

participation of the t_{2g} metal orbitals in the exciplex bond is also possible.

Scale models of $cis\text{-Ir(phen)}_2\text{Cl}_2^+$ and naphthalene show that there is no steric hindrance for the approach of naphthalene to a phenanthroline ligand in the way shown in Figure 2. One can easily see that there are four almost equivalent configurations of the type shown in the figure. In each of these configurations hydrogen bonding between naphthalene and a chloride ligand can contribute to the stability of the exciplex. The approach of naphthalene to the other side of the phenanthroline ligands is also possible, but in this case two out of the four bonding positions are sterically hindered by the presence of the other phenanthroline ligand.

Preliminary experiments have shown that excited $cis\text{-Ir(phen)}_2\text{Cl}_2^+$ also forms exciplexes with 2-acetonaphthone and that excited $cis\text{-Ir(5,6-Me}_2\text{phen)}_2\text{Cl}_2^+$ forms exciplexes with naphthalene. We are now carrying out a systematic investigation in order to establish the role played by the metal, ligands, ligand substituents, solvent, etc., in the formation of this new type of exciplexes.

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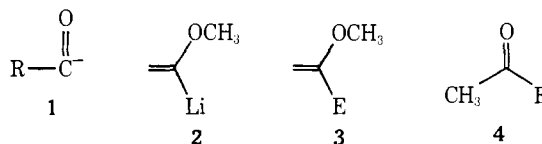
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α -Methoxyvinyl lithium and Related Metalated Enol Ethers. Practical Reagents for Nucleophilic Acylation

Sir:

Considerable effort has been recently devoted toward the discovery of useful synthetic equivalents of the acyl anion **1**.¹⁻¹¹ We now communicate our finding that α -



methoxyvinyl lithium (MVL) (**2**) and related species are readily prepared acyl anion equivalents of considerable synthetic value.¹² The reaction products, e.g., **3**, of these species with electrophiles (E^+) contain vinyl ethers which may be further elaborated as such or, more usually, can be converted by mild treatment (aqueous methanolic 0.02 *N* HCl, 25°) to their corresponding carbonyl compounds **4** in high isolated yield. Thus in a typical procedure *tert*-butyllithium (100 mmol, 62.5 ml, 1.6 *M* in *n*-pentane) was added dropwise to a solution of methyl vinyl ether (9.2 g, 160 mmol) in dry tetrahydrofuran at -65° under nitrogen.¹³ After removal of the cooling bath the yellow precipitate¹⁴ redissolved and the solution became colorless between -5 and 0°. This solution which contains quantitatively MVL was cooled to -65° for most reactions, the electrophilic species being added, in solution of tetrahydrofuran, at this temperature. If the vinyl ether product be required, the reaction is quenched (0°) with ammonium chloride solution (20% aqueous). The conversion to the carbonyl compound required reaction with aqueous methanolic 0.02 *N* HCl (30 min, 20°). The results of reaction of MVL with a selection of different electrophiles are described in Table I, all yields quoted being those of isolated and purified products. As is evident from the table the reaction of **2** with aldehydes and ketones is an efficient route to hydroxyl enol ethers **5** and α -ketols **6**, in excellent yield. The reagent reacts with relatively hindered carbonyl groups, e.g., 17-keto steroids (*cf.* Table I) and it is noteworthy that smooth nucleophilic addition was observed even with substrates which are prone to enolization, e.g., phenylacetone.

MVL is also reactive toward benzonitrile and benzoic acid (0.5 equiv), providing in each instance the hemiprotected diketone **7** and ultimately α -diketone **8**. Along with **7**, a small amount (*ca.* 10%) of the bis

(1) For a review, see D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **8**, 639 (1969).

(2) Protected cyanohydrin method: G. Stork and L. Maldonado, *J. Amer. Chem. Soc.*, **93**, 5286 (1971).

(3) J. E. McMurray and J. Melton, *J. Amer. Chem. Soc.*, **93**, 5309 (1971).

(4) Lithiodithiane derivatives: (a) review, D. Seebach, *Synthesis*, **17** (1969); (b) T. Mukaiyama, K. Naraska, and M. Furusato, *J. Amer. Chem. Soc.*, **94**, 8641 (1972); (c) E. J. Corey and D. Crouse, *J. Org. Chem.*, **33**, 298 (1968); (d) E. L. Eliel and A. A. Hartmann, *ibid.*, **37**, 505 (1972); (e) R. J. Cregge, J. H. Herrmann, J. E. Richman, R. F. Romanet, and R. H. Schlessinger, *Tetrahedron Lett.*, 2595 (1973); (f) J. L. Herrmann, J. E. Richman, and R. H. Schlessinger, *ibid.*, 2599 (1973); (g) P. Stutz and P. A. Stadler, *Helv. Chim. Acta*, **55**, 75 (1972).

(5) Acyl transition metal reagents: (a) E. J. Corey and L. S. Hege-
dus, *J. Amer. Chem. Soc.*, **91**, 1233 (1969); (b) E. J. Corey and L. S. Hege-
dus, *ibid.*, **91**, 4926 (1969); (c) M. P. Cooke, Jr., *ibid.*, **92**, 6080
(1970); (d) J. P. Collman, S. R. Winter, and D. R. Clark, *ibid.*, **94**,
1788 (1972); (e) W. O. Siegl and J. P. Collman, *ibid.*, **94**, 2516 (1972);
(f) Y. Sawa, M. Ryang, and S. Tsutsumi, *J. Org. Chem.*, **35**, 4183
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33, 2159 (1968); (h) J. P. Collman and N. W. Hoffman, *J. Amer. Chem.*
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Komoto, *ibid.*, **95**, 249 (1973).

(6) Metalloaldimines: (a) H. M. Walborsky and G. E. Niznik,
J. Amer. Chem. Soc., **91**, 7778 (1969); (b) H. M. Walborsky, W. H.
Morrison, III, and G. E. Niznik, *ibid.*, **92**, 6675 (1970); (c) G. E.
Niznik, W. H. Morrison, III, and H. M. Walborsky, *J. Org. Chem.*,
39, 600 (1974); (d) Y. Yamamoto, K. Kondo, and I. Moritani, *Tetra-*
hedron Lett., 793 (1974).

(7) α -Thiosulfoxides: (a) K. Ogura and G. Tsuchihashi, *Tetrahedron Lett.*, 3151 (1971); 1383, 2681 (1972); (b) J. E. Richman, J. L. Herrmann, and R. H. Schlessinger, *ibid.*, 3267 (1973); (c) J. L. Herrmann, J. E. Richman, and R. H. Schlessinger, *ibid.*, 3271 (1973); (d) J. L. Herrmann, J. E. Richman, P. J. Wepple, and R. H. Schlessinger, *ibid.*, 4707 (1973); (e) G. Schill and P. R. Jones, *Synthesis*, 117 (1974).

(8) E. J. Corey and J. I. Schulman, *J. Org. Chem.*, **35**, 777 (1970).

(9) R. M. Carlson and J. L. Isidor, *Tetrahedron Lett.*, 4319 (1973).

(10) K. Oshima, H. Takahashi, H. Yamamoto, and H. Nozaki, *J. Amer. Chem. Soc.*, **95**, 2694 (1973).

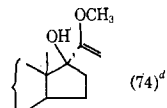
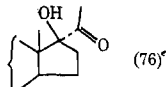
(11) Acyl carbanions themselves generally lack sufficient stability to be useful synthetic intermediates; *cf.* L. S. Trzupek, T. L. Newirth, E. G. Kelly, N. E. Sbarbati, and G. M. Whitesides, *J. Amer. Chem. Soc.*, **95**, 8118 (1973); however, recent reports describe species related to **1** which may have discrete lifetimes: U. Schöllkopf and F. Gerhart, *Angew. Chem., Int. Ed. Engl.*, **6**, 805, 970 (1967); P. Jutzi and F. W. Schröder, *ibid.*, **10**, 339 (1971); G. K. Koch and J. M. M. Kop, *Tetrahedron Lett.*, 603 (1974).

(12) While our work was in progress it was reported that ethyl vinyl ether could be metalated by *tert*-butyllithium-tetramethylethylenediamine and the lithiated derivative reacted with benzaldehyde: U. Schöllkopf, personal communication; *cf.* U. Schöllkopf and P. Hänssle, *Justus Liebigs Ann. Chem.*, **763**, 208 (1972). Professor G. Büchi of this department has made related observations; G. Büchi and H. Wuest, personal communication.

(13) This is exothermic and should be maintained between -65 and -55°.

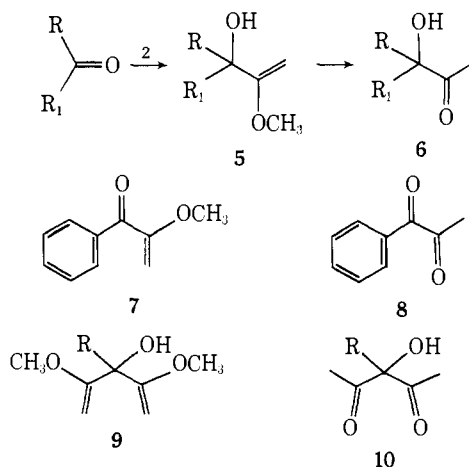
(14) This is a complex of *tert*-butyllithium and tetrahydrofuran (2:1); *cf.* F. A. Settle, M. Haggerty, and J. F. Eastham, *J. Amer. Chem. Soc.*, **86**, 2076 (1964).

Table I. Reactions of MVL with Electrophiles

| Electrophile | Adduct (yield, ^a %) | Hydrolysis product (yield, ^a %) |
|-----------------------|---|---|
| Benzaldehyde | 5 (R = Ph, R ₁ = H) (78) | 6 (R = Ph, R ₁ = H) (91) |
| Butyraldehyde | 5 (R = <i>n</i> -Pr, R ₁ = H) ^b | 6 (R = <i>n</i> -Pr, R ₁ = H) (63) ^c |
| Cyclohexanone | 15 | 6 (R, R ₁ = -(CH ₂) ₅ -) (90) |
| Cyclopentanone | 5 (R, R ₁ = -(CH ₂) ₄ -) (88) | 6 (R, R ₁ = -(CH ₂) ₄ -) (86) |
| Estrone methyl ether |  (74) ^d |  (76) ^e |
| Phenylacetone | 5 (R = PhCH ₂ , R ₁ = CH ₃) (90) | 6 (R = PhCH ₂ , R ₁ = CH ₃) (85) |
| Mesityl oxide | 11 (75) | 12 (61) ^e |
| Crotonaldehyde | 5 (R = CH ₃ CH=CH-, R ₁ = H) (74) | 6 (R = CH ₃ CH=CH-, R ₁ = H) (55) ^{e,f} |
| Methyl benzoate | 9 (R = Ph) (74) | 10 (R = Ph) (64) ^e |
| Methyl valerate | 9 (R = <i>n</i> -Bu) (82) | 10 (R = <i>n</i> -Bu) (83) |
| Methyl crotonate | 9 (R = CH ₃ CH=CH-) ^b | 10 (R = CH ₃ CH=CH-) (46) ^{e,f} |
| Benzonitrile | 7 (70) | 8 (77) ^g |
| Benzoic acid | 7 (62) | |
| Octyl iodide | <i>n</i> -C ₈ H ₁₇ C(OCH ₃)=CH ₂ ^b | 2-Decanone (80) ^{e,d} |
| Phenacyl bromide | 13 ^b | 14 (58) ^{e,f} |
| Dimethylallyl bromide | (CH ₃) ₂ C=CHCH ₂ C(OCH ₃)=CH ₂ ^b | (CH ₃) ₂ C=CHCH ₂ COCH ₃ (74) ^e |

^a Unless otherwise noted, all yields are for isolated and distilled or recrystallized products, and hydrolytic conditions were aqueous methanolic HCl at 20°. ^b The adducts were characterized by spectral data and were hydrolyzed without purification. ^c In these runs, the intermediate enol ethers were hydrolyzed directly without purification; yields are based on the electrophile. ^d The reagent **2** was used in 70% excess. ^e Hydrolysis with methanolic aqueous acetic acid. ^f Hydrolysis by shaking with 0.1 M aqueous oxalic acid. ^g Hydrolysis by brief warming under conditions in footnote *a*.

adduct **9** (R = Ph) is formed by reaction of **2** with benzoic acid. These novel enol ethers **9** are available in high yield upon reaction of an ester with 2 equiv of MVL. This process is general for aliphatic and aromatic esters providing a direct synthetic approach to substituted hydroxypentanediones **10**.¹⁵



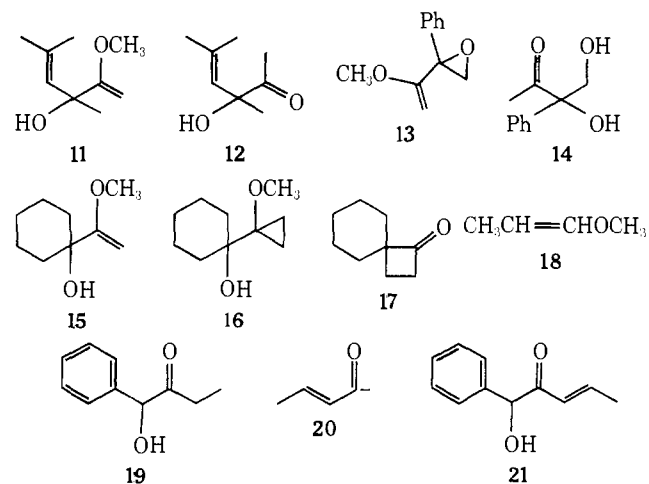
Although several carbonyl anion equivalents react in a conjugate fashion with unsaturated carbonyl compounds,^{3,4b,e,f,5a,7c} only lithiodithianes have been reported to add to the carbonyl carbon of such substrates.^{4c} We have observed that MVL undergoes exclusively 1,2-addition with α,β -unsaturated systems. Thus, mesityl oxide affords adduct **11** which may be hydrolyzed to the unsaturated ketol **12** without allylic hydroxyl migration.¹⁶ Unsaturated aldehydes and

(15) Few compounds related to **10** have been described. For characterization of **10**, R = CH₃, see F. S. Ramirez, S. B. Bhatia, and C. P. Smith, *J. Amer. Chem. Soc.*, **89**, 3026 (1967). This substance has been prepared in 65% overall yield from ethyl acetate by the present method.

(16) E. A. Braude and C. J. Timmons, *J. Chem. Soc.*, 3131, 3138 (1953).

esters also provide carbonyl adducts, and the relative ease of hydrolysis of enol ethers makes this procedure an attractive alternative to the use of 2-lithio-2-methyl-dithiane.^{4c}

We have examined the reaction of MVL with halides. For example, 2-decanone was obtained in 80% overall yield from *n*-octyl iodide. Although **2** readily displaces allylic halides (*cf.* Table I) only 1,2-diphenylethane was formed on reaction of **2** with benzyl bromide, presumably *via* an initial halogen exchange reaction to generate benzyl lithium as an intermediate. With phenacyl bromide the reaction apparently proceeds by attack of **2** at the carbonyl carbon, followed by intramolecular displacement of bromide to provide the epoxide **13** as the sole product. The diol **14** was obtained upon hydrolysis of the epoxide.



In addition to their hydrolytic behavior, the adducts from MVL and electrophiles are subject to further elaboration, thereby extending their utility as synthetic intermediates. Thus **15** may be converted (Simmons-

Smith) to the cyclopropyl ether **16** which hydrolytically rearranges in high yield to the spirocyclobutanone **17**, a system which has already been shown to be amenable to further transformations.¹⁷

Metalation of monosubstituted enol ethers is also possible. Thus the *cis* and *trans* mixture of methylpropenyl ether **18**, with *tert*-butyllithium in the presence of tetramethylethylenediamine (1 equiv) followed by benzaldehyde gave, after hydrolysis, ketol **19** (55% isolated).¹⁸ The crotonyl anion equivalent **20** was obtained by metalation (conditions as for MVL) of 1-methoxy-1,3-butadiene which after reaction with benzaldehyde and hydrolysis provided ketol **21** (30% recrystallized).

In summary, metalated enol ethers are versatile and efficient acyl anion equivalents which provide simple routes to some otherwise difficultly accessible functionalities.

Acknowledgments. We wish to thank the National Science Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, Eli Lilly & Co., Meick Sharp and Dohme, and Hofmann-La Roche for their generous support.

(17) See B. M. Trost, *Accounts Chem. Res.*, **7**, 85 (1974), and references cited therein.

(18) We have not yet been able to successfully α -metalate β,β -disubstituted enol ethers.

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The Effect of Oxygen on Rhodium-Catalyzed Ring Openings of Bicycloalkenes¹

Sir:

There is considerable current interest in the metal-catalyzed valence isomerization and ring opening of strained cyclic hydrocarbons. Attention in most of these systems has been directed to the detailed mechanisms involved, including the nature of the active catalytic species and whether the processes are stepwise or concerted.²⁻⁶ During the course of our studies of metal complex catalyzed rearrangements of the 6-substituted bicyclo[3.1.0]hex-2-enes of the general formula I,⁷ we have discovered a dramatic effect of oxygen on the reaction rates. Our results unequivocally demonstrate the necessity of O₂ for efficient ring opening when the catalyst employed is (PPh₃)₃RhCl or (PPh₃)₂Rh(CO)Cl. Reported herein are the preliminary results of this study.

(1) Presented in part at the Eighth Great Lakes Regional Meeting of the American Chemical Society, West Lafayette, Ind., June 3-5, 1974, Abstract No. 114.

(2) Pertinent reviews include: (a) F. D. Mango and J. H. Schachtschneider in "Transition Metals in Homogeneous Catalysis," G. N. Schrauzer, Ed., Marcel Dekker, New York, N. Y., 1971; (b) J. Halpern, "Collected Accounts of Transition Metal Chemistry," Vol. 1, F. Basolo, J. F. Bunnett, and J. Halpern, Ed., American Chemical Society, Washington, D. C., 1973; (c) L. A. Paquette, *Accounts Chem. Res.*, **4**, 280 (1971).

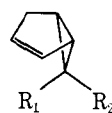
(3) P. G. Gassmann and R. R. Reitz, *J. Amer. Chem. Soc.*, **95**, 3057 (1973).

(4) G. Zon and L. A. Paquette, *J. Amer. Chem. Soc.*, **95**, 4456 (1973).

(5) R. Noyori, Y. Kamagai, and H. Takaya, *J. Amer. Chem. Soc.*, **96**, 634 (1974).

(6) H. Hogeveen and B. J. Nusse, *Tetrahedron Lett.*, 159 (1974).

(7) D. L. Garin and K. O. Henderson, *Tetrahedron Lett.*, 2009 (1970).

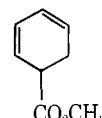


Ia, R₁ = CO₂CH₃; R₂ = H

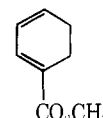
b, R₁ = H; R₂ = CO₂CH₃

c, R₁ = CO₂CH₃; R₂ = CH₃

d, R₁ = CH₃; R₂ = CO₂CH₃



II



III

All reactions were performed in nmr tubes for the purpose of monitoring reaction progress by proton nmr spectroscopy.⁸ Typically, 1.0 mmol of the organic substrate and 0.1 mmol of rhodium catalyst were dissolved in 1.0 ml of CHCl₃, and the solution was charged to an nmr tube which was subsequently capped and stored in the dark at room temperature. Spectra were recorded at appropriate intervals. In all cases the reported reactions were catalytic.

The system we have studied most intensively to date is the endo ester Ia. Regardless of the rhodium catalyst employed, the major products (95% yield) are the conjugated cyclohexadienes II and III. Both major products were isolated in pure form by preparative vpc (6 ft \times 1/4 in. Carbowax on Chromasorb W) and characterized by mass spectrometry, uv, and proton nmr spectroscopy.⁹ Compounds II and III were obtained in an approximately 40:60 ratio when Ia was completely consumed. Although nmr traces of the reaction mixtures very accurately portray the extent of reaction, other methods are needed to show the presence of small amounts of the other cyclohexadiene products.⁹⁻¹² If the reaction is not terminated by quenching with hexane and subsequent removal of the precipitated rhodium catalyst when Ia has completely reacted, a slow conversion ($t_{1/2} \cong 5$ days)^{12b} of II to III is observed.

When samples of Ia with (PPh₃)₃RhCl are prepared under inert atmosphere with argon-purged solvent, no ring opening is observed after 48 hr, but the reaction may be initiated by bubbling oxygen through the system for 15-20 sec. Intentional oxidation of a methylene chloride solution of (PPh₃)₃RhCl by the method reported by Bennett and Donaldson¹³ affords the O₂-containing complex [(PPh₃)₂RhCl(O₂)₂]. This complex was isolated in solid form and placed in an nmr tube equipped with a vacuum fitting and the endo-ester Ia was added. The tube was placed under high vacuum, and chloroform, which had been rigorously degassed on the vacuum line, distilled into the nmr tube, which was sealed under vacuum. Ring opening was found to occur at a rate comparable to that observed when O₂ was bubbled through a chloroform solution of Ia and (PPh₃)₃RhCl. This rate is approximately seven times faster than the rate of reaction of Ia with (PPh₃)₃RhCl

(8) We have observed catalyst poisoning due to small amounts of acid in several commercial samples of deuteriochloroform. For this reason all experiments were carried out in freshly distilled CHCl₃ solvent using tubes which had been washed with dilute sodium bicarbonate.

(9) W. J. Bailey, R. Barclay, Jr., and R. A. Baylouny, *J. Org. Chem.*, **27**, 1851 (1962).

(10) R. Grewe and I. Hinrichs, *Chem. Ber.*, **97**, 443 (1964).

(11) M. E. Kuehne and B. F. Lambert, *Org. Syn.*, **43**, 22 (1963).

(12) (a) Ia and Ib ring-open to give all five possible cyclohexadiene isomers as shown by vpc. Regardless of the extent of reaction, II and III constitute at least 95% of the product mixture. (b) Values of $t_{1/2}$ represent time required for conversion of 50% of starting material, based on nmr integrations.

(13) (a) M. J. Bennett and P. B. Donaldson, *J. Amer. Chem. Soc.*, **93**, 3307 (1971); (b) We find that an essentially stoichiometric amount of triphenylphosphine oxide is formed in this reaction.