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# BRIDGEHEAD POLYFLUORO-GRIGNARD REAGENTS.

By

S.F. CAMPBELL, J.M. LEACH, R. STEPHENS and J.C. TATLOW.

(Department of Chemistry,
University of Birmingham,
P. O. B. 363,
Edgbaston, Birmingham, 15.).

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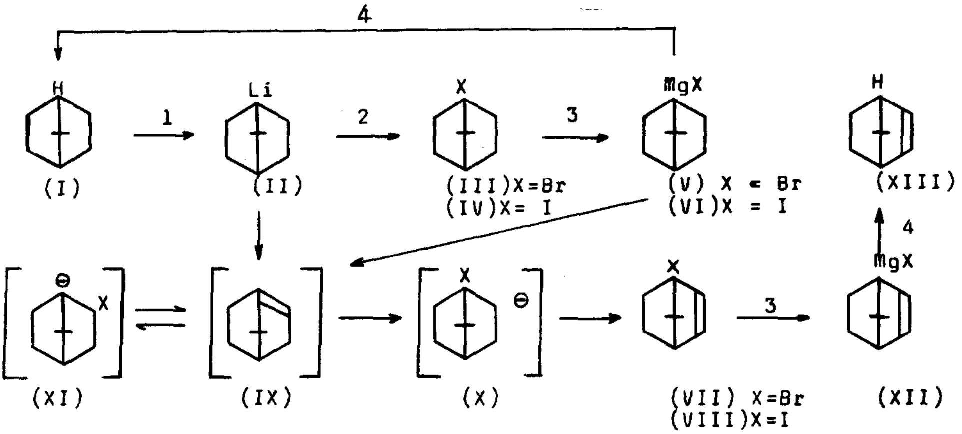
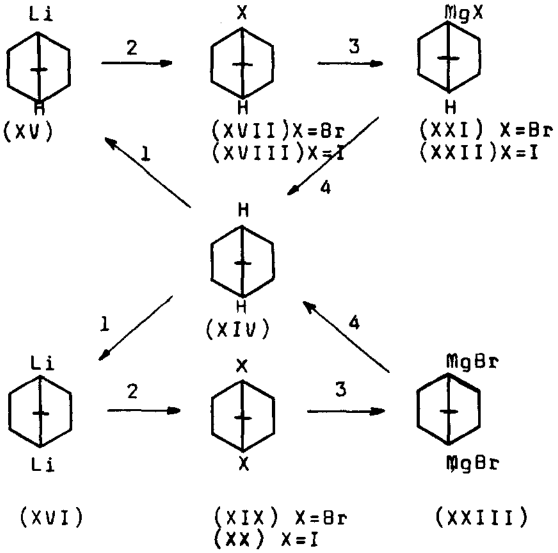
UNDECAFLUOROBICYCLO[2,2,1]HEPTYL LITHIUM (II), formed from 1H-undecafluorobicyclo[2,2,1]heptane (I) and methyl lithium in ether at -50°,[1] reacts readily with bromine and with iodine to give the corresponding bromide (III) (68%) and iodide (IV) (73%); these in turn readily give saturated bridgehead Grignard reagents (V) and (VI), compounds of a type not known hitherto[2].

The iodide (IV) with activated magnesium in ether at -50° for 2 hr. and at -20° for 4 hr. gave a moderate yield of the Grignard reagent (VI), as indicated by hydrolysis to 1H-undecafluorobicyclo[2,2,1]heptane (I) (36%); unchanged (IV) (50%) was also present. However, (IV) with 1 mol. of magnesium at 35° for 1 hr. gave, after hydrolysis, 1-iodononafluorobicyclo[2,2,1]hept-2-ene (VIII) (45%), unchanged (IV) (25%), and small amounts of 1H-nonafluorobicyclo[2,2,1]hept-2-ene(XIII) and 1H-undecafluorobicyclo[2,2,1]heptane (I). With an excess of magnesium at 35° for 4 hr., (IV) gave, after hydrolysis, only 1H-nonafluorobicyclo[2,2,1]hept-2-ene (XIII) (83%). Likewise, the 1-bromo-compound (III) with an excess of magnesium at 35° for 4 hr. gave, after hydrolysis, only the 1H-olefin (XIII).

The above observations can be rationalised in terms similar to those used to explain the production in ether at room temperature [1] of 1-bromo- or 1-iodo-nonafluorobicyclo-[2,2,1]hept-2-ene, (VII) and (VIII), from undecafluorobicyclo[2,2,1]heptyl lithium (II), formed using methyl lithium prepared from methyl bromide or methyl iodide, respectively. Elimination from (V) or (VI)





All unmarked substituents are fluorine.

Reagents: 1,MeLi; 2,$Br_2$ or $I_2$; 3,Mg; 4,$H_3O^+$

of magnesium halogeno-fluoride (a well-known reaction of perfluoroalkyl Grignard reagents [3]) gives a transient bridgehead olefin or di-radical [1] (IX), to which the rapid addition of a bromide or an iodide ion affords the unstable intermediates (X) and (XI). The former then undergoes a facile β-elimination to give the olefin (VII) or (VIII), which is isolated when 1 mol. of magnesium is used, but which will react in turn with magnesium, if an excess is present, to form an unsaturated Grignard reagent (XII). This was found [1] to be stable in refluxing ether, and so on hydrolysis will give the known 1-H-nonafluorobicyclo[2,2,1]-hept-2-ene (XIII). The extent of decomposition of the Grignard reagent (VI) after varying times of reflux suggested a higher stability than that of the lithio-compound (II). This would be expected from its less ionic character; ease of elimination of fluoride ion should increase with increase in carbonionic character.

A parallel study was based on 1H,4H-decafluorobicyclo[2,2,1]heptane (XIV). Thus, methyl lithium was added to an ethereal solution of (XIV) at -55° until methane evolution ceased and bromine added to give 1H-4-bromo- and 1,4-dibromo-decafluorobicyclo[2,2,1]heptane (XVII) and (XIX),(12 and 45%, respectively); iodine addition gave the 1H,4-iodo-and 1,4,-di-iodo-analogues (XVIII) and (XX) (54 and 7%, respectively).

In contrast to the saturated 4-fluoro-substituted Grignard reagents (V) and (VI), those derived from compounds (XVII), (XVIII) and (XIX) were stable in refluxing ether and, after hydrolysis, only 1H, 4H-decafluorobicyclo[2,2,1] heptane (XIV) could be isolated.

The lower stability of the 4-fluoro-substituted Grignard reagents (V) and (VI), *cf*. (XXI)-(XXIII), is thought to arise from the transmission through the central molecular cavity [2,4] of the dipole associated with the carbon-fluorine bond of the other bridgehead carbon. This will inductively enhance the ionic character of the carbon-magnesium bond, which in turn will favour loss of fluoride ion from $C_2$.

Another significant effect, due apparently to a bridgehead fluorine, is found in the deuteriation of compounds (I) and (XIV). Though both were deuteriated in the presence of base,[1] with deuterium oxide alone at room temperature no deuteriation of the 1H,4H-compound (XIV) could be detected by mass spectrometry after 27 days, whereas the 1H- compound (I) was 49% deuteriated after 5 days. Quantitative measurements of their acidities also show a substantial difference.[5]

Compounds (I),(III),(V),(VII),(VIII),(XIII),(XIV) and (XVII)-(XX) had correct elemental analyses and consistent IR-, NMR- and mass-spectra.

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