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Unusual Reactions of C_{60} with Aldehydes in the Presence of Aqueous Ammonia

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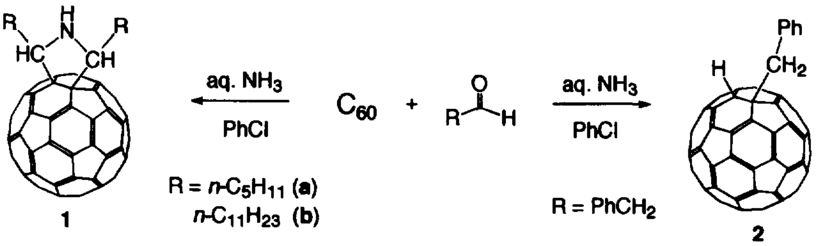
Abstract: Fullerene C_{60} reacts with alkylaldehydes in the presence of aqueous ammonia to give 2,5-dialkyl-substituted pyrrolidine derivatives. The reaction of phenylacetaldehyde under similar conditions afforded $C_{60}(H)(CH_2Ph)$ via possible decarbonylation. On the basis of the product analysis, reaction mechanisms are proposed in which C_{60} plays the role of a dipolarophile or radical scavenger.

The chemistry of fullerenes has attracted much attention in connection with the search for new functional materials.[1] Various heteroatoms were introduced in fullerene materials, and in some cases fullerene-fused 5-membered heterocycles, such as pyrazoline,[2] oxazolidine,[3] and pyrrolidine,[4,5] were obtained by use of 1,3-dipolar reagents. In the course of our study on alkyl-substituted fullerene derivatives,[6] we unexpectedly found a novel synthetic route to fullerene-fused pyrrolidine derivatives (Scheme 1, left). Two alkyl groups can be introduced to C_{60} simultaneously according to this reaction. Furthermore, another type of reaction was found when phenylacetaldehyde was used as the starting material (Scheme 1, right). We report in this letter an outline of these reactions and propose the possible reaction mechanisms.

The following synthetic procedure is typical. A mixture of C_{60} (14.5 mg, 0.020 mmol), hexanal (41.7 mg, 0.42 mmol), aqueous ammonia (25%, 35 mg, 0.52 mmol), and chlorobenzene (4 mL) was stirred at 50-60°C for 48 h under argon. The solution turned brown. After passing through a silica-gel short column using toluene as an eluent, evaporation of the solvent under reduced pressure left a black residue. Separation of the products on an HPLC (LC 908, Japan Analytical Industry) by using gel permeation columns (Jaigel 1H+

Scheme 1.



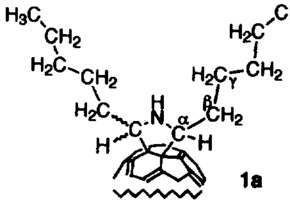
1H) and toluene as an eluent afforded 3.0 mg of **1a** (16% yield) together with 8.7 mg of C_{60} recovered (60%). A similar reaction using dodecanal instead of hexanal gave **1b** in 35% yield (40% C_{60} recovered).

The SIMS and FABMS of **1a** were measured on a Finnigan Mat. TSQ 700 by positive and negative ionizations from a matrix of *m*-nitrobenzyl alcohol. The spectra of **1a** showed $M^{\bullet -}$ at *m/z* 903 and MH^+ at *m/z* 904. The tandem MS/MS analysis suggested that the molecule consisted of a C_{60} moiety ($C_{60}^{\bullet -}$ at *m/z* 720) and a substituent $C_{12}H_{25}N$ ($C_{12}H_{26}N^+$ at *m/z* 184). The elemental analysis confirmed the formula $C_{72}H_{25}N$, indicating that two alkyl groups were introduced to C_{60}.[7]

The ^1H NMR spectrum of **1a** was found to be a superimposition of two isomers (Fig. 1) which, so far, have not been separable by the HPLC method. The H-H COSY measurements of the mixture clarified that two alkyl groups are symmetrically equivalent in each isomer and that a chiral center resided at C_α in the alkyl chain. The ^{13}C NMR indicated the major isomer to have C_s symmetry.[8] Therefore, the major and minor isomers can be assigned to *cis-meso*-**1a** and *trans-d,l*-**1a**, respectively. The *cis* isomer is thermodynamically preferred to the *trans* one because the two alkyl groups are arranged at equatorial sites in the former but one alkyl group is at an axial position in the latter.[9] Steric effects generally cause ^1H signals to be shifted to a lower field. The H_α signals are reasonably assigned as follows: 4.56 ppm for *cis*-**1a** and 4.74 ppm for *trans*-**1a**.[11] The *cis* / *trans* ratio was determined to be 81 / 19 by the H_α signal integrals.

The MS, UV-vis, IR and NMR spectra of **1b** confirmed the corresponding pyrrolidinofullerene structure. Similar spectral analysis determined the *cis*/ *trans* ratio to be 79/21. It is noteworthy that the solubility of **1b** in organic solvents is considerably improved in comparison with that of C_{60}.

In the case of the reaction with phenylacetaldehyde, the isolated product was not a pyrrolidine derivative but **2**[12] (12% yield). The substituents on the 6-ring/6-ring junction are CH_2Ph and H. The benzyl group undoubtedly is generated by decarbonylation of phenylacetaldehyde.



1a

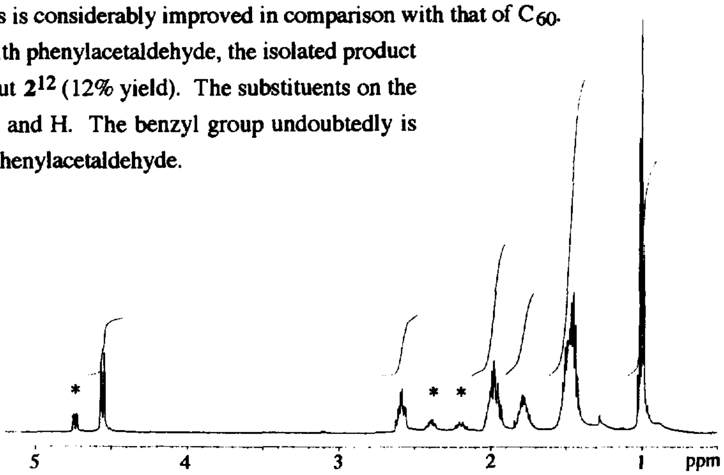
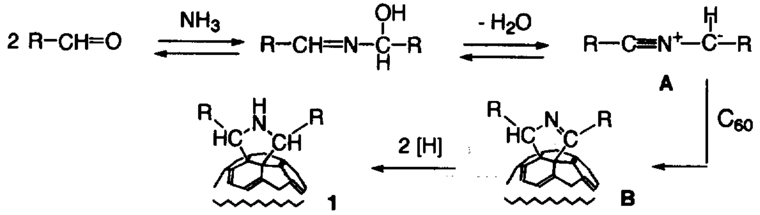


Fig. 1. ^1H NMR spectrum of **1a** (500 MHz, 1/4 CS_2-C_6D_6). *cis*-**1a**: δ 4.56 (dd, *J* = 11, 2 Hz, H_α), 2.61-2.55 (m, $H_{\beta 1}$), 2.00-1.92 (m, $H_{\beta 2}$+$H_{\gamma 1}$), 1.80-1.73 ($H_{\gamma 2}$), 1.53-1.40 (m, 4H), 0.99 (t, *J* = 7 Hz, 3H). *trans*-**1a** (denoted by asterisks): δ 4.74 (dd, *J* = 11, 2 Hz, H_α), 2.42-2.35 ($H_{\beta 1}$), 2.23-2.15 ($H_{\beta 2}$).

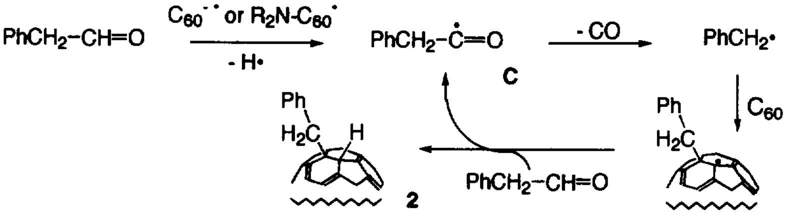
We obtained two types of adducts for alkylaldehydes and phenylacetaldehyde, notwithstanding the use of the same synthetic procedure. We propose a reaction mechanism involving 1,3-dipolar cycloaddition reaction as the key step for the pyrrolidine synthesis (Scheme 2) and a radical mechanism for the benzyl adduct (Scheme 3).

In Scheme 2, a nitrile ylide (**A**) is considered to be a reactive intermediate. In order to investigate this reaction mechanism, all of the products obtained from the C_{60}-dodecanal-ammonia system were analyzed by

Scheme 2.



Scheme 3.



means of FABMS after HPLC separation. The molecular ions $C_{60}(C_{24}H_{47}N)(C_{36}H_{71}N)$, $C_{60}(C_{24}H_{47}N)_2$, $C_{60}(C_{36}H_{72}N)$, and $C_{60}(C_{24}H_{49}N)$ were observed at *m/z* 1587, 1420, 1239, and 1072, respectively, in positive FABMS. The MS/MS experiments revealed that the fragmentation of the moieties shown in parentheses occurred. No product of possible stepwise reactions was detected.[13]

Reductants are, however, not specified in Scheme 2. It is possible that aldehydes become a hydrogen donor or that some amine derivatives become an electron donor. Preliminary results on the reaction with benzaldehyde indicated the generation of a product exhibiting $M^{\bullet-}$ at *m/z* 913 in FABMS. The product can be tentatively assigned to **B** (R = Ph). This finding is rationalized by the stability due to the conjugation of a phenyl group with a pyrroline C=N bond. Product **B** is a normal adduct of 1,3-dipolar addition of **A** (R = Ph) to C_{60}.[14] Thus, the mechanism described in Scheme 2 is plausible for the synthesis of **1**.

In the synthesis of **2**, the decarbonylation strongly suggests that this reaction involves an acyl radical (**C**),[15] as shown in Scheme 3. The generation of a relatively stable benzyl radical may be the driving force in this reaction. This type of reaction competes with the reaction in Scheme 2. The product analysis of the reaction with hexanal after HPLC separation revealed the presence of a trace amount of $C_{60}(H)(COC_5H_{11})$ (*m/z* 820 in FABMS). When alkyl aldehydes were used as the starting material, decarbonylation did not occur because a primary alkyl radical is less stable than an acyl radical. On the other hand, the reaction with benzaldehyde gave no benzoyl adduct. The 1,3-dipolar addition mechanism is favorable probably because the conjugation of the phenyl group facilitates the formation of **A** (R = Ph).

The benzyl addition investigated here was found to occur even in the dark. The initiator of hydrogen abstraction may be thermally generated aminofullerene radicals or charge-transfer complexes of C_{60} and amines, taking the electron-accepting nature of C_{60} into account. There have been a number of examples of radicals and ion radicals prepared from C_{60} and amines in the literature.[16] However, ammonia and imines are less electron-donating than amines. Alkylamines, such as hexahydro-1,3,5-triazine derivatives formed in equilibria, can be considered to be electron donors or nucleophiles to C_{60}.

The mechanisms proposed above are derived from the reactivities of C_{60} as a good dipolarophile, an efficient radical scavenger, and an electron acceptor. Although it remains to be clarified whether these reaction mechanisms can be applied to substrates other than C_{60}, they may provide a new synthetic approach such as a facile generation of benzyl radicals.

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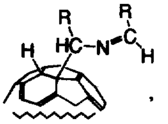
REFERENCES AND NOTES

1. Taylor, R.; Walton, D. R. M. *Nature* **1993**, *363*, 685-693; Diederich, F.; Isaacs, L.; Philp, D. *Chem. Soc. Rev.* **1994**, 243-255; Hirsch, A. *The Chemistry of the Fullerenes*, Thieme, Stuttgart, 1994; Śliwa, W. *Fullerene Sci. Technol.* **1995**, *3*, 243-281; Diederich, F.; Thilgen, C. *Science* **1996**, *271*, 317-323; *Symposium-in-Print on Fullerene Chemistry* ed by Smith, A. B. *Tetrahedron* **1996**, 52, 4925-5262.
2. Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* **1991**, *114*, 7301-7302.
3. Meier, M. S.; Poplawska, M. *J. Org. Chem.* **1993**, *58*, 4524-4525.
4. Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798-9799; Zhang, X.; Willems, M.; Foote, C. S. *Tetrahedron Lett.* **1993**, *34*, 8187-8188.
5. Wilson, S. R.; Wang, Y.; Cao, J.; Tan, X. *Tetrahedron Lett.* **1996**, *37*, 775-778.
6. Kawasumi, M.; Ishida, T.; Nogami, T. *Fullerene Sci. Technol.* in press.
7. Mp. >300°C (from toluene). Anal. Calcd for $C_{72}H_{25}N$: C, 95.66; H, 2.79; N, 1.55%. Found: C, 93.14; H, 2.97; N, 1.54%. UV-vis (cyclohexane) 220, 256, 308, 430, 702 nm which are characteristic of closed [6,6] C_{60}-adducts. IR (KBr) $\nu_{N\text{-}H}$ 3350 cm^{-1} (broad).
8. *cis*-**1a**: ^{13}C NMR (125 MHz, 1/4 C_6D_6-CS_2) δ_C 154.80(2), 153.96(2), 147.22(2), 146.84(2), 146.63(2), 146.52(2), 146.40(2), 146.24(2), 146.16(2), 145.92(1), 145.62(1), 145.58(2), 145.55(2), 145.53(2), 145.40(2), 144.79(2), 144.54(2), 143.57(1), 143.33(1), 143.03(2), 142.98(2), 142.93(2), 142.51(2), 142.45(2), 142.32(2), 142.20(2), 141.99(2), 140.43(2), 140.09(2), 136.54(2), 135.89(2), 80.18(2), 74.19(2), 34.01(2), 32.83(2), 28.97(2), 23.61(2), 14.84(2). The carbon abundances shown in parentheses were determined by the relative signal intensity. Some of the 36 signals of C_2 *trans*-**1a** could not be detected because they were buried under those of *cis*-**1a**.
9. MM2 calculation[10] indicated the total steric energies of 407.22 and 408.18 kcal/mol for *cis*- and *trans*-**1a**, respectively.
10. Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127-8134.
11. Very recently, Wilson *et al.* reported the opposite assignment of ^{1}H NMR signals for 2,5-disubstituted pyrrolidinofullerene.[5]
12. Chen, J.; Cai, R.-F.; Huang, Z.-E.; Wu, H.-M.; Jiang, S.-K.; Shao, Q.-F. *J. Chem. Soc., Chem. Commun.* **1995**, 1553-1554.

13. Possible adducts are, for example,



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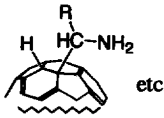

etc.

14. Averdung, J.; Albrecht, E.; Lauterwein, J.; Luftmann, H.; Mattay, J.; Mohn, H.; Müller, W. H.; ter Meer, H.-U. *Chem. Ber.* **1994**, *127*, 787-789; Iyoda, M.; Sultana, F.; Komatsu, M. *Chem. Lett.* **1995**, 1133-1134.
15. Carey, F. A.; Sundberg, R. J. "*Advanced Organic Chemistry, Part A,*" Plenum, New York (1990), Chap. 12.
16. Skiebe, A.; Hirsch, A.; Klos, H.; Gotschy, B. *Chem. Phys. Lett.* **1994**, *220*, 138-140; Allemand, P.-M.; Khemani, K. C.; Koch, A.; Wudl, F.; Holczer, K.; Donovan, S.; Grüner, G.; Thompson, J. D. *Science* **1991**, *253*, 301-303; Schick, G.; Kampe, K.-D.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1995**, 2023-2024. For photoinduced electron transfer reactions, see Lawson, G. E.; Kitaygorodskiy, A.; Ma, B.; Bunker, C. E.; Sun, Y.-P. *J. Chem. Soc., Chem. Commun.* **1995**, 2225-2226 and references cited therein.

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