

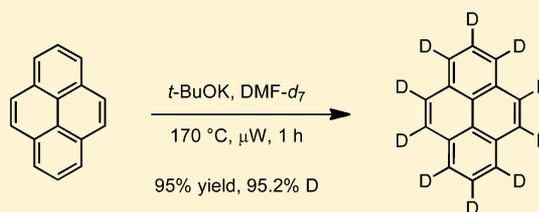
Rapid, Microwave-Assisted Perdeuteration of Polycyclic Aromatic Hydrocarbons

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S Supporting Information

ABSTRACT: A simple and convenient method for the perdeuteration of polycyclic aromatic hydrocarbons that does not require strong acid has been developed. Using commercially available reagents, the one-step procedure provides a new route to perdeuterated derivatives of both common and exotic polycyclic aromatic hydrocarbons. Microwave irradiation of the hydrocarbons in a solution of dimethylformamide- d_7 containing potassium *tert*-butoxide affords rapid and essentially complete H/D exchange. For example, corannulene is converted to corannulene- d_{10} with >98% deuterium incorporation in just 1 h of microwave irradiation in a solution of *t*-BuOK/DMF- d_7 .



Many methods for the efficient H/D exchange of polycyclic aromatic hydrocarbons (PAHs) have been studied in recent years.¹ A variety of metal-,² acid-,³ and base⁴-catalyzed H/D exchange reactions of PAHs have been reported. Furthermore, utilization of near-critical or supercritical D₂O has provided a “green” route to perdeuterated PAHs.⁵ All of these methods, however, typically involve some specialized apparatus, high temperatures, and/or long reaction times. Aiming to provide a general method for the convenient and efficient deuterium exchange of aromatic hydrogen atoms, we have developed a rapid, low-cost method that uses commercially available DMF- d_7 (**1**) as the deuterium source and potassium *tert*-butoxide (**2**) as a basic catalyst.

It has been well-documented that *N,N*-dimethylformamide (DMF) undergoes decomposition to carbon monoxide and dimethylamine in the presence of base, especially at elevated temperatures.⁶ Decomposing DMF with sodium hydride provides a route to sodium dimethylamide, which has been used as a base for a variety of reactions.⁷ One drawback of this method for preparing sodium dimethylamide, however, is that it also evolves hydrogen gas and carbon monoxide gas, which, on scale, is a serious concern. More importantly, the rate of DMF decomposition is fast, but only after an unpredictable incubation period, causing uncontrollable exothermic reactions, even at room temperature.

Owing to these concerns, we examined other bases for the decomposition of DMF. It had been shown that potassium *tert*-butoxide reacts in a controllable manner with DMF and that the solutions can even be heated to elevated temperatures.⁶ The decomposition was expected to generate equal amounts of carbon monoxide, potassium dimethylamide- d_6 (**3**), and *tert*-butyl alcohol- d_1 (**4**), which will equilibrate to form dimethylamine- d_7 (**5**) and **2**, as shown in Scheme 1. It should also be possible to use DMF- d_1 , which would decompose in the presence of **2** to form dimethylamine- d_1 , but the price is comparable to that of DMF- d_7 .

We speculated that this combination of bases, at high temperatures in a highly polar, aprotic solvent, might promote H/D exchange of PAHs by a deprotonation/reprotonation mechanism. Thus, **1** and **2** were combined, a planar or curved polycyclic aromatic hydrocarbon was added, and the mixture was heated by microwave irradiation for 1 h at 170 °C. In every case studied, the corresponding perdeuterated PAH was obtained with a high % deuterium incorporation (Table 1). The facility of this exchange is surprising, in light of the difference of ~20 pK_a units between *tert*-butyl alcohol and benzene,⁸ an aromatic hydrocarbon with C–H bonds similar to those in large PAHs.

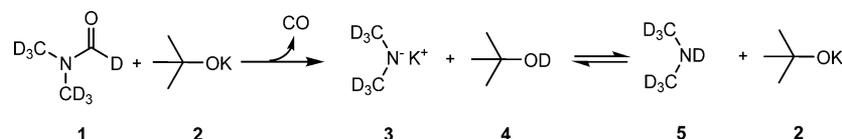
Initial conditions were optimized with pyrene (**6**), a commercially available PAH (see abstract graphic). It was found that 20 equiv of potassium *tert*-butoxide in a 0.20 M solution of **6** in DMF- d_7 under microwave irradiation provides deuterated pyrene (**7**) in 95% yield with 95.2% deuterium incorporation (Table 1, entry 1). This reaction was also run on the benchtop, without microwave heating, in a sealed glass pressure vessel, at 150 °C, for 24 h (entry 2), and the result was identical to that found using microwave irradiation for 1 h.

Analysis of **7** by electron impact mass spectrometry (EI-MS) revealed that the reaction had incorporated 10 deuterium atoms onto pyrene. As shown in Figure 1, pyrene- d_{10} (m/z 212) is the most abundant species in the EI-MS; however, lesser amounts of pyrene- d_9 (m/z 211), pyrene- d_8 (m/z 210), and pyrene- d_7 (m/z 209) can also be detected in the product mixture. In order to determine the efficiency of this H/D exchange process, deuterium incorporation was determined quantitatively using integration of the ¹H NMR spectrum with an internal standard, which allowed for quantification of any residual hydrogen

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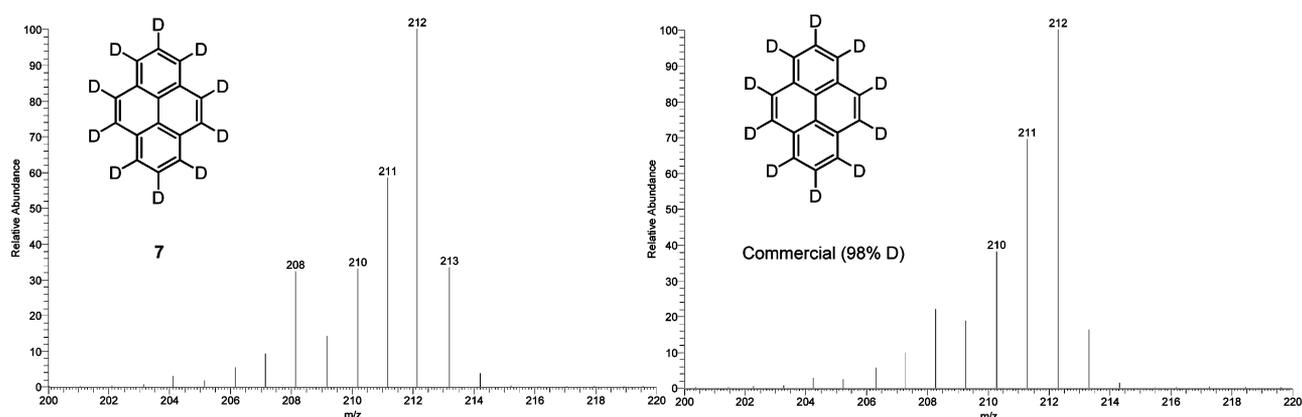
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Scheme 1. Decomposition of DMF- d_7 by Potassium *tert*-ButoxideTable 1. H/D Exchange of Polycyclic Aromatic Hydrocarbons^a

Entry	PAH	Time (h)	Temp. (°C)	Product	Yield (%)	% D ^b
1		1	170 ^c		95	95.2
2		24	150 ^d		95	95.0
3		1	170 ^c		75	94.4
4		1	170 ^c		80	>98
5		1	170 ^c		71	95.5

^aReaction conditions: 20 equiv of *t*-BuOK (sublimed) and [0.20 M] DMF- d_7 . ^bDeuterium incorporation was determined by ¹H NMR integration with 1,3,5-trimethoxybenzene as an internal standard. ^cReaction was run in a microwave reactor. ^dReaction was run in a pressure vessel.

Figure 1. EI-MS of pyrene- d_{10} .

atoms present in the mixture. This analysis indicated a 95.2% deuterium incorporation for 7.

Further optimization of this method, aiming to exchange the remaining hydrogen atoms in the product mixture with deuterium, was explored. It was found that a decrease in the reaction time under microwave irradiation led to diminished

deuterium incorporation. Conversely, increasing the reaction time did not result in an increase in deuterium incorporation. Pyrene- d_{10} was then resubjected to the same reaction conditions again. Curiously, however, the H/D ratio was not significantly improved. Increasing the amount of solvent (1) and/or increasing the equivalents of the base (2) likewise failed

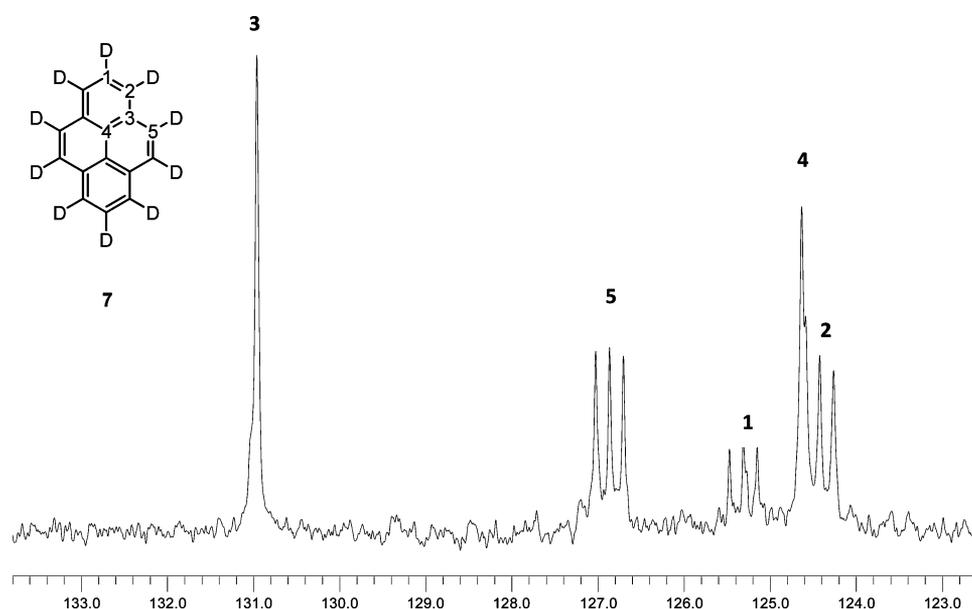


Figure 2. ^{13}C NMR of pyrene- d_{10} (150 MHz, CDCl_3 , no proton decoupling, 300 pulses, 60 s pulse delay).

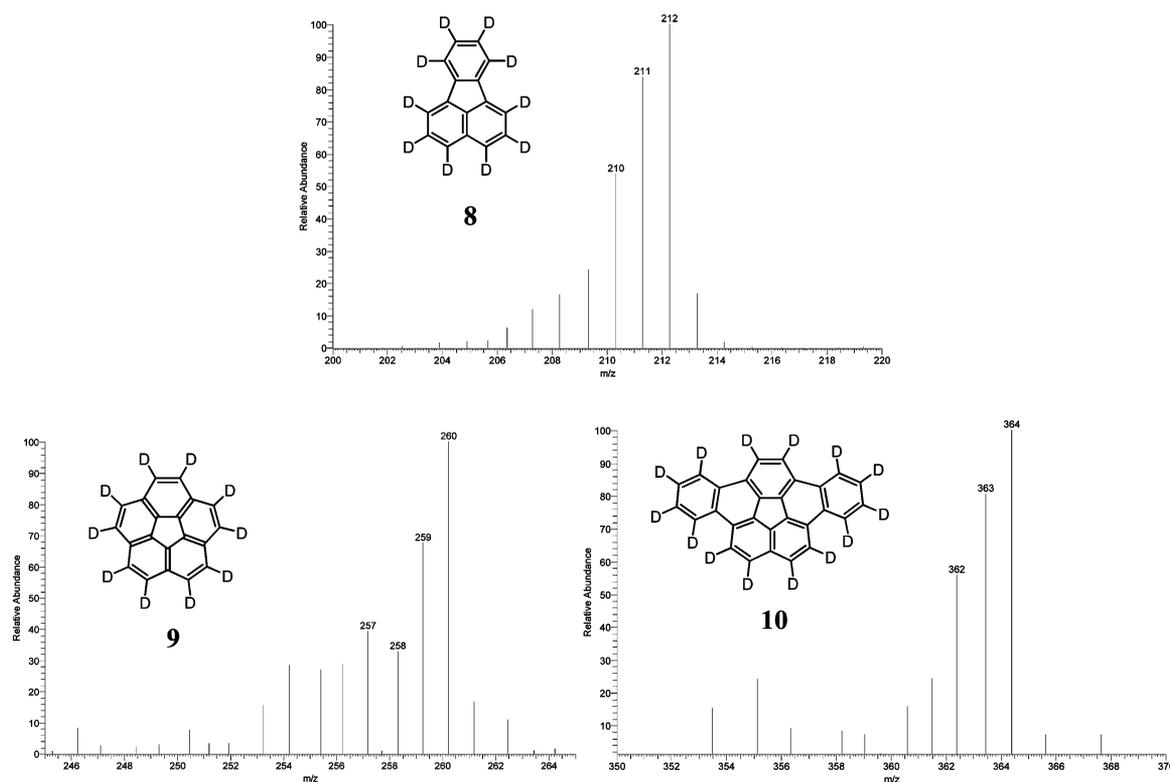


Figure 3. EI-MS of perdeuterated polycyclic aromatic hydrocarbons.

to improve the percent of deuterium incorporation. It was further determined that the purity and moisture content of the base (**2**) play a significant role in the percent of deuterium incorporation; best results were obtained with freshly sublimed **2** or with freshly opened, commercially available sublimed **2**.

The product mixture was analyzed by two different mass spectrometric methods; EI-MS and high-resolution DART-TOF. The two independent methods show almost identical ratios of peak heights, which indicates that the D/H ratio is probably not eroding in the mass spectrometer during the analysis. As another confirmation, commercially available **7**

(98% D) was analyzed, and it was found to have a mass spectrum comparable to that of **7** prepared by the present method (Figure 1). The commercially available **7** was also analyzed by ^1H NMR, with an internal standard, and was confirmed to have a deuterium incorporation of 98.6%. ^{13}C NMR spectroscopic analysis of the deuterated pyrene prepared under our new conditions (Figure 2) confirms the incorporation of 10 deuterium atoms in the majority of the molecules.

This method is not limited to pyrene. It was also applied to another commercially available PAH, fluoranthene. Fluoranthene- d_{10} was prepared under the same conditions as **7** in a

75% yield with 94.4% deuterium incorporation (Table 1, entry 3). The method was further applied to less generic PAHs, specifically, geodesic polyarenes, which have been utilized as building blocks for organic electronic materials. Applying this simple and convenient method to these larger, curved polycyclic aromatic hydrocarbons enabled the synthesis of perdeuterated compounds that were not previously accessible so easily by other methods.⁹ The perdeuteration of two geodesic polyarenes was explored. Corannulene¹⁰ and dibenzo[*a,g*]corannulene¹¹ are both curved polycyclic aromatic hydrocarbons that have attracted widespread interest for a variety of synthetic and materials applications. Accessing these molecules in their perdeuterated form will allow further studies of these molecules as synthetic intermediates. Applying the potassium *tert*-butoxide/DMF-*d*₇/microwave irradiation conditions to both corannulene (Table 1, entry 4) and dibenzo[*a,g*]corannulene (Table 1, entry 5) affords the corresponding perdeuterated geodesic polyarenes in good yields with high deuterium incorporation. All compounds were again analyzed by EI-MS (Figure 3), and the degree of deuterium incorporation was determined by ¹H NMR analysis with the same internal standard.

Thus, a convenient and relatively inexpensive method for the preparation of perdeuterated polycyclic aromatic hydrocarbons has been developed. Using commercially available reagents and short reaction times, both common and exotic perdeuterated PAHs are now easily accessible. Most importantly, this method affords efficient H/D exchange, delivering deuterium incorporation levels comparable to those found in commercially available perdeuterated standards (Figure 1). The ease, convenience, short reaction times, and accessibility of reagents presage a wide variety of applications of this method in the future.

EXPERIMENTAL SECTION

All chemicals were purchased and used without further purification unless otherwise noted. Deuterated materials, *N,N*-dimethylformamide-*d*₇ (99.5% D) and pyrene-*d*₁₀ (98% D), were purchased from Cambridge Isotope Laboratories; independent analysis of these materials by ¹H NMR integration with an internal standard and EI-MS confirmed the percent deuterium incorporation. Potassium *tert*-butoxide (sublimed grade, 99.99% trace metals basis) was purchased from Aldrich and stored sealed under nitrogen in a desiccator. Exposure to moisture resulted in diminished deuterium incorporation. Potassium *tert*-butoxide that was freshly sublimed in our laboratory worked just as well as freshly opened, sublimed grade potassium *tert*-butoxide purchased from Aldrich. Microwave irradiation was performed with a CEM Discover LabMate reactor with the IntelliVent pressure control system; temperatures of the reaction mixtures were monitored by a vertically focused IR temperature sensor and not by an internal temperature probe. EI-MS data were obtained with a unit resolution quadrupole mass spectrometer. High-resolution mass spectrometry was performed using a DART time-of-flight mass spectrometer. NMR shifts are referenced in parts per million downfield from TMS, using chloroform-*d*₁ ($\delta_{\text{H}} = 7.26$ ppm, $\delta_{\text{C}} = 77.23$ ppm). ¹³C NMR spectra were recorded at 125 MHz with no proton decoupling and a 60 s pulse delay. Deuterium incorporation was determined by ¹H NMR integration (500 MHz) with 1,3,5-trimethoxybenzene as an internal standard. For example, pyrene-*d*₁₀ (0.0573 mmol) and 1,3,5-trimethoxybenzene (0.00238 mmol) were mixed in 0.70 mL of CDCl₃. The residual hydrogen signals from pyrene-*d*₁₀ were integrated (8.5 per 1H) versus the internal standard (7.34 per 1H). From the integration, the number of moles of residual hydrogen present in the pyrene-*d*₁₀ sample was calculated based on the known moles of the internal standard and found to be 0.00276 mmol. The moles of residual hydrogen present in the pyrene-*d*₁₀ sample (0.00276 mmol)

were divided by the total number of moles of pyrene-*d*₁₀ (0.0573 mmol), providing the percent residual hydrogen (4.8% H). Chromatography was performed with Sorbent Technologies silica gel (porosity = 60 Å, particle size = 32–63 μm).

Pyrene-1,2,3,4,5,6,7,8,9,10-*d*₁₀ (7). To a flame-dried, nitrogen-purged 10 mL microwave vessel equipped with a magnetic stir bar were added 50.0 mg (0.248 mmol) of pyrene and 1.00 mL of dimethylformamide-*d*₇. The mixture was stirred, and sublimed potassium *tert*-butoxide was added (0.555 g, 4.95 mmol). The microwave vessel was capped and placed in a microwave reactor for 1 h at 170 °C. The mixture was cooled to room temperature and immediately flushed through a short pad of silica gel with dichloromethane as the eluent. Evaporation of the solvent provided 49.9 mg (95%) of deuterated pyrene as a tan solid. ¹H NMR analysis (500 MHz, CDCl₃) with 1,3,5-trimethoxybenzene as an internal standard showed 95.2% deuterium incorporation. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.21 (s, 4H), 8.10 (s, 4H), 8.03 (s, 2H). ¹³C NMR (125 MHz, CDCl₃, no proton decoupling, 300 pulses, 60 s pulse delay) δ (ppm): 130.9 (s), 126.8 (t, *J* = 24.0 Hz), 125.3 (t, *J* = 24.5 Hz), 124.6 (s), 124.4 (t, *J* = 24.0 Hz). See Figure 1 for EI-MS data. HRMS (DART-TOF): calcd for C₁₆HD₁₀ (*M* + 1)⁺ 213.1488, found 213.1490. DART-TOF % deuterium incorporation: 45% *d*₁₀:38% *d*₉:8.5% *d*₈.¹²

Fluoranthene-1,2,3,4,5,6,7,8,9,10-*d*₁₀ (8). The same general procedure above was used with fluoranthene (50.0 mg, 0.248 mmol), 1.00 mL of dimethylformamide-*d*₇, and sublimed potassium *tert*-butoxide (0.555 g, 4.95 mmol) to afford 39.0 mg (75%) of deuterated fluoranthene as a tan solid. ¹H NMR analysis (500 MHz, CDCl₃) with 1,3,5-trimethoxybenzene as an internal standard showed 94.4% deuterium incorporation. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.99–7.97 (m), 7.95 (s), 7.93–7.92 (m), 7.85 (s), 7.64 (s), 7.39 (s). ¹³C NMR (125 MHz, CDCl₃, no proton decoupling, 376 pulses, 60 s pulse delay) δ (ppm): 139.1 (s), 136.6 (s), 132.2 (s), 129.6 (s), 127.2 (t, *J* = 23.9 Hz), 126.9–126.6 (m), 125.9 (t, *J* = 24.0 Hz), 121.2–120.8 (m), 119.2 (t, 24.0 Hz). See Figure 3 for EI-MS data. HRMS (DART-TOF): calcd for C₁₆D₁₀ (*M*⁺) 212.1410, found 212.1418.

Corannulene-1,2,3,4,5,6,7,8,9,10-*d*₁₀ (9). The same general procedure above was used with 20.0 mg (0.0800 mmol) of corannulene, 0.40 mL of dimethylformamide-*d*₇, and sublimed potassium *tert*-butoxide (0.179 g, 1.60 mmol) to afford 16.7 mg (80%) of deuterated corannulene as a tan solid. ¹H NMR analysis (500 MHz, CDCl₃) with 1,3,5-trimethoxybenzene as an internal standard showed >98% deuterium incorporation. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.77 (s, 10H). ¹³C NMR (125 MHz, CDCl₃, no proton decoupling, 3184 pulses, 60 s pulse delay) δ (ppm): 134.9 (s), 125.6 (t, *J* = 22.0 Hz). See Figure 3 for EI-MS data. HRMS (DART-TOF): calcd for C₂₀D₁₀ (*M*⁺) 260.1410, found 260.1411.

Dibenzo[*a,g*]corannulene-1,2,3,4,5,6,7,8,9,10,11,12,13,14-*d*₁₄ (10). The same general procedure above was used with 20.0 mg (0.0571 mmol) of dibenzo[*a,g*]corannulene, 0.30 mL of dimethylformamide-*d*₇, and sublimed potassium *tert*-butoxide (0.128 g, 1.14 mmol) to afford 14.7 mg (71%) of deuterated dibenzo[*a,g*]corannulene as a tan solid. ¹H NMR analysis (500 MHz, CDCl₃) with 1,3,5-trimethoxybenzene as an internal standard showed 95.5% deuterium incorporation. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.73–8.66 (m), 8.34 (s), 8.26 (m), 7.98 (m), 7.78 (s). ¹³C NMR (125 MHz, CDCl₃, no proton decoupling, 2696 pulses, 60 s pulse delay) δ (ppm): 135.8 (s), 134.8 (s), 134.1 (s), 133.0 (s), 132.9 (s), 130.0 (s), 128.5 (s), 128.3 (s), 126.8–126.2 (m), 125.6–125.3 (m), 124.7–123.9 (m). See Figure 3 for EI-MS data. HRMS (APPI): calcd for C₂₈D₁₄ (*M*⁺) 364.1968, found 364.1959.

ASSOCIATED CONTENT

Supporting Information

All ¹H NMR and ¹³C spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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