

4-(Difluoroiodo)tricyclene, an Isolable Compound of Type RIF₂ from an Aliphatic Iodide

Gregory W. Bradley,^a John H. Holloway,^b Han Joong Koh,^a David G. Morris^{*,a} and Paul G. Watson^b

^a Dept. of Chemistry, University of Glasgow, Glasgow, G12 8QQ, UK

^b Dept. of Chemistry, University of Leicester, Leicester LE1 7RH, UK

The synthesis, characterisation and reactivity are reported for the title compound which is the first isolable compound of type RIF₂ from an aliphatic iodide.

Examples of difluoroiodo compounds such as C₆H₅IF₂,¹ CF₃-IF₂² and CH₃IF₂² are known, the last of which can be made and used immediately in solution. Presently we wish to report the synthesis and characterisation of 4-(difluoroiodo)tricyclene **1**, which represents the first example of an isolable compound in which the IF₂ functionality is linked to an aliphatic hydrocarbon residue. 4-Iodotricyclene was chosen as the starting material for this investigation for the following reasons: (a) we have previously shown that the 4-position of tricyclene is the bridgehead site from which a nucleofuge departs most reluctantly in any S_N1 reaction hitherto investigated;³ (b) rate-determining formation of bridgehead radicals takes place with less reluctance than formation of the corresponding carbocation, though there is a correlation between the two processes;⁴ (c) we consider it unlikely that C₄I bond heterolysis will occur to give a positively charged iodine group either in **2** or, more particularly, **1**; (d) the reaction does not contain the ingredients for a C₄I bond cleavage to occur readily *via* an SET pathway.

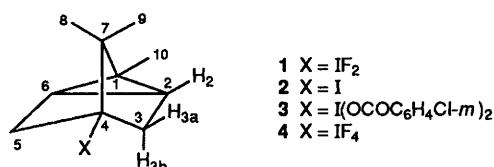
Treatment of a solution of 4-iodotricyclene **2** in carbon tetrachloride with a six-fold molar excess of XeF₂ at ambient temperature for 1 h, followed by removal of solvent and excess of XeF₂ by evacuation at 10⁻² mmHg at room temperature gave a pale yellow solid product. Assignment of structure **1** to this product was made from NMR spectral data. Both ¹H and ¹³C NMR spectra indicated that the plane of symmetry present in **2** was preserved in the product, and also that the ¹H NMR spectrum of **1**, by virtue of the AB pattern for protons H_{3a} and H_{3b} in particular at δ 1.56 and 1.21 (*J* 11 Hz), showed that the three-membered ring had been preserved [in these systems *J*(H_{3a}H₂) = *J*(H_{3b}H₂) ≤ 0.5 Hz].

The ¹³C NMR spectrum of **1** shows that the heavy-atom effect, by which carbons bonded to monovalent iodine resonate at abnormally high fields,⁵ is not present in this compound. One noteworthy feature of the spectrum of **1** is a triplet coupling, ²*J*(C₄IF) 9 Hz. ¹³C Chemical shift data for **1** and **2** and a previously made related compound **3**⁶ are presented in Table 1. The absence of a heavy-atom effect for carbon atoms bonded to trivalent iodine⁷ can be most economically rationalised in terms of the increased electronegativity of -IF₂ over -I, although other factors previously considered cannot presently be excluded. Recently, further examples of the absence of the heavy-atom effect in trivalent iodine compounds have been provided.⁸

One resonance was observed in the ¹⁹F NMR spectrum, a sharp singlet at δ -193.3 (ext. std. CCl₃F) in the region associated with RIF₂.^{1,2}

In our experiments we detected no evidence for the presence of 4-(tetrafluoroiodo)tricyclene **4** either from fluorination by an excess of XeF₂ or by disproportionation of the observed RIF₂. We feel that a compound of the type RIF₄ would be fairly hindered, even allowing for the tied-back nature of the 4-tricyclene system employed.

Table 1 ¹³C NMR data for compounds **1**, **2** and **3** in CDCl₃



	1	2	3
C ₁	24.77	23.74	23.85
C ₂	20.66	20.55	20.00
C ₃	37.26	43.40	38.26
C ₄	80.99	43.90	80.29
C ₇	49.27	47.34	49.27
C ₈	20.23	19.52	20.23
C ₁₀	12.23	11.77	12.23

Two pieces of available NMR evidence support this contention. Firstly, the ¹³C NMR spectra of some I^V compounds⁹ indicate that C₄ of **4** would resonate at significantly higher field than our observed value for **1**. Secondly, the four equivalent coplanar fluorines of **4** would show a ¹⁹F resonance in a very different region of the spectrum⁹ from those in **1**. The NMR evidence that we have adduced is supported by mass spectral analysis which showed a parent ion for **1** at *m/z* 300 (70 eV, electron impact) with no evidence for a tetrafluoroiodo product.

4-(Difluoroiodo)tricyclene **1** is a pale yellow waxy solid which is stable in air for up to 4 h and in CCl₄ solution, under an inert atmosphere, indefinitely. Compound **1** is probably an optimum structure for conferring longevity on aliphatic compounds of type RIF₂ and very likely places an upper limit on the lifetime of such compounds.

We were interested in the reactivity of **1** as a fluorinating agent, as has been observed for ArIF₂.¹⁰ Accordingly **1** was allowed to react with norbornadiene to give by ¹H NMR analysis, albeit in a different solvent, sensibly the same products as found previously.

As an extension of this work we found that reaction of Cl₄ with XeF₂, under the same conditions, led to extensive decomposition rather than tetra(difluoroiodo)methane.

Experimental

The reaction was carried out in standard Schlenk apparatus under an N₂ atmosphere.

To a stirred, degassed solution of 4-iodotricyclene (30 mg, 0.12 mmol) in CCl₄, a sample of XeF₂ (120 mg, 0.7 mmol), pre-weighed into a sample bottle in a dry-box, was added. After 1 h, the colourless solution had turned pale yellow and was subjected to high vacuum for 15 min to remove solvent and

excess of XeF₂. The resulting yellow solid was then dissolved in CDCl₃ and transferred to an NMR tube by a Pasteur pipette.

References

- 1 D. F. Shellhammer, R. J. Conner, R. E. Richardson and V. L. Heasley, *J. Org. Chem.*, 1984, **49**, 5015.
- 2 J. A. Gibson, R. K. Marat and A. F. Janzen, *Can. J. Chem.*, 1975, **53**, 3044.
- 3 S. A. Sherrod, R. G. Bergman, G. J. Gleicher and D. G. Morris, *J. Am. Chem. Soc.*, 1972, **94**, 4615.
- 4 C. Rüchardt, V. Golzke and G. Range, *Chem. Ber.*, 1981, **114**, 2769.
- 5 F. W. Wehrli, A. P. Marchand and S. Wehrli, *Interpretation of Carbon-13 NMR Spectra*, 2nd edn., Wiley, Chichester, 1983.
- 6 D. G. Morris and A. G. Shepperd, *J. Chem. Soc., Chem. Commun.*, 1981, 1250.
- 7 K. Friedrich, W. Amanu and H. Fritz, *Chem. Ber.*, 1978, **111**, 2099; T. M. Balthazor, D. E. Godar and B. R. Stults, *J. Org. Chem.*, 1979, **44**, 1447.
- 8 A. R. Katritzky, J. K. Gallos and H. D. Durst, *Magn. Reson. in Chem.*, 1989, **27**, 815.
- 9 G. Oates and J. M. Winfield, *J. Chem. Soc., Dalton Trans.*, 1974, 119.
- 10 A. Gregoričič and M. Zupan, *J. Chem. Soc., Perkin Trans. 1*, 1977, 1446.

Paper 2/04909K

Received 14th September 1992

Accepted 17th September 1992