-3; Ni(I)₂ (X = NO₂), 54975-67-6; Cu(I)₂ (X = NO₂), 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 = CO₂H), 89710-95-2; Ni(I)₂ (X = CO₂H), 89710-96-3; Cu(I)₂ (X = CO₂H), 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* **1984**, *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 6th 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.; Helba, 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.; Prabhandu, 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) Bowle, J. H.; Lewis, G. E.; 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.

Received for review September 6, 1983. Accepted December 2, 1983.

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

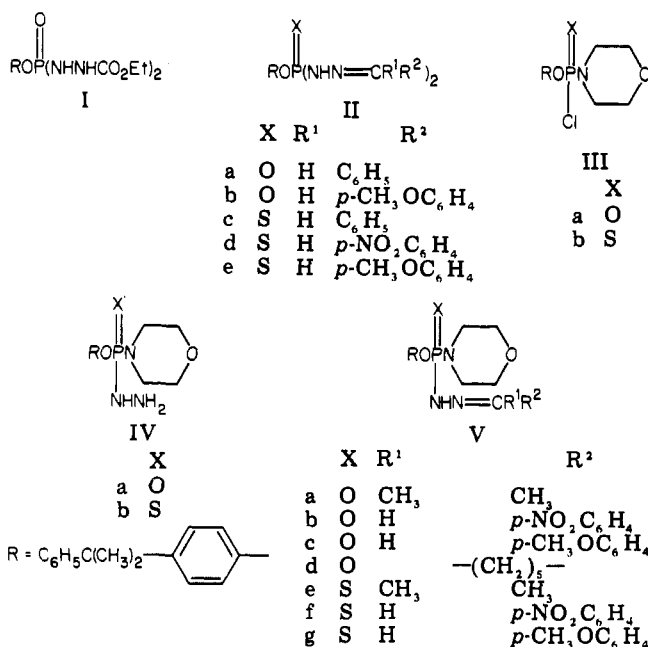
Richard J. Cremlyn* and Luke Wu

Division of Chemistry, Hatfield Polytechnic, Hatfield, Hertfordshire, England AL109AB

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

β-Phenyl-*p*-cumylphosphorobis(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



[†] Part of the M. Phil. Dissertation of L.W., Hatfield Polytechnic, Hertfordshire, England, 1983.