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REACTIONS OF SOME (POLYHALOARYL)COPPER COMPOUNDS WITH ACID CHLORIDES AND CHLOROSILANES

A. E. JUKES, S. S. DUA AND H. GILMAN
Department of Chemistry, Iowa State University, Ames, Iowa, 50010 (U.S.A.)

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SUMMARY

(Polyhaloaryl)copper compounds or their complexes, where the aryl group is pentafluorophenyl, pentachlorophenyl, or 2,3,5,6-tetrachloro-4-pyridyl, have been prepared by three methods: (*i*) via a polyhaloaryllithium compound; (*ii*) via a polyhaloaryl Grignard reagent; and (*iii*) via addition of polyhaloarene to lithium dimethylcopper. The copper compounds react readily with acid chlorides but slowly or not at all with chlorosilanes.

INTRODUCTION

Recently there has been considerable interest in the use of organocopper compounds for the synthesis of a variety of substances. In some earlier studies of organometallic compounds we prepared, among several organocopper compounds, the insoluble methylcopper[1], the soluble "ate" complex lithium dimethylcopper[1], and phenylcopper[2]. Several broad generalizations were made[2] on the order of decreasing thermal stability of organometallic compounds, including those of copper. It has long been recognized that the introduction of halogens, particularly fluorine and chlorine, may enhance the thermal stability of many organometallic compounds. This has been found to be the case for (perfluoroalkyl)copper[3] and -silver[4] compounds (pentafluorophenyl)copper[5,6,7,8], and other (polyhaloaryl)copper compounds[8,9]. We have found that the copper compounds are good intermediates for the preparation of polyhaloaryl ketones in high yields, but exhibit a low order of reactivity or are unreactive towards chlorosilanes in ethereal solvents.

RESULTS AND DISCUSSION

Prior to our work, (pentafluorophenyl)copper had been prepared by addition of a copper(I) halide to a (pentafluorophenyl)magnesium halide[5,6]. Three methods were mentioned previously[8,10], for the preparation of (polyhaloaryl)copper compounds or their complexes, where the aryl group is pentafluorophenyl, pentachlorophenyl, or 2,3,5,6-tetrachloro-4-pyridyl. They were: method A, addition of a copper(I) halide to a polyhaloaryllithium compound; method B, addition of a copper(I) halide to a polyhaloaryl Grignard reagent; and method C, addition of a polyhaloarene to lithium dimethylcopper containing a small excess of methyllithium. The (polyhaloaryl)copper compounds, prepared by all methods, react exothermally with acid halides to give high yields of polyhaloaryl ketones. We have previously reported[8a,10] the preparation of some polyhaloaryl diketones by similar procedures.

This facile reaction may complement organocadmium compounds for the preparation of ketones[11]. As the copper compounds were used without isolation and no substances arising from reaction of the copper compound with the carbonyl group were isolated they may be less reactive than organocadmium compounds[12].

We have prepared the respective polyhaloaryl methyl and phenyl ketones in yields as high as 85%. Methods A and B are, in many cases, the preferred preparations of the (polyhaloaryl)copper compounds or their complexes, although in some cases method C can give high yields of the copper compounds via rapid reactions, *e.g.* pentafluorobenzene and lithium dimethylcopper. Generally, slightly higher yields of the ketones, and hence the copper compounds, are obtained when copper(I) iodide is used rather than copper(I) chloride, and via method A.

Addition of pentafluorobenzene ($2x$ moles) to lithium dimethylcopper (x moles), containing a small excess of methyllithium, at −10° in ether was accompanied by rapid evolution of nearly the theoretical quantity ($2x$ moles) of methane to give a new copper compound. Pentafluorobenzene, pentafluoroiodobenzene, and 4-iodotetrachloropyridine were the only arenes of those investigated which reacted with lithium dimethylcopper in ether: for the other arenes a mixture of THF and ether was found to be necessary. In all of these reactions, except that with pentafluorobenzene, a yellow precipitate resembling methylcopper was observed during the addition of the arene to the lithium dimethylcopper, perhaps indicating the following sequence of reactions, although this may be an over-simplification.

$$C_6Cl_5X + Li[Me_2Cu] \rightarrow C_6Cl_5Li + MeCu + MeX \rightarrow Li[(C_6Cl_5)CuMe]$$

$$C_6Cl_5X + Li[(C_6Cl_5)CuMe] \rightarrow Li[(C_6Cl_5)_2Cu] + MeX$$

$$X = H \text{ or } Cl$$

In this connection it was found that the polyhaloaryllithium compounds dissolve methylcopper to give clear but usually colored solutions, which on derivatization with benzoyl chloride afforded a mixture of acetophenone and the respective polyhaloaryl phenyl ketone.

In studies concerning the reaction of organocopper compounds with α,β-unsaturated ketones[13], investigation of solutions of lithium dimethylcopper in ether by NMR spectroscopy and its low order of reactivity with carbonyl functions indicated that the equilibrium (1) may be far to the right. Possibly, the addition of a

$$(MeCu)_n + MeLi \leftrightarrows Li^+[Me_2Cu]^- \qquad (1)$$

polyhaloarene upsets this equilibrium and metalation or metal–halogen exchange proceeds rapidly via a small quantity of methyllithium.

A small excess of methyllithium appears to be necessary for the metalation of polyhaloarenes by lithium dimethylcopper. For reactions in which the evolution of methane was very slow, addition of a further small quantity (*ca.* 5%) of methyllithium resulted in a rapid evolution of methane. Furthermore no hydrogen–copper exchange was observed between pentafluorobenzene and methylcopper or phenylcopper. The presence of a small excess of methyllithium in the lithium dimethylcopper may account for the observed difference in the reaction with polyhaloarenes and some organic monohalides[14].

No appreciable reaction occurred between hexafluorobenzene and lithium dimethylcopper in THF/ether or DME/ether at 0°. There was isolated *ca.* 3–5% yields of pentafluorophenyl ketones subsequent to the addition of acid halides, indicating replacement of fluorine by a metal, possibly via free radicals which may arise from decomposition of lithium dimethylcopper. Although such observations have previously been made[15,16], fluorine–metal exchange is generally not considered likely under the usual conditions of halogen–metal exchange and Grignard reagent formation. Recently there has been a report of an anomalous reaction of a Grignard reagent with decafluorobiphenyl in which the intermediacy of a polyfluoroaryl Grignard reagent was postulated[17].

An indication of the lower reactivity of the (polyhaloaryl)copper compounds is their reactions with chlorosilanes. A mixture of (pentafluorophenyl)copper and chlorotrimethylsilane in ether/hexane was kept at the ambient temperature for 4.5 days, although VPC analysis indicated no apparent further reaction after 12 h. The products were (pentafluorophenyl)trimethylsilane (25%) and decafluorobiphenyl (10.5%). (Pentafluorophenyl)copper and chlorodimethylphenylsilane on heating in dioxane at 95° afforded (pentafluorophenyl)dimethylphenylsilane in 59% yield, identical to a sample prepared in excellent yield via pentafluorophenyllithium. A reaction with chlorotriphenylsilane under similar conditions gave only a low yield of (pentafluorophenyl)triphenylsilane. Similar reactions of (pentachlorophenyl)copper and (2,3,5,6-tetrachloro-4-pyridyl)copper with chlorosilanes were unsuccessful.

So far, no significant measure of success has been obtained in reactions of the (polyhaloaryl)copper compounds with some sulfur compounds: thionyl chloride, sulfuryl chloride and *p*-toluenesulfonyl chloride.

EXPERIMENTAL

All reactions were carried out in an atmosphere of dry, oxygen-free nitrogen. Ethereal solvents were dried over sodium and, excepting ether, further purified by distillation from sodium benzophenone ketyl. n-Butyllithium in hexane, methyllithium in ether, and phenyllithium in ether/benzene were from the Foote Mineral Co. Copper(I) iodide was either prepared[18] or purchased from Alfa Inorganic Chemicals. Copper(I) chloride was prepared by purification[19] of commercial samples.

Polyhaloaryllithium and Grignard reagents

The following were prepared by reported procedures: pentachlorophenyllithium[20], (pentachlorophenyl)magnesium chloride[21], 2,3,5,6-tetrachloro-4-pyridyllithium[22], (2,3,5,6-tetrachloro-4-pyridyl)magnesium chloride[9,23], pentafluorophenyllithium[24], and (pentafluorophenyl)magnesium chloride[25].

2.3.5.6-Tetrachloro-4-pyridyllithium was prepared by addition of n-butyllithium in hexane to pentachloropyridine (equimolar proportions) in THF at −70°. The lithium compound is best used within one hour as it decomposes, even at −70°.

Preparation of polyhaloarylcopper compounds

Method A: *From polyhaloaryllithium compounds.* To the polyhaloaryllithium compound (from *x* moles of the respective arene) in THF at −70° was added a copper (I) halide (*x* moles) and the mixture stirred at −70° until Color Test I[32] was negative. The mixture was allowed to warm to the ambient temperature before use. The time taken for Color Test I to become negative was at least several hours. For example, pentafluorophenyllithium and copper(I) iodide in THF at −70° gave a negative Color Test I only after 5 h had elapsed. The combination of pentafluorophenyllithium and copper(I) chloride in ether under our conditions gave poor yields of ketones subsequent to the addition of an acid chloride, and should be avoided.

Method B: *From polyhaloaryl Grignard reagents.* To the Grignard reagent (from *x* moles of the respective arene) in THF at 0° was added a copper(I) halide (*x* moles) and the mixture stirred for up to 16 h. Color Test I is usually negative within one hour. However, an investigation of the sensitivity of Color Test I[32] towards (pentafluorophenyl)magnesium chloride in THF has shown that a weak positive Color Test is obtained with a 0.05 *M* solution of the Grignard reagent but not with a 0.04 *M* solution. Similar results were reported previously for (2,3,5,6-tetrachloro-4-pyridyl)magnesium chloride[9]. The malachite green color is often masked by excess iodine which can be reduced by addition of a few drops of a sodium thiosulfate solution. Ample time was allowed at each stage of the test as the reactions involved appeared to be slow in dilute solution. When Color Test I was performed during the preparation of a copper compound, there was present a pale green aqueous layer [due to oxidation of copper(I) salts].

Method C: *Via lithium dimethylcopper.* Lithium dimethylcopper[1] was prepared by a slow, dropwise addition of methyllithium (2.2*x* moles) in ether to copper(I) iodide (*x* moles) in ether or THF at −10° (or lower). Copper(I) chloride could be used when the solvent was THF (eventually a THF/ether mixture), but was unsatisfactory when ether alone was the solvent. Fresh, clear solutions of methyllithium were used at the strength determined by the supplier. To the lithium dimethylcopper at −10° was added a polyhaloarene (*x* or 2*x* moles) dissolved in a small quantity of ether or THF, depending on the medium in which the "ate" complex was prepared. For preparations involving hydrogen-containing arenes the reaction could be followed by the rate of evolution of methane. For perhalogenated arenes, VPC examination of a hydrolyzed aliquot on a suitable column was used to follow the progress of the reaction (usually taking about 4 h).

Lithium dimethylcopper containing none or only a small excess of methyllithium does not give a positive Color Test I, as previously stated[1].

Polyhaloaryl ketones (*Tables* 1 *and* 2)

To the copper compound at 0° was added an excess of an acid halide and the mixture stirred for several hours. In many cases the reaction was noticeably exothermic and stirring need not be prolonged. If left for too long a period before hydrolysis with aqueous ammonia and ammonium chloride, fission of the ether by the acid halide in the presence of metal salts produces ω-halo esters[26], particularly in reactions employing THF as solvent. After the customary work-up[10], the products were separated by distillation or crystallization. These were: 2′,3′,4′,5′,6′-pentafluoroacetophenone, b.p. 82–85°/28 mm, $n_D^{17.5}$ 1.4335, [cited[27]: 48–50°/5 mm, $n_D^{17.5}$ 1.4330], with

TABLE 1

POLYHALOARYL KETONES FROM COPPER COMPOUNDS PREPARED BY METHOD A AND B

Copper compound[a] (scale[b] moles)	Method[c]	Acid halide	Product (% yield)
C_6F_5Cu (0.05)	A[d]	AcBr	C_6F_5Ac (82.5)
C_6F_5Cu (0.05)	A[d]	AcCl	C_6F_5Ac (84)
C_6F_5Cu[e] (0.05)	A[d]	AcCl	C_6F_5Ac (37.5), $(C_6F_5)_2$ (36)
C_6F_5Cu[e] (0.10)	B	AcCl	C_6F_5Ac (69.5)
C_6F_5Cu (0.05)	A	AcBr	C_6F_5Ac (76)
C_6F_5Cu[e] (0.05)	A	AcCl	C_6F_5Ac (64)
C_6F_5Cu (0.05)	A	BzCl	C_6F_5Bz (70)
C_6Cl_5Cu[f] (0.05)	A	AcBr	C_6Cl_5Ac (65)
C_6Cl_5Cu[f] (0.05)	A	BzCl	C_6Cl_5Bz (82)
C_6Cl_5Cu[f] (0.05)	A	BzCl	C_6Cl_5Bz (85)
C_6Cl_5Cu[e,f] (0.03)	A	BzCl	C_6Cl_5Bz (71)
C_5NCl_4Cu (0.05)	A	AcBr	$(C_5Cl_4N)Ac$-4 (64)
C_5NCl_4Cu (0.05)	A	BzCl	$(C_5Cl_4N)Bz$-4 (47)
C_5NCl_4Cu[e] (0.04)	B	BzCl	$(C_5Cl_4N)Bz$-4 (61)
C_5NCl_4Cu (0.04)	B	BzCl	$(C_5Cl_4N)Bz$-4 (63)
C_6Cl_5Cu[f,g] (0.05)	A	BzCl	C_6Cl_5Bz (82)

[a] No structures are to be implied in the notation for the copper compounds. Unless otherwise stated, copper(I) iodide was used. [b] Scale is based on the quantity of the polyhaloarene used in preparation. [c] The copper compound was prepared in THF/hexane unless otherwise specified. [d] Solvent was ether/hexane. [e] Copper(I) chloride used. [f] From C_6Cl_5H. [g] MeLi used in place of BuLi.

TABLE 2

POLYHALOARYL KETONES FROM COPPER COMPOUNDS PREPARED BY METHOD C

$LiCuMe_2$[a] (moles)	Arene (moles)	Solvent	Acid halide	Product (% yield)
0.05	C_6F_5H (0.05)	Et_2O	AcCl	C_6F_5Ac (68)
0.05	C_6F_5H (0.10)	Et_2O	AcCl	C_6F_5Ac (79)
0.05	C_6F_5I (0.05)	Et_2O	AcCl	C_6F_5Ac (59)
0.05	C_6F_5I (0.10)	Et_2O	AcCl	C_6F_5Ac (64)[d] C_6F_5I (20)
0.05	C_6F_6[e] (0.10)	THF/Et_2O (4/1)	BzCl	C_6F_5Bz (5)
0.05	C_6F_6[e] (0.10)	DME/Et_2O (4/1)	AcCl	C_6F_5Ac (4)
0.03	C_6Cl_5H (0.025)	Et_2O	AcCl	C_6Cl_5H (72)[f]
0.025	C_6Cl_5H (0.05)	THF/Et_2O (4/1)	BzCl	C_6Cl_5Bz (65)
0.02	C_6Cl_6 (0.02)	THF/Et_2O (4/1)	BzCl	C_6Cl_5Bz (63) $CH_3COC_6H_5$
0.02[b]	C_6Cl_6 (0.02)	THF/Et_2O (4/1)	BzCl	C_6Cl_5Bz (68)
0.015	$(C_5Cl_4N)I$-4 (0.015)	Et_2O	AcBr	$(C_5Cl_4N)Ac$-4 (44)
0.03	$(C_5Cl_4N)H$-4[c] (0.03)	THF/Et_2O (3/1)	BzCl	$(C_5Cl_4N)Bz$-4 (31) $CH_3COC_6H_5$
0.04	C_5Cl_5N (0.04)	THF/Et_2O (4/1)	BzCl	$(C_5Cl_4N)Bz$-4 (66) $CH_3COC_6H_5$ (35)
0.05	C_5Cl_5N (0.05)	Et_2O	AcCl	C_5Cl_5N (90)[f]

[a] 10% Excess methyllithium. Copper(I) iodide used unless otherwise stated. [b] Copper(I) chloride used. [c] Insufficient methane was liberated (250 ml). [d] Yield based on the C_6F_5I consumed. [e] Kept 24 h at 0° before addition of the acid chloride. [f] No reaction occurred.

UV and IR spectral data in agreement with that published[28]; 2,3,4,5,6,-pentafluorobenzophenone, b.p. 92–94°/0.2 mm, m.p. 30–31° [cited[28]: m.p. 33°] with UV and IR spectral data in agreement with that published; 2',3',4',5',6'-pentachloroacetophenone, m.p. 90–91°, [cited[29]: 90°], ν_{max} 1726 cm^{-1} (C=O); 2,3,4,5,6-pentachlorobenzophenone, m.p. 153–154°, [cited[30]: 154°], ν_{max} 1684 cm^{-1} (C=O); 4-benzoyltetrachloropyridine, m.p. 134–135°, identical to a sample prepared in this laboratory[23]; and 4-acetyltetrachloropyridine, m.p. 120–121°, ν_{max} 1724 cm^{-1} (C=O). (Found: C, 32.51; H, 1.26. $C_7H_3Cl_4NO$ calcd.: C, 32.43; H, 1.16%.)

The reactions are summarized in Tables 1 and 2.

Addition of polyhaloaryllithium compounds to methylcopper

Methylcopper was prepared[1] by addition of methyllithium (x moles) to copper(I) iodide (x moles) in ether at −10°.

(*a*). *Pentafluorophenyllithium* (from 0.05 mole C_6F_5H) in ether at −70° was added to methylcopper (0.05 mole) in ether at −70°. The methylcopper dissolved, and on warming slowly to room temperature a clear solution was obtained. Subsequent to addition of excess benzoyl chloride and the usual work-up there were obtained acetophenone (2.03 g, 34%) and 2,3,4,5,6-pentafluorobenzophenone (10.18 g, 80%), m.p. 32.5–33° [cited[28]: 33°].

(*b*). *Pentachlorophenyllithium* (from 0.05 mole C_6Cl_6) at −70° in THF was added to methylcopper (0.05 mole) in ether at −70°. The methylcopper gradually dissolved and on allowing to warm slowly to room temperature gave a clear wine-red solution. Subsequent to addition of excess benzoyl chloride, acetophenone (2.07 g, 35%) and 2,3,4,5,6-pentachlorobenzophenone (4.22 g, 47%), m.p. 152–154°, were isolated.

(*c*). 2,3,5,6-*Tetrachloropyridyllithium* (from 0.05 mole C_5Cl_5N) in THF at −70° was added to methylcopper (0.05 mole) in ether at −20°. After allowing to warm slowly to room temperature the solution was red and clear. The complex was kept 12 h at the ambient temperature. Subsequent to addition of excess benzoyl chloride, 4-benzoyltetrachloropyridine (7.30 g, 45.5%), m.p. 134–135° (from ethanol) was isolated. Distillation of the residue afforded acetophenone (2.52 g, 42%).

Pentafluorobenzene and phenylcopper

Phenylcopper[31] was prepared by addition of phenyllithium (0.05 mole) in ether/benzene to a suspension of copper(I) iodide (10.47 g, 0.055 mole) in ether at 0°. Pentafluorobenzene (8.4 g, 0.05 mole) was added and the mixture stirred at 0° for 24 h. The color changed from pale yellow, through brown to a copper color. Iodobenzene (20.4 g, 0.1 mole) was added, the solvent evaporated, and the residue heated at 100° for 44 h. Work-up in the usual manner afforded biphenyl (6.55 g), m.p. 64–65°. Crystallization from ethanol gave white needles, m.p. 69–70°, identical to an authentic sample (mixed m.p.). The chloroform-insoluble residue (2.5 g), was insoluble in aqueous ammonia/ammonium chloride and appeared to be copper. No 2,3,4,5,6-pentafluorobiphenyl was present.

Pentafluorobenzene and methylcopper

To methylcopper, prepared by addition of methyllithium (0.05 mole) in ether to copper(I) iodide (9.50 g, 0.05 mole) in ether at −10°, was added pentafluorobenzene (8.4 g, 0.05 mole). No methane was liberated and no 2',3',4',5',6'-pentafluoroacetophenone was isolated subsequent to the addition of acetyl chloride and the customary work-up.

(Pentafluorophenyl)dimethylphenylsilane from pentafluorophenyllithium

To pentafluorophenyllithium (from 0.05 mole C_6F_5H) in ether/hexane at $-70°$ was added chlorodimethylphenylsilane (8.5 g), and the mixture stirred until Color Test I[32] was negative. Work-up in the usual manner followed by distillation afforded (pentafluorophenyl)dimethylphenylsilane as a colorless liquid (14.55 g, crude yield 96%), b.p. 90–94°/0.15 mm, 98% pure by VPC. Redistillation afforded a sample b.p. 94.5–95.5°/0.15 mm, n_D^{20} 1.5068. (Found: C, 55.83; H, 3.85. $C_{14}H_{11}F_5Si$ calcd.: C, 55.62; H, 3.67%.)

Reaction of (pentafluorophenyl)copper with chlorosilanes

(*a*). *Chlorotrimethylsilane.* Pentafluorophenylcopper [0.10 mole, from C_6F_5H, n-BuLi and copper(I) iodide] and chlorotrimethylsilane in ether/hexane were kept at 25° for 4.5 days. After hydrolysis with water, copper salts were removed by addition of aqueous ammonia and ammonium chloride and the ether phase separated and dried ($MgSO_4$). Distillation afforded (pentafluorophenyl)trimethylsilane (3.02 g, 25%), b.p. 58–60°/15 mm, identical to a sample prepared by the reported procedure[33]. Crystallization of the residue from petroleum ether (b.p. 60–70°) afforded decafluorobiphenyl (0.88 g, 10.5%), m.p. 67–68°.

(*b*). *Chlorodimethylphenylsilane.* (Pentafluorophenyl)copper (0.05 mole) and chlorodimethylphenylsilane (8.5 g, 0.05 mole) were heated in dioxane 95° for 40 h. Work-up as before afforded (pentafluorophenyl)dimethylphenylsilane (8.96 g, 59%), b.p. 90–94°/0.15 mm.

(*c*). *Chlorotriphenylsilane.* In a similar reaction in dioxane at 100° for 20 h, from pentafluorophenylcopper (0.05 mole) and chlorotriphenylsilane (10.3 g, 0.035 mole) was obtained (pentafluorophenyl)triphenylsilane (1.92 g, 9%), m.p. 131–133°, identical to a sample prepared[34] in this laboratory. The residue afforded triphenylsilanol (7.6 g).

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REFERENCES

1 H. Gilman, R. G. Jones and L. A. Woods, *J. Org. Chem.*, 17 (1952) 1630.
2 H. Gilman and J. M. Straley, *Rec. Trav. Chim. Pays-Bas*, 55 (1936) 821.
3 I. M. White, J. Thrower and V. C. R. McLoughlin, *4th Int. Symp. Fluorine Chem.*, Estes Park, Colorado (U.S.A.), July 24–28, 1967.
4 W. T. Miller, Jr., and R. J. Burnard, *J. Amer. Chem. Soc.*, 90 (1968) 7367.
5 A. Cairncross and W. A. Sheppard, *J. Amer. Chem. Soc.*, 90 (1968) 2186.
6 R. J. DePasquale and C. Tamborski, *J. Org. Chem.*, 34 (1969) 1736.
7 C. Tamborski, E. J. Soloski and R. J. DePasquale, *J. Organometal. Chem.*, 15 (1969) 494.

8 (a) S. S. DUA, A. E. JUKES AND H. GILMAN, *J. Organometal. Chem.*, 12 (1968) P24.
(b) A. E. JUKES, S. S. DUA AND H. GILMAN, *J. Organometal. Chem.*, 12 (1968) P44.
9 S. S. DUA, A. E. JUKES AND H. GILMAN, *Organic Preparations and Procedures*, 1 (3) (1969) 187.
10 S. S. DUA, A. E. JUKES AND H. GILMAN, *J. Org. Chem.*, in press.
11 D. A. SHIRLEY, *Org. Reactions*, 8 (1954) 28.
12 J. KOLLONITSCH, *J. Chem. Soc.*, (1966) 453, 456.
13 H. O. HOUSE, W. L. RESPESS AND G. M. WHITESIDES, *J. Org. Chem.*, 31 (1966) 3128.
14 E. J. COREY AND G. H. POSNER, *J. Amer. Chem. Soc.*, 89 (1967) 3911.
15 F. L. M. PATTISON, W. J. COTT AND W. C. HOWELL, *J. Org. Chem.*, 22 (1957) 464; F. L. M. PATTISON AND W. C. HOWELL, *J. Org. Chem.*, 21 (1956) 879.
16 H. GILMAN AND L. L. HECK, *J. Amer. Chem. Soc.*, 53 (1931) 377.
17 W. L. RESPESS AND C. TAMBORSKI, *156th ACS Meeting*, Atlantic City, Sept. 8–13, 1968, abstracts, Fluorine section No. 22.
18 G. B. KAUFFMAN AND R. P. PINNELL, *Inorg. Syn.*, 6 (1960) 3.
19 R. N. KELLER AND H. D. WYCOFF, *Inorg. Syn.*, 2 (1946) 1.
20 C. TAMBORSKI, E. J. SOLOSKI AND C. E. DILLS, *Chem. Ind. (London)*, (1965) 2067; M. D. RAUSCH, F. E. TIBBETTS AND H. B. GORDON, *J. Organometal. Chem.*, 5 (1966) 493.
21 S. D. ROSENBERG, J. J. WALBURN AND H. E. RAMSDEN, *J. Org. Chem.*, 22 (1957) 1606.
22 S. S. DUA AND H. GILMAN, *J. Organometal. Chem.*, 12 (1968) 299.
23 S. S. DUA AND H. GILMAN, *J. Organometal. Chem.*, 12 (1968) 234.
24 R. J. HARPER, E. J. SOLOSKI AND C. TAMBORSKI, *J. Org. Chem.*, 29 (1964) 2385.
25 A. E. JUKES AND H. GILMAN, *J. Organometal. Chem.*, 17 (1969) 145.
26 YA. L. GOL'DFARB AND M. L. SMORGANSKĬI, *J. Gen. Chem. (USSR)*. 8 (1938) 1516.
27 N. N. VOROZHTSOV, V. A. BARKHASH, N. G. IVANOVA, S. S. ANICHKINA AND O. I. ANDREEVSKAYA. *Dokl. Akad. Nauk. (USSR)*, 159 (1964) 125.
28 A. K. BARBOUR, M. W. BUXTON, P. L. COE, R. STEPHENS AND J. C. TATLOW, *J. Chem. Soc.*, (1961) 808.
29 G. LOCK AND E. BOCK, *Chem. Ber.*, 70B (1937) 916.
30 G. LOCK AND E. RODIGER, *Chem. Ber.*, 72B (1939) 861.
31 G. COSTA, A. CAMUS, L. GATTI AND N. MARSICH, *J. Organometal. Chem.*, 5 (1966) 568.
32 H. GILMAN AND F. SCHULZE, *J. Amer. Chem. Soc.*, 47 (1925) 2002.
33 M. FILD, O. GLEMSER AND G. CHRISTOPH, *Angew. Chem. Int. Ed. Engl.*, 3 (1964) 801.
34 F. W. G. FEARON AND H. GILMAN, *J. Organometal. Chem.*, 10 (1967) 409.