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One-step Synthesis of Fullerene Hydride $C_{60}H_2$ via Hydrolysis of Acylated Fullerenes

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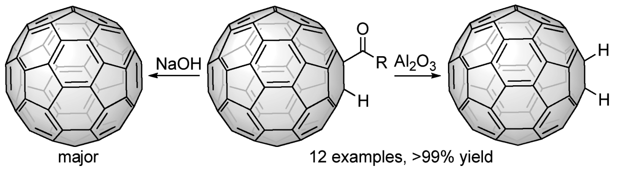

The hitherto unexplored class of acylated fullerene compounds has been shown to be excellent $C_{60}H_2$ precursors. Upon a simple treatment with basic Al_2O_3, they are hydrolyzed quantitatively into $C_{60}H_2$. This key feature led to the development of a new, straightforward protocol for the selective synthesis of the simplest [60] fullerene hydride, $C_{60}H_2$. This protocol may offer an advantageous alternative to previously known methods for the synthesis of $C_{60}H_2$ allowing for a rapid access to $C_{60}H_2$ in good yield and high purity without tedious separating processes.

Reduced fullerenes, also known as fullerene hydrides, are the simplest derivatives of the fullerene family of carbon allotropes.[1] Due to its unique molecular structure, fullerene is the only form of carbon which potentially can be chemically hydrogenated and dehydrogenated reversibly,[2] thereby making such structures of interest as high-capacity hydrogen-storage materials.[3,4] Furthermore, hydrogenated fullerenes, and especially $C_{60}H_2$, have attracted considerable interest due to their synthetic utility as a versatile starting material for further fullerene derivatization.[5] This utility arises from the high acidity of the fullerenyl C−H bond (for $C_{60}H_2$, pK_{a1} = 4.7, pK_{a2} = 16),[6] which facilitates deprotonation of hydrogenated fullerenes (with very mild bases) to afford fullerene anions for further functionalization. $C_{60}H_2$ is also of fundamental interest as a model compound for other fullerene derivatives[7,8] and has been the subject of several experimental and theoretical studies.[9] In addition, $C_{60}H_2$ has been shown to be an effective hole transport material with potential applications in organic field-effect transistors (OFETs) and organic light-emitting devices (OLEDs).[10] These diverse applications of $C_{60}H_2$, the simplest possible hydride of C_{60}, have made any synthetic method leading to its preparation of considerable practical interest.

Established routes toward the synthesis of the hydrogenated fullerene $C_{60}H_2$ include hydroboration,[11,12] hydrozirconation,[13] photoinduced electron transfer,[14] dissolving metal reductions,[15,16] ultrasonically irradiating solutions of C_{60} in decahydronaphthalene,[17] electrochemical reduction to $C_{60}{}^{2-}$ followed by protonation,[18] as well as chemical reduction with diimide or chromous acetate[19,12] and $NaBH_4$.[20,5b] Since hydrogen reduction of C_{60} is of fundamental interest, catalytic hydrogenation has been also utilized for the synthesis of $C_{60}H_2$ in solution with rhodium(0) on alumina,[21] palladium or palladium on carbon,[22] as well as in the solid phase.[23,4]

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Most of these methods afford a single regioisomer of $C_{60}H_2$, the 1,2-addition product which has the lowest energy of the 23 possible all-*exo* isomers of $C_{60}H_2$,[8,24] along with a mixture of highly hydrogenated derivatives ($C_{60}H_n$, $n \geq 2$). The yields of the desired $C_{60}H_2$ are typically low, while the purification procedure requires extensive use of preparative or semipreparative high-pressure liquid chromatography (HPLC);[25] there are only a few cases where the $C_{60}H_2$ yields lie in the range of 60−70%.[13−15, 20] Thus, the mild and selective hydrogenation of C_{60} remains a major goal in fullerene chemistry.

Recently, we have developed an effective method for the direct acylation of [60]fullerene by using commercially available alkyl or aryl aldehydes.[26] Acylated fullerenes represent a novel class of fullerene compounds, and their chemical properties are of fundamental interest. Our present studies on their reactivity revealed, in accordance with earlier studies reported by Mattay et al.[27] and Saigo et al.,[28] that these compounds could be converted into $C_{60}H_2$ under mild conditions. This result prompted us to conduct further investigations for addressing this reactivity and explore potential applications. For this purpose, a series of acylated fullerenes **1**−**13** (Figure 1) was prepared according to the previously reported method.[26] We found that these compounds could be used as efficient reagents for the selective synthesis of 1,2-$C_{60}H_2$ in quantitative yield and high purity (Scheme 1). Several studies under different experimental conditions have been also conducted to explore this functionalization and gain a valuable mechanistic insight.

For the purposes of the present study, ketones **1** and **11** were initially used as model compounds for alkyl- and aryl-substituted ketones, respectively, and treated under different reaction conditions. These conditions included treatment with silica or alumina gel, acidic or alkaline solutions of different concentration, and the presence or absence of molecular oxygen. All these reactions have been carried out by using a toluene solution of ketone **1** or **11** (8×10^{-4} M). Some representative results obtained from these studies are summarized in Table 1.

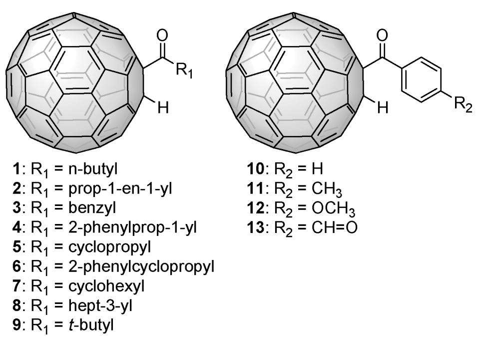
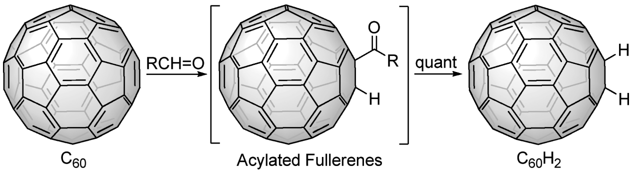


FIGURE 1. Acylated [60]fullerenes investigated in this study.

SCHEME 1. Indirect Approach for the Synthesis of $C_{60}H_2$ through a Sequential Acylation/Hydrolysis Process



Initially, treatment of **1** with SiO_2 or *p*-toluenesulfonic acid (PTSA) did not result in any reaction for several hours, suggesting that this compound is stable under acidic conditions (cf. entries 1 and 2 in Table 1). In contrast, **1** was smoothly converted to C_{60} and $C_{60}H_2$ when treated with aqueous NaOH (entries 3−10, Table 1). Indisputably, hydroxide anions are responsible for this transformation, presumably via the conventional nucleophilic attack on the carbonyl carbon and/or abstraction of the acidic fullerenyl hydrogen (vide infra). Further studies revealed that both NaOH and dissolved oxygen affect the rate of this reaction. In particular, the reaction rate was found to vary considerably when three identical samples of **1** were treated under argon, ambient, or oxygen atmosphere (cf. entries 3−8 in Table 1), respectively. Although the reaction of **1**, under an argon atmosphere, was hardly observed, it proceeded faster under ambient atmosphere. The effect of dissolved oxygen became more pronounced when a pure oxygen atmosphere was maintained over the reaction mixture, thus resulting in a much faster reaction. For example, the time required for achieving a 15% conversion of **1** was 21 h under inert conditions, while under oxygen atmosphere, only 90 min was needed (cf. entries 4 and 7 in Table 1). Apparently, the presence of oxygen is necessary for this process. In addition, a substantial increase in the reaction rate was observed with increase of NaOH concentration (cf. entries 5, 6 and 9, 10 in Table 1). It should also be mentioned that prolonged reaction time and/or increased NaOH concentration led to the consumption of both $C_{60}H_2$ and C_{60} and the formation of a brown sludge, partially soluble in water. This is probably due to the polyhydroxylation of C_{60}, which results in the formation of water-soluble fullerenols; this process is known to occur upon treatment of C_{60} with NaOH under O_2 atmosphere.[29]

At this point, it is worth mentioning that the $C_{60}/C_{60}H_2$ ratio increases with increasing reaction time (cf. entries 9 and 10 in Table 1; see also below). This observation implies that $C_{60}H_2$ should be considered as an intermediate compound in the conversion of **1** to C_{60}. To probe further this possibility, we prepared a pure sample of $C_{60}H_2$ which was then treated under the same experimental conditions mentioned above with aqueous NaOH. Indeed, under these alkaline conditions, $C_{60}H_2$ was readily converted to C_{60}. Moreover, the exclusion of oxygen from the reaction mixture inhibited this process. This result is substantially consistent with that of Wang et al.[20] and provides further experimental evidence for the intermediacy of oxygen in the reaction mechanism. More importantly, this result may also rationalize the previously reported lability of $C_{60}H_2$, and especially its conversion back to C_{60} in the presence of oxygen.[16,21]

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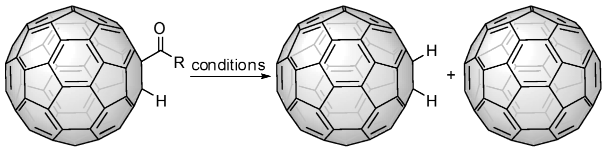
TABLE 1. Conversion of Ketones 1 and 11 to $C_{60}H_2$ and/or C_{60} under Various Conditions[a]



1: R = butyl
11: R = *p*-$CH_3C_6H_4$

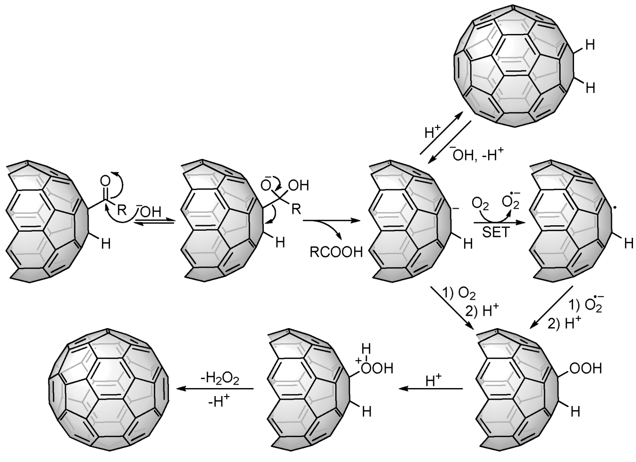
				relative yield[b] (%)	
entry	substrate/conditions	time (h)	conversion[b] (%)	$C_{60}H_2$	C_{60}
1[c]	**1**/SiO_2		0		
2[d]	**1**/PTSA	15	0		
3[e]	**1**/NaOH 1 M, Ar	5	3	33	67
4[e]	**1**/NaOH 1 M, Ar	21	15	27	73
5[f]	**1**/NaOH 1 M, air	6	10	34	66
6[f]	**1**/NaOH 1 M, air	22	54	28	72
7[g]	**1**/NaOH 1 M, O_2	1.5	15	38	62
8[g]	**1**/NaOH 1 M, O_2	16	58	33	67
9[h]	**1**/NaOH 10 M, air	0.25	26	40	60
10[h]	**1**/NaOH 10 M, air	2	83	15	85
11[i]	**1**/basic Al_2O_3		**> 99**	**> 99**	
12[c]	**11**/SiO_2		0		
13[d]	**11**/PTSA	15	0		
14[e]	**11**/NaOH 1 M, Ar	2	20	53	47
15[f]	**11**/NaOH 1 M, air	2	92	71	22
16[f]	**11**/NaOH 1 M, air	27	100	10	90
17[g]	**11**/NaOH 1 M, O_2	2	95	44	56
18[g]	**11**/NaOH 1 M, O_2	22	100	6	94
19[i]	**11**/basic Al_2O_3		**> 99**	**> 99**	

[a] All reactions were carried out by using 8×10^{-4} M **1**or **11** in toluene (3 mL) at ambient temperature. Further details can be found in the Supporting Information. [b] Determined by HPLC analysis. These values are typically consistent with the obtained isolated yields. [c] The reaction mixture was passed through a column packed with silica gel. [d] Three milliliters of H_2O containing ca. 80 mg of PTSA was added into the reaction mixture. [e] Three milliliters of aqueous NaOH solution (1 M) was added. The reaction was carried out by using degassed solvents under argon atmosphere. [f] NaOH (1 M, 3 mL) was added, and the reaction mixture was kept under ambient atmosphere. [g] As above but under oxygen atmosphere (760 Torr). [h] NaOH (10 M, 3 mL) was added under ambient atmosphere. [i] The reaction mixture was passed through a column packed with Al_2O_3 (basic).

Finally, a toluene solution of **1** was treated with basic Al_2O_3, under essentially the same conditions mentioned above in the case of SiO_2. To our delight and in contrast to what was observed so far, ketone **1** was readily converted to $C_{60}H_2$ in a quantitative yield without further conversion to C_{60} (entry 11, Table 1).[28] In this case, alumina surface groups (i.e., negatively charged hydroxyl groups) are most likely responsible for mediating this reaction. We surmised that this solid material provides mild alkaline conditions for the selective hydrolysis of **1** to $C_{60}H_2$; subsequent conversion of $C_{60}H_2$ to C_{60} should be relatively slow, thereby facilitating the selective formation of $C_{60}H_2$ in essentially quantitative yield. To substantiate this assumption, a pure sample of $C_{60}H_2$ was treated similarly with basic Al_2O_3. Under these conditions, $C_{60}H_2$ was indeed converted to C_{60}, albeit at a much lower rate (i.e., several hours, see the Supporting Information for details).

The next set of experiments assessed the reactivity of ketone **11**, which was expected to be different from that of **1** (Figure 1), due to the presence of an aryl instead of an alkyl substituent. Indeed, benzyl ketone **11** was found to be much more reactive than aliphatic ketone **1** as evidenced by the shortening of the time required for completion of the reaction (compare entries 3−8 with 14−18 in Table 1). For example, a 58% conversion of **1** was observed over 16 h, whereas the time required for an almost quantitative conversion of **11** was only 2 h (cf. entries 8 and 17). This result clearly indicates that the susceptibility of the C_{60}-attached carbonyl group toward a nucleophilic attack by a hydroxide anion is directly determined by the α-carbonyl substituent. The lability of the aryl ketone moiety in **11**, by virtue of the resonance stability in the newly formed benzoic acid derivative (the major hydrolysis product, see below), may account for the observed reactivity. In this case, the rapid hydrolysis of **11** to $C_{60}H_2$ combined with the relatively slow conversion of $C_{60}H_2$ to C_{60} results in the accumulation of significant amounts of $C_{60}H_2$ at short reaction times. On the other hand, as seen in Table 1 (cf. entries 15−18), the $C_{60}/C_{60}H_2$ ratio increases over time and C_{60} can be almost quantitatively obtained as the final product at prolonged reaction times in the presence of molecular oxygen. This result corroborates the aforementioned conclusion that molecular oxygen plays an important role in this reaction and that C_{60} is primarily, if not exclusively, derived from $C_{60}H_2$. Moreover, in line with our previous findings, **11** was quantitatively converted into $C_{60}H_2$ upon simple treatment with basic Al_2O_3 (entry 19, Table 1). The practical utility of this latter process, which is largely based on its simplicity, was then established by studying a series of structurally diverse ketones **2**−**10**, **12**, and **13** (Figure 1). An almost quantitative conversion of these substrates to $C_{60}H_2$ was again achieved, indicating the great synthetic potential of this approach in the selective synthesis of the otherwise

SCHEME 2. Proposed Mechanism for the Conversion of Acylated Fullerenes to C_{60} and $C_{60}H_2$



hardly accessible $C_{60}H_2$ (eq 1).

$$\mathbf{1{-}13} \xrightarrow{Al_2O_3} C_{60}H_2 \qquad (1)$$
$$\mathbf{1{-}7}, \mathbf{9{-}13}, > 99\%$$
$$\mathbf{8}, 10\%$$

Another important result obtained from these latter studies concerns the steric effect on the rate of this reaction. This was evidenced by the longer time required for the hydrolysis of ketones **7**−**9** which have secondary or tertiary substitution at the α-carbon, respectively (see Supporting Information). Accordingly, we conclude that this reaction is sensitive to steric, in addition to electronic factors.

Scheme 2 depicts a mechanistic approach for the transformations of acylated fullerene adducts under alkaline conditions, consistent with the results described in the preceding discussion, as well as with previous findings.[20,28] This process should be initiated by nucleophilic attack of a hydroxide anion at the carbonyl carbon, leading to the formation of HC_{60}^- anion and carboxylic acid RCOOH. The fullerene anion acts as a good leaving group, due to the strong electron-withdrawing ability of the fullerene moiety.[28,30] This mechanistic pathway has been experimentally verified by studying the hydrolysis of ketone **12** with 1 M NaOH; in this case, *p*-methoxybenzoic acid, along with a mixture of $C_{60}/C_{60}H_2$, has been isolated as the reaction product (see the Supporting Information for details). On the other hand, the accumulation of $C_{60}H_2$ molecules is giving rise to a second equilibrium process, which is also induced under basic conditions. In this process, hydroxide anions abstract a proton from $C_{60}H_2$ to form $C_{60}H^-$ anion which is then converted to fullerene hydroperoxide $HC_{60}OOH$ via two distinct pathways, both of which involve the intervention of molecular oxygen.[20] In one route, direct electron transfer from $C_{60}H^-$ to O_2 results in two radical intermediates, namely superoxide radical anion ($O_2^{\bullet-}$) and fullerene radical ($HC_{60}^{\bullet}$). Coupling of these radical intermediates and subsequent protonation affords the fullerene hydroperoxide $HC_{60}OOH$. Alternatively, direct nucleophilic addition of fullerene anion (HC_{60}^-) to oxygen followed by protonation results in the same fullerene hydroperoxide $HC_{60}OOH$. Subsequently, the elimination of a H_2O_2 molecule affords fullerene C_{60}. This latter pathway, namely the conversion of $C_{60}H_2$ to C_{60} is much slower in basic Al_2O_3, thus giving selective access to the formation of $C_{60}H_2$ in high yield.

In conclusion, we have shown that acylated [60]fullerenes can be either converted quantitatively to $C_{60}H_2$ or regenerate C_{60} under certain reaction conditions. Regeneration of C_{60} is of fundamental interest as a measure of the chemical stability of several C_{60} compounds, while the synthesis of the simplest fullerene hydride, $C_{60}H_2$, is of considerable practical interest. Thus, the decatungstate-catalyzed acylation of C_{60} followed by hydrolysis represents a new, straightforward, route to the selective synthesis of $C_{60}H_2$. This facile methodology obviates the need for HPLC separation, thus allowing for rapid access to $C_{60}H_2$ through a simplified purification procedure, in high yield and purity.

Experimental Section

Representative experimental procedures are described here. Full experimental details for all reactions can be found within the Supporting Information.

General Procedure for the Synthesis of Acylated Fullerene Adducts 1−13. A solution of C_{60} (20 mg, 0.028 mmol) in a mixture of chlorobenzene/acetonitrile 85:15 (80 mL) was added in a 150-mL glass flask containing a magnetic stirring bar. This solution was degassed by performing three freeze−pump−thaw cycles under argon, and then TBADT (18.5 mg, 0.0056 mmol) and the corresponding aldehyde (2.78 mmol) were added. This solution was subsequently irradiated at ca. 5 °C under argon atmosphere. The progress of all reactions was monitored by HPLC. Then, the solvent and aldehyde were distilled from the reaction mixture under reduced pressure, and the remaining crude product was washed with acetonitrile. The isolated product was further purified by flash column chromatography (hexane/toluene 4:1 v/v) to afford the fullerene adducts **1**−**13** (30−50% isolated yield).

Synthesis of $C_{60}H_2$. Ketone **1** (10 mg, 0.012 mmol) was passed through a long column packed with activated alumina (basic, Brockmann I) to afford $C_{60}H_2$ quantitatively. This simple procedure was similarly applied to ketones **2**−**13**. Again, a quantitative conversion of **2**−**7** and **9**−**13** to $C_{60}H_2$ was readily achieved. Hydrolysis of ketones **7** and **9** to $C_{60}H_2$ was found to be relatively slow. Thus, **7** and **9** were effectively converted to $C_{60}H_2$ after three consecutive passages through a short column of basic alumina. On the other hand, ketone **8** was hardly converted to $C_{60}H_2$ even after consecutive passing of **8** through the alumina column three times (ca. 10% conversion). The isolated yield for this reaction sequence (acylation/hydrolysis) was routinely 30−50% with respect to the starting C_{60} material, being depended on the ketone used. For example, a 50% of $C_{60}H_2$ (0.014 mmol) was isolated via acylation of C_{60} (20 mg, 0.028 mmol) with valeraldehyde followed by hydrolysis. **$C_{60}H_2$:** IR (KBr) ν (cm^{-1}) = 2914, 1426, 1182, 577, 526; UV−vis ($CHCl_3$) λ_{max} (nm) = 257, 328, 405, 433; MS (MALDI, positive, DCTB) *m*/*z* 722; ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.00 (s, 1H); ^{1}H NMR (500 MHz, C_6D_6): δ 5.91 (s, 1H); ^{1}H NMR (300 MHz, ODCB-d_4) δ 6.85 (s, 1H); ^{13}C NMR (ODCB-d_4) δ 152.49, 147.79, 147.40, 146.39, 146.33, 146.11, 145.52, 145.44, 144.73, 143.31, 142.55, 141.98, 141.96, 141.61, 140.38, 136.36, 53.32.

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Supporting Information Available: Detailed experimental procedures, spectral data, ^{1}H and ^{13}C NMR, FT-IR, and UV−vis spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(30) For similar transformations, see: (a) Timmerman, P.; Anderson, H. L.; Faust, R.; Nierengarten, J.-F.; Habicher, T.; Seiler, P.; Diederich, F. *Tetrahedron* **1996**, *52*, 4925–4947. (b) Murata, Y.; Motoyama, K.; Komatsu, K.; Wan, T. S. M. *Tetrahedron* **1996**, *52*, 5077–5090.