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Chemical Transformations on the Surface of [60]Fullerene: Synthesis of [60]Fullereno[1',2':4,5]oxazolidin-2-one

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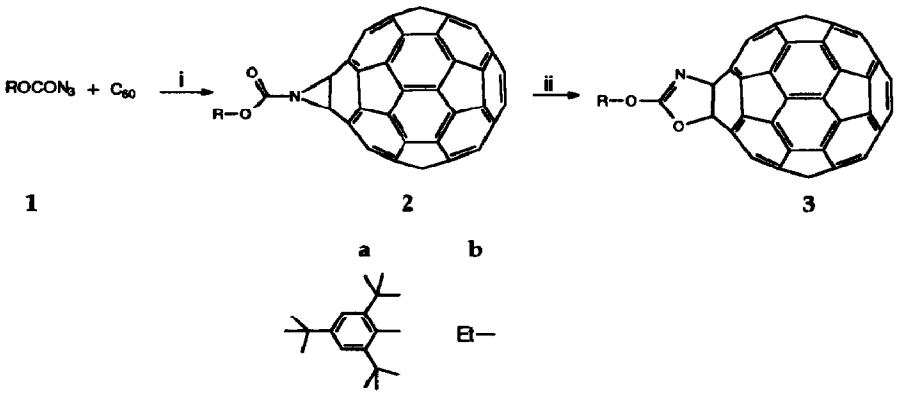
Abstract: Base-induced α-elimination from substituted *O*-4-nitrophenylsulfonylhydroxamic acids has been used as a mild source of nitrenes for capture by [60]fullerene; rearrangment of the resulting [60]fullereno[1',2':2,3]aziridine bearing a *N*-ethoxycarbonyl grouping under the influence of phenol/chlorotrimethylsilane results in the quantitative formation of the title compound which can be cleaved to yield 1-hydroxy-2-*N*-methylamino[60]fullerene.

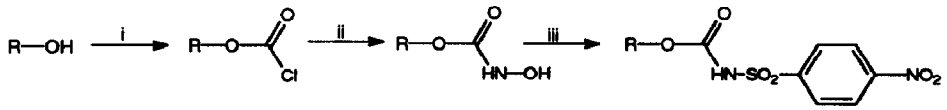
The chemical modification of [60]fullerene (C_{60}) continues to fascinate chemists and hitherto many methods to bring about its mono-functionalization have been reported[1,2]. By comparison, reports of subsequent chemical manipulation of these mono-adducts remain sparse, and the examples observed so far have targetted on functionalities at least two or three atoms away from the point of attachment to the fullerene surface [3]. Of the various successful attempts to functionalize C_{60}, its reaction with alkyl azides in boiling chlorobenzene (132°C) for 24 hours has been reported to yield open fulleroid 5,6-compounds[4,5,6], presumably via 1,3-dipolar addition and subsequent elimination of nitrogen from the resultant triazoline adduct[7]. In contrast, we have observed[8] that treatment of C_{60} with 2,4,6-tri-tert-butylphenyl(supermesityl) azidoformate **1a** at 147°C in 1,1,2,2-tetrachloroethane (TCE) led to a closed 6,6- [60]fullereno[1',2':2,3]aziridine **2a**, and argued that this product arose by nitrene addition to C_{60}. Furthermore, we demonstrated that heating of **2a** resulted in a quantitative rearrangement to isomeric 3-(2,4,6-tri-*tert*-butylphenyl)oxy[60]fullereno[1',2':4,5]oxazole **3a** with both *O* and *N* vicinally bound to the fullerene skeleton at a closed 6,6-junction (Scheme 1).



Scheme 1. Conditions: (i) TCE, 147°C, 5 min, 70%; (ii) TCE, 147°C, 12h, 100%.

This finding exemplified the possibilities of being able to carry out chemical manipulations of functionalities on the fullerene surface. In this respect ^{13}C NMR spectroscopy proved to be a powerful tool for unravelling the structures of mono-adducts of C_{60} due to symmetry arguments[9]. In this letter we describe a much milder method for the preparation of fullerenoaziridines **2a,b** involving the capture of C_{60} by nitrenes generated at room temperature from the base-induced decomposition of substituted *O*-4-nitrophenylsulfonylhydroxamic acids **6**[10,11], and also report on their subsequent chemical manipulation to produce the parent [60]fullereno[1',2':4,5]oxazolidin-2-one **8**, which can be further modified to afford 1-hydroxy-2-*N*-methylamino[60]fullerene **9**.

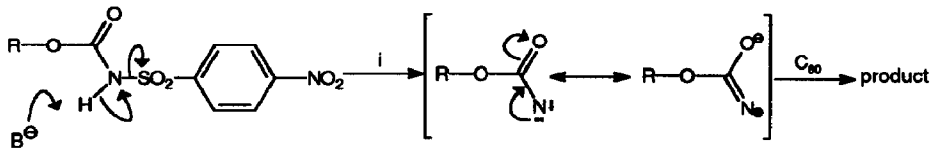
In light of our experience with the nitrene-mediated reaction of supermesitylazidoformate to C_{60}[4] at elevated temperatures, for our initial study we synthesised *O*-4-nitrophenylsulfonyl-2,4,6-tri-*tert*-butylphenylhydroxamic acid[12] **6a** in a sequence of high yielding steps from supermesitylphenol (Scheme 2). Thus, treatment of the readily formed chloroformate **4a**[8] with hydroxylamine hydrochloride, potassium carbonate and calcium hydride in boiling DME (85°C) gave the hydroxamic acid **5**. Coupling of *O*-lithiated hydroxamic acid **5a** with 4-nitrophenylsulfonyl chloride at -78°C in diethyl ether gave the required *O*-4-nitrophenylsulfonylhydroxamic acid **6a**.



4a **5a** **6a**

Scheme 2. Reagents and conditions: (i) *n*-butyl lithium, phosgene, DME, 0°C, 98%; (ii) hydroxylamine hydrochloride, potassium carbonate, calcium hydride, DME, 85°C, 94%, (iii) *n*-butyl lithium, *n*-hexane:diethyl ether, -78°C, then 4-nitrophenylsulfonyl chloride, 85%.

Treatment of a rapidly stirred mixture of C_{60} (1 equiv) and **6a** (5 equiv) under argon in dichloromethane (DCM)/water with an aqueous solution of sodium hydrogen carbonate (5 equiv) and benzyltriethylammonium chloride (10 equiv)[13] over 5 min produced an 86% yield of crude product. HPLC analysis (FullereneSep®, 7% ethyl acetate:n-hexane, 2 ml.min^{-1}, 258 nm)[14] showed that **2a** had been formed together with **3a** in a 5:1 ratio. The formation of **3a** at room temperature in this case was unexpected but can be explained by addition of the nitrene intermediate **7** in its 1,3-dipolar mesomeric form to C_{60} (Scheme 3).



6 **7**

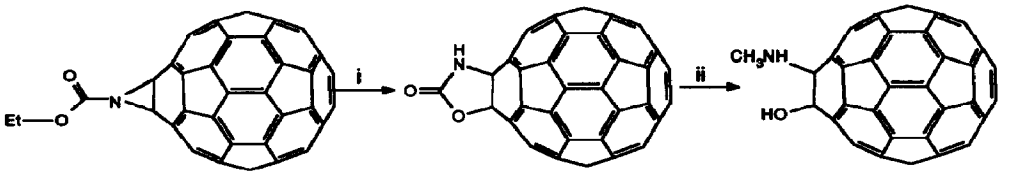
Scheme 3: Conditions: (i) sodium hydrogen carbonate, benzyltriethylammonium chloride, water/DCM, 20°C.

Following this demonstration of the applicability of the base-induced α-elimination reaction as a practicable route to [60]fullerenoaziridines **2** we turned our attention to an investigation of the effect of substituting an alkyl group in place of the supermesityl moiety. To this end we synthesised *O*-4-nitrophenylsulfonylethylhydroxamic acid **6b**[10] in good yield. When C_{60} was treated with the ethyl analogue under phase-transfer conditions at room temperature, *N*-ethoxycarbonyl[60]fullereno[1',2':2,3]aziridine **2b** was formed in 65% yield and could be easily separated from unreacted C_{60} by flash chromatography on silica (toluene:hexane 1:10). The ^{13}C NMR spectrum (62.5 MHz, CS_2/$CDCl_3$) of isolated **2b** was as

expected for a derivative of C_{60} with C_{2v} symmetry and consisted of 13 lines of intensity 4 and 3 lines of intensity 2 in the sp^2 region between δ 139.7 and 144.9, together with a diagnostic line of intensity 2 in the sp^3 region at δ 80.5; the resonances for the ethoxycarbonyl moiety were observed at δ 14.5 (CH_3), 64.0 (CH_2) and 155.5 (C=O). The ^{1}H NMR spectrum of **2b** consisted of a triplet (δ 1.60, J = 7.1 Hz) and a quartet (δ 4.5, J = 7.1 Hz), whilst its FT-IR spectrum exhibited strong bands at 1743 (C=O) 1228 (C-O), and 526 cm^{-1}. FAB-MS analysis confirmed that the product was indeed a mono-adduct [(M^++1) 808.04274, $C_{63}H_5NO_2$ requires 808.03985].

During the course of this work a report[15] by Japanese workers appeared describing the synthesis of **2b** by heating a mixture of C_{60}, sodium azide, ethyl chloroformate and 15-crown-5-ether in toluene. It was claimed that the compound remained unchanged upon heating under reflux in *o*-dichlorobenzene (180°C) for 8 h. In our hands, it was found to rearrange to 3-ethoxy-[60]fullereno[1',2':4,5]oxazole **3b** under the same conditions. An HPLC study (FullereneSep®) of the rearrangement showed that at this temperature the process was accompanied by the formation of significant amounts of C_{60}. The rearrangement was also carried out in boiling TCE (147°C) and the products were easily separated by preparative HPLC. The ^{13}C NMR (62.5 MHz, CS_2-$CDCl_3$) spectrum of **3b** showed the presence of diagnostic sp^2 carbon atoms that resonated at δ 96.8 and 88.3, along with C=N at δ148.3; the rest of the fullerene sp^2 carbon atoms were observed between δ 136 and 148 (28 lines of intensity 2 and 2 lines of intensity 1). The ^{1}H NMR (250 MHz) spectrum of the product consisted of a triplet (δ 1.71, J = 7.1 Hz) and a quartet (δ 4.82, J = 7.1 Hz) and its FT-IR spectrum showed characteristic absorptions at 1653 (C=N) and 526 (fullerene) cm^{-1}. FAB-MS data confirmed this product to be an isomer of **2b** [(M^++1) 808.04049, $C_{63}H_5NO_2$ requires 808.03985]. These data compare favourably with that previously reported[11] for the fullerenooxazole **3a** obtained from supermesitylazidoformate. The failure of the Japanese workers to detect the rearrangement of **2b** may lie in the relative slowness of the process which required heating for 65 h to bring about 50% conversion at 147°C; *cf.* 19% conversion at 180°C for 19h, and 100% conversion in 12 h for the supermesityl analogue **2a**.

In a further significant development to these findings treatment of a solution of **2b** in DCM with a pre-mixed solution of phenol and trimethylsilyl chloride[16] (3:1) in DCM led to dealkylation and the propitious formation of the parent fullerenooxazolidin-2-one **8** in 95% yield (Scheme 4). FAB-MS analysis of the product showed (M^++1) at 780.00831 ($C_{61}H_2NO_2$ requires 780.00855) and the FT-IR exhibited strong bands at 3420 (br., NH), 1760 (C=O), and 527 (fullerene) cm^{-1}. The ^{13}C NMR (62.5 MHz, d^5-pyridine) consisted of 32 fullerene lines as expected for a derivative with C_s symmetry, the most diagnostic resonances being at δ 157.9 (C=O) and two lines in the sp^3 region at δ 94.0 and 74.4; the sp^2 carbon atoms of the fullerene skeleton were found between δ 135.2 and δ 147.8.



2b **8** **9**

Scheme 4: Reagents and conditions: (i) phenol/chlorotrimethylsilane, (3:1), DCM, 20°C, 95%; (ii) DIBAL in DCM, DME, 20°C, 90%.

The mechanism of formation of **8** awaits further study, but in the meantime it is worth noting that its isolation highlights the opportunities of conducting reactions on functionalities attached to the surface of C_{60} by the following chemical transformation.

Fullerenooxazolidin-2-one **8** was suspended in DME and added dropwise to 1M DIBAL[17] in DCM at ambient temperature with stirring for 1 h. Careful addition of concentrated ammonia to the reaction mixture produced a brown precipitate in the DCM layer which was easily isolated. FT-IR showed that the carbonyl group in the starting material (1760 cm^{-1}) had disappeared and that the strongest feature in the spectrum was a broad band at 3447 cm^{-1}. FAB-MS analysis of the product confirmed that the starting material had been reduced to $C_{61}H_3NO$ [(M^++1) 768.04371, $C_{61}H_4NO$ requires 768.04494]. This evidence would suggest that **8** had been reduced to yield 1-hydroxy-*N*-methylamino[60]fullerene **9**.

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12. Selected data for O-4-nitrophenylsulfonyl-2,4,6-tri-*tert*-butylphenylhydroxamic acid **6a**: EI-MS (M^+) 506.20771 $C_{25}H_{34}N_2O_5S$ requires 506.20867; mp 190°C (decomp.); ^1H NMR (250 MHz, $CDCl_3$) δ 1.15 (s, 18H, o-Bu^t), 1.25 (s, 9H, p-Bu^t), 8.28 (AB quartet, 4H, -$SO_2C_6H_4$-NO_2), 8.59 (bs, 1H, NH); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 154.1 (C=O), 152.9, 151.2, 148.2, 144.2, 141.1, 138.8, 131.2, 124.0, 123.6, 35.4, 34.7, 31.3; FTIR ν_{max} 3277 (s, NH), 1792 (s, C=O), 1527, 1394 (s, NO_2), 1350, 1192 (s, SO_2) cm^{-1}.
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