July, 1975] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (7), 2001—2005 (1975) 2001

Studies on Bond Character in Phosphorus Ylides by Combustion Heat and X-Ray Photoelectron Spectroscopy

Manabu Senō, Shinji Tsuchiya, Hideo Kise, and Teruzo Asahara
Institute of Industrial Science, The University of Tokyo, 7-22, Roppongi, Minato-ku, Tokyo 106

(Received October 24, 1974)

In order to clarify the electron structure of carbonyl-stabilized phosphorus ylides, measurements of X-ray photoelectron spectroscopy (XPS) and combustion heat were performed. NMR and IR spectra were also measured as complementary methods. The results suggest that carbomethoxymethylenetriphenylphosphorane has a major contribution of polar bond $(\overset{+}{P}-\overset{-}{C})$ structure, whereas benzoylmethylenetriphenylphosphoranes have a larger contribution of covalent bond (P=C). A $d\pi$—$p\pi$ interaction in the P–C bond was interpreted for XPS and NMR. The data for heat of combustion suggest that a large contribution of the polar bond structure brings about stabilization of the ylide molecule. These results show that XPS and combustion heat measurements are useful means for the analysis of ylide bonding.

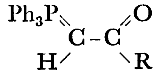
It has been considered that the phosphorus atom in phosphorus ylides has an oxidation number between P(IV) and P(V) and forms a multiple bond with an adjacent atom possessing lone-pair electrons *via* a $d\pi$-$p\pi$ bonding. The nature of the P–C bonding in phosphorus ylides has been discussed mainly on the basis of their chemical properties. Recently, IR, NMR, dipole moment, and X-ray diffraction techniques have also been used for the elucidation of the bond character, but an uncertainty still seems to remain especially on the variation of the character with the substituents on the carbon atom.

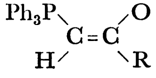
It has been reported that X-ray photoelectron spectroscopy (XPS) is especially useful in the investigation of the bonding or the formal oxidation state of atoms in a variety of compounds.[1] This induced us to use XPS as a tool for probing the bond character of the phosphorus ylides, expecting the direct elucidation of the electronic environment of the phosphorus atom.

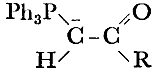
In the present work, we have analyzed the bonding mainly by means of XPS, and the ambiguities in electronic structure have been clarified through the examination of the binding energies. The measurement of combustion heat is also considered to give useful pieces of information on the bond energy in thermodynamic sense, and the results on the phosphorus ylides will be described as well as the data of IR, and NMR spectroscopy.

Results and Discussion

The compounds used for the present investigation are the carbonyl-stabilized phosphorus ylides, which have been already studied by IR,[2] NMR,[3] dipole moment,[4] and X-ray diffraction.[5] Measurement of p*K*a value and chemical reactivities[6] have also been carried out in order to clarify the effect of substituent on the carbonyl carbon. By these investigations, three resonance structures shown below have been presented:


Ia

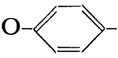
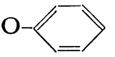
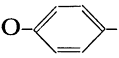
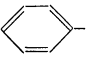
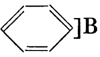
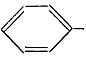

Ib


Ic

The contribution of each structure is considered to vary with the substituents R through their inductive, mesomeric and steric effects. In the present investigation, we tried to clarify the degree of contribution of each resonance structure in differently substituted ylides.

IR Studies. The C=O stretching bands in phosphorus compounds are summarized in Table 1. The bands of the phosphonium salts appear at higher frequencies by 135—189 cm^{-1} than those of the ylides. This suggests that the contribution of the structure **Ib** is large in the ylides, whereas the phosphonium salts have not the contribution of this type of resonance structure.

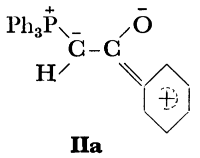
Table 1. Stretching bands of C=O groups in the ylides and their salts

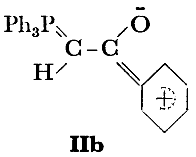
Compounds	C=O band (cm^{-1})
1 $Ph_3P=CHCO-$$-NO_2$	1540—1500
2 $Ph_3P=CHCO-$	1527
3 $Ph_3P=CHCO-$$-OMe$	1503
4 $Ph_3P=CHCO-OMe$	1620
5 $[Ph_3\overset{+}{P}-CH_2CO-$$-NO_2]Br^-$	1689
6 $[Ph_3\overset{+}{P}-CH_2CO-$$]Br^-$	1662
7 $[Ph_3\overset{+}{P}-CH_2CO-$$-OMe]Cl^-$	1652
8 $[Ph_3\overset{+}{P}-CH_2CO-OMe]Br^-$	1725

In the salts (**5**), (**6**), and (**7**) an electron donating substituent on phenyl ring yields a low frequency shift by the conjugation of the carbonyl group with the phenyl ring.

In the ylides (**1**), (**2**), and (**3**), we also find the same aspect of the effect of substituents on phenyl ring with that mentioned above in the salts (**5**), (**6**), and (**7**).

Thus, we should consider not only the resonance structure **Ib**, but also **IIa** and **IIb**:


IIa


IIb

The ylide (**4**) exhibits a C=O band at higher frequency by as much as about 100 cm^{-1} than those of other ylides. Furthermore, the difference of the C=O frequency between the salt (**8**) and the ylide (**4**) is the smallest (105 cm^{-1}) among the pairs of the salt and the ylide listed in Table 1. These results indicate that the contribution of the resonance structure **Ia** and/or **Ic** is significant in the ylide (**4**).

NMR Studies. The chemical shift and coupling constant of methylene and methine protons are summarized in Table 2.

Table 2. NMR data of the ylides and their salts

Compounds	^{1}H (methylene or methine)		^{31}P (ppm)	^{13}C$^{a)}$	
	Shift (ppm)	J_{P-C-H} (Hz)		Shift (ppm)	J_{P-C} (Hz)
1	4.46	21.6	−16.8	52.5	108
2	4.40	24.3	−16.3	49.7	108
3	4.34	24.3	−16.7	48.4	107
4	2.82	—	−17.4	28.9	131
5	6.60	13.5	−20.5	—	—
6	6.40	13.5	−20.6	—	—
7	6.36	13.5	−20.4	—	—
8	5.25	15.8	−20.5	32.6	57

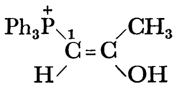
a) Methylene or methine carbons.

Comparison of the salts with ylides shows that the methylene signals of the salts appear in lower magnetic field than methine signals of the ylides. This may be attributed to higher electron densities on methine carbon atoms in the ylides than those on methylene carbon atoms in the salts, although, as generally observed, the partially olefinic character of the methine proton in the ylides would compensate the high field shift. Moreover, the difference in coupling constants between the ylides and the salts shows the existence of dπ-pπ interaction in P–C bond of the ylides.

The methylene protons in the salts (**5**), (**6**), and (**7**) give signals at lower field by 1.11—1.35 ppm than that of the salt (**8**). The same tendency is observed between the ylides (**1**), (**2**), (**3**), and (**4**), and this may be attributed to the electron releasing character of the phenyl ring. The ylide (**4**) is distinct from others also in that the shift of the signal in going from the salt (**8**) to the ylide (**4**) is large (2.43 ppm) compared to the shift in other pairs of the salts and the ylides (2.00—2.14 ppm). It was supposed from the IR measurement that the ylides (**1**), (**2**), and (**3**) have a larger contribution of the resonance structure **Ib**, whereas the ylide (**4**) is considered to have the major resonance structure **Ia** or **Ic**. The present results of NMR suggest a high degree of negative charge on the methine carbon and this seem to support the structure **Ic** rather than **Ia** for the ylide (**4**).

The signals of ^{31}P NMR of the salts appear at lower magnetic field than those of the ylides as shown in Table 2; this may be attributed to less positive charge on phosphorus atoms in the ylides. The substituent effect is not found for the phosphonium salts. In the case of the ylides, the substituents on carbonyl carbon have a clear effect on phosphorus atom through dπ-pπ bonding. The ^{31}P NMR peak of the ylide (**4**) appears at the lowest magnetic field among the ylides, probably because of the more positive charge on the phosphorus atom of the ylide. These results are consistent with those of IR and ^{1}H NMR, indicating the large contribution of resonance structure **Ic** in the ylide (**4**). The shift of the ylides (**1**), (**2**), and (**3**) suggests that the nature of P–C bonding in these ylides is of more double bond character. Hence, it is likely that the ylides (**1**), (**2**), and (**3**) have a larger contribution of resonance structure **IIb**.

The ^{13}C chemical shift and ^{13}C–^{31}P nuclear spin coupling constant are especially useful in the investigation of the bondings of phosphorus ylides. The shifts in Table 2 were assigned on the basis of previous studies.[3k,31] Gray showed that the ylides such as $Ph_3P(CR)CO_2R'$ should not be considered to have primarily **Ib** type electron structure, on the basis of comparison with value, $\delta_{13C}=70.92$ ppm and $J_{C-P}=99.2$ Hz, for C-1 of enol form **III**.



III

The results in Table 2 suggest a considerable carbanion character of P–C carbons especially for ylide (**4**), whereas the ylides (**1**), (**2**), and (**3**) seem to have considerable olefinic character by comparison with data for **III**. Especially, the values of the ^{13}C–^{31}P coupling constant are close to that of **III**. That is, since the ^{13}C–^{31}P coupling constant reflects the s character of the ylide bond,[31] the ylide bond in (**1**), (**2**), and (**3**) is considered to have the character of sp^2.

The substituent effect on ^{13}C NMR is consistent with IR and other NMR data shown above, and the order of ^{13}C NMR chemical shift is parallel with p*K*a values.[6]

Combustion Heat Studies. Two main factors have been suggested to account for bond strengthening in covalent bonds. The first reflects a certain amount of polar character of the bond. This ionic-covalent resonance causes lowering of energy of the molecule and a strengthening of the bonds. Another factor of bond strengthening has been attributed to some additional π-bonding. Pi-bonding involving d-orbital is often found in phosphorus compounds. It is of interest to see whether this type of bonding makes an important contribution to the overall energy content of the molecule. For phosphorus compounds there are much thermochemical data available and the effects of dπ–pπ bonding are much more apparent.[7] Thus, the measurement of combustion heat may be useful for the studies of bonding of phosphorus ylides. The data of combustion heat of the ylides $Ph_3P{=}CHCOR$ and related compounds are summarized in Table 3. Now we consider the thermochemical cycle shown below:

$$\begin{tikzcd}
\mathrm{Ph_3P} \arrow[d, "\Delta H_1"] & +\ \mathrm{CH_3COR} \arrow[d, "\Delta H_2"] \arrow[r, "\Delta H"] & \mathrm{Ph_3P{=}CHCOR} \arrow[d, "\Delta H_3"] & +\ \mathrm{H_2} \arrow[d, "\Delta H_4"] \\
\text{(combustion} & \text{products)} \arrow[r, phantom, "\equiv"] & \text{(combustion} & \text{products)}
\end{tikzcd}$$

Thus, the enthalpy change ΔH of the P–C bond formation is derived from the combustion heats, ΔH_1, ΔH_2, ΔH_3, and ΔH_4

$$\Delta H = (\Delta H_1 + \Delta H_2) - (\Delta H_3 + \Delta H_4) \qquad (1)$$

where $\Delta H_4 = -68$ kcal·mol^{-1}. The results calculated by the above equation are given in Table 3.

TABLE 3. COMBUSTION HEATS (ΔH_{comb}) AND ENTHALPY CHANGES OF THE P–C BOND FORMATION (ΔH) OF YLIDES

R	ΔH_2 of CH_3COR (kcal·mol^{-1})	ΔH_3 of Ph_3P=CHCOR (kcal·mol^{-1})	ΔH (kcal·mol^{-1})
p-$NO_2C_6H_4$	−940.0	−3398.1	−0.9
Ph	−989.6	−3420.9	−27.7
p-$MeOC_6H_4$	−1116.1	−3535.4	−39.7
OMe	−378.3	−2701.7	−135.6

Ph_3P; $\Delta H_1 = -2527.0$ kcal·mol^{-1}

The value for the ylide with substituent R=OMe shows that this substituent brings about a large decrease in ΔH, compared to the other substituents R=p-NO_2-C_6H_4, Ph, and p-$MeOC_6H_4$. Since the decrease in ΔH indicates the stabilization of the P–C bond, the bond of the ylide (**4**) is thought to be most stable among four ylides.

According to NMR data, the ylide (**4**) is considered to have the smaller contribution of the covalent bond through dπ–pπ interaction, and the results obtained from the combustion heat measurement seem to show that a large contribution of **Ic** brings about stabilization of the ylide molecule. We also found a substituent effect in the combustion heat of the ylides (**1**), (**2**), and (**3**), and the change in these values is consistent with that of NMR data. Furthermore, Jolly *et al.* have shown that XPS shifts do correlate well with thermochemical data.[8] It is expected that a relation is established between XPS shifts and combustion heat data for phosphorus ylides.

XPS Studies. A survey of the literature reveals the utility of X-ray photoelectron spectroscopy (XPS) on the investigation of the electronic environment of anomalous covalent atom and this induced us to use XPS as a tool for probing the ylide bonds. Most recently, Mixan *et al.* reported the XPS measurement on sulfur-nitrogen ylides and related compounds attempting to probe the nature of the S–N polar bonds.[1f]

TABLE 4. P–2p ELECTRON BINDING ENERGIES IN PHOSPHORUS YLIDES AND THEIR SALTS, THE RATE CONSTANTS OF WITTIG REACTION AND BASICITIES, pK_a[a]

Compounds	Binding energies (eV)	log k of Wittig reaction (k; l·mol^{-1}·s^{-1})	pK_a
Ph_3P=O	131.5		
Ph_3P=S	131.6		
1	130.8	−5.19	4.2
2	131.2	−3.92	6.0
3	131.3	−3.39	6.7
4	131.7	−1.84	8.8
5	131.8		
6	132.0		
7	132.0		
8	132.5		

a) Reaction with benzaldehyde.[6]

The electron binding energies in phosphorus atom measured in the present work are summarized in Table 4.

The phosphorus 2p binding energies were recorded with reference to the C 1s line at 284 eV. Distinct differences are found between the spectra of the ylides and those of their salts; the binding energies of the salts are higher than those of the corresponding ylides. It is also found that P-2p electron binding energies in the ylides decrease in the order (**4**)>(**3**)>(**2**)>(**1**), reflecting the substituent effect. It is likely that the large binding energy of the ylide (**4**) is due to a large contribution of resonance structure **Ic** rather than **Ia** and **Ib**, as revealed already by the measurements of IR, NMR, and combustion heat. Aryl substituents seem to bring about an increase in the electron density on phosphorus atom, compared to the methoxy group in the ylide (**4**). By considering the results of IR and NMR, the increase of electron density is thought to be the result of a large contribution of the structure **IIb** rather than that of **Ib**.

The binding energy of the ylide (**4**) is almost the same with those of Ph_3P=O and Ph_3P=S, and this implies that the polarity of P–C bond in (**4**) is comparable to those of P–O and P–S bonds in the phosphine oxide and sulfide. For the salts (**5**), (**6**), and (**7**), the substituent effect on the binding energies is not found; a distinct difference in chemical shift of the salt (**8**) has not been explained yet.

Siegbahn *et al.* demonstrated[9] that the chemical shift in the total screening constant can be written as

$$\Delta\sigma_A = \frac{-\Delta E_A}{3mc^2} + \frac{\pi e}{3mc\mu_0 g_A}\Delta\sum_{\alpha} C_{A,\alpha\alpha} I_{\alpha\alpha} \qquad (2)$$

where ΔE_A: XPS shift, $C_{A,\alpha\alpha}$: spin-rotation constant for nucleus A along the αth molecular inertial axis, $I_{\alpha\alpha}$: corresponding principal moment of inertia of the molecule, μ_0: nuclear magneton, g_A: g-factor for nucleus A. From this relation, they concluded that the first term in equation (2) is the part of the shift in the diamagnetic constant and is proportional to the XPS shift. This term is only of the size of a few ppm. The second term is the part of the shift in the paramagnetic constant and is one or two orders of magnitude larger than the first term. Thus, no linear correlation between XPS and NMR shift can be expected even for the same kind of compounds.

In the present work, the shifts in the compounds having different kind of bondings vary largely as seen among Ph_3P=O, Ph_3P=S, and phosphorus ylides, and the correlation between XPS and NMR shift is not observed. However, in the series of phosphorus ylides and their salts, a correlation between XPS and ^{31}P NMR is found. The results seem to indicate that both the phosphorus ylides and salts used for the present investigation have almost the same contribution of paramagnetic term, and the diamagnetic term contributes mainly to the change in the shift of these spectra. For quaternary phosphonium compounds, Swartz *et al.* also reported that a linear relationship was established between the P-2p binding energies and the ^{31}P NMR chemical shifts.[1c)]

It has been elucidated that the overall rate of the Wittig reaction depends on the rate of electrophilic reaction of ketones or aldehydes onto the α-carbon of ylide compounds.[10)] This step would be affected by the electronic character as well as the steric one. With respect to a series of ylides used here, a linear relationship between the basicity of the ylides and the reaction rate with benzaldehyde has been established.[6)] This indicates that the rate determining step mentioned above is affected only by the electronic effect. Thus, more positive charge on phosphorus atom would favor the reaction. Since the binding energy of XPS is proportional to the positive charge, a relationship between the binding energy and the reactivity is expected, and this is actually the case as shown in Table 4.

Conclusion

1) In the present investigation it was concluded that the electronic structure of carbomethoxymethylenetriphenylphosphorane (**4**) has a major contribution of resonance structure **Ic**. Measurements of ^{31}P NMR and XPS support localization of positive charge on phosphorus atom, and combustion heat data also convince us of the large contribution of resonance structure **Ic**.

2) With respect to ylides (**1**), (**2**), and (**3**), the large lower shift of C=O stretching bands show that the carbonyl groups in the ylides are polar $(>\overset{\delta+}{\mathrm{C}}-\overset{\delta-}{\mathrm{O}})$, and it was clarified by ^{13}C NMR that the hybrid orbital of the methine carbon is close to sp^2 hybrid. These results indicate that these ylides have a large contribution of resonance structure **Ib**, **IIa**, and **IIb**. However, ^{31}P NMR and XPS measurements show that these ylides have less positive charge on phosphorus atom than ylide (**4**). Thus, the resonance structure **IIb** is considered to have a primary contribution.

3) In the ylides (**1**), (**2**), and (**3**), the substituent effect is found on both the methine proton and the phosphorus atom, whereas in the salts (**5**), (**6**), and (**7**), the substituent effect is observed only on methylene protons. This observation indicates that P–C bonds in the ylides are semipolar with dπ-pπ interaction. P–C–H Coupling constant in Table 2 also support the above discussion. Thus, these results experimentally clarify dπ-pπ interaction in phosphorus ylides.

4) The result of the analysis by XPS is consistent with those by IR and NMR, and gives additional informations on polar bondings. A correlation between P-2p binding energies of XPS and ^{31}P NMR shifts was observed in phosphorus ylides and phosphonium salts, and a relation was also established between the binding energies and combustion heat of ylides. These suggest that XPS may be a useful tool for the elucidation of the electronic structure of some organic compounds.

Experimental

The compounds used in this study were prepared, purified and characterized according published methods.[4,6,11)] All the ylides were prepared by dehydrohalogenation of corresponding phosphonium salts. The results of elemental analyses are as follows.

	Calcd			Found		
	C	H	N	C	H	N
(**1**)	73.30	4.95	3.28	73.11	4.75	3.35
(**2**)	82.08	5.58	—	82.09	5.61	—
(**3**)	79.10	5.64	—	79.03	5.68	—
(**4**)	75.41	5.74	—	75.65	5.74	—

IR Spectroscopy. All the infrared spectra were obtained as mulls with Nujol on a JASCO IRA-2 infrared spectrometer. All the spectra have sharp absorption bands of C=O stretching except that of ylide (**1**) which has a broad peak due to the overlap with the absorption peak of the nitro group.

NMR Spectroscopy. ^{1}H NMR spectra were recorded on a Hitachi R-22 spectrometer (90 MHz) using deuteriochloroform as a solvent and TMS as an internal standard.

The measurement of ^{31}P NMR were made using a Hitachi R-20A NMR spectrometer at 24.3 MHz using 85% phosphoric acid as an external reference. The spectra were taken in chloroform; the concentration 1.0—0.5 M was needed for detection of the signals.

^{13}C NMR spectra were obtained using a Hitachi R-26 NMR spectrometer in Fourier transform mode, and was operated at 10 MHz. ^{13}C–H Couplings were eliminated using broad band ^{1}H-noise-modulated decoupling. The ylides and salts were run in saturated deuteriochloroform solutions in 10 mm sample tubes, and TMS was used as an internal standard.

X-Ray Photoelectron Spectroscopy. The measurements were performed with a JASCO ESCA-1 or a McPherson ESCA-36 electron spectrometer with Mg$K\alpha$ radiation. The spectra were obtained on powdered samples mounted on an aluminum plate. In order to compensate for the charging of the insulating samples during the phtoelectron ejection process, all the spectra were referenced to the photoelectron line of C ls; $E_b=284$ eV. An attempt was also made to reference the spectra to the Au 4f$_{7/2}$; $E_b=83$ eV by vacuum deposition of gold onto the samples, and the results from the two methods were consistent with each other. The binding energies were read at the midway point of the full peak at half height.

Combustion Heat. Combustion heat data were obtained using a Shimadzu automatic bomb calorimeter CA-3. Powdered samples were wrapped in Gampi paper, and liquid samples were placed in gelatin capsule. The given data were averaged values of ten measurements.

References

1) (a) M. Plavin, D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *J. Phys. Chem.*, **74**, 1116 (1970). (b) W. E. Morgan, W. T. Stec, R. G. Albridge, and J. R. V. Wazer, *Inorg. Chem.*, **10**, 926 (1971). (c) W. E. Swartz and D. M. Hercules, *Anal. Chem.*, **43**, 1066 (1971). (d) W. E. Swartz, J. K. Ruff, and D. M. Hercules, *J. Amer. Chem. Soc.*, **94**, 5227 (1972). (e) W. T. Stec, W. E. Moddeman, R. G. Albridge, and T. R. V. Wazer, *J. Phys. Chem.*, **75**, 3975 (1971). (f) C. E. Mixan and J. B. Lambert, *J. Org. Chem.*, **38**, 1350 (1973).

2) (a) A. J. Speziale and K. W. Ratts, *J. Amer. Chem. Soc.*, **85**, 2790 (1963). (b) A. J. Speziale and K. W. Ratts, *J. Org. Chem.*, **28**, 465 (1963).

3) (a) K. W. Ratts and A. N. Yao, *J. Org. Chem.*, **31**, 1185 (1967). (b) J. E. Lancaster, *Spectrochim. Acta*, **23A** 1449 (1967). (c) F. J. Randall and A. W. Johnson, *Tetrahedron Lett.*, 2841 (1968). (d) H. J. Bestmann and J. P. Snyder, *J. Amer. Chem. Soc.*, **89**, 3936 (1967). (e) D. M. Crouse, A. T. Wehman, and E. E. Schweizer, *Chem. Commun.*, **1968**, 866. (f) A. W.

Johnson, "Ylide Chemistry," Academic Press, Inc., New York (1966), p. 76. (g) M. Halman and I. Blatzner, *J. Phys. Chem.*, **70**, 580 (1966). (h) M. M. Crutchfield, J. R. V. Wazer *et. al.*, "Topics in Phosphorus Chemistry," vol. 5, John Wiley & Sons, New York (1967), p. 227. (i) H. Schmidbaur and W. Fronic, *Chem. Ber.*, **101**, 604 (1968). (j) S. O. Grim *et. al.*, *J. Chem. Eng. Data*, **15**, 497 (1970). (k) G. A. Gray, *J. Amer. Chem. Soc.*, **95**, 5092 (1973). (l) G. A. Gray, *ibid.*, **95**, 7736 (1973).

4) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957).

5) (a) A. J. Speziale and K. W. Ratts, *J. Amer. Chem. Soc.*, **87**, 5603 (1965). (b) J. C. J. Bart, *J. Chem. Soc. B*, **1969**, 350. (c) J. C. J. Bart, *Angew. Chem.*, **80**, 697 (1968).

6) S. Flizar, R. F. Hudson, and G. Salvadori, *Helv. Chim. Acta*, **172**, 1580 (1963).

7) (a) H. H. Jaffe, *J. Inorg. Nucl. Chem.*, **4**, 372 (1957). (b) C. L. Chernick and H. A. Skinner, *J. Chem. Soc.*, **1956**, 1401. (c) H. O. Prichard and H. A. Skinner, *Chem. Rev.*, **55**, 745 (1955). (d) C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press Ltd., London (1962). (e) R. T. Sanderson, "Chemical Bonds and Bond Energy," Academic Press, New York and London (1971).

8) W. L. Jolly, "Electron Spectroscopy," ed. by D.A. Shirley North-Holland Publ. Co., Amsterdam (1972). (b) W. L. Jolly and D. N. Hendrickson, *J. Amer. Chem. Soc.*, **92**, 1863 (1970). (c) W. L. Jolly, *ibid.*, **92**, 3260 (1970).

9) U. Gelius, G. Johansson, H. Siegbahn C. J. Allan, D. A. Allison, J. Allison, and K. Siegbahn, *J. Electron Spectrosc. Relat. Phenomena*, **1**, 285 (1972/1973).

10) A. J. Speziale and D. E. Bissing, *J. Amer. Chem. Soc.*, **85**, 3875 (1963).

11) (a) O. Isler, H. Guttman, M. Motaron, R. Ruegg, G. Ryser, and P. Zeller, *Helv. Chim. Acta*, **40**, 1242 (1957). (b) C. Screttas and A.F. Isbell, *J. Org. Chem.*, **27**, 2573 (1962).