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Carbenes in polycyclic systems: generation and fate of potential adamantane-1,3-dicarbenes

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Potential formation and reactions of adamantane-1,3-dicarbenes 1–3 generated under different conditions and from different precursors, such as sodium salt of adamantane-1,3-dicarbaldehyde ditosylhydrazone (4a), sodium salt of 1,3-diacetyladamantane ditosylhydrazone (5a), sodium salt of 1,3-dibenzoyladamantane ditosylhydrazone (6a), and 1,3-bis(diazobenzyl)adamantane (7) are reported. Carbene species generated thermally from 4a yielded bishomoadamantane (15), as a final product, via intramolecular insertion into adjacent C—C bond and formation of putative anti-Bredt olefin species, followed by hydrogen abstraction. Pyrolysis of the same sodium salt 4a in the presence of hydrogen donor n-Bu₃SnH afforded 1,3-dimethyladamantane (17). Thermal decomposition of sodium salt 5a afforded 1,3-divinyladamantane (14). However, thermal decomposition of sodium salt 6a and diazo-precursor 7 gave benzonitrile as a sole identified product. On the contrary, photolysis of 7 afforded dimeric azine 21. Finally, the synthetic pathways of novel tosylhydrazone derivatives 4, 5, 6 and their corresponding sodium salts, as well as bis-diazocompound 7 are described. Copyright © 2008 John Wiley & Sons, Ltd.

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INTRODUCTION

Carbene-intermediates have been the subject of extensive experimental and theoretical investigation.^[1–5] Carbenes, which are readily generated by decomposition of corresponding diazocompounds, are versatile synthetic intermediates in organic chemistry. For example, intramolecular carbene cycloaddition to the olefinic bond has been used as a successful strategy for preparation of small ring propellanes.^[6–13] Likewise, the carbene route has been employed for generation of bridgehead double bonds as in anti-Bredt olefins.^[14] Bridgehead double bonds are readily accommodated in larger ring systems, but in the small rings they are unstable.^[15] The bridgehead-olefin carbene rearrangement has also been documented.^[16–22] Recently, we reported the evidence for the formation of mono- and dialkylidene species.^[23,24,25] The reactivity profile of carbene and dicarbene species is highly dependent on the carbene structure.

In order to gain insight into the chemical reactivity of alkyldicarbene species, we studied the generation and reactions of potential adamantane-1,3-dicarbenes 1-3. By introduction of two potential carbene centers onto the adamantane framework, we were able to study both the possibility of simultaneous ringexpansion to its higher homologue and the introduction of two double bonds into bridgehead positions of the parent system. Carbenes were generated via pyrolysis of corresponding precursors [i.e., dry sodium salt of adamantane-1,3dicarbaldehyde *p*-toluenesulfonylhydrazone (**4a**), sodium salt of 1,3-diacetyladamantane *p*-toluenesulfonylhydrazone (**5a**), sodium salt of 1,3-dibenzoyladamantane *p*-toluenesulfonylhydrazone (**6a**), and 1,3-bis(diazobenzyl)adamantane (**7**)] *in vacuo*, or by photolysis of bis-diazocompound **7** in benzene solution.

RESULTS AND DISCUSSION

The routes to prepare the carbene precursors **4a**, **5a**, **6a**, and **7** are shown in Scheme 1. The synthesis started from 1,3-dibromoadamantane via corresponding diacid **8** and dialdehyde **10** or diketones **11** and **12**. Hitherto unknown dicarbonyl compounds **10**, **11**, and **12** were converted in a high yield to new corresponding tosylhydrazones **4**, **5**, and **6**. Subsequent conversion to their tosylhydrazone sodium salts **4a**, **5a**, and **6a**, was achieved using our previously developed procedure.^[11,12] Novel bis-diazo precursor **7** was prepared in 75% overall yield via reaction of **12** with hydrazine monohydrate followed by oxidation of dihydrazone **13** with BaMnO₄^[26] in the presence of CaO.

Flash vacuum pyrolysis of dry Na-salts 4a and 5a were carried out at 210°C and $1\times10^{-3}\,mm$ Hg. The products were collected

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Scheme 1.

into a trap cooled by liquid nitrogen, dissolved in C_6D_6 and analyzed by NMR and GC-MS. Pyrolysis of **5a** (Scheme 2) afforded 1,3-divinyladamantane (**14**) as a sole product in 42% yield. Olefin **14** forms as a product of 1,2-CH insertion which is favored to C—C insertion when both reactions are possible.^[2,4,5]

Therefore we presumed, that by having the carbon-hydrogen bonds at a larger distance from the carbene center, as it is in carbene species **1**, the carbon-carbon insertion reaction will be preferred, enabling us to test the generation of anti-Bredt olefin. However, a problem that could arise here stems from the fact that **1** has several bonds for ring-expansion. Carbene insertion into different C—C bonds would lead to the formation of several related bridgehead alkenes (Scheme 3).

The ¹H NMR spectrum of the product obtained by pyrolysis of Na-salt **4a** was complex, but all signals were in the aliphatic region showing no olefinic protons. We hypothesized that two carbene centers subsequently underwent carbene-rearrangements which are known to take place through exclusive migration of the shorter bridges.^[27,28] Hypothesized highly strained and reactive anti-Bredt intermediates would tend to

achieve stabilization through hydrogen abstraction leading to the formation of saturated bishomoadamantane product. Given that bishomoadamantane 15 is a stable product of high symmetry and a product of migration into a shorter bridge, it seemed likely that 15 would be the main product. Analysis of the crude product by GC-MS exhibited a single peak with mass M⁺(164) and some polymers which appeared at high temperature. To test our hypothesis, an authentic sample of bishomoadamantane 15^[29] was prepared and compared with the product obtained by pyrolysis of 4a. MS fragmentation patterns as well as GC-retention time (compared by two different capillary columns, HP-5 and DB-210) proved identical with the data obtained for the authentic sample of 15 prepared from 2,6-adamantanedione. When Na-salt 4a was subjected to the pyrolysis with simultaneous introduction of n-Bu₃SnH into the system, 1,3-dimethyladamantane (17) was obtained as the sole hydrocarbon product. The formation of bishomoadamantane 15 and 1,3-dimethyladamantane (17) entails the generation of either dicarbene species 1 or sequential formation of monocarbene species as shown in Scheme 3.



Scheme 2.



Scheme 3.

To achieve stabilization of putative bridgehead olefin through conjugative effect, phenyl-substituted precursors **6a** and **7** were prepared. The introduction of substituents to bridgehead olefins is believed to alter their stability and reactivity. Schleyer^[15] and Jones^[30] proposed that replacement of the vinyl hydrogen by bulky groups with steric protection or substituents which provide electronic stabilization could aid the formation of observable species. In that regard, Eguchi *et al.*^[31] reported conjugative stabilization of the double bond at the bridgehead of homoadamantene through the 1,2-C shift of 1-adamantylcarbene intermediate generated from (1-adamantyl)diazophenylmethane. However, flash vacuum pyrolysis of Na-salt **6a**, at 210°C under reduced pressure (~1 × 10⁻³ mm Hg) afforded benzonitrile (**18**) as the only isolated product (Scheme 4). To exclude the fragmentation of Na-salt **6a** prior to the formation of diazo-precursor **7**, we prepared pure **7** by a direct method (refer to Experimental section for details) and carried out the vacuum pyrolysis at 600° C (Scheme 5).









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A benzene solution of **7** was injected into a quartz tube inserted into an oven preheated to 600° C. The quartz tube was connected to the vacuum line $(1 \times 10^{-1} \text{ mm Hg})$ and product was collected in a trap cooled by liquid nitrogen. Again, analysis of the product showed **18** to be the main product apart from some polymers and traces of unidentified material.

Based on these results, we propose the formation of monocarbene intermediate species **19** which undergoes intramolecular gas phase reaction with the second diazo-group to yield cyclic azine **20** as shown in Scheme 5. Subsequent homolytic cleavage of azine **20** at higher temperature affords benzonitrile (**18**) and adamantane-diradical which polymerizes.

To generate carbene species 3 photochemically, a benzene solution of 7 was irradiated with a high-pressure Hg-lamp through a Pyrex filter until the red color of the diazo-compound completely disappeared. The product obtained in 88% yield was identified as azine-dimer 21 (Scheme 5). The ¹H and ¹³C NMR spectra of the product were identical to the spectra of the azine 21 obtained by the coupling reaction of the dihydrazone 13 and diketone 12 performed in refluxing xylene and catalyzed with p-toluenesulfonic acid.^[32] Since the product was stable toward thermolysis in solution at 140°C, a control experiment under conditions of flash vacuum pyrolysis was carried out. Likewise, when azine-dimer 21 was subjected to the pyrolysis at 210°C and 0.5×10^{-3} mm Hg, no benzonitrile was obtained, and **21** was recovered quantitatively. However, pyrolysis of azine 21 at 600°C and 1×10^{-1} mm Hg led to homolytic cleavage whereupon benzonitrile was obtained as the sole volatile product.

CONCLUSIONS

The potential generation of two carbene centers attached to the 1,3-bridgehead position of an adamantane system such as 1 has been investigated. The results can be interpreted such that, in the gas-phase and absence of trapping reagent, pyrolysis of sodium salt 4a generates potential dicarbene 1, which is forced to undergo insertion reaction into adjacent C-C bonds of adamantane framework leading to generation of an anti-Bredt olefin, 1,8-bishomoadamantanediene. Stabilization by hydrogen abstraction leads to the formation of bishomoadamantane 15, as confirmed by comparison with authentic sample. On the contrary, when sodium salt 4a was subjected to the pyrolysis in the presence of trapping reagent (n-Bu₃SnH) 1,3-dimethyladamantane (17) was formed possibly as a product of hydrogen abstraction by adamantane-1,3-dicarbene (1). Pyrolysis of sodium salt **5a** produced 1,3-divinyladamantane (**14**)^[33] in 41.3% vield, possibly as the product formed by 1,2-H shift reaction from adamantane dicarbene 2. However, the consecutive reaction and formation of monocarbene species like 1a, 1b and 1c or 2a and 2b cannot be excluded. All of the products can be rationalized by sequential reactions of monocarbenes as well as by reactions of dicarbenes. Generation of dicarbene species 3 proved to be unsuccessful both by pyrolysis of sodium salt **6a** and corresponding 1,3-bis(diazobenzyl)adamantane (7) or by photolysis of 7. The formed products, azines 20 and 21, suggest that gas-phase pyrolysis of **6a** and **7** proceed through the formation of monocarbene intermediate 19, which then reacts intramolecularly with the second diazo-group to yield cyclic azine **20**. On the other hand, photolysis of bis-diazo precursor 7 affords monocarbene **19** which in solution reacts intermolecularly furnishing azine-dimer 21 as the only product.

EXPERIMENTAL

General

The purity of all compounds was determined by GC and/or ¹³C NMR spectral analysis. GC analyses were performed using a Varian 3380 gas chromatograph equipped with either a DB-210 or a DB-1701 capillary column. GC-MS analyses were performed on a HP 5890-II, MSD 5970 equipped with HP-5 column (25 m \times 0.2 mm), operated over temperature range 60–250°C. ¹H and ¹³C NMR spectra were recorded on 300 MHz and 600 MHz Brucker spectrometers using TMS or CDCl₃ as the internal standard. IR spectra were recorded on a Perkin Elmer M-297 and ABB Bomem M-102 spectrophotometers. UV-spectra were recorded on 100 Bio UV/VIS spectrophotometers. Melting points were determined on a Koffler apparatus or Electrothermal 9100 and are uncorrected. Elemental microanalyses were performed on Perkin Elmer Series II CHNS/O Analyzer 2400. Adamantane-1,3dicarboxylic acid^[34] and the dimethyl ester of adamantane-1,3dicarboxylic acid^[35] were prepared according to the literature procedures. Unless stated otherwise, reagent grade solvents were used.

1,3-bis(hydroxymethyl)adamantane (9)

To a suspension of LiAlH₄ (1.56 g, 41.8 mmol) in dry THF (200 ml) was added dropwise a solution of dimethyl ester of adamantane-1,3-dicarboxylic acid (2.63 g, 10.5 mmol) in dry THF (150 ml) and the mixture was heated to reflux. After 70 h of reflux, the reaction mixture was cooled down to rt and diluted with THF (70 ml). The excess of LiAlH₄ was quenched with water (13 ml), THF solution was decanted off and the white solid was washed with THF (2 × 30 ml). Organic extracts were dried over anhydrous MgSO₄, filtered, and evaporated to give **9** as a colorless crystalline solid (1.776 g, 86.7%): mp 181°C (lit.^[35] 180.5–182.0°C); ¹H NMR (CD₃OD) δ 1.24 (s, 2H), 1.40–1.55 (m, 8H), 1.66 (br.s, 2H), 2.06 (br.s, 2H), 3.14 (s, 4H); ¹³C NMR (CD₃OD) δ 30.0 (d, 2C), 36.2 (t, 1C), 38.0 (t, 1C), 40.1 (t, 4C), 42.0 (s, 2C), 74.0 (t, 2C); IR (KBr) $\tilde{\nu}$ 3264 (s), 2898 (s), 2844 (s), 1452 (m), 1045 (s), 1026 (m) cm⁻¹.

Adamantane-1,3-dicarbaldehyde (10)

To a suspension of pyridinium chlorochromate (PCC; 0.850 g, 4.0 mmol) in CH₂Cl₂ (~10 ml) was added a suspension of **9** (0.196 g, 1.0 mmol) in dry THF (~5 ml). The reaction mixture was stirred at rt for 2.5 h, whereupon it was diluted with dry diethyl ether (~50 ml) and filtered through a plug of florisil. The filtrate was evaporated *in vacuo* to afford **10** (0.183 g, 95%). According to GC analysis (DB 210, 150°C) product **10** had a purity of over 95%. Since dialdehyde **10** is unstable and decomposes on silica gel, it was used in the next step without further purification. ¹H NMR (CDCl₃) δ 1.60–1.84 (m, 12H), 2.29 (br.s, 2H), 9.39 (s, 2H); ¹³C NMR (CDCl₃) δ 26.6 (d, 2C), 34.2 (t, 1C), 35.0 (t, 4C), 35.3 (t, 1C), 44.5 (s, 2C), 204.4 (d, 2C); IR (KBr) $\tilde{\nu}$ 2910 (s), 2850 (m), 2800 (w), 2700 (w), 1720 (s), 1450 (m) cm⁻¹.

Adamantane-1,3-dicarbaldehyde ditosylhydrazone (4)

To a solution of **10** (0.317 g, 1.7 mmol) in abs. MeOH (8 ml) was added *p*-toluenesulfonylhydrazine (0.672 g, 3.3 mmol) in small portions and the reaction mixture was stirred at rt for 2 days. The progress of the reaction was monitored by TLC (2% MeOH in CH_2Cl_2). After the reaction was completed, water (20 ml) was

added and the resulting white suspension was extracted with diethyl ether (3 × 20 ml). The combined organic extracts were dried over anhydrous MgSO₄, filtered and concentrated *in vacuo* to give crude **4** (1.108 g). Further purification by column chromatography on silica gel (0–3% MeOH in CH₂Cl₂) yielded **4** (0.824 g, 92%) as a white microcrystalline solid: mp 163–165°C; ¹H NMR (CD₃OD) δ 1.40–1.75 (m, 14H), 2.12 (s, 2H), 2.50 (s, 6H), 7.03 (s, 2H), 7.46 (d, 4H, *J* = 7.6 Hz), 7.83 (d, 4H, *J* = 7.6 Hz); ¹³C NMR (CD₃OD) δ 21.8 (2C), 29.4 (2C), 36.8 (1C), 38.5 (1C), 40.2 (4C), 42.7 (2C), 129.2 (4C), 130.8 (4C), 137.5 (2C), 145.5 (2C), 159.5 (2C); IR (KBr) $\tilde{\nu}$ 3160 (s), 2900 (s), 2840 (s), 1620 (w), 1590 (m), 1480 (w), 1430 (s), 1350 (s), 1310 (s), 1150 (s) cm⁻¹; Anal. Calcd. for C₂₆H₃₂N₄S₂O₄ (528.70): C, 59.07; H, 6.10; N, 10.60. Found: C, 59.06; H, 6.04; N, 10.80.

Preparation and pyrolysis of sodium salt of adamantane-1,3-dicarbaldehyde ditosylhydrazone (4a)

To a solution of **4** (0.351 g, 0.664 mmol) in dry THF (3.5 ml) was added NaH (50% dispersion in mineral oil, 0.063 g, 1.31 mmol) in small portions over 2 h at rt. The solvent was removed under reduced pressure, and the crude product was additionally dried under high vacuum ($\sim 1 \times 10^{-3}$ mm Hg) for several hours. The dry **4a** (1.0 mmol) was pyrolyzed at 210°C and 1×10^{-3} mm Hg for 20 min. The volatile product was collected into a trap cooled by liquid nitrogen and subsequently dissolved in C₆D₆ (0.5 ml) under a nitrogen atmosphere. The crude product was analyzed by GC-MS (as in Supplementary data).

1,3-Diacetyladamantane (11)

Adamantane-1,3-dicarbaldehyde (0.231 g, 1.2 mmol) was dissolved in dry THF (10 ml) under a nitrogen atmosphere and cooled to 0°C. To the resulting solution was added dropwise 2 M solution of CH₃Li in hexane (1.2 ml, 2.4 mmol). The reaction mixture was stirred for 48 h at rt, quenched with saturated aqueous NH₄Cl (15 ml) and water (5 ml) and extracted with diethyl ether (4 \times 30 ml). The combined organic extracts were dried over anhydrous MgSO₄, filtered, and concentrated in vacuo to afford 0.183 g (65%) of the crude product. The crude product was dissolved in CH₂Cl₂ (5 ml), and added in small portions to a solution of pyridinium chlorochromate (0.707 g, 3.3 mmol) in CH₂Cl₂ (5 ml). The reaction mixture was stirred at rt for 2 h and then was diluted with dry diethyl ether (\sim 50 ml), and filtered through a small plug of florisil. The organic filtrate was concentrated in vacuo to give 0.180 g of the mixture of products which, according to GC (DB-210, 150°C) contained 60% of diacetyladamantane. Purification by column chromatography on silica gel (10-30% diethyl ether in pentane) yielded 11 (0.137 g, 51.8%) as a white solid. Analytical sample of 11 was obtained by sublimation: mp 52°C; ¹H NMR (CDCl₃) δ 1.66–1.85 (m, 12H), 2.11 (s, 6H), 2.18–2.23 (br.s, 2H); ¹³C NMR (CDCl₃) δ 24.3 (d, 2C), 27.7 (q, 2C), 35.3 (t, 1C), 37.3 (t, 4C), 38.4 (t, 1C), 46.5 (s, 2C), 212.8 (s, 2C); IR (KBr) $\tilde{\nu}$ 2931 (w), 2905 (w), 2851 (w), 1707 (s), 1450 (m), 1343 (m), 1252 (m), 1191 (s), 596 (s) cm⁻¹; Anal. Calcd. for C₁₄H₂₀O₂ (220.31): C, 76.33; H, 9.15. Found: C, 76.47; H, 9.11.

1,3-Diacetyladamantane ditosylhydrazone (5)

To a solution of **11** (0.137 g, 0.6 mmol) in abs. MeOH (2.5 ml) was added *p*-toluenesulfonylhydrazine (0.236 g, 1.2 mmol) in small portions. The solution was stirred at rt for 24 h. The reaction was monitored by TLC (2% MeOH in CH_2CI_2). While stirring, a white

residue precipitated out of the reaction mixture. The residue was collected by filtration, washed with MeOH and dry diethyl ether to yield **5** (0.345 g, 100%) as a white powder: mp 217–219°C; ¹H NMR (CD₃OD) δ 1.28 (s, 2H), 1.45–1.73 (m, 18 H, with strongly expressed singlet at 1.72 (CH₃)), 2.06 (br.s, 2H), 2.41 (s, 6H), 7.35 (d, 4H, J = 8.3 Hz), 7.81 (d, 4H, J = 8.3 Hz); ¹³C NMR (CD₃OD) δ 11.9 (d, 2C), 21.8 (q, 2C), 30.0 (q, 2C), 37.1 (t, 1C), 40.1 (t, 4C), 42.6 (t, 1C), 42.7 (s, 2C), 129.7 (d, 4C), 130.5 (d, 4C), 137.6 (s, 2C), 145.3 (s, 2C), 165.6 (s, 2C); IR (KBr) $\tilde{\nu}$ 3230 (s), 2920 (m), 2850 (w), 1600 (w), 1340 (s), 1160 (s) cm⁻¹; Anal. Calcd. for C₂₈H₃₆N₄S₂O₄ (556.75): C, 60.41; H, 6.52; N, 10.06. Found: C, 60.52; H, 6.53; N, 10.23.

Preparation and pyrolysis of sodium salt of 1,3-diacetyladamantane ditosylhydrazone (5a)

To a suspension of NaH (50% dispersion in mineral oil; 0.112 g, 2.3 mmol) in dry THF (4 ml) heated to 60°C was added 5 (0.493 g, 0.9 mmol) in small portions. After 2 h at 60°C, the reaction mixture was cooled to rt and the solvent was removed in vacuo. The product was additionally dried under high vacuum $({\sim}1\times10^{-3}\,\text{mm\,Hg})$ for 2 h and the resulting salt was used in the pyrolysis without further purification. The dry 5a (1 mmol) was heated at 210°C and $1\times 10^{-3}\,\text{mm\,Hg}$ for 20 min, during which, salt changed its color from white to pink. The volatile product was collected in a liquid nitrogen cooled trap, and the product was dissolved in C₆D₆ under a nitrogen atmosphere. Analysis of the crude product by GC (DB 210, 100°C, 1 min; 10°C/ min; 200°C) showed the presence of one product with 90% purity. Purification of the crude product by chromatography on neutral Al₂O₃ (activity 1) with pentane as the eluent afforded 1,3-divinyladamantane (14) as a colorless oil (0.069 g, 41.3%). Spectral data for 14¹H NMR, ¹³C NMR and IR, were identical with published data ^[33] (as in Supplementary Data).

1,3-Dibenzoyladamantane (12)

A solution of **8** (1.5 g, 6.7 mmol) in SOCl₂ (15 ml) was refluxed overnight. Evaporation of excess of SOCl₂ afforded adamantane-1,3-dicarboxylic acid dichloride as a white solid (1.726 g, 99%), which was characterized by IR spectroscopy: IR (KBr) $\tilde{\nu}$ 2915 (m), 2863 (m), 1794 (s), 1455 (s), 1446 (s), 1061 (s), 1040 (s), 943 (s), 833 (s), 670 (s) cm⁻¹. The compound was used in the next step without further purification due to its instability.

To the magnesium turnings (0.488 g, 20.1 mmol) in dry diethyl ether (7 ml) was added dropwise a solution of bromobenzene (2.1 ml, 20.1 mmol) in dry diethyl ether (10 ml) under a nitrogen atmosphere, and the reaction mixture was stirred at rt. The reaction mixture changed color from turbid white to brown. After addition of the reagent had been completed, the resulting mixture was refluxed until the magnesium turnings disappeared. Reaction mixture was cooled in an ice bath and to the suspension was added CdCl₂ (1.842 g, 10 mmol) in several portions within 10 min. After the addition of CdCl₂ had been completed, mixture was heated to reflux for 1.5 h. The mixture was cooled down to rt and the solvent was removed under vacuum. The residue was suspended in dry benzene (15 ml), a solution of adamantane-1,3-dicarboxylic acid dichloride (1.73 g, 6.6 mmol) in dry benzene (15 ml) was added dropwise, and the reaction mixture was refluxed overnight. The reaction mixture was poured on the ice and subsequently was added 10% sulfuric acid (20 ml). Organic layer was separated and the aqueous layer was extracted with diethyl ether (4 \times 25 ml). The combined organic extracts

were washed with water (25 ml) and dried over anhydrous MgSO₄. Solvent was removed *in vacuo* and the resulting residue was purified by column chromatography on silica gel (0–10% ethyl acetate in hexane). Fractions eluted with 100% hexane afforded biphenyl (0.062 g) as a side product, while fractions eluted using (3–5%) ethyl acetate in hexane afforded compound **12** (1.87 g, 81.9%) as a colorless crystalline solid: mp 108–110°C; ¹H NMR (CDCl₃) δ 1.75 (br.s, 2H), 1.95–2.12 (m, 8H), 2.27 (br.s, 4H), 7.37–7.49 (m, 6H), 7.54–7.60 (m, 4H); ¹³C NMR (CDCl₃) δ 28.0 (d, 2C), 35.3 (t, 1C), 38.1 (t, 4C), 40.0 (t, 1C), 47.1 (s, 2C), 127.0 (d, 4C), 127.9 (d, 4C), 130.4 (d, 2C), 138.9 (s, 2C), 208.8 (s, 2C); IR (KBr) $\tilde{\nu}$ 2934 (m), 2891 (m), 2854 (w), 1660 (s), 1444 (m), 1241 (m), 917 (m), 707 (m), 651 (m) cm⁻¹; Anal. Calcd. for C₂₄H₂₄O₂ (344.46): C, 83.69; H, 7.02. Found: C, 83.74; H, 6.76.

1,3-Dibenzoyladamantane ditosylhydrazone (6)

To a solution of 12 (0.580 g, 1.7 mmol) in abs. MeOH (8 ml) was added p-toluenesulfonylhydrazine (0.939 g, 5.0 mmol) in small portions and the reaction mixture was stirred at reflux for 4 days. The reaction was monitored by TLC (2% MeOH in CH₂Cl₂). While stirring, a white residue precipitated out of the reaction mixture. The residue was collected by filtration, washed with methanol and diethyl ether to afford product 6 (0.938 g, 82%) as a white powder solid: mp 172–174°C; ¹H NMR (DMSO- d_6) δ 1.31–1.54 (m, 12H), 1.97 (br.s, 2H), 2.39 (s, 6H), 6.87 (br.s, 4H), 7.36 (d, 4H, J = 7.6 Hz), 7.42 (br.s, 6H), 7.69 (d, 4H, J = 7.6 Hz), 9.27 (br.s, 2H); ¹³C NMR (CDCl₃) δ 21.6 (q, 2C), 27.9 (d, 2C), 35.1 (t, 1C), 38.7 (t, 4C), 40.6 (s, 2C), 41.5 (t, 1C), 127.5 (d, 4C), 127.7 (d, 4C), 129.2 (d, 4C), 129.3 (d, 2C), 129.4 (d, 4C), 130.8 (s, 2C), 135.2 (s, 2C), 143.9 (s, 2C), 164.3 (s, 2C); IR (KBr) $\tilde{\nu}$ 3276 (w), 3208 (w), 2927 (m), 2904 (m), 2854 (w), 1598 (w), 1442 (w), 1385 (m), 1338 (m), 1168 (s), 704 (m), 674 (m), 555 (s) cm⁻¹; Anal. Calcd. for C₃₈H₄₀N₄S₂O₄ (680.89): C, 67.03; H, 5.92; N, 8.23. Found: C, 66.56; H, 5.60; N, 8.06.

Preparation and pyrolysis of sodium salt of 1,3-dibenzoyladamantane ditosylhydrazone (6a)

To a suspension of 6 (0.681 g, 1.0 mmol) in dry THF (5 ml) was added NaH (50% dispersion in mineral oil, 0.096 g, 2.0 mmol) in small portions during 2 h at rt. Upon addition of NaH, stirring was continued for additional 20 min, whereupon solvent was removed in vacuo. Crude product was dried under high vacuum $(\sim 1 \times 10^{-3} \text{ mm Hg})$ for several hours. The salt was used in the pyrolysis without further purification. The dry 6a (1 mmol) was pyrolyzed at 210°C and 1×10^{-3} mm Hg for 10 min during which the salt changed its color from white to pink. Volatile products were collected in a trap cooled by liquid nitrogen, and the resulting crude product was dissolved in benzene under a nitrogen atmosphere. Analysis of the crude product by GC (DB 210, 60°C, 10 min; 15°C/min; 200°C) and GC-MS (HP-5) showed the presence of benzonitrile and polymeric material. Benzonitrile was confirmed by comparison of the GC and GC-MS analysis of the authentic sample: GC-MS (HP-5; 60°C, 10 min; 15°C/min; 250°C); $t_{\rm R} =$ 14.01; m/e: 103 (M⁺ 100%), 76 (39%), 50 (23%).

1,3-Dibenzoyladamantane dihydrazone (13)

A solution of **12** (1.0 g, 2.9 mmol) and hydrazine monohydrate (2.8 ml, 58 mmol) in abs. EtOH (25 ml) was refluxed for 4 days. The solvent was removed *in vacuo* and the resulting solid purified by

column chromatography on silica gel (50–80% EtOAc in hexane) to yield **13** (0.827 g, 76.4%), as a white solid: mp 169.7–173.3°C; ¹H NMR (CDCl₃) δ 1.4–1.8 (m, 12H), 2.0 (s, 2H), 4.7 (s, 4H), 6.8–7.5 (m, 10H); ¹³C NMR (CDCl₃) δ 28.5 (d, 2C), 35.7 (t, 1C), 39.4 (t, 4C), 39.8 (s, 2C), 42.8 (t, 1C), 128.0 (d, 4C), 128.2 (d, 4C), 128.7 (d, 2C), 133.1 (s, 2C), 159.8 (s, 2C); IR (KBr) $\tilde{\nu}$ 3369 (m), 2925 (s), 2897 (s), 2848 (s), 1621 (w), 1491 (w), 1439 (w), 1073 (w), 1021 (w), 712 (s) cm⁻¹; Anal. Calcd. for C₂₄H₂₈N₄ (372.51): C, 77.38; H, 7.58; N, 15.04. Found: C, 76.96; H, 7.83; N, 14.98; MS El M⁺ calcd. 372.2308, found 372.2309.

In some reactions besides **13**, the sideproduct, 1-(phenylcarbinol)-3-benzoyladamantane hydrazone, was formed in various percentage (from 13.6 to 36.3%): mp 208.9–210°C; ¹H NMR (CDCl₃) δ 1.19–2.29 (m, 14H), 4.25 (s, 1H), 4.78 (s, 2H), 6.94-7.33 (m, 10H); ¹³C NMR (CDCl₃) δ 28.3 (d, 2C); 36.0 (t, 1C); 36.5 (t, 1C); 37.4 (s, 1C); 37.7 (s, 1C); 39.7 (t, 2C); 41.0 (t, 2C); 82.5 (d, 1C); 127.2 (d, 1C); 127.4 (d, 2C); 127.6 (d, 2C); 128.0 (d, 1C); 128.2 (d, 2C); 128.8 (d, 2C); 133.2 (s, 1C); 140.9 (s, 1C); 160.1 (s, 1C); IR (KBr) $\tilde{\nu}$ 3403 (s), 3304 (m), 2901 (s), 2847 (s), 1490 (m), 1449 (m), 709 (s) cm⁻¹.

1,3-bis(diazobenzyl)adamantane (7)

To a suspension of a barium manganate (BaMnO₄; 0.635 g, 2.48 mmol) and powdered CaO²⁶ (0.959, 17.1 mmol) in dry THF (10 ml) was added a solution of **13** (0.115 g, 0.31 mmol) in dry THF (10 ml) under a nitrogen atmosphere. The reaction mixture was stirred at rt for 1 h. Filtration of solids and evaporation of the solvent afforded **7** (0.111 g, 98.2%), as a red-wine colored oil. IR spectrum with characteristic absorption band at 2031 cm⁻¹ confirmed formation of diazo-compound **7** which was used in the further experiments without purification. ¹H NMR (C₆D₆) δ 1.30-2.10 (m, aliphatic H), 6.92–7.30 (m, Ph-H); ¹³C NMR (C₆D₆) δ 29.3 (d, 2C), 33.1 (t, 1C), 35.6 (s, 2C), 40.1 (t, 4C), 44.4 (t, 1C), 124.7 (d, 2C), 125.8 (d, 4C), 129.2 (d, 4C), 131.1 (s, 2C); IR (KBr) $\tilde{\nu}$ 2901 (s), 2848 (s), 2031 (m), 1655 (m), 1449 (m), 1025 (m), 737 (s) cm⁻¹; UV (EtOH) $\lambda_{max/nm}$ (log ε): 501.2 (1.18).

Pyrolysis of 1,3-bis(diazobenzyl)adamantane (7)

Diazo-compound **7** (1.0 mmol) was subjected to the pyrolysis at 600°C under reduced pressure $(1 \times 10^{-1} \text{ mm Hg})$. Volatile products were collected in a trap cooled by liquid nitrogen, and subsequently dissolved in benzene under an atmosphere of nitrogen. Analysis of the crude product by GC (DB 210 and DB 1701; 60°C, 10 min; 15°C/min; 200°C) and GC-MS analysis showed the presence of two compounds. GC-MS analysis (HP-5) showed that the major peak has mass of M⁺(103) and corresponding to the benzonitrile (**18**): GC-MS (HP-5; 60°C, 10 min; 15°C/min; 250°C); $t_{\rm R} = 14.01$; m/e: 103 (M⁺ 100%), 76 (35%), 50 (15%).

Photolysis of 1,3-bis(diazobenzyl)adamantane (7)

A degassed solution of **7** (0.046 g, 0.13 mmol) in C₆D₆ (0.675 ml) was irradiated with a high pressure Hg-lamp through a Pyrex filter until the characteristic color of the diazo-compound disappeared. Evaporation of the solvent afforded azine **21** (0.048 g) as a pale yellow solid: ¹H NMR (C₆D₆) δ 1.15–2.11 (m, aliphatic H), 6.87–7.36 (m, Ph-H); ¹³C NMR (C₆D₆) δ 28.8, 35.9, 39.7, 40.7, 43.0, 127.3, 127.7, 128.0, 137.1, 165.3; IR (KBr) $\tilde{\nu}$ 2902 (s), 2851 (s), 1743 (w), 1593 (m), 1490 (w), 1444 (m), 1341 (m), 1238 (w), 1067 (m), 764 (m), 697 (s) cm⁻¹. HRMS for C₄₈H₄₈N₄ [M + 1]⁺ calcd. 681.3957, found 681.3951.

Preparation of authentic azine 21

To a solution of **12** (0.092 g, 0.27 mmol) and **13** (0.100 g, 0.27 mmol) in xylene (10 ml) was added catalytic amount of *p*-TsOH. The mixture was heated to reflux and the reaction was monitored by TLC (ethyl acetate:hexane = 70:30). After 3 h under reflux, the bright yellow solution was cooled down to rt, washed with 0.1 M NaOH (2×15 ml) and water (2×20 ml) and dried over anhydrous MgSO₄. The solvent was evaporated *in vacuo* to give **21** (0.120 g, 65%), as a yellowish solid.

SUPPLEMENTARY MATERIAL

The following data are available in WILEY Interscience: ¹H and ¹³C NMR spectra of compounds **4**, **5**, **6**, **7**, **9**, **10**, **11**, **12**, and **13**, as well as GC-MS data and/or NMR spectra of products **14**, **15**, **17**, **18**, and **21**.

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