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NOTE

INTERACTION OF SOME POLYFLUORINATED ALKANES AND ALKENES WITH LITHIUM OR MAGNESIUM AND CHLOROTRIMETHYLSILANE

DAVID H. BALLARD* AND HENRY GILMAN
Department of Chemistry, Iowa State University, Ames, Iowa 50010 (U.S.A.)

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Incidental to a study concerned with the preparation of thermally stable silicon monomers containing polyhalogenated groups, we have investigated the *in situ* reactions of a number of mono- and polyhalogenated aromatic compounds with lithium or magnesium and chlorotrimethylsilane in tetrahydrofuran (THF)[1-4]. Many highly halogenated substrates gave tetrakis(trimethylsilyl)allene, (I)[5]. The facile formation of (I) by these methods[2-4] was further exemplified by an extension of the study to some aliphatic systems[6]. Using magnesium in place of lithium, extensive reduction occurred with hexachloro-1,3-butadiene, and bis(trimethylsilyl)-butadiyne was formed as the major product[7].

The easy replacement of chlorine under these conditions to give highly silylated unsaturated compounds has prompted us to investigate the reactions of highly fluorinated substrates under similar conditions, (Table 1).

The reaction of 1,2-dibromotetrafluoroethane with an excess of lithium and chlorotrimethylsilane gave an almost quantitative yield of bis(trimethylsilyl)acetylene, whereas the similar reaction using magnesium produced only tetrafluoroethylene; in neither experiment was any 1,2-bis(trimethylsilyl)tetrafluoroethane isolated. The easy removal of the fluorine atoms as lithium fluoride was further demonstrated in

TABLE 1

TRIMETHYLSILYLATION OF SOME POLYFLUORINATED ALKANES AND ALKENES AT 0° IN THF

Compound	Metal	Products (%)
CF_2BrCF_2Br	Li	$Me_3SiC{\equiv}CSiMe_3$ (99)
$CF_3CCl{=}CCl_2$	Li	$(Me_3Si)_2C{=}C{=}C(SiMe_3)_2$ (59)
$CF_3CFBrCF_2Br$	Li	$(Me_3Si)_2C{=}C{=}C(SiMe_3)_2$ (32)
$CF_3CCl_2CClFCF_3$	Li	$(Me_3Si)_3C{-}C{\equiv}C{-}C(SiMe_3)_3$ (15)
CF_2BrCF_2Br	Mg	$CF_2{=}CF_2$
$CF_3CFBrCF_2Br$	Mg	$CF_3CF{=}CF_2$
$CF_3CCl_2CFClCF_3$	Mg	Unidentified

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* Present address: Department of Chemistry, University College, Gower Street, London W.C.1 (England).

the other systems, and in no case was any of the trimethylsilylated fluorocarbon obtained. The production of tetrafluoroethylene from 1,2-dibromotetrafluoroethane, and hexafluoropropene from 1,2-dibromohexafluoropropane, presumably proceeds by initial Grignard formation followed by elimination of magnesium bromide in a similar manner to that envisaged for 1,2-dibromoethane.

$$CF_2BrCF_2Br \xrightarrow{Mg} [BrMgCF_2CF_2Br] \xrightarrow{-MgBr_2} CF_2{=}CF_2$$

The results obtained using lithium closely follow those obtained from the reaction of chlorinated hydrocarbons, lithium and chlorotrimethylsilane. Three-carbon systems (1,1,2-trichloro-3,3,3-trifluoropropene and 1,2-dibromohexafluoropropane) gave (I) in fairly good yields whereas 1,1,1,2,4,4,4-heptafluoro-2,3,3-trichlorobutane reacted similarly to hexachlorobutadiene giving hexakis(trimethylsilyl)-2-butyne as the major product[1].

Magnesium, chlorotrimethylsilane and the heptafluorotrichlorobutane gave an inseparable mixture of two oils (2/1); the infrared spectrum showed the presence of C=C, $SiMe_3$ and C–F groups, and it is tentatively suggested that the oil may be a mixture of *cis* and *trans*-2-(trimethylsilyl)heptafluoro-2-butene.

EXPERIMENTAL

All reactions were carried out under an atmosphere of dry oxygen-free nitrogen. THF was dried over sodium and distilled from sodium benzophenone ketyl before use. VPC analyses were carried out with an F and M Model 500 Gas Chromatograph using an $18 \times \frac{1}{4}''$ column packed with silicone rubber gum, SE 30, on Chromosorb W (1/20).

Interaction of lithium, chlorotrimethylsilane and 1,2-dibromotetrafluoroethane

1,2-Dibromotetrafluoroethane (13.00 g, 0.05 mole) dissolved in THF (50 ml) was added dropwise to lithium (3.47 g, 0.5 g-atom) and chlorotrimethylsilane (38.01 g, 0.35 mole) in THF (150 ml) at 0°. An exothermic reaction occurred with darkening of the system and precipitation of lithium salts. After stirring for a total of 20 h, excess lithium was removed and hexane (100 ml) was added to the filtrate. The precipitated lithium salts were removed by filtration and the filtrate was fractionally distilled to give bis(trimethylsilyl)acetylene (8.56 g, 99%), b.p. 133–135°, n_D^{20} 1.4261; (lit.[8] b.p. 133–135°, n_D^{20} 1.4260). The IR spectrum was identical with that of an authentic specimen of bis(trimethylsilyl)acetylene[7].

Interaction of lithium, chlorotrimethylsilane and 1,1,2-trichloro-3,3,3-trifluoropropene

Trichlorotrifluoropropene (9.97 g, 0.05 mole) dissolved in THF (50 ml) was added dropwise to lithium (6.94 g, 1 g-atom) and chlorotrimethylsilane (54.30 g, 0.5 mole) in THF (150 ml) at 0°. An exothermic reaction occurred with darkening and the precipitation of lithium salts. After vigorously stirring for 16 h, excess lithium was removed and the products hydrolysed with 2 *N* HCl. The organic products were extracted with ether, the ethereal layer dried ($MgSO_4$) and the volatiles removed to give a yellow oil. Distillation of this oil afforded tetrakis(trimethylsilyl)allene (I) (9.68 g, 59%), b.p. 58–60°/0.05 mm, n_D^{20} 1.4767 [(I) has b.p. 69–70°/0.2 mm, n_D^{20} 1.4770)][9].

Interaction of lithium, chlorotrimethylsilane and 1,2-*dibromohexafluoropropane*

Dibromohexafluoropropane (15.49 g, 0.05 mole) dissolved in THF (40 ml) was added dropwise to lithium (6.94 g, 1 g-atom) and chlorotrimethylsilane (54.30 g, 0.5 mole) in THF (150 ml) at 0°. An exothermic reaction occurred with separation of lithium salts. After vigorously stirring for 18 h, work-up as above afforded a dark oil which, by VPC, contained only one component. Distillation afforded 5.2 g, (32%) of the allene (I), b.p. 69–70°/0.2 mm, n_D^{20} 1.4768. The IR spectrum was identical with that of an authentic sample of (I).

Interaction of lithium, chlorotrimethylsilane and 1,1,1,2,4,4,4-*heptafluoro*-2,3,3-*trichlorobutane*

Heptafluorotrichlorobutane (14.38 g, 0.05 mole) dissolved in THF (50 ml) was added dropwise to lithium (6.94 g, 1 g-atom) and chlorotrimethylsilane (54.30 g, 0.5 mole) in THF (150 ml) at 0°. The normal exothermic reaction occurred. After stirring for 16 h, the usual work-up afforded a dark solid which was washed several times with ethanol (0°) and recrystallised from hexane. Hexakis(trimethylsilyl)-2-butyne (3.6 g, 15%), m.p. and m.m.p. with an authentic specimen[7] 276–278°, was isolated as white crystals.

Reactions using magnesium

The polyfluoroalkane (0.05 mole) dissolved in THF (40 ml) was added dropwise to magnesium (0.5 g-atom) and chlorotrimethylsilane (0.5 mole) in THF (150 ml) at 0°. After initiation with a few drops of 1,2-dibromoethane an exothermic reaction occurred. The exit gases were passed through a cold trap (−196°) to collect any volatile fluorocarbons evolved. After vigorously stirring for 18 h, the reactions were worked up as before.

(*a*). 1,2-*Dibromotetrafluoroethane*. The cold trap collected tetrafluoroethylene, identified by comparison of its IR spectrum with a standard spectrum[10] and by bromination to 1,2-dibromotetrafluoroethane. Apart from hexamethyldisilane and hexamethyldisiloxane, no other products were isolated.

(*b*). 1,2-*Dibromohexafluoropropane*. The cold trap collected hexafluoropropene identified by comparison of its IR spectrum with a standard spectrum[10] and by derivatization with bromine to 1,2-dibromohexafluoropropane. Apart from hexamethyldisilane and hexamethyldisiloxane, no other products were isolated.

(*c*). 1,1,1,2,4,4,4-*Heptafluoro*-2,3,3-*trichlorobutane*. No gaseous products were isolated but fractional distillation of the oily product afforded a fraction b.p. 143–147° which contained two components that have not been separated by VPC or by fractional distillation. The IR spectrum of this mixture revealed the presence of olefinic, carbon–fluorine and silicon–methyl groups.

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REFERENCES

1 D. H. Ballard, T. Brennan, F. W. G. Fearon, K. Shiina, I. Haiduc and H. Gilman, *Pure Appl. Chem.*, to be published; also papers in the series, *Polyhaloorganometallic and -organometalloidal Compounds.*

2 T. Brennan and H. Gilman, *J. Organometal. Chem.*, 11 (1968) 185; F. W. G. Fearon and H. Gilman, *Chem. Commun.*, (1967) 86.

3 T. Brennan and H. Gilman, *Chem. Ind. (London)*, (1967) 1489.

4 T. Brennan and H. Gilman, *J. Organometal. Chem.*, 12 (1968) 291.

5 R. West, P. A. Carney and I. C. Mineo, *J. Amer. Chem. Soc.*, 87 (1965) 3788

6 D. H. Ballard and H. Gilman, *J. Organometal. Chem.*, 12 (1968) 237.

7 D. H. Ballard and H. Gilman, *J. Organometal. Chem.*, 15 (1968) 321.

8 A. D. Petrov and L. L. Shchukovskaya, *Dokl. Akad. Nauk SSSR*, 86 (1952) 551; *Chem. Abstr.*, 47 (1953) 12225.

9 K. Shiina and H. Gilman, *J. Amer. Chem. Soc.*, 88 (1966) 5367.

10 H. A. Szymanski (Ed.), *Infrared Band Handbook*, Plenum Press, New York, 1963.