91. *Organometallic Compounds of Group II. Part IV.*[1] *Preparation and Reactions of Organocalcium Halides.*

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The preparation of organocalcium halides has been investigated. Convenient preparations of methylcalcium iodide and bromide, n-butylcalcium iodide, phenylcalcium iodide and bromide, and 1-naphthylcalcium iodide are described. Reactions between calcium and organic halides require ethereal media. The presence of traces of magnesium in the calcium is advantageous, and of sodium disadvantageous. Superficial amalgamation of the calcium with mercury strongly promotes these reactions. Ease of reaction with calcium follows the order RI > RBr > RCl. Reaction of 2-iodothiophen with calcium followed by carboxylation, anomalously gives thiophen-2,5-dicarboxylic acid and 2-iodothiophen-5-carboxylic acid, but no thiophen-2-carboxylic acid.

Chemically, organocalcium halides resemble organolithium compounds more than Grignard reagents. Carboxylation gives the corresponding carboxylic acid, and in some cases the ketone and tertiary alcohol. Examples are described of addition to carbonyl compounds, halogen–calcium exchange, and metallation. Phenylcalcium iodide and pyridine give 2-phenylpyridine and either 2,5- or 2,6-diphenylpyridine, depending on the conditions.

The rates of decomposition of some organocalcium halides in tetrahydrofuran have been measured, and some cleavage products identified.

Few organocalcium compounds other than the acetylide have been described. This is surprising in view of the extensive studies of Grignard reagents and organometallic derivatives of other light metals. The formation of organocalcium iodides from calcium and various organic iodides has been reported from time to time.[2-5] The reactions tended to be slow, erratic, and difficult to initiate, and only in the case of iodobenzene was a good yield reported (but see below).[3] Organocalcium bromides and chlorides are apparently unknown. Payne and Sanderson recently obtained dimethylcalcium after a reaction between methyl iodide and calcium in pyridine.[6] Fischer and Stolzle obtained biscyclopentadienylcalcium from cyclopentadiene and calcium in tetrahydrofuran or dimethylformamide.[7] Gilman and Woods have prepared complex calcium–zinc alkyls by partial displacement of zinc from zinc alkyls;[8] but calcium appears unable to displace mercury from organomercury compounds.[2]

Preliminary attempts to prepare organocalcium halides in the manner conventionally used for Grignard reagents confirmed the previous reports of erratic behaviour and other difficulties.[2-4] Various factors which might influence the reactions were then examined.

A number of commercially available samples of calcium were found to contain either sodium or magnesium as the principal impurity (1—5 atom %). In comparison with pure calcium, the use of the sodium alloys led to lower, and the magnesium alloys to higher, yields. This effect of sodium contrasts with the need for traces of sodium in metallic lithium used for the direct preparation of organolithium compounds.[9] Magnesium was more effective as a promoter when alloyed than when added separately to the reaction mixture: the use of a little preformed Grignard reagent was approximately as beneficial

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[1] Part III, Bryce-Smith and Cox, *J.*, 1961, 1175. For a preliminary account of the present work see Bryce-Smith and Skinner, *Chem. and Ind.*, 1960, 1106.

[2] Gilman and Schultz, *J. Amer. Chem. Soc.*, 1926, **48**, 2463; cf. Schultz, *Iowa State Coll. J. Sci.*, 1933, **8**, 225.

[3] Gilman, Kirby, Lichtenwalter, and Young, *Rec. Trav. chim.*, 1936, **55**, 79.

[4] Glacet, *Bull. Soc. chim. France*, 1938, **5**, 895.

[5] Meals, *J. Org. Chem.*, 1944, **9**, 211.

[6] Payne and Sanderson, *J. Amer. Chem. Soc.*, 1958, **80**, 5324.

[7] Fischer and Stolzle, *Chem. Ber.*, 1961, **94**, 2187.

[8] Gilman and Woods, *J. Amer. Chem. Soc.*, 1945, **67**, 520.

[9] West and Glaze, *J. Org. Chem.*, 1961, **26**, 2096, and references therein.

as the addition of an equivalent amount of free magnesium. Calcium amalgam containing equiatomic proportions of the metals reacted much more readily than pure calcium with organic halides; but appreciable amounts of organomercury compounds were formed. Activation without any significant accompanying tendency for formation of organomercury compounds was achieved by superficial amalgamation of the calcium particles under argon with 2 atoms % of mercury, and this will subsequently be termed " activated calcium."

No reaction between various organic iodides and activated calcium could be induced in the absence of ethereal media. Light-metal alkoxides, which are effective in promoting the direct formation of non-ethereal Grignard reagents,[10] did not initiate corresponding reactions of activated calcium. Reactions generally occurred more rapidly in tetrahydrofuran than in diethyl ether, but diethyl ether was found to be preferable in the preparation of n-butylcalcium iodide. Both of these ethers are cleaved by organocalcium halides, reactions which are further discussed below.

By attention to the foregoing factors, the following organocalcium halides have been prepared directly in satisfactory yields: methylcalcium bromide and iodide, n-butylcalcium iodide, phenylcalcium bromide and iodide, and *p*-tolylcalcium iodide. Secondary and tertiary alkyl halides failed to react with activated calcium. With n-butyl and phenyl halides, the ease of reaction was RI > RBr > RCl. Some of the main results are summarised in the Table. The reactions for which diethyl ether is shown as the medium occurred much more rapidly in tetrahydrofuran, but the yields of organocalcium compounds were negligible because of Wurtz-type coupling reactions unless temperatures of *ca.* —30° were used: even then, yields tended to be lower than in the ethereal preparations. Gilman *et al.* reported a 90% yield of phenylcalcium iodide from the reaction of iodobenzene and calcium in ether.[3] In our hands, this reaction gave yields of 27% and 30% in duplicated preparations. These yields were determined by carboxylation and isolation of benzoic acid, but the yields indicated by the single titration method employed by Gilman *et al.* were 77% and 80%, respectively. The discrepancy can be attributed to the formation of a calcium ethoxide by ether-cleavage: this obviously cannot be distinguished from the organocalcium compound by hydrolysis and titration of the liberated base. Preliminary attempts to use benzyl chloride in a double-titration procedure (cf. Gilman and Haubein [11]) gave unpromising results.

Yields of organocalcium halides from organic halides and activated calcium.

	Medium	Temp.	Yield (%)	Note		Medium	Temp.	Yield (%)	Note
MeCaBr *	T †	−35°	81	*a*	Bu^nCaBr	T	−25°	24	*b*
MeCaI	T	−55	81	*a*	Bu^nCaI	E	35	63	*a, c*
EtCaCl	T	50	20	*a*	$n\text{-}C_5H_{11}{\cdot}CaI$	E	35	24	*b*
EtCaBr	T	−30	33	*a*	PhCaCl	T	65	<1	*b*
EtCaI	E ‡	35	39	*a*	PhCaBr	T	−10	45	*b, c*
Pr^nCaI	E	35	25	*a*	PhCaI	T	−30	90	*b, c*
Bu^nCaCl	T	65	22	*a*	$p\text{-}Me{\cdot}C_6H_4{\cdot}CaI$	T	−30	46	*b*

* These conventional formulæ are given for brevity and may imply too high a proportion of halogen (see below). † T = Tetrahydrofuran. ‡ E = Diethyl ether.

(*a*) Yield determined by hydrolysis and collection of the evolved hydrocarbon. (*b*) Yield determined by isolation of the products of carboxylation. (*c*) Calcium containing 5 atoms % of magnesium was used.

Reactions of Organocalcium Halides: General.—In view of the position of calcium in the Periodic Table, it was of interest to examine the chemical behaviour of organocalcium compounds in comparison with that of organometallic compounds of sodium, lithium, magnesium, and aluminium. It may be stated at once that the greatest resemblances have been found to organolithium compounds (contrast ref. 12). To avoid ambiguity,

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[10] Blues and Bryce-Smith, *Chem. and Ind.*, 1960, 1533.

[11] Gilman and Haubein, *J. Amer. Chem. Soc.*, 1944, **66**, 1515.

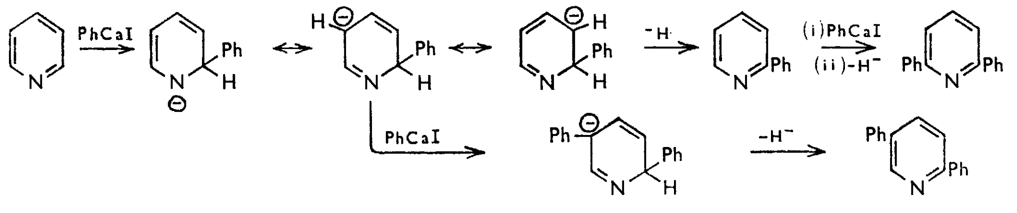
[12] Sharpe, *Ann. Reports*, 1960, **57**, 118.

and at some expense in yields, most of the reactions have been studied with reagents prepared from magnesium-free calcium.

Addition to Carbonyl Compounds.—Reaction of n-butylcalcium iodide with gaseous carbon dioxide at 20—25° gave valeric acid together with dibutyl ketone and tributylcarbinol (5-butylnonan-5-ol). More ketone than acid was formed even when an excess of solid carbon dioxide was used, in contrast to the behaviour of n-butyl-lithium.[13] n-Pentylcalcium iodide behaved similarly. Organolithium compounds, but not Grignard reagents or organosodium or aluminium compounds, show a marked tendency to form ketones on reaction with carbon dioxide (Gilman's ketone synthesis[13]). Trialkylaluminium compounds react with carbon dioxide to give the corresponding carboxylic acid and tertiary alcohol: alkylaluminium halides are inert to carbon dioxide.[14] On the other hand, carboxylation of phenylcalcium iodide, bromide, and chloride normally gave only benzoic acid: this behaviour resembles that of the corresponding Grignard reagents. The bromide, but not the iodide, gave also a little benzophenone when carboxylated slowly: no triphenylcarbinol was found in either case.

Previous authors have indicated that phenylcalcium iodide is substantially inert towards acid chlorides such as benzoyl chloride.[2,4] Such inertness is not to be expected. Phenylcalcium iodide has now been found in fact to react rapidly with benzoyl chloride at −30°[*] to give triphenylmethanol in 94% yield. It appears that the reagents used previously must have consisted largely of calcium alkoxides formed by ether-cleavage, and little if any phenylcalcium iodide. Blues and Bryce-Smith have observed that the reactivity of alkylmagnesium halides can be markedly reduced by complex-formation with certain alkoxides.[10,15] Reaction of phenylcalcium iodide with ethyl benzoate and benzophenone gave triphenylmethanol in 80% yields. Methylcalcium iodide and benzaldehyde gave 2-phenylpropan-2-ol (10%) together with apparently polymeric matter.

Addition to Pyridine.—The adduct of an organolithium compound and pyridine loses lithium hydride at *ca.* 100° to give a 2-substituted pyridine. Grignard reagents have been reported to react with pyridine under forced conditions, though the results are disputed.[16] No analogous reaction of an organoaluminium compound has apparently been described. Phenylcalcium iodide added to pyridine very readily. Elimination of hydride occurred even at room temperature, and it appeared to be more rapid than the corresponding elimination of lithium hydride. The products were 2-phenylpyridine, and either 2,5- or 2,6-diphenylpyridine. The 2,6-isomer was obtained when the reaction was performed under conditions which favoured the more rapid elimination of hydride. Phenylation of 2-phenylpyridine by phenylcalcium iodide gave only the 2,6-isomer. It therefore seems likely that the 2,5-isomer is formed in a reaction of a second molecule of phenylcalcium iodide with the first-formed adduct. The annexed scheme is tentatively proposed.[†]



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[*] Owing to a typographical error, this temperature was given as +30° in a preliminary report.[1]

[†] The intermediates are depicted as anions merely for simplicity, and no implication is intended concerning the precise degree of polarity of the Ca–N and Ca–C bonds.

[13] Gilman and Van Ess, *J. Amer. Chem. Soc.*, 1933, **55**, 1258.

[14] Ziegler in " Organometallic Chemistry," ed. Zeiss, Reinhold, New York, 1960, p. 194.

[15] Blues and Bryce-Smith, unpublished work.

[16] Bergstrom and McAllister, *J. Amer. Chem. Soc.*, 1930, **52**, 2845; see, however, Goetz-Luthy, *ibid.*, 1949, **71**, 2254.

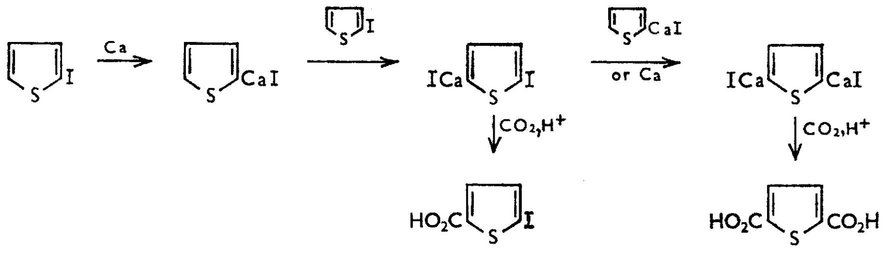
The substitution at the 5-position is unusual, and is a possibly controversial stage in the above proposal. Models indicate that there are steric objections to substitution at the 3-position. 5,6-Addition of phenylcalcium iodide to the initial adduct is considered improbable as it would lead to the formation of two adjacent negative centres: but for this objection, an addition mechanism would seem attractive. Direct 2,5-disubstitution of pyridine has not hitherto been reported. The 2,5-derivatives are often only accessible by lengthy indirect routes (see, *e.g.*, ref. 17). In a comparative experiment, phenyllithium and pyridine gave no diphenylpyridines.

Calcium–Bromine Exchange.—Phenylcalcium iodide reacted very readily with 1-bromonaphthalene, and carboxylation gave 1-naphthoic acid in 98% yield. This therefore provides an excellent preparation of 1-naphthylcalcium iodide. Organolithium compounds are well known to undergo reactions of this type, but Grignard reagents usually only do so under forced conditions.[18]

Metallation.—Phenylcalcium iodide failed to metallate toluene. In this, it resembled phenyl-lithium more than phenylsodium. Phenylcalcium iodide, like phenyl-lithium, metallated anisole in an *ortho*-position. Carboxylation gave *o*-anisic acid in 16% yield. Guaiacol (11%) was also obtained, presumably by fortuitous aerial oxidation of the organocalcium product. Thiophen was metallated by methylcalcium iodide, and carboxylation gave thiophen-2-carboxylic acid.

p-Tolylsodium readily rearranges to benzylsodium at 80—100°, presumably by intermolecular metallation.[19] *p*-Tolylcalcium iodide, like *p*-tolyl-lithium,[19] failed to rearrange at 95°.

Anomalous Reaction of 2-*Iodothiophen with Calcium.*—2-Iodothiophen reacted readily with activated calcium in tetrahydrofuran at —35°. Carboxylation gave thiophen-2,5-dicarboxylic acid and 2-iodothiophen-5-carboxylic acid, but none of the expected thiophen-2-carboxylic acid. The reaction sequence shown involves metallation and calcium–halogen exchange reactions related to those described above.



It is interesting that reaction of lithium with 2-iodothiophen in tetrahydrofuran at —35°, followed by carboxylation, gave thiophen-2-carboxylic acid as the only acidic product. Magnesium and ethereal 2-iodothiophen have been reported to react similarly.[20]

Reaction with Tetrahydrofuran.—Although tetrahydrofuran is becoming widely used as a medium for organometallic preparations, and is known to be cleaved more readily than diethyl ether by, *e.g.*, organolithium compounds,[21] little seems to be known of the cleavage products. Normant [22] obtained some compounds $R\cdot[CH_2]_4\cdot OH$ from reactions of alkenylmagnesium halides, RMgHal, and tetrahydrofuran above 200°, and Jensen and

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[17] Wiley, Jarboe, Callahan, and Nielsen, *J. Org. Chem.*, 1958, **23**, 780; Wiley, Callahan, Jarboe, Nielsen, and Wakefield, *ibid.*, 1960, **25**, 366.

[18] Jones and Gilman, *Org. Reactions*, 1951, **6**, 339.

[19] Bachmann and Clarke, *J. Amer. Chem. Soc.*, 1927, **49**, 2089; Gilman and Pacevitz, *ibid.*, 1940, **62**, 673; Gilman, Pacevitz, and Baine, *ibid.*, p. 1514.

[20] Schlenk and Ochs, *Ber.*, 1915, **48**, 679.

[21] Gilman and Gaj, *J. Org. Chem.*, 1957, **22**, 1165.

[22] Normant, *Compt. rend.*, 1954, **239**, 1510.

Bedard[23] obtained the corresponding alcohol from triphenylmethylmagnesium bromide. Rembaum *et al.* obtained evidence for the formation of ethane, ethylene, acetaldehyde, and hexan-1-ol from ethyl-lithium and tetrahydrofuran.[24] Benzylsodium reacts with tetrahydrofuran to give butadiene and, after hydrolysis, a mixture of phenylpentenes derived by addition of benzylsodium to butadiene.[25] The present solutions of organocalcium compounds in ether and tetrahydrofuran slowly decomposed at 20°. Methylcalcium iodide and tetrahydrofuran evolved a mixture of methane (9 mol. %), ethane (1 mol. %), and ethylene (90 mol. %). A little propan-2-ol was formed, together with much tarry undistillable matter. C_4 Hydrocarbons and pentan-1-ol were not detected. No simple explanation for the formation of propan-2-ol is apparent to the authors.* The small proportion of methane indicates that metallation plays only a small part. As 1·0 equivalent of methylcalcium iodide gave 0·81 mol. of ethylene, this hydrocarbon is clearly a cleavage product of tetrahydrofuran. In contrast, 1·0 equivalent of phenylcalcium iodide in tetrahydrofuran gave 0·75 mol. of benzene: the fission process is evidently different in this case.

The decomposition of phenyl- and methyl-calcium iodide in a large excess of tetrahydrofuran showed the expected first-order kinetics. The half-lives at 20° were 13·5 and 13 days, respectively. These reagents were initially prepared at $-30°$ and $-55°$, respectively. About 30% of each was destroyed rapidly on warming to 20° in 1 hour. This unexpected result seems to imply that the reagents as initially prepared contained at least two species differing greatly in their stabilities. It was demonstrated for methylcalcium iodide that only the less stable of these was soluble in tetrahydrofuran at $-55°$: the other species gave, at 20°, the moderately stable solution referred to above. Both species evolved methane on hydrolysis, and at $-70°$ the freshly prepared solution of methylcalcium iodide gave one equivalent of hydroxyl ion per mol. of methane: thus no cleavage products were present in solution. The ratio of hydroxyl to iodide ions (base : halide ratio) formed on hydrolysis of the solution was 6·3 : 1. This is consistent with an empirical formula $(Me_2Ca)_{2\cdot 65},MeCaI$. Whatever the species actually present may be, the use of a general formula RCaI is probably not justified except to simplify the stoicheiometry of equations. The base : halide ratios for solutions of the more stable species are difficult to interpret because of the presence of cleavage products; they were, however, invariably greater than unity. The connection between the nature of the halogen in the reagents and the tendency to cleave ethers has not been established in any general sense; but it may be significant that solutions of methylcalcium bromide in tetrahydrofuran (half-life *ca.* 70 days at 20°) were more stable than those of the iodide. Methylcalcium chloride has not been obtained, but n-butylcalcium chloride was remarkably stable in tetrahydrofuran, even at the boiling point.

EXPERIMENTAL

Calcium was provided as blocks by A.W.R.E., Aldermaston. This contained <0·5% of magnesium and <0·2% of sodium, and was the purest material obtainable by the authors.

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* It might at first sight seem that cleavage of tetrahydrofuran might produce acetaldehyde (and thence propan-2-ol on addition of methylcalcium iodide) by a process analogous to that observed by Letsinger and Pollart in the formation of acetophenone from tetrahydro-2-phenylfuran and propylsodium.[25a] It seems unlikely that our propan-2-ol arose in this way. Letsinger and Pollart obtained no products of addition of propylsodium to acetophenone, and stressed that acetophenone was not initially formed as such, but as the sodium enolate (which would not of course add propylsodium); acetophenone was only obtained after hydrolysis. Analogous reactions in the present case would give the iodocalcium enolate of acetaldehyde, which could not give rise to propan-2-ol since methylcalcium iodide had completely decomposed before the hydrolysis.

[23] Jensen and Bedard, *J. Org. Chem.*, 1959, **24**, 874.

[24] Rembaum, Shiao-Ping Siao, and Indictor, *J. Polymer Sci.*, 1962, **56**, S 17.

[25] Bryce-Smith, unpublished work.

[25a] Letsinger and Pollart, *J. Amer. Chem. Soc.*, 1956, **78**, 6079.

" Distilled " calcium (Union Carbide) was a gift from Ethyl Corporation and contained *ca.* 5% of magnesium, *ca.* 1% of strontium, and $<0\cdot01\%$ of sodium. Calcium powder (Ethyl Corporation) obtained by dissolution of sodium–calcium alloy in methanol contained *ca.* 1·5% of sodium, as did lump calcium from Hopkin and Williams. These are designated calcium " A," " B," " C," and " D," respectively. Bulk metal was milled under liquid paraffin to an average particle size of $3 \times 1 \times 0\cdot2$ mm. and stored as a slurry.* The liquid paraffin was removed by dry ether in a Soxhlet apparatus: simple washing with ether was unsatisfactory.

Ether was dried over sodium, and tetrahydrofuran over calcium hydride. Alkyl halides were purified by conventional methods. Reactions were conducted under argon, except where otherwise indicated. Organocalcium halides were estimated as indicated in the Table, footnotes *a* and *b*.

" Activated " calcium was prepared by stirring the millings under argon with 2 atoms % of mercury. Much heat was evolved. The prior heating previously mentioned [1] has now been found unnecessary.

Preparation of Reagents.—(*a*) *Methylcalcium bromide.* A solution of methyl bromide (14·3 g.) in tetrahydrofuran (25 ml.) were added at 0° to activated calcium " A " (7·5 g. of Ca) in tetrahydrofuran (25 ml.). A grey precipitate began to be formed after 30 minutes' stirring at 0—5° under nitrogen. Tetrahydrofuran (100 ml.) was then added, and the mixture was stirred at −35° for 3 hr. The yield was 81%.

(*b*) *Methylcalcium iodide.* About 10 ml. of a solution of methyl iodide (21·3 g.) in tetrahydrofuran (25 ml.) was added at −3° to activated calcium " A " (7·5 g. Ca) in tetrahydrofuran (50 ml.) under nitrogen. Reaction commenced almost immediately. Tetrahydrofuran (80 ml.) was then added. The rest of the methyl iodide solution was run in during 1 hr. with stirring at −55°, and stirring was continued for a further 4 hr. at this temperature. The yield was again 81%.

A similar preparation conducted in refluxing diethyl ether gave a yield of 37%.

(*c*) *Ethylcalcium chloride.* Ethyl iodide (2·34 g.) was added to an unstirred gently refluxing (50°) mixture of ethyl chloride (9·7 g.) and activated calcium " A " (8 g. Ca) in tetrahydrofuran (40 ml.) (condenser at −70°) under nitrogen. Ethyl iodide was consumed in an initial rapid reaction, which soon subsided: a sample of the mixture then gave a negative test with the Michler's ketone reagent,[26] so ethylcalcium iodide was absent. The mixture was stirred under reflux for a further 5 hr., and a sample then gave a strong positive test with the Michler's ketone reagent. The yield was 20%.

(*d*) *Ethylcalcium bromide.* About 10 ml. of a solution of ethyl bromide (15·4 g.) in tetrahydrofuran (30 ml.) were added to activated calcium "A" (7·5 g. Ca) in tetrahydrofuran (30 ml. at 20° under nitrogen. The reaction commenced after 45 minutes' stirring. The rest of the ethyl bromide solution was then run in, during 2 hr., at −30°, and stirring was continued at this temperature for a further 5 hr. The yield was 33%.

(*e*) *Ethylcalcium iodide.* About 10 ml. of a solution of ethyl iodide (23·4 g.) in ether (25 ml.) were stirred under gentle reflux with activated calcium " A " (7·5 g. Ca). Reaction commenced within 10 min., and the remainder of the solution was added dropwise during 2½ hr. Heating under reflux was continued for a further 3 hr. The yield was 39%.

A similar preparation conducted at −65° in tetrahydrofuran gave a yield of 32%. The use of 1 : 1 tetrahydrofuran–methylcyclohexane at −65° led to a 35% yield. It was hoped that the hydrocarbon would minimise side reactions by making the product less soluble.

(*f*) *n-Propylcalcium iodide.* The preparation was conducted essentially as in (*e*) with an equivalent amount of propyl iodide in ether and gave a 25% yield.

A preparation in tetrahydrofuran at −50° gave a yield of 27%.

(*g*) *n-Butylcalcium chloride.* A solution of butyl chloride (13·9 g.) in tetrahydrofuran (25 ml.) was stirred under reflux (75°) for 1 hr. with activated calcium " A " (8 g. of Ca). No reaction was apparent. Ethyl iodide (2·34 g.) was then added as entraining agent. Reaction commenced immediately and had subsided after 30 min. A test with the Michler's ketone reagent was negative at this stage. The mixture was stirred at 65° for a further 5½ hr. The

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* A more finely divided form of calcium could not be obtained by mechanical means. It is suspected that the yields here reported could be improved, and the range of suitable halides extended, if sodium-free calcium powder were used.

[26] Gilman and Schultz, *J. Amer. Chem. Soc.*, 1925, **47**, 2002.

product gave a positive test with the Michler's ketone reagent, and a 22% yield of butane on hydrolysis. Butane (29%) and butene (22%) were evolved during the reaction, and octane (23%) was also obtained. These figures suggest that little cleavage of tetrahydrofuran had occurred.

The use of activated calcium " B " in the above preparation obviated the need for an entrainment technique and led to a 20% yield of n-butylcalcium chloride after 24 hr. at the b. p. In a further experiment, the use of a two-fold excess of activated calcium " B " led rather surprisingly to an identical yield.

(*h*) *n-Butylcalcium bromide.* The use of n-butyl bromide (20·5 g.) as in experiment (*d*), followed by carboxylation in an ethereal slurry of solid carbon dioxide, gave valeric acid (15%) [4-bromophenacyl ester, m. p. and mixed m. p. 75° (higher-melting form)[27]] and di-n-butyl ketone (9%) (semicarbazone, m. p. and mixed m. p. 89°). No 5-butylnonan-5-ol was found.

(*i*) *n-Butylcalcium iodide.* A solution of butyl iodide (18·4 g.) in ether (15 ml.) was added with stirring during 30 min. to activated calcium " B " (4·5 g. of Ca) in refluxing ether (35 ml.). The mixture was stirred for a further 30 min. under reflux. Hydrolysis gave a 63% yield of butane. The use of activated calcium " A " and " D " led to yields of 40 and 15%, respectively. Activated calcium " D " with 10 equiv. % of n-butylmagnesium iodide added as promoter gave a 45% yield. Tetrahydrofuran was unsatisfactory as a reaction medium. Thus, at the reflux temperature (65°) the yield of butylcalcium iodide from activated calcium " D " was zero, and at $-30°$ (activated calcium " A ") the yield was 6% based on valeric acid and dibutyl ketone obtained on carboxylation.

(*j*) *n-Pentylcalcium iodide.* A solution of pentyl iodide (19·8 g.) in ether (20 ml.) was added with stirring in 1 hr. to activated calcium " A " (6·5 g. of Ca) in refluxing ether (40 ml.). Refluxing and stirring were continued for 6 hr., and the cooled product was poured on an ethereal slurry of solid carbon dioxide, to give hexanoic acid (9%) (4-bromophenacyl ester, m. p. 72°), di-n-pentyl ketone (15%), b. p. 220°, n_D^{20} 1·4290, and decane (21%), b. p. 170—173°, n_D^{20} 1·413.

The use of tetrahydrofuran at $-20°$ in place of ether in the above preparation gave hexanoic acid (7%), di-n-pentyl ketone (12%), and decane (23%).

(*k*) *Phenylcalcium chloride.* The procedure in experiment (*g*) was followed, with chlorobenzene (44 g.) and activated calcium " A." The product gave a weak positive test with the Michler's ketone reagent. Carboxylation gave benzoic acid (0·01 g.), m. p. 118° and mixed m. p. 120°. Chlorobenzene (30 g.) was recovered. No trace of benzophenone or triphenylmethanol was found.

(*l*) *Phenylcalcium bromide.* The general procedure of experiment (*d*) was followed with bromobenzene (10·0 g.) and a main reaction temperature of $-10°$. Carboxylation by passage of a stream of carbon dioxide at $-10°$ to $-20°$ gave benzoic acid (43%), m. p. and mixed m. p. 121°, and benzophenone (2%) (2,4-dinitrophenylhydrazone, m. p. 247°). No triphenylmethanol was found.

In a duplicate preparation, carboxylation as in (*j*) gave benzoic acid (45%), and no benzophenone or triphenylmethanol. Slow carboxylation of organolithium compounds is known to favour the formation of ketones.

No reaction between bromobenzene and activated calcium " B " could be induced in diethyl ether, even by use of iodobenzene as entraining agent.

(*m*) *Phenylcalcium iodide.* A solution of iodobenzene (20·4 g.) in tetrahydrofuran (30 ml.) was added in 3 hr. to activated calcium " B " (4·6 g. of Ca) in tetrahydrofuran (70 ml.) at $-30°$ with stirring. Stirring was continued at $-30°$ for a further 2 hr., and a stream of carbon dioxide was then passed through the mixture at $-50°$ to $-30°$. Benzoic acid (90%), m. p. and mixed m. p. 121·5°, was obtained. Neither benzophenone (contrast *l*) nor triphenylmethanol was detected.

Six repetitions of the above procedure with activated calcium " A " gave yields within the range 68—72%. A yield of 55% was obtained with the use of activated calcium " C."

When the above preparation (calcium " B ") was performed at 10—15°, the yield of benzoic acid was 27%. At the b. p. (*ca.* 70°), the yield was 15%. Neither the yield nor the rate of reaction was significantly increased when this reaction was repeated in the presence of 5 equivalents % of aluminium t-butoxide (cf. ref. 10).

[27] Bryce-Smith and Cox, *J.*, 1958, 1050.

Gilman, Kirby, Lichtenwalter, and Young's preparation of phenylcalcium iodide [3] in ether was repeated with unactivated calcium " B." The yield indicated by titration of hydrolysed aliquot portions of the stirred suspension was 77% (reported [3] 90%), but carboxylation gave only a 30% yield of benzoic acid.

(*n*) p-*Tolylcalcium iodide.* The use of *p*-iodotoluene (20·05 g.) according to the procedure of experiment (*m*) (calcium " A "), followed by carboxylation as in experiment (*j*), gave *p*-toluic acid (46%), m. p. and mixed m. p. 179°.

Reaction of 2-*Iodothiophen with Calcium.*—About 5 ml. of a solution of 2-iodothiophen (10·5 g.) in tetrahydrofuran (10 ml.) were stirred with activated calcium " A " (5 g. of Ca) in tetrahydrofuran (20 ml.) at 0°. A transient yellow colour (iodine?) appeared after 5 min. The remainder of the halide solution was then added in 3 hr. at −35°. Stirring at this temperature was continued for a further 2 hr. Carboxylation as in experiment (*j*) gave a mixture of acids (4·4 g.) which was extracted (Soxhlet) with light petroleum (b. p. 100—120°) for 2½ hr. The insoluble material was recrystallised from water (charcoal), to give thiophen-2,5-dicarboxylic acid (0·8 g.), m. p. >400° [dimethyl ester m. p. 143° (lit.,[28] 144°)] [Found: equiv., 89·0. Calc. for $C_6H_4O_4S$ (dibasic): equiv., 86·0]. Removal of solvent from the extract, and recrystallisation of the residue from water, gave 5-iodothiophen-2-carboxylic acid (1·2 g.), m. p. and mixed m. p. 133° [29] (Found: equiv., 255. Calc. for $C_5H_3IO_2S$: equiv., 254). The 4-*bromophenacyl ester* had m. p. 145° (Found: C, 34·6; H, 1·6. $C_{13}H_8BrIO_3S$ requires C, 34·65; H, 1·75%). Examination of the mother-liquors from recrystallisation of the iodocarboxylic acid revealed no thiophen-2-carboxylic acid.

Reaction of 2-*Iodothiophen with Lithium.*—The previous experiment was repeated with lithium (1·5 g.) in place of activated calcium. The only acid reaction product found was thiophen-2-carboxylic acid (4·4 g., 69%), m. p. 127° (lit.,[20] 127°) (Found: equiv., 126·5. Calc. for $C_5H_4O_2S$: equiv., 128).

Reaction of n-Butylcalcium Iodide with Carbon Dioxide.—An ethereal solution of n-butylcalcium iodide was prepared from activated calcium " A " as in experiment (*i*). Passage of a slow stream of carbon dioxide at 20—25° led to the production of n-valeric acid (1·05 g., 10%) [4-bromophenacyl ester, m. p. and mixed m. p. 75° (higher-melting form) [27]], di-n-butyl ketone (1·5 g., 21%) (semicarbazone, m. p. and mixed m. p. 89°), and 5-butylnonan-5-ol (1·31 g.), identified by its ready dehydration to 5-butylnon-4-ene, b. p. 215—220°, n_D^{20} 1·4371 (lit., b. p. 216°, n_D^{20} 1·4375).

Several other carboxylations are referred to in preceding experiments.

Reactions of Phenylcalcium Iodide.—(i) *Benzoyl chloride.* Phenylcalcium iodide was prepared from activated calcium " A " as in experiment (*m*). A solution of benzoyl chloride (14·4 g.) in tetrahydrofuran (17 ml.) was added with stirring at −30°. The reaction was exothermic. Extraction of the steam-involatile products with 70% sulphuric acid, followed by dilution of the filtered extract with water, gave triphenylmethanol (8·4 g., 94%), m. p. 159°. A single recrystallisation from alcohol gave material having m. p. and mixed m. p. 162°.

(ii) *Benzophenone.* The use of benzophenone (18·3 g.) in place of benzoyl chloride in the foregoing experiment gave triphenylmethanol in 80% yield.

(iii) *Ethyl benzoate.* The use of ethyl benzoate (16·6 g.) in place of benzoyl chloride in experiment (i) gave triphenylmethanol in 80% yield.

(iv) *Pyridine* (2-*phenylation and* 2,5-*diphenylation*). Pyridine (12·0 g.) was added at −60° to phenylcalcium iodide (0·084 equiv.) in tetrahydrofuran (175 ml.). The mixture was allowed to warm to room temperature during 40 hr. Toluene (100 ml.) was then added, and solvents were distilled off until the temperature of the contents of the reaction flask reached 95°: this temperature was maintained for 2 hr. Hydrolysis followed by distillation of the organic products gave 2-phenylpyridine (4·9 g., 41%), b. p. 120—130°/2·5 mm. (picrate, m. p. and mixed m. p. 178°), and 2,5-diphenylpyridine (0·5 g., 6%), b. p. 250—255°/2 mm. (Found: C, 88·5; H, 5·75; N, 5·8. Calc. for $C_{17}H_{13}N$: C, 88·3; H, 5·65; N, 6·05%). This material had m. p. 168°. Three recrystallisations from alcohol raised the m. p. to 171° (lit.,[17] 174—175°). The infrared and ultraviolet spectra were identical with those of 2,5-diphenylpyridine [17] (Professor Wiley kindly provided a copy of the infrared spectrum). The *picrate* had m. p. 187° (decomp.) (Found: C, 59·8; H, 3·75; N, 12·3. $C_{23}H_{26}N_4O_7$ requires C, 60·0; H, 3·50; N, 12·15%).

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[28] Messinger, *Ber.*, 1885, **18**, 567.

[29] Gattermann and Römer, *Ber.*, 1886, **19**, 692.

(v) *Pyridine* (2-*phenylation and* 2,6-*diphenylation*). The foregoing experiment was repeated, except that the pyridine was added at −20°, and the mixture was allowed to warm from −20° to room temperature in 5 hr. Working up as previously gave 2-phenylpyridine (42%) and 2,6-diphenylpyridine (10%), m. p. 82° (lit.,[30] 82°) [picrate m. p. 169° (lit.,[31] 169°); 1,3,5-trinitrobenzene adduct m. p. 113° (lit.,[32] 113°)]. No 2,5-diphenylpyridine was found.

Phenyl-lithium in tetrahydrofuran reacted with pyridine under the conditions of experiment (iv) to give 2-phenylpyridine. No diphenylation was detected.

(vi) 1-*Bromonaphthalene*. A solution of 1-bromonaphthalene (31·1 g.) in tetrahydrofuran (20 ml.) was added at −30° to a solution of phenylcalcium iodide (0·043 equiv.) in tetrahydrofuran (150 ml.). The stirred mixture was allowed to warm to room temperature in 90 min., and was then poured on an ethereal slurry of solid carbon dioxide. 1-Naphthoic acid (7·3 g., 98%), m. p. 159°, was obtained which after recrystallisation from aqueous alcohol had m. p. and mixed m. p. 162°.

(vii) *Anisole*. A solution of phenylcalcium iodide (0·075 equiv.) in tetrahydrofuran (115 ml.) and anisole (100 ml.) was stirred in the dark at room temperature for 14 days, then carboxylated with an ethereal slurry of solid carbon dioxide. Working up gave *o*-anisic acid (1·8 g., 16%), m. p. 97°. Recrystallisation from aqueous alcohol gave material having m. p. and mixed m. p. 99—100°. No benzoic acid was found. A phenolic product was identified as guaiacol (10·5%) through the tribromide, m. p. and mixed m. p. 117°. Although this experiment was performed under argon, it seems probable that a little air must have entered the system during the prolonged reaction period.

(viii) *Toluene*. A suspension of phenylcalcium iodide (0·175 equiv.) in toluene (150 ml.) was prepared by solvent exchange and was heated at 105—107° with stirring for 3 hr. Carboxylation gave only benzoic acid (10%). The characteristic odour of phenylacetic acid was not in evidence.

A similar experiment performed for 12 hr. likewise gave no phenylacetic acid.

Attempted Rearrangement of p-*Tolylcalcium Iodide*.—A suspension of *p*-tolylcalcium iodide (0·1 equiv.) in methylcyclohexane (100 ml.) was stired at 95° for 90 min. Carboxylation gave *p*-toluic acid (90%), m. p. 179°. No trace of phenylacetic acid was detected.

Metallation of Thiophen by Methylcalcium Iodide.—Thiophen (6·7 g.) was added at −30° to methylcalcium iodide (0·092 equiv.) in tetrahydrofuran (200 ml.). No evolution of gas was detected. The mixture was warmed to room temperature; gas, presumably methane, was then slowly evolved during 4 days. Carboxylation gave thiophen-2-carboxylic acid (2·15 g., 21%), m. p. 126° (lit.,[30] 127°). Two recrystallisations from water (charcoal) raised the m. p. to 129°. The mixed m. p. with authentic material (m. p. 127°) (from carboxylation of 2-thienyllithium) was 128—129°. No dimetallation product was detected.

Reaction of Methylcalcium Iodide with Benzaldehyde.—Benzaldehyde (11·6 g.) was added at −50° to methylcalcium iodide (0·087 equiv.) in tetrahydrofuran (150 ml.). Heat was evolved and a green colour developed. After 10 min. at −45° to −50°, a test with the Michler's ketone reagent was negative.[26] The mixture was hydrolysed at room temperature, to give α-methylbenzyl alcohol (1·3 g., 10%) b. p. 96—98°/15 mm., n_D^{20} 1·527, and a viscous undistillable residue (8 g.), apparently polymeric.

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[30] Paal and Strasser, *Ber.*, 1887, **20**, 2764.
[31] Scholtz, *Ber.*, 1895, **28**, 1731.
[32] Sudborough and Beard, *J.*, 1920, **117**, 794.