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Cycloaddition reactions of 2,4-diphenyl-1,3-diazabuta-1,3-dienes with isocyanates and isothiocyanates

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Abstract—The cycloaddition reactions of 1-*p*-tolyl and 1-benzyl- 2,4-diphenyl-1,3-diazabuta-1,3-dienes with a variety of aryl and alkyl isocyanate and isothiocyanate are described. The reaction mechanism is also discussed.

1. Introduction

In the last decades the cycloaddition reactions of 1,3-diazabuta-1,3-dienes represented a useful tool for the synthesis of a wide variety of four, five and six member nitrogen-containing heterocycles.[1] The involvement of these azadienes in cycloaddition reactions with isocyanides,[2] phosphoric compounds,[3] the Simmons–Smith reagent,[4] acetylenes,[5] enamines,[6] sulfenes,[7] oxazolinones,[8] acrylates,[9] the Reformatsky reagent,[10] nitriles[11] and α-nitrostyrenes,[12] have been reported. Nevertheless the cycloaddition reactions of 1,3-diazabuta-1,3-dienes with ketenes represent the most studied application of 1,3-diazabutadienes in heterocyclic synthesis,[13] leading up to a wide variety of azetidinones and pyrimidinones. Recently in our laboratories we investigated the reactions of 2,4-diphenyl-1,3-diazabuta-1,3-dienes **1a** and **1b** with mono and disubstituted ketenes[14] and the thermal and photochemical transformations of the [2+2] cycloadduct into the corresponding [4+2] adduct.[15] We also extended our study to the cycloaddition reactions of 1-benzyl-2,4-diphenyl-1,3-diazabuta-1,3-diene **1b** with some chiral ketenes leading up to optically active azetidinones.[16] In connection with our ongoing interest in this research area, we widened our study to cycloaddition reactions of 2,4-diphenyl-1,3-diazabuta-1,3-dienes **1a** and **1b** with isocyanates[17] and isothiocyanates.[18] In the literature there are only a few reports of the reactions of simple acyclic azadienes and they mainly involve 4,4-disubstituted azadienes[11a,19] or 2,4-heterosubstituted azadienes.[20] On the contrary azadienes **1a** and **1b** are marked out by the monosubstitution on C-4 and by the all-carbon substitutions on the diene chain.

Keywords: 1,3-diazabuta-1,3-dienes; isocyanates; isothiocyanates; [4+2] cycloaddition; triazin-2-ones; triazin-2-thiones.
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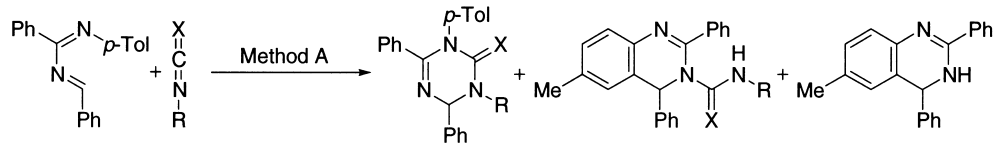
2. Results and discussion

We tested the reactivity of the 1,3-diaza-1,3-butadienes **1a-b** with arylisocyanates **2a-c**, benzylisocyanate **2d**, alkylisocyanates **2e**,**f**, arylisothiocyanates **2g**,**h** and benzylisothiocyanate **2i**. In the first stage of the study the reactions were performed in a sealed tube under nitrogen atmosphere by addition of the appropriate heteroallene **2a–i** (2 equiv.) to a stirred solution of 1,3-diaza-1,3-diene **1a** or **1b** (1 equiv.) in dry benzene and in the presence of few crystals of hydroquinone to avoid heterocumulene polymerisation (Method A). The reactions of azadiene **1a** were performed at 80–110°C while **1b** reacted at lower temperatures. After usual work up, the reaction mixtures were purified by flash chromatography over silica gel or by crystallisation. The structures were assigned on the basis of analytical and spectral data.

As summarised in Table 1 the reactions of the azadiene **1a**, bearing a *p*-tolyl group on N-1 with arylisocyanates **2a-c** gave rise to the 3,4-dihydro-1*H*-[1,3,5]triazin-2-ones **3a-c** in satisfactory yields; the presence of an electron withdrawing group on the isocyanate moiety positively affected the reaction, increasing the yields and reducing the reaction times (Table 1, entries 1–3). The reaction with benzylisocyanate **2d** resulted in the isolation of a modest amount of triazin-2-one **3d** besides the *N*-substituted 3,4-dihydroquinazoline **4d** (Table 1, entry 4). This trend was emphasized in the reactions of **1a** with alkylisocyanates **3e**,**f** yielding the *N*-substituted 3,4-dihydroquinazolines **4e**,**f** as the sole isolated products (Table 1, entries 5 and 6). Finally no reaction was observed between **1a** and the isothiocyanates **2g**,**h** and the 3,4-dihydroquinazoline **5** was the exclusive detected product (Table 1, entries 7–8).

The reactions performed with 1,3-diaza-1,3-butadiene **1b**, bearing a benzyl group on N-1, and heteroallenes **2a-i**

Table 1. Reactions of **1a** with **2a-h** (Method A)



1a **2a-h** **3a-h** **4a-h** **5**

Entry	Compound	R	X	Yield (%)			Time (h)	Temperature (°C)
				3	**4**	**5**		
1	**2a**	Ph–	O	68	–	–	31	80
2	**2b**	*m*-Cl–Ph–	O	84	–	–	5	110
3	**2c**	*p*-CH_3–Ph–SO_2–	O	91	–	–	1	80
4	**2d**	Ph–CH_2–	O	39	60	–	24	110
5	**2e**	*c*-C_6H_{11}–	O	–	78	–	25	100
6	**2f**	$CH_3CH_2CH_2$–	O	–	63	–	75	100
7	**2g**	*p*-NO_2–Ph–	S	–	–	77	24	80
8	**2h**	Ph–	S	–	–	82	22	80

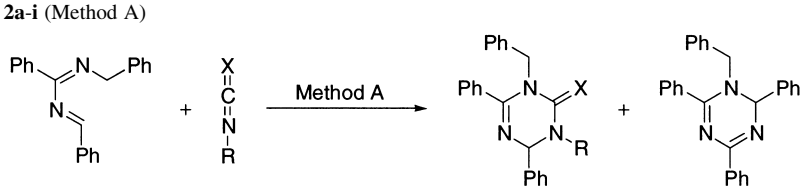
resulted in the isolation of the [4+2] cycloaddition reaction products, the triazin-2-ones/thiones **6a-i** besides a variable amount of the 1,2-dihydro-1,3,5-triazine **7** as by-product (Table 2).

The behavior of azadiene **1b** in the reactions with the aryl and benzyl isocyanates **2a–d** was closely related to those observed for **1a** (Table 2, entries 1–4). In contrast, **1b** was able to react with the alkyl isocyanates **2e**,**f** affording the 3,4-dihydro-1*H*-[1,3,5]triazin-2-ones **6e**,**f** in low yields beside a considerable amount of triazine **7** (Table 2, entries 5 and 6). Moreover, the reaction of **1b** with the isothiocyanates **2g–i** gave the corresponding 3,4-dihydro-1*H*-[1,3,5]triazin-2-thiones **6g–i** in moderate yields (Table 2, entries 7–9). In all performed reactions the use of an excess of heteroallene did not give any adduct arising from the reaction of two molecules of iso(thio)cyanate with one molecule of diene, such as has been reported.[21]

It is well known that the chemistry of 1,3-diazabuta-1,3-dienes is dominated by pronounced charge alternation and high electron deficiency. On the basis of perturbation theory the N-1 is placed in a more favorable position of the diene system and with respect to N-3 is much prone to act as nucleophile.[13c] On the other hand the reactivity of isocyanates and isothiocyanates can be well understood by considering both electronic and steric effect of the groups attached to the nitrogen atom; the reactions of hetero-cumulenes with nitrogen nucleophile involve the attack on the central carbon of iso(thio)cyanate; consequently, in absence of steric hindrance any electron-withdrawing group linked to the NCO/NCS moiety amplifies the positive charge on carbon atom increasing the reactivity toward nucleophiles; on the contrary, the opposite effect is shown when an electron-donating group is attached to NCO/NCS cluster.[22]

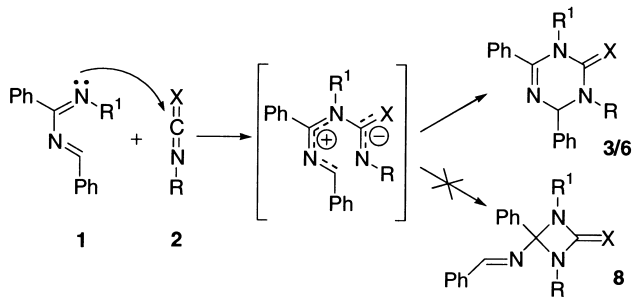
On the basis of these considerations and in analogy with the reactions of azadienes **1a**,**b** with ketenes[14] the proposed mechanism for the reaction between **1a**,**b** and the iso

Table 2. Reactions of **1b** with **2a-i** (Method A)



1b **2a-i** **6a-i** **7**

Entry	Compounds	R	X	Yield (%)		Time (h)	Temperature (°C)
				6	**7**		
1	**2a**, **6a**	Ph–	O	72	13	26	25
2	**2b**, **6b**	*m*-Cl–Ph–	O	76	–	20	25
3	**2c**, **6c**	*p*-CH_3–Ph–SO_2–	O	82	–	5	25
4	**2d**, **6d**	Ph–CH_2–	O	42	19	24	25
5	**2e**, **6e**	*c*-C_6H_{11}–	O	15	48	72	25
6	**2f**, **6f**	$CH_3CH_2CH_2$–	O	17	56	72	25
7	**2g**, **6g**	*p*-NO_2–Ph–	S	52	18	48	25
8	**2h**, **6h**	Ph–	S	42	23	96	60
9	**2i**, **6i**	Ph–CH_2–	S	35	10	120	60



Scheme 1.

(thio)cyanates **2a–i** is a two-step process. As previously reported for cyclic azadienes,[23] the first step involves the nucleophilic attack of the N-1 of the azadiene on the central carbon atom of heterocumulene followed by the intramolecular attack of the C-4 of the diene system on the nitrogen atom of the heteroallene to afford six member heterocycles **3** or **6** (Scheme 1). It is worthy to note that, whereas **1b** reacts with ketenes giving rise to [2+2] cycloaddition products,[14] the reactions of **1b** with iso(thio)cyanates did not afford any [2+2] cycloaddition product and the hypothetical diazetidinone/thione **8** was never detected or isolated (Scheme 1).

In the reactions of **1a** with alkylisocyanates **2d–f** the formation of the *N*-substituted 3,4-dihydroquinazolines **4d–f** (Table 1, entries 4–6) can be explained as consequence of the competitive sequential thermal 6π electrocyclic ring closure/[1,5] sigmatropic hydrogen shift of azadiene **1a** to give 3,4-dihydroquinazoline **5**,[24] followed by nucleophilic addition to isocyanate **2d–f** (Scheme 2).

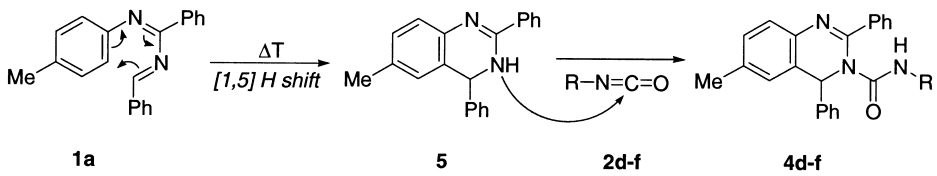
Nevertheless the quinazoline **5** did not react with isothiocyanate **2g–h** which are unreactive under these reaction conditions.[25]

On the other hand, in the reactions between **1b** and heteroallenes, the formation of 1,2-dihydro-1,3,5-triazine **7** (formally derived from two molecules of azadiene **1b**) was competitive with the cycloaddition reaction (Table 2, entries 1, 4–7); the mechanism of formation of **7** was widely discussed in a previous paper.[26]

The lower reactivity of **1a** with respect to **1b** is probably related to the poor nucleophilicity of the N-1 in the fully conjugated system **1a** and to the steric hindrance exerted by the phenyl group directly linked to the N-1 atom in **1a**. The reactive center in **1b** is less hindered by the insertion of a methylene spacer between N-1 and the phenyl group. Moreover the presence of a methylene group in **1b** decrease the conjugation and increase the nucleophilicity of the system.

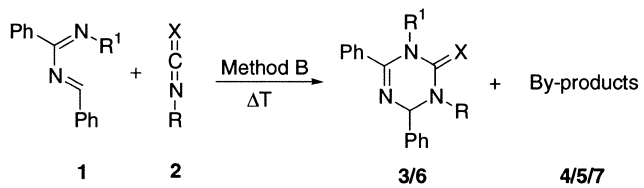
With the aim to improve the yields and avoid or minimize the formation of by-products we performed some new experiments for the reactions that failed or gave low yields by the way of method A. Thus, the reactions of **1a** with **2d**,**f**,**g** and **1b** with **2d–f**,**i** were carried out without solvent by stirring a mixture of 100 mg of azadiene **1** and 1 mL of the appropriate heterocumulene **2** at 25–122°C (Method B). The obtained results are reported in Table 3.

By this way, it was possible to improve the yields of reaction of the azadiene **1a** with benzylisocyanate **2d** from 39 to 61%



Scheme 2.

Table 3. Reactions of **1a** and **1b** with **2d-g**,**i** (Method B)



Entry	Compound	Compound	Time (h)	Temperature (°C)	Products		Gain (%)[a]	By-products	
					3/6	Yield (%)		**4/5/7**	Yield (%)
1	**1a**	**2d**	44	25	**3d**	61	+56	**4d**	tr.
2	**1a**	**2f**	48	25–60	–	–	–	**4f**	91
3	**1a**	**2g**	72	122[b]	–	–	–	**5**	68
4	**1b**	**2d**	48	25	**6d**	64	+52	**7**	tr.
5	**1b**	**2e**	72	40	**6e**	46	+206	**7**	tr.
6	**1b**	**2f**	48	25	**6f**	43	+153	**7**	tr.
7	**1b**	**2i**	72	60	**6i**	54	+54	**7**	tr.

[a] Calculated as: (yield method B−yield method A)×100/yield method A.
[b] The reaction was performed in melted *p*-nitrophenylisothiocyanate **2g**.

(Table 3, entry 1) whereas also in these new reaction conditions and even at high temperatures, each attempt to react **1a** with alkylisocyanate **2f** and isothiocyanate **2g** failed (Table 3, entries 2–3). On the other hand the yields of cycloaddition reactions of **1b** with all iso(thio)cyanates (**2d**–**f**,**i**) tested were increased with a gain from 52 to 206% (Table 3, entries 4–7).

The presented study allowed us to confirm the good reactivity of the ready available 2,4-diphenyl-1,3-diaza-buta-1,3-dienes **1a** and **1b** toward heteroallenes. As a result, we have shown that the [4+2] cycloaddition reactions of **1a** and **1b** with isocyanates and isothiocyanates led in satisfactory yields to a great variety of 3,4-dihydro-1*H*-[1,3,5]triazin-2-ones and 3,4-dihydro-1*H*-[1,3,5]triazin-2-thiones.

3. Experimental

3.1. General details

All chemicals and solvents are commercially available and were used after distillation or treatment with drying agents. Merck silica gel 60 F_{254} thin-layer plates were employed for thin layer chromatography (TLC). Merck silica gel (230–400 mesh) was employed for flash column chromatography. Melting points, measured with a Stuart Scientific SMP3 apparatus, are uncorrected. Infrared spectra were recorded on a FT-IR Perkin–Elmer Spectrum One spectrophotometer using KBr tablets. Proton NMR spectra were recorded at room temperature in $CDCl_3$, on Varian-Gemini 200 at 200 MHz, with residual chloroform as the internal reference (δ_H=7.27 ppm). ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$, on the same spectrometer, at 50.3 MHz, with the central peak of chloroform as the internal reference (δ_C=77.3 ppm). The APT or DEPT sequences were used to distinguish the methine and methyl carbon signals from those due to methylene and quaternary carbons. Two-dimensional NMR experiments (NOESY) were used, where appropriate, to aid in the assignment of signals in the proton spectra. Azadienes **1a**,**b** were prepared according to described method.[12] The isocyanates **2a**–**f** and isothiocyanate **2g**–**j** were purchased from standard chemical suppliers. The 6-Methyl-2,4-diphenyl-3,4-dihydro-quinazoline **5**[24] and the 1,2-dihydro-1,3,5-triazine **7**[26] are known compounds. 'PE' refers to the fraction of petroleum ether with boiling point of 40–60°C. 'EtOAc' means ethyl acetate. TEA means triethylamine.

3.2. Reactions of azadienes 1 with heteroallenes 2

Method A. In a sealed tube, under a nitrogen atmosphere, the appropriate heteroallene **2** (1.34 mmol) was added to a solution of **1a** or **1b** (0.200 g, 0.67 mmol) in dry benzene (5 mL) in the presence of few crystals of hydroquinone. The reaction mixture was stirred at 25–110°C for 1–120 h until no more starting azadiene was detectable by TLC. The solvent was then removed in vacuum. The crude product was purified by crystallisation or by flash chromatography over silica gel column (for yields, times and temperatures see Tables 1 and 2).

Method B. In a sealed tube, under a nitrogen atmosphere, **1a** or **1b** (0.200 g, 0.67 mmol) was added to the appropriate heteroallene **2** (2 mL) in the presence of few crystals of hydroquinone. The reaction mixture was stirred at 25–122°C for 44–72 h until no more starting azadiene was detectable by TLC. When liquid, the excess of heteroallene was removed by distillation at reduced pressure. The crude product was purified by flash chromatography over silica gel column (for yields, times and temperatures see Table 3).

3.2.1. 3,4,6-Triphenyl-1-*p*-tolyl-3,4-dihydro-1*H*-[1,3,5]triazin-2-one (3a). Crystallised from methanol. White solid. Mp: 144°C. IR (KBr) ν=1699, 1636 cm^{-1}. ^1H NMR: δ=2.24 (s, 3H, CH_3), 6.46 (s, 1H, CH), 6.96 (m, 4H, arom.), 7.12–7.62 (m, 15H, arom.) ppm. ^{13}C NMR: δ=21.1, 77.1, 125.7, 126.2, 126.5, 127.9, 128.6, 128.8, 129.0, 129.1, 129.2, 129.3, 129.9, 134.2, 134.9, 137.3, 140.1, 14.0.4, 152.1, 155.3 ppm. $C_{28}H_{23}N_3O$ (417.50): calcd C 80.55, H 5.55, N 10.06; found C 80.67, H 5.58, N 10.10.

3.2.2. 3-(3-Chlorophenyl)-4,6-diphenyl-1-*p*-tolyl-3,4-dihydro-1*H*-[1,3,5]triazin-2-one (3b). Eluent for chromatography: PE/EtOAc (8:2). Pale yellow solid. Mp: 73°C. IR (KBr) ν=1698, 1645 cm^{-1}. ^1H NMR: δ=2.24 (s, 3H, CH_3), 6.23 (s, 1H, CH), 6.91 (d, ^3J=8.4 Hz, 2H, arom., AA′ part of an AA′BB′ system), 6.98 (d, ^3J=8.4 Hz, 2H, arom., BB′ part of an AA′BB′ system), 7.16–7.60 (m, 14H, arom.) ppm. ^{13}C NMR: δ=21.1, 76.8, 123.5, 126.1, 126.5, 126.6, 126.9, 127.8, 127.9, 128.2, 128.7, 128.8, 129.2, 130.0, 134.5, 134.6, 137.5, 139.0, 139.6, 141.5, 151.9, 155.3 ppm. $C_{28}H_{22}ClN_3O$ (451.95): calcd C 74.41, H 4.91, N 9.30; found C 74.31, H 4.90, N 9.34.

3.2.3. 4,6-Diphenyl-3-(toluene-4-sulfonyl)-1-*p*-tolyl-3,4-dihydro-1*H*-[1,3,5]triazin-2-one (3c). Crystallised from diisopropyl ether. White crystals. Mp: 145–149°C. IR (KBr) ν=1715, 1645, 1326, 1171 cm^{-1}. ^1H NMR: δ=2.21 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 6.85 (d, ^3J=8.1 Hz, 2H, arom., AA′ part of an AA′BB′ system), 6.87 (d, ^3J=8.1 Hz, 2H, arom., BB′ part of an AA′BB′ system), 7.11 (s, 1H, CH), 7.17 (m, 4H, arom.), 7.27 (m, 3H, arom.), 7.36 (m, 4H, arom.), 7.64 (d, ^3J=8.4 Hz, 2H, arom.), 7.88 (m, 1H, arom.) ppm. ^{13}C NMR: δ=21.2, 21.7, 73.5, 126.4, 128.0, 128.5, 129.0, 129.2, 129.4, 129.9, 130.1, 131.4, 133.4, 133.7, 135.0, 135.5, 138.1, 138.6, 144.9, 149.4, 154.2 ppm. $C_{29}H_{25}N_3O_3S$ (495.59): calcd C 70.28, H 5.08, N 8.48; found C 70.40, H 5.02, N 8.45.

3.2.4. 3-Benzyl-4,6-diphenyl-1-*p*-tolyl-3,4-dihydro-1*H*-[1,3,5]triazin-2-one (3d). Eluent for chromatography: PE/TEA (8:2). White solid. Mp: 140–143°C. IR (KBr) ν=1692, 1648 cm^{-1}. ^1H NMR: δ=2.27 (s, 3H, CH_3), 3.90 (d, ^2J=15.4 Hz, 1H, CH_2), 5.37 (d, ^2J=15.4 Hz, 1H, CH_2), 6.01 (s, 1H, CH), 7.01 (m, 4H, arom.), 7.14–7.50 (m, 15H, arom.) ppm. ^{13}C NMR: δ=21.1, 48.4, 74.2, 126.5, 127.8, 127.9, 128.4, 128.7, 128.8, 128.9, 129.0, 129.1, 129.2, 129.6, 134.6, 135.2, 136.3, 137.3, 139.7, 153.1, 154.5 ppm. $C_{29}H_{25}N_3O$ (431.53): calcd C 80.72, H 5.84, N 9.74; found C 80.60, H 5.86, N 9.77.

3.2.5. 6-Methyl-2,4-diphenyl-4*H*-quinazoline-3-carboxylic acid benzylamide (4d). Eluent for chromatography: PE/TEA

(8:2). White crystals. Mp: 150–156°C. IR (KBr) ν=3256, 1659, 1541 cm^{-1}. ^1H NMR: δ=2.40 (s, 3H, CH_3), 4.19 (dd, ^2J=14.5 Hz, ^3J=4.7 Hz, 1H, CH_2), 4.27 (dd, ^2J=14.5 Hz, ^3J=5.9 Hz, 1H, CH_2), 4.49 (bm, 1H, NH, exchange with D_2O), 6.70 (s, 1H, H^4), 6.77 (m, 2H, arom.), 7.06 (s, 1H, H^5), 7.10–7.50 (m, 13H, arom.), 7.60 (m, 2H, arom.) ppm. ^{13}C NMR: δ=21.5, 45.6, 56.4, 125.6, 127.4, 127.5, 127.6, 127.9, 128.1, 128.5, 128.7, 128.8, 129.2, 129.7, 131.3, 135.9, 137.6, 137.7, 139.8, 140.9, 150.7, 154.9, 156.8 ppm. $C_{29}H_{25}N_3O$ (431.53): calcd C 80.72, H 5.84, N 9.74; found C 80.72, H 5.82, N 9.76.

3.2.6. 6-Methyl-2,4-diphenyl-4*H*-quinazoline-3-carboxylic acid cyclohexylmethylamide (4e). Eluent for chromatography: PE/EtOAc (8:2). White crystals. Mp: 145°C. IR (KBr) ν=3292, 1654, 1543 cm^{-1}. ^1H NMR: δ=0.70–2.80 (m, 10H, CH_2 cyclohexyl), 2.39 (s, 3H, CH_3), 3.51 (m, 1H, CH cyclohexyl), 4.17 (bd, ^3J=8.2 Hz, 1H, NH, exchange with D_2O), 6.64 (s, 1H, H^4), 7.05 (s, 1H, H^5), 7.20–7.59 (m, 10H, arom.), 7.61 (m, 2H, arom.) ppm. ^{13}C NMR: δ=21.4, 24.4, 24.5, 25.4, 32.1, 33.1, 49.9, 55.9, 125.3, 127.2, 127.5, 127.8, 127.9, 128.3, 128.6, 128.9, 129.4, 131.1, 135.9, 137.3, 139.7, 141.1, 150.8, 153.8 ppm. $C_{29}H_{31}N_3O$ (437.58): calcd C 79.60, H 7.14, N 9.60; found C 79.68, H 7.16, N 9.55.

3.2.7. 6-Methyl-2,4-diphenyl-4*H*-quinazoline-3-carboxylic acid propylamide (4f). Eluent for chromatography: PE/EtOAc (9:1). White crystals. Mp: 156°C. IR (KBr) ν=3270, 1658, 1542 cm^{-1}. ^1H NMR: δ=0.54 (t, ^3J=7.5 Hz, 3H, CH_3–CH_2–CH_2), 1.14 (sexs., ^3J=7.5 Hz, 2H, CH_3–CH_2–CH_2), 2.90 (m, 1H, CH_3–CH_2–CH_2), 3.10 (m, 1H, CH_3–CH_2–CH_2), 4.25 (bm, 1H, NH, exchange with D_2O), 6.65 (s, 1H, H^4), 7.05 (s, 1H, H^5), 7.20–7.50 (m, 10H, arom.), 7.64 (m, 2H, arom.) ppm. ^{13}C NMR: δ=11.8, 21.2, 22.4, 40.4, 56.0, 125.3, 127.2, 127.7, 127.9, 128.3, 128.6, 128.9, 129.4, 131.2, 131.3, 135.7, 137.4, 139.7, 140.9, 150.7, 154.7 ppm. $C_{25}H_{25}N_3O$ (383.49): calcd C 78.30, H 6.57, N 10.96; found C 78.52, H 6.54, N 10.92.

3.2.8. 1-Benzyl-3,4,6-triphenyl-3,4-dihydro-1*H*-[1,3,5]triazin-2-one (6a). Eluent for chromatography: PE/TEA (9:1). White solid. Mp: 127–129°C. IR (KBr) ν=1678, 1659, 1595 cm^{-1}. ^1H NMR: δ=4.49 (d, ^2J=15.0 Hz, 1H, CH_2), 5.29 (d, ^2J=15.0 Hz, 1H, CH_2), 6.34 (s, 1H, CH), 6.90 (d, ^3J=8.1 Hz, 2H, arom.), 7.10–7.51 (m, 18H, arom.) ppm. ^{13}C NMR: δ=48.4, 76.2, 125.1, 126.2, 126.3, 127.3, 128.1, 128.3, 128.5, 128.7, 128.8, 129.1, 130.3, 133.7, 137.1, 139.9, 140.5, 152.7, 155.9 ppm (one signal obscured). $C_{28}H_{23}N_3O$ (417.50): calcd C 80.55, H 5.55, N 10.06; found C 80.29, H 5.52, N 10.09.

3.2.9. 1-Benzyl-3-(3-chlorophenyl)-4,6-diphenyl-3,4-dihydro-1*H*-[1,3,5]triazin-2-one (6b). Eluent for chromatography: PE/TEA (95:5). White solid. Mp: 132–134°C. IR (KBr) ν=1689, 1645, 1591 cm^{-1}. ^1H NMR: δ=4.49 (d, ^2J=15.0 Hz, 1H, CH_2), 5.27 (d, ^2J=15.0 Hz, 1H, CH_2), 6.33 (s, 1H, CH), 6.67 (d, ^3J=7.0 Hz, 2H, arom.), 7.00–7.50 (m, 17H, arom.) ppm. ^{13}C NMR: δ=48.5, 76.2, 122.8, 125.2, 126.2, 126.3, 127.4, 128.0, 128.3, 128.5, 128.7, 128.9, 129.9, 130.4, 133.8, 134.5, 136.9, 139.4, 141.6, 152.5, 155.9 ppm (one signal obscured). $C_{28}H_{22}ClN_3O$ (451.95): calcd C 74.41, H 4.91, N 9.30; found C 74.30, H 4.89, N 9.33.

3.2.10. 1-Benzyl-4,6-diphenyl-3-(toluene-4-sulfonyl)-3,4-dihydro-1*H*-[1,3,5]triazin-2-one (6c). Eluent for chromatography: PE/EtOAc (9:1). Yellow solid. Mp: 139–141°C. IR (KBr) ν=1690, 1632, 1360, 1180 cm^{-1}. ^1H NMR: δ=2.46 (s, 1H, CH_3), 4.37 (d, ^2J=15.4 Hz, 1H, CH_2), 5.13 (d, ^2J=15.4 Hz, 1H, CH_2), 6.42 (d, ^3J=7.3 Hz, 2H, arom.), 6.94 (dd, ^3J=7.3, 7.7 Hz, 2H, arom.), 7.06 (d, ^3J=7.3 Hz, 1H, arom.), 7.12 (s, 1H, CH), 7.22–7.52 (m, 11H, arom.), 7.84 (d, ^3J=8.4 Hz, 2H, arom) ppm. ^{13}C NMR: δ=21.8, 48.1, 72.7, 126.3, 127.5, 127.7, 128.3, 128.4, 128.6, 128.8, 129.2, 129.4, 130.6, 133.2, 135.7, 135.8, 138.4, 145.1, 149.9, 155.4 ppm (one signal obscured). $C_{29}H_{25}N_3O_3S$ (495.59): calcd C 70.28, H 5.08, N 8.48; found C 70.38, H 5.04, N 8.45.

3.2.11. 1,3-Dibenzyl-4,6-diphenyl-3,4-dihydro-1*H*-[1,3,5]triazin-2-one (6d). Eluent for chromatography: PE/EtOAc (95:5). White solid. Mp: 138–140°C. IR (KBr) ν=1682, 1654 cm^{-1}. ^1H NMR: δ=3.81 (d, ^2J=15.4 Hz, 1H, CH_2), 4.59 (d, ^2J=15.4 Hz, 1H, CH_2), 5.23 (d, ^2J=15.4 Hz, 1H, CH_2), 5.39 (d, ^2J=15.4 Hz, 1H, CH_2), 5.91 (s, 1H, CH), 6.80 (m, 2H, arom.), 7.11–7.50 (m, 18H, arom.) ppm. ^{13}C NMR: δ=43.3, 74.0, 126.6, 127.4, 127.8, 127.9, 128.1, 128.3, 128.4, 128.5, 128.6, 128.7, 128.8, 130.1, 134.4, 136.4, 137.6, 139.4, 153.4, 155.4 ppm. $C_{29}H_{25}N_3O$ (431.53): calcd C 80.72, H 5.84, N 9.74; found C 80.82, H 5.85, N 9.74.

3.2.12. 1-Benzyl-3-cyclohexylmethyl-4,6-diphenyl-3,4-dihydro-1*H*-[1,3,5]triazin-2-one (6e). Eluent for chromatography: PE/EtOAc (95:5). White solid. Mp: 129°C. IR (KBr) ν=1671, 1647 cm^{-1}. ^1H NMR: δ=0.90–2.01 (m, 10H, CH_2 cyclohexyl), 4.27 (m, 1H, CH cyclohexyl), 4.42 (d, ^2J=14.7 Hz, 1H, CH_2), 5.19 (d, ^2J=14.7 Hz, 1H, CH_2), 6.04 (s, 1H, CH), 6.78 (m, 2H, arom.), 7.02–7.46 (m, 13H, arom.) ppm. ^{13}C NMR: δ=25.5, 26.0, 26.1, 31.1, 31.5, 48.6, 49.4, 55.4, 126.4, 127.5, 128.2, 128.4, 128.5, 128.6, 128.8, 128.9, 130.7, 137.3, 141.1, 152.9, 157.0 ppm (one signal obscured). $C_{29}H_{31}N_3O$ (437.58): calcd C 79.60, H 7.14, N 9.60; found C 79.52, H 7.18, N 9.63.

3.2.13. 1-Benzyl-4,6-diphenyl-3-propyl-3,4-dihydro-1*H*-[1,3,5]triazin-2-one (6f). Eluent for chromatography: PE/TEA (95:5). Yellow solid. Mp: 129–133°C. IR (KBr) ν=1681, 1526 cm^{-1}. ^1H NMR: δ=0.94 (t, ^3J=7.3 Hz, 3H, CH_3–CH_2–CH_2), 1.66 (m, 2H, CH_3–CH_2–CH_2), 2.85 (m, 1H, CH_3–CH_2–CH_2), 3.85 (m, 1H, CH_3–CH_2–CH_2), 4.49 (d, ^2J=15.0 Hz, 1H, CH_2), 5.19 (d, ^2J=15.0 Hz, 1H, CH_2), 5.96 (s, 1H, CH), 6.78 (m, 2H, arom.), 7.02–7.50 (m, 13H, arom.) ppm. ^{13}C NMR: δ=11.4, 21.2, 47.6, 48.0, 74.9, 126.3, 127.3, 128.3, 128.6, 128.8, 129.3, 134.4, 137.7, 140.1, 153.2, 155.7 ppm (two signals obscured). $C_{25}H_{25}N_3O$ (383.49): calcd C 78.30, H 6.57, N 10.96; found C 78.42, H 6.59, N 11.00.

3.2.14. 1-Benzyl-3-(4-nitro-phenyl)-4,6-diphenyl-3,4-dihydro-1*H*-[1,3,5]triazin-2-thione (6g). Eluent for chromatography: PE/TEA (95:5). Yellow solid. Mp: 144–148°C. IR (KBr) ν=1645, 1363 cm^{-1}. ^1H NMR: δ=4.77 (d, ^2J=15.0 Hz, 1H, CH_2), 6.08 (d, ^2J=15.0 Hz, 1H, CH_2), 6.34 (s, 1H, CH), 6.48 (d, ^3J=7.0 Hz, 2H, arom.), 6.94 (m, 2H, arom.), 7.09 (m, 1H, arom.), 7.30–7.49 (m, 8H, arom.), 7.59 (d, ^3J=9.2 Hz, 2H, arom., AA′ part of an AA′BB′ system),

8.23 (d, ^3J=9.2 Hz, 2H, arom., BB′ part of an AA′BB′ system) ppm. ^{13}C NMR: δ=53.5, 76.9, 124.6, 126.5, 127.4, 128.0, 128.2, 128.5, 128.7, 129.0, 129.1, 130.8, 133.5, 135.9, 138.2, 146.2, 149.4, 154.4, 180.8 ppm (one signal obscured). $C_{28}H_{22}N_4O_2S$ (478.57): calcd C 70.27, H 4.63, N 11.71; found C 70.39, H 4.66, N 11.70.

3.2.15. 1-Benzyl-3,4,6-triphenyl-3,4-dihydro-1*H*-[1,3,5]triazin-2-thione (6h). Eluent for chromatography: PE/EtOAc (95:5). White solid. Mp: 146°C. IR (KBr) ν=1641, 1363 cm^{-1}. ^{1}H NMR: δ=4.75 (d, ^2J=15.0 Hz, 1H, CH_2), 6.17 (d, ^2J=15.0 Hz, 1H, CH_2), 6.32 (s, 1H, CH), 6.25 (d, ^3J=7.0 Hz, 2H, arom.), 6.97 (m, 2H, arom.), 7.10 (m, 1H, arom.), 7.29–7.45 (m, 15H, arom.) ppm. ^{13}C NMR: δ=53.6, 77.4, 126.8, 127.4, 127.7, 128.1, 128.3, 128.5, 128.7, 128.8, 129.0, 129.3, 129.5, 130.6, 134.1, 13.6, 139.0, 144.3, 154.5, 180.9 ppm. $C_{28}H_{23}N_3S$ (433.57): calcd C 77.57, H 5.35, N 9.69; found C 77.68, H 5.38, N 9.64.

3.2.16. 1,3-Dibenzyl-4,6-diphenyl-3,4-dihydro-1*H*-[1,3,5]triazin-2-thione (6i). Eluent for chromatography: PE/EtOAc (95:5). Yellowish oil. IR (KBr) ν=1643, 1371 cm^{-1}. ^{1}H NMR: δ=4.36 (d, ^2J=15.0 Hz, 1H, CH_2), 4.71 (d, ^2J=15.0 Hz, 1H, CH_2), 6.10 (d, ^2J=15.0 Hz, 1H, CH_2), 6.12 (s, 1H, CH), 6.32 (d, ^2J=15.0 Hz, 1H, CH_2), 6.53 (d, ^3J=7.0 Hz, 2H, arom.), 6.92 (m, 2H, arom.), 7.08 (m, 1H, arom.), 7.22–7.44 (m, 15H, arom.) ppm. ^{13}C NMR: δ=53.9, 55.7, 73.3, 126.4, 127.3, 128.0, 128.1, 128.2, 128.3, 128.6, 128.7, 128.8, 129.0, 129.1, 130.5, 134.1, 135.7, 136.9, 138.7, 154.9, 180.9 ppm. $C_{29}H_{25}N_3S$ (447.60): calcd C 77.82, H 5.63, N 9.39; found C 77.74, H 5.66, N 9.44.

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