Fullerene Mechanochemistry

Guan-Wu Wang

*Department of Chemistry, University of Science and Technology of China,
Hefei, Anhui 230026, China*

CONTENTS

1. INTRODUCTION

According to the type of energy source supplied to the system, the different fields of chemistry are classified as thermochemistry, electrochemistry, photochemistry, etc. The term mechanochemistry was proposed by Ostwald as early as 1919 as an energy source for chemical reactions [1]. A narrow field, tribochemistry, was used for reactions initiated by friction during milling of solid reagents [2].

Mechanochemistry involves the transformation of mechanical energy into the driving force for the chemical reactions of solid reagents. Mechanochemistry is generally done in the absence of any solvent. The external dynamic force generated from the mechanical agitation can induce the solid to its vibrationally and electronically excited structures, thus destabilizing the electronic structure of the bonding and making the solid prone to chemical reaction. The activation of the local reaction sites by the mechanical energy caused by the stress, friction, shear deformation, etc., together with the high concentration and closest contact of the reacting species due to the lack of solvation, would be particularly advantageous for the chemical reaction in the solid state.

A recent overview on mechanochemistry by Fernández-Bertrán [3] and an excellent and lengthy review on mechanical alloying and milling by Suryanarayana [4] have appeared. Mechanochemistry was mainly applied to processes related to inorganic materials, such as alloy, ceramics, cermets, ferrites, semiconductors and superconductors, ferroelectrics, mineral fertilizers, catalysts, ceramic construction materials, etc. Fewer examples of mechanochemical reactions by ball milling involving organic compounds have been reported [5–14].

Fullerenes (mainly C_{60} and C_{70}) were first discovered in 1985 [15], and macroscopic amount of fullerenes was made available in 1990 [16]. The discovery and availability in large quantity of fullerenes have stimulated their extensive research in a wide variety of fields such as physics, chemistry, material science, biology, etc. Initially viewed as aromatic and quite chemically inert molecules, fullerenes can actually undergo various chemical reactions characteristic of electron-deficient alkenes. Several review articles [17–21] and an excellent monograph [22] regarding fullerene chemistry have been published.

The solubility of fullerenes in common organic solvents is so low that the use of a large amount of solvents is inevitable in their solution reactions. The reactions of fullerenes in the absence of any solvent have advantages over their solution reactions from the viewpoint of the solubility problem of fullerenes and benign environmental concern by eliminating the usage of harmful organic solvent. Therefore solvent-free reaction of fullerene is an attractive and appealing method to synthesize fullerene derivatives. Fullerene chemistry and mechanochemistry started to merge in the mid-1990s. A review article on the mechanochemical approach to fullerene chemistry at a very early stage of fullerene mechanochemistry was published by Braun in 1997 [23]. Since then, much more work on various solvent-free reactions of fullerenes has been done. The solid-state mechanochemical reaction of fullerene C_{60} based on the authors' own work was reviewed in 1999 [24]. Here a full coverage of fullerene mechanochemistry, including most recent research work in this field, is presented.

2. MECHANOCHEMICAL DEVICES

Different types of mechanochemical devices have been used to provide mechanical activation energy. They differ in their capacity and efficiency, and can be generally classified into two categories: grinding devices and milling devices.

2.1. Grinding Device

The most convenient and easy method for a mechanochemical reaction is the use of a mortar and pestle, which promotes the reaction through grinding, mixing, and triturating. This method has been widely used by Toda and co-workers to investigate various solvent-free organic reactions [25–27]. A new version of mortar and pestle called Mortar Grinder RM 100 is available from Retsch GmbH & Co. KG; the rotary speed of the mortar is 90 rpm.

2.2. Milling Devices

2.2.1. Shaker/Mixer Mill

Shaker mills such as SPEX mills are most commonly used for laboratory investigations. A shaker mill contains a vial, consisting of the sample and grinding balls, secured in the clump and swung energetically back and forth several thousand times a minute. SPEX mills are manufactured by SPEX CertPrep, Metuchen, NJ. A SPEX shaker mill can process about 10–20 g of the sample at a time.

Most of the reactions described in this article were done with the so-called "high-speed vibration mill." This high-speed vibration mill has almost the same working mechanism as the SPEX shaker mill, and consists of a capsule and a milling ball, which are made of stainless steel (Fe-Cr-Ni with a composition of 74:18:8 wt%). The inner diameter and length of the capsule are 9.0 mm and 26 mm, respectively, and the diameter of the milling ball is 6.0 mm. The capsule containing the sample and milling ball was fixed in a home-built vibrating machine so that the capsule was shaken along its long axis horizontally with a slight fluctuation. The vibration frequency is 3500 cycles per minute [28]. Because of the small size of the presently used capsule, only a small amount (usually not more than 200 mg) of sample can be handled.

2.2.2. Planetary Ball Mill

The planetary ball mill owes its name to the planet-like movement of its vials. These vials are arranged on a rotating support disk and a special drive mechanism causes them to rotate around their own axes. The centrifugal force produced by the vials rotating around their own axes and that produced by the rotating support disk both act on the material and grinding balls in the vial. Because the vials and supporting disk rotate in opposite directions, the centrifugal forces alternately act in like and opposite directions. The material in the vial is ground due to the running down, lifting off, traveling, and colliding of the grinding balls. Planetary ball mills (Pulverisette) are available from Fritsch, GmbH in Germany. Compared to the SPEX shaker mills, Fritsch Pulverisettes are lower-energy mills. A few hundred grams of the sample can be milled in a planetary ball mill at a time.

2.2.3. Attritor Mills

A conventional ball mill consists of a rotating horizontal drum half-filled with small steel balls. In contrast, an attritor consists of a vertical drum with a series of impellers inside it. A powerful motor rotates the impellers. Set progressively at right angles to each other, the impellers energize the steel balls. The operation of an attritor is simple. The material to be ground and the grinding medium are placed in the stationary tank. The mixture is then agitated by a shaft with arms, rotating at a high speed of about 250 rpm. The laboratory attritor works up to ten times faster than the conventional ball mills. Commercial attritors are available from Union Process, Akron, OH. Attritors are the mills in which a large quantity of the sample from about 0.5 to 40 kg can be milled at a time.

3. MECHANOCHEMICAL REACTIONS OF FULLERENES

The simplest method of mechanochemistry is the use of mortar and pestle, while ball milling is suitable when a prolonged reaction time is required. Various organic reactions have been shown to take place in the solid state when a mortar and pestle is used without solvents [25–27]. In these examples, essentially the same reactions are reported to occur regardless of the presence or absence of solvent. For most of the reactions shown in the following sections, the so-called "high-speed vibration milling" (HSVM) technique is utilized. The stainless-steel capsule is vigorously shaken at a frequency of 3500 cycles per minute. The effective maximum local pressure in the stainless-steel capsule is not less than 15,000 bars during the high-speed milling process [29]. Some solid-state reactions can be totally different from those in the liquid phase under such extreme conditions. Indeed, some novel solvent-free reactions of fullerenes have been observed to occur only under HSVM conditions, and will be discussed in the following sections.

3.1. Nucleophilic Addition of Organozinc Reagent to C_{60}

The nucleophilic addition of amines, organolithiums, and Grignard reagents to C_{60} is one of the most common and widely used reactions to functionalize C_{60}. All these reactions were done in organic solvents such as benzene and toluene [19]. The first application of HSVM technique to fullerene chemistry was the Reformatsky-type reaction of C_{60}. The addition of organozinc reagents to C_{60}, which had not even been attempted in solution, was investigated under solvent-free HSVM conditions. The reactants of C_{60}, zinc powder, and ethyl bromoacetate in a molar ratio of 1:20:5 along with a stainless-steel milling ball were put into a stainless-steel capsule. This mixture was vigorously milled for 20 min by shaking the capsule at the speed of 3500 cycles per minute by the use of a high-speed vibration mill. The reaction mixture was acidified and separated to afford mainly the expected product **1** in 17.2% and some minor side products along with 72.5% recovered C_{60} (Fig. 1) [30]. It was found that longer reaction time increased the yield of compound **3** at the expense of the main product **1**.

3.2. Synthesis of Fullerene Dimers and Trimers

The formation, structure, and characteristics of all-carbon fullerene oligomers and polymers are of particular interest because of their potential application in molecular devices
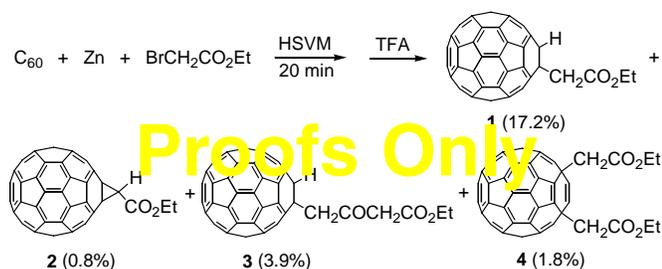
Figure 1. Reaction of C_{60} with zinc and ethyl bromoacetate under HSVM conditions [30].

optoelectronics, and nanotechnology. These materials have been prepared by photochemical irradiation [31–37], by alkali metal doping [38–40], and under high-pressure/high-temperature condition [41–45]. However, the insolubility of these materials in any organic solvent has precluded their characterization from the organic chemistry point of view; therefore, their detailed structures remain to be elucidated. It has been suggested that fullerene dimer with $[2+2]$ structure is the essential subunit in the fullerene oligomers and polymers. Obviously, the preparation and characterization of fullerene dimers and trimers are of paramount importance for understanding the structure and properties and eventual application of the fullerene oligomers and polymers. Fortunately, fullerene dimers and trimers can be uniquely obtained by mechanochemical reactions.

3.2.1. Synthesis of C_{60} Dimer, C_{120}

The reaction of cyanide ion with C_{60} in a solution of *o*-dichlorobenzene (ODCB)-DMF gives a stable $(CN)C_{60}^-$ anion, which can be quenched with various electrophiles to afford cyanated C_{60} derivatives [46]. In sharp contrast to the reaction in liquid phase, the solid-state reaction of C_{60} with KCN under HSVM conditions for 30 min unexpectedly and selectively afforded the formal $[2+2]$-type dimer C_{120} (**6**) in 18% other than the cyanated C_{60} derivative **5**, along with 70% of unconsumed C_{60} (Fig. 2) [47]. The X-ray crystal structure unequivocally showed that the dumbbell-shaped C_{120} is connected by a cyclobutane ring and this four-membered ring is square rather than rectangular as predicted theoretically. Furthermore, the $[2+2]$ structure of C_{120} is stable and does not rearrange to other C_{120} isomers such as those with peanuts-shaped structure.

The amount of KCN need not necessarily be equivalent to that of C_{60}; a small amount such as 0.2 molar equivalent
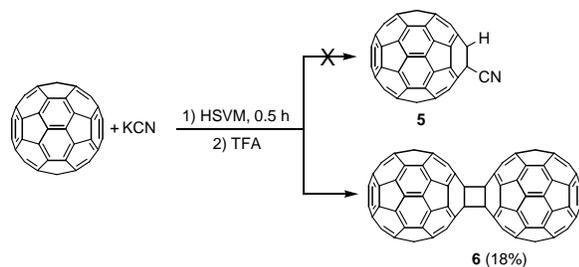
is enough [28]. Apparently, the solid-state reaction of C_{60} with cyanide proceeds in a quite different reaction pathway from the solution reaction. Formation of C_{120} can also be obtained by the reaction of C_{60} with potassium salts such as K_2CO_3 and CH_3CO_2K, metals such as Li, Na, K, Mg, Al, and Zn, and organic bases such as 4-(dimethylamino)- and 4-aminopyridine [28]. This mechanochemical reaction appears to reach an equilibrium state with a ratio of C_{60} to C_{120} in about 7:3 either starting from a mixture of C_{60} and a chosen reagent or from pure C_{120}. For these reactions, the formation of C_{120} was most probably initiated by electron transfer reaction. Once the radical anion $C_{60}^{\cdot-}$ is formed, it would couple with a neutral C_{60} to give $C_{120}^{\cdot-}$, which would transfer one electron to another C_{60} to afford the neutral C_{120}. Helium-3 labeled C_{60} dimer, $^3He@C_{120}$ (**7**) (Fig. 3), was prepared by the above-mentioned HSVM reaction using a helium-3 labeled C_{60} sample in which the approximate ratio of $^3He@C_{60}$ to empty C_{60} is about 1:1000 [28]. $^3He@C_{120}$ and its derivatives can be monitored by helium-3 nuclear magnetic resonance (^3He NMR) [48]. Similarly, $N@C_{120}$ has been synthesized by the mechanochemical reaction of C_{60} containing approximately 0.01% of $N@C_{60}$ with additives such as KCN, $CuSO_4$, $CaCl_2$, and P_2O_5 [49]. $N@C_{120}$ has been measured by electron paramagnetic resonance (EPR).

[60]Fullerene dimer was also obtained as the main product from the HSVM reaction of C_{60} and C_{70} with 4-aminopyridine, which was designed to synthesize cross dimer C_{130} [50]. Dimerization of C_{60} was also found to occur without the presence of any catalyst. Treatment of C_{60} itself under HSVM conditions resulted in a small amount of C_{120} and a large amount of insoluble C_{60} polymers; the latter was not formed in the reaction of C_{60} and KCN [28]. A similar phenomenon was observed by prolonged mechanical milling in a conventional horizontal ball mill at a rotational speed of 95 ± 1 rpm [51, 52].

H. Shinohara and coworkers described the preparation of C_{120} in 15% overall yield by simply hand-grinding a mixture of C_{60} and K_2CO_3 [53]. The same research group also reported that C_{120} was obtained as the main product (8%) from a hand-ground reaction mixture of C_{60} and C_{70} with K_2CO_3 aiming to synthesize cross dimer C_{130}, which was isolated in 3% yield [54].

It should be mentioned that C_{120} has been synthesized in high yield (~80%) by squeezing the organic molecular crystal $(ET)_2C_{60}$ at 5 GPa and 200 °C using a wedge-type cubic anvil high-pressure apparatus [55]. While C_{60} powder itself was squeezed in a simple piston-cylinder pressure cell at 1 GPa and ~200 °C for a few minutes, only ca. 3% of C_{120} and mainly insoluble residue of C_{60} oligomers and polymers along with 15–20% unchanged C_{60} were obtained [56]. Longer treatment resulted in a decrease in the yield of C_{120} and an increase in the insoluble portion.

Figure 2. Synthesis of C_{120} from C_{60} and KCN under HSVM conditions [47].
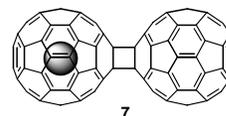
Figure 3. The structure of $^3He@C_{120}$ [48].

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C$_{60}$ + C$_{70}$ ⟶ C$_{120}$ +

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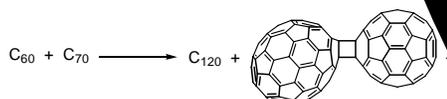
8:   HSVM, 4-aminopyridine
8, **9**: grinding, K$_2$CO$_3$

Figure 4. Synthesis of cross dimer C$_{130}$ from C$_{60}$ and C$_{70}$ un
and grinding conditions [50, 54].

3.3. [2 + 4] Cycloaddition Reactions of C$_{60}$

3.3.1. Diels–Alder Reaction of Condensed Aromatics to C$_{60}$

The [4 + 2] cycloaddition of C$_{60}$ with anthracene is a well-studied reaction in solution [59–61]. The highest yield of the monoadduct is 39% in the conventional thermal conditions [59]. The Diels–Alder reaction of a 1:1.2 mixture of C$_{60}$ and anthracene for 1 h under HSVM conditions was very efficient and gave 55% of the corresponding monoadduct and isomeric mixture of bisadducts in 19% [62]. The reaction appeared to reach an equilibrium state between the reactants and products after a reaction time of about 30 min. The reverse reaction (dissociation) of the monoadduct was found to give a similar component ratio. These results demonstrate that a chemical equilibrium is established under the present solid-state reaction system in spite of the heterogeneous reaction conditions. The HSVM reaction of C$_{60}$ with one equivalent of pentacene afforded the double [4 + 2] adduct **21** (11%) in addition to the symmetrical monoadduct **20** (19%) and positional isomers of bisadducts **22** (15%) (Fig. 7) [62]. Apparently adduct **21** was formed by trapping the thermodynamically less favorable monoadduct **23** by another molecule of C$_{60}$ (Fig. 8). In contrast, the reaction of C$_{60}$ with pentacene in solution selectively gave the monoadduct **20** which has higher thermodynamic stability [63]. Adduct **21** could not be obtained from the solution reaction. Thus, in this particular case, the solid-state reaction appears to be advantageous in trapping the kinetic product. The HSVM treatment of C$_{60}$ with 9,10-dimethylanthracene, tetracene, naphtha[2,3-α]pyrene afforded the corresponding [4 + 2] cycloadducts in fairly good yields.

3.3.2. Diels–Alder Reaction of Phthalazine to C$_{60}$

When the reaction of C$_{60}$ with one equivalent of phthalazine was carried out in a solution of 1-chloronaphthalene at 255 °C for 1 h, the open-cage fullerene derivative **24** was obtained in 44% yield together with 23% of recovered C$_{60}$ by a one-pot reaction. In contrast, the HSVM reaction of
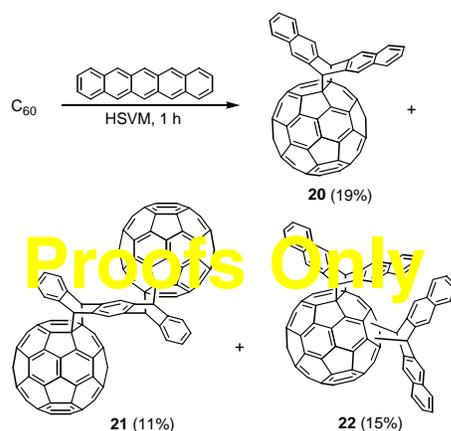
23

Figure 8. Structure of less stable [4 + 2] adduct from C$_{60}$ and pentacene [62].

C$_{60}$ with four equivalents of phthalazine for 1 h followed by heating this solid reaction mixture at 200 °C for 2 h afforded dimeric derivative **25** as the sole product in 14% along with 61% of unchanged C$_{60}$ (Fig. 9) [64]. Compound **25** underwent intramolecular [2 + 2] cycloaddition between the two C$_{60}$ cages located in proximity to give a new C$_{60}$ dimer in quantitative yield either upon irradiation with visible light in chloroform or by heating in ODCB.

3.3.3. Diels–Alder Reaction of Di(2-pyridyl)-1,2,4,5-tetrazine to C$_{60}$

Upon HSVM treatment of a mixture of C$_{60}$ and di(2-pyridyl)-1,2,4,5-tetrazine under HSVM conditions for 30 min, a highly efficient reaction took place and adduct **26** was obtained as a single product quantitatively [65]. The yield of compound **26** obtained by HSVM method is obviously higher than that carried out in refluxing toluene (50–60%) [66]. Compound **26** is highly sensitive to moisture and is transformed by the addition of water molecule followed by an unusual series of rearrangements to give the novel and unexpected 1,2,3,4-tetrahydro-C$_{60}$ derivative **27** (Fig. 10). Other nucleophiles such as alcohols, thiols, and primary and secondary amines react with **26** similarly. The reaction is catalyzed by weak acid catalyst such as silica gel and requires ambient light [67].

The synthesis of dimeric compound **28** was achieved by the HSVM reaction of C$_{60}$ with 0.5 equivalent of di(2-pyridyl)-1,2,4,5-tetrazine, followed by the [4 + 2] cycloaddition of the resultant **26** with C$_{60}$ by heating the solid mixture at 150 °C for 2 h to afford 27% of **28** along with 40% of recovered C$_{60}$ (Fig. 10) [65]. This dimeric compound **28** was obtained only by the solid-state reaction.

Figure 7. Reaction of C$_{60}$ with pentacene under HVSM conditions affording the monoadduct, bisadducts, and C$_{60}$ dimer derivative [62].
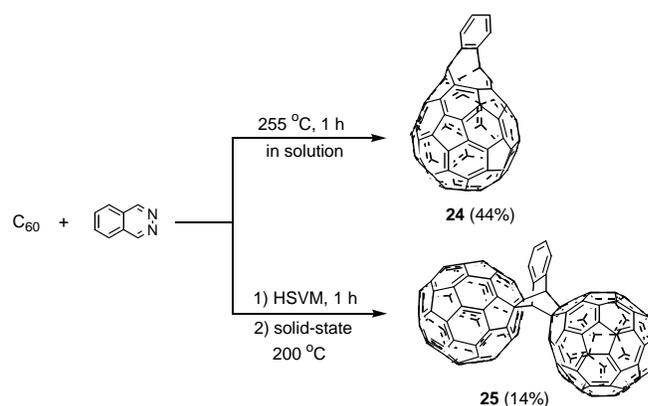
Figure 9. Diels–Alder reaction of C$_{60}$ with phthalazine under HSVM conditions and in solution [64].
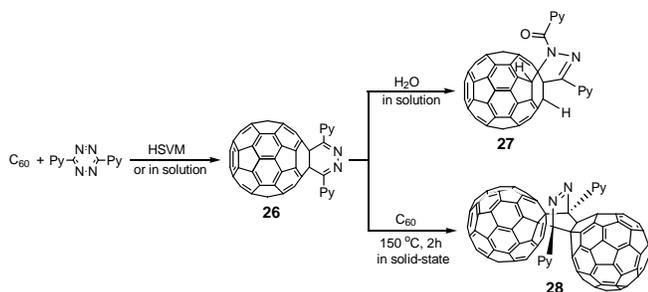
Figure 10. Reaction of C_{60} with di(2-pyridyl)-1,2,4,5-tetrazine under HSVM conditions and in solution [65–67].

The reaction in solution has been reported to result in only hydrogenation of **26** [66, 67]. A new novel C_{60} dimer with direct intercage bonds was formed quantitatively by the intramolecular $[2 + 2]$ cycloaddition when a solution of **28** in ODCB was irradiated with room light for 3 h [65].

3.4. $[2 + 3]$ Cycloaddition Reactions of C_{60}

3.4.1. 1,3-Dipolar Cycloaddition of Organic Azides to C_{60}

Upon the thermal reaction in solution, it is reported that organic azides and C_{60} give triazoline derivatives only at low temperature and the triazolines are converted to 5,6-open and 6,6-closed azafullerenes by heating the solution at 100 °C [68]. The HSVM reaction of C_{60} and azides for 30 min afforded triazoline derivatives **29** in 62–76%. The triazoline **29b** was then heated in the solid state at 120 °C for 2 h to give the 5,6-open and 6,6-closed azafullerenes **30b** and **31b** in higher yields than in solution (Fig. 11). The fact that triazoline derivative **29b** could not be converted to azafullerenes **30b** and **31b** under HSVM conditions indicates that the temperature in the current HSVM system does not rise up to 100 °C [24].

3.4.2. 1,3-Dipolar Cycloaddition of Diazo Compounds to C_{60}

The HSVM reaction of C_{60} with 9-diazofluorene did not allow the isolation of azo-compound **32** but gave 9,9-fluorenofullerene **33** produced by denitrogenation (Fig. 12) [24].
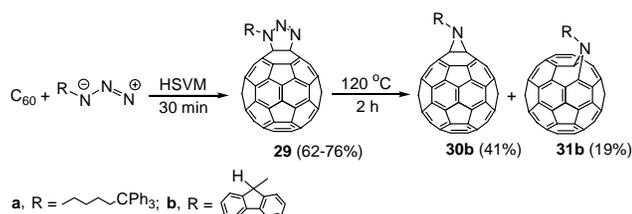
Figure 11. Reaction of C_{60} with azides under HSVM conditions followed by thermal solid-state reaction [24].

Figure 12. Reaction of C_{60} with 9-diazofluorene [24].

3.4.3. 1,3-Dipolar Cycloaddition of Azomethine Ylide to C_{60} and C_{70}

The 1,3-dipolar cycloaddition of azomethine ylide generated *in situ* from *N*-methylglycine and paraformaldehyde to C_{60} to give fulleropyrrolidine was reported at a very early stage of fullerene chemistry by Prato and co-workers [69]. The HSVM technique is applied to the Prato reaction of C_{60} under solvent-free conditions. A mixture of C_{60}, one equivalent of *N*-methylglycine, and one equivalent of an aldehyde was vigorously shaken under HSVM conditions for 1 h; the expected fulleropyrrolidines **34a–e** were obtained in moderate yields (Fig. 13) [70].

Similarly, the HSVM reaction of C_{70} with one equivalent of *N*-methylglycine and one equivalent of paraformaldehyde for 1 h gave three monoadduct isomers **35**, **36**, and **37** in 41% yield with a ratio of 47 : 36 : 16 (Fig. 14).

3.4.4. Cycloaddition of Glycines to C_{60} and C_{70} [70]

While working on the Prato reaction of C_{60}, besides the corresponding fulleropyrrolidines, compound **34a** was isolated unexpectedly as a minor product in all reactions of C_{60} with sarcosine and aldehydes. Intrigued by this observation, the novel reactions between fullerenes and *N*-substituted glycines were found. The HSVM reaction of C_{60} with sarcosine (1:1) for 1 h gave **34a** and C_{120} in 19% and 23%, respectively. Furthermore, when sarcosine was substituted by *N*-ethylglycine, the same kind of reaction occurred, and **38** and C_{120} were obtained in 16% and 19%, respectively (Fig. 15).

When a mixture of C_{70} and *N*-methylglycine was treated with HSVM, the reaction gave monoadducts **35** and **36** in total yield of 23% with relative ratio of 1.5:1 (Fig. 16). The reason for the absence of **37** is not known. It should be noted that there is no evidence of the formation of C_{70} dimer, C_{140}, either from the Prato reaction of C_{70} or the direct reaction of C_{70} with *N*-methylglycine. This is consistent with the failure of formation of C_{140} from the reactions of C_{70} with potassium salts, metals, and amines under HSVM conditions.
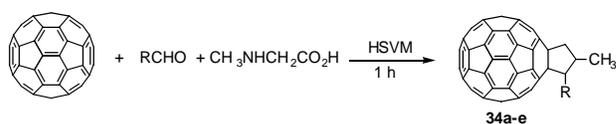
Figure 13. Prato reaction of C_{60} under HSVM conditions [70].

Figure 14. Prato reaction of C_{70} under HSVM conditions [70].

3.5. Reaction of Organic Bromides and Alkali Metals with C_{60}

Reaction of C_{60} with organolithiums and Grignard reagents affording alkyl, aryl, or alkynyl C_{60} derivatives is one of the earliest studied reactions in solution [17–22]. A mixture of C_{60}, aryl or alkyl bromide, and metal (Li, Na, K, Mg) in a molar ratio of 1:2 ~ 3:4 ~ 6 was vigorously shaken for 30 min under HSVM conditions. The resulting black reaction mixture was acidified to give the corresponding aryl or alkyl C_{60} derivatives **39** in moderate yield and small amount of C_{120} (Fig. 17) [71]. The HSVM reaction of C_{60} with metals with higher reducing power is known to give a mixture of C_{60} and C_{120} in a 30:70 ratio. The formation of either the C_{60} dimer or the C_{60} polymer is suppressed by the presence of organic bromide. Alkali metals were found effective for these reactions, while the usage of magnesium gave poor result.

3.6. Reaction of Dichlorodiphenylsilane and Lithium with C_{60}

The silicon species such as silylene [72, 73], disilirane [74, 75], and silyllithium [76] have been reported to react with C_{60} to give mono- or disilyl derivatives of C_{60} [72–81]. Unlike the above-mentioned HSVM reaction of C_{60} with alkyl bromide and lithium which gave the alkyl C_{60} derivatives, the HSVM reaction of C_{60} with dichlorodiphenylsilane and lithium powder for 30 min gave 7.5% of adduct **40**, a C_{60} dimer fused with a silacyclopentane ring, together with 67.4% of recovered C_{60} (Fig. 18) [82]. The reaction mechanism is not quite clear yet, but it was assumed that the C_{60} radical anion formed by one-electron transfer from lithium was playing an important role in the reaction.

3.7. Formation of Fullerene Complexes

Braun and co-workers studied the mechanochemical synthesis of the supramolecular host-guest complex of C_{60} and gamma-cyclodextrin (γ-CD) [83]. The equipment used in the mechanochemical investigation was a 50 ml agate ball mill (diameter: 70 mm, height: 15 mm) (Pulverisette, Type 701, Fritsch, Germany). A homogenized mixture of 10 mg of C_{60} and 100 mg of γ-CD was ball-milled for about 20 h
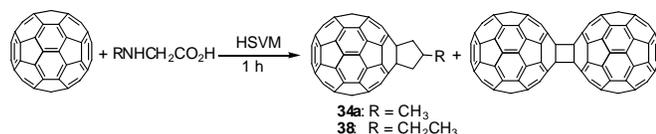
Figure 15. Reaction of C_{60} with *N*-alkylglycines under HSVM conditions [70].
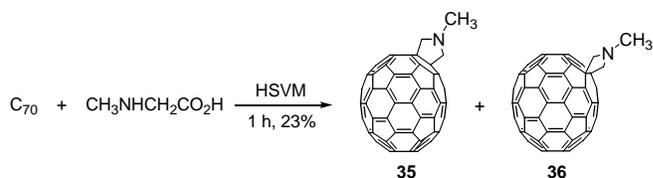
Figure 16. Reaction of C_{70} with *N*-methylglycine under HSVM conditions [70].

at room temperature. A 1:2 C_{60}-γ-CD complex **41** with a bicapped structure was supposed to be formed (Fig. 19). It has been proposed that the mechanochemical enhancement of the reactivity of C_{60} towards γ-CD proceeds via the amorphization of both the originally crystalline phases and guest molecules followed by a solid phase dissolution in amorphous media under vigorous mechanochemical treatment [83]. The C_{60}/δ-CD and C_{70}/δ-CD inclusion complexes have been prepared by the same method [84]. The solid-state inclusion complexation of C_{60} and C_{70} as well as some derivatives of C_{60} with γ-CD, and that of C_{60} and C_{120} with sulfocalix[8]arene, was attained under HSVM conditions more efficiently than classical ball milling [85]. The efficiency of complex formation under HSVM conditions was reflected in the very short reaction time (10 min) for the complexation of C_{60} with γ-CD as compared to about 20 h by classical ball milling [83] or more than 24 h in refluxing aqueous solution [86], and highest solubility of the formed complexes in water.

Another type of complex, that is, charge transfer complex, was reported to be obtained by grinding 1,4-diazabicyclooctane (DABCO) and C_{60} at room temperature in a dry atmosphere. A number of mixtures were prepared with different mole ratios of DABCO : C_{60}. The formed charge transfer complex was found to dissolve readily in water due to its charge separation and increase in dipole moment. However, the reaction of an aqueous solution of DABCO with C_{60} stirred vigorously for 2 h at 60 °C failed to afford the complex formed in the solid state [87].

4. CONCLUSIONS

Various solvent-free mechanochemical reactions of fullerenes have been investigated. Most of the studied mechanochemical reactions of fullerenes were done by high-energy HSVM technique, and many fewer reactions were done by low-energy ball milling and hand-grinding. It has been found that some mechanochemical reactions under HSVM conditions have the same reaction mechanisms as
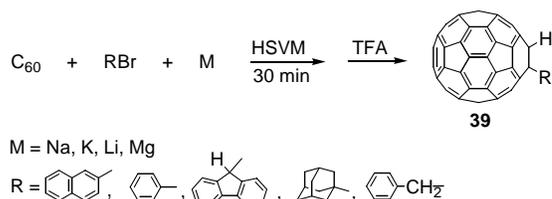
Figure 17. Reaction of C_{60} with alkali metals and bromides under HSVM conditions [71].
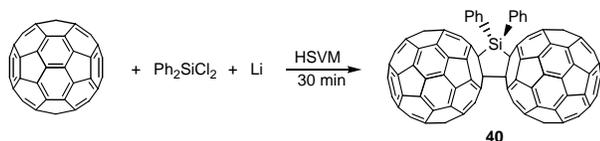
Figure 18. Reaction of C_{60} with dichlorodiphenylsilane and lithium under HSVM conditions [82].

in the solution reactions, but some other mechanochemical reactions under HSVM conditions undergo quite different reaction pathways from those in the solution reactions and therefore give totally different products. Some fullerene derivatives can be uniquely obtained only under solvent-free and HVSM conditions. The fullerene mechanochemistry is still in its infancy. Even though knowledge of the fullerene mechanochemistry has been accumulated over the past years, many more experiments including more various reactions and the adjustment of variables, such as type of mill, milling speed, milling time, and ball to sample weight ratio, have to be done in order to fully understand the unique mechanochemical behavior and be able to propose a possible theoretical model for the fullerene chemistry under HSVM conditions. Furthermore, the extension of the HSVM technique to more general organic reactions (without the involvement of fullerenes) would be a promising research field to produce some unusual results.

GLOSSARY

Fullerene The third form of carbon, it is a family of caged compounds composed of only carbon element. A fullerene C_n consists of 12 pentagonal rings and any number of hexagonal ones, m, such that $m = (C_n - 20)/2$ (Euler's theorem). The most abundant fullerenes are C_{60} and C_{70}.

Fullerene chemistry The chemistry of fullerenes. Fullerenes undergo various kinds of reactions such as nucleophilic addition, Dields–Alder reaction, 1,3-dipolar cycloaddition, radical addition, oxidation, reduction, etc.

High-speed vibration milling (HSVM) It is a technique used to effectively activate the reaction system by vigorous milling of the reaction mixture.

Mechanochemistry Mechanical energy is provided as the driving force for the chemical reactions. The activation of the local reaction sites by the mechanical energy caused by the stress, friction, shear deformation, etc. Mechanochemistry is generally done under solvent-free condition.

Solvent-free reaction Reaction conducted in the absence of any solvent.
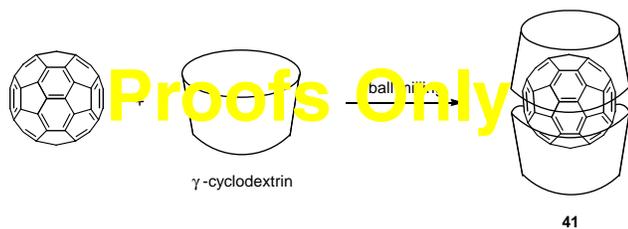
Figure 19. Formation of inclusion complex of C_{60} and γ-CD by ball milling [83].

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