either before or after preparative GLPC. The $CDCl_3$ for the NMR studies was purified by elution through a column of silica gel and was stored over Linde 4A molecular sieves. The $Eu(fod)_3$ shift reagent was handled in a nitrogen-filled glovebox and was dissolved in the purified $CDCl_3$ to form a 0.54 M solution. The NMR samples of **20h** and **20i** were placed in nitrogen-filled sample tubes sealed with small serum stoppers, and aliquots of the $Eu(fod)_3$ solution were added with a 50-μL syringe. The NMR spectra were recorded on a Varian HFT-80 spectrometer, and the decoupling experiments were performed with a Hewlett-Packard Model 3320A frequency synthesizer. The data from the shift reagent studies are shown in Table IV. The isomeric heptenols **22b** and **22c** were studied by the same procedure, and the corresponding data for these compounds are also given in Table IV. The isomeric purities of these two compounds could not be determined by GLPC because the two isomers were not separable with any of the several columns that were employed.

Acknowledgment. We thank Professor Alan B. Levy of this department for many fruitful discussions concerning this work and for confirming many of our findings in his subsequent studies of reactions related to our methods. We also express our gratitude to Professor Charles S. Springer for his advice concerning the lanthanide shift reagent studies. Preliminary work was performed by Mr. Robert Kramer. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Joint Awards Council and University Awards Committee, administered by the Research Foundation of the State University of New York, for support of this research.

Registry No. 15, 54678-23-8; **19a**, 4588-18-5; **19b**, 763-88-2; **19c**, 67356-84-7; **19d**, 67356-85-8; **19e**, 67356-86-9; **20a**, 71360-09-3; **20b**, 71360-10-6; **20c**, 71360-11-7; **20d**, 67356-87-0; **20e**, 71360-12-8; *cis*-**20f**, 71360-13-9; *trans*-**20f**, 71392-87-5; **20g**, 71360-14-0; **20h**, 69417-95-4; **20i**, 69417-96-5; **20j**, 71360-15-1; **20k**, 71360-16-2; **20l**, 71360-17-3; **20m**, 110-93-0; **20n**, 71360-18-4; **22a**, 67356-88-1; **22b**, 13679-01-1; **22c**, 13679-00-0; **22d**, 71360-19-5; **22e**, 71360-20-8; **22f**, 71360-21-9; **22g**, 71360-22-0; **22h**, 71360-23-1; **22i**, 68705-77-1; **23**, 4630-06-2; 1-octyne, 629-05-0; 1-propyne, 74-99-7; 1-hexyne, 693-02-7; ammonium chloride, 12125-02-9; allyl bromide, 106-95-6; acetyl chloride, 75-36-5; ethyl bromide, 74-96-4; hexyl bromide, 111-25-1; butyl bromide, 109-65-9; methyl bromide, 74-83-9; propyl bromide, 106-94-5; 1-butyne, 107-00-6; 1-pentyne, 627-19-0; 2-cyclohexen-1-one, 930-68-7; 1-acetylcyclohexene, 932-66-1; coumarin, 91-64-5; 1,1-dimethyl-(2*H*)-naphthalenone, 23230-52-6; 2-cyclopenten-1-one, 930-30-3; chalcone, 94-41-7; benzalacetone, 122-57-6; methyl vinyl ketone, 78-94-4; ethylene oxide, 75-21-8; 1,2-epoxypropane, 75-56-9; 1,2-epoxyheptane, 5063-65-0; styrene oxide, 96-09-3; cyclohexene oxide, 286-20-4; 2-ethyl-1-octene, 51655-64-2.

Active Metal Slurries by Metal Vapor Techniques. Reactions with Alkyl and Aryl Halides[1]

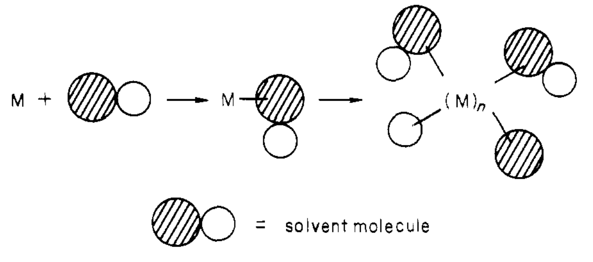
Kenneth J. Klabunde*[2] and Thomas O. Murdock

Department of Chemistry, University of North Dakota, Grand Forks, North Dakota 58202

Received May 1, 1979

The low-temperature codesposition of metal vapors with solvents in high excess, followed by warming and subsequent partial reclustering of metal atoms, allows preparation of very active metal particles in slurry form. Thus, slurries of Al, In, Zn, Cd, Sn, Pb, and Ni were prepared in either xylene, toluene, hexane, tetrahydrofuran, or diglyme. These metal–organic dispersions were allowed to react with alkyl and aryl halides: $(Al)_n$/solvent with ArX yielded Ar_xAlX_{3-x}; $(In)_n$/solvent with RX yielded R_xInI_{3-x}; $(Zn)_n$/solvent with RX yielded R_2Zn, which could readily be isolated in nonsolvated form, and $(Zn)_n$/solvent with CH_2X_2/olefin yielded Simmons–Smith chemistry in fair to poor yields; $(Cd)_n$/solvent with RX yielded RCdX, in some cases in nonsolvated form; $(Sn)_n$/solvent with RX yielded R_xSnI_{4-x}; $(Pb)_n$/solvent with RX yielded R_3PbX; and $(Ni)_n$/solvent with RX yielded organic products resulting from R or RNiX intermediates. The active powders prepared from the slurries by solvent evaporation were storable for many months without significant loss in activity, as measured by RX reaction rates after readdition of pure solvent.

When metal atoms are codeposited at −196 °C with high excesses of solvents, unexpected reactions often take place.[3,4] These reactions usually occur during matrix warmup, and with Ni even C–C cleavage in alkanes can occur efficiently as low as −130 °C. Also during matrix warmup, M–M clustering takes place, and this can occur quite rapidly (even below −196 °C)[5] if the solvent possesses no available complexing π or nonbonding electrons, such as with alkanes.[6] Therefore, in all such systems where metal atoms and weakly complexing solvents (considering the metal atom in question) are codeposited, upon warmup a competition exists between M–M *bond reformation* (clustering) and *reaction* of the atoms and/or clusters with



---

(1) Clustering of Metal Atoms in Organic Media. VII. For part VI, see: Klabunde, K. J.; Ralston, D.; Zoellner, R.; Hattori, H.; Tanaka, Y. *J. Catal.* **1978** 55, 213.

(2) Address correspondence to this author at the Department of Chemistry, Kansas State University, Manhattan, Kans. 66506.

(3) Davis, S. C.; Klabunde, K. J. *J. Am. Chem. Soc.* **1978**, *100*, 5973.

(4) For a description of metal vapor chemistry and techniques, cf. Klabunde, K. J.; Timms, P. L.; Skell, P. S.; Ittel, S. *Inorg. Synth.* **1979**, *19*, 59.

(5) Klotzbucher. W. E.; Mitchell, S. A.; and Ozin, G. A. *Inorg. Chem.* **1977**, *16*, 3063.

(6) Klabunde, K. J. *Acc. Chem. Res.* **1975**, *8*, 393.

0022-3263/79/1944-3901$01.00/0 © 1979 American Chemical Society

the solvent. In fact, at least in the case of Ni, it is believed that only the small clusters, not the atoms, react with alkanes.[3] The result of this competition is a nearly amorphous "pseudoorganometallic" powder in very fine slurry form. On the surface of each cluster or crystallite is an organic coating of adsorbed molecules and fragments of these molecules. The amount of bound organic depends on the metal involved, the solvent involved, and the rate of warmup of the matrix. Very slow matrix warmups usually favor higher organic incorporation.[3]

We have carried out a broad investigation of the activities of these metal slurries in reactions with organohalides. We believe the data reported herein clearly show that this metal vapor–solvent vapor codeposition method represents a major new advance in active metals preparation, especially in light of recent information regarding the relatively low cost for large scale preparation of metal vapor produced chemicals.[7]

A Short History of Metal Activation Procedures

A detailed review of metal activation procedures used over the last 100 years has shown that there are seven basic methods:[8] (1) mechanical reduction or machining of the metal under inert atmosphere and/or solvents;[9] (2) preparation of alloys or couples, e.g., ZnCu;[10] (3) addition of catalysts or activators to the reaction mixture, e.g., I_2 or R_3N addition;[11] (4) chemical cleansing of the metal surface, e.g., addition of $BrCH_2CH_2Br$;[12] (5) reduction of metal salts by alkali metals, e.g., $MgCl_2 + 2K \rightarrow Mg^* + KCl$;[13a] (6) reduction of metal salts by hydrogen or hydride donors;[13b–l] and (7) metal vapor–solvent vapor codeposition procedures, e.g., Mg/THF,[14] Mg/hexane,[14] Zn/diglyme,[15] or Cd/THF,[15] metal vaporizations into inert gas atmospheres,[16] and decompositions of organometallics in the vapor phase, e.g., $Ni(CO)_4$.[17]

The two methods that appear to reproducably yield the most active metals are the metal halide–alkali metal reduction procedure recently developed by Rieke and coworkers[13a] and our metal vapor–solvent vapor method.[14,15,18,19] These two methods appear to be complementary in a variety of ways. The Rieke method can be carried out in conventional glassware and yields extremely active metals. However, there are some limitations on solvent choice for preparation of the active metal since at least a small amount of the metal halide salt must be soluble in the solvent (a less polar solvent can be substituted afterwards, however). Furthermore, a great deal of sometimes unwanted KX is also formed. With our metal vapor–solvent vapor method, more elaborate glassware is needed (but see ref 4 for some rather simplified and inexpensive designs), and often the reactivities of the metal slurries produced are not quite as high as those with the Rieke method. However, essentially any solvent (alkanes, arenes, ethers) can be used, and no KX byproduct is produced.

Rieke

$$MX_2 + K \xrightarrow{\text{solvent}} (M)_n^* + 2KCl$$

$$\text{solvent} = \text{ether or arene}$$

metal vapor–solvent vapor codeposition

$$M_{\text{vapor}} + \text{solvent} \rightarrow [\text{M-sol}] \rightarrow (M)_n^*\text{-sol}$$

The following results describe our recent findings with regard to the preparation, properties, and reactivities of a variety of vapor deposition slurries with organohalides. The metals discussed here include Al, In, Zn, Cd, Sn, Pb, and Ni.

Activated Aluminum

Commercial scale evaporation of Al is quite commonplace in industry today, and it is used for the purpose of coating plastics and other materials with conducting and/or reflection coatings.[20] Also, the activation of Al metal is a vital requirement for the commercial preparation of aluminum alkyls.[21] Therefore, it is evident that the Al vapor–solvent vapor codeposition procedure is potentially very useful for Al activation on a large scale.

Previous Al activation procedures have included the following.

Wittenberg[22] has reported that grinding granular aluminum with $AlCl_3$, $AlBr_3$, and NaCl imparts some added activity for reaction with chlorobenzene to yield the phenylaluminum sesquichloride $[Ph_3Al_2Cl_3]$. Aluminum–magnesium alloys have been employed for the facilitation of RXAl reactions as well.[23] Recently, Rieke and Chao[24] have reduced $AlCl_3$ with potassium to produce a highly active aluminum slurry intermixed with KCl. In hot xylene, this active aluminum consumed aryl halides rapidly to yield phenylaluminum sesquihalides (from 66 °C to reflux temperature).

---

(7) On a multiton 1 year basis, approximate costs of $10–30/pound have been estimated; private communications with P. L. Timms.

(8) Murdock, T. O., Ph.D. Thesis, 1977, University of North Dakota, Grand Forks, N. Dak., 58202.

(9) (a) Gilman, H.; Peterson, J. M. *Proc. Iowa Acad. Sci.* **1926**, *33*, 173. (b) Gilman, H.; Meyers, C. H. *J. Am. Chem. Soc.* **1923**, *45*, 159. (c) Shaw, M. C. *J. Appl. Mech.* **1948**, *15* (1), 37.

(10) (a) Gilman, H.; Peterson, J. M.; Schulze, F. *Recl. Trav. Chim. Pays-Bas* **1928**, *47*, 19. (b) Gladstone, J. H.; Tribe, A. *J. Chem. Soc.*, **1879**, *35*, 567. (c) LeGoff, E. *J. Org. Chem.* **1964**, *29*, 2048.

(11) (a) Gilman, H.; Kirby, R. H. *Recl. Trav. Chim. Pays-Bas* **1935**, *54*, 577. (b) Ashby, E. C.; Reed, R. *J. Org. Chem.* **1966**, *31*, 971. (c) Leigh, T. *Chem. Ind. (London)* **1965**, 426. (d) Marvel, C. S.; Whitford, R. G. *J. Org. Chem.* **1958**, *22*, 1658. (e) Ashby, E. C.; Yu, S. H.; Beach, R. G. *J. Am. Chem. Soc.* **1970**, *92*, 433.

(12) (a) Grignard, V. *C. R. Hebd. Seances Acad. Sci.* **1934**, *198*, 625. (b) Ramsden, H. E.; Leebrick, J. R.; Rosenberg, S. D.; Miller, E. H.; Walburn, J. J.; Balint, A. E.; Serr, R. C. *J. Org. Chem.* **1959**, *24*, 504. (c) Pearson, D. E.; Cowan, P.; Beckler, J. D. *J. Org. Chem.* **1959**, *24*, 504.

(13) (a) Rieke, R. D. *Acc. Chem. Res.* **1977**. *10*, 301. (b) Brown, C. A.; Brown, H. C. *J. Org. Chem.* **1966**, *31*, 3989. (c) Paul, R.; Buisson, P.; Joseph, N. *C. R. Hebd. Seances Acad. Sci.* **1951**, 627. (d) Brown, H. C.; Brown, C. A. *J. Am. Chem. Soc.* **1962**, *84*, 2827. (e) Paul, R.; Buisson, P.; Joseph, N. *Ind. Eng. Chem.* **1952**, *44*, 1006. (f) Brown, C. A.; Ahuja, V. K. *J. Org. Chem.* **1973**, *38*, 2226. (g) Eaborn, C.; Pant, D. C.; Peeling, E. R. A.; Taylor, S. C. *J. Chem. Soc. C*, **1969**, 2823. (h) Seaborg, G. T.; and Katz, J. J. "The Actinide Elements"; McGraw-Hill: New York, 1954. (i) Starks, D. F.; Streitwieser, Jr. *J. Am. Chem. Soc.* **1977**, *99*, 4833. (j) Lamprey, H.; Ripley, R. L. *J. Electrochem. Soc.* **1977**, *109*, 713. (k) Anderson, J. R. "Structure of Metallic Catalysts"; Academic Press: New York, 1975. (l) Ciapetta, F. G.; Plank, C. J. "Catalysis"; Emmett, P. H., Ed.; Reinhold: New York, 1954; Vol. 1, p 315.

(14) Klabunde, K. J.; Efner, H. F.; Satek, L.; Donley, W. *J. Organomet. Chem.* **1974**, *71*, 309.

(15) Murdock, T. O.; Klabunde, K. J. *J. Org. Chem.* **1976**, *41*, 1076.

(16) (a) Kimoto, K.; Kamiya, Y.; Nonoyama, M.; Uyeda, R. *Jpn. J. Appl. Phys.* **1963**, *2*, 702. *Chem. Abstr.* **1963**, *59*, 14965f. (b) Wada, N. *Jpn. J. Appl. Phys.* **1967**, *6*, 553. *Chem. Abstr.* **1967**, *67*, 5829u. (c) Maier, G. M. German Patent 1 458 174; *Chem. Abstr.* **1971**, *74*, P6052t. (d) National Research Corporation, British Patent 930 402; *Chem. Abstr.* **1964**, *60*, P14219a.

(17) (a) Schlecht, L.; Kippel, H. U.S. Patent 2 791 283; *Chem. Abstr.* **1957**, *51*, P11226f. (b) Suzuki, S.; Morita, U. Japanese Patent 2470 (A57); *Chem. Abstr.* **1958**, *52*, 8924f.

(18) (a) Klabunde, K. J. *Acc. Chem. Res.* **1975**, *8*, 393. (b) Klabunde, K. J. *CHEMTECH*. **1975**, Nov, 624.

(19) Klabunde, K. J.; Davis, S. C.; Hatorri, H.; Tanaka, Y. *J. Catal.* **1978**, *54*, 254.

(20) Baer, C. A. *Res. Dev. Ind.* **1974**, Feb, 51.

(21) (a) Mole, T.; Jeffrey, E. A. "Organoaluminum Compounds"; Elsevier: Amsterdam, 1972; p 11 and 63. (b) Ziegler, K.; Gellert, H. G.; Lehmkuhl, H.; Pfohl, W.; Zosel, K. *Justus Liebigs Ann. Chem.* **1960**, *629*, 14. (c) Coates, G. E.; Green, M. L. H.; and Wade, K. "Organometallic Compounds", 3rd ed.; Muthuen and Co.: London, 1967; Vol. 1, p 299.

(22) Wittenberg, D. *Justus Liebigs Ann. Chem.*, **1962**, *654*, 23.

(23) Mardykin, V. P.; Gaponik, P. N. *Izv. Vyssch. Ucheb. Zaved., Khim. Tekknol.* **1969**, *12*, 963. *Chem. Abstr.* **1970**, *72*, 3888 m.

(24) Rieke, R. D.; Chao, L. *Synth. React. Inorg. Met.-Org. Chem.* **1974**, *4*, 101.

Table I. Reaction of Aluminum Slurries with Aryl Halides

solvent	aryl halide	mmol of ArX	mg-atom of Al	reflux time, h	% yield based on $Ph_3Al_2X_3$[a]
toluene	C_6H_5I	6.5	1.9	4	95
toluene	C_6H_5Br	14.0	4.6	5	75
xylene	C_6H_5I	10.0	3.0	1	62
xylene	C_6H_5Br	5.5	1.8	5	39
hexane	C_6H_5I	42.0	14.0	4	24
hexane	C_6H_5Br	4.0	36.4	1	N.R.
diglyme	C_6H_5Br	50.0	13.5	23	5.8

[a] The reaction mixture was hydrolyzed with methanol, and the yield was determined by measuring the quantity of benzene present, using an internal GLC standard.

Skell and Wolf[25] have previously reported that aluminum atoms react with alkenes to form Al–C bonded species in a low-temperature (77 K) matrix. Alkyl halides also reacted with aluminum atoms to yield sesquihalides.[26] This, of course, is not surprising since nonactivated bulk aluminum metal reacts readily with *alkyl* halides. A better test of high activity is with aryl halides, in particular, chlorobenzene. And, indeed, we have found that both chlorobenzene and bromobenzene reacted with aluminum atoms to give the expected sesquihalides. However, our primary interest was in learning if storable, active-aluminum slurries could be prepared by metal-vaporization procedures.

Results and Discussion (Al). Cocondensation of aluminum vapor with toluene or xylene at 77 K yielded a dark green matrix, apparently due to a π-arene–Al complex,[18] which is stable only at low temperature. On warmup, the matrix darkened and, subsequently, melted to form a brown-black to black, finely-divided aluminum slurry. Similarly, codeposition of aluminum vapor with hexane yielded a black matrix that also allowed the formation of a fine slurry. These slurries were extremely pyrophoric in air and were handled by syringe.

Addition of halobenzenes to the slurries followed by reflux for 1 to 5 h produced high yields of organoaluminum halides.

$$Al^*/\text{solvent} + 3C_6H_5X \rightarrow (C_6H_5)_xAlX_{3-x}$$

The toluene and xylene slurries were found to be the most active, and the metal particles were finer than those formed in hexane. However, the Al–hexane slurry still possessed higher activity than normal Al powder. Finer Ni slurries have also been found with toluene as solvent rather than hexane.[27]

Aluminum slurries could not be prepared in diglyme or other ethereal solvents due to extensive reductive cleavage of the solvent by the aluminum atoms and particles. Aluminum oxide and various hydrocarbon fragments were obtained from these codepositions. A complete study of these processes has been made and will be reported soon.[28]

In addition to aryl halides, the Al/toluene slurry was allowed to react with diphenylmercury. Triphenylaluminum was formed in 54% yield in 3 h. In contrast, much longer reaction times are required for unactivated aluminum chips,[9]

$$Al^*/\text{toluene} + (C_6H_5)_2Hg \rightarrow (C_6H_5)_3Al + Hg \quad (4)$$

and this reaction is not possible with active aluminum prepared by reduction of $AlCl_3$ with potassium due to the formation of KCl, which complexes with triphenylaluminum.[24,29]

Storage of the aluminum slurries as dry powders under nitrogen for several months did not adversely affect their activities.

Table II. Reaction of Indium Slurries with Ethyl Iodide

solvent	mmol of RI	mg-atom of In	reflux time, h[a]	% yield of Et_2InI, $EtInI_2$
diglyme	20.0	6.2	21	64
dioxane	20.0	3.7	19	41
xylene	20.0	5.9	24	10
THF	10.0	6.3	2	9

[a] All reactions were carried out in the metal atom reactor with reflux, under reduced pressure.

Activated Indium

Only under extreme conditions will bulk indium metal react with organic halides. Spencer and Wallace[30] reported that iodobenzene reacted with indium metal during 15 h of reflux at 250 °C. More active halides, such as iodopentafluorobenzene (which yielded tris(pentafluorophenyl)indium)[31] and alkyl iodides and bromides (which yielded R_2InX and $RInX_2$),[32] also have been examined. Rieke[13a] has employed the potassium reduction procedure in boiling xylene for conversion of $InCl_3$ to active indium powder and was able to obtain quantitative yields of R_2InI and $(C_6H_5)_2InI$ at 80–150 °C by reaction of RX and C_6H_5I with this very active form of indium.

Results and Discussion (In). Indium is vaporized readily, and so it is quite easy to prepare large amounts of active indium slurries by this metal atom–solvent cocondensation procedure. A wide range of solvents was found amendable to study since, in the case of indium, ethereal solvents also could be employed. The activities of the slurries prepared in diglyme, dioxane, xylene, and tetrahydrofuran are compared in Table II. Note that the yields were highest when high-boiling, polar solvents were employed.

$$2In^*/\text{solvent} + (C_2H_5)_2InI + C_2H_5InI_2 + \text{In salts}$$

However, both polar and nonpolar solvents have been used. Our products were found to be mixtures of R_2InI, $RInI_2$, and InI, which is in agreement with Gynane, Waterworth, and Worrall.[32]

The indium/solvent frozen matrices initially melted forming finely-divided, black slurries. However, various degrees of particle sintering or agglomeration occurred on

---

(25) Skell, P. S.; Wolf, L. R. *J. Am. Chem. Soc.* **1972**, *94*, 7919.

(26) McGlinchey, M. J.; Skell, P. S. "Cryochemistry"; Moskovits, M.; Ozin, G., Eds.; Wiley-Interscience: New York, 1976; p 158.

(27) Klabunde, K. J.; Efner, H. E.; Murdock, T. O.; Ropple, R., *J. Am. Chem. Soc.* **1976**, *98*, 1021.

(28) Klabunde, K. J.; Murdock, T. O. *J. Org. Chem.*, to be submitted.

(29) Laubengayer, A. W.; Wade, K.; Lengnick, G. *Inorg. Chem.* **1962**, *1*, 632, discussion of adducts of triphenylalane.

(30) Spencer, J. F.; Wallace, M. L. *J. Chem. Soc.* **1908**, *93*, 1827.

(31) Deacon, G. B.; Parrot, J. C. *Aust. J. Chem.* **1971**, *24*, 1771.

(32) Gynane, M. J. S.; Waterworth, L. G.; Worrall, I. J. *J. Organomet. Chem.* **1972**, *40*, C9. **1972** *43*, 257.

Table III. Simmons-Smith Reaction, Using Active Zinc Slurries

solvent	halide	mg-atom of Zn	mmol of CH_2X_2	mmol of c-C_6H_{10}	reflux time, h	% yield of norcarane
diglyme	CH_2Br_2	86	220	150	2	24
dioxane	CH_2Br_2	21	220	150	2	18
THF	CH_2Br_2	78	90	80	2.5	4.6
hexane	CH_2Br_2	76	90	80	4	0.2

Table IV. Attempted Activation of Cadmium Slurries with Salts and Supports

solvent	mg-atoms of Cd	support	mol of support	reflux time, h	% yield of Pr-CdX[a]
diglyme	120	none		13	10
diglyme	31	KI	80	20	98
diglyme	28	KI	0.7	23	6
diglyme	25	KCl	90	22	5
diglyme	37	Al_2O_3[b]	50	19	8
THF	23	KI	40	16	13

[a] 0.04 mol of *n*-PrBr. [b] A high surface area γ-Al_2O_3 calcined prior to use.

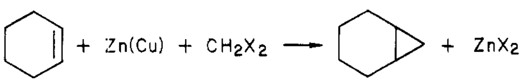
warming to room temperature, which seemed to be dependent on the nature of the solvent. Severe particle agglomeration occurred with the In/xylene and In/THF systems. The In/THF slurry was initially black and finely divided, but on slow warming to room temperature a smooth shiny piece of indium sponge formed. This sintering phenomenon was not a problem in the diglyme or dioxane systems, which seems to be reflected in their superior reactivities.

Activated Zinc

Earlier we reported on the reactions of zinc atoms with perfluoroalkyl iodides[33] and on the preparation of active zinc slurries by the metal atom method.[15] These versatile slurries were used for the facile preparation of dialkylzinc compounds in quantitative yield.[15] An example of particular relevance is the preparation of pure $(CH_3)_2Zn$ in hexane solvent that can be freed of zinc salts simply by distillation. Ethereal, aromatic, and alkane solvents were all successfully employed.

$$Zn^*/\text{hexane} + CH_3I \rightarrow \underset{\substack{\text{distilled off}\\ \text{with hexane}}}{(CH_3)_2Zn} + ZnI_2$$

It was noted[18] that Rieke, Uhm, and Hudnall[34] also have prepared extremely active zinc slurries by their potassium reduction method. Since zinc is so readily vaporized in large amounts, and since we find that our resulting zinc slurries are storable as dry powders for up to seven months without diminishing activity, we considered it worthwhile to find additional uses for these materials. We report here application of these slurries in Simmons–Smith chemistry (cyclopropanation of olefins, using CH_2X_2–Zn).[35]



Results and Discussion (Zn). Active zinc slurries were prepared in diglyme, dioxane, THF, and hexane. The slurries were removed from the reactor by syringe and then treated with CH_2Br_2 and cyclohexane with short reflux times. Table III summarizes the results which were quite reproducible. The cyclopropanation did not occur in very good yield, but note that CH_2Br_2 could be used. The entire procedure is carried out in the absence of any hydroxylic solvents, acids, or oxygen (no metal washings are necessary).

Activated Cadmium

Our earlier work on cadmium slurries[15] has been extended to elaborate the preparation of nonsolvated RCdI species. This was a desirable extension in view of the work of others which had suggested that the direct reaction of cadmium metal with alkyl halides required the presence of very polar solvents such as Me_2SO, DMF, or HMPA (hexamethylphosphoric triamide).[36] Alternatively, a different approach was used in an attempt to prepare RCdI, which involved the reaction between Et_2Cd and CdI_2 in ether, and Sheverdina and co-workers[37] isolated EtCdI in Me_2SO and other solvents. Also of current interest in this regard is the recent report of Habeeb, Osman, and Tuck on the electrochemical synthesis of RCdX species.[38] This interesting paper reported the preparation of a series of ligand-stabilized RCdX(L–L) species, but nonligand-stabilized CH_3CdI could not be isolated.[38]

We have noted that our active cadmium slurries reacted with alkyl iodides in any solvent, polar or nonpolar, to yield RCdI (not R_2M as with zinc).

$$Cd^*/\text{solvent} + C_2H_5I \rightarrow C_2H_5CdI$$

solvent = hexane, toluene, THF, or dioxane

Results and Discussion (Cd). Usually 5–10 g of cadmium was vaporized and converted to slurry per experiment. Addition of ethyl iodide to the slurry was followed by reflux for several hours. In each solvent (hexane, toluene, THF, or dioxane), EtCdI was formed. In the ethereal solvents, the product remained in solution due to solvation, whereas in the hydrocarbon solvents white, nonsolvated EtCdI precipitated.[39] This compound could be taken up (solvated) in THF or acetone for filtration and spectral studies.

The cadmium slurries which were prepared were stable on storage as dry powders. For example, a seven month old Cd/toluene powder reacted with EtI to yield EtCdI in 67% yield, compared with 55% for a fresh sample under identical conditions.

Cadmium slurries did not react vigorously with alkyl bromides. In diglyme, only a 10% yield of alkylcadmium

---

(33) Klabunde, K. J.; Key, M. S.; Low, J. Y. F. *J. Am. Chem. Soc.* **1972**, *94*, 999.

(34) Rieke, R. D.; Uhm, S. J.; Hudnall, P. M. *J. Chem. Soc., Chem. Commun.* **1973**, 269.

(35) Simmons, H. E.; Smith, R. D. *J. Am. Chem. Soc.* **1959**, *81*, 4256.

(36) (a) Chenault, J.; Tatibouet, F. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1967**, *264*, 213. Also **1966**, *266*, 499. *Chem. Abstr.* **1967**, *67*, 32758c. **1966**, *64*, 17632c. (b) Gaudemar, M. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1969**, *268*, 1439.

(37) (a) Sheverdina, N. I.; Paleeya, I. E.; Delinshaya, E. D.; and Kocheshkov, K. A. *Dokl. Akad. Nauk SSSR* **1959**, *125*, 1959 348. (b) Radionov, A. N.; Paleeva, I. E.; Shigorin, D. N.; Sheverdina, N. I.; Kocheshkov, K. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1967**, 1031. *Chem. Abstr.* **1967**, *67*, 63634p. (c) Paleeva, I. E.; Sheverdina, N. I.; Kocheshkov, K. A. *Izv. Akad. Nauk SSSR Ser. Khim.* **1967** 1263. *Chem. Abstr.* **1968**, *68*, 22031s. (d) Radionov, A. N.; Paleeva, I. E.; Shigorin, D. N.; Sheverdina, N. I.; Kocheshkov, K. A. *Izv. Akad. Nauk, SSSR, Ser. Khim.* **1967**, 1031. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1967**, 996.

(38) Habeeb, J. J.; Osman, A.; Tuck, D. G. *J. Chem. Soc., Chem. Commun.* **1976**, 379.

(39) See ref 4, p 78.

Table V. Reaction of Tin Slurries with Methyl Iodide

solvent	mmol of tin	RX[a]	reflux time, h	% of $MeSnI_3$	% of Me_2SnI_2	% of Me_3SnI	% yield of organotin compds	% yield of SnI_4
toluene	4.27	MeI	16	71.7	21.5	6.8	51	14
dioxane	3.32	MeI	21	41.9	48.8	9.3	35	4
THF	8.74	MeI	20	16.3	40.8	42.9	28	12
hexane	5.72	MeI	22	trace	74.9	25.1	8	13

[a] 50 mmol of methyl iodide.

bromide was obtained with *n*-propyl bromide on overnight reflux. Other solvents such as *p*-dioxane, THF, toluene, and hexane allowed yields of only 1–3%.

Recalling previous work of Rieke and co-workers,[13a,40] demonstrating increased activity of magnesium slurries by addition of salts such as potassium iodide, we believed it would be worthwhile trying to further activate our cadmium slurries in a similar way. We considered that the high activity realized in some of the Rieke work is probably due to the high dispersion of the small particles on the crystals of KCl or KI. Thus, we prepared our slurries in the presence of excesses of supports such as KCl, KI, and high-surface Al_2O_3. The fine Cd–diglyme or THF dispersions were allowed to melt down onto varying amounts of support, and then the activity of the resultant cadmium slurry was tested by reaction with *n*-propyl bromide. Table IV summarizes our findings. Large amounts of KI dramatically increased the *n*-PrCdX yield. If this were due simply to higher dispersion of the Cd due to the KI surface, then other supports should work as well. However, KCl and Al_2O_3 did not enhance the Cd-slurry activity. Neither did a catalytic amount of KI enhance activity. Thus, we suspected that an S_N2 process, whereby the more reactive *n*-PrI was formed from *n*-PrBr and KI prior to reaction to form *n*-PrCdI, was occurring. Indeed, a control experiment showed that under the reaction conditions in the absence of cadmium, *n*-PrI formation was complete in 1 h.

Activated Tin

A variety of reports can be found in the chemical literature dealing with the direct reaction between alkyl iodides and metallic tin under special conditions. For example, alkyl iodides and tin metal have been heated in a sealed tube at 130–180 °C for 35 h to yield R_2SnI_2.[41] Smith and Rochow have prepared dimethyltin dichloride by passing gaseous methyl chloride through molten tin.[42] Matsuda and co-workers have published several articles which describe the preparation of alkyltin halides (Cl, Br, and I) by the reaction of tin metal with alkyl halides in the presence of various catalysts.[43–46] A catalytic amount of the corresponding alkyl alcohol (5%) and magnesium metal (<1%) were also added to the reaction mixture. Sisido and co-workers have prepared alkyl- and benzyltin halides in refluxing toluene in the presence of catalytic amounts of $HgCl_2$ and various amines.[47–49] A mixture of alkyltin halides was obtained when powdered tin, methyl bromide, and methanol were heated for 72 h in an autoclave at 700 °C and 79 atm of pressure.[50] Oakes and Hutton have prepared dibutyl- and dioctyltin iodides from the alkyl iodide, metallic tin, lithium or LiCl, and a high-boiling, polar solvent such as 2-ethoxyethanol, DMF, or butyl acetate.[51,52] However, use of a lower boiling solvent such as THF or *p*-dioxane gave no products under these conditions. A recent report described the direct reaction between organic halides and metallic tin in hexamethylphosphoric triamide, using cuprous iodide as a catalyst.[53] It is interesting to note that in order to facilitate the reaction between metallic tin and alkyl halides one or more of the following conditions must be met: (a) long reaction times, (b) polar solvent media, (c) high temperature, or (d) the presence of a catalyst.

Results and Discussion (Sn). Tin vapor cocondensed with excess toluene, THF, *p*-dioxane, diglyme, or hexane yielded tin slurries of varying activity in reactions with alkyl iodides. The tin slurries were initially black and very finely divided, but on further warming and stirring considerable particle agglomeration occurred. Only the tin/diglyme slurry remained fine enough that it could be removed from the reactor by means of a syringe and a long Teflon needle. The slurries were transferred under nitrogen to a 250-mL round-bottom flask equipped with a reflux condenser, magnetic spin bar, and an inert gas inlet. Methyl iodide (0.05 mol) was added to the tin slurry, and the reaction mixture was heated to reflux overnight to complete reaction. The reaction mixture was cooled to room temperature and filtered to remove unreacted tin and tin(IV) iodide. Most of the organic solvent was then removed by cryogenically pumping it into a liquid N_2 trap. The remaining methyltin iodide compounds were dissolved in CCl_4, and a weighed amount of acetonitrile (CH_3CN) was added to the solution as an internal standard for a nuclear magnetic resonance experiment. The NMR experiment indicated the presence of Me_3SnI (~1.0 ppm), Me_2SnI_2 (~1.7 ppm), and $MeSnI_3$ (~2.5 ppm) relative to Me_4Si.[54,55] Tetramethyltin was not observed in any of the reaction mixtures. The molar quantities of methyltin iodide compounds were determined by comparison of the peak area relative to the peak area of the acetonitrile. The results of the reaction between various tin slurries and methyl iodide are illustrated in Table V. Note that different solvents caused differences in the ratios of $MeSnI_3$ to Me_2SnI_2 to Me_3SnI. No sensible trends are evident, except perhaps that the higher boiling toluene allowed a higher total yield with $MeSnI_3$ favored.

Even higher yields of Me_xSnI_{4-x} could be obtained in less time when Sn/diglyme slurries were employed. However,

---

(40) Rieke, R. D. *Top. Curr. Chem.* **1975**, *59*, 1.

(41) Karantassis, T.; Basileiadon, K. *C. R. Hebd. Seances Acad. Sci.* **1937**, *205*, 460. *Chem. Abstr.* **1937**, *31*, 8505.

(42) Smith, A. C.; Rochow, E. G. *J. Am. Chem. Soc.* **1953**, *75*, 4103.

(43) Matsuda, H.; Matsuda, S. *Kogyo Kagaku Zasshi* **1960**, *63*, 1958. *Chem. Abstr.* **1961**, *56*, 7342c.

(44) Matsuda, S.; Matsuda, H.; Nakamura, M. *Kogyo Kagaku Zasshi* **1961**, *64*, 1948. *Chem. Abstr.* **1962**, *57*, 2239i.

(45) Matsuda, S.; Matsuda, H.; and Hayashi, J. *Kogyo Kagaku Zasshi* **1961**, *64*, 1951. *Chem. Abstr.* **1962**, *57*, 2240a.

(46) Matsuda, S.; Matsuda, H. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 208.

(47) Sisido, K.; Takeda, Y. *J. Org. Chem.* **1961**, *26*, 2301.

(48) Sisido, K.; Takeda, Y.; Kinugawa, Z. *J. Am. Chem. Soc.* **1961**, *83*, 538.

(49) Sisido, K.; Takeda, Y.; Nozaki, H. *J. Org. Chem.* **1962**, *27*, 2411.

(50) Irmacher, R.; Knoephe, W.; Kunze, H. German Patent 1 050 336; *Chem. Abstr.* **1961**, *55*, 2485b.

(51) Oakes, V.; Hutton, R. E. *J. Organomet. Chem.* **1965**, *3*, 472.

(52) Oakes, V.; Hutton, R. E. *J. Organomet. Chem.* **1966**, *6*, 133.

(53) Fostein, P.; Pommier, J. C. *J. Organomet. Chem.* **1976**, *114*, C7.

(54) Grant, D.; Van Wazer, J. R. *J. Organomet. Chem.* **1965**, *4*, 229.

(55) van den Berghe, E. V.; van der Kelen, G. P. *J. Organomet. Chem.* **1966**, *6*, 522.

Table VI. Reaction of Alkyl halides with Nickel/THF Slurries

mmol of Ni	RX	reflux time, h	% of ethene	% of ethane	% of propene	% of propane	% of *cis*-2-butene	% of *trans*-2-butene	% of 1-butene	% of butane	overall yield, %
17.5	EtI	18	38.0	62.0							24
28.9	CH_2I_2	7	100.0								52
14.3	*n*-PrBr	20			31.0	69.0					22
17.3	*i*-PrI	24			34.0	66.0					26
7.3	*n*-BuBr	20					4.4	5.0	21.6	69.0	30
19.2	2-BuBr	20					11.5	9.1	12.7	66.7	19

the presence of this high-boiling solvent made isolation of the organotin compounds very difficult, and for this reason toluene is the preferred solvent.

Thus, active tin slurries in a variety of common solvents can be prepared by the metal vapor–solvent vapor codeposition method. Addition of activating agents or use of extremely high-boiling polar solvents is not necessary.

Activated Lead

Although the reaction of organic halides with Pb–Na alloy is well known, we have found no reports describing the reaction of normal alkyl halides with active Pb in the absence of Na. Closely related studies have been reported by Gilman and Jones where tetramethyllead was prepared from PbI_2:[56]

$$3CH_3Li + PbI_2 + CH_3I \rightarrow (CH_3)_4Pb + 3LiI$$

Tetraethyllead has been prepared from powdered lead and ethylene in 250 atm of H_2[57] in 1–3% yields. Similarly, low yields of tetrabenzyllead have been prepared by reducing the particle size of lead partially in a vibrating mill in the presence of benzyl chloride.[58]

We have prepared active Pb slurries in diglyme and dioxane and have allowed them to react with CH_3I. Trimethyllead iodide was formed in ca. 10% yield. It is possible that $(CH_3)_2PbI_2$ is an intermediate, as this compound would be expected to disproportionate:[59]

$$(CH_3)_2PbI_2 \rightarrow (CH_3)_3PbI + PbI_2 + CH_3I$$

Other iodides also reacted with the active Pb slurries. For example, CF_3I reacted rapidly, yielding an unstable (and as yet uncharacterized) $(CF_3)_xPb(I)_{4-x}$ species.

Activated Nickel

We have reported previously on the preparation of highly active Ni catalysts, using metal vapor–solvent vapor codeposition techniques.[1,19,27] Also, we have reported on the efficient low-temperature *reaction* of the small Ni clusters with solvents, particularly alkanes, to yield "pseudoorganometallic" powders.[3]

Herein we report that these "pseudoorganometallic" powders are very active in reactions with some alkyl halides. In this regard, extremely active Ni/THF slurries have been prepared by the codeposition of nickel vapor and THF. Initially, a light yellow Ni–THF etherate was formed (−196 °C), and on warming a very fine black slurry resulted, which could be readily handled by syringe.

The Ni/THF slurry was allowed to react with alkyl and aryl halides while under gentle reflux under reduced pressure (40–50 °C). The products that resulted were generally gaseous alkenes and alkanes, resulting from radical-like reactions and/or reactions of intermediate "RNiX" species. Table VI summarizes some of these results. No radical coupling products were formed, but instead reduction to alkane was favored. This finding indicates that if "RNiX" is formed, it probably decomposes in a radical-like process, and R· picks up hydrogen readily from the excess ethereal solvents present. β-Hydride elimination from "RNiX" does not seem as likely, since more alkene formation would be expected.

In the CH_2I_2 reaction, the exclusive formation of C_2H_4 is very interesting. Apparently species such as "CH_2INiI" are stable enough that two such molecules can come together to yield C_2H_4 and $2NiI_2$.

Benzyl chloride reacted with the Ni/THF slurry to yield mainly the coupling product, bibenzyl (88% of total; 42% overall yield based on Ni vaporized), and only 12% of toluene. In a similar way, allyl bromide reacted vigorously in only 10 min at 25 °C to yield considerable portions of hexadienes (50%) and propene (50%).

Unfortunately, high yields of coupling products did not result from the reaction of the Ni/THF slurry with aryl halides, such as iodobenzene, where an overall 8% yield of biphenyl resulted.

The results of these Ni/THF studies indicate that the most active halides are those that would be expected to form more stabilized RNiX species, such as those with allyl, benzyl, and CH_2X_2 halides. Also, the product analyses show that coupling products (R–R) are only observed for these more stabilized systems, which suggests that stabilized RNiX (R = allyl, benzyl, and CH_2X) live long enough under the reaction conditions that intermolecular interactions can occur. In contrast, the presumed unstabilized RNiX (R = CH_3, Et, and Pr) yield no coupling products and mainly RH, which is probably formed by H abstraction from solvent.

Conclusions

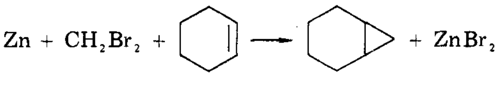
Active metal slurries of Al, In, Zn, Cd, Sn, Pb, and Ni can be prepared in a variety of solvents, polar and nonpolar, by cocondensation of metal vapors with organic solvents followed by warming to room temperature. Many of the resulting fine slurries can be manipulated by syringe. For the low-boiling metals Zn, Cd, Sn, and Pb, relatively large amounts (~10 g of metal) can be readily prepared, and much larger amounts could be prepared without anticipated difficulty. In all cases tested, the active metal powders prepared by vacuum removal of solvent are stable to long-term storage under nitrogen.

The reactions of these active slurries with alkyl and aryl halides are summarized:

$$Al + ArX \rightarrow Ar_2AlX + ArAlX_2$$

$$In + RI \rightarrow R_2InI + RInI_2 + InI$$

$$Zn + RX \rightarrow R_2Zn + 2nX_2$$



$$Cd + RI \rightarrow RCdI$$

---

[56] Gilman, H.; Jones, R. E. *J. Am. Chem. Soc.* **1950**, *72*, 1760.

[57] Malatesta, A. U.S. Patent 3045035; *Chem. Abstr.* **1962**, *57*, 166566.

[58] Grohn, H.; Paudert, R. *Z. Chem.* **1963**, *3*, 89. *Chem. Abstr.* **1963**, *59*, 7549b.

[59] Greninger, D.; Kollonitsch, V.; Kline, C. H. "Lead Chemicals"; International Lead Zinc Research Organization, Inc., New York, 1975.

$$\mathrm{Sn} + \mathrm{RX} \rightarrow \mathrm{R_3SnX} + \mathrm{R_2SnX_2} + \mathrm{RSnX_3}$$

$$\mathrm{Pb} + \mathrm{RI} \rightarrow \mathrm{R_3PbI}$$

$$\mathrm{Ni} + \mathrm{RX} \rightarrow \mathrm{R{-}R} + \mathrm{RH} + \text{alkene}$$

Experimental Section

The metal slurries were produced by codeposition of metal vapors (atoms) and an excess of solvent on the wall of a metal atom reactor at -196 °C, followed by warming. Aluminum was vaporized from tungsten or tantalum boats or tungsten baskets with graphite insert crucibles, and indium was vaporized from an aluminum oxide coated tungsten wire crucible. Zn, Cd, Sn, Pb, and Ni were vaporized from alumina crucibles with external tungsten basket heaters. Metal atom reactors or vapor synthesis reactors are commercially available from Kontes-Martin Glass Co., Vineland, N. J. Several reviews have also been published on metal vapor chemistry,[6,60] and our simple apparatus has been described previously.[4] Solvents employed were freshly distilled toluene and hexane from benzophenone ketyl under nitrogen, THF and *p*-dioxane from sodium wire, and diglyme from lithium aluminum hydride (under vacuum). All were freeze–thaw degassed just prior to use.

All yields are based simply on g-atoms of metal vaporized regardless of reaction stoichiometry.

Aluminum slurries are prepared by the cocondensation of aluminum vapor (>0.1 g) and about 50 mL of solvent (toluene, xylene, or hexane) at -196 °C. A dark-green frozen matrix was obtained for toluene and xylene, while hexane gave a black matrix. The matrices were allowed to melt and warm to room temperature, which resulted in the formation of finely divided, black, aluminum slurries. The slurries were transferred under dry nitrogen by syringe and a long Teflon needle to a 250-mL round-bottomed flask equipped with a condenser, magnetic spin bar, and an inert gas inlet. (Caution: Aluminum slurries and metal slurries in general are extremely pyrophoric). The aryl halide (3ArX–Al) was added to the flask by syringe, and the reaction mixture was heated at reflux for a period of 1–48 h, depending on the slurry and the aryl halide. After reaction, the phenylaluminum sesquihalide yields generally were determined by hydrolysis by addition of about 5 mL of methanol to the crude reaction mixture. The hydrolyzed reaction mixture was filtered, a weighed amount of cyclohexane was added as an internal GLC standard, and GLC studies were carried out. The presence of the hydrolysis product, benzene, prior to hydrolysis was generally not considered a problem, as similar yield results were obtained if volatiles were removed prior to hydrolysis.

Indium slurries were produced by the cocondensation of indium vapor (>0.5 g) and about 60 mL of solvent at -196 °C. Brightly colored matrices were formed (diglyme, bright yellow; *p*-dioxane, red-brown; and THF, brown), indicating the presence of indium etherates stable only at low temperature. Ethyl iodide was condensed into the reactor, and the matrix was then allowed to melt and warm to room temperature, initially forming a black, finely-divided, indium slurry. Considerable particle agglomeration occurred on stirring at room temperature for about 10 min, thus exposing a smaller metal surface to the organic halide. The reaction mixtures were heated to reflux for about 18 h, at which time the ethylindium iodides were hydrolyzed by the addition of 5 mL of 6 M HCl. The ethane was isolated by fractional condensation through a series of cold traps at -77, -116, and -196 °C, and the amount of ethane was determined by a simple PVT measurement and GLC measurements.

Alternatively, the alkylindium iodides could be isolated. An example with CH_3I is given below.

Indium vapor, 0.5784 g (5.04 mg-atom), was cocondensed with 50 mL of dioxane during a 45 min reaction (2.4 V; 50 A) to produce a yellow-brown matrix. Then 2 mL (32 mmol) of CH_3I was condensed into the reactor and the matrix allowed to melt to a black slurry which was refluxed for 20 h. The solution had a small amount of red brown precipitate which was filtered and dried, under nitrogen. The solid material appears to be a mixture of InI and In. The dioxane was removed from the filtrate, leaving 1.22 g of a white-light purple solid. NMR studies of this solid in $CDCl_3$ showed 19% dioxane (singlet at 3.8 ppm), 45% CH_3InI_2 (singlet at 0.9 ppm [lit = 1.1 ppm in CH_2Cl_2]),[32] and 36% $(CH_3)_2InI$ (singlet at 0.75 ppm) in $CDCl_3$. The yields were corrected for dioxane content. Based on In vaporized, they were: CH_3InI_2, 28%; and $(CH_3)_2InI$, 32%. Heating of the $(CH_3)_2InI$–dioxane material in the mass spectrometer yielded first dioxane evolution and then a clean mass spectrum, clearly showing the expected parent ions for both In compounds (largest peaks in the spectrum).

Zinc slurries were prepared by the codeposition of zinc vapor (~8 g) and about 50 mL of solvent in about 1 h (diglyme, *p*-dioxane, THF, or hexane). With ether solvents, yellow, brown, and black matrices, which turned black upon melt-down and slurry formation, were initially observed. With hexane, the matrix initially was black. The zinc slurries were transferred to conventional glassware under a fast flow of nitrogen, and cyclohexene and CH_2X_2 (X = Br or I) were added dropwise over a 15 min period, while the reaction mixture was heated and stirred. The mixture was refluxed for several hours (cf. Table II) and cooled; volatiles were removed under vacuum and trapped at -196 °C. This fraction was analyzed by GLC for norcarane on a 5 ft × 0.25 in. 25% Carbowax 550 column at 90 °C.

Cadmium slurries were prepared by codeposition of cadmium vapor (~7 g) with about 50 mL of solvent in about 1 h (diglyme, *p*-dioxane, THF, toluene, or hexane). Brown to black matrices, which turned black on melt-down, were initially formed. The slurry was again cooled to -196 °C and 7.8 g of C_2H_5I (0.05 mol) distilled in. The upper portion of the reactor was wrapped with 3–4 turns of Tygon tubing with water flowing through it, which served as a means of condensing the solvent and EtI vapors. The slurry was refluxed overnight. With toluene as solvent, a colorless solution and white precipitate were formed (Cd completely consumed). Removal of toluene and other volatiles under vacuum left yellow-white crude EtCdI. The volatile fractions contained about 3% $(C_2H_5)_2Cd$, as determined by hydrolysis with 10% HCl. The nonvolatile EtCdI was removed by washing with dry degassed THF (several 10-mL portions). The combined fractions were filtered under nitrogen, and solvent was removed under vacuum until some solid separated. At this point, the solution was cooled at -10 °C overnight. A 50% yield of EtCdI (THF solvated) was realized in this way, as determined by isolating it, drying it under vacuum, and weighing it in a Vacuum Atmospheres inert atmosphere box. Hydrolyses of the solid with 10% HCl–H_2O yielded 1 mol of ethane/mol of EtCdI, as identified by GLC, MS, and IR.

Nonsolvated ethylcadmium iodide is a white, nonvolatile solid that is insoluble in pentane, toluene, or chloroform but quite soluble in THF and acetone. It is very air-sensitive. In a sealed ampule, it darkens slightly at 145 °C and decomposes at 160–170 °C: NMR [$(CD_3)_2CO$] δ 1.00 (triplet, area 3), 0.50 (quartet, area 2, $J_{CH_3-CH_2}$ = 6.9 Hz).

Tin slurries were prepared by the codeposition of tin vapor (~0.5 g) with about 50 mL of solvent in about 1 h. The colors of the matrices varied as those of toluene (yellow), dioxane (brown-black), THF (black), and hexane (black). On warming the solution, finely divided black slurries were formed that were transferred under fast N_2 flush to a 100 mL one-necked round-bottom flask equipped with a condenser, magnetic spin bar, and inert gas inlet. Methyl iodide (50 mmol) was added via syringe and the reaction mixture heated to reflux for 21 h. All of the metal was consumed, and a yellow precipitate was formed (SnI_4). The reaction mixture was filtered to remove SnI_4, the toluene was evaporated under vacuum, the resultant viscous liquid ($(CH_3)_xSnI_{4-x}$) was dissolved in 25 mL of CCl_4, and a weighed amount of CH_3CN was added to the solution as an NMR standard. An NMR spectrum[54,55] of the solution revealed the presence of singlet resonances for CH_3SnI_3 (δ 2.30, 72%), $(CH_3)_2SnI_2$ (δ 1.56, 22%), and $(CH_3)_3SnI$ (δ 0.82, 7%) for an overall yield of 51% of organotin compounds based on the amount of tin vaporized. A 14% yield of SnI_4 was also isolated.

Lead slurries were prepared as described for Sn slurries, although about 5 g of lead with 50 mL of solvent was codeposited. The solvents employed were diglyme or THF. Addition of 50 mmol of CH_3I followed by reflux for 24 h under N_2 yielded a yellow precipitate mixed with unreacted lead. Vacuum distillation of volatile products yielded a fraction that was a mixture of solvent

---

[60] Timms, P. L. In "Cryochemistry"; Moskovits, M.; Ozin, G., Eds.; Wiley-Interscience: New York, 1976.

and a small amount (~10%) of $(CH_3)_3$ PbI, as shown by mass studies showing the expected isotope pattern. For the 208 isotope: *m*/*e* 380, $(CH_3)_3$PbI; *m*/*e* 65, $(CH_3)_2$PbI; *m*/*e* 350, CH_3PbI; *m*/*e* 253, PbI; *m*/*e* 223, CH_3Pb; and *m*/*e* 208, Pb.

Nickel slurries were prepared as described for tin slurries, except that ~1 g of Ni was codeposited with about 60 mL of solvent in about 1 h. The colors of the matrices were: toluene (red-brown), THF (yellow), and hexane (black). Generally, THF was employed as the slurry solvent, the resultant very fine black slurry was transferred by syringe to a three-necked round-bottom flask equipped with a reflux condenser, addition funnel, stirring bar, and N_2 bubbler, and about 40 mmol of alkyl halide were slowly added (15 min) followed by reflux for about 20 h. The volatile products formed (no stable organometallics were isolable) were fractionated by trap-to-trap distillation through cold traps at −77, −116, and −196 °C. The gases were analyzed by PV measurements and GLC techniques.

When less volatile products were being analyzed, no trap-to-trap distillation was carried out. The reaction mixture was simply filtered and GLC analyses carried out. For example, biphenyl and bibenzyl were analyzed on a 5 ft × 0.25 in. SE-30 column at 170 °C (bibenzyl was used as an internal standard when biphenyl was being analyzed and vice versa).

Acknowledgment. We gratefully acknowledge the National Science Foundation (CHE-7402713) for generous support and Thomas Groshens for experimental assistance.

Registry No. Aluminum, 7429-90-5; indium, 7440-74-6; zinc, 7440-66-6; cadmium, 7440-43-9; tin, 7440-31-5; lead, 7439-92-1; nickel, 7440-02-0; phenyl iodide, 591-50-4; phenyl bromide, 108-86-1; ethyl iodide, 75-03-6; diethyliodoindium, 31145-95-6; ethyldiiodoindium, 37865-57-9; methyl iodide, 74-88-4; iododimethylindium, 14799-83-8; diiodomethylindium, 37865-56-8; methyl dibromide, 74-95-3; methyl diiodide, 75-11-6; diethylcadmium, 592-02-9; ethyliodocadmium, 17068-35-8; triiodomethyltin, 3236-97-3; diiododimethyltin, 2767-49-9; iodotrimethyltin, 811-73-4; tetraiodotin, 7790-47-8; iodotrimethyllead, 17546-36-0; propyl bromide, 106-94-5; isopropyl bromide, 75-30-9; butyl bromide, 109-65-9; 2-bromobutane, 78-76-2.

Orbital Interactions. 5. Through-Space Effects of Substituents on the Reactivity of a Double Bond toward Diels–Alder and Epoxidation Reactions[1]

Michael N. Paddon-Row,*[2a] Harish K. Patney,[2a,c] and Ronald N. Warrener[2b]

Chemistry Departments, New South Wales Institute of Technology, Broadway, N.S.W. 2007, Australia, and Australian National University, Canberra, A.C.T. 2600, Australia

Received January 3, 1979

A series of 9-substituted octahydrodimethanonaphthalenes (**17a–f**) have been synthesized, and the kinetics of their Diels–Alder cycloaddition reactions with 3,6-di(2′-pyridyl)-*s*-tetrazine (**2**) have been determined. The rate of reaction of the syn alcohol **17d** is strongly solvent dependent, being some 500 times faster in Me_2SO than in $CHCl_3$ solution. This result is explained in terms of the different conformational preferences of the hydroxyl group in the two solvents, being intramolecularly H bonded (**26**) in $CHCl_3$ and intermolecularly H bonded (**27**) in Me_2SO. The remaining compounds lie in the order of decreasing reactivity **17e** > **17a** > **17f** > **17c** in both $CHCl_3$ and Me_2SO solvents. Activation parameters have been measured for the reactions of **17a**, **17c**, **17e**, **17f**, and the octahydrodimethanonaphthalen-2-one **18** with the *s*-tetrazine **2**. All these results may be explained in terms of a PMO treatment of orbital interactions through space (OITS) between the 9-substituent and the double bond of **17**. The presence of OITS in the ketone (**17c**) is further supported from UV spectral measurements of the compounds **17a**, **17c**, **18**, **29**, and **30**. The relative rates of epoxidation of the compounds **17a**, **17c**, **17e**, and **17f** by *m*-chloroperbenzoic acid were determined by using the competition method. The relative reactivities were in the same order as those for the tetrazine cycloaddition reactions, i.e., **17e** > **17a** > **17f** > **17c**, and are in agreement with the PMO predictions.

A few years ago we reported that the rates of Diels–Alder reactions of several tricyclononadienes (**1a–d**) with 3,6-di(2′-pyridyl)-*s*-tetrazine (**2**) to give **3a–d** (Scheme I) were sensitive to the nature of the substituent at the 9-position, the order of reactivity being syn methoxy (**1c**) > **1a** > ketone (**1d**).[3,4] The same sequence of reactivities was observed in the epoxidation of these compounds.[5]

Using a frontier molecular orbital (FMO) model, Paddon-Row[6] explained these observations in terms of orbital interactions through space (OITS)[7] operating between the substituents and the cyclobutene double bond. Thus the n_1–π interaction of the syn methyl ether, in the conformation depicted by **4**, is predicted to enhance the dienophilicity of the cyclobutene toward dienes having inverse electron demand[9] such as **2**. The FMO model also explained the 470-fold increase in the reactivity of the syn

---

(1) Part 4: M. N. Paddon-Row, H. K. Patney, and R. N. Warrener, *J. Chem. Soc., Chem. Commun.*, 296 (1978).

(2) (a) New South Wales Institute of Technology. (b) Australian National University. (c) ARGC Research Assistant 1976–1978.

(3) I. W. McCay, M. N. Paddon-Row, and R. N. Warrener, *Tetrahedron Lett.*, 1401 (1972).

(4) M. N. Paddon-Row and R. N. Warrener, *Tetrahedron Lett.*, 1405 (1972).

(5) M. G. Hymann, M. N. Paddon-Row, and R. N. Warrener, *Synth. Commun.*, **5**, 107 (1975).

(6) M. N. Paddon-Row, *Tetrahedron Lett.*, 1409 (1972); M. N. Paddon-Row cited in I. W. McCay, Ph.D. Thesis, Australian National University, Canberra, 1971. A similar FMO model has been advanced by Sustmann to account for substituent effects on the Diels-Alder and 1,3-dipolar cycloaddition reactions.[8]

(7) Review: R. Hoffmann, *Acc. Chem. Res.*, **4**, 1 (1971).

(8) R. Sustmann, *Tetrahedron Lett.*, 2717, 2721 (1971).

(9) J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **6**, 16 (1967).

0022-3263/79/1944-3908$01.00/0 © 1979 American Chemical Society