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.

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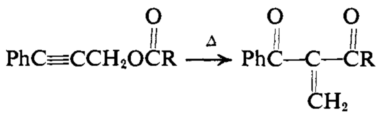
Formation of 2-Alkylidene-1,3-diones and α,β-Unsaturated Ketones from the Pyrolysis of Propargyl Esters[1]

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



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

1

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$_3$CO), 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

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[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).

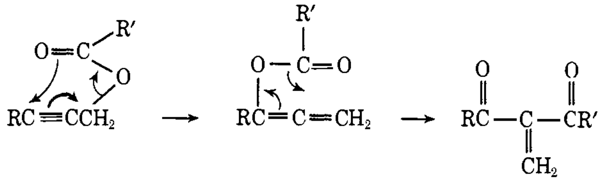
[9] J. Dickstein and R. M. Hoegerle, U. S. Patent 3,042,710 (1962); *Chem. Abstr.*, **57**, 14946c (1962).

Table II. Yields of α,β-Unsaturated Ketones from the Pyrolysis of Propargyl Esters

Propargyl ester	Pyrolysis temp, °C	Product	Yield, %^{a}	Recovered starting material, %^{a}
$PhC{\equiv}CCH_2OCOH^b$	670	$PhCOCH{=}CH_2$	94	Trace
	640		82	16
	560		34	55
$HC{\equiv}CCH_2OCOPh^c$	660	$PhCOCH{=}CH_2$	80	3
	640		82	8
$HC{\equiv}CCH(Ph)OCOCH_3{}^d$	645	$CH_3COCH{=}CHPh$	79	7
	640		87	7
	670		48	4
$HC{\equiv}CCH_2OCOPh^e$	630	$PhCOCH{=}CH_2$	54	11
	630		56	10
$HC{\equiv}CCH_2OCOCH_3{}^c$	630	$CH_3COCH{=}CH_2$	60	Trace

[a] Yields determined by nmr spectroscopy using an internal standard, ethyl benzoate or propiophenone. [b] This ester was prepared from the alcohol and 97% formic acid. See ref 5. [c] See ref 4 and A. M. Sladkov, V. V. Korshak, and A. G. Makhsumov, *Vysokomol. Soedin.*, **6**, 1642 (1964); *Chem. Abstr.*, **61**, 14163 (1964). [d] See ref 4 and M. Barrelle, D. Plovin, and R. Glenat, *Bull. Soc. Chim. Fr.*, 449 (1967). [e] See ref 4 and 5.

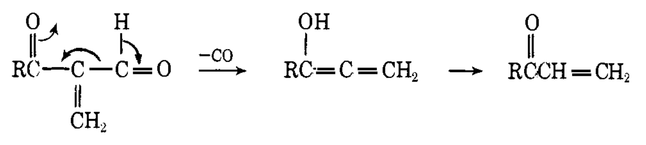
of propargyl esters to allenyl esters have been reported,[10]



and vinyl esters are known to undergo 1,3-acyl shifts in the gas phase at 500–600°.[11]

Instead of alkylidenediones, α,β-unsaturated ketones are obtained from the pyrolysis of propargyl esters which would give rise to alkylidenediones that have a hydrogen atom attached to one carbonyl group. In Table II are listed the yields of the α,β-unsaturated ketones obtained from various propargyl esters. The products were identified by their nmr spectra which, with the exception of the new compound cyclohexyl vinyl ketone,[12] were compared with spectra of commercial samples or published data.

An attractive explanation for these results is that the intermediate enedione undergoes a facile decarbonylation reaction to give an enol which rearranges to the ketone.



Since propargyl alcohol is readily available and inexpensive, the pyrolysis of propargyl esters offers a synthetically useful means of preparing vinyl ketones in reasonable yields from the corresponding carboxylic acid.

$$RCOOH + HOCH_2C{\equiv}CH \xrightarrow[\text{2. pyrolysis}]{\text{1. esterification}} RCOCH{=}CH_2 + CO$$

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[10] (a) A. I. Zakharova, *Zh. Obshch. Khim.*, **15**, 429 (1949); (b) P. D. Landor and S. R. Landor, *J. Chem. Soc.*, 1015 (1956); (c) G. Saucy, R. Marbert, H. Lindlarand, and O. Isler, *Helv. Chim. Acta*, **42**, 1945 (1959); (d) V. T. Ramakrishnan, K. V. Narayanan, and S. Swaminathan, *Chem. Ind. (London)*, 2082 (1967); (e) W. R. Benn, *J. Org. Chem.*, **33**, 3113 (1968).

[11] (a) A. B. Boese, Jr., and F. G. Young, Jr., U. S. Patent 2,395,800 (1946); *Chem. Abstr.*, **40**, 3130 (1946); (b) F. G. Young, F. C. Frostick, Jr., J. J. Sanderson, and C. R. Hauser, *J. Amer. Chem. Soc.*, **72**, 3635 (1950).

[12] This compound gave an acceptable elemental analysis by Spang Microanalytical Laboratory, Ann Arbor, Mich.

[13] Alfred P. Sloan Research Fellow, 1970–1972.

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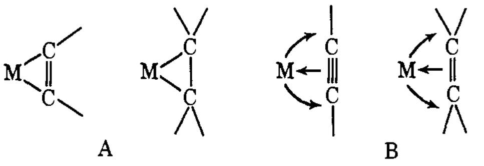
A Comparison of the Bonding in Zero- and Divalent Platinum–Olefin and –Acetylene Complexes from Carbon-13 Nuclear Magnetic Resonance Parameters[1]

Sir:

Metal–olefin and –acetylene bonding is dominated by the relative energies of the π and π^* orbitals of the unsaturated hydrocarbon and the metal dsp hybrid orbitals used in the bonding.[2] This model leads to a continuum of bonding and incorporates the original Chatt–Dewar–Duncanson[3] bonding descriptions shown below.



Much debate has been devoted (a) to an appraisal of the relative magnitudes of the σ and π interactions, (b) to the choice of metal orbitals employed in the bonding, and hence (c) to the formal oxidation state and coordination number of the metal.[4–8] We wish to present the

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[1] Part XXII. For part XXI, see A. H. Lawrence, D. R. Arnold, J. B. Stothers, and P. Lapouyade, *Tetrahedron Lett.*, in press.

[2] E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Can. J. Chem.*, **46**, 3879 (1968).

[3] M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, 79 (1951); J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

[4] M. A. Bennett, Second Coordination Conference of the Coordination and Metal Organic Chemistry Division of the Royal Australian Chemical Institute, Monash, Australia, May 1968.

[5] F. R. Hartley, *Chem. Rev.*, **69**, 799 (1969), and references cited therein.

[6] (a) J. H. Nelson, K. S. Wheelock, L. C. Cusachs, and H. B. Jonassen, *J. Amer. Chem. Soc.*, **91**, 7005 (1969); (b) *ibid.*, **92**, 5100 (1970).

[7] J. H. Nelson and H. B. Jonassen, *Coord. Chem. Rev.*, **6**, 27 (1971).

[8] V. Belluco, B. Crociani, R. Pietropaolo, and P. Uguaglia, *Inorg. Chim. Acta*, 19 (1969).