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POLYFLUOROBICYCLO(2,2,1)HEPTANES
PART VI DERIVATIVES FROM 1-IODO-NONAFLUOROBICYCLO(2,2,1)-HEPT-2-ENE *

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SUMMARY

1-Iodo-nonafluorobicyclo(2,2,1)hept-2-ene gives a Grignard reagent and organolithium derivative with thermal stabilities in diethyl ether much higher than those hitherto associated with structures carrying magnesium or lithium adjacent to a β $>CF_2$ group. Their synthetic potential is indicated by the preparation of 1-(nonafluorobicyclo(2,2,1)hept-2-ene-1-yl)ethanol and 1-methylethanol and nonafluorobicyclo(2,2,1)hept-2-ene-1-carboxylic acid.

INTRODUCTION

The synthetic utility of highly fluorinated organometallics is severely limited in general by rapid olefin-forming β-eliminations[2]. Lithium derivatives of polyfluorobicyclo(2,2,1)heptanes are exceptional in being very useful synthetically since the β-elimination involved is hindered, giving a bridgehead olefin[3]. Even these can decompose around 0°, however, and the preparation of an analogous Grignard reagent is greatly hindered by the same elimination process[4,5]. This paper describes nonafluorobicyclo(2,2,1)hept-2-ene-1-yl magnesium iodide and lithium, which contain β $>CF_2$ groups and yet are stable in diethyl ether at 35° for a long period of time.

RESULTS AND DISCUSSION

Our earlier studies on polyfluorobicyclo(2,2,1)heptane derivatives have indicated an unusually high thermal stability for bridgehead organometallic

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* For Part V, see ref. 1.

derivatives of polyfluorobicyclo(2,2,1)hept-2-enes, *viz.*, nonafluorobicyclo(2,2,1)-hept-2-ene-1-yl lithium, and magnesium iodide and bromide[1,5], 4-iodo- and 4*H*-octafluorobicyclo(2,2,1)hept-2-ene-1-yl lithium, and magnesium iodide[6], and 4-trifluoromethyloctafluorobicyclo(2,2,1)hept-2-ene-1-yl lithium and magnesium iodide[7]. In some cases such effects have been noted during characterisation procedures, and some of the thermal decomposition products of saturated polyfluorobicycloalkyl lithiums could only be explained by invoking high stabilities for lithio derivatives of unsaturated intermediates.

These preliminary indications have now been fully substantiated by a more detailed study of magnesium and lithium derivatives of 1-iodo-nonafluorobicyclo-(2,2,1)hept-2-ene (I)[3].

Thus, after 24 h at 35° in diethyl ether, nonafluorobicyclo(2,2,1)hept-2-ene-1-yl magnesium iodide (II) gave the 1*H*-olefin (III) (60%) when treated with dilute acid. After 3 h at 35°, (II) gave 1-(nonafluorobicyclo(2,2,1)hept-2-ene-1-yl)-ethanol (IV) (64%) and 1-(nonafluorobicyclo(2,2,1)hept-2-ene-1-yl)-1-methyl-ethanol (V) (73%) when treated with acetaldehyde and acetone, respectively, in the usual way. The Grignard (II) did not react with carbon dioxide under the standard conditions of carbonation.

Nonafluorobicylo(2,2,1)hept-2-ene-1-yl lithium (VI) was prepared from the iodo-olefin (I) and n-butyl-lithium in pentane–ether at room temperature. The iodo-olefin (I) (90%) was recovered after ½ h with the reagent at −40°, and was not completely metallated after ½ h at room temperature. The absence of any significant substitution[8] of butyl for vinylic fluorine (actually addition–elimination) which might be expected with such a strained –CF=CF– bond, was surprising at room temperature, although there may be some steric impedance with this reaction.

After 6 h at 35°, the solution of the lithio compound (VI) so obtained gave the 1*H*-olefin (III) (60%) with dilute acid. After 3 h at room temperature (VI) gave (IV) (66%) and (V) (65%) with acetaldehyde and acetone, respectively, in the usual way. With carbon dioxide the solution of (VI) gave nonafluorobicyclo-(2,2,1)hept-2-ene-1-carboxylic acid (VII) (79%) which was characterised as its s-benzylthiuronium salt (VIII).

The appreciably higher stabilities of the organometallics (II) and (VI) as compared to the saturated perfluoro analogues[3,5,7] may derive from the even greater strain associated with the olefinic bridgehead diradical octafluorobicyclo-(2,2,1)hept-1,5-diene (IX) which would result from an olefin-forming β-elimination between the carbanionic centre at C_1 and the adjacent $>CF_2$ group. Indeed, alternative modes of decomposition (Fig. 1) might be more likely, *viz.*, oligomer (X) formation by nucleophilic substitution between the carbanionic centre and the strained –CF=CF– group, or heterolytic fission of the bridge to give (XI) and thence the triene (XII). An indication that one or more of such decomposition pathways may be followed was obtained when the Grignard (II) was generated in tetrahydrofuran, using a large excess of magnesium, and kept at 50° for 20 h before acid hydrolysis; this gave a small amount of a mixture of unidentified fluorocarbons in addition to the 1*H*-olefin (III) (30%).

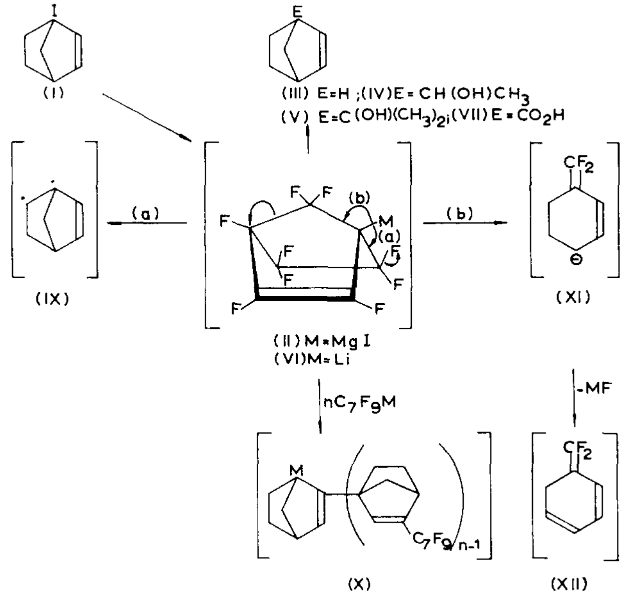

Fig. 1. Characterisation and possible modes of decomposition of nonafluorobicyclo(2,2,1)hept-2-ene-1-yl lithium and magnesium iodides.
(All unmarked substituents are fluorine; species in brackets were not isolated).

Since groups other than fluorine can be attached to C_4 in compounds of the type exemplified by (I)[6, 7], a wide synthetic potential is available for derivatives of the type (1)*X*-C_7F_8-*Y*(4).

EXPERIMENTAL

Gas chromatography

Analytical work was carried out using a 6 m glass column (4 mm diameter) packed with dinonyl phthalate–celite (1:10) (col. A). For preparative work copper columns (4.88 m long and 35 mm diameter) were used packed with dinonyl phthalate–celite (1:5) (col. B) and silicon gum-celite (1:5) (col. C).

NMR spectroscopy

The proton spectra were measured with a Varian instrument at 60 MHz and the chemical shifts are quoted from TMS as external reference. The fluorine-19 spectra were measured on a Perkin–Elmer R10 instrument at 56.46 MHz with $CFCl_3$ as external reference, or on a Varian HR100 at 94.1 MHz using trifluoroacetic acid as external reference.

Mass spectra

These were measured on an A.E.I. MS9 instrument.

Nonafluorobicyclo(2,2,1)hept-2-ene-1-yl magnesium iodide

1-Iodononafluorobicyclo(2,2,1)hept-2-ene[3] (1.0 g) in ether (15 ml) was added drop-wise to a well-stirred suspension of magnesium turnings (0.25 g) in dry refluxing ether (50 ml) containing a crystal of iodine. After 24 h reflux, the faintly cloudy solution was decanted from excess magnesium, washed with water, dried ($MgSO_4$), filtered and evaporated through a vacuum jacketed column (15 cm) packed with glass helices. The residue (3.1 g) was separated by GLC (col. B; 80°; N_2, 15 l/h) to give ether (1.5 g) and 1*H*-nonafluorobicyclo(2,2,1)hept-2-ene[3] (0.4 g) with a correct IR spectrum.

1-(Nonafluorobicyclo(2,2,1)hept-2-ene-1-yl)ethanol

Nonafluorobicyclo(2,2,1)hept-2-ene-1-yl magnesium iodide was prepared in the manner previously described from 1-iodononafluorobicyclo(2,2,1)hept-2-ene (1.0 g) and magnesium turnings (0.25 g) in refluxing ether (60 ml). After 3 h, acetaldehyde (2 ml) was quickly added. A white precipitate formed immediately and, after 2 h reflux, water was added followed by 4 *N* HCl. The ether extract was dried ($MgSO_4$), filtered and evaporated. The residue (5.1 g) was separated by GLC (col. C; 120°, N_2, 16 l/h) to give ether (2.9 g) and 1-(nonafluorobicyclo-(2,2,1)hept-2-ene-1-yl)ethanol (nc) (0.5 g), b.p. 165° (Found: C, 36,0; H, 1.8. $C_9H_5F_9O$ requires C, 36.0; H, 1.7%), $\nu_{max.}$ 3400 (OH) and 1760 cm^{-1} (–CF=CF–), its ^1H NMR spectrum consisted of a doublet (CH_3), a pentuplet ($>$CH) and a doublet (OH) at 8.5 τ 5.4 τ and 6.8 τ, respectively, in the relative intensity ratio of 3:1:1, respectively; there was also slight coupling of the methyl and tertiary protons with the hydroxyl proton.

1-(Nonafluorobicyclo(2,2,1)hept-2-ene-1-yl)-1-methyl-ethanol

In exactly the same manner as described previously, the Grignard reagent from 1-iodononafluorobicyclo(2,2,1)hept-2-ene (1.0 g) reacted with acetone (2 ml; dried by shaking with K_2CO_3 for 24 h and distilling from $CaCl_2$) to give an immediate precipitate. After 3 h reflux, dilute acid was added and the ether extract dried ($MgSO_4$), filtered and fractionated (15 cm column packed with glass helices). The residue (5.3 g) was separated by GLC (col. C; 130°; N_2, 17 l/h) to give ether (3.0 g) and 1-(nonafluorobicyclo(2,2,1)hept-2-ene-1-yl)-1-methyl-ethanol (nc) (0.6 g) m.p. 37° (Found: C, 38.4; H, 2.5. $C_{10}H_7F_9O$ requires C, 38.2; H, 2.2%), $\nu_{max.}$ 3450 (OH) and 1770 cm^{-1} (–CF=CF–), *m*/*e* 314 ($C_{10}H_7F_9O$), its ^1H NMR spectrum consisted of a doublet (–CH_3) and a broad band (OH) at 8.4 τ and 7.8 τ, respectively, in the relative intensity ratio of 6:1.

Nonafluorobicyclo(2,2,1)hept-2-ene-1-yl lithium

A 2.5 *N* solution of butyl-lithium (0.6 ml, in pentane) in dry ether (10 ml) was added drop-wise to a stirred solution of 1-iodo-nonafluorobicyclo(2,2,1)-

hept-2-ene (0.5 g) in ether (100 ml) at room temperature; this solution was then stirred for 2 h, refluxed for 6 h and hydrolysed with dilute acid. The ether extract was dried ($MgSO_4$), filtered and evaporated, and the residue separated by GLC (col. B; 80°; N_2, 17 l/h) to give 1*H*-nonafluorobicyclo(2,2,1)hept-2-ene (0.2 g) with a correct IR spectrum.

A solution of nonafluorobicyclo(2,2,1)hept-2-ene-1-yl lithium, from the iodide (1.0 g) and 2.47 *N* butyl-lithium (1.5 ml, in pentane) in ether, was stirred for 3 h at room temperature, and acetaldehyde (1 ml) added. After 6 h reflux, dilute acid was added. The dried ($MgSO_4$) ether extract was filtered and fractionally distilled (15 cm column of glass helices) to yield a residue (4.0 g) which was separated by GLC (col. C; 120°; N_2, 16 l/h) to give ether (2.1 g) and 1-(nonafluorobicyclo(2,2,1)hept-2-ene-1-yl)ethanol (0.52 g) with a correct IR spectrum.

To a solution of nonafluorobicyclo(2,2,1)hept-2-ene-1-yl lithium prepared from the iodo-olefin (1.0 g) in the manner described above, acetone (2 ml) was added and the mixture refluxed for 6 h. The usual isolation procedure gave a residue (4.5 g) which was separated by GLC (col. C; 125°; N_2, 17 l/h) to give ether (2.5 g) and 1-(nonafluorobicyclo(2,2,1)hept-2-ene-1-yl)-1-methyl-ethanol (0.53 g) with a correct IR spectrum.

Nonafluorobicyclo(2,2,1)hept-2-ene-1-carboxylic acid

Carbon dioxide, generated by sublimation of "Drikold", dried over silica gel and phosphoric oxide, was bubbled through an ethereal solution of nonafluorobicyclo(2,2,1)hept-2-ene-1-yl lithium, prepared from the iodo-olefin (1.0 g) in the usual way, at room temperature for 18 h. The reaction mixture was then hydrolysed with dilute acid and extracted with ether. The combined ethereal extracts were washed with 1 *N* NaOH (100 ml) and the carboxylic acid was precipitated with dil. HCl, and extracted with ether. The combined extracts were dried ($MgSO_4$) and evaporated to a brown viscous liquid which could not be crystallised but was "distilled" at 0.05 mmHg across a short path length to give the white, waxy, hygroscopic nonafluorobicyclo(2,2,1)hept-2-ene-1-carboxylic acid (nc) (0.6 g) m.p. *ca.* 20° (Found: C, 31.4; H, 1.0 $C_8HF_9O_2$ requires C, 32.0; H, 0.3%), $\nu_{max.}$ 3600–2400 (COOH) 1760 (–CF=CF–) and 1745 cm^{-1} (>C=O), *m/e* 256 (C_7F_9H), 44 (CO_2), its ^1H NMR spectrum in CCl_4 consisted of a band at 1.95 τ. A small portion of the acid in aqueous ethanol and a saturated aqueous solution of s-benzylthiuronium chloride gave a precipitate which was washed with water and dried to give s-benzylthiuronium nonafluorobicyclo(2,2,1)hept-2-ene-1-carboxylate (nc) m.p. 125° (Found: C, 41.5; H, 2.6. $C_{16}H_{11}F_9N_2O_2S$ requires C, 41.2; H, 2.4%).

REFERENCES

1 P. J. N. Brown, R. Stephens, J. C. Tatlow and J. R. Taylor, *J. Chem. Soc.*, in the press.
2 W. A. Sheppard and C. M. Sharts, *Organic Fluorine Chemistry*, W. A. Benjamin, Inc., New York, 1969, p. 279.
3 S. F. Campbell, R. Stephens and J. C. Tatlow, *Tetrahedron*, *21* (1965) 2997.
4 S. F. Campbell, J. M. Leach, R. Stephens and J. C. Tatlow, *Tetrahedron Letters*, (1967) 4269.
5 S. F. Campbell, J. M. Leach, R. Stephens and J. C. Tatlow, *J. Fluorine Chem.*, *1* (1971/72) 85.
6 S. F. Campbell, J. M. Leach, R. Stephens, J. C. Tatlow and K. N. Wood, *J. Fluorine Chem.*, *1* (1971/72) 103.
7 R. Stephens, J. C. Tatlow and K. N. Wood, *J. Fluorine Chem.*, *1* (1971/72) 165.
8 D. R. Sayers, R. Stephens and J. C. Tatlow, *J. Chem. Soc.*, (1964) 3035.