

Synthetic and Mechanistic Aspects of Acid-Catalyzed Disproportionation of Dialkyl Diarylmethyl Ethers: A Combined Experimental and Theoretical Study

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The disproportionation reactions of various dialkyl diarylmethyl ethers have been carried out in the presence of a catalytic amount (10 mol-%) of *o*-benzenedisulfonimide as a Brønsted acid catalyst; the reaction conditions were mild, and the yields of the diarylmethane target products were good. The catalyst was easily recovered and purified, ready to be used in further reactions. The theoretical study confirmed

that the reaction proceeds in two steps: The formation of a carbocation from the protonated ether followed by hydride transfer. Although the hydride transfer is the rate-determining step, it is the stability of the carbocation that determines the reaction rate and therefore the yields.

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Introduction

We recently reported the use of *o*-benzenedisulfonimide (**1**; Figure 1) in catalytic amounts as a safe, non-volatile, and noncorrosive Brønsted acid in some acid-catalyzed organic reactions such as etherification,^[1] esterification,^[1,2] acetalization,^[1] and the Nazarov electrocyclozation^[3] under very mild and selective conditions. The catalyst was easily recovered and purified, ready to be used in further reactions with economic and ecological advantages.

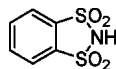
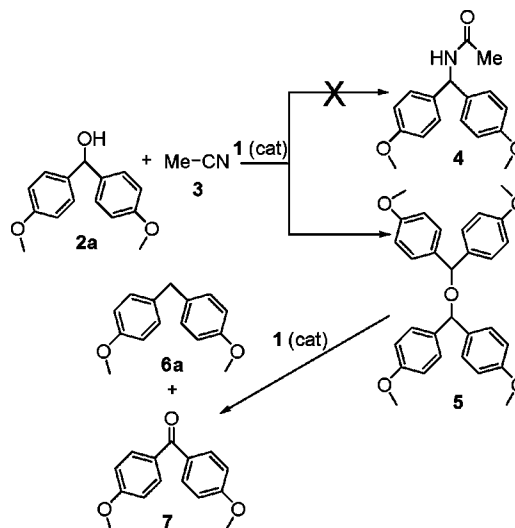


Figure 1. *o*-Benzenedisulfonimide (**1**).

In a recent paper we reported the results of a study of the Ritter reaction^[4] between various alcohols and nitriles in the presence of **1** as catalyst.^[5] In particular, on treatment of bis(4-methoxyphenyl)methanol (**2a**) with acetonitrile (**3**) in the presence of 10 mol-% of **1** no traces of the Ritter product **4** were observed, but we obtained an approximately 1:1 mixture of bis(4-methoxyphenyl)methane (**6a**) and 4,4'-dimethoxybenzophenone (**7**) derived from a disproportionation reaction of the intermediate bis[bis(4-methoxyphenyl)methyl] ether (**5**; Scheme 1). It is known from the literature that diarylmethyl isopropyl ethers under catalytic acid con-

ditions, typically using trifluoroacetic acid, undergo disproportionation with selective hydride transfer to form the corresponding diarylmethanes and acetone.^[6]



Scheme 1. Disproportionation of bis[bis(4-methoxyphenyl)methyl] ether (**5**).

It has also been reported that diphenylmethyl isopropyl ether is transformed into the corresponding diphenylmethane in good yields by using supercritical isopropyl alcohol at 350 °C.^[7]

Moreover, various diarylmethanols or benzylic alcohols can undergo disproportionation reactions, but they require strong acidic activation and/or harsh conditions and give equimolar amounts of arylalkanes or diarylmethanes and the corresponding aldehydes or ketones.^[8]

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Apart from this, there are four main methods for the synthesis of diarylmethanes:^[9] (1) The reduction of diaryl ketones, (2) Friedel–Crafts alkylation, (3) transition-metal-catalyzed coupling of either a benzyl halide with an aryl-metal species or an aryl halide with a benzylmetal species, and (4) the addition of organometallic reagents to aldehydes and subsequent reduction. The preparation of diarylmethanes is an important synthetic goal as the diarylmethane unit is present in molecules of biological, medicinal, or pharmacological interest,^[10] supramolecular structures such as macrocycles, catenanes, and rotaxanes,^[11] chain extenders in polymers,^[12] and intermediates in the preparation of di- and triaryl dyes, for example, malachite green lactone and crystal violet.^[13]

Results and Discussion

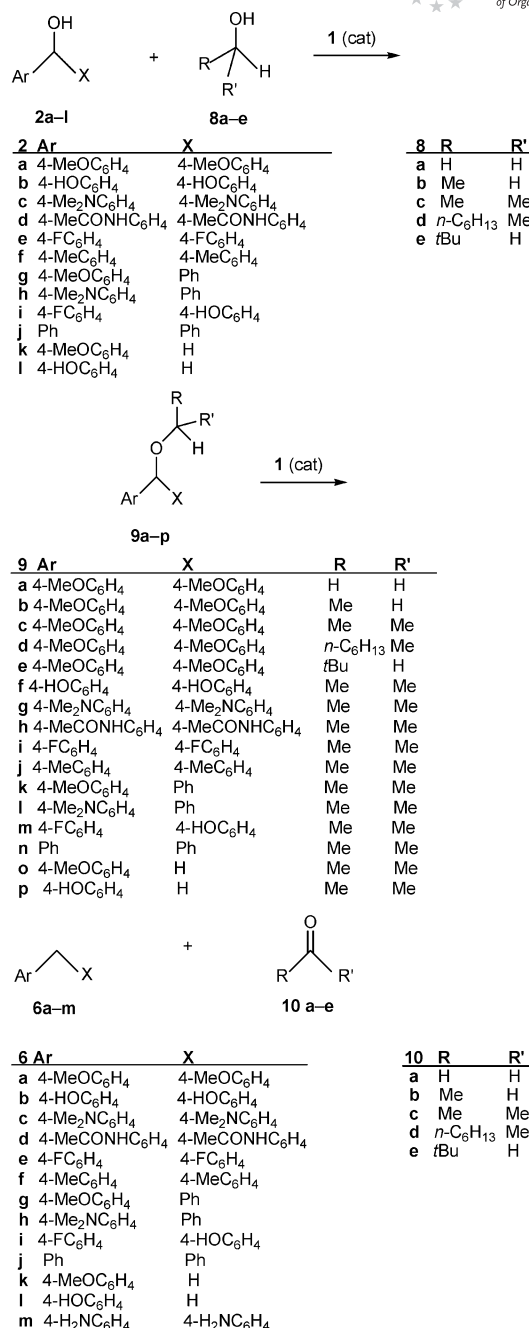
Hence, in this paper we wish to propose the disproportionation reaction of various dialkyl diarylmethyl ethers **9a–p**, synthesized in situ by treating diarylmethanols or benzylic alcohols **2a–l** with alcohols **8a–e** in the presence of **1** as catalyst (Scheme 2).

First, we treated **2a** with **8a–e** in the presence of 10 mol-% of **1**; the preliminary results are reported in Table 1.

On heating of **2a** and **8c** in approximately equimolar amounts in the presence of 10 mol-% of **1** at 80 °C for 3 h we obtained a quantitative yield of **6a** (Entry 3). Furthermore, **1** was recovered in excellent yield (91%) by simply concentrating the aqueous layer and washings under reduced pressure, as reported in the Experimental Section. By monitoring the progress of the reaction by GC and GC/MS it was possible to verify the immediate formation of **9c** and its gradual disappearance in parallel with the immediate appearance and gradual increase of **6a**. To check the possibility of using the ethers **9a,b,d,e** in the disproportionation reactions, the reaction was performed by using **8a** instead of **8c** (Entry 1). We observed the immediate formation of **9a**, but no disproportionation reaction occurred. In fact, after 24 h of heating, no traces of **6a** were detected. In the reaction with **8b** we obtained almost the same results, although, after 24 h, traces of **6a** were detected by GC/MS analysis (Entry 2).

We also used **8d** and **8e**, and the reactions were complete after 2 and 8 h, respectively, with the formation of a quantitative yield of **6a** (Entries 4 and 5). However, it was necessary to perform column chromatography to separate **6a** from ketone **10d**. On the basis of the above results, the best reaction conditions involve the use of **8c**.

To compare the catalytic activity of **1** we treated **2a** with **8c** in the presence of 10 mol-% of six different Brønsted acids. The results, reported in Table 2, show that in all six cases the formation of **9c** is almost immediate, but the disproportionation reaction is slower, and only with 2,4-dinitrobenzenesulfonic acid and HBF₄·OEt₂ did we observe the complete disappearance of **9c** (Entries 5 and 6).



Scheme 2. Disproportionation of dialkyl diarylmethyl ethers **9a–p**.

Having found the optimal conditions, we used the same conditions in the reactions of diarylmethanols **2b–i**; the results are reported in Table 3. Excellent results were obtained with identical (Entries 1–6) or different (Entry 9) electron-donating groups on aromatic rings; also in Entries 7 and 8 with only one electron-donating group we also achieved good yields of unsymmetrical diarylmethanes **6g,h**, although the reaction times were longer.

The reaction did not occur in the absence of electron-donating groups. In fact, in Entry 10, while monitoring the progress of the reaction with GC and GC/MS, we immediately observed the formation of **9n** and the disappearance

Table 1. Preliminary reactions.

Entry	Reactants	Products, yield ^[a,b] [%]	Time [h]
1	2a, 8a	6a , –	24
2	2a, 8b	6a , traces	24
3	2a, 8c	6a , 100 ^[c]	3
4	2a, 8d	6a , 100 ^[d]	2
5	2a, 8e	6a , 100 ^[e]	8

[a] The reactions were performed at 80 °C. [b] The yields refer to the pure products. [c] In the GC/MS analysis of the crude residue, acetone (**10c**; $m/z = 58$ [M]⁺) was detected. Clearly, it was not possible to isolate this due to its volatility. [d] Octan-2-one (**10d**; $m/z = 128$ [M]⁺, 0.58 g, 90% yield) was also isolated by flash chromatography on a short column (eluent: petroleum ether/diethyl ether, 9:1). [e] In the GC/MS analysis of the crude residue, 2,2-dimethylpropanal (**10e**; $m/z = 86$ [M]⁺) was detected. However, it was not possible to isolate it due to its volatility.

Table 2. Reactions of **2a** and **8c** with various Brønsted acids.

Entry	Acid	Yields ^[a,b,c] [%]		Time [h]
		6a	9c	
1	HCOOH	traces	95	24
2	CF ₃ COOH	40	45	24
3	MeSO ₃ H	80	19	24
4	4-MeC ₆ H ₄ SO ₃ H	79	20	24
5	2,4-(O ₂ N) ₂ C ₆ H ₃ SO ₃ H	95	–	8
6	HBF ₄ ·Et ₂ O	77	–	22
7	1	100	–	3

[a] The reactions were performed at 80 °C with 5 mmol of **2a** and 5.5 mmol of **8c**. [b] The yields refer to the pure products. [c] Compounds **6a** and **9c** were isolated by flash chromatography on a short column (eluent: petroleum ether/diethyl ether, 9:1). Isopropyl bis(4-methoxyphenyl)methyl ether (**9c**): Colorless oil. ¹H NMR (200 MHz, CDCl₃, 25 °C): $\delta = 7.40$ and 6.98 (2 d, 1:1, $J = 8.76$ Hz, 4 H), 5.57 (s, 1 H), 3.84 (s, 6 H), 3.83 – 3.73 (m, 1 H), 1.36 (d, $J = 6.11$ Hz, 6 H) ppm. ¹³C NMR (50 MHz, CDCl₃, 25 °C): $\delta = 159.1$, 135.8 , 128.6 , 114.0 , 79.9 , 69.0 , 55.4 , 22.6 ppm. MS (EI): $m/z = 286$ [M]⁺. C₁₈H₂₂O₃ (286.37): calcd. C 75.50, H 7.74; found C 75.52, H 7.80.

Table 3. Disproportionation reactions.

Entry	Reactants ^[a]	Products, yields ^[b] [%]	Time [h]	m/z for [6]⁺
1	2a	6a , 100	3	228
2	2b	6b , 100	3	200
3	2c	6c , 92	8	254
4	2d	6d , ^[c] 89	8	282
5	2e	6e , 97	8	204
6	2f	6f , 100	5	196
7	2g	6g , 90	24	198
8	2h	6h , 85	36	211
9	2i	6i , 92	6	202
10	2j	6j , traces ^[d]	24	168
11	2k	6k , traces	24	124
12	2l	6l , traces	24	138

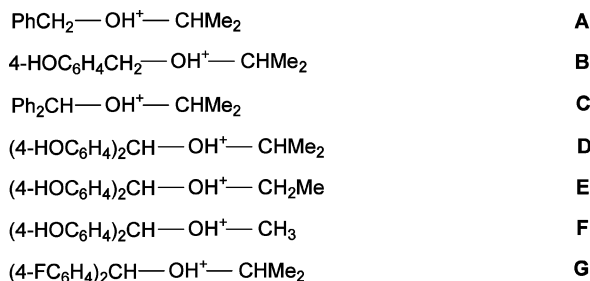
[a] All the reactions were performed with **8c** at 80 °C. [b] The yields refer to the pure products. [c] Product **6d** was hydrolyzed as reported in the literature^[14] to give bis(4-aminophenyl)methane (**6m**), as reported in the Experimental Section. [d] The reaction was also performed at 150 °C with **8d**. After 24 h, GC/MS analysis showed diphenylmethyl 1-methylheptyl ether ($m/z = 296$ [M]⁺) as the main product as well as traces of **6k**.

of **2j**, but, after 24 h of heating, we detected only traces of **6j**. Even with **8d** and heating at reflux (about 150 °C) we obtained the same results.

We also attempted the reactions between benzylic alcohols **2k,l** and **8c**, but we obtained disappointing results. We observed by GC and GC/MS the immediate formation of the ethers **9o,p**, but, after 24 h of heating, only traces of **6k,l** were detected, and no disproportionation reactions occurred.

The acid-catalyzed disproportionation of diaryl ethers^[15] was first observed by Kny-Jones and Ward in 1930.^[16] A two-step mechanism via the protonated ether carbocation followed by hydride transfer was proposed in the 1950s.^[17,18] More recently, Provot and co-workers^[6] stated that the reaction occurs after a selective disproportionation of the ether by a concerted selective hydride transfer, as in the Meerwein–Ponndorf–Verley reduction. However, the role of acid catalysis in that article was not clearly explained.

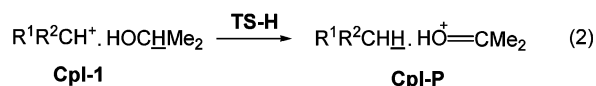
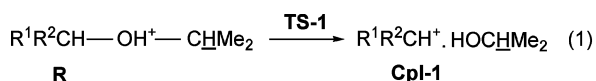
To elucidate the mechanism and rationalize the experimental results described above we performed a theoretical study. We started by assuming the protonated ethers obtained from some diarylmethanols or benzylic alcohols and isopropyl alcohol (**8c**) to be the reactants. Four cases were studied in detail (Scheme 3): **A**, **B** (corresponding to the protonated ether **9p**), **C** (protonated ether **9n**), and **D** (protonated ether **9f**). The energies of the products only were also calculated for the disproportionation of the ethers obtained from bis(4-hydroxyphenyl)methanol and ethanol (**8b**; case **E**) and methanol (**8a**; case **F**). These ethers were not studied experimentally but by inspection of Table 3 we can safely assume that the hydroxyphenyl group behaves like the methoxyphenyl group. A the final case, **G** (protonated ether **9i**) was also partially studied.



Scheme 3. Protonated ethers used for the theoretical study.

In all cases the reaction was found to take place in two steps (Scheme 4 and Figure 2). In step (1) we observe the decomposition (**TS-1**) of the protonated ether (**R**) and the formation of a complex (**Cpl-1**) between the aromatic carbocation and the isopropyl alcohol. The second step is the hydride transfer (**H**) from the alcohol to the carbenium ion (**TS-H**) yielding a complex (**Cpl-P**) between the substituted methane and the protonated acetone. With the exception of case **A**, the hydride transfer is the rate-determining step, confirmed by the observation of an isotope effect (1.8–2.6).^[18]

The second aromatic ring and the hydroxy groups stabilize the carbocations. These become less reactive with an increase in the energy barrier for the hydride transfer (from less than 1 kcal mol⁻¹ in case **A** to 8 kcal mol⁻¹ in case **D**).



Scheme 4. Reaction mechanism for the disproportionation of protonated ethers.

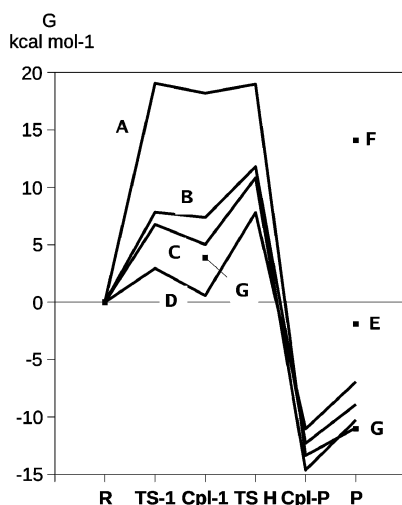


Figure 2. Potential solvated free-energy profiles for the disproportionation of protonated ethers $\text{R}^1\text{R}^2\text{CH}-\text{OH}^+-\text{CHR}^a\text{R}^b$. For R^1 , R^2 , R^a , and R^b (A–G) see Scheme 3.

However, this effect is overwhelmed by the strong lowering of the whole energy profile. Therefore, stabilization of the carbocations seems to be required to obtain good yields. We found the most stable carbocation in case **D**, which leads to the fastest reaction: The energy of **TS-H** is less than 8 kcal mol^{-1} above the protonated ether **R**, and the yield of the disproportionation is in fact 100% after 3 h (Table 3, Entry 2). In cases **B** and **C**, the relative energies of the **TS-Hs** are $11\text{--}12 \text{ kcal mol}^{-1}$ above the corresponding reactant, and the reaction yields are less than 2% after 24 h (Table 3, Entries 12 and 10, respectively). Case **A** was not studied experimentally, but from Figure 2 we can clearly expect no products. Bartlett and McCollum^[18] observed that a more stable protonated ketone will lead to a larger rate constant. In case **E** the reaction is only slightly exoergic: Products are found less than 2 kcal mol^{-1} below the protonated ether **R**, whereas in cases **A–D** they are found 7 kcal mol^{-1} or more below **R**. By assuming an energy barrier for the reverse hydride transfer equal to the value found for the same carbocation (case **D**, ca. $14\text{--}15 \text{ kcal mol}^{-1}$) we can estimate the energy of **TS-H** for case **E** to be around $12\text{--}13 \text{ kcal mol}^{-1}$. This would lead to a yield close to that found for cases **B** and **C**, which is in fact less than 2% after 24 h (Table 1, Entry 2). In case **F** the reaction is endoergic, and products were not found even in trace amounts (Table 1, Entry 1). However, it must be stressed that the exoergicity of the reaction is not sufficient a condition. Case **A** should be a favored reaction because the product is found to be

11 kcal mol^{-1} below **R**, but the reaction yield is very poor, confirming the determinant role of the stabilization of the carbocation. This role is confirmed in case **G**: The complex formed between the fluoroaromatic carbocation and the isopropyl alcohol (**Cpl-1**) is energetically between those formed in cases **C** and **D** (4 kcal mol^{-1}). Thus, a yield of 97% is obtained, but after 8 h (Table 3, Entry 5). The stabilizing effect of the fluorine atoms on the carbocation is not surprising if we consider that it presents a small negative σ^+ value (-0.07).

Conclusions

The advantages of performing the disproportionation reactions of ethers **9** in the presence of **1** as catalyst can be summarized as follows: (1) Use of a safe, nonvolatile, non-corrosive Brønsted acid, (2) very good recovery of **1** at the end of the reactions simply by removing aqueous washings by evaporation, and (3) target products **6** are obtained in excellent yields under easy and mild reaction conditions. It must be stressed that in these easy operative conditions we obtained in excellent yields products **6c** and **6m**, which are important intermediates as chain extenders in polymers^[11] or in the preparation of di- and triaryl dyes, for example, malachite green lactone and crystal violet.^[13] They are most commonly synthesized in low yields by the acid-catalyzed condensation reaction of anilines with formaldehyde.^[19] The theoretical study confirmed that the reaction proceeds in two steps: The formation of a carbocation from the protonated ether followed by hydride transfer. Although the latter is the rate-determining step, the whole reaction rate is determined by the stability of the carbocation: The more stable ions lead to a lower potential energy profile and therefore a faster reaction. The formation of a stable protonated ketone is also a preliminary condition but is not the determining factor.

Experimental Section

General: All reactions were conducted in open-air vials. Analytical-grade reagents and solvents were used, and reactions were monitored by GC and GC/MS. Mass spectra were recorded with an HP 5989B mass-selective detector connected to an HP 5890 GC and using a cross-linked methyl silicone capillary column. Petroleum ether (PE) refers to the fraction boiling in the range $40\text{--}70 \text{ }^\circ\text{C}$. ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance 200 spectrometer at 200 and 50 MHz, respectively. *o*-Benzenedisulfonamide (**1**) was prepared as reported in the literature;^[20] diarylmethanols **2b,d,h,i** were prepared by reduction of commercially available benzophenones with LiAlH_4 or NaBH_4 , as described in the literature.^[21] All other diarylmethanols **2a,c,e–h**, benzylic alcohols **2i,j**, and alcohols **8a–e** were purchased from Sigma–Aldrich. The structures and purities of the diarylmethanes **6a–f,m** were confirmed by comparison of their physical and spectroscopic data with those of available commercial samples (Sigma–Aldrich). The physical and spectroscopic data of **6g,h** are identical to those reported in the literature.^[22a,22b] Satisfactory microanalyses were obtained for the new compounds **6i** and **9c**.

Representative Procedure for the Disproportionation Reaction. Synthesis of Bis(4-methoxyphenyl)methane (6a): *o*-Benzenedisulfonimide (**1**; 10 mol-%; 0.11 g, 0.5 mmol) was added to a mixture of bis(4-methoxyphenyl)methanol (**2a**; 1.22 g, 5 mmol) and propan-2-ol (**8c**, 0.30 g, 5.5 mmol). The mixture was stirred at 80 °C. The reaction was monitored by GC and GC/MS; after 15 min, **2a** had disappeared, and both isopropyl bis(4-methoxyphenyl)methyl ether (**9c**; $m/z = 286$ [M]⁺) and the title compound **6a** ($m/z = 228$ [M]⁺) were observed. As the reaction progressed, GC and GC/MS analyses showed that **9c** decreased and **6a** increased. After 3 h, **6a** remained, and acetone (**10c**; $m/z = 58$ [M]⁺) could also be observed. The reaction mixture was poured into diethyl ether/water (1:1, 100 mL). The aqueous layer was separated and extracted with diethyl ether (2 × 50 mL). The combined organic extracts were washed with water (2 × 50 mL), dried with Na₂SO₄, and concentrated under reduced pressure. The crude residue (1.14 g, 100% yield) was virtually pure **6a** (GC, GC/MS, ¹H NMR). The aqueous layer and aqueous washings were collected and concentrated under reduced pressure. After removal of water, virtually pure (¹H NMR) *o*-benzenedisulfonimide (**1**) was recovered [0.10 g, 91% yield; m.p. 192–194 °C (toluene; ref.^[19] m.p. 192–194 °C)].

(4-Fluorophenyl)(4-hydroxyphenyl)methane (6i): Colorless oil. ¹H NMR (200 MHz, CDCl₃, 25 °C): $\delta = 8.78$ (br. s, 1 H) 7.70–7.67 and 7.08–7.03 (2 m, 1:1, 4 H), 7.62 and 6.84 (2 d, 1:1, $J = 8.75$ Hz, 4 H), 3.95 (s, 2 H) ppm. ¹³C NMR (50 MHz, CDCl₃, 25 °C): $\delta = 165.1$ (d, $^1J_{CF} = 251.5$ Hz), 161.2, 134.6 (d, $^4J_{CF} = 3.0$ Hz), 132.8, 132.3 (d, $^3J_{CF} = 9.0$ Hz), 129.1, 115.5, 115.3 (d, $^2J_{CF} = 15.5$ Hz), 46.6 ppm. MS (EI): $m/z = 202$ [M]⁺. C₁₃H₁₁FO (202.23): calcd. C 77.21, H 5.48, F 9.39; found C 77.22, H 5.51, F 9.44.

Hydrolysis of 6d: As reported in the literature,^[14] Fe(NO₃)₃·9H₂O (0.40 g, 1.0 mmol) was added to a solution of **6d** (0.56 g, 2.0 mmol) in MeOH (10 mL). The reaction mixture was stirred at room temperature for 24 h. The solvent was then removed under reduced pressure, and the crude residue was poured into diethyl ether/water (1:1, 100 mL). The aqueous layer was separated and extracted with diethyl ether (2 × 50 mL). The combined organic extracts were washed with water (2 × 50 mL), dried with Na₂SO₄, and concentrated under reduced pressure. The residue was virtually pure (GC, GC/MS, ¹H NMR) bis(4-aminophenyl)methane (**6m**, 0.35 g, 88% yield). M.p. 90–92 °C (MeOH). MS (EI): $m/z = 198$ [M]⁺, identical to a commercial sample (Sigma–Aldrich).

Theoretical Methods: The theoretical study was performed by using density functional theory (DFT)^[23] making use of the mPWB1K functional.^[24] This functional was developed by Truhlar and co-workers for the accurate evaluation of energy barriers. All geometries were fully optimized with the 6-311+G(d,p) basis set^[25a,25b] and characterized by vibrational frequency analysis.^[26] Single-point energy calculations were performed with the 6-311+(3df,2p) basis set,^[25b,25c] including the electrostatic and nonelectrostatic solvent effects with the polarized continuum method.^[27] Finally, these data were combined with the gas-phase zero-point energy corrections. All energy values are reported in the Supporting Information. Calculations were performed by using the Gaussian 03 program.^[28]

Supporting Information (see footnote on the first page of this article): Total (in a.u.) and relative (in kcal mol⁻¹) energies and nuclear coordinates (in Å).

Acknowledgments

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