with one short Co–Co distance of 2.474 (2) Å and two long Co–Co distances of 2.649 (1) Å resulting in an averaged value of 2.591 Å. The shorter Co–Co distance compares favorably with those in $Co_3(h^5\text{-}C_5H_5)_3(CO)(S)$, while the two longer distances are similar to those in $Co_3(h^5\text{-}C_5H_5)_3S_2$. All of these variations in metal–metal distances are in complete accord with our bonding model[5] which assumes *no* antibonding electrons for $Co_3(h^5\text{-}C_5H_5)_3(CO)(S)$, *one* such electron for the $[Co_3(h^5\text{-}C_5H_5)_3S_2]^+$ monocation, and *two* such electrons for $Co_3(h^5\text{-}C_5H_5)_3S_2$. The 0.1-Å longer Co–Co distances in $Co_3(h^5\text{-}C_5H_5)_3(CO)(S)$ compared to those in the electronically equivalent $Co_3(h^5\text{-}C_5H_5)_3(CO)(O)$ may be readily attributed to the influence of the larger triply bridging sulfur ligand.

The nontrivial singlet–triplet equilibrium indicated from the temperature-dependent magnetic measurements of $Co_3(h^5\text{-}C_5H_5)_3S_2$ together with the structural information that $Co_3(h^5\text{-}C_5H_5)_3S_2$ shows no detectable distortion of the Co_3S_2 fragment from D_{3h} geometry[19] at room temperature in contradistinction to the large C_{2v} deformation of this fragment in the $[Co_3(h^5\text{-}C_5H_5)_3S_2]^+$ monocation illuminates a key point with regard to the electronic structures of these complexes. For $Co_3(h^5\text{-}C_5H_5)_3S_2$ the nmr paramagnetic shift data, which strongly indicate that the singlet–triplet energy separation in the non-Curie region is temperature dependent, may be rationalized on the basis that at $T > 260°$ the triplet state arising from double occupancy of a doublet degenerate level is more likely the ground state than one arising from occupancy of two close-lying energy levels (with one level nondegenerate and the other degenerate).[20] On the other hand, at $T < 260$°K the observed nmr solution data can be explained in terms of two close-lying levels of which the lowest one is nondegenerate. This situation may arise if the antibonding $1a'_2$ level[5] is assumed to be lower in energy and therefore fully occupied at $T < 173$°K. With an increase in temperature the $1a'_2$ level is then presumed to be destabilized relative to the antibonding 3e′ one[5] such that a crossover occurs to give the 3e′ level as the occupied lower one at room temperature.[21] The solid-state magnetic data, whose interpretation is complicated by the observed phase transition,[7,9] are consistent with these bonding hypotheses. We feel (in harmony with Sorai, *et al.*[9]) that the change in electronic structure may be primarily a consequence of the metal–cyclopentadienyl interactions due to a vibronic effect caused by more restricted ligand motion at lower temperatures. The C_{2v} geometry of the $[Co_3(h^5\text{-}C_5H_5)_3S_2]^+$ monocation may be explained by a Jahn–Teller splitting of a doublet ^2E ground state (which presumably would occur for a symmetrical triangular tricobalt cluster system. The unpaired electron would cause the 3e′ (under D_{3h}) to break down into $a_1 + b_2$ (under C_{2v}), but it is not possible to predict which nondegenerate energy level is lower and hence the directional nature of the geometrical deformation. The observed one short and two long Co–Co distances are compatible with the unpaired electron occupying the a_1 orbital. This work will be reported in full upon completion of closely related studies which have included the preparation and structural characterization of $Rh_3(h^5\text{-}C_5H_5)_3(CO)(S)$, a complex which is isosteric with its electronically equivalent cobalt analog.

Acknowledgment. These investigations were made possible by the financial support of the National Science Foundation (No. GP-19175X). The use of the UNIVAC 1108 computer at the Academic Computing Center, University of Wisconsin (Madison), was made available through partial support of NSF and the Wisconsin Alumni Research Foundation administered through the University Research Committee. We also express special thanks to Mr. Boon Keng Teo at the University of Wisconsin, to Dr. C. H. Wei at Oak Ridge National Laboratory (Biology Division), and to Dr. H. Vahrenkamp at the Institut für Anorganische Chemie der Universität München for helpful consultations.

P. Douglas Frisch, Lawrence F. Dahl*
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706
Received March 1, 1972

[19] For all $P6_3/m$ twinned structures,[1,4] a significant distortion from D_{3h} (or C_{3v}) symmetry may be undetected due to the twinning as well as the added possibility of a threefold crystal disorder of an unsymmetrical metal triangle. For this reason we stress that the averaged geometry is D_{3h} (or C_{3v}). However, the thermal ellipsoids of the metal atoms in $Co_3(h^5\text{-}C_5H_5)_3S_2$ did not give an indication of either any distortion or crystalline disorder.

[20] A Jahn–Teller distortion of the molecule would be anticipated for such an electronic configuration (*e.g.*, the antibonding $1a'_2$ energy level being slightly lower than the antibonding 3e′ one).

[21] Another possibility is that the 3e′ level is lower, but the degeneracy is broken due to some unknown and structurally nondetectable change in the $Co_3(h^5\text{-}C_5H_5)_3S_2$ molecule from threefold symmetry (presumably involving the cyclopentadienyl rings and/or the Co_3S_2 cluster fragment).

Carbon-13 Spectra of Allenes

Sir:

As a result of technical advances carbon-13 nmr has finally begun to achieve its obvious place as a convenient and powerful tool for the elucidation of organic structures[1] and the probing of ground-state electronic distributions of molecules.[2] The unusual bonding situation in the allene functionality has prompted us to undertake a systematic study of this class of compounds.[3,4] Determination of the spectra[5] of over 50 allenes has provided data which show definite chemical-shift trends as a function of substitution. Moreover, these trends are correlated with theoretical calculations of electron density. Representative carbon-13 nmr chemical shifts for allenes with simple alkyl substituents are given in Table I.

In general, for allenes bonded to nonfunctionalized carbon, the sp-hybridized carbons are found in the sparsely populated region at lower field than CS_2 (−20 to −5 ppm) whereas the sp^2 carbons appear at slightly

[1] (a) E. F. Mooney and P. H. Winson, *Annu. Rev. Nucl. Magn. Resonance Spectrosc.*, **2**, 153 (1969); (b) J. B. Stothers, *Quart. Rev., Chem. Soc.*, **19**, 144 (1965).

[2] Examination of electronic environments in aromatic compounds by carbon-13 nmr has been quite successful. See, for instance, R. J. Pugmire, M. J. Robins, D. M. Grant, and R. K. Robins, *J. Amer. Chem. Soc.*, **93**, 1887 (1971), and references therein.

[3] (a) R. A. Friedel and L. Retcofsky, *ibid.*, **85**, 1300 (1963); (b) R. Steur, J. P. C. M. van Dougen, M. J. A. de Bie, and W. Drenth, *Tetrahedron Lett.*, 3307 (1971).

[4] W. W. Conover, J. K. Crandall, and S. A. Sojka, paper presented at the International Symposium on Acetylenes, Allenes, and Cumulenes, Nottingham, England, July 5–8, 1971.

[5] Spectra were obtained by using equipment previously described: A. Allerhand, D. Doddrell, V. Glushko, D. W. Cochran, E. Wenkert, P. T. Lawson, and F. R. N. Gurd, *J. Amer. Chem. Soc.*, **93**, 544 (1971).

Table I. Chemical-Shift Data for Allenes

$R_1R_2C_3{=}C_2{=}C_1R_3R_4$				δ_{CS_2}			
R_1	R_2	R_3	R_4	C_1	C_2	C_3	Other
H	H	H	H	120.2	−18.9		
CH_3	H	H	H	120.3	−15.7	109.5	R_1 (180.5)
CH_3	H	CH_3	H	108.8	−12.8		$R_{1,3}$ (179.1)
CH_3	CH_3	H	H	122.0	−13.2	100.7	$R_{1,2}$ (174.6)
CH_3	CH_3	CH_3	H	110.2	−9.8	99.6	$R_{1,2}$ (173.0) R_3 (178.7)
CH_3	CH_3	CH_3	CH_3	101.6	−6.3		$R_{1,2,3,4}$ (173.7)
C_2H_5	H	H	H	119.0	−15.1	102.1	C_4 (172.1), C_5 (180.5)
n-C_3H_7	H	H	H	119.1	−15.8	103.8	C_4 (163.2), C_5 (174.4), C_6 (180.0)
n-C_4H_9	H	H	H	119.9	−15.3	104.1	C_4 (162.6), C_5 (166.1), C_6 (171.9), C_7 (180.5)
n-C_5H_{11}	H	H	H	118.7	−15.7	103.3	C_4 (161.8), C_5 (164.2), C_6 (164.9), C_7 (170.5), C_8 (179.1)
i-C_3H_7	H	H	H	117.5	−14.1	95.9	C_4 (165.8), C_5 (170.8)
t-C_4H_9	H	H	H	116.7	−13.3	91.3	C_4 (162.0), C_5 (162.9)

higher fields (90–120 ppm) than normal olefinic and aromatic carbons. The former signal is particularly useful in the qualitative determination of the allene function which is difficult to detect by other spectroscopic methods with tri- and tetrasubstituted examples. In fact, the exact position of the sp signal can be used to indicate the number or alkyl substituents on the allene: monosubstituted compounds appear in the range −16 to −14 ppm, disubstituted (either 1,3 or 1,1) at −14 to −11, trisubstituted at −10 to −6, and tetrasubstituted at −7 to −5. These values appear to hold reasonably well for compounds possessing other functional groups as long as they are at least one carbon atom removed form the allene moiety. However, the accumulation of bulky substituents, such as *tert*-butyl groups, adjacent to the allene results in slightly more positive chemical shifts for the sp carbon than those indicated above. This effect finds analogy with the γ shift in saturated hydrocarbons.[6]

The chemical-shift trends for allene and its five possible methyl-substituted analogs are illustrated in Figure 1. There is a strikingly regular upfield shift of the sp carbon with increasing number of substituents, 3 ppm for each added methyl group. To a first approximation, the sp^2 carbons fall into three groups depending on the number of directly attached methyl groups.[7] There is an 11 ± 1 ppm downfield shift in going from $=CH_2$ to $=CHCH_3$ and a 9 ± 1 ppm downfield shift between $=CHCH_3$ and $=C(CH_3)_2$. The effect of changing the substitution pattern at the remote group is more subtle but appears to be approximately 2 ppm upfield for $=CHCH_3$ to $=C(CH_3)_2$ and 1 ppm downfield for $=CH_2$ to $=CHCH_3$. The actual increments are given in Figure 1.

There is relatively little effect of increasing the length of the side chain of monosubstituted allenes from methyl to n-pentyl on either the sp carbon or the remote sp^2 center. The substituted sp^2 carbon behaves very much like an internal carbon of the corresponding alkene series.[8] For this limited set of data the α effect was −10.7 ppm, the β effect was −7.4 ppm, and the γ effect was +1.6 ppm. Increasing methyl substitution at a carbon bonded directly to the allene group results in a small but consistent upfield trend on the chemical shift of the sp carbon. The substituted sp^2 center shows an attenuated β effect similar to the corresponding alkane and alkene series.[6,8] There is a parallel but diminished effect at the remote sp^2 center. This latter trend may be a result of steric interactions between the substitutent methyls and the remote double bond.[9]

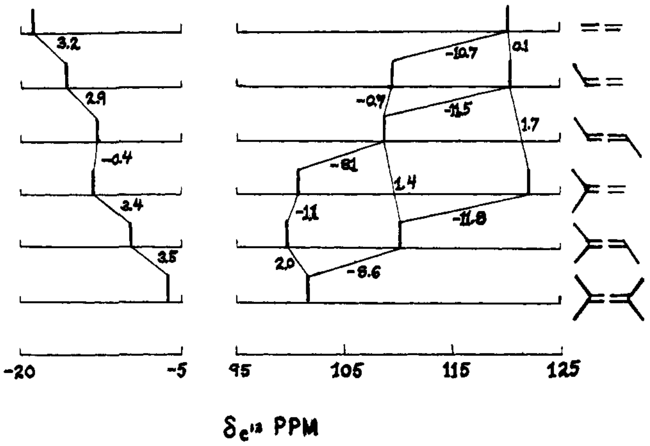


Figure 1. Correlation diagram for methylallenes.

According to current chemical-shift theory,[10] the paramagnetic term of the carbon-13 chemical-shift expression predominates over the diamagnetic and anisotropic terms. The paramagnetic term is given by a complex expression depending in part on the electron density associated with the carbon nucleus. To ascertain whether a simple relationship exists between the observed chemical shifts and electron densities, theoretical calculations were performed on the allenes using the CNDO/2 method of Pople.[11] These calculations are known to give quite reliable atomic electron densities.[11,12] An excellent correlation (ρ = 0.983) was obtained when the total electron density of the sp carbons was plotted against the corresponding chemical shifts.

Attempts to correlate electron densities with sp^2 carbon chemical shifts gave poorer results. One possibility is that the diamagnetic term becomes important

---

(6) D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, **86**, 2984 (1964).

(7) In fact, considering all the simple substituted allenes studied, $=CH_2$ resonates at 120 ± 2 ppm, $=CHCH_3$ at 109 ± 2 ppm (methyls resonate at 179 ± 1 ppm), and $=C(CH_3)_2$ at 98 ± 2 ppm (methyls at 173 ± 1 ppm).

(8) D. E. Dorman, M. Jautelat, and J. D. Roberts, *J. Org. Chem.*, **36**, 2757 (1971).

(9) J. B. Grutzner, M. Jautelat, J. B. Dence, R. A. Smith, and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 7107 (1970).

(10) (a) M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963); (b) R. Ditchfield, D. P. Miller, and J. A. Pople, *Chem. Phys. Lett.*, **6**, 573 (1970).

(11) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., p 214.

(12) J. W. McIver, Jr., P. Coppens, and D. Nowak, *Chem. Phys. Lett.*, **11**, 82 (1971).

at the sp^2 carbon since its value changes with substitution. A plot of chemical shifts, δ', corrected for the diamagnetic contribution,[13] gives a good correlation ($\rho = 0.990$) in keeping with this idea.

It appears that chemical-shift data can be efficiently utilized as a probe for studying ground-state electron densities. We are currently examining allene with heteroatomic, polar, and other unusual substituents to elaborate on this idea.

Acknowledgments. Acknowledgment is made to the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We thank Dr. R. Saxena-Bindra and Mr. W. W. Conover for experimental assistance.

[13] J. Mason, *J. Chem. Soc. A*, 1038 (1971).

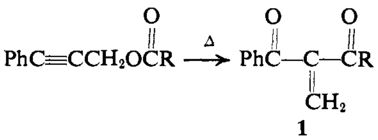
[14] (a) Alfred P. Sloan Fellow, 1968–1970; John Simon Guggenheim Fellow, 1970–1971; (b) Mead-Johnson Predoctoral Fellow, 1970–1971.

J. K. Crandall,*[14a] S. A. Sojka[14b]
Contribution No. 2076
Department of Chemistry, Indiana University
Bloomington, Indiana 47401
Received January 13, 1972

Formation of 2-Alkylidene-1,3-diones and α,β-Unsaturated Ketones from the Pyrolysis of Propargyl Esters[1]

Sir:

We have found that the low-pressure (10^{-3}–10^{-5} Torr) gas-phase pyrolysis[2] of 3-phenylpropargyl acetate and benzoate[4,5] gives rise to the corresponding alkyl or aryl phenyl 2-methylene-1,3-dione (**1**). The yields



$$\mathrm{PhC{\equiv}CCH_2O\overset{\overset{\displaystyle O}{\|}}{C}R \xrightarrow{\Delta} Ph\overset{\overset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle CH_2}{\|}}{C}{-}\overset{\overset{\displaystyle O}{\|}}{C}R}$$

1

of these products from pyrolyses at various temperatures are reported in Table I.

Table I. Yields of 2-Methylene-1,3-diones from the Pyrolysis of 3-Phenylpropargyl Acetate and Benzoate

Propargyl ester	Pyrolysis temp, °C	PhCO-C(=CH$_2$)COR yield, %[a]	Recovered starting material, %[a]
R = CH$_3$	680	72	
	630	62	21
	580	38	45
R = Ph	660	88	Trace
	660	85	
	620	67	4

[a] Yields determined by nmr spectroscopy using an internal standard, ethyl benzoate.

From these data it is seen that reasonably good yields of these methylenediones are obtained with pyrolysis temperatures at *ca.* 650°. Because of the lability of the methylenediones, they were washed out of the trap with solvent and spectra were taken on the crude material. The nmr spectra indicated that less than 5% impurities were present.

1-Acetyl-1-benzoylethene showed the following characteristics: nmr ($CDCl_3$) δ 7.95–7.15 (m, 5), 6.40 (s, 1), 5.99 (s, 1), and 2.36 (s, 3); ir (neat) 1735 (medium), 1660 (strong, broad), and 1594 (medium) cm^{-1}.

1,1-Dibenzoylethene showed the following characteristics: nmr (CCl_4) δ 7.85–7.14 (m, 10) and 6.15 (s, 3); ir (CCl_4) 1731 (medium), 1683 (shoulder), 1675 (strong), 1667 (strong), and 1583 (medium) cm^{-1}.

Further confirmation of the structures of the methylenediones was obtained by converting them to the corresponding alkanes by catalytic hydrogenation over palladium on carbon in ethyl acetate.

1-Acetyl-1-benzoylethane showed the following characteristics: nmr (CCl_4) keto form δ 8.10–7.20 (m, 5), 4.52 (q, 1, J = 7 Hz), 2.13 (s, 3, CH_3CO), and 1.39 (d, 3, CH_3CH, J = 7 Hz), which is consistent with published data;[6] enol form δ 6.3 (s, 1,–OH), 7.60–7.25 (m, 5), 2.20 (s, 3), and 1.90 (s, 3).

1,1-Dibenzoylethane showed the following characteristics: nmr (CCl_4) δ 8.04–7.04 (m, 10), 5.16 (q, 1, J = 7 Hz), and 1.43 (d, 3, J = 7 Hz).[5]

The preparation of 1,1-dibenzoylethene has been previously claimed,[7] but we repeated this work and the nmr spectrum of the product we obtained, which has a similar melting point (175–177°) to that reported for their product (177–179°), indicates that it is 1,1,3,3-tetrabenzoylpropane: nmr ($CDCl_3$) δ 8.25–7.20 (m, 20), 5.70 (t, 2, CH, J = 7 Hz), and 2.75 (t, 2, CH_2, J = 7 Hz).

Acetylacetone and formaldehyde have been shown[8] to give mainly 2:1 and no 1:1 condensation products, an observation consistent with our results with the dibenzoylmethane–formaldehyde condensation. These workers[8] were able to isolate the normal 1:1 condensation products of acetylacetone and higher aldehydes.

The report[9] that a 1:1 condensation product between acetylacetone and formaldehyde was obtained must be incorrect. The boiling point reported for this material (139–140° (1.7 mm)) is much higher than that expected for the 1:1 condensation product.

In order to gain support for the methylenediones as intermediates in the formation of these 2:1 condensation products, and to confirm the identity of our product, we allowed our 1,1-dibenzoylethene to react with dibenzoylmethane and diethylamine. The product of this reaction had the same melting point and nmr spectrum as the 1,1,3,3-tetrabenzoylpropane obtained from the Knoevanagel reaction.

We propose that the progargyl esters rearrange to allenyl esters which then undergo 1,3-acyl shifts to give the methylenediones. Metal-catalyzed rearrangements

---

[1] (a) Based on work by P. W. M. in partial fulfillment of the requirements for the Ph.D. degree at Iowa State University; (b) we thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work by Grant No. 3219-A.

[2] The pyrolysis apparatus has been previously described.[3]

[3] W. S. Trahanovsky, C. C. Ong, J. G. Pataky, F. L. Weitl, P. W. Mullen, J. C. Clardy, and R. S. Hansen, *J. Org. Chem.*, **36**, 3575 (1971).

[4] These esters were prepared by the addition of the acid chloride in ether to an ether solution of the alcohol and triethylamine.

[5] These compounds gave acceptable elemental analyses by Chemalytics Inc., Tempe, Ariz., and expected nmr spectra.

[6] F. Ramirez, S. B. Bhatia, A. V. Patwardhan, and C. P. Smith, *J. Org. Chem.*, **32**, 3547 (1967).

[7] G. W. Cannon, A. A. Santilli, and P. Shenian, *J. Amer. Chem. Soc.*, **81**, 1660 (1959).

[8] (a) B. D. Wilson, *J. Org. Chem.*, **28**, 314 (1963); (b) J. K. O'-Loane, C. M. Combs, and R. L. Griffith, *ibid.*, **29**, 1730 (1964).

[9] J. Dickstein and R. M. Hoegerle, U. S. Patent 3,042,710 (1962); *Chem. Abstr.*, **57**, 14946c (1962).