Addition of diphenylphosphinoyl azide to [60]fullerene

I. P. Romanova,* O. G. Sinyashin, G. G. Yusupova, V. I. Kovalenko, Yu. Ya. Efremov, Yu. V. Badeev, I. I. Vandyukova, and I. A. Arakelyan

> A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center of the Russian Academy of Sciences, 8 ul. Akad. Arbuzova, 420083 Kazan, Russian Federation. Fax: +7 (843 2) 75 2253. E-mail: romanova@iopc.kcn.ru

The reaction of [60] fullerene with diphenylphosphinoyl azide in toluene or in o-dichlorobenzene in the presence of traces of water affords 2-[N-(diphenylphosphoryl)amino]-1-hydroxy[60] fullerene. This reaction in THF gives a mixture of (N-diphenylphosphoryl)[60] fullereno[1,2-b] aziridine and a product of partial hydrolysis of the bisadduct of phosphorylated azide and fullerene.

Key words: [60]fullerene, phosphorylated azide, cycloaddition, aminohydroxyfullerene, phosphorylated aziridinofullerene, synthesis, structure, hydrolysis.

Recently, reactions of cycloaddition of dipolarophilic reagents with fullerene and studies of the thermal and hydrolytic stabilities of the resulting adducts have received much attention.¹⁻³ This is associated with the necessity of solving an important problem of the chemistry of fullerenes, namely, the introduction of functional groups into molecules of these compounds, which are then accessible for further modifications.

Previously, we have demonstrated⁴ that di(isopropoxy)phosphorylformonitrile oxide reacted with fullerene (C_{60}) according to the scheme of [3+2] cycloaddition to form phosphorus-containing isoxazoline mono- and diadducts. Subsequent HPLC studies of the hydrolytic and thermal stability of the monoadduct demonstrated that the phosphorus-containing isoxazoline ring is highly stable upon heating as well as with respect to the action of proton-donor reagents (H₂O or ROH), which prevented one from using these reactions for introducing functional groups into the fullerene molecule.

In this connection, we undertook the investigation of the reactions of C_{60} with phosphorylated azides. It is known^{5,6} that the reactions of organic azides with fullerenes afford either triazolino- and aziridinofullerenes or azafulleroids. Data on the hydrolytic stability of aziridine heterocycles in fullerene derivatives are lacking in the hiterature. As for the thermal stability, it is known^{7,8} that prolonged heating of aziridinofullerenes, which are formed in the reactions of fullerene with azidoformates, in toluene or dichloroethane leads either to isomerization to the corresponding fullerene derivatives with the insertion of the oxygen atom into the six-membered ring or to elimination of the radical at the nitrogen atom to form aziridinofullerene with the N—H bond. Cycloaddition of phosphorylated azides to fullerene is poorly understood. Only one patent was published,⁹ in which it was demonstrated that UV irradiation of a series of phosphorylated azides in a mixture with fullerene afforded compounds of the general formula $C_{20+2m} = NR$ $(R = P(O)R_2', P(S)R_2', or PR_2'; m = 2-100)$. Data on the structures of the latter were not reported and the structures of the reaction products of fullerene with phosphorylated azides are still open questions.

Of the known phosphorylated azides, we used diphenylphosphinoyl azides (1) as the most thermally stable compounds. The reaction of azide 1 with C_{60} was studied in toluene, o-dichlorobenzene (DCB), and THF. Toluene and DCB are most often used for performing reactions of fullerenes with dipolarophiles, and THF is widely used in reactions of phosphorylated azides with unsaturated compounds. It was of interest to study the effect of the nature of the solvent on the rate and direction of the addition of azide 1 to C_{60} .

According to the data of HPLC, heating (at the boiling temperatures of the solvents) of solutions of C_{60} and azide 1 in anhydrous toluene or DCB for 20 h afforded several products, which were present in the reaction mixtures at low concentrations. The major peak on the chromatogram corresponded to the starting fullerene. It was impossible to separate fullerene and the reaction products by column chromatography because of the low concentrations of the latter. When this reaction was performed in toluene or DCB containing trace amounts of water under analogous conditions, we succeeded in isolating two products (Scheme 1). According to the data of IR and ¹H and ³¹P NMR spectroscopy, one of these products, which is readily soluble in organic solvents, is diphenylphosphinic acid (2).

Translated from Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 11, pp. 2168-2172, November, 1999. 1066-5285/99/4811-2144 \$22.00 © 1999 Kluwer Academic/Plenum Publishers

The second product is a powdered black compound insoluble in usual organic solvents. Because of this, its structure was established only by IR spectroscopy and mass spectrometry and its composition was determined by elemental analysis. The IR spectrum has absorption bands of phenyl groups, the P=O bond, the fullerene fragment, and the P-N-C bond and a broad absorption band at 3440 cm⁻¹, which corresponds to NH and OH stretching vibrations. In the IR spectrum of this compound, the absorption band at 2146 cm⁻¹ characteristic of the initial azide is absent. Based on the IR spectrum and the data of elemental analysis, the structure of 2-[N-(diphenylphosphoryl)amino]-1-hydroxy-[60] fullerene (3) was assigned to the reaction product. In the mass spectrum of compound 3, which was obtained by the electron impact method, the molecular ion peak of 3 was not detected. However, the spectrum has molecular ion peaks of fullerene, diphenylphosphinic acid, and the amide of diphenylphosphinic acid, which can be formed only as a result of thermal decomposition of product 3 in a tube containing the sample at 250 °C.

Scheme 1



Reagents and conditions: *i.* DCB or PhMe, (H_2O) , Δ ; *ii.* THF, (H_2O) .

The reaction of C_{60} with azide 1 in THF proceeded at ~20 °C and the resulting product precipitated within several minutes after the reagents had been mixed. As a result, a pale-brown compound, which is insoluble in most organic solvents, was isolated. Hence, it was identified only by mass spectrometry (electron impact). According to the data obtained, the precipitate that formed was a mixture of two adducts. The mass spectrum of the precipitate has a molecular ion peak $[M]^+$ at m/z 935, which corresponds to phosphorylated azirido-fullerene 4, and a peak at m/z 1168, which belongs to bisadduct 5 containing the aziridine, N-(diphenyl-phosphoryl)amino, and hydroxyl fragments.

The conclusion that the structure of bisadduct 5 has exchangeable protons was confirmed by the deuterium exchange between compound 5 and D_2O (MeOD) established by mass spectrometry. However, the exchange of only one proton for deuterium was experimentally observed. Thus, in the mass spectrum of a mixture of compounds 4 and 5 obtained after treatment with deuterium-containing solvents, the intensity of the peak at m/z1169 is higher than that of this peak in the mass spectrum of a mixture of compounds 4 and 5 before treatment. The intensity of the peak at m/z 1170 remains virtually unchanged. In our opinion, this situation is attributable to a low degree of exchange (~10%) due to the low solubility of compound 5 in water and alcohol.

Previously, compounds 3 and 5 have not been prepared by the reactions of fullerene with organic azides. Apparently, the formation of these compounds is associated with the presence of trace amounts of water in the solvents, which is evidenced by the release of acid 2, which can be formed only as a result of partial hydrolysis of the initial azide. In addition, there are good grounds to believe that the reaction of azide with fullerene can take several pathways, depending on the reaction conditions (the solvent, the temperature, and the presence of proton-donor reagents), to give structurally different fullerene derivatives.

Two mechanisms of the reactions of azides with fullerene were discussed in the literature. In the case of alkyl- and arylazides, it was established that the reactions with fullerene occurred as dipolarophilic [3+2] cycloaddition to form triazolinofullerenes. Under the reaction conditions, the latter decomposed with elimination of nitrogen to give azafulleroids.⁶ In the case of azidoformates, aziridinofullerenes were isolated as the major products. Their formation was attributed to the fact that under the reaction conditions, azide decomposed to nitrene, which added to fullerene.⁷

Based on the published data and taking into account the low yield of product 3 and the duration of the reaction of C_{60} with azide 1 in a solution of toluene or DCB, we suggest that this reaction proceeds as dipolar [3+2] cycloaddition to form the triazoline derivative of fullerene 6 in the first stage. The decomposition of the latter can occur according either to the synchronous or two-step mechanism^{10,11} (Scheme 2).

When the reaction was performed in anhydrous solvents, aziridinofullerene 4, whose formation is independent of the mechanism of decomposition of triazolino-fullerene $\mathbf{6}$, should be obtained as the final product. It is



Reagents and conditions: i. PhMe, DCB, or THF; ii. in the absence of H₂O.

not inconceivable that it was product 4 that we detected by HPLC and its low yield is associated with the low reaction rate. Besides, according to the HPLC data, cycloaddition of azide 1 to fullerene under these condition was, most likely, not terminated in the stage of formation of product 4. The chromatograms of the reaction mixtures have peaks of several compounds, which we failed to identify, along with the peak of the starting fullerene.

The structures of the products of the reaction of C_{60} with azide 1 in toluene or DCB containing trace amounts of water depend on the direction of decomposition of triazolinofullerene 6. When decomposition of compound 6 proceeds according to the synchronous mechanism (pathway a), aziridinofullerene 4, which is initially formed, can by hydrolyzed to form the final product 3. When decomposition of triazolinofullerene 6 proceeds according to the two-step mechanism (pathway b), compound 3 is formed as a result of addition of water to intermediate bipolar ion 7. In this case, compound 3 immediately precipitates due to its poor solubility and does not react with azide 1. Based on the data on hydrolysis of phosphorus-containing isoxazoline derivatives of fullerene and taking into account the absence of products of the opening of the aziridine heterocycles in fullerene derivatives containing organic radicals at the nitrogen atoms, we believe that hydrolysis of aziridinofullerene 4 accompanied by heterocycle opening (pathway a) is highly improbable.

As for the reaction of fullerene with diphenylazidophosphinate in THF, it can be suggested that product 4 is formed as a result of synchronous elimination of nitrogen from triazolinofullerene 6, which is formed in the first stage, and the formation of the new C-N bond, which is favored by milder reaction conditions (see Scheme 2, pathway c). However, taking into account that the reaction is rapid, we are inclined to believe that the addition of azide 1 to fullerene in THF proceeds through the formation of nitrene, which is a product of decomposition of azide (Scheme 3).

It has long been known that azide 1 can decompose to nitrene.¹² In the case under consideration, fullerene, which generates a reactive species due to its sensitizing ability, as well as THF can promote decomposition. Under the reaction conditions, monoadduct 4 adds one more molecule of azide 1 to form a bisadduct containing two aziridine heterocycles, one of which is hydrolyzed under the action of traces of moisture to form product 5. The formation of the bisadduct and compound 5 agrees with the data on the hydrolytic stability of monoheterocycles in fullerene.³ It is not inconceivable that the ease of hydrolysis of one of the aziridine heterocycles in the bisadduct is associated with the higher reactivity of the latter compared to the monoadduct.

To summarize, the study of the reaction of azide 1 with C_{60} demonstrated that, unlike the reactions of the latter with organic azides, the nature of the solvent and



the presence of proton-donor reagents in the reaction mixture substantially affect the reaction pathway. Phosphorylated 1,2-aminohydroxy derivatives of fullerene, which have not been observed previously in the reactions of C_{60} with organic azides, were prepared for the first time.

Experimental

The IR spectra were obtained on a Bruker IFS-113V Fourier spectrometer in KBr pellets. The ³¹P NMR spectra were recorded on a Bruker CXP-100 instrument (36.47 MHz) relative to 85% H₃PO₄ (external standard). The ¹H NMR spectra were measured on a Bruker WM-250 instrument (250.13 MHz) (Me₄Si as the internal standard). HPLC analysis was carried out on a Laboratorni pristroje Praha chromatograph (Czechoslovakia) (7-µm Separon SGX C₁₈ column, a mixture of PhMe (60%) and PrOH (40%) as the eluent, 0.3 mL min⁻¹, a UV-VIS Detector LCD 2563 detector, λ 365 nm). The mass spectra (electron impact) were obtained on an MKh-1310 instrument at the resolution R = 15000 (the energy of electrons was 60 eV) with direct introduction of the sample into the ion source; the temperature of the sample was varied from 50 to 460 °C; the precise masses in the range of 50-1000 were determined by the secondary processing of the mass spectra; the precise values of the ion masses with m/z > 1000 were obtained by the method of superimposition of the ion peaks of the compound under study and of the reference compound (perfluorokerosene and Ultramark). Dry toluene was prepared by prolonged heating over sodium followed by repeated distillation over LiAlH₄. Dry DCB was prepared by repeated distillation over P2O5. With the aim of retaining traces of moisture, toluene was distilled over sodium without previous prolonged heating and DCB was subjected to simple distillation with separation of water as an azeotrope; THF was previously refluxed over an alkali and then repeatedly distilled over LiAlH4. All reactions were performed under an argon atmosphere and the solvents were degassed.

2-[N-(Diphenylphosphoryl)amino]-1-hydroxy[60]fullerene (3). Solutions of C_{60} (110 mg, 0.15 mmol) and azide 1 (112 mg, 0.41 mmol) in toluene or DCB (50 mL) containing traces of moisture were heated at the boiling temperatures of the solvents for 16 h. The black precipitate that formed was filtered off, washed with toluene and MeOH, and dried *in vacuo* (0.2 Torr) at 60-70 °C. Compound 3 was obtained in a yield of 15 mg (10%). Found (%): P, 3.75. $C_{72}H_{12}NO_2P$. Calculated (%): P, 3.25. IR (KBr), v/cm⁻¹: 727, 751, 1437, 1573, 1593 (Ph); 1135 (P=O); 528 (fullerene fragment); 1063 (P-N-C); 3440 (NH, OH). MS: found: m/z 217.0704 [M]⁺; $C_{12}H_{12}NOP$; calculated: M = 217.0656; found: m/z 218.0491 [M]⁺; $C_{12}H_{11}O_2P$; calculated: M = 218.0497; found: m/z 719.9956 [M]⁺; C_{60} ; calculated: M = 720.0000.

After separation of compound **3**, the filtrate was concentrated *in vacuo*, the residue was recrystallized from CHCl₃, and diphenylphosphinic acid (**2**) was obtained in a yield of 85 mg (85%), m.p. 194 °C (*cf.* Ref. 13: 194 °C). Found (%): C, 65.99; H, 5.02; P, 14.11. $C_{12}H_{11}O_{2}P$. Calculated (%): C, 66.05; H, 5.04; P, 14.22. IR (KBr). v/cm⁻¹: 527, 554, 694, 729, 1439, 3055, 3075 (Ph); 1131 (P=O); 960, 1673, 2151, 2629, 3427 (OH). ³¹P NMR (CHCl₃), &: 31.7. ¹H NMR (CDCl₃), &: 7.31-7.48 (m, 6 H, C₆H₅); 7.68-7.76 (m, 4 H, C₆H₅); 8.87 (s, 1 H, OH).

Reaction of [60]fullerene with azide 1 in THF. Azide 1 (38 mg) was added to a solution of C_{60} (38 mg) in THF (150 mL) at -20 °C. The reaction solution was stirred for 1-2 min, after which precipitation started. The mixture was stirred for 8 h at -20 °C. The precipitate was filtered off, washed with toluene and MeOH, and dried *in vacuo* (0.2 Torr) at 60-70 °C. A mixture of compounds 4 and 5 was obtained in a yield of 27 mg as a pale-brown powder. MS: found: m/z 935.0504 [M]⁺; $C_{72}H_{10}NOP$; calculated: M = 935.0500; found m/z 1168.1106 [M]⁺; $C_{84}H_{22}N_2O_3P_2$; calculated: M = 168.1105. After separation of the precipitate, the signal of the starting fullerene was detected in the filtrate by HPLC (the retention time was 5.6 min).

This work was performed within the framework of the Russian Scientific and Technical Program "Current Trends in Physics of Condensed Matter," the Direction "Fullerenes and Atomic Clusters" (Project No. 96156).

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Received November 20, 1998; in revised form August 25, 1999