Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

SILYLATION AS A PROTECTIVE METHOD FOR TERMINAL ALKYNES IN ORGANOMETALLIC SYNTHESIS

PREPARATION OF 1,4-DIETHYNYLTETRAFLUOROBENZENE AND (PENTAFLUOROPHENYL)ACETYLENE

F. WAUGH and D. R. M. WALTON

School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)

(Received January 14th, 1972)

SUMMARY

Hexafluorobenzene reacts with $Et_3SiC{\equiv}CLi$ to give *p*- $Et_3SiC{\equiv}CC_6F_4C{\equiv}CSiEt_3$ and pentafluorophenylcopper couples with $BrC{\equiv}CSiEt_3$ to give $C_6F_5C{\equiv}CSiEt_3$ in good yield. Treatment of the products with aqueous methanolic alkali gives *p*-$HC{\equiv}CC_6F_4C{\equiv}CH$ and $C_6F_5C{\equiv}CH$ respectively.

INTRODUCTION

The ease with which fluoride ion is displaced from perfluoroaromatic compounds by relatively weak nucleophiles[1] allows acetylene derivatives to be synthesised by direct couplings involving alkynyllithium reagents[2,3], but these reactions possess certain drawbacks. With hexafluorobenzene for example, it is necessary to use a large excess of fluorocarbon if mono-substitution is desired, because the acetylene group introduced activates the fluorine atom *para* to it and further substitution ensues [*e.g.* eqn. (1)][3]. Furthermore, reactions with ethynyllithium are reported to yield only

$$C_6F_6+RC{\equiv}CLi \rightarrow p\text{-}RC{\equiv}CC_6F_4C{\equiv}CR \qquad (1)$$

insoluble polymers because, it is thought[3], the strongly electron withdrawing pentafluorophenyl group enhances the acidity of the terminal ethynyl hydrogen in the initial product which in turn leads to hydrogen–lithium exchange and to further couplings [eqns. (2, 3)]. Consequently a multistep procedure was developed to prepare (pentafluorophenyl)acetylene[4].

$$\begin{tikzcd} C_6F_5C{\equiv}CH+LiC{\equiv}CH \arrow[r] & C_6F_5C{\equiv}CLi+C_2H_2 \arrow[d, "C_6F_6"] & (2) \\ p\text{-}HC{\equiv}CC_6F_4C{\equiv}CC_6F_5 & C_6F_5C{\equiv}CC_6F_5 \arrow[l, "LiC{\equiv}CH"'] & (3) \end{tikzcd}$$

Ethynyl–silicon bonds are broken less readily than ethynyl–hydrogen bonds by nucleophiles[5], an observation which permits trialkylsilyl groups to be used as a protecting agent for terminal alkynes in certain organometallic syntheses[6,7]. We have now employed this principle to prepare 1,4-diethynyltetrafluorobenzene for the first time and to provide an alternative route to (pentafluorophenyl)acetylene.

RESULTS AND DISCUSSION

Coupling between $Et_3SiC{\equiv}CLi$ and an excess of C_6F_6 in THF gave substantially the same result as recorded previously for other $RC{\equiv}CLi$ reagents, namely that *para*-disubstitution predominated[3]. Use of two equivalents of $Et_3SiC{\equiv}CLi$ gave the product, *p*-$Et_3SiC{\equiv}CC_6F_4C{\equiv}CSiEt_3$, in ca. 60% yield. Bis(triethylsilyl)acetylene was isolated as a minor product of the first reaction, and a small quantity of yellow polymer was obtained from the second, indicating that some breaking of ethynyl–silicon bonds had also occurred, but the quantities involved were too small to be troublesome. The triethylsilyl protecting groups were removed cleanly without interference from fluoride ion displacement by treating the product with aqueous methanolic alkali. The process can usefully be followed by associated ultraviolet spectral changes (Fig. 1).

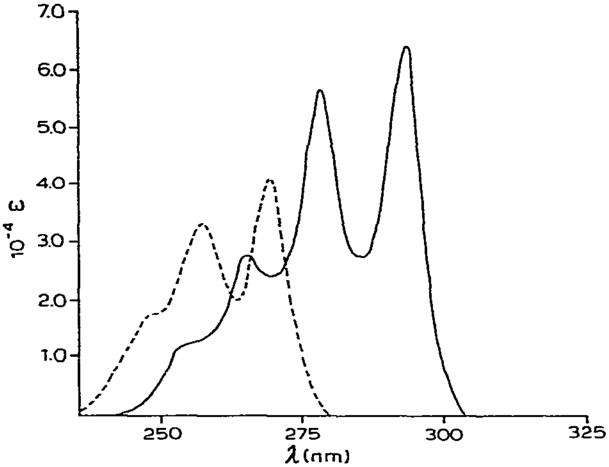

Fig. 1. UV Spectra (methanol solution); ——, *p*-$Et_3SiC{\equiv}CC_6F_4C{\equiv}CSiEt_3$; ------, *p*-$HC{\equiv}CC_6F_4C{\equiv}CH$.

In view of the difficulties encountered in introducing only one acetylene residue via the organolithium method, an alternative coupling scheme was sought in order to obtain (pentafluorophenyl)acetylene silylated on the ethynyl group. Organocopper compounds seemed a possible choice since alkynylcopper reagents have been successfully coupled with (bromoethynyl)triethylsilane[7], furthermore cuprous chloride is known to catalyse coupling of Grignard reagents with haloalkynes[8]. At the first attempt, pentafluorophenylcopper coupled cleanly with (bromoethynyl)triethylsilane to give [(pentafluorophenyl)ethynyl]triethylsilane in excellent yield [eqn. (4)] and treatment of this product with aqueous methanolic alkali gave (pentafluorophenyl)-acetylene.

$$C_6F_5Cu + BrC{\equiv}CSiEt_3 \rightarrow C_6F_5C{\equiv}CSiEt_3 \ 85\% \qquad (4)$$

We note that the two couplings described may serve as prototypes for the preparation of a wide range of arylacetylenes.

EXPERIMENTAL

Coupling of $Et_3SiC{\equiv}CLi$ (2 equivalents) with C_6F_6 (1 equivalent)

1,4-Bis[(triethylsilyl)ethynyl]tetrafluorobenzene. n-Butyllithium (100 ml of 0.96 *M* ether solution) was added at 0° during 1 h to ethynyltriethylsilane (14 g, 0.1 mole) in THF (100 ml). The resulting colourless solution was subsequently stirred for a further 30 min then added during 3 h to hexafluorobenzene (9.3 g, 0.05 mole) in THF (100 ml) maintained at 20–25°. The mixture which gradually changed through yellow and brown to deep purple was stirred for 12 h, then poured into cold dilute hydrochloric acid and organic products were extracted with ether. The ether extracts were dried ($MgSO_4$), concentrated, and the crude product was absorbed onto neutral alumina. Elution with light petroleum (< 60° fraction) gave a pale brown liquid (shown by IR and UV spectroscopy to contain the desired product). Further elution with ether/petrol (1/20) gave solutions which fluoresced strongly. Distillation of the initial fractions afforded 1,4-bis[(triethylsilyl)ethynyl]tetrafluorobenzene (nc) (12.3 g, 58%) b.p. 125–130°/10^{-3} mm which solidified in the receiver, to give material m.p. 28° (from chloroform/methanol at −15°) (Found: C, 62.0; H, 7.0. $C_{22}H_{30}F_4Si_2$ calcd.: C, 61.9; H, 7.1%.) IR (film): 2172 m (C≡C); 1490 vs, 1480 vs (C_6F_4) cm^{-1}, UV (methanol) [λ_{max} ($10^{-4}\varepsilon$)]: 292 (6.39), 278 (5.63), 265 (2.75), 254 sh (1.13) nm. Concentration of the petrol/ether fractions gave a yellow solid which could not be positively identified.

Coupling of $Et_3SiC{\equiv}CLi$ (1 equivalent) with C_6F_6 (4 equivalents)

(Triethylsilyl)ethynyllithium, prepared from n-butyllithium (0.048 mole) and ethynyl(triethyl)silane (7 g, 0.05 mole) in THF (30 ml) was added during 3 h at 0° to hexafluorobenzene (37.2 g, 0.20 mole) in THF (30 ml). The mixture was subsequently stirred at 20–25° for 12 h then treated with dilute acid and worked up as described above. Distillation yielded material b.p. ca. 50°/0.01 mm (1.34 g) followed by bis[(triethylsilyl)ethynyl]tetrafluorobenzene (4.52 g, 42.5%) b.p. 125°/10^{-3} mm. The first fraction was separated by preparative GLC into two components, identified by molecular weights (mass spectrum), elemental analyses and GLC retention times (comparison with authentic samples) as bis(triethylsilyl)acetylene and [(pentafluorophenyl)ethynyl]triethylsilane (*vide infra*).

Coupling of C_6F_5Cu with $BrC{\equiv}CSiEt_3$: [(pentafluorophenyl)ethynyl]triethylsilane

Pentafluorophenylmagnesium bromide[8] was prepared by adding bromopentafluorobenzene (23 g, 0.09 mole) in THF (50 ml) during 15 min to ethylmagnesium bromide (0.1 mole) in THF (100 ml) at 0°. The resulting clear solution was subsequently stirred at 20–25° for 90 min, then cooled to 0° and finely powdered cuprous iodide (19.5 g, 0.10 mole) was added in portions with *vigorous* stirring during 45 min. The white suspension thus formed was stirred at 0–20° for 36 h[9].

(Bromoethynyl)triethylsilane (22 g, 0.1 mole) in THF (50 ml) was then added and the mixture, which became slightly warm, turned green and was stirred for a further 1 h then boiled under reflux for 10 h. Treatment with dilute acid and petrol led to precipitation of grey cuprous salts which were removed by filtration. The filtrate was extracted with petrol, and the petrol layer was dried ($MgSO_4$) and distilled to give [(pentafluorophenyl)ethynyl]triethylsilane (nc) (24.3 g, 85%) b.p. 60–62°/0.1 mm, n_D^{20} 1.4710. (Found: C, 55.0; H, 5.1. $C_{14}H_{15}F_5Si$ calcd.: C, 54.9; H, 4.9%.) IR (film): 2171 m (C≡C); 1518 vs, 1504 vs (C_6F_4) cm^{-1}. UV (methanol) [λ_{max} ($10^{-4}\varepsilon$)]: 257 (1.93), 246 (2.14), 236 (1.32) nm.

1,4-Diethynyltetrafluorobenzene

Aqueous 0.1 *M* sodium hydroxide (10 ml) was added with stirring to a solution of 1,4-bis[(triethylsilyl)ethynyl]tetrafluorobenzene (4.14 g, 0.0097 mole) in methanol (300 ml) at 20°. After 90 min the UV spectrum (Fig. 1) revealed cleavage to be complete. The mixture was then neutralised with dilute hydrochloric acid and extracted with ether. The ether layer was dried ($MgSO_4$) and solvent was distilled leaving a residue which was chromatographed on alumina to give hexaethyldisiloxane upon elution with petrol. Subsequent elution with ether/petrol (1/20) gave after concentration of the fractions, 1,4-diethynyltetrafluorobenzene (nc) (1.6 g, 84%) m.p. 132–133° (from chloroform/methanol). (Found: C, 60.2; H, 0.9. $C_{10}H_2F_4$ calcd.: C, 60.6; H, 1.0%.) IR (CCl_4): 3300 vs (C≡C–H); 2128 w (C≡C); 1480 vs (C_6F_4) cm^{-1}. UV (methanol) (λ_{max} ($10^{-4}\varepsilon$)]: 269 (4.07), 257 (3.31), 250 sh (1.79) nm.

(Pentafluorophenyl)acetylene

Treatment of [(pentafluorophenyl)ethynyl]triethylsilane (16.7 g, 0.055 mole) in methanol (300 ml) with aqueous 0.05 *M* sodium hydroxide (20 ml) during 2.5 h followed by a similar working up procedure, culminating in fractional distillation, afforded pentafluorophenylacetylene (8.1 g, 77%) b.p. 50–52°/37 mm, (lit.[4] b.p. 130–131°). IR (film): 3305 vs (C≡C–H); 2130 w (C≡C) cm^{-1}. UV (methanol) (λ_{max}): 243, 234, 222 nm [lit.[4] (λ_{max}): 243, 234, 222 nm].

1,4-Bis(pentafluorophenyl)butadiyne

Air was bubbled through an acetone solution of (pentafluorophenyl)acetylene in the presence of Hay CuCl/TMEDA catalyst[11] to give 1,4-bis(pentafluorophenyl)-butadiyne (nc) m.p. 113–114° (from chloroform/methanol at −15°). (Found: C, 49.9. $C_{16}F_{10}$ calcd.: C, 50.3%.) IR (CCl_4): 1432 s, 1490 m, 1647 m (C_6F_5) cm^{-1}. UV (methanol) [λ_{max} ($10^{-4}\varepsilon$)]: 325 (2.38), 305 (3.00), 287 (2.17), 269 (1.35), 258 (2.90), 246 (3.05) nm.

ACKNOWLEDGEMENTS

We thank Ciba-Geigy (U.K.) Ltd. for financial support, Drs. J. Grigor and W. Hoyle for their interest and encouragement, and Prof. J. C. Tatlow for spectral data.

REFERENCES

1 J. C. Tatlow, *Endeavour*, 22 (1963) 89.
2 M. R. Wiles and A. G. Massey, *Chem. Ind. (London)*, (1967) 663; M. R. Wiles and A. G. Massey, *Tetrahedron Lett.*, (1967) 5137.
3 P. L. Coe, J. C. Tatlow and R. C. Terrell, *J. Chem. Soc. C*, (1967) 2626.
4 P. L. Coe, R. G. Plevey and J. C. Tatlow, *J. Chem. Soc. C*, (1966) 597.
5 C. Eaborn and D. R. M. Walton, *J. Organometal. Chem.*, 4 (1965) 217.
6 C. Eaborn, A. R. Thompson and D. R. M. Walton, *J. Chem. Soc. C*, (1967) 1364.
7 R. Eastmond and D. R. M. Walton, *Chem. Commun.*, (1968) 204; C. Eaborn, A. R. Thompson and D. R. M. Walton, *J. Chem. Soc. B*, (1970) 357.
8 H. K. Black, D. H. S. Horn and B. C. L. Weedon, *J. Chem. Soc.*, (1954) 1704.
9 W. L. Respass and C. Tamborski, *J. Organometal. Chem.*, 11 (1968) 619.
10 A. E. Jukes and H. Gilman, *J. Organometal. Chem.*, 17 (1969) 145.
11 A. S. Hay, *J. Org. Chem.*, 27 (1962) 3320.