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THE GEMINAL 1,1'-BIADAMANTYL GROUP AS A STABILIZER OF REACTIVE FUNCTIONS

1,1'-BIADAMANTYLDIAZOMETHANE, 1,1'-BIADAMANTHYLEMETHYLENE-IMINOXYL AND 1,1'-BIADAMANTHYLMETHYLENE-IMINYL

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Abstract—The syntheses and main properties of the title compounds are described. The diazocompound **3** and the iminoxyl radical **21** proved to be very stable crystalline compounds; the iminyl radical **25** has been characterized by its EPR spectrum and by its typical fragmentation pattern.

The use of adamantyl groups for the stabilization of certain functional groups has proven to be of great value.[1-3] Initial experiments with two adamantyl groups attached to one carbon have led to the isolation of remarkably stable imines.[4] In this respect it seems that a 1,1'-gem.-biadamantyl group is superior to the t-butyl analogue, since a 1-adamantyl group is not prone to rearrangement and elimination processes as is the t-butyl group. The two groups seem to be approximately similar in steric effect. The high crystallinity of adamantyl compounds forms an additional advantage with regard to isolation and product stability. With these properties in mind we set out to synthesize 1,1'-biadamantyldiazomethane, since the t-butyl derivative could not be prepared.[5]

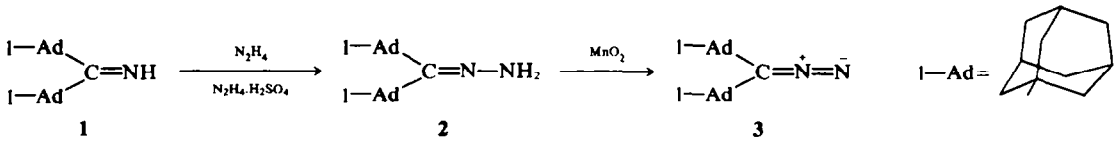
RESULTS

The diazocompound **3** was prepared from the imine **1**[4] by conversion of **1** into the hydrazone **2**, followed by oxidation (Fig 1).

The diazocompound **3** was obtained as a pink solid, m.p. 140–141·5° (corr.). It is a perfectly stable, but still reactive compound. The presence of traces of water in the manganese dioxide sometimes caused partial hydrolysis to the carbinol **4**. The latter was also obtained by reduction of 1,1'-biadamantylketone **5**[4] with $LiAlH_4$ (Fig 2).

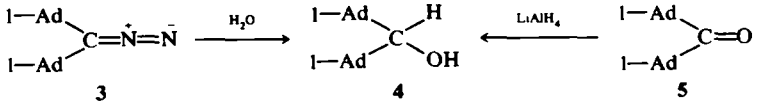
The behavior of **3** was tested under various conditions. The results are depicted in Fig 3.

Prolonged heating of **3** in refluxing benzene caused quantitative conversion to the azine **6**, This compound was characterized by its very low C=N stretching absorption at 1560 cm^{-1}. The corresponding absorption in the IR spectrum of the azine of adamantanone was at 1660 cm^{-1}.[6] An attempt to cyclo-add **3** to 1,1'-biadamantylketene **7**[7] proved unsuccessful. The ketene remained unchanged, while **3** was converted to the azine **6**. With 2-carbonyladamantane **8**[8] cycloaddition took place readily, however in an unusual way to give **9**. A similar type of cycloaddition has been described by Kirmse.[9] The irradiation of **3** in hexane with a Hanau S 81 lamp with pyrex or quartz filters did not lead to insertion products, but gave mainly the hydrocarbon **10**, the azine **6**, the carbinol **4** and an



1 2 3

Fig 1.



3 4 5

Fig 2.

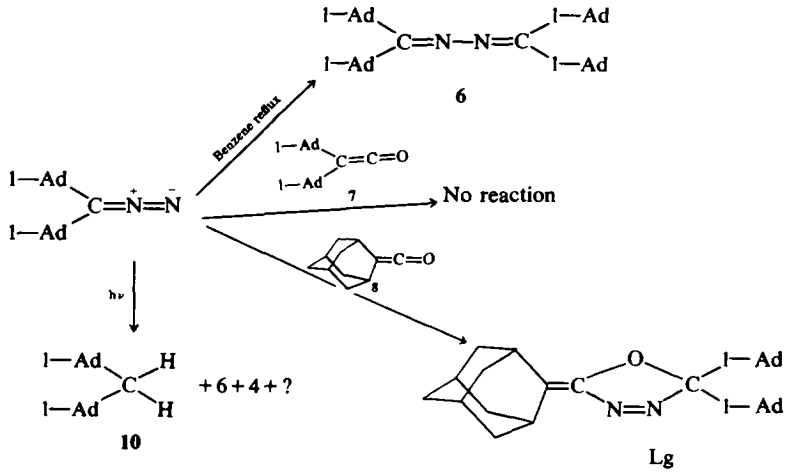


Fig 3.

insoluble material of undefined structure in varying ratios. In benzene solutions irradiation gave mainly **4**, despite careful attempts to expel water and oxygen. The hydrocarbon **10** was identified as 1,1'-biadamantylmethane by comparison with an authentic sample prepared by the route illustrated in Fig 4.

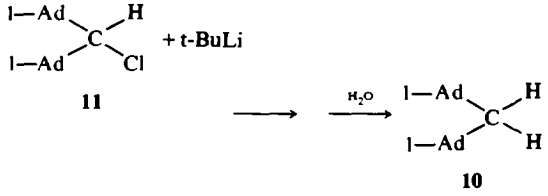


Fig 4.

The mother liquor from the crystallization of crude hydrazone **2**, which turned to a pink red solution (λ_{max} = 564 nm) after a few weeks, was found to consist mainly of 1,1'-biadamantylketone **5**. Although the origin of the colour has not been established, it was found by EPR that various samples gave rise to low concentrations of stable radicals with nitrogen splittings of 8 and 10 gauss, respectively. A more precise determination of the structure of these two radicals was possible by independent generation from unambiguous substrates. The radical exhibiting a nitrogen triplet with a_N = 8 gauss was suspected to be an acylnitroxide, given its low a_N value.[10] Because this type of radicals can be generated from N-hydroxycarbonamides, we set about a synthesis of **14** by reaction of the acid chloride **12**[11] and the hydroxylamine **13**.[12] However, O- instead of N-acylation took place and **15** was obtained (Fig 5)[13] as evidenced by its spectroscopic properties.

To our surprise **15** gave intense signals of the acylnitroxide **16** upon oxidation. We suggest that a rearrangement takes place, but no quantitative correlation was established between signal strength and radical concentration. The identity of the radical as **16** was confirmed by still another synthesis from the aldehyde **17** and nitrosocompound **18** (Fig 6).[10,12,14]

The EPR spectrum of the nitroxide **16** proved to be identical with that present in the hydrazone mother liquor. Its a_N value was 8 gauss. The formation of this radical in the hydrazone mother liquor can be understood by assuming a rapid oxidation of the residual imine **1** to the oxaziridine-N-oxide **20** which then rearranges to the N-hydroxy-carbonamide **14**, the compound generating **16** (Fig 7).

N-Substituted structures like **20** have been assumed in the literature to explain the formation of

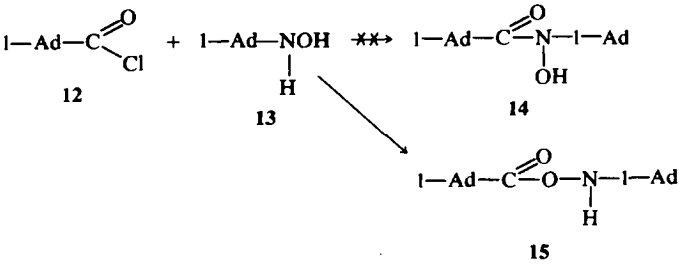


Fig 5.

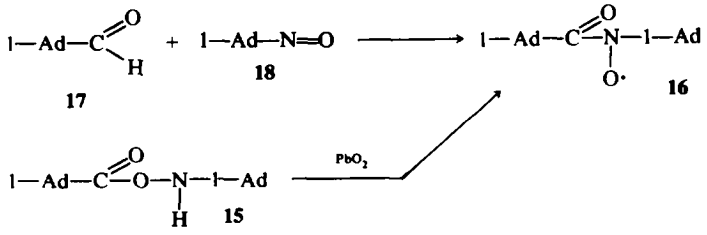


Fig 6.

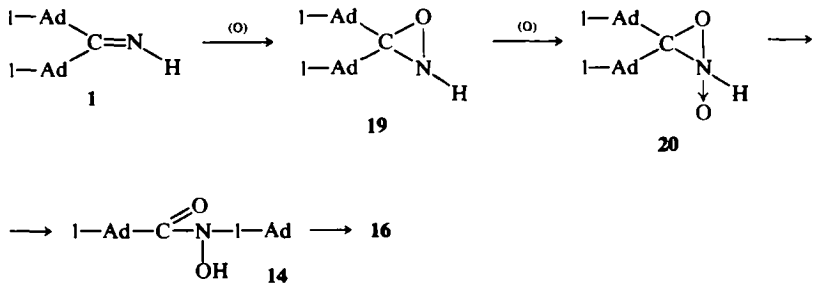


Fig 7.

several products.[15,16] Although the oxidation of Schiff bases is a well documented reaction, it is not entirely obvious in the case of the imine **1**, since this represents a reasonably hindered substrate.[17] Hence we carried out the oxidation of **1** with one equivalent of m-chloroperbenzoic acid under mild conditions. A white crystalline material was obtained. Its spectral properties (IR, NMR) were in accordance with the proposed oxaziridine structure **19**. Unfortunately, the compound could not be purified by recrystallization. Attempted chromatographic purification gave almost complete conversion to the amide **24** and the ketone **5**. This is in accordance with the chemical properties of oxaziridines.[18,19] As oxaziridines are also known to rearrange to oximes, possibly via nitrones[20,21] we presumed that the other radical present in the hydrazone mother liquor might be the iminoxyl radical **22**, formed by homolysis of the oxime O—H bond. However, this type of radical is known to have a large hfs constant of about 30 gauss.[22] Yet to exclude the possibility and inspired by recent interest in the preparation of stable iminoxyl radicals[23-25] we prepared 1,1'-biadamantylmethylene-iminoxyl by mild oxidation of the oxime **21**. The oxime was obtained from the imine **1** (Fig 8).

The iminoxyl compound was isolated as a sky-blue solid (λ_{max} = 745 nm, ϵ = 5·1), with m.p. 118·4–118·6° (corr.); its mass spectrum was identical with that of the parent oxime **21** (M^+ at *m/e* 313), a phenomenon which was also observed by Ingold studying di-t-butylmethylene-iminoxyl.[25]

The infrared spectrum is dominated by an intense absorption at 1600 cm^{-1}; its EPR spectrum showed only hyperfine splitting due to nitrogen with a coupling constant of 32 gauss. The compound proved to be stable at room temperature in the solid phase; in solution it decomposed slowly to a colourless material, mainly consisting of the amide **24**, which was synthesized separately from the acid chloride **12** and the amine **23** (Fig 9). No evidence for dimerization of the radical to a blue nitroso compound was obtained.

The second radical present in the hydrazone mother liquor (see above) exhibiting a nitrogen triplet with a_N = 10 gauss, was suspected on the basis of its a_N value[26,27] to be the iminyl type. We succeeded in generating the same radical from the imine **1** by hydrogen abstraction. These radicals were generated by *in situ* oxidation of **1** with PbO_2 in tetrachloromethane solution.

The identity of this species as 1,1'-biadamantylmethylene-iminyl **25** was substantiated by its typical decay pattern as depicted in Fig 10.

Although dimerization of iminylradicals to azines is known[26,28] and also occurs here to some extent, fragmentation is the principal reaction here. This decomposition pathway is hitherto unknown, but

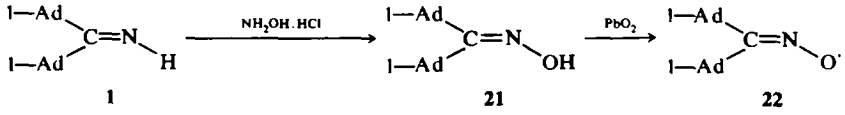


Fig 8.

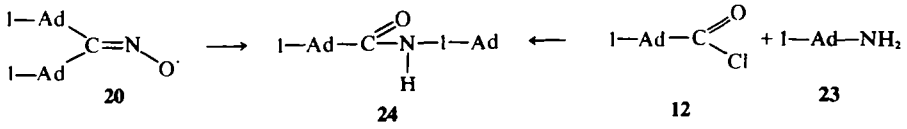


Fig 9.

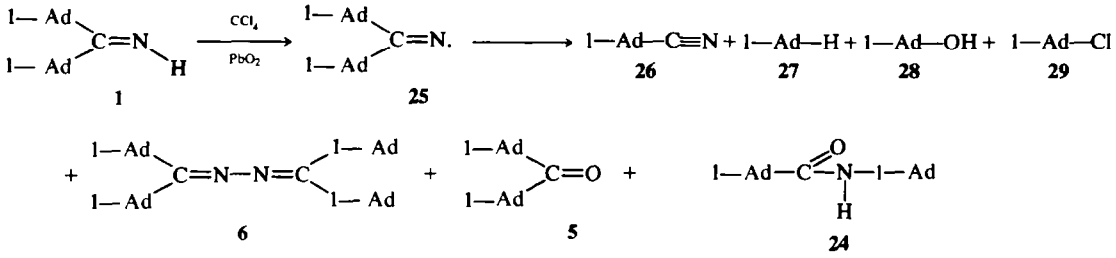


Fig 10.

contributes profoundly to the structural assignment of **25** as an iminyl type radical.

Coupling of iminyl radicals to azines requires considerable orbital readjustment[26] and this may contribute to the apparent stability of the iminyl radical. In addition to the nice correlation between the value of a_N and the position of the odd electron in an p-orbital there is now a chemical fit for this positioning in a preferred fragmentation *vs* coupling decay.

The mechanism of the formation of **25** is unknown but we suppose that PbO_2 initiates a chain reaction in which the trichloromethyl radical abstracts the imine hydrogen atom. The iminyl radical **25** thus formed can react with tetrachloromethane to give the N-chloro imine, which rearranges to the amide **24** (Fig 10). Alternatively it fragments to the cyanide **24** and a 1-adamantyl radical which abstracts chlorine from the solvent to give 1-chloroadamantane **29** and a new trichloromethyl radical. Experiments with other solvents did not lead to detectable quantities of **25**.

EXPERIMENTAL

M.ps are corrected. Microanalyses were performed by the Analytical Department of our Laboratory under supervision of Mr. W. M. Hazenberg. NMR spectra were recorded on Varian A-60 and A-60-D instruments, using TMS as internal standard. IR spectra were taken on a Perkin–Elmer 257 grating spectrophotometer. Mass spectra were recorded on an AEI MS 902 instrument by Mr. A. Kiewiet. UV spectra were measured on a Zeiss PMQ II spectrometer by Mr. S. Vrugt. EPR spectra were recorded on a Varian EPR-4 apparatus.

1,1'-Biadamantylketone hydrazone **2**. 100 mg (0·377 mmole) of **1** was suspended in about 3 ml of pure hydrazine hydrate, to which a few drops of sulfuric acid had been added. The mixture was refluxed for 5 days, cooled, diluted with water and extracted with 4 × 150 ml of ether. After drying and evaporating the solvent, 60 mg (0·19 mmole = 56%) of crude **2** remained. The compound was recrystallized twice from hexane, m.p. 196–200° (dec.). (Found: C, 80·65; H, 10·34; N, 8·81. Calc. for $C_{21}H_{32}N_2$: C, 80·72; H, 10·32; N, 8·96%); IR: 3240, 3320, 3390, 1570, 1640 cm^{-1}; NMR (CCl_4): τ = 7·5–8·75 (30 H); MS: M^+ at *m/e* 312, $M^+ - C_{10}H_{15}$ at *m/e* 177 (100%).

1,1'-Biadamantyldiazomethane **3**. 1·0 g (3·22 mmole) of **2** was dissolved in 100 ml of dry ether (distilled from $LiAlH_4$); 4·0 g of active basic manganese dioxide[29] and 5·0 g of flamed calciumdioxide were introduced and the mixture was stirred for 2 h at room temperature. The suspension was filtered and the residual solution concentrated. The resulting **3** (1·0 g = 3·22 mmole = 100%) was purified by recrystallization from hexane or acetone at −60°, m.p. 140–141·5° (dec.). (Found: C, 81·38; H, 9·67; N, 8·23. Calc. for $C_{21}H_{30}N_2$: C, 81·24; H, 9·73; N, 9·03%); IR: 2030, 1100, 820, 755 and 715 cm^{-1}; NMR (CCl_4): τ = 7·8–8·6 (complex multiplet); MS: M^+ at *m/e* 310, $M^+ - N_2$ at *m/e* 282 (100%); UV (cyclohexane): λ_{max} = 480 nm, ϵ = 6.

1,1'-Biadamantylcarbinol **4**. To a solution of 298 mg (1 mmole) of 1,1'-biadamantylketone[4] in 40 ml of dry ether was added 50 mg (1·5 mmole) of $LiAlH_4$ and the suspension subsequently refluxed for 2 h. Water was added dropwise and the organic layer washed with dil HCl and water. After drying and evaporating the solvent, 300 mg (1 mmole = 100%) of **4** remained, purified by repeated crystallization from methanol, m.p. 192·3–193·4°. (Found: C, 83·92; H, 10·62; Calc. for $C_{21}H_{32}O$: C, 83·94; H, 10·73%); IR: 3630 (sharp), 3480 (broad), 1015 and 935 cm^{-1}; NMR (CCl_4): τ = 7·50 (1 H, J = 6 Hz, d), τ = 8·80 (OH, d, J = 6 Hz); MS: M^+ at *m/e* 300, M–H_2O at *m/e* 135 (100%).

1,1'-Biadamantylmethyleneazine **6**. A solution of 300 mg (0·97 mmole) of **3** in 20 ml of benzene was refluxed under N_2 during 12 h. After removal of the solvent a colourless material remained, which was recrystallized twice from dichloromethane/methanol (1:1), subsequently from chloroform; thoroughly drying at 80° and 0·001 mm for 2 h gave pure **6**, m.p. 248·7–249·2° (dec.). (Found: C, 84·88; H, 10·08; N, 4·73. Calc. for $C_{42}H_{60}N_2$: C, 85·07; H, 10·19; N, 4·72%); IR: 1560, 1005 cm^{-1}; NMR (CCl_4): τ = 7·6–8·5 (complex multiplet with major peaks located at τ = 7·75, 7·95 and 8·30); MS: *m/e* 135 (100%), ½ M at *m/e* 296, and *m/e* 457.

Attempted cycloaddition of the diazocompound **3** *to the ketene* **7**. A solution of 27 mg (0·087 mmole) of **7** and **3** in xylene was refluxed for 1 h under N_2. The infrared

spectrum of the residue showed unchanged **7**. The diazo absorption had disappeared; instead the characteristic absorption of the azine was readily discernible at 1560 cm^{-1}.

2, 2 - (1, 1' - *Biadamantyl*) - 5 - *adamantylidene* - 2, 5 - *dihydro* - 1, 3, 4 - *oxadiazole* **9**. A mixture of 411 mg (1·48 mmole) of 2-bromoadamantane-2-carboxylic acid chloride, 200 mg of zinc wool (BDH), 50 mg of zinc powder (UCB) and 60 ml of dry ether were refluxed for 45 min under N_2 to produce 2-carbonyladamantane.[8] Then 444 mg (1·48 mmole) of **3**, dissolved in 30 ml of ether, was introduced at 0° while stirring. The solution turned green. After 15 min the ice bath was removed and stirring continued until the mixture had reached room temperature. The insoluble materials were filtered off and the solvent was removed. The residue was chromatographed on Florisil (column 30 × 1 cm) with chloroform/tetrachloromethane (2:1) (300 ml). This afforded 320 mg (0·67 mmol = 46%) of crude **9**. Continued elution with pure chloroform gave an additional 170 mg of a colourless oil of undefined composition. The curde **9** was recrystallized from acetone/dichloromethane (1:1) but purification finally only succeeded by chromatography on a silica gel plate (20 × 20 × 0·2 cm) with dichloromethane elution. An additional crystallization from acetone/benzene gave analytically pure **9**, m.p. 190–194° (dec.). (Found: C, 81·20; H, 9·13; N, 5·55. Calc. for $C_{32}H_{44}O$: C, 81·31; H, 9·38; N, 5·92%); IR: 1660 cm^{-1} (very weak), 1000 and 1160 cm^{-1}; NMR (CCl_4): τ = 7·15 (1 H), τ = 7·8–8·6 (42 H); MS: M^+ at *m/e* 472, *m/e* 135 (100%); UV (cyclohexane): λ_{max} = 328 nm, ϵ = 2200.

Irradiation of the diazocompound **3**. A solution of 100 mg (0·32 mmole) of **3** in 130 ml of dry hexane (distilled from $LiAlH_4$), which had previously been placed in the reaction vessel, was boiled in order to become free of oxygen for 10 min. The irradiation was started (a Hanau S 81 lamp with pyrex or quartz filter). After six days the solution was free of **3** and the products were examined with GLC and IR. The major product was **10**; minor quantities of **6** and **4** could be detected.

1,1'-*Biadamantylmethylchloride* **11**. In 5 ml of distilled thionylchloride 150 mg (0·5 mmole) of **4** was dissolved. After the spontaneous reaction had ceased, reflux was applied for 10 min. After evaporation 158 mg (0·5 mmole = 99%) of fairly pure **11** remained. Repeated recrystallization from methanol gave pure **11**, m.p. 156·0–157·4°. (Found: C, 78·90, H, 9·74; Cl, 11·27. Calc. for $C_{21}H_{31}Cl$: C, 79·08; H, 9·80; Cl, 11·11%); IR: 693, 715 and 980 cm^{-1}; NMR (CCl_4): τ = 6·75 (1 H), τ = 7·9–8·5 (30 H); MS: No M^+, fragments at *m/e* 282 and 135 (100%).

1,1'-*Biadamantylmethane* **10**. To a solution of **11** (300 mg = 0·945 mmole) in 80 ml of dry hexane under N_2 was added 2 ml of 2 N t-butyllithium (pentane solution, Fluka) and reflux was applied for 1·5 h. After hydrolysis and washing, followed by drying and evaporating the solvent, 250 mg (0·88 mmole = 93%) of crude **10** remained. A pure sample was obtained by recrystallization from methanol and acetone, m.p. 171–177°. (Found: C, 88·35; H, 11·25. Calc. for $C_{21}H_{32}$: C 88·65; H 11·34%). (Mol. weight, osmometric in benzene): (Found: 285·4. Calc. 284·5); IR: 850, 990 and 1105 cm^{-1}; NMR (CCl_4): τ = 8·0–8·6 (complex multiplet); MS: M^+ at *m/e* 284, *m/e* 135 (100%).

1-*Adamantylcarboxylic acid ester of* 1'-*adamantylhydroxylamine* **15**. A solution of 360 mg (2 mmole) of 1-adamantanecarboxylic acid[30] in 20 ml of thionylchloride was refluxed for 5 min. The excess of thionylchloride was then removed *in vacuo*. To the residual **12** was added 400 mg (2·4 mmole) of recrystallized 1-adamantylhydroxylamine **13**[12] together with 30 ml of tetrahydrofuran. The solution was boiled for 3 min, the solvent was evaporated and the residue chromatographed on aluminium oxide (AN_1, Merck) sheets with benzene. From this 150 mg (0·46 mmole = 23%) of fairly pure **15** was obtained. A pure sample was obtained after decolourization with charcoal and recrystallization from methanol, m.p. 246·0–246·9° (dec.). (Found: C, 76·14; H, 9·49; N, 4·17; Calc. for $C_{21}H_{31}O_2N$: C, 76·55; H, 9·48; N, 4·25%); IR: 3215 cm^{-1} (NH, sharp), 1725, 1075 and 1240 cm^{-1}; NMR (CCl_4): τ = 2–4 (NH, broad), τ = 7·8–8·6 (complex multiplet); MS: M^+ at *m/e* 329, *m/e* 135 (100%).

Generation of **16** *from* **17** *and* **18**. A solution of 20 mg of **17** and **18** in 1 ml of benzene was transferred to an EPR tube and heated to about 40°. The EPR spectrum was readily discernible and showed the signals of both **16** and 1,1'-biadamantylnitroxide, both having identical g values.

Attempted preparation of 3,3-(1,1'-*biadamantyl*)-*oxaziridine* **19**. To a solution of 70 mg (0·236 mmole) of **1** in 30 ml of dichloromethane was added 50 mg (0·25 mmole) of m-chloroperbenzoic acid at 0°. The solution was placed in a refrigerator (−30°) for 7 days. Then additional dichloromethane was introduced and the organic layer was washed with water and sodium sulphite solution. After drying and evaporating the solvent 50 mg of a white solid remained, which was recrystallized from methanol. In the IR spectrum the intense C=N stretching absorption present in the substrate at 1592 cm^{-1} had disappeared. Significant peaks are found at 3340 cm^{-1} (NH), 1240, 1105, 1085, 818 and 735 cm^{-1}. The NMR spectrum showed a broad NH absorption at τ = 6·5 and a complex multiplet at τ = 7·8–8·6 (30 H). Both recrystallization and chromatography led to a decomposition with formation of **24** and **5**.

Oxime of 1,1'-*biadamantylketone* **21**. To a solution of 297 mg (1 mmole) of **1** in 30 ml of ethanol and 6 ml of water, 350 mg (5 mmole) of hydroxylamine-HCl salt and 410 mg (5 mmole) of sodiumacetate were added and the mixture was refluxed for 18 h. After cooling crystals of **21** appeared, which were filtered off (164 mg = 0·52 mmole = 52%). Extra water was added and the new precipitate was filtered off also (110 mg consisting of a mixture of **21** and **5**). The oxime was purified by recrystallization from benzene, m.p. 254–255°. (Found: C, 80·73; H, 10·0; N, 4·42. Calc. for $C_{21}H_{31}NO$: C, 80·46; H, 9·97; N, 4·47%). IR: 3150–3400 cm^{-1} (OH), 1620 (weak), 1010, 980, 940 and 755 cm^{-1}; NMR (CCl_4:$CDCl_3$, 5:1): τ = 2·75 (OH), τ = 7·5–7·7 (6 H), τ = 7·85–8·2 (12 H): τ = 8·25–8·4 (12 H); MS: M^+ at *m/e* 313, M- OH at *m/e* 296, *m/e* 135 (100%).

1,1'-*Biadamantylmethylene-iminoxyl* **22**. In a centrifuge tube 100 mg (0·32 mmole) of **21** was dissolved in 10 ml of benzene. To this solution 500 mg of leaddioxide was added. The mixture was stirred at room temperature for 20 min. Centrifugation was applied and the sky blue solution was decanted. After evaporation of the solvent remained 100 mg of a blue solid, which was recrystallized from hexane at −80°. Yield: 80 mg = 0·256 mmole = 80%. Repeated crystallization afforded an analytically pure sample, m.p. 118·4–118·6°. Found: C, 80·72; H, 9·64; N, 4·37. Calc. for $C_{21}H_{30}ON$: C, 80·72; H, 9·67; N, 4·48%); IR: 1600 cm^{-1} (intense), 1285, 1245, 1008, 820, 760 and 715 cm^{-1}; MS: see **21**; UV (hexane); λ_{max} at 745 nm, ϵ = 5·1.

1-Adamantylcarboxylic acid-1'-adamantylamide **24**. 180 mg (1 mmole) of 1-adamantylcarboxylic acid was converted to the acid chloride **12** as described for **15**. The acid chloride was dissolved in 20 ml of triethylamine and 151 mg (1 mmole) of 1-adamantylamine **23** was added with vigorous stirring. Reflux was applied for 5 min. The mixture was diluted with ether and water. The organic layer was washed thoroughly, dried and concentrated; 240 mg (0·76 mmole = 76%) of crude **24** was obtained. It was purified by recrystallization from acetone, m.p. above 300°. (Found: C, 80·30; H, 10·00; N, 4·44. Calc. for $C_{21}H_{31}ON$: C, 80·46; H, 9·97; N, 4·47%); IR: 3340 cm^{-1} (NH), 1640, 1540, 1365 and 1360, 1000 cm^{-1}; NMR (CCl_4): $\tau = 5{\cdot}60$ (*N*H), $\tau = 7{\cdot}2$–$8{\cdot}5$ (complex multiplet); MS: M^+ at *m/e* 313, *m/e* 135 (100%).

Generation of **25** *from* **1**. To a solution of 200 mg of **1** in 20 ml of tetrachloromethane, 500 mg of leaddioxide was added and the mixture stirred for 24 h. The solution was filtered and concentrated. The remaining solid was analyzed by GLC and TLC, combined with IR.

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