The Organometallic Chemistry of the Alkaline-earth Metals. Part 3.[1] Preparation and Properties of Alkylhalogenometal Compounds and Related Species of Calcium, Strontium, and Barium †

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Alkyliodo-strontium and -barium compounds can be prepared in tetrahydrofuran (thf) solution at −78 °C in good yields, and solids of composition $[MR(I)]\cdot n$thf (R = Me, Et, Pr^n, or Bu^n, M = Sr, n = 2 or 3; R = Et, M = Ba, n = 1) may be isolated. Characterisation of these products by analysis and other studies is reported. Co-condensation of alkyl halides with Ca, Sr, or Ba metal vapour at low temperature *in vacuo* gives products which contain solvent-free alkylhalogenometal species (10—25%) which are also investigated. Dicyclopentadienyl compounds, $[M(cp)_2]$ (M = Ca, Sr, or Ba), and di-indenyl compounds, $[M(C_9H_7)_2]$ (M = Sr or Ba), are prepared in high yield by co-condensation reactions. Reactions between various unsaturated organic molecules and iodo(methyl)-strontium and -barium compounds are reported and, except from Ph_2CO, low yields of alkyl addition products are formed. The thermal decomposition of (ethyl)iodostrontium species produces a variety of hydrocarbon and other products, and studies on this system at 18 °C indicate the occurrence of some saturated C–C bond-cleavage reactions under mild conditions.

STUDIES on the preparation and reactivity of simple organometallic compounds of the alkaline-earth elements, especially of the heavier metals strontium and barium, have been few. In contrast to the Grignard reagents of magnesium, analogues of the other Group 2A metals are not well known and even for calcium species somewhat conflicting reports have appeared.[2] Aryl (R) derivatives of the general formula $[MR(X)]$ (M = Ca, X = Cl, Br, or I;[2] M = Sr[3] or Ba,[4,5] X = I) have been prepared in solution and reactions of $[CaR(I)]$ studied in some detail. Solutions of alkyl (R′) species, $[CaR'(X)]$, have been described, although low yields were reported for tertiary and secondary alkyl groups and, in some cases, where X = Cl or Br.[2] Reactions of alkyliodocalcium compounds with organic molecules have also been studied.

Reactions of alkyl halides with strontium and barium in ether solvents have previously been reported not to form organometallic products,[6] but more recent work has indicated that alkyliodobarium species can be formed in solution in low yields (20—30%).[5]

We have reinvestigated the products formed between strontium or barium metal and alkyl iodides in solution, and also studied the reactions of the alkaline-earth metals with alkyl halides and other organic substrates when co-condensed *in vacuo* at low temperatures.

RESULTS AND DISCUSSION

(*i*) *Preparation of Alkylhalogenometal Compounds.*—(*a*) *Reactions in solution.* Alkylhalogenocalcium compounds have been produced in solution by various groups of workers but there is only one report involving the isolation of a solid ether adduct of such species, *i.e.* $[CaBu^n(I)]\cdot OEt_2$.[7] No previous reports of similar strontium compounds have been recorded and no alkyl species of barium isolated from solution.

We have found that reactions of finely divided strontium or barium with 1-iodoalkanes in tetrahydrofuran (thf) at −78 °C give solutions of the respective alkyliodometals which may be isolated, after filtration and crystallisation, as microcrystalline colourless products of general formula $[MR'(I)]\cdot n$thf. Using this technique, the compounds with R′ = Me, Et, Pr^n, or Bu^n, and M = Sr, and R′ = Et and M = Ba, have been prepared and characterised analytically (Table 1). Other alkyl derivatives of Ba (R′ = Me, Pr^n, or Bu^n) have also been produced without complete analytical characterisation. Yields of these adducts with thf are relatively high (68—87%). If preparations are carried out at higher temperatures poorer yields are obtained and it was also found that, although amalgamated metals (5% Hg) could be utilised, the pure metals react as easily in a finely divided state.

The compounds are very reactive solids, decomposing rapidly in a moist atmosphere and slowly *in vacuo* at ambient temperatures to give species insoluble in ethers. The freshly prepared products are moderately soluble in the more polar ether solvents, from which recrystallisation is possible. They are sparingly soluble in hydrocarbon solvents and attempts to prepare these species in such media at various temperatures met with no success; this is in contrast to a report of calcium reactions in hydrocarbon solvents.[8]

Tetrahydrofuran itself was found to react with the

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[1] Part 2, K. A. Allan, B. G. Gowenlock, and W. E. Lindsell, *J. Organometallic Chem.*, 1974, **65**, 1.

[2] B. G. Gowenlock and W. E. Lindsell, *J. Organometallic Chem. Library*, 1977, **3**, 1 and refs. therein.

[3] L. F. Kozhemyakina, N. I. Sheverdina, Z. E. Paleeva, V. A. Chernoplekova, and K. A. Kocheshkov, *Izvest. Akad. Nauk. S.S.S.R., Ser. khim.*, 1976, 431.

[4] H. Gilman and F. Schulze, *Bull. Soc. chim. France*, 1927, **41**, 1333.

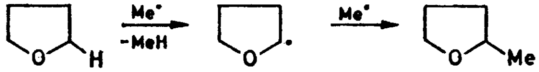
[5] I. I. Lapkin, M. N. Rybakova, M. I. Belonovich, and L. M. Novoselitskaya, *Zhur. obshchei Khim.*, 1972, **42**, 2681.

[6] F. Schulze, *Iowa State J. Sci.*, 1933, **8**, 225; B. J. Wakefield, *Adv. Inorg. Chem. Radiochem.*, 1968, **11**, 390.

[7] M. A. Zemlyanichenko, N. I. Sheverdina, I. M. Viktorova, N. P. Barminova, and K. A. Kocheshkov, *Dolkady Akad. Nauk S.S.S.R.*, 1970 **194**, 95.

[8] N. Kawabata, A. Matsumura, and S. Yamashita, *J. Org. Chem.*, 1973, **38**, 4268.

species at ambient temperatures so that all the manipulations involving this solvent were carried out at low temperatures. In thf (8 h, 19 °C), [SrMe(I)] liberates 32 mol % of a volatile product ($CH_4 : C_2H_6 : C_2H_4 = 5 : 2 : 2$) and produces 2-methyltetrahydrofuran (2Me-thf) (5%) and an insoluble residue. Likewise, [BaMe(I)] in thf (5 h, 19 °C) liberates $CH_4 : C_2H_6 : C_2H_4$ (1.9 : 1 : 1.4) and produces 2Me-thf (6%). The mechanism of decomposition in thf is open to speculation, but the production of methane indicates that hydrogen (or proton) abstraction from the solvent occurs. Ethylene may be formed (at least in part) by cleavage of thf, as found in the decomposition of alkyl-lithium compounds in this solvent.[9] Ethane and 2Me-thf may arise from radical-coupling reactions, *e.g.* equation (1). The compound



(1)

[SrEt(I)]·2thf in the solid state produces 2-ethyltetrahydrofuran (2Et-thf) (4%) and hexanol (2%), accompanied by volatile hydrocarbons, on decomposition [see section (*iii*)].

The compounds in Table 1 gave consistent analyses for M and I, and thf was determined qualitatively, and quantitatively in one case, by g.l.c. Hydrolysis or methanolysis of the freshly prepared products liberates the gases indicated. The principal gaseous component from hydrolysis of [MR'(I)]·*n*thf is the saturated hydrocarbon, R'H, and mass-spectral analysis of the product from D_2O and [SrEt(I)]·2thf showed this to be mainly EtD. However, some alkene, R' − H, and some coupled product, R'_2, are also produced together with smaller amounts of other hydrocarbons. After standing *in vacuo* at room temperature, decomposition of the solids takes place so that subsequent hydrolyses yield differing relative amounts of hydrocarbon and hydrogen. It is also to be noted that the mol % of volatile product collected is only 60—77% of that expected for pure RH and this quantity was found to decrease if the hydrolysis was delayed. Both the complex mixture of volatile products and the low volumes of gaseous product formed from presumed ' fresh ' organometallic compound may indicate some decomposition of this product in handling prior to gas analysis.

TABLE 1

Properties of isolated [MR(I)]·*n*thf compounds

Compound	Analysis (%) [a] N	I	Hydrocarbons liberated on hydrolysis Mol % volatile [b]	Composition [c]	Prominent i.r. bands (cm^{-1}) [d]
[SrMe(I)]·3thf	19.6(19.65)	28.0(28.5)	77	$CH_4(100), C_2H_6(16)$	1 032s, 918s, 876s, 368m
[SrEt(I)]·2thf	22.8(22.6)	33.7(32.7)	66—76	$CH_4(2), C_2H_6(100), C_2H_4(1), C_2H_2(2), C_3H_6(1), C_4H_{10}(<1)$	1 033s, 920s, 876s, 385m
[SrPr^n(I)]·2thf	21.9(21.8)	31.8(31.6)	67	$CH_4(16), C_2H_6(1), C_3H_8(100)$, 1-$C_3H_6(24), C_6H_{14}$ [e]	1 032s, 918m, 876s, 373m
[SrBu^n(I)]·3thf	18.0(18.0)	26.2(26.0)	60	CH_4(t), C_2H_6(t), $C_4H_{10}(100)$, 1-$C_4H_8(20)$, C_8H_{18} [e]	
[BaEt(I)]·thf [f]	37.2(37.6)	34.5(34.7)	71	$CH_4(5), C_2H_6(100)$	

[a] Calculated values are given in parentheses. [b] Above −78 °C trap. [c] Relative molar amounts are given in parentheses (g.l.c.). The amount of hydrogen formed was negligible. t = Trace. [d] In Nujol mull, between CsI windows. [e] Determined separately. [f] thf, 18.7 (g.l.c.) (calc. 19.6%).

Base titration of solutions of hydrolysed products gave results close to the theoretical values for [SrR'(I)]·3thf (R' = Me or Bu^n), but were consistently low for other species and this may also have arisen from some decomposition.

Laser-Raman spectroscopy of the solids was inapplicable since the products decomposed in the beam and it was impossible to obtain i.r. spectra without some decomposition. However, i.r. spectra were obtained in the solid state for some compounds and these show typical alkyl C–H bands, bands from co-ordinated thf (*e.g.* at 1 033 ± 1 and 876 cm^{-1}), and low-frequency bands (at *ca.* 370 cm^{-1}) which may be either ν(M–C) or ν(M–O) vibrations (see Table 1).

Hydrogen-1 n.m.r. spectra of these compounds (in 1,2-dimethoxyethane) show resonances attributable to thf (δ 1.8 p.p.m., β-CH_2) but *no* resonances are observed at high fields ($\delta < 0.5$ p.p.m.) which might be expected from metal-bound methyl or methylene groups.[10] Cooling to −55 °C caused no changes in these spectra. The only other resonances present are in the range δ 1.5—0.8 p.p.m. [for ' SrR'(I),' R' = Me, Et, or Bu^n] which may be assignable to metal-bound alkyl groups but could alternatively be due to hydrocarbons in solution. It is of interest that [CaBu^n(I)]·OEt_2, prepared as described in the literature,[7] also does not show high-field resonances [observed spectrum in C_6D_6: δ 3.36 (q) and ∼1.1 p.p.m. (complex m)].

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[9] A. Rembaum, S-P Siao, and N. Indicator, *J. Polymer Sci.*, 1962, **56**, S17; A. Maercker and H. M. Neumann, *J. Organometallic Chem.*, 1975, **102**, Cl.

[10] M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Adv. Organometallic Chem.*, 1965, **3**, 1.

The thf adducts listed in Table 1 are probably structurally related to analogous Grignard reagents.[11]

(*b*) *Solvent-free alkylhalogenometal species*. The co-condensation procedure has been used recently with much success to prepare main-group and transition-metal compounds which are unobtainable, or which are prepared only in low yields, by normal reaction techniques.[12,13] This vapour-phase technique has been applied by Skell and Girard[14] to the preparation of solvent-free Grignard reagents and the products so obtained show unusual reactivity. Klabunde has produced alkylhalogeno-species from Ni, Pd, and Pt,[13] and from Zn,[15] by this method. It has also been shown that defluorination of perfluorohydrocarbons occurs on co-condensation with calcium metal, and oxidative addition of C–F bonds to calcium was proposed as the mechanism in these reactions.[16] An uncharacterised unstable intermediate $[Ca(C_6F_5)F]$ was postulated to be formed from perfluorobenzene,[16] but no other such organometallic co-condensation products of the alkaline-earth metals have been reported.

We have found that co-condensation of calcium, strontium, or barium metal vapours with excess of alkyl halide (*ca.* 1 : 100) at −196 °C leads to the formation of alkylhalogenometal species. The metals are conveniently vaporised from a heated tungsten-wire basket in an evacuated vessel (10^{-4} Torr) * and condensed synchronously with alkyl halide on to a rotating glass surface. The matrices so formed (−196 °C) are black. If these matrices are subsequently warmed quickly to the melting point, analyses of the resulting products show very low yields of alkylmetal species and indicate that reaction is slow at −196 °C. (This phenomenon was also observed by Skell and Girard[14] in magnesium reactions.) In order to obtain reasonable yields of organometallic product the matrices are warmed to 10—20 °C below their melting points for 1—8 h. During this time the matrices became lighter in colour, and finally melting and evaporation of excess of alkyl halide at low temperature gave white-grey coloured solids which contained alkyl metal species. Yields calculated by analyses of the gas liberated on hydrolysis are in the range 10—25% (based on metal evaporated).

$$R'\text{–}X + M \xrightarrow[-196\,^{\circ}C]{\text{co-condense}} \underset{\text{(dark matrix)}}{R'\text{–}X,M} \xrightarrow{\text{warm up}} \underset{\text{(colourless)}}{R'\text{–}M\text{–}X} \ (+\ \text{other products}) \qquad (2)$$

The range of reactions studied is listed in Table 2. Primary, secondary, and tertiary alkyl halides do react under these conditions to give organometallic products. In normal solution reactions, secondary halides react only with difficulty with Ca and tertiary alkyl halides give <1% yield of organometallic product.[2,17] Calcium, Sr, and Ba react but the ease of reaction follows the order Ca < Sr ⩽ Ba. This order is evident in the rate of lightening of the matrix during the warm-up period and also in the higher percentage of hydrogen in the gases liberated on hydrolysis of products from reactions of tertiary alkyl halides with Ca (due to the presence of unchanged calcium metal). A variety of halides R'X (X = Cl, Br, or I) may be employed, and it should be noted that reactions between Ca and R'X (X = Cl or Br) in solution often proceed with difficulty and in many cases negligible yields are obtained[18] or special initiation procedures must be employed.[17]

Hydrolyses of the solid products liberated the gaseous mixtures listed in Table 2. The molar ratios were not completely constant and varied somewhat with preparation but the values given are representative. The major component from R'X is R'H except in the few cases where the percentage of hydrogen is very high. This latter occurrence is probably due to the presence of unchanged metal in these products. Coupled products R'_2 and alkene R' — H occur in significant amounts and these may arise from radical processes. Other products, however, are also significant. Acetylene may originate from metal carbide, MC_2, formed in the co-condensation process or prior to hydrolysis. Products such as methane and ethane, formed from higher alkyl halides and present in many cases, must be formed by C–C bond cleavage. This may occur during co-condensation, during a subsequent decomposition reaction prior to hydrolysis, or during the hydrolysis process itself, but at all times the solid was kept well below ambient temperature and for hydrolysis *in vacuo* melted ice was used.

The product of deuteriolysis (with D_2O) of the solid from co-condensation of EtI and Sr were subjected to mass-spectral analysis. The ethane formed is largely EtD, although the presence of other hydrocarbons producing ions at *m/e* 26—31 ($C_2H_{2-x}D_x$ and $C_2H_{4-x}D_x$) made quantitative analysis impossible. The hydrogen produced (above the −196 °C trap) comprises HD and D_2 (*ca.* 3 : 1), the former presumably arising from metal hydride impurity and the latter from free metal. Above the −196 °C trap, ions at *m/e* 18, 17, and 16, assignable to non-oxygen-containing species CH_2D_2, CH_3D, or CHD_2, and CH_4 or CH_2D respectively, are present (intensities *m/e* 18 < 17 < 16). Thus it must be concluded that the order of the amounts of methanes present in the deuteriolysis is $CH_2D_2 < CH_3D < CH_4$.

The solid products of co-condensation are partially

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* Throughout this paper: 1 Torr = (101 325/760) Pa.

[11] M. Vallino, *J. Organometallic Chem.*, 1969, **20**, 1; G. D. Stucky and R. E. Rundle, *J. Amer. Chem. Soc.*, 1964, **86**, 4825.

[12] P. L. Timms, *Adv. Inorg. Chem Radiochem.*, 1972, **14**, 121; D. Young and M. L. H. Green, *J. Appl. Chem. Biotechnol.*, 1975, **25**, 641.

[13] K. J. Klabunde, *Accounts Chem. Res.*, 1975, **8**, 393 and refs. therein.

[14] P. S. Skell and J. E. Girard, *J. Amer. Chem. Soc.*, 1972, **94**, 5518.

[15] K. J. Klabunde, M. S. Key, and J. Y. F. Low, *J. Amer. Chem. Soc.*, 1972, **94**, 999.

[16] K. J. Klabunde, M. S. Key, and J. Y. F. Low, *J. Fluorine Chem.* 1972, **2**, 207.

[17] N. Kawabata, A. Matsumura, and S. Yamashita, *Tetrahedron*, 1973, **29**, 1069.

[18] D. Bryce-Smith and A. C. Skinner, *J. Chem. Soc.*, 1963, 577.

soluble in thf. Dissolution in thf of the product from the reaction of EtI and Sr, filtration, and crystallisation by addition of n-pentane gave a solid product with Sr and I analysis as required for [SrEt(I)]·2thf, identical to the species produced by reaction between EtI and Sr in solution.

It may be concluded that the solid products of co-condensation are solvent-free alkylhalogenometal species, ' MR'(X),' accompanied by impurities including free metal, metal halide, metal hydride, metal carbide, and possibly other metal–carbon species.

TABLE 2

Co-condensation reactions

Reactants		Volatiles liberated on hydrolysis of solid products [a]									
Alkyl halide	Metal	H_2	CH_4	C_2H_6	C_2H_4	C_2H_2	C_3H_8	C_3H_6	n-C_4H_{10}	1-C_4H_8	Others
MeI	Ca	1	100	36	2		t		t		
	Sr	0.5	100	11.5	1	t	t		t		
	Ba	0.8	100	21	2	t	t		t		
EtI	Ca	0.3	12	100	12	50	4		33	11	
	Sr	0.4	10	100	13	49	t		27	8	
	Ba	1	6	100	9	52	t		15	11	
Pr^{n}I	Ca	12	8	3	2	14	100	26	t		
	Sr	14	18	3	2		100	32	t		
	Ba	22	16	5	3	2	100	28	t	t	
Bu^{n}I	Ca	n.m. [b]	16	4	1	14	t		100	20	n-C_8H_{18}
	Sr	n.m.	15	6	3	23	t		100	32	n-C_8H_{18}
	Ba	n.m.	11	3	1	18			100	26	n-C_8H_{18}
Pr^{i}I	Sr	55	24	2	1	33	100	74			C_6 products (32)
	Ba	76	37	3	1.5	40	100	85			C_6 products (15)
Bu^{t}I	Ca	168	28	1		14	50		t		i-C_4H_{10}(100), i-C_4H_8(66), C_8 products
	Sr	7	5.5	3		70	1		t	t	i-C_4H_{10}(100), i-C_4H_8(46), C_8 products, *etc.*
MeBr	Ca	11	100	12	1.5	28	9		t	t	
	Sr	16	100	22	1	20	2		t	t	
	Ba	9	100	11	1	21	0.5		3	0.5	*c*
EtBr	Ca	14.5	3.5	100	45	21	0.5		41	8	
	Sr	6	1.5	100	3.5	43.5	0.5		36	5	*c*
	Ba	40	25	100	20	30	1		22		*c*
Pr^{n}Cl	Ca	41	4.5	0.3	0.2	1.5	100	36	0.2	0.2	n-C_6H_{14}(0.3) [d]
	Sr	22	2	0.3	0.2	11	100	38	0.3	5	n-C_6H_{14}(1) [d]
	Ba	130	18.5	3	0.8	55	100	32		0.6	n-C_6H_{14}(1.5) [d]
Bu^{t}Cl	Ca	132	23.5	6.5	t	t	4				i-C_4H_{10}(100), i-C_4H_8(81) [e]
	Sr	16	7	3	1.2	t	1				i-C_4H_{10}(100), i-C_4H_8(47) [e]
	Ba	30	7.5	1.5	1	t	6.5				i-C_4H_{10}(100), i-C_4H_8(89) [e]

[a] Given as relative molar amounts determined by g.l.c.; t = trace. [b] n.m. = Not measured. [c] Trace amounts of higher products. [d] Also trace amounts of C_5 and higher products. [e] Also trace amounts of C_8 products.

(*c*) *Preparation of dicyclopentadienyl- and di-indenyl-metal compounds by co-condensation.* The dicyclopentadienyl compounds, [M(cp)$_2$] (M = Ca, Sr, or Ba), were the first well characterised organometallics of the alkaline-earth metals[19] and have been subjected to some chemical studies.[20] The direct methods used to prepare [M(cp)$_2$] (M = Sr or Ba) led, however, to low or negligible yields of product[19] (4.1 and 0.2 % respectively).

We have found that co-condensation of the vapour of Ca, Sr, or Ba with cyclopentadiene at −196 °C, warming to −98 °C for 1—3 h, and then warming to room temperature with evaporation of excess of cyclopentadiene yields the dicyclopentadienyl compounds [M(cp)$_2$] (90—100%). Thus co-condensation constitutes a very useful method for their preparation, especially [Ba(cp)$_2$]. The compounds [M(cp)$_2$] (M = Sr or Ba) are negligibly soluble in thf and ^{1}H n.m.r. spectra (each comprising one singlet resonance) were obtained in $P(NMe_2)_3O$.

The related di-indenyl compounds, [M(C_9H_7)$_2$] (M = Sr or Ba), can also be obtained in 80—90% yield by co-condensation of excess of indene with metal at −196 to −78 °C. These species have been described in solution,[21] but again the vapour-phase preparation is very convenient. The ^{1}H n.m.r. spectra of [M(C_9H_7)$_2$] are typical of ' ionic ' indenyl compounds (see Experimental section), and virtually identical to spectra described in the literature.[21]

(*ii*) *Reactions of Alkyliodo-strontium and -barium Compounds with Organic Substrates.*—With a view to assessing the efficacy of organo-strontium and -barium compounds in synthetic organic chemistry we have investigated the reactions of ' MMe(I) ' (M = Sr or Ba) in thf with a variety of unsaturated molecules. Reactions of ' CaMe(I) ' have previously been reported by different groups[22] of workers. The results have been somewhat inconsistent but in some cases high yields of

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[19] E. O. Fischer and G. Stölzle, *Chem. Ber.*, 1961, **94**, 2187.

[20] M. Kirilov, G. Petrov, and C. Angelov, *J. Organometallic Chem.*, 1976, **113**, 225; K. A. Allan, B. G. Gowenlock, and W. E. Lindsell, *ibid.*, 1973, **55**, 229.

[21] P. West and M. C. Woodville, U.S.P. 3,718,703/1973; I. G. Hargis and R. A. Livigni, G.P. 2,144,322/1972.

[22] N. Kawabata, H. Nakumura, and S. Yamashita, *J. Org. Chem.*, 1973, **38**, 3403; M. Chastrette and R. Gauthier, *J. Organometallic Chem.*, 1974, **66**, 219; *Compt. rend.*, 1973, **277**, 805.

addition products were formed from organic carbonyl compounds.

Results of reactions of ' MMe(I) ' (M = Sr or Ba) are listed in Table 3. At between −78 and −30 °C (4—12 h) it is found that significant amounts of hydrocarbon gases were liberated during the reaction (principally methane). Thus hydrogen (or proton) abstraction must be occurring and, since the solvent is only slowly attacked at these low temperatures, this reaction must involve the organic substrate. Final hydrolysis of the reaction mixture with dilute hydrochloric acid led to the products listed.

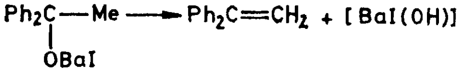
TABLE 3

Reactions of ' SrMe(I)' and ' BaMe(I) ' in tetrahydrofuran solution [a]

Re-actant	Products			
	Reaction with ' SrMe(I) ' [b]		Reaction with ' BaMe(I) ' [c]	
	Volatiles formed in reaction	Isolated after hydrolysis [d]	Volatiles formed in reaction	Isolated after hydrolysis [d]
Ph_2CO	CH_4 + other hydrocarbons	$Ph_2C(Me)OH$ (69)	CH_4(31)	$Ph_2C{=}CH_2$(21), $[Ph_2CHOH + Ph_2C(Me)OH]$ (2)
PhCHO	n.a.	PhCH(Me)OH(21), $PhCH{=}CH_2$(4) $PhMeC{=}CH_2$(2)	n.a.	PhCH(Me)OH(16), $PhCH{=}CH_2$ (11), $PhCMe{=}CH_2$(4)
PhCOCl	CH_4	$PhCMe{=}CH_2$(11)	CH_4	*e*
PhCN	n.a.	PhCOMe(6), PhCHO(t)	n.a.	PhCOMe(1)
Me_2CO	CH_4(26), C_2H_6(t)	Me_3COH(8)	CH_4(24), C_2H_6(5)	Me_3COH(18), Me_2CHOH(8)
MeCOCl	CH_4(21)	Me_2CO(t)	CH_4, C_2H_6(mol ratio 5 : 2)	*e*
MeCN	CH_4(27)	Me_2CO(t)	CH_4(21), C_2H_6(8)	*e*
$MeCO_2Me$	CH_4	Me_3COH(3)	CH_4	*e*

[a] At between −78 and −30 °C. n.a. = Not analysed, t = trace. [b] Yields (%) (g.l.c.) given in parentheses were based on the amount of [SrMe(I)]·2thf used. [c] Yields (%) (g.l.c.) given in parentheses were based on the amount of MeI used to prepare the organometallic. [d] Starting material (or a hydrolysis product) and volatile hydrocarbons (mainly CH_4 and C_2H_6) were also obtained. [e] No addition or reduction products.

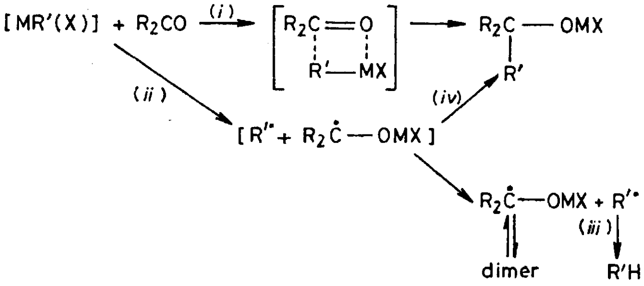
Only in the reaction of ' SrMe(I) ' with benzophenone is a high yield (69%) of addition product, 1,1-diphenylethanol, obtained. In the corresponding reaction with ' BaMe(I) ' the alkene, 1,1-diphenylethylene (21%), is the main product, possibly formed by further reaction of an alkoxoiodobarium intermediate, *e.g.* as in equation (3).



$$Ph_2C(OBaI){-}Me \longrightarrow Ph_2C{=}CH_2 + [BaI(OH)] \qquad (3)$$

Russian workers have also reported high yields of alkenes from solution reactions of alkylbarium compounds with benzophenone at room temperature, although the alkylbarium species themselves were only produced in low yields.[5] In the reaction with ' SrMe(I) ' the deep blue colour of the radical anion of diphenylketyl is observed so that radicals are produced in the reaction, and when the temperature is allowed to rise above −30 °C lower yields of 1,1-diphenylethanol and the minor product, diphenylmethanol, are isolated. The mechanism of alkyl transfer from Grignard reagents to organic substrates is a subject of much active research [23] and both a heterolytic polar process [24] and a single electron transfer (s.e.t.) mechanism [25,26] have been shown to occur: it is possible that reactions of ' SrMe(I) ' also proceed, at least partly, by a s.e.t. process. This would also explain the methane produced during the reaction.

Other aromatic substrates, benzaldehyde, benzoyl chloride, and benzonitrile, give lower yields of addition product and alkenes are also produced from the aldehyde. With these substrates ' SrMe(I) ' gives higher yields of products than ' BaMe(I) '. With aliphatic substrates yields of addition product are very low (see Table 3) and much hydrocarbon is liberated during the reaction, possibly due to enolisation of the substrate. From acetone ' BaMe(I) ' gives a higher yield of 2-methylpropan-2-ol than ' SrMe(I) ' but this is accompanied by the reduction product propan-2-ol. Negligible amounts of mesityl oxide or other condensation products are observed in both reactions and essentially all (>94%) the unchanged acetone is recovered from the reaction with ' SrMe(I) '.



(*i*) Polar mechanism; (*ii*) s.e.t. mechanism; (*iii*) solvent; (*iv*) reaction in solvent cage

The products of co-condensation of methyl iodide with

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[23] E. C. Ashby, J. Laemmle, and H. M. Neumann, *Accounts Chem. Res.*, 1974, **7**, 272.

[24] E. C. Ashby, J. Laemmle, and H. M. Neumann, *J. Amer. Chem. Soc.*, 1972, **94**, 5421.

[25] C. Blomberg, R. M. Salinger, and H. S. Mosher, *J. Org. Chem.*, 1969, **34**, 2385.

[26] E. C. Ashby, J. D. Buhler, I. G. Lopp, T. L. Wiesemann, J. S. Bowers, and J. T. Laemmle, *J. Amer. Chem. Soc.*, 1976, **98**, 6561.

Ca, Sr, and Ba were allowed to react with acetone at −78 °C. In these reactions, CH_4, C_2H_6, and C_2H_4 (mol ratio 3.7—5.3 : 1—1.3 : 1—2) are evolved during the reaction. The organic products after hydrolysis are unchanged acetone, 2-methylpropan-2-ol, and propan-2-ol [yields of the latter two compounds (based on metal evaporated) were 6 and 2 (Ca), 3 and 2 (Sr), and 7 and 1% (Ba) respectively]. The presence of reduction products here may reflect the presence of hydride species in the co-condensed product (*cf.* Mg).[26]

Methyl methacrylate is polymerised to 56% conversion by [SrEt(I)]·2thf in 1,2-dimethoxyethane at −78 °C (31 h). Hydrogen-1 n.m.r. spectroscopy showed the polymer to be mainly syndiotactic (72%) but this degree of regularity is lower than observed for poly(methyl methacrylate) produced from some organocalcium species.[27]

(*iii*) *Thermal Decomposition of Ethyliodostrontium Species*.—All the alkylhalogenometal species of Sr and Ba decomposed thermally in the solid state *in vacuo* and the rate of decomposition was marked even at room temperature.

The decomposition of [SrEt(I)]·2thf at 18 °C was investigated and the results are presented graphically in Figures 1 and 2. Over a period of several hours, gases are liberated as shown (Figure 1). Ethane predominates initially but its production virtually ceases after *ca.* 4 h when methane and, to a lesser extent, ethylene production becomes significant. There are also small amounts of hydrogen and n-butane. The total amount of gas liberated per mol of [SrEt(I)]·2thf is variable but is *ca.* 30 mol % in 35 h.

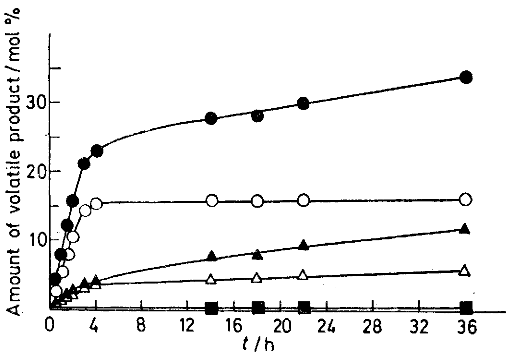

FIGURE 1 Volatile products formed during the thermal decomposition (18 °C) of [SrEt(I)]·2thf: (●) total; (○) C_2H_6; (▲) CH_4; (△) C_2H_4; (■) H_2 + n-C_4H_{10}

The solid residue formed during decomposition has also been analysed by hydrolysis after various intervals of time. The gases liberated (Figure 2) show that the total amount of gas decreases from *ca.* 76 mol % {per mol [SrEt(I)]·2thf} when first analysed to *ca.* 27 mol % after 2 h. The amount of ethane decreases from >93 to <1% in 3 h, whereas hydrogen increases from <1 to >76% in the same time. The only other gases produced in significant, but smaller, amounts after 3 h are methane and acetylene. n-Butane and ethylene are only produced in small quantities within the first 3 h.

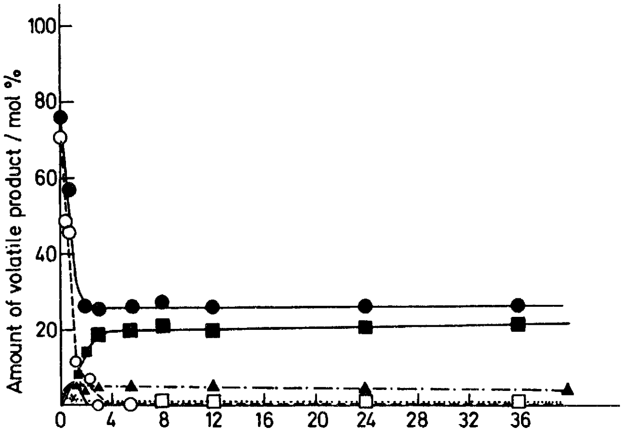

FIGURE 2 Variation in volatile products formed on hydrolyses of the solid residue formed in thermal decomposition (18 °C) of [SrEt(I)]·2thf, as a function of time: (●) total; (○) C_2H_6; (▲) CH_4; (△) C_2H_4; (■) H_2; (□) C_2H_2; (×) C_4H_{10}

Mass-spectral analysis of the gases formed by reaction of D_2O with the decomposed solid shows that hydrogen (over the −196 °C trap) is principally HD and that *no* D_2 is present. Analysis of the methane liberated is less clear but, above the −196 °C trap, peaks at *m/e* 18 (very small), 17, and 16, assignable to non-oxygen-containing CH_xD_y fragments, are observed, indicating that CH_2D_2 (trace), CH_3D, and CH_4 are being produced.

The percentages of Sr and I in the solid increase slightly during decomposition [after 4 h: Sr, 23.9; I, 34.8% (see Table 1 for calc. values)] and other less volatile products observed after hydrolysis (72 h) are 2Et-thf (4%) and n-hexanol (2%).

The decomposition of solvent-free ' SrEt(I) ' formed by co-condensation of EtI with Sr was also monitored at 18 °C. Some results (mol %) for hydrocarbons present in the decomposition products after intervals of time and also for gaseous products formed by hydrolyses of the decomposing solid are given in Table 4. Compared to [SrEt(I)]·2thf there is a wider range of hydrocarbons produced on decomposition, but the main gases are, similarly, ethane and methane ($C_2H_6 > CH_4$). Hydrolysis of the solid ' SrEt(I) ' initially produces a greater mixture of hydrocarbons than [SrEt(I)]·2thf but after 25 h the predominant gas is analogously hydrogen (63%) with acetylene > ethylene > methane > ethane as minor products. The absence of thf of solvation, although changing the absolute yields of the various products of thermal decomposition, does not markedly affect their nature.

The mechanisms of decomposition seem to be complex. Hydride formation (liberation of HD on deuteriolysis) must be one process. This must partially involve β-H abstraction from ethyl groups with liberation of ethylene, but quantitative analyses indicate that this is not the

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[27] K. A. Allan, B. G. Gowenlock, and W. E. Lindsell, *J. Polymer Sci.*, 1974, **12**, 1131.

only process of hydride formation. Ethane–ethylene and butane may be formed by radical disproportionation and coupling processes, and ethane by hydrogen abstraction from organic groups or thf. Attack of thf in the solvated species does occur as evidenced by the isolation of 2Et-thf and hexanol. Acetylene probably arises from metal carbide (or similar) precursors. Methane is produced in significant quantities both on thermal decomposition and in hydrolysis of the solid residues of decomposition. Hence C–C bond cleavage must be occurring at 18 °C, liberating CH_4 and probably forming $Sr–CH_x$ fragments which themselves liberate CH_4 on hydrolysis. The products obtained with D_2O ($CH_4 + CH_3D > CH_2D_2$) do not completely clarify the nature of $Sr-CH_x$, but species having $x = 3$ and 2 may be the precursors for CH_3D and CH_2D_2. The species $Mg(CH_2)$ has been described in the literature.[28]

TABLE 4

Decomposition of products from co-condensation of ethyl iodide and strontium [' SrEt(I) '] at 18 °C

	Relative mol % of volatiles formed by decomposition [a]							
t/h	H_2	CH_4	C_2H_6	C_2H_4	C_2H_2	C_3H_8	n-C_4H_{10}	1-C_4H_8 [b]
1	n.m.	36.2	44.1	16.0	1.0	2.1	3.6	
2	n.m.	32.6	44.2	15.2	t	2.0	6.1	
3	n.m.	33.2	44.4	13.6	t	1.6	7.2	
13	n.m.	29.4	49.0	9.1	t	2.3	9.7	0.4
25	n.m.	26.3	52.4	8.3	t	2.1	11.0	0.3
	Relative mol % of volatiles formed by hydrolysis of the solid [a]							
ca. 0	0.4	4	56	2	17	1	17	3
25	63	5	2	13	16	0.2	1	0.2

[a] Determined by g.l.c.; n.m. = not measured, t = trace. [b] Trace amount of C_5 hydrocarbons.

Ethylhalogenomagnesium species show little thermal decomposition below 150 °C; at 180—275 °C C_2—C_6 hydrocarbons are produced, but it is interesting that negligible quantities of methane or hydrogen are formed.[29] Hydrolyses of the pyrolysis residues give hydrogen as the main gaseous product with smaller amounts of acetylene, propyne, and allene, but again *no* methane is produced. Thus it appears that there is a marked difference in both the stability and decomposition mechanisms between the alkyl compounds of magnesium and those of strontium (and, from our qualitative results, also barium).

EXPERIMENTAL

All the reactions, and as many manipulations as possible, were carried out under high vacuum ($<10^{-4}$ Torr). Reaction vessels were of Schlenk-type design, fitted with high-vacuum Rotaflo Teflon stopcocks. Pre-dried deoxygenated nitrogen could be admitted to such vessels and solids, and occasionally liquids, were briefly handled in a nitrogen atmosphere. Samples of organometallic compounds, which were found to be very reactive, were prepared as freshly as possible before further investigations and, when brief storage was required, they were kept under high vacuum at 77 K. Solvents were rigorously dried with suitable reagents and finally distilled from lithium tetrahydridoaluminate or sodium diphenylketyl in thf. All the reagents were purified by standard techniques, redistilled before use, and checked for purity by g.l.c.

Hydrogen-1 n.m.r. spectra were recorded in evacuated tubes with a JEOL JNM-MH 100-MHz (room temperature) or Perkin-Elmer R12 60-MHz (35 °C) spectrometer; chemical shifts (δ) are quoted relative to $SiMe_4$. Infrared spectra were obtained in a nitrogen atmosphere with a Perkin-Elmer 457 spectrometer. G.l.c. was performed with appropriate columns, using either flame-ionisation or katharometer detectors, a vacuum sampling valve for analyses of reactions, and internal standards for quantitative analyses. Decompositions and solvolyses of products were carried out and subjected to analyses completely under high vacuum using a gas burette and a gas–liquid chromatograph equipped with a sampling valve.

Metals (Ca >99.9, Sr >99, and Ba >99.5%) were finely divided shortly before use by grinding in a mill under a stream of pure nitrogen, or by shaving to small particle size under a constant stream of liquid paraffin using a rotating lathe, and were carefully washed and dried *in vacuo*. Strontium and barium were determined by titration with ethylenediaminetetra-acetic acid, and iodine by the Volhard method. Organic compounds were determined by g.l.c. (Analyses for C and H were found to be unreliable.)

Preparation of Alkyliodometals in Tetrahydrofuran.—[SrMe(I)]·3thf. Tetrahydrofuran (30 cm^3) followed by MeI (1.1 cm^3, 17.6 mmol) was distilled *in vacuo* on to Sr metal (1.9 g, 21.7 mmol) at −196 °C. The reaction mixture was warmed to −78 °C and stirred for 8 h. More thf (50 cm^3) was then distilled into the mixture and the solution quickly filtered under nitrogen at as low a temperature as possible. The filtrate was re-evacuated, and by evaporation of thf and distillation of n-pentane (*ca.* 50 cm^3) into the solution a colourless microcrystalline solid was precipitated. Decantation, washing, and drying at low temperatures gave the product, 6.3 g (80%).

[SrEt(I)]·2thf. This (3.3 g, 87%) was prepared similarly from Sr (1.2 g) and EtI (0.80 cm^3) in thf (25 cm^3) for 7 h. Also prepared similarly were [SrPr^n(I)]·2thf (68%), [SrBu^n(I)]·3thf (78%), [BaEt(I)]·thf (86%), [BaMe(I)]·*n*thf, and other alkyliodobarium compounds.

Co-condensation Reactions.—The apparatus used was similar to that described by Timms, Green, and other workers.[12,13] A matrix was formed on the surface of a rotating (*ca.* 120 revolution min^{-1}) evacuated ($<10^{-4}$ Torr)

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[28] K. Ziegler, K. Nagel, and M. Patheiger, *Z. anorg. Chem.*, 1955, **282**, 345.

[29] M. Lefrancois and Y. Gault, *J. Organometallic Chem.*, 1969, **16**, 7.

Pyrex vessel cooled to −196 °C at the centre of which was a stationary, electrically heated, tungsten-wire (0.4 mm diameter) basket (10—15 A, 0—10 V). A typical reaction is described below.

Strontium metal (0.22 g, 2.5 mmol) was evaporated from the tungsten basket as MeI (25 cm^3) was admitted slowly into the vessel (1 h). After co-condensation at −196 °C the black matrix was heated to −117 °C for 1 h and then to −78 °C for 4 h. Eventually, increasing the temperature slowly, excess of MeI was evaporated off leaving a white solid which could be collected under nitrogen (0.54 g). Hydrolysis and gas analysis gave the yield of 'SrMe(I)' as 18%. Similar co-condensation reactions of MeI and Ca or Ba gave 'CaMe(I)' (13%) and 'BaMe(I)' (15%) respectively. Co-condensations with other halogenoalkanes were carried out similarly (yields 10—25%). Temperatures employed during warming up of the matrices were: EtI (−117 to −78), Pr^{n}I (−78), Bu^{n}I (−78), Pr^{i}I (−63), Bu^{t}I (−63), MeBr (−98), EtBr (−126), Pr^{n}Cl (−126), and Bu^{t}Cl (−126 °C).

Preparation of Dicyclopentadienylmetals [M(cp)$_2$].—Calcium, Sr, or Ba metal (*ca.* 0.1—0.5 g) and cyclopentadiene (35 cm^3) were co-condensed at −196 °C. The matrix was warmed to −98 °C for 1—3 h and then to room temperature with removal of excess of cyclopentadiene *in vacuo*. The products, with properties analogous to the species described in the literature,[2,19—21] were formed as follows: [Ca(cp)$_2$] (100%), ^{1}H n.m.r. in P(NMe$_2$)$_3$O, 5.62 p.p.m.; [Sr(cp)$_2$] (90%), δ 5.65 p.p.m.; and [Ba(cp)$_2$] (100%), δ 5.58 p.p.m.

Preparation of Di-indenylmetals.—Strontium or Ba metal (*ca.* 0.2 g) and indene (25 cm^3) were co-condensed at −196 °C (or higher). The temperature was increased to −63 °C for 2 h and then slowly to room temperature when excess of indene was removed under nitrogen. Solid products analogous to compounds described in the literature[21] were obtained: [Sr(C$_9$H$_7$)$_2$] (80%), ^{1}H n.m.r. in thf, δ 5.58 (d) (3.3 Hz), 6.40 (t) (3.3 Hz), and 6.58 and 7.30 p.p.m. (AA'BB'); [Ba(C$_9$H$_7$)$_2$] (90%), δ 5.58 (d) (3.3 Hz), 6.37 (t) (3.3 Hz), and 6.57 and 7.25 (AA'BB').

Reactions with Organic Substrates (*see Table* 3).—(*a*) [SrMe(I)]·3thf. The metal compound (0.5—2.5 g) in thf (10—20 cm^3) and equimolar quantities of organic reactant were mixed and stirred *in vacuo* under the following conditions: Me$_2$CO, −78 °C, 10 h; Ph$_2$CO, −78 °C, 12 h; PhCHO, −30 °C, 6 h; MeCO$_2$Me, −30 °C, 6 h; PhCOCl, −30 °C, 6 h; MeCOCl, −30 °C, 10 h; MeCN, −30 °C, 8 h; and PhCN, −30 °C, 6 h.

(*b*) 'BaMe(I).' The metal compound was prepared in thf solution from MeI (0.1—0.4 g), the solution was filtered, and an equimolar amount of organic reactant added *in vacuo* under similar conditions to the above.

Gases evolved during reactions were analysed by g.l.c. and in some cases by use of a gas burette. Hydrolysis was accomplished with dilute HCl.

Polymerisation of Methyl Methacrylate.—The compound [SrEt(I)]·2thf (20 mg) in 1,2-dimethoxyethane (15 cm^3) and methyl methacrylate (10 cm^3) were sealed *in vacuo* at −78 °C for 31 h. Polymer (56%) was isolated in the ratio syndiotactic : heterotactic : isotactic (^{1}H n.m.r., 120 °C) = 72 : 23 : 5.

Analysis of Organometallic Products.—(*a*) *Solvolysis.* Water, methanol, or D$_2$O at the melting point was allowed to mix with the solid *in vacuo*. The gases evolved were analysed by g.l.c. and also by use of a gas burette.

(*b*) *Thermal decomposition of* [SrEt(I)]·*n*thf (*n* = 0 *or* 2). Gaseous products evolved *in vacuo* at 18 °C from the solid were analysed by g.l.c. and also by use of a gas burette.

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