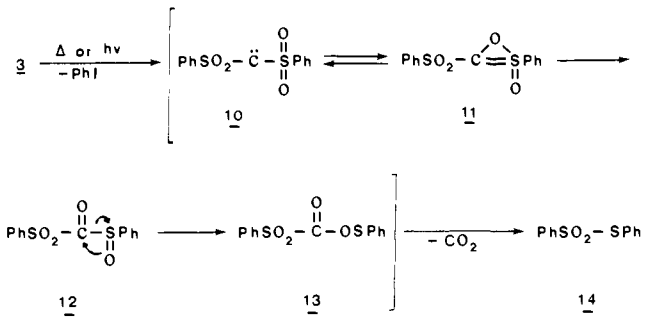
Scheme III



formation of **9c** is noteworthy since, unlike **9a** and **9b**, **9c** cannot be prepared by direct iodination of **2**.[13]

$$3 + \text{N–X succinimide} \xrightarrow[\text{room temperature}]{CH_2Cl_2} (PhSO_2)_2CX_2$$

9a, X = Cl (54%)
9b, X = Br (81%)
9c, X = I (79%)

Compounds **9b** and **9c** were also formed from **3** and the corresponding elemental halogen, while **9a** was obtained from **3** with SO_2Cl_2. The ylide **3** has oxidizing properties: thus **3** reacts with aniline to give *trans*-azobenzene, with anthracene to give 9,10-anthraquinone, and with diphenylacetylene to give benzil, all in low yields. Furthermore, phenylalkenes such as styrene, *trans*-stilbene, and ethyl cinnamate undergo cleavage of the double bond with **3** at room temperature to afford benzaldehyde as the main product. Acrylonitrile was polymerized by **3** exothermically.

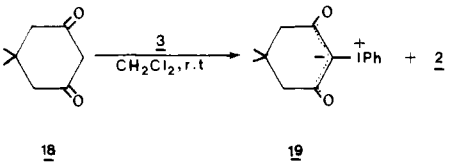
When **3** was heated in such diverse H-containing solvents as AcOH, CH_2Cl_2, MeCN, etc., the formation of iodobenzene and the disulfone **2** was observed. However, when **3** was heated under reflux in *t*-BuOH in the presence of $Cu(acac)_2$ and under N_2, CO_2 was evolved, and the unexpected product phenyl benzenethiosulfonate (**14**) was obtained, in 80% yield. The same ester was formed in varying amounts in most of the reactions of **3**. We propose the mechanism shown in Scheme III for the formation of **14**. Apparently the solvent plays a passive role since CO_2 evolution has been detected during the thermolysis of solid **3**. Support for this mechanism is provided by an attempted synthesis of ylide **16** from (phenylsulfonyl)(phenylthio)methane (**15**) and **1**, where the decomposition product of the expected ylide diphenyl disulfide (**17**) was obtained. The formation of **17** probably proceeds analogously to the pathway in Scheme III.

$$\underset{\mathbf{15}}{PhSO_2CH_2SPh} \xrightarrow[MeOH,\ KOH,\ -10\ ^\circ C]{1} [PhI^{+-}C(SO_2Ph)(SPh)] \xrightarrow[-PhI]{} \underset{\mathbf{17}}{PhSSPh} + CO_2$$
$$\mathbf{16}$$

The reactions of **3** with nucleophiles as well as its thermolysis probably involve dissociation of the ylide into iodobenzene and bis(phenylsulfonyl)carbene (**10**).[14] Carbene formation from iodonium ylides has previously been suggested in two cases.[4,15] The carbene **10** is apparently in equilibrium with **11**, as oxirenes are with ketocarbenes.[16] Rearrangement of **11** into **12** followed by intramolecular nucleophilic collapse of **12** to **13** and decarboxylation of **13** would give **14**. This stage (**13** → **14**) is possibly responsible for the production of free radicals and the polymerization of acrylonitrile.

There is precedent[17] for *O*-sulfonyl attack at highly electrophilic C. The enhanced nucleophilic character of the sulfonyl oxygen of **3** or **10** must be responsible for the oxidations effected by **3** under mild conditions. Both **3** and **10** are probably stabilized by resonance so that considerable negative charge may be acquired by the sulfonyl oxygens. However, carbene formation here and in reactions of **3** with electrophiles seems unlikely. The formation of transient iodonium salts is more justifiable. We note, for example, that phenyliodonium dinitromethylide gives isolable iodonium salts[18] with FSO_3H.

Scheme IV



Iodobenzene is a byproduct in all the above reactions of **3**. A different type of reactivity was observed when **3** was allowed to react with dimedone (**18**) in non-hydroxylic solvents. In this case, "reversed" transylidation occurred, and the phenyliodonio dimedonate (**19**) was obtained in 50% yield (Scheme IV). This reaction may involve proton transfer from **18** (pK_a = 5) to **3** (estimated[19] pK_a of protonated **3** is ~4) and subsequent attack of the dimedonate ion on protonated **3**.

Registry No. **1**, 3240-34-4; **2**, 3406-02-8; **3**, 98858-34-5; **4**, 98858-35-6; **5**, 38564-68-0; **6** (Z = pyridine), 98858-36-7; **6** (Z = Ph_3P) (P(V) entry), 96415-47-3; **6** (Z = Ph_3P) (ylide entry), 25809-68-1; **6** (Z = $(Me_2N)_2CS$), 77134-48-6; **6** (Z = Me_2S), 2292-72-0; **6** (Z = PhSMe), 53799-65-8; **7**, 98858-37-8; **8**, 98858-38-9; **9a**, 603-35-0; **9b**, 2782-91-4; **9c**, 75-18-3; **14**, 1212-08-4; **15**, 15296-86-3; **17**, 882-33-7; CS_2, 75-15-0; *N*-chlorosuccinimide, 128-09-6; *N*-bromosuccinimide, 128-08-5; *N*-iodosuccinimide, 516-12-1; aniline, 62-53-3; azobenzene, 103-33-3; 9,10-anthraquinone, 84-65-1; diphenylacetylene, 501-65-5; benzyl, 2154-56-5; styrene, 100-42-5; *trans*-stilbene, 103-30-0; ethyl cinnamate, 103-36-6; benzaldehyde, 100-52-7; acrylonitrile, 107-13-1; polyacrylonitrile, 25014-41-9; anthracene, 120-12-7.

(13) Jarvis, B.; Fried, H. E. *J. Org. Chem.* **1975**, *40*, 1278.
(14) The formation of **10** has been proposed in reactions of the unusually stable bis(phenylsulfonyl)diazomethane,[11] but no reaction occurred with benzene and alkenes, whereas triphenylphosphine did react to give the phosphazene. Therefore formation of **10** from this precursor is unlikely.
(15) Hood, J. N. C.; Lloyd, D.; MacDonald, W. A.; Shepherd, T. M. *Tetrahedron* **1982**, *38*, 3355.
(16) Csizmadia, I. G.; Font, J.; Strauss, O. P. *J. Am. Chem. Soc.* **1968**, *90*, 7360.
(17) Chalkey, G. R.; Snodin, D. J.; Stevens, G.; Whiting, M. C. *J. Chem. Soc. C* **1970**, 682. Braverman, S.; Reisman, D. *Tetrahedron Lett.* **1977**, 1753.
(18) Semenov, V. V.; Shevelev, S. A.; Fainzilberg, A. A. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1978**, 2348.
(19) Neiland, O.; Karele, B. *Zh. Org. Khim.* **1971**, *7*, 1611.

Oxidative Nucleophilic Addition of Organovanadium Reagents to Aldehydes with Formation of Ketones

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A variety of organometallic reagents have been developed for selective molecular elaboration.[1,2] In particular, alcohol formation via carbonyl addition reactions constitutes one of the important C–C bond construction methods. Herein we describe a new methodology for carbonyl alkylation which involves an organovanadium compound as a key reagent for oxidative nucleophilic addition.

The organovanadium reagents employed here were generated in situ in dichloromethane from equimolar amounts of vanadium trichloride and organolithium or magnesium compounds. The reactions of the reagents thus obtained with aldehydes resulted in oxidative C–C bond formation leading to the corresponding ketones (Scheme I). For example, vanadium trichloride was

(1) For example: Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333. Mukaiyama, T. *Ibid.* **1977**, *16*, 817. Reetz, M. T. *Topics Curr. Chem.* **1982**, *106*, 1. Imamoto, T.; Tawarayama, Y.; Kusumoto, T.; Yokoyama, M. *J. Synth. Org. Chem. Jpn.* **1984**, *42*, 143.
(2) Seebach, D. In "Modern Synthetic Methods"; Scheffold, R., Ed.; Wiley: New York, 1983; Vol. 3, p 217.

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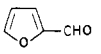
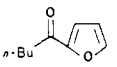
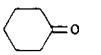
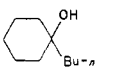
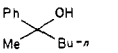
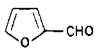
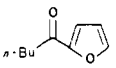
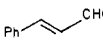
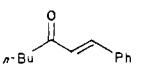
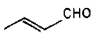
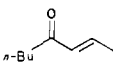
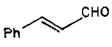
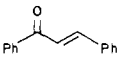
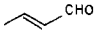
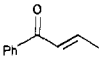
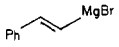
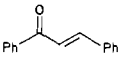
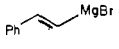
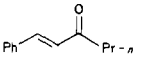
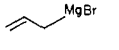
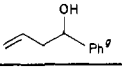
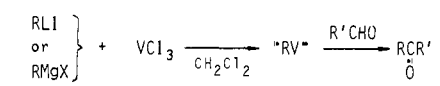
Table I. Reactions of Organovanadium Reagents[a]

RM ("RV")	R'CHO	solvent	temp	time, h	product	isolated yield, %
n-BuLi	PhCHO	CH_2Cl_2	−78 °C	2	*n*-BuC(=O)Ph *n*-BuC(OH)Ph	89 (0:100)
		CH_2Cl_2	reflux	16		60 (42:58)
		PhMe	reflux	10		58 (45:55)
		hexane	reflux	10		53 (23:77)
		THF	reflux	10		0
		ether	rt[g]	24		0
		CH_2Cl_2, PhMe[b]	reflux	16		42 (100:0)
n-BuMgBr	PhCHO	CH_2Cl_2, PhMe[b]	reflux	16	*n*-BuC(=O)Ph *n*-BuC(OH)Ph	54 (100:0)
n-BuMgBr[c]	PhCHO	CH_2Cl_2, PhMe[b]	reflux	16	*n*-BuC(=O)Ph *n*-BuC(OH)Ph	64 (1:99)
n-BuMgBr[d]	PhCHO	CH_2Cl_2, PhMe[b]	reflux	16	*n*-BuC(=O)Ph *n*-BuC(OH)Ph	64 (5:95)
n-BuMgBr[e]	PhCHO	CH_2Cl_2, PhMe[b]	reflux	16	*n*-BuC(=O)Ph *n*-BuC(OH)Ph	72 (15:85)
n-BuLi	*p*-$MeOC_6H_4CHO$	CH_2Cl_2, PhMe[b]	reflux	16	*n*-BuC(=O)C_6H_4OMe-*p*	56
n-BuLi	*p*-ClC_6H_4CHO	CH_2Cl_2, PhMe[b]	reflux	16	*n*-BuC(=O)C_6H_4Cl-*p*	54
n-BuLi		CH_2Cl_2, PhMe[b]	reflux	16		64
n-BuLi		CH_2Cl_2	rt[f]	12		63
n-BuMgBr	PhC(=O)Me	CH_2Cl_2	rt[f]	2		81
n-BuMgBr		CH_2Cl_2, PhMe[b]	reflux	16		66
n-BuMgBr	*n*-PrCHO	CH_2Cl_2, PhMe[b]	reflux	16	*n*-BuC(=O)-*n*-Pr	50
n-BuMgBr	*n*-HepCHO	CH_2Cl_2, PhMe[b]	reflux	16	*n*-BuC(=O)-*n*-Hep	48
MeMgI	PhCHO	CH_2Cl_2, PhMe[b]	reflux	16	MeC(=O)Ph	64
PhMgBr	PhCHO	CH_2Cl_2, PhMe[b]	reflux	16	PhC(=O)Ph	66
PhMgBr	*n*-PrCHO	CH_2Cl_2, PhMe[b]	reflux	16	PhC(=O)-*n*-Pr	55
n-BuLi		CH_2Cl_2, PhMe[b]	reflux	16		46
n-BuMgBr		CH_2Cl_2, PhMe[b]	reflux	16		36
PhMgBr		CH_2Cl_2, PhMe[b]	reflux	16		43
PhMgBr		CH_2Cl_2, PhMe[b]	reflux	16		46
	PhCHO	CH_2Cl_2, PhMe[b]	reflux	16		38
	*n*-PrCHO	CH_2Cl_2, PhMe[b]	reflux	16		47
	PhCHO	CH_2Cl_2, PhMe[b]	reflux	16		42

[a] Unless otherwise stated, the reaction was carried out using an aldehyde or ketone, an organolithium or magnesium compound, and vanadium trichloride in a ratio of 1:1:1. [b] Toluene was added to the mixture which was kept at −78 °C for 2 h after the addition of an aldehyde. [c] *n*-BuMgBr/VCl_3 = 3:1. [d] *n*-BuMgBr/VCl_3 = 2:1. [e] *n*-Butylvanadium species/R'CHO = 2:1. [f] Room temperature. [g] The corresponding ketone was not obtained.

Scheme I



X=Br, I

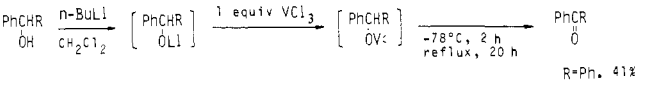
treated with 1 equiv of *n*-BuLi/hexane in dichloromethane at −78 °C, followed by the addition of benzaldehyde (1 equiv) at the same temperature. After heating the resultant mixture under reflux, valerophenone was formed (Table I). The generation of the organovanadium species should be done at a low temperature (−78 °C) because generation at −20 °C resulted in a poor yield of the desired ketone.

The success of the present transformation is strongly dependent on the choice of solvent. Dichloromethane was found to be superior to toluene or hexane. The oxidative nucleophilic addition reaction did not occur at all in ether or THF solvent, which is in sharp contrast to the normal reactions with known nucleophilic organometallic reagents. Therefore, the concentration of the ethereal Grignard reagent should be as high as possible. To get a higher yield of ketones, toluene was added to the reaction mixtures obtained by the addition of aldehydes to the organovanadium compound in dichloromethane.[3] By use of this procedure, alcohol formation was completely depressed, maybe due to the increase of the refluxing temperature. The conversion yield was almost quantitative in every case and the only side product was some starting aldehyde. Attempts to increase ketone yields by using an excess amount of organovanadium compounds per aldehydes failed and gave predominantly alcohols.

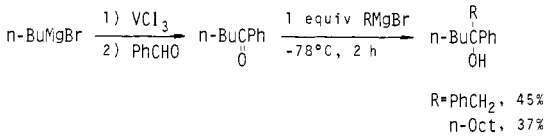
Aryl aldehydes were smoothly converted to the corresponding ketones as listed in Table I. In the case of *p*-chlorobenzaldehyde,

(3) A typical procedure is as follows. To a suspension of VCl_3 (1.0 mmol) in dichloromethane (2 mL) was added *n*-BuMgBr (1.88 M in ether; 1.0 mmol) at −78 °C over 10 min. The resultant mixture was stirred at the same temperature for 20 min. An aldehyde (1.0 mmol) was added at −78 °C and stirring was continued for 2 h. The mixture was warmed to room temperature. After the addition of toluene (2 mL), the mixture was heated at reflux for 16 h. Workup with saturated $NaHCO_3$ solution and column chromatography gave the desired ketone.

Scheme II

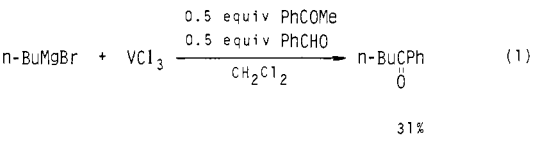


Scheme III



the chloro substituent was inert under the conditions employed here. Starting from alkyl aldehydes and the organovanadium reagent from *n*-BuLi, the oxidation process did not proceed. The successful transformation to ketones was performed by use of the Grignard reagent instead. Various Grignard reagents such as vinyl- or arylmagnesium halides were employed in the ketone synthesis via organovanadium compounds. The reagent from allylmagnesium bromide did not undergo the oxidation reaction with benzaldehyde but only gave the alcohol. Noteworthy is the fact that conjugated aldehydes underwent regioselective 1,2-addition of organovanadium reagents to produce α,β-unsaturated ketones exclusively.

Ketones were also reactive enough toward these organovanadium reagents, but it should be noted that high chemoselectivity was observed in the reaction of *n*-butylvanadium species with a mixture of benzaldehyde and acetophenone (eq 1).



(1)

Acetophenone was recovered and the only product was valerophenone derived from benzaldehyde.

Although an intermediate organovanadium species has not been isolated, ketone synthesis is considered to be characteristic of presumed $RVCl_2$.[4a] Use of more than 2 equiv of *n*-butylmagnesium bromide per vanadium trichloride resulted in alcohol formation.[4b] The present transformation was unsuccessful when VCl_4 or $V(O)Cl_3$ was employed.

Treatment of the reaction mixture under reflux is important since workup at −78 °C gave alcohols exclusively. The intermediacy of the secondary alkoxyvanadium species seems likely. In fact, when lithium alkoxides were treated with vanadium trichloride in dichloromethane, oxidation to the corresponding ketones occurred (Scheme II). This oxidation step might be formally explained by a β-elimination reaction.

An application of this selective ketone synthesis was demonstrated by a facile one-pot synthesis of tertiary alcohols as exemplified in Scheme III.

A useful synthesis of unsymmetrical ketones from aldehydes is now possible by organovanadium chemistry. Vanadium-mediated synthetic reactions have scarcely been studied.[2,4,5] Further investigation is in progress.

Registry No. *n*-BuLi, 109-72-8; *n*-BuMgBr, 693-03-8; MeMgI, 917-64-6; PhMgBr, 100-58-3; PhCH=CHMgBr, 30094-01-0; CH_2=CHCH_2MgBr, 13291-18-4; PhCHO, 100-52-7; *p*-MeC_6H_4CHO, 104-87-0; *p*-ClC_6H_4CHO, 104-88-1; PhCOMe, 98-86-2; *n*-PrCHO, 123-72-8; $CH_3(CH_2)_6CHO$, 124-13-0; PhCH=CHCHO, 104-55-2; CH_3CH=CHCHO, 4170-30-3; $CH_3(CH_2)_3COPh$, 1009-14-9; $CH_3(CH_2)_3CH$(OH)Ph, 583-03-9; $CH_3(CH_2)_3COC_6H_4$-*p*-OMe, 1671-76-7; 4-*n*-$BuCOC_6H_4Cl$, 25017-08-7; *n*-BuCOPr, 589-63-9; *n*-$BuCO(CH_2)_6CH_3$, 19780-10-0; PhCOPh, 119-61-9; PhCOPr, 495-40-9; BuCOCH=CHPh, 4071-84-5; $BuCOCH$=$CHCH_3$, 4643-27-0; $PhCOCH$=CHPh, 94-41-7; $PhCOCH$=$CHCH_3$, 495-41-0; $PhCH$=CHCOPr, 4646-80-4; CH_2=$CHCH_2CH$(OH)Ph, 936-58-3; 2-furancarboxaldehyde, 98-01-1; cyclohexanone, 108-94-1; butyl 2-furyl ketone, 3194-17-0; 1-butylcyclohexanol, 5445-30-7; 2-phenyl-2-hexanol, 4396-98-9; vanadium trichloride, 7718-98-1.

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Competitive C–H Activation and C≡C Coordination in the Reactions of Acetylenes with a Binuclear Rhodium Complex

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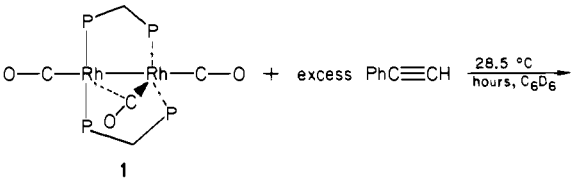
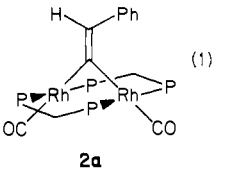
Terminal alkynes react with transition-metal complexes either by coordination of the C≡C bond as $2e^-$ or $4e^-$ donor[2] or by C–H bond activation to form acetylide complexes, which often undergo subsequent transformations.[3] In this paper, we describe a detailed study of the reaction between phenylacetylene and the binuclear complex $Rh_2(CO)_3(dppm)_2$ (**1**, dppm = bis(diphenylphosphino)methane) which provides insight into the factors influencing modes of acetylene reactivity and shows that in this system η^2 coordination between the two Rh atoms (μ_2-η^2) does not lie on the reaction profile leading to C–H activation.

Complex **1**, which was recently been found to possess an $18e^-/16e^-$ non-A-frame structure,[4] reacts readily with a 10-fold excess of PhCCH in benzene at 28.5 °C to form an intensely purple colored product **2a** cleanly and without observable intermediates, eq 1.[5] This product has been established by a single-crystal X-ray study to be a phenylvinylidene bridged A-frame complex having the structure shown in Figure 1.[6] **2a** possesses approximate mirror symmetry with no formal Rh–Rh bond and



1



2a

(1)

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(2) See, for example: (a) Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858 and references therein. (b) Lukehart, C. M. "Fundamental Transition Metal Organometallic Chemistry"; Brooks/Cole Publishers: Monterey, CA, 1985; pp 154–163 and references therein.

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(5) Spectroscopic data for **2a**. ^1H NMR (C_6D_6) (CH_2 region) δ 3.85 (m, 2 H), 2.25 (m, 2 H); $^{31}P\{^1H\}$ NMR δ 31.22 (m); IR (Nujol mull) ν(CO) 1934 (s), 1910 (s) cm^{-1}.

(6) Crystal data for **2a**: $P\bar{1}$ with a = 14.684 (4) Å, b = 14.818 (4) Å, c = 13.527 (2) Å, α = 102.56 (2)°, β = 101.56 (2)°, γ = 73.13 (2)°, and V = 2719.3 $Å^3$; Z = 2, d_{calcd} = 1.377 g cm^{-3}; convergence with R_f = 0.048, R_w = 0.069, and GOF = 1.93 (631 variables, 4562 reflections with $I > 3\sigma(I)$, all non-hydrogen atoms anisotropic). Full details of the structure solution will be presented in a separated report.

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