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Unusual redox-type addition of nitroalkanes on the C_{60} surface

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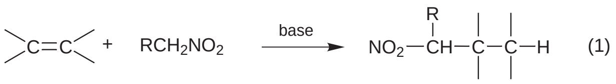
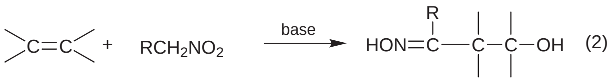
Nitroethanes underwent base-catalyzed addition to C_{60} to give 2-hydroxy-1,2-dihydrofulleryl ketoximes by way of a unique intramolecular redox process, which is not observed in normal alkenes.

Usual base-catalyzed reaction of nitroalkanes with electron-deficient alkenes is known to proceed in a 1,4-addition manner to give γ-nitro-functionalized products [eqn. (1)].[1] While fullerenes possess similar reactivity with nucleophilic reagents because of their low LUMO level,[2] this reaction with C_{60} was found to proceed with a different addition pattern to give β-hydroxy oxime products [eqn. (2)].

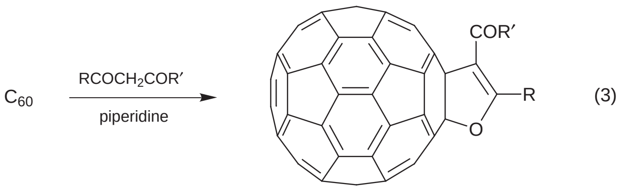


$$>C=C< \; + \; RCH_2NO_2 \xrightarrow{\text{base}} NO_2-\overset{R}{CH}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-H \qquad (1)$$

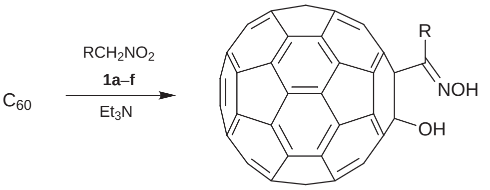


$$>C=C< \; + \; RCH_2NO_2 \xrightarrow{\text{base}} HON=\overset{R}{C}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-OH \qquad (2)$$

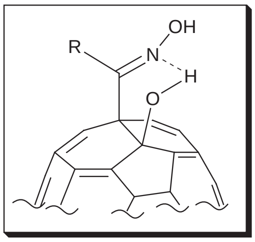
This result is not observed with standard alkenes and is ascribable to the specific nature of the double bonds on the C_{60} surface. So far, remarkable oxidative (cyclo)additions of C_{60} have been recorded in nucleophilic cyclization of 1,2-diamines,[3] photoinduced cyclization of Et_3N,[4] F-promoted cyclopropanation of a silyl enol ether,[5] 1,4-bisaddition of Grignard reagents,[6,7] and 1,2-bisaddition of alkoxy anions.[8] In our studies on heterocyclization of C_{60}, base-catalyzed oxidative [3+2]cycloaddition of β-dicarbonyl compounds has also been shown to give dihydrofuran-fused C_{60} derivatives [eqn. (3)].[9] Likewise, ambiphilic nitroalkanes could undergo an analogous addition but instead lead to the formation of a 1,2-bifunctionalized hydroxy oxime derivative as a result of an intramolecular redox process, which is reported here with a proposed mechanism.

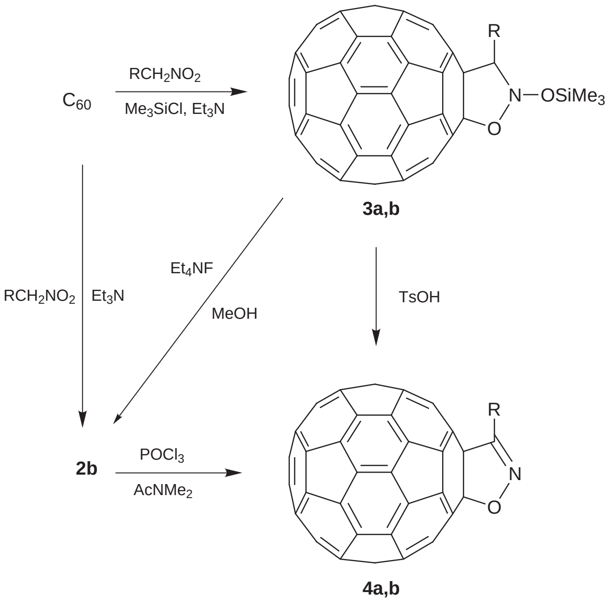


Previously, nitromethane **1a** was demonstrated to react with C_{60} in the presence of Et_3N and TMSCl to give the parent *N*-silyloxyisoxazolidine **3a** as the result of 1,3-dipolar cycloaddition of the *in situ* formed *N*-silyloxynitrone; a following acid-catalyzed elimination reaction gave isoxazoline **4a** (Scheme 1).[10] The same reaction conditions in the absence of the silylating reagent were anticipated to allow the oxidative [3+2]cycloaddition as observed in β-dicarbonyl compounds, but this did not take place. Despite this failure, homologous nitroethane **1b** could be reacted smoothly with C_{60} at room temperature for 2 h by employing excess reagents (20 equiv.), and a brown product was obtained after silica gel chromatography (toluene). Unexpectedly, the FAB mass spectrum included a molecular ion peak at *m/z* 795 (exact sum of molecular weights of C_{60} + $C_2H_5NO_2$), which revealed that the product was certainly a 1 : 1 adduct but not an oxidative cycloadduct (M^+ must be reduced by 2 amu). Nevertheless, the IR (KBr) and UV–VIS (dioxane) spectra showed absorptions at 527 cm^{-1} and 428 nm, respectively, which are characteristics of a C_{60} derivative arising from 1 : 1 addition at a 6,6 junction. The ^1H NMR signals were observed at δ 2.83 (3 H), 4.20 (1 H), and 6.45 (1 H), all as singlet peaks, with the integrations of the last two decreased by addition of D_2O, implying the existence of OH groups but no methylene or methine groups in the molecule. The ^{13}C NMR signals were observed at δ 14.95, 83.58, 99.59, 135.65–149.86 (52 lines),† and 156.53. The first three peaks and next low field aromatic peaks were assignable to sp^3



		2	Yield
a	R = H	**a**	0%
b	R = Me	**b**	46%
c	R = CO_2Et	**c**	0%
d	R = $CH_2CH_2CO_2Et$	**d**	34%
e	R = $CH_2CH_2CO_2Bu^t$	**e**	29%
f	R = Bn	**f**	45%





Scheme 1

carbons due to methyl and junction carbons and spherical sp^2 carbons, respectively; the total 52 lines due to C_{60}, seemingly, suggested no molecular symmetry. The last peak might be due to a C=N moiety. These data were difficult to completely assign. Consequently, the suggestion that an intramolecular redox process may split the nitro group to give nitroso (tautomeric oxime) and hydroxy groups, as shown below, prompted us to determine the structure *via* an independent synthesis. Recently, Hassner reported that β-hydroxy ketoximes were obtained by the fluoride-induced ring cleavage of *N*-silyloxyisoxazolidines derived from 1,3-dipolar cycloaddition reaction of *N*-silyloxynitrones.[11] This method was applied to the chemistry of C_{60}. Thus, C_{60} was allowed to react with **1b** in the presence of Et_3N and TMSCl,[10] and the prepared **3b** was successively treated with Et_4NF in MeOH at −20 °C for 1 h to give the ring-cleaved product, 2-hydroxy-1,2-dihydrofulleryl methyl ketoxime **2b**. As a result, the HPLC retention time and spectral data of this authentic sample were consistent with those of the addition product obtained from the base-catalyzed reaction with **1b**. This identification was supported by chemical conversion of the product into isoxazoline **4b** by cyclodehydration with $POCl_3$ and $AcNMe_2$. Intuitively, the confirmed β-hydroxy oxime structure might have C_s symmetricity, but this was not supported by the ^{13}C NMR data; however, the spectrally observed lack of symmetry could be explained by considering a boat-like form (as shown in Scheme 1) composed of an intramolecular hydrogen-bond between the oxime and hydroxy groups. In fact PM3 calculations suggested that a coplanar hydrogen-bonded structure was much less stable than the boat-like one. From a synthetic point of view, the above new 1,2-bifunctionalization of C_{60} can be applied to nitroethanes but not to nitromethanes. Whereas the similar reaction with ethyl nitroacetate **1c** was unsuccessful, those with ethyl and *tert*-butyl 4-nitrobutanoates **1d**,**e** and β-nitroethylbenzene **1f** under the same conditions lead to the formation of the corresponding bifunctionalized **4d**–**f** in moderate yields (Scheme 1).

As a clue to understanding the mechanism of the above unusual addition reaction, it is considered likely that a nitro group can essentially serve as an oxygen donor (*i.e.* reduction to a nitroso group), a β-hydrogen to this group being necessary for the reaction to occur. Since the use of active methylene compounds in oxidative [3+2]cycloadditions has precedent from our previous work,[9a] a formal intramolecular redox process is proposed as follows (Scheme 2). First, addition of a nitronate anion at the carbon site to a double bond on C_{60} is followed by 1,5-hydrogen shift and subsequent addition at the oxygen site to give an isoxazoline *N*-oxide intermediate (**i** → **ii** → **iii**; this resembles the foregoing reaction with β-dicarbonyl compounds[9]). Second, two hydrogens migrate to a fused isoxazoline ring *via* tautomerization from a nitrone form to a *N*-hydroxyenamine species (this step requires the β-H); abstraction of an acidic hydrogen on the core by the enamine is followed by a 1,4-hydrogen shift and subsequent hydride attack on an iminium cation (**iii** → **iv** → **v** → **vi**). This sequence is regarded as an intramolecular redox process. Finally, eliminative ring cleavage to a nitroso alcohol intermediate and subsequent tautomerization gives the product β-hydroxy ketoxime (**vi** → **vii** → **viii**).

In conclusion, nitroethanes were shown to undergo redox-type addition to a double bond of C_{60} under base-catalyzed conditions to give 2-hydroxy-1,2-dihydrofulleryl ketoximes. The mode of addition as seen in this reaction is quite unique, compared with normal electron-deficient alkenes which simply act as a Michael acceptor in the common nucleophilic reaction of nitroalkanes. While some previous oxidative additions to C_{60} were reported to occur with C_{60} itself as an oxidant,[4b,8a] in this case, a nitro group played such a part intramolecularly. This pattern is peculiar in fullerene chemistry and provides a new methodology for its bifunctionalization.

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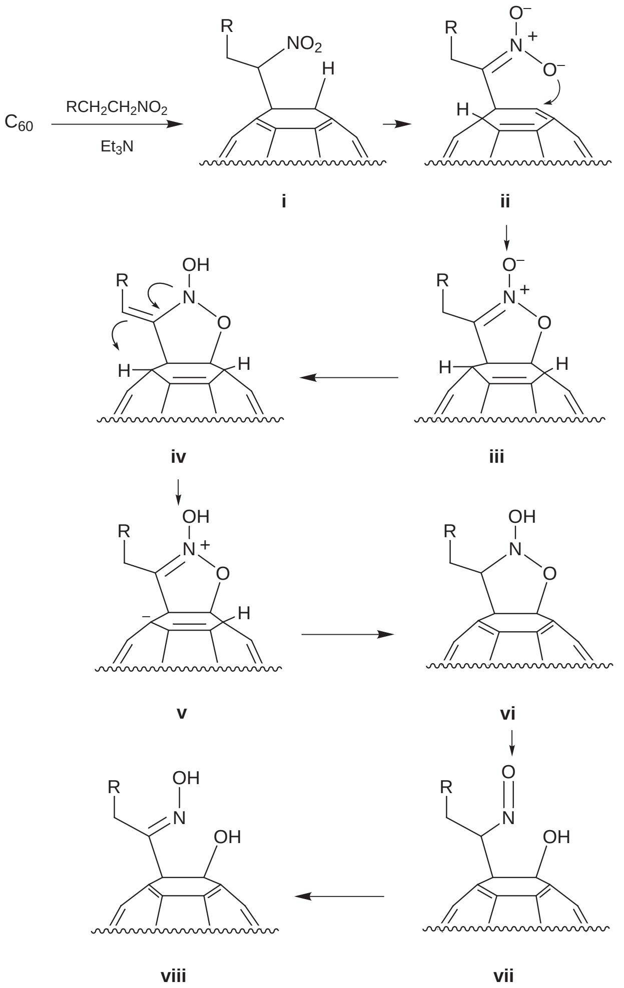

Scheme 2

Notes and references

† The ^{13}C NMR signals due to C_{60} sp^2 carbons (52 lines) were 135.65, 136.55, 137.15, 138.46, 139.77, 141.41, 141.60, 141.76, 142.10, 142.59, 142.79, 142.86, 143.08, 143.30, 143.44, 143.61, 143.82, 143.87, 143.96, 144.32, 144.50, 144.58, 144.63, 144.65, 144.75, 144.79, 144.94, 145.03, 145.11, 145.23, 145.24, 145.54, 145.56, 145.65, 145.98, 146.18, 146.50, 146.59, 146.67, 146.93, 147.07, 147.26, 147.39, 147.44, 147.75, 148.16, 148.42, 149.08, 149.49, 149.57, 149.73 and 149.86.

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