Synthesis of Bis(α-alkylaminobenzylidene)hydrazines and their Transformation into 4-Alkyl-4*H*-1,2,4-triazoles

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Sterically hindered 4-alkyl-3,5-diphenyl-4*H*-1,2,4-triazoles have been prepared by reacting bis(α-chlorobenzylidene)hydrazine with alkylamines. Under mild conditions this reaction gives, as intermediates, bis(α-alkylaminobenzylidene)hydrazines, a new class of compound. The stability of these compounds appeared to increase with increasing bulk of the alkyl substituent. Upon being heated the compounds, either neat or in a variety of solvents, were transformed into the corresponding triazoles in high yields.

Bis(α-alkylaminobenzylidene)hydrazines with sterically bulky groups, e.g. *tert*-butyl or 1-adamantyl, undergo cyclization in conjuction with elimination to form, as the major product, 3,5-diphenyl-1*H*-1,2,4-triazole.

Recently we reported an investigation of the thermal rearrangement of 4-alkyl substituted 4*H*-1,2,4-triazoles.[1] The rearrangement appeared to involve an ion-pair mechanism or a bimolecular nucleophilic displacement reaction, even though a concerted mechanism could not be excluded. In the course of this work, there were strong indications that the rate of reaction and product distributions may depend on the size of the 4-alkyl group. We therefore undertook an investigation of the thermolysis of a series of triazoles in which the steric bulk of the 4-alkyl groups was increased.

Synthetic methods leading to this type of compound have been extensively reviewed.[2] We have tested a series of the more promising methods. Thus, triazoles were prepared by the reaction between phenyltetrazole and *N*-alkylimidoyl chlorides as described by Huisgen *et al.*,[3] by the reaction of oxadiazoles with alkylamines[4] and also by modifications of the reaction between dibenzoylamine and semicarbazide.[5]

Results and discussion

None of the above methods have so far proved successful as general methods for preparation of the hindered 4-alkyl-3,5-diphenyl-4*H*-1,2,4-triazoles (**1**). Huisgens classical tetrazole method was useful only for less hindered compounds, Scheme 1. We found that for sterically bulky 4-alkyl groups, this reaction failed to produce the desired products. Thus, for reactions with imidoyl chlorides, **2**, in which R was *tert*-butyl or 1-adamantyl, none of the desired triazoles could be detected in the products. The reactions yielded *tert*-butyl chloride or 1-chloroadamantane respectively (**3**), together with benzonitrile (**4**). These observations agree well with the results reported by Ugi *et al.*,[6] that *tert*-butylimidoyl chlorides easily undergo von Braun degradations to the corresponding nitrile and alkyl chloride.[7] However, under mild reaction conditions ($SOCl_2$/room temp.), the appropriate *N*-alkylbenzamides were transformed into the imidoyl chlorides **2**, which could be identified by the IR bands at 1663 cm^{-1}, characteristic of the imidoyl C=N bond. The products were thermally unstable, and decomposed upon standing or being heated to benzonitrile and *tert*-butyl chloride and 1-chloroadamantane, respectively. We may therefore conclude, that this method as a general route towards the triazoles failed, because, under the mild conditions where hindered imidoyl chlorides were stable, the reaction between tetrazole and imidoyl chloride did not proceed and at the higher temperatures required for the reaction the imidoyl chlorides undergo von Braun type reactions.

Bis(α-aminobenzylidene)hydrazines. We therefore looked for alternative synthetic methods. In our previous work we once made use of the reaction between bis(α-chlorobenzylidene)hydrazines (**5**) and primary alkylamines for the preparation of triazoles, Scheme 2. As this appeared to be a promising, convenient and selective method for the synthesis of the desired class of hindered 4-alkyltriazoles, we initiated a more thorough study of this reaction.

Our first experience with this reaction was in the preparation of the triazole **1** (R = 2-butyl) by the reaction between **5** and 2-butylamine in benzene at 140 °C. However, when the reaction was carried out at a lower temperature, 63 °C, in neat, refluxing amine, a product different from the triazole was formed in an essentially quantitative yield. This product was identified spectroscopically as

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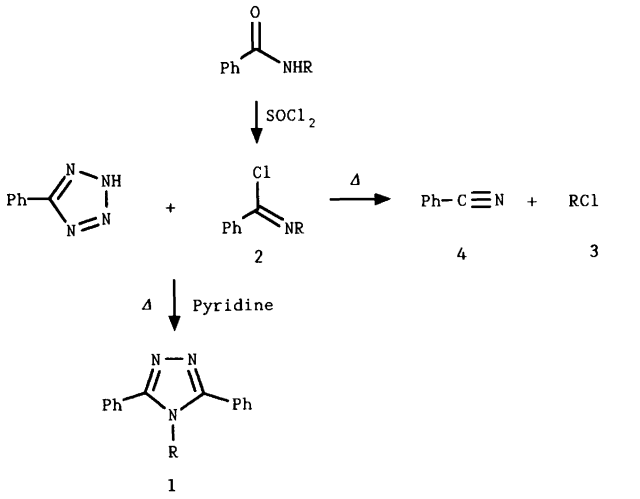


Scheme 1.

bis[α-(2-butylamino)benzylidene]hydrazine, **6** (R = 2-butyl).

Synthesis of triazoles **1** using reactions similar to those described above was first reported by Stollè and Thomä[8] and the synthesis of a series of 4-aryl-[9,10] and 4-alkyl-triazoles[11] were later described by Lange and Tondys, and have appeared in a number of patents for the synthesis of biologically active triazoles.[12] Bis(α-chlorobenzylidene)hydrazine is known to undergo a series of similar nucleophilic addition–cyclization reactions with other nucleophiles. Examples are the formation of oxazoles, thiazoles and 4-amino- and 4-hydroxy-substituted triazoles.[8,13] In none of these examples have bis-adducts corresponding to **6** been reported as intermediates.

Several methods for the preparation of bis(α-chlorobenzylidene)hydrazines **5** have been reported.[10,14–16] In this work the synthesis of **5** was easily accomplished by the action of chlorine on the corresponding bis(α-benzylidene)-hydrazine in carbon tetrachloride.[10]

To the best of our knowledge, bis(α-alkylaminobenzylidene)hydrazines **6** constitute a new class of compound that has not previously been reported. They have, however, been suggested as intermediates in other reactions.[17] The observation that 2-butylamine reacts with **5** to form the corresponding bis-adduct **6** (R = 2-butyl), while less bulky amines have been reported to form triazoles, suggests that steric hindrance and reaction conditions may play an important role in determining the course of the reaction.

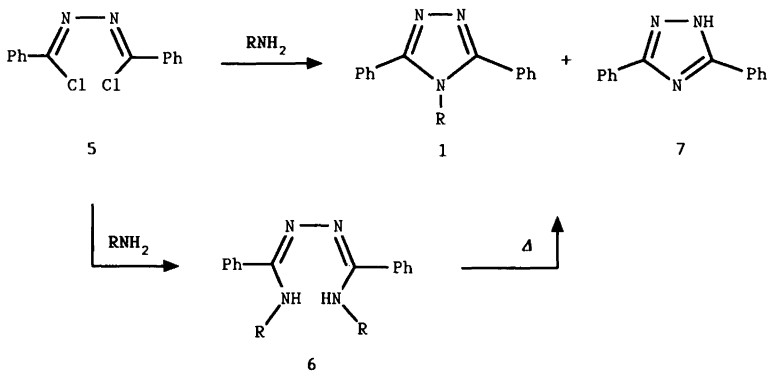
We therefore studied the reaction between **5** and a series of primary alkylamines, with alkyl groups of increasing steric bulk. The amines used in the reaction yielded varying amounts of the corresponding bis(α-alkylaminobenzylidene)hydrazines.

The results in Table 1 show that if sufficiently mild reaction conditions were employed, all of the alkylamines reacted with **5** to form the corresponding bis-adduct **6**, usually in close to quantitative yields. Some loss of product was experienced upon recrystallization. For the more bulky primary alkylamines, elevated temperatures were required. If the reaction temperature used for the less hindered alkylamines was too high, subsequent ring closure took place to form the corresponding triazoles. Thus, when **5** was allowed to reflux in methylamine (40 % in water) or ethylamine (70 % in water), triazoles could be isolated in essentially quantitative yields. When performed at room temperature, no ring closure was observed. With the more bulky alkylamines, even at high temperatures, only the bis-adducts **6** could be isolated.

We conclude, therefore, that **6** can routinely be prepared from **5** and in high yields. The stability of these products increased with the increasing bulk of the *N*-alkyl groups.

*4-Alkyl-3,5-diphenyl-4*H*-1,2,4-triazoles.* Some triazoles have been synthesized before by other workers according to Scheme 2. Our investigation confirmed and extended the significance of this reaction, as a series of triazoles could be prepared. Representative results are shown in Table 2.

We have simplified some of the earlier procedures that called for high temperature reactions under pressure.[9,11] For R = methyl or ethyl the triazoles were readily prepared by reflux of **5** in methylamine or ethylamine, respectively. For the somewhat larger alkyl groups, the reaction required more forcing conditions. Thus, in most other cases the triazoles could be isolated only after reaction at higher temperatures, e.g. 140–190 °C, using benzene, toluene or *N,N*-dimethylaniline, DMA, as the solvents. For the prep-



Scheme 2.

Table 1. Synthesis of bis(α-alkylaminobenzylidene)hydrazines **6**.

Entry	R	Temp./°C	Time/h	Yield (%)
1	Methyl	20	3.5	46[a]
2	Ethyl	20	2	66[a]
3	2-Propyl	35[b]	18	71
4	2-Butyl	65[b]	48	67
5	Cyclohexyl	20	6.5	62
6	*tert*-Butyl	46[b]	23	67
		140[c]	40	24
7	1-Adamantyl	193[d]	62	17

[a]The compound was thermally unstable. No well defined m.p. could be determined. GLC analysis showed only one signal corresponding to the related triazole. [b]Reaction in refluxing alkylamine. [c]Reaction in benzene solution in a pressure tube. [d]Reaction in refluxing *N,N*-dimethylaniline, DMA.

aration of 4-cyclohexyl-3,5-diphenyl-4*H*-1,2,4-triazole, Lange and Tondy reported that after reaction of **5** with cyclohexylamine at 140 °C for 8 h, an unidentiied product different from the desired triazole was formed. In the light of the present work, we propose that they actually observed the bis-amino adduct of type **6**. We succeeded in forming the triazole for this substituent simply by increasing the reaction time to 4 days. It appears from the results shown in Table 2, that the reaction readily proceeds for alkyl groups of small or moderate size.

The ring closure products could be derived either via **6**, or from a monoamino-monochloro intermediate, where the dichloro starting material only partly reacted with the alkylamine. These mixed intermediates have never been isolated or detected in the reaction mixtures, but cannot be excluded in the cyclization process. However, we have demonstrated that the corresponding bis(aminobenzylidene)hydrazines can function as precursors for triazoles upon thermolysis.

For sterically more constraining groups, e.g. *tert*-butyl or 1-adamantyl, the formation of the 4-alkyl-substituted triazoles eluded detection. However, from the reaction mixtures could be isolated varying amounts of the corresponding 3,5-diphenyl triazole, **7**. Thermolysis of neat **6** (R = *tert*-butyl, 1-adamantyl) in both cases resulted in the formation of **7**. This appeared to indicate that cyclization to the triazole did actually take place, but the bulky alkyl groups were subsequently eliminated, presumably due to steric strain. Considering the knowledge compiled so far about rearrangements of 4-alkyltriazoles,[1] an ion-pair mechanism may explain the tendency towards elimination. Bond cleavage is promoted by steric repulsion between the bulky 4-alkyl groups and the two flanking phenyl groups, together with the higher temperatures required to initiate the cyclization in the first place.

In conclusion, this study has demonstrated that **5** reacts with alkylamines to form triazoles **1**, presumably via the bis-adducts **6**, and that the reactivity and the direction of the reactions depends on the steric characteristics of reagents and intermediates. We have also established that the method is a viable route to a series of hindered 4-alkyltriazoles that are otherwise difficult to obtain, although the 4-*tert*-butyl and 4-(1-adamantyl) bis-adducts undergo cyclization only in conjunction with elimination, yielding as the major product 3,5-diphenyl-1*H*-1,2,4-triazole.

Experimental

General. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX-100 NMR spectrometer using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. IR spectra were obtained on a Nicolet 20-SXC FT-IR spectrometer, and mass spectra on an AEI MS-902 spectrometer at 70 eV (IP) and 200 °C inlet temperature where nothing else is reported. GLC measurements were performed on a Varian 3700 gas chromatograph equipped with a BP-5 capillary column (25 m); injection temperature: 280 °C. Preparative TLC was performed on 20 × 20 cm glass plates covered with a 1 mm layer of Merck silica gel HF254+366, using chloroform as the eluent. All melting points are uncorrected.

Table 2. Synthesis of 4-alkyltriazoles **1**, from bis(α-chlorobenzylidene)hydrazine **5**.

Entry	R	Temp./°C	Time/h	Solvent	Yield (%)
1	Methyl	48	18	Methylamine	60
2	Ethyl	40	18	Ethylamine	84
3	1-Propyl	48	72	Propylamine	69
4	2-Propyl	20	600	2-Propylamine	30
		63	48		79
5	2-Butyl	193	24	DMA	87
6	Cyclohexyl	145	96	Benzene	48
7	1-Octyl	145	47	Benzene	79
8	2-Octyl	165	26	2-Octylamine	95
9	*tert*-Butyl	232	3.5	Neat	NR(58)[a]
10	1-Adamantyl	193	14	DMA	NR

[a]The number in parentheses indicates the isolated yield of 3,5-diphenyl-1*H*-1,2,4-triazole.

General procedure for the synthesis of bis(α-alkylaminobenzylidene)hydrazines. Bis(α-chlorobenzylidene)hydrazine (0.20 g, 0.72 mmol) in alkylamine (20 ml) was stirred for 2 h at room temperature, unless otherwise stated. The mixture was then concentrated under reduced pressure. The residue was dissolved in dichloromethane (15 ml), washed with water (3 × 10 ml), dried, the solvent evaporated and the crude product recrystallized from aqueous ethanol, unless otherwise reported.

Bis(α-methylaminobenzylidene)hydrazine. Bis(α-chlorobenzylidene)hydrazine (0.09 g, 0.32 mmol), dissolved in diethyl ether (5 ml), was added to a 40 % aqueous solution of methylamine (5 ml) and stirred for 3.5 h at room temperature. The yield was 0.04 g (46 %) and the product was obtained as pale yellow crystals, which exhibited the following spectroscopic properties.

^{1}H NMR (100 MHz): δ 2.79 (d, 6 H, J = 5.4 Hz), 6.29 (br s, 2 H), 7.38–7.50 (m, 6 H), 7.50–7.69 (m, 4 H). Upon addition of D_2O the doublet at 2.79 collapsed to a singlet, while the broad signal at 6.29 disappeared. ^{13}C NMR (25.0 MHz): δ 31.1, 128.2, 128.5, 129.1, 134.1, 159.9. IR (KBr): 3365, 3255, 1608, 1589, 1565, 1499, 1476, 1354, 1019 cm^{-1}. MS [*m/z* (% rel. int.)]: 266 (17, M^+), 236 (51), 235 (73), 234 (78), 133 (34), 118 (100), 104 (52), 103 (20), 77 (58). Found: M^+ 266.1537. Calc. for $C_{16}H_{18}N_4$: M 266.1531.

Bis(α-ethylaminobenzylidene)hydrazine. For this reaction, a 70 % aqueous ethylamine solution (20 ml) was used. Pure product, 0.14 g (66 %), was isolated as pale yellow crystals which exhibited the following spectroscopic properties.

^{1}H NMR (100 MHz): δ 1.08 (t, 6 H, J = 7.3 Hz), 3.13 (quintet, 4 H, J = 6.8 Hz), 6.34 (br t, 2 H), 7.20–7.50 (m, 6 H), 7.50–7.72 (m, 4 H). ^{13}C NMR (25.0 MHz): δ 16.6, 38.9, 128.1, 128.5, 129.0, 134.7, 159.2. IR (KBr): 3317, 3288, 2984, 2965, 2946, 2925, 1607, 1593, 1569, 1493, 1466, 1443, 1413, 1377, 1328, 1278, 1141 cm^{-1}. MS [*m/z* (% rel. int.)]: 295 (5), 294 (21, M^+), 250 (22), 249 (44), 248 (34), 147 (100), 132 (30), 104 (99). Found: M^+ 294.1848. Calc. for $C_{18}H_{22}N_4$: M 294.1844.

Bis(α-isopropylaminobenzylidene)hydrazine. The pure product, 70 mg (30 %) was isolated as white crystals of m.p. 146.5–147 °C.

^{1}H NMR (100 MHz): δ 1.08 (d, 12 H, J = 6.3 Hz), 3.31–3.78 (m, 2 H), 6.23 (br d, 2 H, J = 10.3 Hz), 7.38–7.50 (m, 6 H), 7.50–7.67 (m, 4 H). ^{13}C NMR (25.0 MHz): δ 24.4, 45.3, 128.1, 128.5, 128.9, 135.2, 158.8. IR (KBr): 3333, 2959, 2929, 1611, 1592, 1568, 1495, 1444, 1414, 1385, 1365, 1179, 783 cm^{-1}. MS [*m/z* (% rel. int.)]: 323 (3), 322 (12, M^+), 163 (18), 161 (100), 104 (69), 77 (17), 58 (22). Found: M^+ 322.2156. Calc. for $C_{20}H_{26}N_4$: M 322.2157.

Bis(α-butylaminobenzylidene)hydrazine. Bis(α-chlorobenzylidene)hydrazine (1.40 g, 0.50 mmol) was refluxed in isobutylamine (5 ml) for 48 h, nd worked up by evaporation of the solvent under reduced pressure. The residue was extracted with ether, the solvent evaporated, and the crude product finally recrystallized from 80 % ethanol. The pure product, 1.21 g (67 %), was isolated as white crystals, m.p. 134–135 °C.

^{1}H NMR (100 MHz): δ 0.85 (t, 6 H, J = 7.3 Hz), 1.06 (d, 6 H, J = 6.8 Hz), 1.29–1.62 (m, 4 H), 3.10–3.56 (m, 2 H), 6.20 (br d, 2 H, J = 13.0 Hz), 7.27–7.50 (m, 6 H), 7.50–7.72 (m, 4 H). ^{13}C NMR (25.0 MHz): δ 10.5, 22.2, 31.2, 50.8, 128.0, 128.5, 128.9, 135.4, 159.3. IR (KBr): 3317, 3302, 2961, 1609, 1595, 1570, 1497, 1420, 1368, 1324, 1164, 1105, 779 cm^{-1}. MS [*m/z* (% rel. int.)]: 351 (3), 350 (12, M^+), 177 (20), 175 (100), 121 (12), 119 (22), 106 (3), 105 (7), 104 (75), 77 (18). Found: M^+ 350.2476. Calc. for $C_{22}H_{30}N_4$: M 350.2470.

Bis(α-tert-butylaminobenzylidene)hydrazine. Bis(α-chlorobenzylidene)hydrazine (2 g, 7.22 mmol) and *tert*-butylamine (50 ml) were refluxed for 23 h. The crude product (2.32 g) was recrystallized to yield 1.70 g (67 %) of white crystals of 99.4 % purity (GC), m.p. 187.5–188.5 °C. The product exhibited the following spectroscopic properties.

^{1}H NMR (100 MHz): δ 1.09 (s, 18 H), 6.43 (br s, 2 H), 7.29–7.48 (m, 6 H), 7.48–7.72 (m, 4 H). ^{13}C NMR (25.0 MHz): δ 31.8, 52.2, 127.5, 128.7, 129.3, 137.5, 159.7. IR (KBr): 3287, 2964, 1608, 1589, 1571, 1442, 1365, 1351, 1225, 1203, 705 cm^{-1}. MS [*m/z* (% rel. int.)]: 352 (3), 351 (19), 350 (75, M^+), 222 (39), 160 (33), 135 (33), 119 (33), 104 (100), 77 (20), 67 (70). Found: M^+ 350.247. Calc. for $C_{22}H_{30}N_4$: M 350.2470.

In an alternative procedure bis(α-chlorobenzylidene)hydrazine (0.47 g, 1.70 mmol) and *tert*-butylamine (0.52 g, 7.11 mmol) were dissolved in dry benzene (2.06 g), and then heated in a sealed pressure glass tube, at 140–150 °C for 40 h in an oil bath. The reaction mixture was cooled to room temperature and resulting crystals were separated by filtration, washed repeatedly with 1 M HCl and then with water and finally recrystallized from ethanol. 0.14 g (24 %) of the pure product were isolated as white crystals. The spectroscopic properties were identical in all details with those described in the above procedure.

Bis(α-cyclohexylaminobenzylidene)hydrazines. The reaction mixture was stirred for 6.5 h at room temperature. The crude product was recrystallized to yield 0.18 g (62 %) of white crystals of 98.2 % purity (GC), m.p. 154.5–156 °C. The product exhibited the following spectroscopic properties.

^{1}H NMR (100 MHz): δ 0.70–1.41 (m, 10 H), 1.41–1.98 (m, 10 H), 2.87–3.40 (m, 2 H), 6.35 (br d, 2 H, J = 10.3 Hz), 7.27–7.50 (m, 6 H), 7.50–7.72 (m, 4 H). ^{13}C NMR (25.0 MHz): δ 25.1, 25.4, 34.9, 52.3, 128.0, 128.4, 128.9, 135.2, 158.7. IR (KBr): 3333, 2935, 2925, 2849, 1609, 1588, 1569, 1497, 1433, 1158, 766 cm^{-1}. MS [*m/z* (% rel. int.)]: 402 (11, M^+), 203 (19), 202 (17), 201 (100), 121 (22), 119 (13), 104 (60), 98 (17), 77 (12). Found: M^+ 402.2789. Calc. for $C_{26}H_{34}N_4$: M 402.2783.

Bis(α-adamantylaminobenzylidene)hydrazine. Bis(α-chlorobenzylidene)hydrazine (2.06 g, 7.44 mmol) and 1-adamantylamine (4.08 g, 27.0 mmol) were dissolved in 12.5 g of *N,N*-dimethylaniline, and refluxed in a nitrogen atmosphere for 62 h. After being cooled to room temperature, the reaction mixture was acidified with 1 M HCl (25 ml) and extracted with dichloromethane (3 × 20 ml). The combined organic phases were washed with 1 M HCl (3 × 15 ml), water (2 × 15 ml), and the solvent evaporated under reduced pressure. The residual oil was recrystallized from 96 % ethanol (ca. 20 ml), to yield 0.65 g (17 %) of a pure compound (GLC) as white crystals with m.p. 228–230.5 °C. ^{1}H NMR (100 MHz): δ 1.48 (br s, 12 H), 1.57–1.79 (m, 12 H), 1.91 (br s, 6 H), 6.32 (br s, 2 H), 7.28–7.48 (m, 6 H), 7.48–7.70 (m, 4 H). ^{13}C NMR (25.0 MHz): δ 29.7, 36.0, 44.8, 52.9, 127.5, 128.7, 129.2, 138.2, 159.3. IR (KBr): 3270, 2900, 2849, 1612, 1592, 1573, 1494, 1443, 1370, 1358, 1343, 1305, 708 cm^{-1}. MS [*m/z* (% rel. int.)]: 508 (3), 507 (25), 506 (37, M^+), 253 (13), 136 (20), 135 (100), 104 (15), 93 (25), 79 (18). Found: M^+ 506.3416. Calc. for $C_{34}H_{42}N_4$: *M* 506.3409.

*4-Methyl-3,5-diphenyl-4*H*-1,2,4-triazole* was prepared by refluxing a solution containing 800 mg of **5** in methylamine (15 ml; 40 % in water) for 18 h. Initially the reaction mixture boiled at 48 °C, but as methylamine evaporated through the condenser, the boiling point increased to ca. 90 °C. During this process the reaction mixture became colourless. Then the solvent was evaporated under reduced pressure and the crude product recrystallized from toluene. The yield of pure product was 61 %. All spectroscopic properties were in total agreement with those of an authentic sample.[1]

*4-Ethyl-3,5-diphenyl-4*H*-1,2,4-triazole* was prepared from **5** (800 mg) and ethylamine (15 ml; 70 % in water), using the procedure described above for the methyltriazole. The yield, after recrystallization from toluene, was 94 % and all spectroscopic properties were consistent with those of an authentic sample.[1]

*3,5-Diphenyl-4-(2-propyl)-4*H*-1,2,4-triazole.* Bis(α-chlorobenzylidene)hydrazine (0.50 g, 1.81 mmol) was dissolved in isopropylamine (50 ml) under nitrogen and stirred at room temperature for 25 days. The reaction mixture was then concentrated under reduced pressure, the residue dissolved in dichloromethane (20 ml), and washed with 1 M HCl (3 × 20 ml), water (20 ml), saturated sodium hydrogencarbonate (20 ml), water (20 ml), and finally the organic solution was dried over anhydrous $MgSO_4$. The solvent was evaporated of under reduced pressure and the residue recrystallized from toluene to give 0.14 g (30 %) of the pure product as colourless crystals (100 % by GLC) of m.p. 176–177 °C.

^{1}H NMR (100 MHz): δ 1.29 (d, 6 H, J = 7.3 Hz), 4.51 (septet, 1 H, J = 7.3 Hz), 7.37–7.70 (m, 10 H). ^{13}C NMR (25.0 MHz): δ 23.0, 49.1, 128.5, 130.0, 155.2. IR (KBr): 3053, 2981, 2941, 1470, 1464, 1444, 1392, 1387, 1373, 1309, 775, 769, 746, 702 cm^{-1}. MS [*m/z* (% rel. int.)]: 265 (2), 264 (19), 263 (93, M^+), 222 (17), 221 (100), 118 (87), 104 (24), 103 (10), 91 (13), 90 (12), 89 (46). Found: M^+ 263.1426. Calc. for $C_{18}H_{19}N_3$: *M* 263.1423.

*4-(2-Butyl)-3,5-diphenyl-4*H*-1,2,4-triazole from bis(α-isobutylaminobenzylidene)hydrazine.* Bis(α-isobutylaminobenzylidene)hydrazine (2.0 g, 5.7 mmol) was dissolved in 5 ml of freshly distilled *N,N*-dimethylaniline, and refluxed under an atmosphere of nitrogen for 24 h. The solvent was then evaporated under reduced pressure, and the residue (1.72 g) recrystallized from 50 % ethanol, to yield 1.31 g (87.3 %) of the pure product as white crystals, m.p. 175–176 °C.

^{1}H and ^{13}C NMR, IR and MS data were identical in every detail with those reported in the literature.[1] Found: M^+ 277.1581. Calc. for $C_{18}H_{19}N_3$: *M* 277.1579.

*4-(1-Octyl)-3,5-diphenyl-4*H*-1,2,4-triazole.* Bis(α-chlorobenzylidene)hydrazine (0.21 g, 0.75 mmol) was dissolved in a mixture of 1-octylamine (0.41 g, 0.33 mmol) and dry benzene (1.00 g), and then heated in a sealed tube for 47 h at 141–152 °C in an oil bath. The reaction mixture was cooled to room temperature, dissolved in dichloromethane (15 ml), and washed with 1 M HCl (6 × 5 ml) and water (2 × 10 ml). The organic solvent was evaporated off under reduced pressure and the crude product recrystallized from aqueous ethanol to yield 0.20 g (79 %) of the pure product as white crystals of m.p. 93.5–94.5 °C.

^{1}H NMR (100 MHz): δ 0.65–1.55 (m, 15 H), 4.08 (t, 2 H, J = 7.3 Hz), 7.32–7.80 (m, 10 H). ^{13}C NMR (25.0 MHz): δ 14.0, 22.5, 25.9, 28.5, 28.8, 29.8, 31.5, 44.8, 127.9, 129.0, 130.0, 155.5. IR (KBr): 3065, 2953, 2918, 2853, 1476, 1444, 1417, 1026, 776, 734, 699, 685 cm^{-1}. MS [*m/z* (% rel. int.)]: 335 (2), 334 (10), 333 (42, M^+), 290 (21), 276 (17), 262 (17), 249 (18), 248 (82), 235 (24), 234 (44), 222 (38), 221 (100), 200 (18), 131 (33), 118 (64), 104 (52), 103 (18), 91 (18), 90 (15), 89 (85), 79 (11), 77 (62). Found: M^+ 333.2213. Calc. for $C_{22}H_{27}N_3$: *M* 333.2205.

*4-(2-Octyl)-3,5-diphenyl-4*H*-1,2,4-triazole.* Bis(α-chlorobenzylidene)hydrazine (2.00 g, 7.22 mmol) was dissolved in 2-octylamine (12.08 g, 93.5 mmol) and refluxed under a nitrogen atmosphere for 26 h. Excess 2-octylamine was then evaporated under reduced pressure. The residue was dissolved in dichloromethane (30 ml) and washed consecutively with water (20 ml), 1 M HCl (3 × 20 ml), 2 M NaOH (3 × 20 ml) and water (20 ml), and the organic phase was dried over anhydrous $MgSO_4$. The solvent was evaporated off under reduced pressure and the residue sublimated, at 160–170 °C and 1–2 Pa, to give a solid product, 2.3 g (95 %) of 90 % purity (GLC). 0.2 g of this product was further purified by preparative TLC ($CHCl_3$). The zone with R_f = 0–0.44, gave 0.17 g pure product [98.9 % (GLC)], of m.p. 89–92 °C and the following spectroscopic properties.

^{1}H NMR (100 MHz): δ 0.77–0.93 (m) and 0.93–1.32 (m) integral for 13 H, 1.53 (d, 3 H, J = 6.8 Hz), 4.08–4.49 (m, 1 H), 7.36–7.73 (m, 10 H). ^{13}C NMR (25.0 MHz): δ 13.9, 22.1, 22.4, 26.0, 28.4, 31.4, 35.6, 53.5, 128.5, 129.9, 155.5. IR (KBr): 3066, 2952, 2934, 2866, 1473, 1459, 1445, 1410, 1388, 1380, 764, 701 cm^{-1}. MS [*m/z* (4 rel. int.)]: 334 (7), 333 (23, M^+), 222 (22), 221 (100), 118 (46), 104 (18), 90 (11), 89 (61), 77 (21), 63 (13), 57 (17). Found: M^+ 333.2213. Calc. for $C_{22}H_{27}N_3$: M 333.2205.

*4-Cyclohexyl-3,5-diphenyl-4*H*-1,2,4-triazole.* The experimental procedure was analogous to that described for the synthesis of 4-(1-octyl)-3,5-diphenyl-4*H*-1,2,4-triazole. The reaction mixture were heated in a sealed tube for 114 h at 144–147 °C in an oil bath. The crude product was recrystallized from aqueous ethanol to yield 0.11 g (48 %) of pure product as white crystals of m.p. 162–163 °C. The product exhibited the following spectroscopic properties.

^{1}H NMR (100 MHz): δ 0.58–2.00 (m, 10 H), 3.83–4.19 (m, 1 H), 7.34–7.72 (m, 10 H). ^{13}C NMR (25.0 MHz): δ 24.8, 25.9, 33.3, 57.8, 128.6, 130.0, 155.3. IR (KBr): 2936, 2863, 2850, 1474, 1460, 1454, 1443, 1387, 1180, 784, 777, 771, 731, 722, 711, 704 cm^{-1}. MS [*m/z* (% rel. int.)]: 304 (13), 303 (48, M^+), 222 (21), 221 (100), 118 (32), 89 (14). Found: M^+ 303.1741. Calc. for $C_{20}H_{21}N_3$: M 303.1736.

*Thermolysis of Bis(α-*tert*-butylaminobenzylidene)hydrazine* was performed by heating 0.11 g (0.314 mmol) of the compound in a nitrogen atmosphere for 3.5 h at 232 °C. The reaction mixture was then dissolved in dichloromethane (10 ml) and extracted with 2 M sodium hydroxide solution. The basic phase yielded, after acidification with 1 M hydrochloric acid and extraction with dichloromethane (2 × 15 ml), 40 mg (58 %) of white crystals identified as 3,5-diphenyl-1*H*-1,2,4-triazole (**8**) m.p. 189–191 °C. Spectroscopic properties were in total agreement with those previously reported.[18]

*Attempted preparation of 4-(1-adamantyl)-3,5-diphenyl-4*H*-1,2,4-triazole.* *N*-(1-adamantyl)benzamide (0.30 g, 1.18 mmol) was dissolved in 5 ml of thionyl chloride, and stirred at room temperature under a nitrogen atmosphere for 3 days. The reaction mixture was then evaporated to dryness under reduced pressure. The residue (131 mg) and 5-phenyltetrazole (158 mg, 1.18 mmol) were then dissolved in 5 ml of dry pyridine at room temperature under nitrogen and heated to reflux for 14 h. After being cooled, the reaction mixture was dissolved in dichloromethane (10 ml) and washed with 1 M HCl (3 × 10 ml), 2 M NaOH (2 × 10 ml), water (10 ml) and finally dried over anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure to yield 58 mg (71 %) of a white product that was identified as 1-chloroadamantane (98 % pure by GLC) by comparison of its spectroscopic properties with those of an authentic sample. From the acidified basic extract was isolated unchanged phenyltetrazole, but no traces of triazoles were detected.

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