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Activated Carbon as the Reagent for the Oxidative Cyclization of Fullerene Adducts

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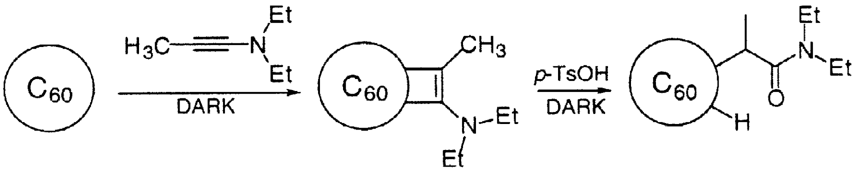
Abstract: Reaction of C_{60} with diethylaminopropyne leads to cyclobutene adduct **1**, which upon acid hydrolysis provides a facile synthetic route to fullerene adduct **2**. Subsequent oxidative cyclization involving activated carbon yields the novel fullerene lactone **3**.

We have reinvestigated the reaction of C_{60} with diethylaminopropyne (DAP). This alkyne is known to react both thermally and photochemically with various substrates.[1-6] DAP was shown previously to add photochemically [2+2] to fullerenes to yield cyclobutene **1**, which undergoes subsequent self-sensitized reaction with singlet oxygen to yield a ketone/amide product.[7] Further investigation revealed that, contrary to previous reports, DAP also reacts thermally with fullerenes.[7] Reaction of C_{60} with DAP in CS_2 in the dark at room temperature gave cyclobutene **1** whose formation can be easily monitored by HPLC and ^{1}H NMR, and which is stable when kept in the dark.



1 2

Scheme 1

Addition of *p*-toluenesulfonic acid hydrate to a solution of compound **1** in the dark quantitatively yields hydrolysis product **2** (Scheme 1). The previously published synthesis provided only a trace of **2**, and involved a lengthy purification.[7]

In an attempt to derivatize cyclobutene **1**, we carried out what we expected to be a simple catalytic hydrogenation using palladium on carbon under H_2 in toluene. Much to our surprise, we found no trace of the expected saturated product. Instead, a product with a simple ^{1}H NMR spectrum was isolated and identified as methyl lactone **3**. This product arises not from a hydrogenation, but from an unexpected oxidation. Lactone **3** was also formed under the same reaction conditions from product **2** (Scheme 2). Thus, we conclude that a trace of acid leads to the formation of **2**, which subsequently oxidizes to lactone **3**.

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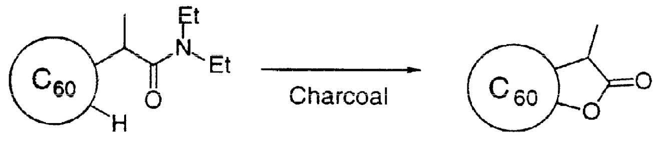


2 **3**

Scheme 2

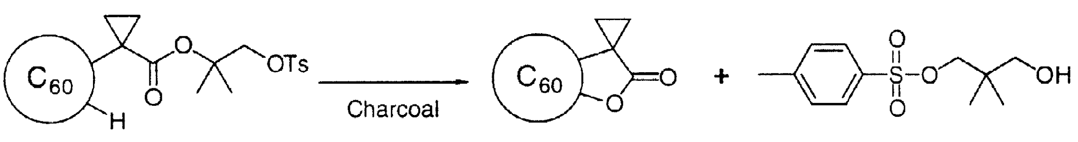
Charcoal is known to adsorb C_{60} and C_{60} derivatives, causing irreversible losses.[8,9] To avoid adsorption of the starting material and reaction products, we attempted to find a charcoal-free catalyst for this reaction. Since oxidation of the fullerene carbon occurs, various oxidants were tried, but only reagents with charcoal gave lactone **3**. Oxidants, bases, and other compounds investigated are listed in Table 1. The common species in all the successful reagents was charcoal. Amazingly, the oxidation of **2** to **3** proceeded cleanly using charcoal alone. Charcoal from various suppliers and of different types were equally effective.

Table 1. Reagents investigated to convert **2** to **3**.

Negative					Positive
Bases	Adsorbents	Oxidants	Metals	Miscellaneous	Charcoal Containing
NH_4OH	Alumina	NaOCl	$Pd(AcO)_2$[c]	H_2SO_4	Pd/C[c,d]
DMAP	Celite	SeO_2	PtO_2[c]	Xenon hυ	Pearlman's Catalyst[c,e]
NaOH[a]	Florisil	MnO_2	$Pd/BaCO_3$[c]	Benzoyl Peroxide	Norit SG§ (EM Science)
CaH_2	SiO_2	$KMnO_4$	$Na_{(s)}$	AIBN	Darco® G-60 (EM Science)
t-BuOK	Molecular Sieves	PCC[b]		$(n\text{-}Bu)_3SnH$	Darco§ G-60 (Aldrich)
$N(Et)_3$		O_2		$FeSO_4/H_2O_2$	

a) Carried out under argon.[10] b) Pyridine Chlorochromate: one equivalent appeared by HPLC analysis to cause a peak at the proper retention time, but the reaction was only 50% complete in 6 months. More than one equivalent resulted in the loss of all HPLC peaks. c) Both in the presence and absence of H_2. d) Palladium on powdered charcoal. 10% catalyst. e) Palladium hydroxide on carbon, Pd content 20%.

To investigate whether structurally similar fullerenes would give this reaction, we looked for a similar substrate. Fullerene derivative **4** was synthesized by Nakamura *et al.*[11] Both **2** and **4** contain a fullerene hydrogen and a carbonyl group attached to a heteroatom. As with derivative **2**, reaction of the cyclopropyl compound **4** with charcoal yielded the cyclopropyl lactone **5**, along with the corresponding alcohol **6** (Scheme 3).



4 **5** **6**

Scheme 3

Discussion

The oxidation of **2** to **3** must involve an oxygen source. To increase the rate of the reaction, and also find the oxygen source for this oxidation, the reaction was performed under an O_2 atmosphere, and with the addition of water. Neither conditions altered the rate compared to a control carried out under argon. The most likely explanation is that oxygen is already adsorbed to the charcoal, and thus the local concentration near the reactive sites is unaffected by the ambient atmosphere.

Because of the affinity of charcoal for fullerenes, there is an inverse relationship between the reaction rate and the yield. Increasing the amount of charcoal increases the reaction rate, but with a decrease in yield. Conversely, if the reaction is done with less charcoal the yields tend to be higher, but the reaction rate is much slower. Carrying out the charcoal reaction in the absence of light has no effect, but heating the reaction results in the formation of C_{60}. The methyl lactone (**3**) is quite robust, surviving irradiation from a xenon lamp and refluxing toluene. It can be stored for many months with no sign of decomposition.

In conclusion, we have demonstrated that activated carbon can be used as a reagent that interacts with certain fullerene derivatives to give an oxidized ring-closed lactone.

Experimental

Materials

C_{60} was purchased from MER Corp.[12], 99.5+%. *p*-Toluenesulfonic acid hydrate and all solvents were used as received from Fisher (Certified A.C.S.). Activated carbon (charcoal), Darco® G-60, 100 mesh powder, was purchased from Aldrich and used without further purification. HPLC analyses were carried out with a Waters 501 pump using toluene/acetonitrile (Fisher, Optima grade) 1:1 v/v, at a flow rate of 1 ml per minute. A Hypersil, C18, 5 micron, 250 mm, 4.6 mm I. D. column was used with UV detection at 340 nm. Column chromatography was performed using Silica Gel 60 (230-400 mesh) purchased from EM Science.

Synthesis of 2

In a 1 liter round bottom flask, 0.45 g of C_{60} was dissolved in ca. 500 ml of carbon disulfide.[13,14] Diethylaminopropyne[15,16] was added in the dark with rapid stirring. The mixture was monitored by HPLC, and an appropriate amount of alkyne was added until the majority of C_{60} had reacted, and the cyclobutene (**1**)/C_{60} peak ratio had grown to 6:1 (ca. 85% complete; this usually required 2-3 equivalents).[17] *p*-Toluene sulfonic acid hydrate, 0.7 g (ca. 6 equiv.), was then added and the reaction was left to stir in the dark until HPLC analysis showed that all of the cyclobutene **1** had been converted to **2** (ca. 4 hours). The reaction was then concentrated by rotatory evaporation and purified by column chromatography. Using CS_2 as the eluent, the characteristic purple C_{60} band was collected. The solvent system was then changed to CH_2Cl_2 and **2** eluted rapidly as a brown band (70%).[18]

Synthesis of methyl lactone 3

In a 300 ml round bottom flask, 0.111 g of **2** was dissolved in carbon disulfide and 0.45 g of activated carbon (Darco® G-60, 100 mesh) was added. The reaction was monitored by HPLC and after 15 days, was concentrated by rotatory evaporation. The mixture was subjected to column chromatography, using carbon disulfide as the solvent; a major brown band was collected and identified as methyl lactone **3**, (30%). Switching the solvent system to CH_2Cl_2 afforded unreacted starting material.[19]

Synthesis of cyclopropyl lactone 5

In a 100 ml round bottom flask, 0.128 g of the cyclopropyl derivative **4**[11] was dissolved in ca. 40 ml carbon disulfide. Activated carbon (Darco® G-60, 100 mesh), 0.17 g, was added, and left to stir. After monitoring by HPLC for 20 days, the reaction was concentrated by rotatory evaporation and subjected to column chromatography. Elution with CS_2 provided crude product (**5**). Switching the solvent to CH_2Cl_2 gave unreacted starting material (**4**). The solvent was then changed to ethyl acetate, which eluted the hydrolyzed product **6**.[20] The carbon disulfide fraction was subjected to a second purification by column chromatography, with the eluent consisting of 4:1 carbon disulfide/toluene. This afforded cyclopropyl lactone **5** (10%).[21]

Acknowledgments

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17. The reaction is usually not carried out to completion because excess diethylaminopropyne leads to diadduct formation.
18. For physical data see ref. 7.
19. **Physical data for methyl lactone 3:** IR (KBr) 1784 cm^{-1}, 1005 cm^{-1}, 970 cm^{-1}. ^{1}H NMR 400 MHz ($CDCl_3$) δ 2.14 (d, J = 7.6 Hz, 3H), 4.71 (q, J = 7.6 Hz, 1H). ^{13}C NMR 100 MHz ($CDCl_3$) δ 16.6, 45.2, 67.0, 96.9, 134.6, 137.0, 137.3, 138.2, 140.0, 140.02, 140.2, 140.5, 141.3, 141.6, 141.9, 142.0, 142.31, 142.32, 142.37, 142.39 142.40, 142.47, 142.49, 142.5, 142.92, 142.99, 143.0, 143.13, 143.18, 144.3, 144.52, 144.55, 144.7, 144.8, 144.9, 145.2, 145.34, 145.37, 145.49, 145.52, 145.56, 145.57, 145.60, 145.62, 145.8, 146.42, 146.46, 146.51, 146.54, 146.58, 146.66, 146.69, 146.7, 146.82, 146.89, 147.9, 148.5, 150.0, 154.6, 177.2. HRMS (FAB) calcd $(M+H)^+$ 793.0289, found 793.029
20. **Physical data for cleavage product 6**: IR (KBr) 3432 cm^{-1}, 2965 cm^{-1}, 1356 cm^{-1}, 1190 cm^{-1}, 966 cm^{-1}. ^{1}H NMR 400 MHz ($CDCl_3$) δ 0.88 (s, 6H), 1.65 (t, J = 6 Hz, 1H), 2.45 (s, 3H), 3.38 (d, J = 6 Hz, 2H), 3.82 (s, 2H) 7.35 (d, J = 8 Hz, 2H), 7.79 (d, J = 8 Hz, 2H). ^{13}C NMR 100 MHz ($CDCl_3$) δ 21.1, 21.8, 36.7, 67.7, 75.1, 128.0, 130.0, 133.0, 145.0. HRMS (EI) calcd $(M+H)^+$ 259.10039, found 259.1009
21. **Physical data for cyclopropyl lactone 5**: IR (KBr) 1780 cm^{-1}, 1508 cm^{-1}, 1148 cm^{-1}, 991 cm^{-1}. ^{1}H NMR 500 MHz ($CDCl_3/CS_2$) δ 1.90 (dd, J = 5 and 8 Hz, 2H), 2.18 (dd, J = 5 and 8 Hz, 2H). ^{13}C NMR 125 MHz ($CDCl_3/CS_2$) δ19.7, 28.9, 65.5, 96.1, 135.6, 137.6, 139.8, 140.1, 141.3, 141.6, 142.0, 142.1, 142.3, 142.4, 142.72, 142.76, 142.9, 144.3, 144.51, 144.52, 144.8, 145.1, 145.30, 145.31, 145.4, 145.6, 146.1, 146.2, 146.3, 146.49, 146.52, 151.2, 176.6. HRMS (FAB) calcd $(M+H)^+$ 805.0289, found 805.029