ChemComm
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Thermic conversion of benzene into 6-phenylfulvene with high yield mediated by GaP nanocrystals†

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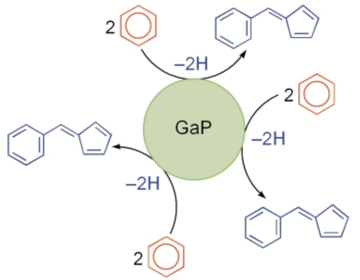
Received (in Cambridge, UK) 19th August 2002, Accepted 10th October 2002
First published as an Advance Article on the web 31st October 2002

With GaP nanocrystals being used in a close reaction system, 6-phenylfulvene is successfully obtained *via* a high yield thermic conversion from benzene, which provides the possibility of applying nanocrystals to mediate organic reactions.

In recent years, research in academia and industry has increasingly emphasized the search for efficient transformations of easily available starting materials into complex organic molecules.[1,2] From the green chemistry point of view, it is very important and even desirable to develop an atom-economy strategy[3–6] to synthesise series of materials in order to reduce consumption and pollution. Currently, another intensive research topic focuses on nanomaterials, which exhibit many intriguing and even unexpected properties derived from the dramatic reduction of the particle size, such as pronounced quantum size effects,[7] large surface and high catalytic activity.[8] This gives us an inspiration that nanoparticles may provide a potential opportunity for the syntheses of organic compounds. Based on this idea, we firstly explore here the possibility of nanocrystalline GaP in an organic reaction to induce thermic rearrangement of benzene, and successfully realize a high yield conversion of benzene to 6-phenlyfulvene under supercritical conditions. It is well known that benzene can undertake photochemical rearrangement easily,[9] but its thermic rearrangement has proved very difficult to achieve. To our best knowledge, this is the first and yet an indirect observation of the thermic rearrangement of benzene. Nanocrystalline GaP plays an important role in the thermic conversion of benzene, supporting our strategy that the use of inorganic nanoparticles would favor some organic reactions and thus open a new application field of inorganic nanoparticles.

Fulvenes are non-aromatic cyclic polyolefins, which undergo the gamut of radical, electrophilic, nucleophilic and concerted reactions.[10] and they also serve as excellent models in judging electronic theories of organic reactivity. Over the past several decades, there were many reports on the syntheses of fulvenes and their corresponding electronic theories of organic reactivity.[11–14] However, little research touched upon the luminescence properties of these compounds mainly because of the low yield and the difficulties in isolation from the complicated reaction systems in previously reported methods. In this communication, a novel atom-economic reaction is established to prepare 6-phenylfulvene from benzene in the presence of GaP nanocrystals, and the luminescence properties of this compound are investigated. The diagram of the preparation process is illustrated in Scheme 1.

Details of a typical experiment are as follows: 0.5 g newly-prepared GaP nanocrystals which were synthesized in the procedure reported in our previous work[15] were added into a stainless steel autoclave with 100 ml capacity, then 80 ml (70.32 g) analytical grade benzene was added into the autoclave to 75% of the total volume. The autoclave was maintained at 450–500 °C for 8–10 h and then naturally cooled to room temperature, resulting in an ashen precipitate with mass of 70.35 g. Products were dissolved in chloroform and the solution was filtered to remove the GaP powder. The final products with a mass of 69.70 g were obtained after vaporizing the chloroform in the solution. According to the mass of original reagent, benzene, the yield of the final product was 99%.



Scheme 1 Schematic illustration of the atom economic protocol for the thermic rearrangement and dimerization of benzene induced by GaP nanocrystals at 450–500 °C.

The structure of the product was analyzed by mass spectroscopy, ^{1}H and ^{13}C NMR, IR and UV-vis absorption spectroscopy, the analytical data are listed in Table 1. The mass spectra were performed with a GC-TOF Mass Spectrometer. The NMR studies were carried out using a General Electric QE 300 (7.05 T). The IR spectra were recorded in the wavenumber range of 4000–350 cm^{-1} with a Nicolet Model 759 Fourier transform infrared (FTIR) spectrometer, using a KBr wafer, and the UV–vis absorption spectra were performed on a UV–vis spectrophotometer (Specord 200) in the wavelength range 190–1100 nm (Analytic Jena GmbH, Germany). The morphology of the product and GaP nanocrystals, were observed using scanning electronic microscopy (SEM) which was performed on an X-650 scanning electron micro-analyzer, and TEM measurements which were made on a Hitachi H-800 transmission electron microscope with accelerating voltage of 200 kV, respectively. A Hitachi 850 fluorescence spectrometer with a Xe lamp at 25 °C (λ_{ex} = 320 nm) was used to measure the fluorescence properties of 6-phenylfulvene. The MS[16] spectrum showed that the molecular formula of the product was $C_{12}H_{10}$. The other data

Table 1 Characterization of the product

^{1}H NMR δ (ppm)	^{13}C NMR δ (ppm)	IR (cm^{-1}) (CCl_4/CS_2)		UV λ_{max}/nm (C_6H_{12})
H-C(1) 6.70	C(1) 120.3	1625s	923m	230
H-C(2) 6.64	C(2) 136.0	1492m-s	900s	237
H-C(3) 6.48	C(3) 130.9	1472m–s	882w–m	318
H-C(4) 6.32	C(4) 128.2	1445m	833w–m	374
H-C(6) 7.20	C(5) 145.0	1397m	761s	
H-C(8- 7.0–7.7 12)	C(6) 138.4	1338m	710m–s	
		1086w–m	690s	
		1080m	620s	
($CDCl_3$)	($CDCl_3$)	1028w-m	601m	
		988m	482m	

DOI: 10.1039/b208076a

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† Electronic supplementary information (ESI) available: MS and ^{13}C NMR spectra of the as-prepared products. See http://www.rsc.org/suppdata/cc/b2/b208076a/

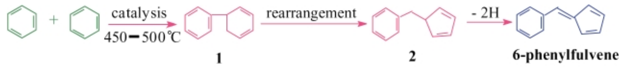

Fig. 1 The mechanism for thermic rearrangement and dimerization of benzene catalyzed by GaP nanocrystals at 450–500 °C.

were all in accord with the literature for the molecular structure of this compound.[17–19]

The yield of this approach for 6-phenylfulvene was assessed to be roughly 100%, according to the following facts: (1) From the experimental data of the mass of reagents and products, the transformation rate of benzene to 6-phenylfulvene is near to 100%. (2) Spectral analysis (Table 1) showed that the ashen precipitate left was qualitatively pure 6-phenylfulvene. This high yield makes it possible to investigate the luminescence properties of this organic compound without a complicated isolation procedure.

From the point of view of the reactant and the end product, the reaction should undergo a process of dimerization of benzene and thermic rearrangement of intermediates. It is well known, however, that benzene was hardly subjected to thermic-rearrangement, because it is a ground-state rearrangement. Therefore, why did benzene achieve thermic rearrangement under the current conditions? The primary reason must be that nanocrystalline GaP plays a crucial role in the procedure. The mechanism is not clear yet, although a relatively reasonable mechanism can be proposed for the thermic rearrangement of benzene, as shown in Fig. 1. The whole reaction may experience three steps. Step (**I**): benzene molecules are chemically adsorbed onto the surface of GaP nanocrystals and undergo dimerization successively at the temperature of 450–500 °C to form compound **1**. Step (**II**): compound **1** transforms into compound **2** since it is unstable compared with compound **2**; which has been proved by their free enthalpies through theoretical calculation using Gaussian 98. Step (**III**): based on a similar theoretical calculation, compound **2** would further transform into the end product, 6-phenylfulvene, *via* elimination of two hydrogen atoms. Due to the larger surface and higher catalytic activity of the newly-prepared GaP nanocrystals, the whole reaction would occur in rapid reaction steps. Thus, this explains why the yield was high enough to form an atom-economy approach for 6-phenylfulvene. Control experiments were carried out to probe the role of GaP nanocrystals. Keeping other conditions unchanged, nanocrystals of GaAs, InP, CdS, were used respectively instead of GaP nanocrystals in the system. No reaction was observed, which suggested the novel effect of GaP nanocrystals. The TEM images of the catalysis nanocrystals before and after the reaction are shown in Fig. 2A and B, respectively, from which one can clearly see that the surface of GaP was capped with something other than benzene molecules and their sizes became obviously larger after reaction.

The SEM image of the obtained 6-phenylfulvene, as shown in Fig. 2C, reveals an interesting net-cross morphology. Fig. 2D shows the photoluminescence (PL) spectra for 6-phenylfulvene in 2 ppm chloroform solution, which consists of a broad emission with a maximum at about 565 nm. When fabricated into thin film, 6-phenylfulvene emits strongly in the yellow–green region of the spectrum (550–570 nm). This bright yellow–green luminescence can easily be observed with the unaided eye under UV excitation (Fig. 2E).

In conclusion, the application of inorganic nanocrystals in mediating organic rearrangement reactions is first explored. In the case of the thermic conversion of benzene into 6-phenylfulvene, this idea has achieved great success with high yield. Benzene, a remarkably inexpensive and fertile source, was used as the raw material, which can greatly reduce the cost, and can also offer an opportunity for the industrial application of this important organic luminophor of 6-phenylfulvene.

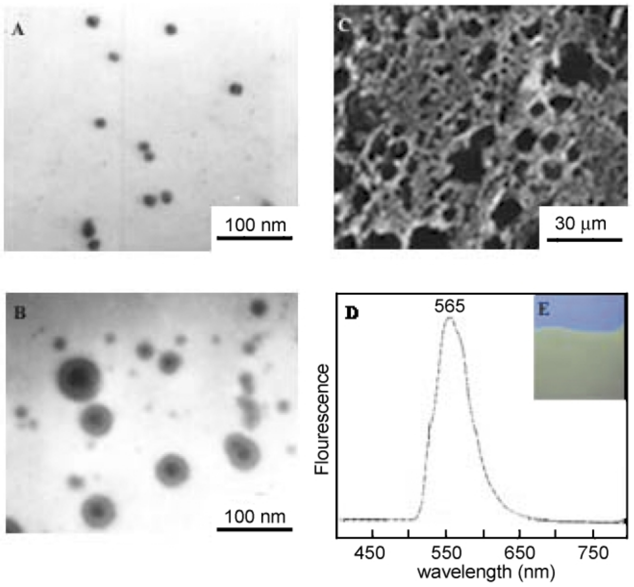

Fig. 2 (A) and (B), TEM images of GaP nanocrystals before and after reaction, respectively. (C) SEM image of the as-prepared 6-phenylfulvene. (D) Photoluminescence (PL) spectrum (with the excitation wavelength 450 nm) of 6-phenylfulvene prepared at 450–500 °C. (E) The photograph of luminescent phenomenon observed under the irradiation of a UV-lamp.

Notes and references

1 B. M. Trost, *Science*, 1991, **254**, 1471.
2 B. M. Trost, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 259.
3 I. Pérez, J. P. Sestelo and L. A. Sarandeses, *J. Am. Chem. Soc.*, 2001, **123**, 4155.
4 B. M. Trost and S. C. Oi, *J. Am. Chem. Soc.*, 2001, **123**, 1230.
5 B. M. Trost and H. Ito, *J. Am. Chem. Soc.*, 2000, **122**, 12003.
6 G. D. Yadav and P. K. Goel, *Green Chem.*, 2000, **2**, 71.
7 C. B. Murray, C. R. Kagan and M. G. Bawendi, *Science*, 1995, **270**, 1335.
8 X. C. Jiang, Y. Xie, J. Lu, L. Y. Zhu, W. He and Y. T. Qian, *Langmuir*, 2001, **17**, 3795.
9 H. Rao, *Progress in photochemistry and photophysics*, ed. J. F. Rabek, CRC, Boca Raton, 1990.
10 K. J. Stone and R. D. Little, *J. Org. Chem.*, 1984, **49**, 1853.
11 T. Kumagai, M. Ohno, K. Mitani, K. Yamamoto and M. Oda, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 301.
12 H. Kurata, T. Ekinaka, T. Kawase and M. Oda, *Tetrahedron Lett.*, 1993, **34**, 3445.
13 D. J. Sardella, C. M. Keane and P. Lemonias, *J. Am. Chem. Soc.*, 1984, **106**, 4962.
14 K. N. Houk and L. J. Luskus, *J. Org. Chem.*, 1973, **38**, 3836.
15 S. M. Gao, D. L. Cui, B. B. Huang and M. H. Jiang, *J. Cryst. Growth*, 1998, **192**, 89.
16 For more detailed MS and ^{13}C NMR data, please see ESI†.
17 P. Bonzli, A. Otter and M. Neuenschwander, *Helv. Chim. Acta*, 1986, **69**, 1052.
18 H. Bircher and M. Neuenschwander, *Helv. Chim. Acta*, 1989, **72**, 1697.
19 M. Neuenschwander and R. Iseli, *Helv. Chim. Acta*, 1977, **60**, 1061.