Journal of Organometallic Chemistry, 114 (1976) C4—C6

Preliminary communication

A NEW SYNTHESIS OF METAL-CENTRED (e.g., GROUP IV ELEMENT) RADICALS FROM AN ORGANOMETALLIC HALIDE AND AN ELECTRON-RICH OLEFIN*

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(Received May 4th, 1976)

Summary

Irradiation of a bulky Group IV element halide, such as $(Me_3Si)_3MHal$ (M = C or Si) or $\{(Me_3Si)_2CH\}_3M'Hal$ (M′ = Ge or Sn), in n-hexane or toluene along with an electron-rich olefin, such as $[:\overline{CN(Me)CH_2CH_2N}Me]_2$ or $C_2(NMe_2)_4$, produces the metal-centred radical, with Hal totally converted into the insoluble $[Hal\overline{CN(Me)CH_2CH_2N}Me]^+\ Hal^-$ or $[C_2(NMe_2)_4]^{2+}(Hal^-)_2$; unsymmetrical substrates $\{(Me_3Si)_2CH\}_2(R')SnHal$ (e.g., RHal = MeI) give the disproportionation product $\{(Me_3Si)_2CH\}_3\dot{S}n$.

We wish to report a new and convenient synthesis of metal-centred radicals, which may prove to have some generality and advantages over established procedures, and is here illustrated by reference to some recently-prepared long-lived Group IV element species. The method involves the photolysis of a hydrocarbon solution of an organometallic halide and an electron-rich olefin, such as I (R = Me or Et) or II, as shown in equations 1 or 2 where *n* is the normal valency of the metal M and Y is a ligand such as an alkyl or aryl group. A convenient solvent is n-hexane or toluene; these have the advantage over, say, cyclohexane or benzene in having low freezing points, thus permitting the low temperature ESR characterisation of the radical. Both the reactants and the radical are hydrocarbon-soluble, whereas the salt is precipitated. Hence a feature of these reactions is that there is quantitative formation of the radical and/or its decomposition products as the sole species in solution at the termination of the reaction, stoichiometries being as follows:

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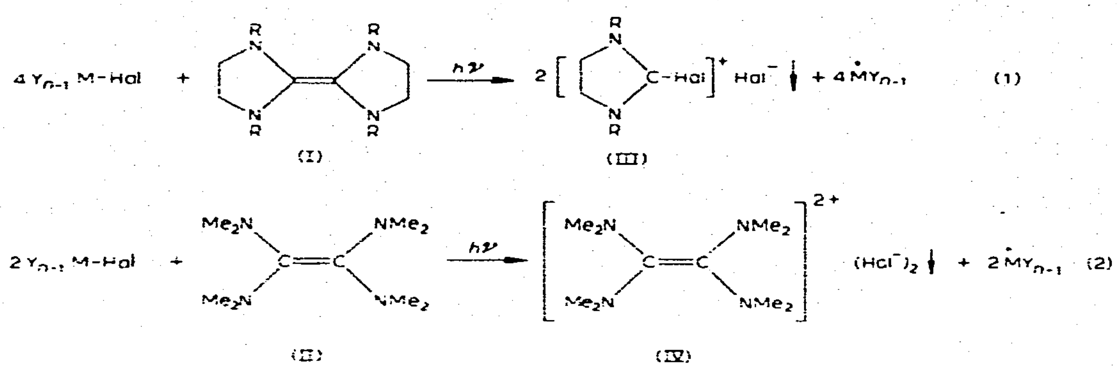

A suitable experimental technique was to dissolve the substrate halide [$(\mathrm{Me_3Si})_3\mathrm{CCl}$ [1], $(\mathrm{Me_3Si})_3\mathrm{SiBr}$ [2], $\{(\mathrm{Me_3Si})_2\mathrm{CH}\}_3\mathrm{GeCl}$ [3], $\{(\mathrm{Me_3Si})_2\mathrm{CH}\}_3\mathrm{SnCl}$ [3], or $\{(\mathrm{Me_3Si})_2\mathrm{CH}\}_2(\mathrm{R'})\mathrm{SnX}$ (R′, X = i-Pr, Cl; t-Bu, Cl; Me, Br; Et, Br; t-Bu, Br; Me, I; Et, I; n-Bu, I; $\mathrm{C_5H_5}$, I)] in either n-hexane or toluene. Photolysis using a 250 W lamp in the cavity of a Varian E3 ESR spectrometer gave no signal. The olefin I (R = Me or Et) or II was then added, again without an ESR signal being observed. However, irradiation at −70°C (or also 20°C for the Ge and Sn species) gave the appropriate strong ESR signal [$(\mathrm{Me_3Si})_3\dot{\mathrm{C}}$ [1]: $g = 2.0027$, $a(\mathrm{H}) = 0.0376$ mT; $(\mathrm{Me_3Si})_3\dot{\mathrm{Si}}$ [2]: $g = 2.0050$, $a(\mathrm{H}) = 0.044$ mT; $\{(\mathrm{Me_3Si})_2\mathrm{CH}\}_3\dot{\mathrm{Ge}}$ [4]: $g = 2.0078$, $a(\mathrm{H}) = 0.38$ mT, $a(\mathrm{Ge}) = 9.2$ mT; or $\{(\mathrm{Me_3Si})_2\mathrm{CH}\}_3\dot{\mathrm{Sn}}$ [4]: $g = 2.0094$, $a(\mathrm{H}) = 0.21$ mT, $a(^{117}\mathrm{Sn}) = 169.8$ mT, $a(^{119}\mathrm{Sn}) = 177.6$ mT]. The hygroscopic salts III or IV were readily distinguished by their $\nu(\mathrm{CN_2})$ IR vibration [5]: ca. 1595 $\mathrm{cm^{-1}}$ for III (Hal = I) and ca. 1660 $\mathrm{cm^{-1}}$ for IV.

The reducing properties of electron-rich olefins such as I or II are well-known, not least from their exceptionally low first ionisation potential of ca. 6 eV [6]. The somewhat less electron-rich analogues I (R = Ph) or $\mathrm{C_2(SMe)_4}$ proved unreactive, although in the case of the former this may be due to its hydrocarbon-insolubility. Interestingly, the irradiation of either of these olefins in suspension or solution in n-$\mathrm{C_6H_{14}}$ or PhMe gave no ESR signal, whereas I (R = Me or Et) or II gave a weak and broad signal ($g = 2.0033$) which may arise from the olefin triplet.

The formation of $\{(\mathrm{Me_3Si})_2\mathrm{CH}\}_3\dot{\mathrm{Sn}}$ rather than $\{(\mathrm{Me_3Si})_2\mathrm{CH}\}_2\mathrm{R'}\dot{\mathrm{Sn}}$ from the mixed tin(IV) halide may be due to photo-disproportionation giving the most stable product; the symmetrical radical has $t_{1/2} >$ ca. 1 year at 20°C [4]. We hope to make use of this property in developing syntheses of, for example the unknown $\{(\mathrm{Me_3Si})_2\mathrm{N}\}_3\dot{\mathrm{Si}}$ and $\{(\mathrm{Me_3Si})_2\mathrm{CH}\}_3\dot{\mathrm{Si}}$ (available in low yield from photolysis of $\mathrm{Si_2Cl_6}/(\mathrm{Me_3Si})_2\mathrm{CHLi}$) [4], starting from $\mathrm{Y_2(R')SiHal}$ species. Reactions such as 1 or 2 are likely to have application far beyond that of the main group IV elements, and for radicals of type $\{(\mathrm{Me_3Si})_2\mathrm{CH}\}_3\dot{\mathrm{M}}$ the isolation of the solvent-free species can now be expected.

We thank Dr. P.L. Pye for useful discussions and I.C.I. Ltd., for the award of a Fellowship to M.J.S.G.

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