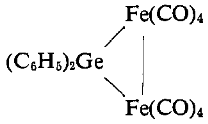
infrared-active carbonyl bands in cyclohexane. The compound may be formulated with some confidence as the C_{2v} structure



It is evident that the ability of R_2M (M = Si, Ge, and Sn) groups to bridge transition metals is more general than suggested by examples known heretofore, and that reactions of R_2MH_2 compounds with metal carbonyls offer a promising synthetic route.

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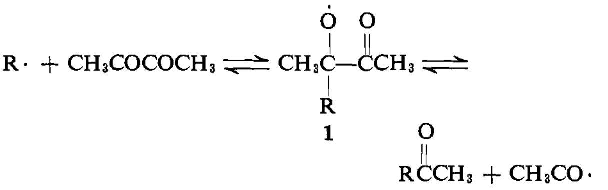
A Free-Radical Acylation

Sir:

We wish to report a free-radical reaction sequence which leads ultimately to acetylation products. When benzoyl peroxide (BPO) is decomposed thermally in deoxygenated dioxane or cyclohexane (RH) to which biacetyl has been added, reasonable yields of acetyl products are formed, as recorded in Table I. The most likely sequence of reactions to rationalize these products is given by eq 1–3. We believe reaction sequence 3

$$\mathrm{BPO} \longrightarrow \mathrm{In}\cdot \qquad (1)$$

$$\mathrm{In}\cdot + \mathrm{RH} \rightarrow \mathrm{InH} + \mathrm{R}\cdot \qquad (2)$$



$$\mathrm{R}\cdot + CH_3COCOCH_3 \rightleftharpoons \underset{\mathbf{1}}{CH_3\overset{\dot{O}}{\underset{R}{C}}-\overset{O}{\overset{\|}{C}}CH_3} \rightleftharpoons \mathrm{R}\overset{O}{\overset{\|}{C}}CH_3 + CH_3CO\cdot \qquad (3)$$

to be one of fundamental importance which has not been well recognized and, to our knowledge, not previously reported in solution.[1] Beyond the novelty of the processes suggested, these reactions are of interest in relation to the question of the direction of radical attack on the carbonyl group and, viewed as a free-radical acetylation sequence, may also have synthetic applications.

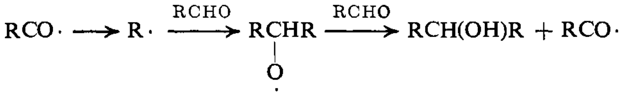
Yields in Table I are based on moles of radicals produced in theory from complete decomposition of the peroxide. If corrected for cage effects these yields would be higher; however, the fact that they are not greater than 100% suggests that the initiation process is very inefficient, or, as seems more likely, the kinetic chain length is extremely short[2] if chains are involved at all. Attempts to maximize the yield of acetyl product from cyclohexane by increasing the concentration of biacetyl (expt 4) were unsuccessful, in part because of the addition of phenyl radicals themselves to biacetyl. The efficient trapping of phenyls and formation of acetophenone in expt 6 should be noted. It is also significant that, whereas phenyl radicals and solvent radicals from dioxane and cyclohexane are apparently readily acetylated, reaction in toluene (not listed in Table I) gave at most traces of acetyl product, the major identified benzyl radical product being bibenzyl. In contrast, dimers (RR) were formed in less than 10% yields from dioxane and cyclohexane. These results suggest that sequence 3 is correctly represented as an equilibrium, the position of which is dependent on the relative stabilities of R· and acetyl.[3]

Table I. Free-Radical Acetylation Reactions[a]

Expt.	Solvent	BPO, *M*	Biacetyl, *M*	% $RCOCH_3$[b]
1	Cyclohexane	0.02	0.04	32
2	Cyclohexane	0.02	0.15	69
3	Cyclohexane	0.02	0.20	66
4	Cyclohexane	0.02	1.0	48[c]
5	Dioxane	0.02	0.20	70
6	Biacetyl	0.02		62[d]

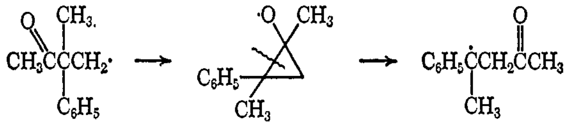
[a] Deoxygenated solutions at reflux (77–80°) for 21–29 hr. [b] Based on the assumed formation of 2 moles of radicals per mole of BPO decomposed. [c] Acetophenone also formed. [d] R = C_6H_5.

Considerable precedent may be found for the individual reaction steps postulated in sequence 3. Radical additions to *carbonyl carbon* have been proposed previously: (a) to explain the formation of secondary alcohols in low yields during the decarbonylation of aldehydes;[4] (b) in the recently reported addition of



$$\mathrm{RCO}\cdot \longrightarrow \mathrm{R}\cdot \xrightarrow{\mathrm{RCHO}} \underset{\dot{O}}{\underset{|}{RCHR}} \xrightarrow{\mathrm{RCHO}} \mathrm{RCH(OH)R} + \mathrm{RCO}\cdot$$

propyl radicals to hexafluoroacetone to give 1,1,1-trifluoro-2-(trifluoromethyl)-2-pentanol;[5] (c) as the first step in the facile 1,2-acetyl shift very recently noted,[6]



and quite likely are involved in the 1,2-carboethoxy migration observed[7] in the thermolysis of substituted carboethoxy bicyclo[2.1.0]pentanes. That acetyl radicals

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(1) The gas-phase reaction of methyl radicals with biacetyl has been proposed to account for the high quantum yields of acetone in the photolysis of biacetyl (D. S. Herr, M. S. Matheson, and W. D. Walters, *J. Am. Chem. Soc.*, 63, 1464 (1941); F. E. Blacet and W. E. Bell, *Discussions Faraday Soc.*, 14, 70 (1953)), but methyls were only reactive in this manner above 80°.

(2) Acetyl radicals would likely not abstract hydrogens readily, and decarbonylation to give chain-carrying methyls probably does not compete efficiently with other processes at these temperatures.

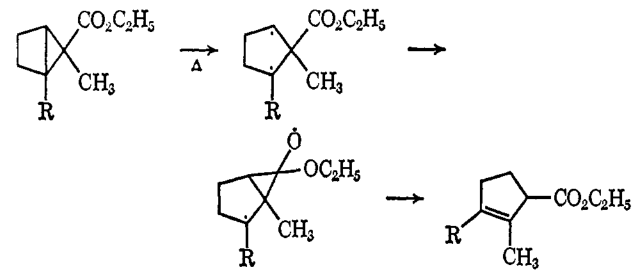
(3) The extremely facile elimination of benzyl *via* β cleavage of alkoxy radicals generated from the corresponding hypochlorite is well documented (C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **85**, 1593 (1963)).

(4) F. F. Rust, F. H. Seubold, and W. E. Vaughan, *ibid.*, 70, 4253 (1948).

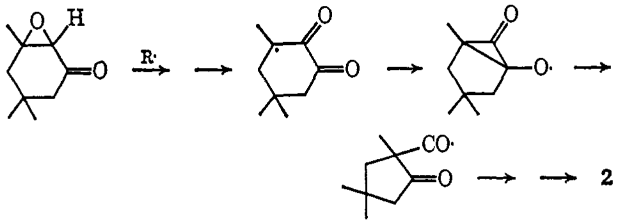
(5) W. H. Urry, A. Nishihara, and J. H. Y. Niu, *J. Org. Chem.*, 32, 347 (1967).

(6) W. Reusch and C. L. Karl, Abstracts of the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, P-79.

(7) M. J. Jorgenson and T. J. Clark, *J. Am. Chem. Soc.*, 90, 2188 (1968).



are readily eliminated in β-cleavage reactions such as suggested in (3) was well demonstrated by the work of Walsh, *et al.*,[8] who studied reactions of a large number of alkoxy intermediates analogous to **1** which were generated from the corresponding hypochlorite precursors. In fact, the previously published radical-catalyzed conversion of isophorone oxide to 2,4,4-trimethylcyclopentanone (**2**) is quite possibly an *intramolecular* acetylation as the authors suggest.[9] The



reaction of methyl radicals with 3-penten-2-one to give 2-butene and acetyl in the gas phase appears to be a closely analogous addition–elimination reaction.[10]

In contrast to the cited examples of attack at carbonyl carbon by alkyl radicals, *alkanoyl*[11] and *benzoyl*[11b] radicals have been shown to give products of *carbonyl oxygen attack* as illustrated by the reaction of butanoyl radicals with hexafluoroacetone to yield the hexafluoro ester.[5] These differences may reflect the influence of polar effects on the direction of attack or may have to do with the ease with which products of carbon or oxygen attack are trapped, since both processes may well be reversible. We are currently looking for products of acyl exchange in reactions of acyl radicals with biacetyl as evidence of carbonyl carbon attack.

We are also attempting to exploit the synthetic potential of these reactions by the selective generation of radicals at desired positions of more complex molecules through reaction of the chloride or bromide with trialkyltin hydride in the presence of biacetyl.

$$RX \xrightarrow[R_3SnH]{CH_3COCOCH_3} RCOCH_3$$

Reactions of radicals with various other carbonyl compounds which may potentially react by addition–elimination to split out stable radicals other than acetyl are also being studied.[12]

Acknowledgment. Support of this work by the Petroleum Research Fund of the American Chemical Society though a research grant (PRF-2439-A4) is gratefully acknowledged.

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[8] E. J. Walsh, Jr., L. Witmer, M. McNeil, T. Wilcko, and B. Orwig, *Tetrahedron Letters*, 77 (1968).

[9] W. Reusch, C. K. Johnson, and J. A. Manner, *J. Am. Chem. Soc.*, **88**, 2803 (1966).

[10] J. N. Pitts, Jr., R. S. Tolberg, and T. W. Martin, *ibid.*, **79**, 6370 (1957).

[11] (a) L. Kaplan, *ibid.*, **88**, 1833, 4970 (1966); E. J. Walsh, Jr., and H. G. Kuivila, *ibid.*, **88**, 576 (1966); E. J. Kupchik and R. J. Kiesel, *J. Org. Chem.*, **29**, 3690 (1964); (b) F. F. Rust, F. H. Seubold, and W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 3258 (1948).

[12] An apparently related reaction is chlorocarbonylation utilizing oxalyl chloride and a free-radical initiator (I. Tabushi, J. Hamuro, and R. Oda, *J. Org. Chem.*, **33**, 2108 (1968); E. Hedaya and L. M. Kyle, *ibid.*, **32**, 197 (1967); M. S. Kharasch, S. S. Kane, and H. C. Brown, *J. Am. Chem Soc.*, **64**, 1621 (1942); M. S. Kharasch, and H. C. Brown, *ibid.*, **64**, 329 (1942)).

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A New Structural Type for Heteropoly Anions. The Crystal Structure of $(NH_4)_2H_6(CeMo_{12}O_{42})\cdot 12H_2O$

As part of a continuing study of the isopoly- and heteropolyanions of molybdenum and tungsten, we wish to report the crystal structure of $(NH_4)_2H_6(CeMo_{12}O_{42})\cdot 12H_2O$[1] which shows two significant features not previously reported in the crystal structures of related compounds.[2–8] First, the structure involves face sharing between MoO_6 octahedra, and, second, the polyhedron formed by the molybdenum atoms is an icosahedron.

$(NH_4)_2H_6(CeMo_{12}O_{42})\cdot 12H_2O$ was prepared by the method of Baker, *et al.*[9] The crystals are trigonal with rhombohedral dimensions: $a = 10.589 \pm 0.004$ Å, $\alpha = 78.108 \pm 0.004°$. There is one formula unit in the rhombohedral cell. With rhombohedral indexing, there are no systematic absences in the X-ray data, but Friedel[10] symmetry indicates space groups R3 or R$\bar{3}$.

X-Ray intensity data were collected by the stationary crystal–stationary counter method and peak heights were converted to integrated intensities by means of an experimental curve. Mo Kα X-radiation (λ 0.7107 Å) was used and 2699 independent reflections were measured up to a 2θ angle of 65°. 1830 of the reflections had peak heights greater than twice the calculated standard deviation of peak height and are regarded as observed.

After application of the usual corrections, a sharpened Patterson map was calculated. While it is realized that the Patterson map would show only relatively large

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[1] When the compound was prepared the major fraction of the product was monoclinic crystals analyzed as $(NH_4)_6H_2(CeMo_{12}O_{42})\cdot 10H_2O$. These crystals proved unsuitable for accurate structural investigation, and the X-ray work was carried out on a very small quantity of rhombohedral crystals which were also present. The small quantity precluded analysis but the structural results indicate the formula $(NH_4)_2H_6(CeMo_{12}O_{42})\cdot 12H_2O$.

[2] J. F. Keggin, *Proc. Roy. Soc.* (London), **A144**, 75 (1934).

[3] A. Perloff, Ph.D. Dissertation, Georgetown University, Washington, D. C., 1966.

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[8] H. T. Evans, Jr., paper presented before Washington Crystal Colloquium, 1967.

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