Cycloadditions of Aryl-Substituted 1,2,4-Triazines with 2-Cyclopropylidene-1,3-dimethylimidazolidine – Zwitterions as Discrete Intermediates

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Dedicated to Professor *Rolf Huisgen* on the occasion of his 85th birthday

Cycloadditions of 2-cyclopropylidene-1,3-dimethylimidazolidine (**1**), a strong, electron-rich C-nucleophile, with a variety of aryl-substituted 1,2,4-triazines occur at temperatures between −100 and +100°, depending on the substitution pattern. At low temperatures, zwitterions, formed by nucleophilic attack of **1** on the triazines, could be detected spectroscopically and, in some cases, isolated. Two types of zwitterions were found: *1*) those where the new bond was linked to C(5) of the triazine and which were formed in a reversible dead-end equilibrium, and *2*) those where the new bond was linked either to C(3) or C(6). The latter exhibited the same regiochemistry as the final cycloadducts, and might be intermediates of a two-step *Diels–Alder* reaction. Energies and structural characteristics for stationary points in the reaction of monosubstituted triazines with **1** in the gas phase and in CH_2Cl_2 solution were calculated at the Becke3LYP/6-311+G(d,p)//Becke3LYP/6-31G(d) level of theory. Different reaction mechanisms are discussed on the basis of steric, electronic, and solvent effects.

1. Introduction. – 3,6-Disubstituted 1,2,4,5-tetrazines react rapidly at room temperature with 2-cyclopropylidene-1,3-dimethylimidazolidine (**1**) to give dispiro adducts *via* [4+2] cycloaddition and consecutive elimination of N_2, in accordance with a generally accepted mechanism [1–3]. The high reactivity of the dienophile [4] in inverse-electron-demand *Diels–Alder* reactions [5] allowed the addition to be performed at low temperatures, and, thus, zwitterions could be isolated as intermediates. A detailed study of unsymmetrically substituted tetrazines showed the importance of steric hindrance in the second step, which determined the overall regiochemistry of the cycloaddition [2]. Similar *Diels–Alder* reactions of electron-rich alkenes with 1,2,4-triazines are known in a large variety, and are regularly used in synthesis [3]. Previous investigations [3][6][7] confirm the strong dependence of the regiochemistry on the substitution pattern of both partners, and on the solvent polarity, but not all effects are well-understood. In some cases, indications for the presence of intermediates in these reactions were found [7]. Here, we report the isolation and characterization of zwitterions as intermediates in [4+2] cycloadditions of **1** with 1,2,4-triazines, and the effect of the substitution pattern on the formation of zwitterions and cycloadducts.

2. Results. – 2.1. *Preparation of Triazines.* The triazines required for our investigation were prepared by two routes. The method of *Saraswathi* and *Srinavasan*

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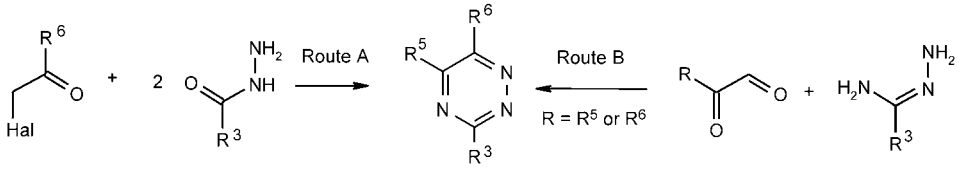
[8], improved by *Zaschke* and co-workers [9], starting with β-halogeno ketones and 2 equiv. of acid hydrazides, was best suited for 3,6-disubstituted 1,2,4-triazines **2** (*Route A*, *Table 1*). Condensation of 1,2-diketones and amidrazones by the method of *Rätz* and *Schroeder* [10], and of *Neunhoeffer et al.* [11], yielded 6-substituted triazines **3**, 5-substituted triazines **4**, and 3,5-disubstituted triazines **5** (*Route B*, *Table 1*). Triazines **4** were usually contaminated with their 6-substituted isomers and 1,2,4,5-tetrazines, but could be separated easily by column chromatography.

Table 1. *Preparation of Different Triazines*



2 – 5, **19**

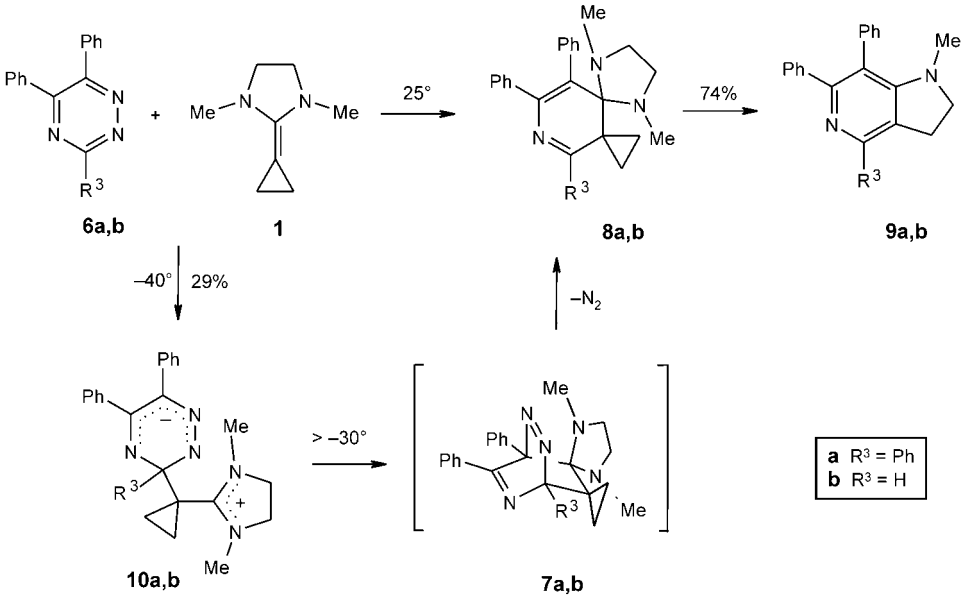
Triazine	R^3	R^5	R^6	Route[a])	Yield [%]
2b	C_6H_5	H	2-Me-C_6H_4	*A*	63
2c	C_6H_5	H	4-MeO-C_6H_4	*A*	42
2e	2-Me-C_6H_4	H	C_6H_5	*A*	16
2f	4-CF_3-C_6H_4	H	C_6H_5	*A*	37
2g	4-NO_2-C_6H_4	H	C_6H_5	*A*	29
2i	4-Me_2N-C_6H_4	H	C_6H_5	*A*	38
2j	4-CF_3-C_6H_4	H	4-MeO-C_6H_4	*A*	39
2k	4-NO_2-C_6H_4	H	4-MeO-C_6H_4	*A*	44
2l	4-MeO-C_6H_4	H	4-NO_2-C_6H_4	*A*	36
2m	4-Me_2N-C_6H_4	H	4-NO_2-C_6H_4	*A*	95
2n	C_6H_5	H	4-NO_2-C_6H_4	*A*	54
3b	H	H	4-MeO-C_6H_4	*B*	3
3c	H	H	4-NO_2-C_6H_4	*B*	59[b])
4b	H	2-Tol	H	*B*	16
4c	H	2,4,6-Me_3-C_6H_2	H	*B*	7
4d	H	4-NO_2-C_6H_4	H	*B*	59[b])
4e	H	4-MeO-C_6H_4	H	*B*	4
5c	C_6H_5	4-MeO-C_6H_4	H	*B*	54
19b	4-NO_2-C_6H_4	H	H	*A*	85

[a]) See *Exper. Part.* [b]) Combined yield.

2.2. *Cycloaddition of 3,5,6-Triphenyl-1,2,4-triazine* (**6a**). 3,5,6-Triphenyl-1,2,4-triazine (**6a**) reacted rapidly with **1** at room temperature in (D_6)benzene (*Scheme 1*). Apparently, in a *Diels–Alder* reaction, the so-far elusive bicyclic intermediate **7a** is formed, which loses N_2 in a fast, consecutive [4+2] cycloreversion. After a few minutes, the N_2 evolution was finished, and the dispiropyridine **8a** was identified by means of ^{1}H- and ^{13}C-NMR spectroscopy [12]. The substitution pattern of **8a** was corroborated after rearrangement to the pyrrolo[3,2-*c*]pyridine **9a**, a thermal rearrangement combined with a fragmentation typical for dispiro systems like **8**, leading to *N*-methylaziridine as the second product [12][13]. The regiochemistry of **9a**

(and, thus, that of **8a**) could easily be determined by NOE and other 2D-NMR experiments. When **6a** and **1** were mixed slowly in CD_2Cl_2 at $-40°$, a clear solution resulted, which was analyzed by ^1H- and ^{13}C-NMR. After 90 min, the mixture consisted of starting materials (53% of **6a** and 41% of **1**), cyloadduct **8a** (18%), and a new substance (29%) to which we assigned the zwitterionic structure **10a** on the basis of spectral similarities [2] to related zwitterions (see below). On stepwise warming to $-30°$, and then to $0°$, the proportion of **10** was reduced to 10 and 0%, and the amount of cycloadduct **8a** increased to 33 and 75%, respectively. The only other products were triazine **6a** (25%) and the reaction product of CD_2Cl_2 with **1**, which, like other 2-alkylidene imidazolidines, is not stable in this solvent for a longer period at temperatures above $-20°$ [2][4]. Unfortunately, we could not find conditions that led to higher concentrations of **10a** to allow the acquisition of unambiguously interpretable 2D-NMR spectra. Thus, structural assignment was based only upon chemical-shift comparisons, and not upon clear connectivities.

Scheme 1

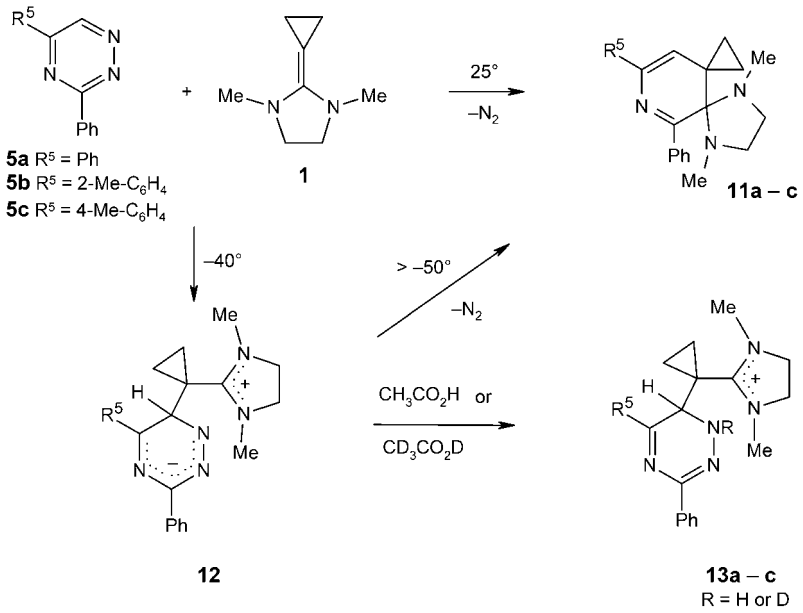


2.3. *Cycloaddition of 5,6-Diphenyl-1,2,4-triazine* (**6b**). Triazine **6b** reacted smoothly with imidazolidine **1** in benzene solution at room temperature to yield **8b** as a single regioisomer in 93% yield (*Scheme 1*). In CH_2Cl_2 solution, **8b** isomerized quantitatively to yield the pyrrolo[3,2-*c*]pyridine **9b**, whose structure was unambiguously identified by COLOCS, HETCOR, and NOE measurements. NMR Investigation of the low-temperature reaction at $-30°$ in CD_2Cl_2 showed, besides **6b** (33%) and **8b** (5%), the zwitterion **10b** (62%). The proportion of the latter could be increased to 70% on warming to $-20°$. Again 2D-NMR spectra unambiguously corroborated the structure of the 3-regioisomer. Especially the ^3J(C,H) couplings of the characteristic CH group between the two neighboring N-atoms, and NOE effects were very convincing. After

warming the solution to room temperature, 80% of the dispiropyridine **8b** were identified, and after seven days, **8b** had rearranged quantitatively to **9b**, with an isolated yield of 80%. In other experiments, we observed that N_2 evolution already starts at temperatures as low as $-50°$.

2.4. *Cycloadditions of 3,5-Disubstituted Triazines* **5**. 3,5-Diphenyl-1,2,4-triazine (**5a**) formed a precipitate with imidazolidine **1** at room temperature in toluene (*Scheme 2*). Within 20 min, the precipitate dissolved under vigorous N_2 evolution to afford the dispiropyridine **11a** in 99% yield after distillation. Similarly, the tolyl and anisyl derivatives **5b** and **5c**, respectively, readily reacted at room temperature under evolution of N_2 to afford **11b** and **11c** in high yields.

Scheme 2

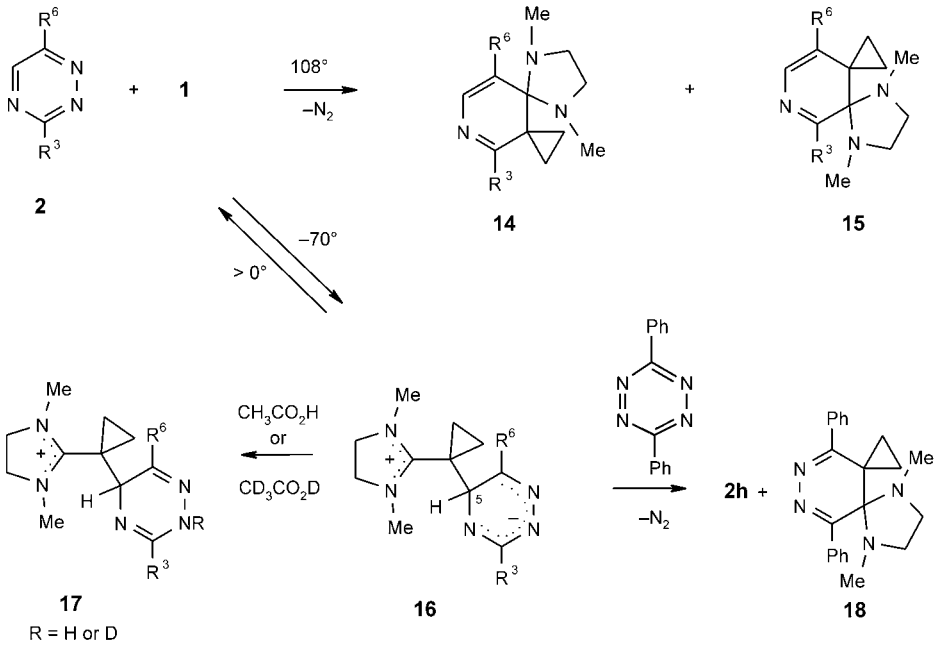


At $-75°$, the orange-yellow precipitate **12a** formed within a few minutes, as above, but no gas evolution occurred. As this precipitate was not soluble in CD_2Cl_2, AcOH was added, and the resulting acetate, which was stable at room temperature, was dissolved in $CDCl_3$. Careful 2D-NMR analysis revealed the structure of the protonated zwitterion **13a** as the main product (97%; *Scheme 2*). Triazine **5c** was treated with **1** in CD_2Cl_2 at $-40°$, and after a few minutes, CD_3COOD was added, and the resulting clear solution was investigated by NMR. Now, the deuterated zwitterion **13c** (61%) was detected, together with starting material and the dispiro adduct **11c** (15%), which was formed even at such low temperature. In both cases, **13a** and **13c**, the cyclopropyl group was undoubtedly connected to the nonsubstituted C-atom of the dihydrotriazine moieties, corroborating the connectivity of the initially precipitating zwitterions **12**.

2.5. *Cycloadditions of 3,6-Disubstituted 1,2,4-Triazines* **2**. Triazines **2** are clearly the least reactive regioisomers of this series with regard to cycloaddition. Gas evolution did

not occur below 50°, and to achieve a reasonable reaction rate, temperatures typically of *ca.* 100° were necessary. Thus, all *Diels–Alder* reactions were run at 108° in sealed tubes. In all cases, regioisomeric mixtures of the dispiropyridines **14** and **15** were found in a ratio of 93 : 7 to 48 : 52, usually with preferred attack of the cyclopropyl C-atom of **1** at the 3-position of **2** (*Scheme 3*, *Table 2*).

Scheme 3



When **1** was added at −40° to the yellow solutions of triazines **2** in THF or toluene, the orange zwitterions **16** rapidly precipitated. The zwitterions **16a**,**g**,**h** were isolated under Ar atmosphere at −40°. Compounds **16a** and **16h** were dissolved in CD_2Cl_2, the insoluble **16g** was treated with $CDCl_3$ containing 4 equiv. of CD_3COOD to achieve a clear solution of **17g**, which is probably the most-stable tautomer [14]. The zwitterions **16d**,**e**,**i** were protonated in the reaction mixture by AcOH without prior isolation, and, after removal of the solvent *in vacuo*, the resulting acetates **17d**,**e**,**i** gave clear solutions in $CDCl_3$. NMR Studies of the solutions of the zwitterions at −20°, and of the protonated or deuterated zwitterions at room temperature, indicated that all nucleophilic additions had occurred at the 5-position of the triazines. Apparently, compound **1** prefers to attack the 5-position of **2** with its nucleophilic β-C-atom to give zwitterions **16**, while, at high temperatures, C(3) and C(6) of **2** form bonds with the same β-C-atom to afford the final products **14** or **15** after elimination of N_2. The reversibility of the nucleophilic addition was verified by two experiments. While the protonated zwitterions **17** were stable at temperatures below 70°, the zwitterions **16** decomposed below room temperature. Thus, when a CD_2Cl_2 solution of isolated **16h**

Table 2. *Isomer Distribution in the Reactions of Triazines* **2** *with* **1**. Conditions: solvent, 19 h, 108°, sealed tube.

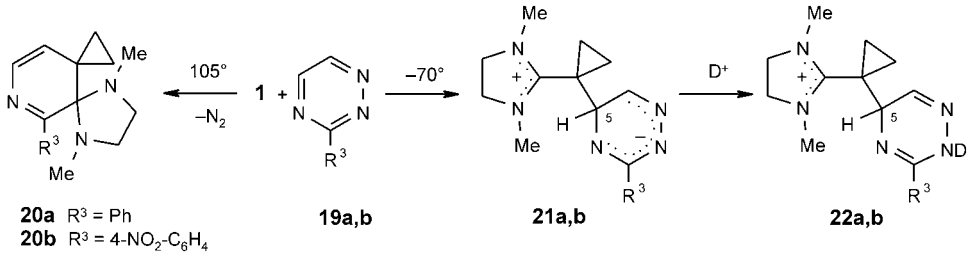
Triazine	R^3	R^6	Solvent[a])	Yield [%]	**14/15**[b])
2a	C_6H_5	C_6H_5	Toluene	100	88 : 12
2a			DMF	78	69 : 31
2b	C_6H_5	2-Me-C_6H_4	Benzene	57[c])	80 : 20
2c	C_6H_5	4-MeO-C_6H_4	Benzene	82	88 : 12
2c			Toluene	65	87 : 13
2d	4-Me-C_6H_4	C_6H_5	Toluene	100	89 : 11
2e	2-Me-C_6H_4	C_6H_5	Benzene	48	83 : 17
2e			Benzene	65[c])	88 : 12
2e			Toluene	80	81 : 19
2f	4-CF_3-C_6H_4	C_6H_5	Benzene	100	70 : 30
2g	4-NO_2-C_6H_4	C_6H_5	Benzene	100	48 : 52
2g			Toluene	100	49 : 51
2h	4-MeO-C_6H_4	C_6H_5	Benzene	52	90 : 10
2h			Toluene	93	89 : 11
2i	4-Me_2N-C_6H_4	C_6H_5	Benzene	100	93 : 7
2j	4-CF_3-C_6H_4	4-MeO-C_6H_4	Benzene	100	75 : 25
2k	4-NO_2-C_6H_4	4-MeO-C_6H_4	Benzene	88	52 : 48

[a]) Fully deuterated in each case. [b]) Determined by ^{1}H-NMR analysis. [c]) Heating for 2 h (instead of 19 h).

was allowed to warm to room temperature, only triazine **2h** and the reaction products of **1** with CD_2Cl_2 [2][4] were detected in the ^{1}H-NMR spectrum. In a second experiment, zwitterion **16h** was suspended in a (D_6)benzene solution of 3,6-diphenyl-1,2,4,5-tetrazine, which reacts rapidly with **1** at room temperature [1][2]. No reaction occurred at room temperature, but on heating above 50°, slow evolution of gas started. After heating to 80° for some hours, the purple color of the tetrazine had vanished, and the ^{1}H-NMR spectrum showed a 1 : 1 mixture of **2h** and **18** (*Scheme 3*) [1][2].

2.6. *Cycloadditions of 3-Substituted Triazines.* When the 3-aryl-substituted triazines **19a** and **b** were treated with **1** in (D_6)benzene at room temperature, a yellow-brown solid precipitated (*Scheme 4*). After heating the mixtures in a sealed tube at 105° for 2 h, clear solutions were formed, and the products were identified by 2D-^{1}H- and -^{13}C-NMR spectroscopy. Thus, the dispiropyridine **20a** (90%) and its nitro derivative **20b** (40%) were identified. We found no indication for the other possible regioisomers.

Scheme 4

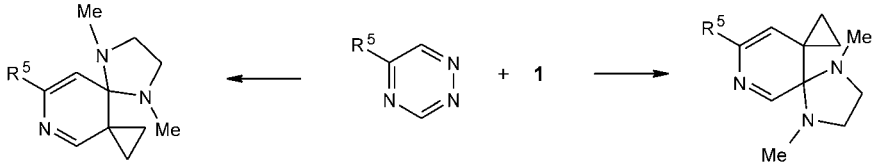


The triazines **19a** and **b** readily reacted with the imidazolidine **1** at temperatures as low as −70°. The precipitates, supposed to be zwitterions **21a** and **b**, respectively, were

not soluble in THF, CH_2Cl_2, or $CHCl_3$. After addition of CD_3COOD, a clear orange solution (in CD_2Cl_2) was obtained, which allowed a detailed 2D-NMR investigation. In addition to small amounts of the triazines, the deuterated cations **22a** (88%) and **22b** (90%) were identified as the only products. Again, the imidazolidine **1** prefers to attack the 5-position of triazines **19** with its nucleophilic β-C-atom to give zwitterions **21**, while, at high temperatures, C(6) of **19** gets bonded to the β-C-atom of **1** to provide **20**.

2.7. *Cycloadditions of 5-Substituted Triazines* **4**. Dropwise addition of a toluene solution of **1**, pre-cooled to $-78°$, to a solution of 5-phenyl-1,2,4-triazine (**4a**) at $-85°$ resulted in the formation of an orange-red precipitate, which dissolved within minutes under rapid gas evolution. After distillation, a yellow oil, consisting of a 60:40 mixture of the dispiropyridines **23a** and **24a**, was isolated in 70% yield. In CD_2Cl_2, no precipitate was formed, but gas evolution occurred rapidly on mixing. When different solvents were used at different temperatures (*Table 3*), some variation of the isomer distribution resulted, which, however, was marginal in terms of energy differences.

Table 3. *Isomer Distribution in the Reactions of Triazines* **4** *with* **1**



23 **4** **24**

Triazine[a])	R^5	Solvent[b])	T [°]	Yield [%]	**23**/**24**[c])
4a	C_6H_5	Toluene	25	76	85:15
		Toluene	−78	84	77:23
		Toluene[d])	−78	83	60:40
		Et_2O	−100	100	80:20
		THF	25	100	83:17
		CD_2Cl_2	−60	48	60:40
		DMF	25	92	70:30
		DMF	−50	57	53:47
		CD_3CN	25	30	71:29
		C_6D_6	25	100	83:17
4b	2-Me-C_6H_4	C_6D_6	25	100	92:8
4c	2,4,6-Me_3-C_6H_2	C_6D_6	25	100	100:0
4d	4-NO_2-C_6H_4	C_6D_6	25	95	73:27
4e	4-MeO-C_6H_4	C_6D_6	25	100	86:14

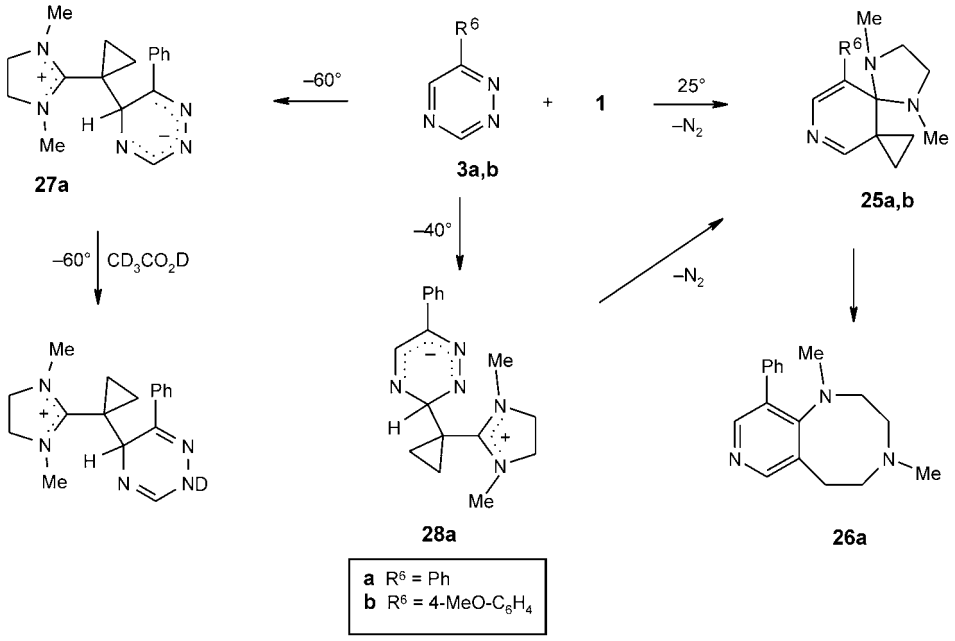
[a]) 0.1–0.3M solution. [b]) Fully deuterated in each case. [c]) Determined by ^{1}H-NMR analysis. [d]) Dilute solution.

Similar results were achieved with the other 5-aryl-substituted triazines **4b–e**. While donor (**4e**) or acceptor (**4d**) substitution did not influence the isomer distribution noticeably, steric hindrance (*e.g.*, in **4b** and **c**) seems to be of stronger influence. In terms of energy, the introduction of a mesityl (=2,4,6-trimethylphenyl) group clearly makes a difference between both pathways. In all cases, we never succeeded to record

the NMR spectra of the first reaction product, supposed to be a zwitterion, or to intercept it by protonation before gas evolution set in.

2.8. *Cycloadditions of 6-Substituted Triazines* **3**. 6-Phenyl-1,2,4-triazine (**3a**) and its MeO derivative **3b** formed red precipitates with imidazolidine **1** at room temperature in benzene or toluene (*Scheme 5*). Within a few minutes, the precipitates dissolved with concomitant, vigorous gas evolution. 2D-NMR Spectra let no doubt that, in both cases, only one regioisomer, **25a** (100%) and **25b** (55%), respectively, was formed in the cycloaddition. However, we did not succeed in isolating **25a**, as it rearranged in solution to the eight-membered ring system **26a**, an often-observed rearrangement of such dispiro systems [12][13].

Scheme 5



The low-temperature reaction between **3a** and **1** in CD_2Cl_2 solution afforded clear solutions at temperatures above $-50°$. At $-60°$, only one product could be identified by 2D-NMR after addition of CD_3OOD, *i.e.*, the deuterated salt **27a**·CD_3CO_2D (89%), together with unreacted **3a** (11%). On mixing **3a** and **1** at -40 or $-15°$, we detected the formation of a second zwitterion, **28a**, in 8 and 15% yield, respectively. Compound **28a** showed the same regiochemistry as the cycloadduct **25a**.

2.9. *Structures of Zwitterions.* All zwitterions showed characteristic spectroscopic data indicative of their structures. The ^{1}H- and ^{13}C-NMR spectra of the dihydroimidazolium rings were very similar to related dihydroimidazolium salts [2][13], thus corroborating the cationic feature of these rings. The anionic dihydrotriazinide rings showed similarities to related dihydrotetrazinides [2], and, likewise, this moiety in the protonated zwitterions resembled those of dihydrotriazines [15]. In comparison with

the starting triazines, significant high-field shifts were found for the ^{13}C-NMR signal of the C-atom connected to the cyclopropyl group, and the same behavior was found for the directly attached H-atom. Thus, the ^{13}C-NMR signals were observed between δ(C) 49.1 and 56.7 for C(4) and C(5), and between 81.5 and 89.2 for C(3), respectively, with δ(H) values of 3.94 and 5.90. There was one notable exception: H–C(3) of the 5,6-diphenyl-substituted zwitterion **10b** showed a resonance at δ(H) 2.08, a value that seems to be at too high a field. The reason for this may be that, in this case (and maybe also for **10a**), the two bulky Ph groups in 5- and 6-position, which cannot both be coplanar with the triazinide ring, force the zwitterion into a different conformation. We knew from a crystal structure of the thermally stable zwitterion **29**, derived from 3,6-diphenyltetrazine and **1**, that its dihydrotetrazinide ring adopts a boat conformation (*Fig. 1*) [13]. That this is also a likely option for the dihydrotriazinide ring in our zwitterions is the result of theoretical studies at the Becke3LYP/SB level of theory (see below). In such a case, two conformations are possible where the substituents can adopt either pseudo-axial or pseudo-equatorial positions.

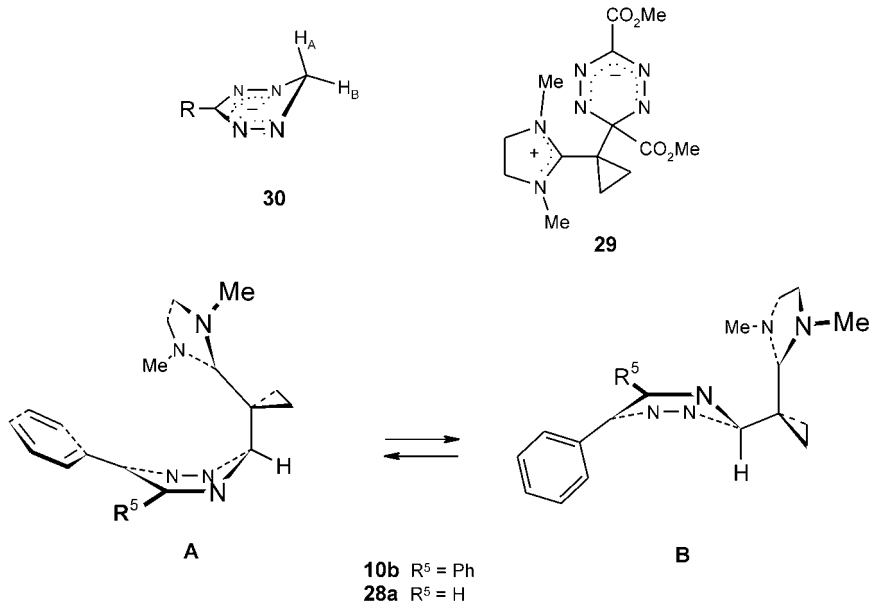


Fig. 1. *Boat conformations of zwitterions*

As shown in *Fig. 1* for the zwitterions **10b** and **28a**, the latter probably prefers conformation **A**, whereas the former adopts conformation **B**. *Van der Plas* and co-workers [16] have shown that the ^{1}H-NMR chemical shifts of the H_a- and H_b-atoms in dihydrotetrazinide anions **30** can differ by as much as 4.8 ppm, H_a being found at higher field. A similar effect is probably responsible for the observed shift difference in **10b** ($\Delta\delta$(H) = 2.08) and **28a** (5.72). Of course, there are also other conformers to be considered, especially those arising from rotation about the bond connecting the

cyclopropyl and triazinide rings. These, however, could hardly rationalize the large differences in ^{1}H-NMR chemical shifts. For all zwitterions (and protonated zwitterions), we found that the rotation barrier for the bond between the cyclopropyl and the dihydroimidazolium rings is relatively high. Therefore, the corresponding NMR signals are not averaged. The two CH_2 groups of the cyclopropyl and dihydroimidazolium rings exhibited *ABCD* spin systems in the ^{1}H-NMR spectra, and two signals each in the ^{13}C-NMR spectra.

3. Discussion. – 3.1. *Selectivity and Reactivity in Nucleophilic Additions.* All triazines investigated (with the possible exception of 5-aryl-triazines **4**) react rapidly with 2-cyclopropylidene-1,3-dimethylimidazolidine (**1**) in nucleophilic additions. The substitution pattern strongly influences the selectivity. Whenever possible, H-bearing C-atoms are attacked preferentially, *e.g.*, in **2**, **5**, and **6b**. When two unsubstituted positions are available, as in **3** and **19**, the reactivity decreased in the order C(5) > C(3) > C(6), as expected from experimental work on other triazines [17]. The substituent effect is probably due to steric hindrance at the reaction center, but may also stem from stabilization of the resulting zwitterions. Electronic effects on the formation of the zwitterions could not be investigated for the donor- or acceptor-substituted triazines, because the reaction did not occur at the centers bearing these substituents. The same was true for steric effects.

3.2. *Selectivity and Reactivity in Cycloadditions.* All triazines investigated gave cycloadditions only *via* atoms C(3) and C(6). We found no indication of the alternative reaction involving C(5) and N(2), followed by elimination of a nitrile [3]. This means that nucleophilic addition to C(5) cannot lead to a dispiro adduct and, thus, is a dead-end equilibrium for the overall reaction. For the cycloaddition reactions at C(3) and C(6), we found tremendous differences in overall reaction rates. For example, imidazolidine **1** formed cycloadducts with the 5-phenyl-substituted triazine **4a** within a few minutes at $-100°$ (see *Table 3*), while the *Diels–Alder* reaction with 3,6-diaryltriazines **2** usually required heating for several hours at $+108°$ (see *Table 1*). But this does not necessarily mean that the actual cycloaddition reaction is slow. It only shows that it is slower than the (very fast) nucleophilic addition to C(5) of **2** to give **16**, which competes with the cycloaddition products **14** and **15**. The rate-determining step then is the fragmentation of **16** back to the starting materials **2** and **1**. That the rate of the cycloaddition of triazines **2** is probably high is shown by comparison with triphenyltriazine **6a**, which reacts quickly at room temperature, although it exhibits the same (or even stronger) steric hindrance at the reacting centers C(3) and C(6), but does not undergo nucleophilic addition at C(5) in a dead-end equilibrium.

The 3,6-diaryl-triazines **2** and 5-aryl-triazines **4** offered a chance to investigate the influence of electronic, steric, and solvent effects upon cycloaddition. For the *para*-substituted derivatives of **2**, the steric influence can be neglected. Donors in *para*-position of the 3-substituent (**2d**,**h**,**i**) increased the ratio of **14**/**15** slightly (93 : 7 for **2i**) in comparison to the diphenyltriazine (88 : 12), and acceptors (**2f**,**g**) showed the opposite effect (48 : 52 for **2g**) (see *Table 2*). A MeO group in *para*-position of the 6-substituent (**2c**) had no influence at all, and donor/acceptor combinations (**2j**,**k**) showed no enhanced effect. All effects can be rationalized by electronic stabilization or destabilization of potential zwitterionic intermediates. As electronic effects are small

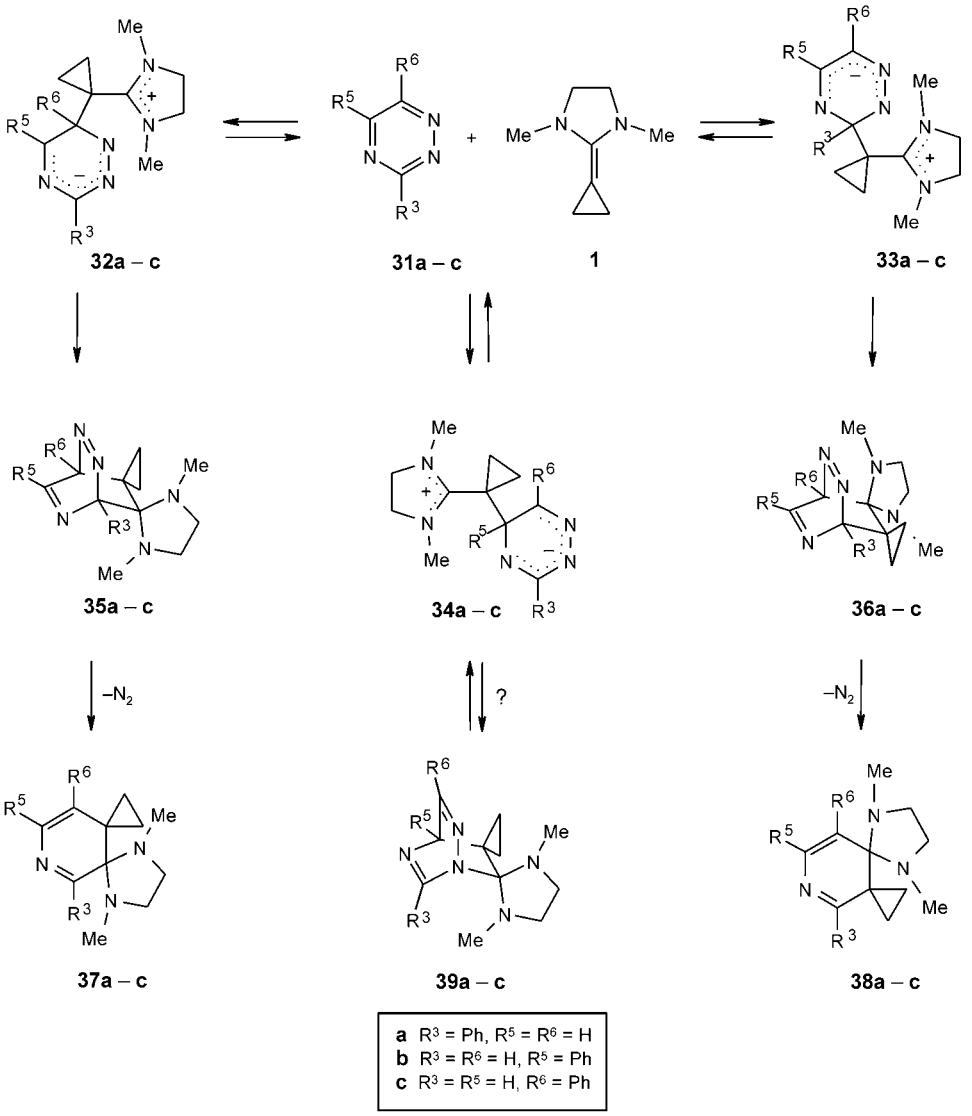
and negligible for a Me group in *para*-position, the effects of *ortho*-Me groups may be seen as merely steric. *ortho*-Tolyl groups in 3-position (**2e**) or 6-position (**2b**) both reduce the ratio of **14**/**15** slightly to 83 : 17 and 80 : 20, respectively. For **2e**, this might be interpreted as a sterically hindered addition to C(3). For **2c**, one would expect the opposite behavior, with the same argumentation. In this case, the second step of a potential two-step *Diels – Alder* reaction may determine the overall regioselectivity, as corroborated for related sterically hindered tetrazines [2]. However, as we could not isolate 3- or 6-substituted zwitterions in these cases, it remains speculation.

A small solvent effect was found for the 3,6-diphenyl-triazine **2a**. While in (D_8)toluene, the ratio **14a**/**15a** was 88 : 12, it dropped to 69 : 31 in (D_7)DMF. All effects are relatively small in terms of energy differences in the transition states ($\leq$ 5 kJ/mol). For 5-phenyltriazine **4a**, we found a 83 : 17 ratio of cycloadducts **23**/**24** in (D_6)benzene at 25° (see *Table 3*). This ratio was reduced in more-polar solvents like CD_3CN (71 : 29) or (D_7)DMF (70 : 30). There was also a dependence on temperature. At lower temperatures, the proportion of **24** increased in toluene (40% at $-85°$) or (D_7)DMF (47% at $-50°$). A MeO substituent in *para*-position of the 5-aryltriazine **4e** increased the ratio **23**/**24** (86 : 14), a NO_2 group (**4d**) reduced it (73 : 27). Again, these effects can be rationalized by stabilization or destabilization of the potential (but not identified) zwitterionic intermediates of a two-step *Diels – Alder* reaction. While donor or acceptor substitution (**4e** *vs.* **4d**) did not influence the isomer distribution noticeably, steric hindrance (**4b**,**c**) seems to be of stronger influence. The *ortho*-tolyl substituent favored cycloadduct **23b** over **24b** by 92 : 8; in case of a mesityl group, only one isomer was be detected (**23c**). In terms of energy, the introduction of a mesityl group clearly makes a difference between both pathways. One can assume that the *ortho*-tolyl and mesityl groups in 5-position are not coplanar with the triazine on the time average and, thus, impede nucleophilic attack at the neighboring C(6)-atom: *ortho*-tolyl from one side, mesityl from both sides.

Two conclusions can be drawn unambiguously: if no 3- or 6-substituents hamper the cycloaddition by steric hindrance, the reaction occurs very fast. If zwitterions in 3- or 6-positions could be detected at low temperatures, the regioselectivity for zwitterion and cycloadduct formation was identical. For example, the cyclopropyl C-atom of **1** was bound to the more-reactive and usually unsubstituted C-atom of the triazines. Except for a few cases, we could not correlate the regioisomeric ratios with the size of orbital coefficients of the triazine LUMOs (lowest-unoccupied molecular orbitals). It seems, that steric or other effects overwhelm the effect of orbital interactions of the starting materials. It may well be that the regiochemistry is not determined in the first, but rather in the second (or maybe even in the third) transition state of these reaction series, such as the elimination of N_2, as calculated for cycloadditions of tetrazines [2].

3.3. *One- or Two-Step* Diels – Alder *Reaction?* To sum up all considerations, there is no definite proof for a one-step or two-step reaction mechanism of the above cycloadditions. All arguments favoring the two-step path – the very existence of zwitterions, the same regiochemistry for the nucleophilic addition and the cycloaddition, the influence of steric or electronic effects on regioselectivities and reaction rates in the first and/or second step – cannot exclude the possibility that a concerted reaction competes with nucleophilic addition. However, there is one argument that makes this possibility very unlikely, at least in the case of the monosubstituted triazines

Scheme 6. *Mechanistic Overview of Triazine Cycloadditions*



31a – c (*Scheme 6*)[2]). The imidazolidine **1** and the 5-phenyltriazine **31b** first form a precipitate at $-100°$, which rapidly dissolves under gas evolution. With very high probability, this precipitate is a mixture of the two zwitterions **32b** and **33b**. If one assumes that the cycloaddition occurs in a concerted reaction, these zwitterions need to fragment back to starting materials, and this fragmentation has to be fast even at

[2]) Some of the structures of *Scheme 6* correspond to compounds specifically numbered before (*e.g.*, **31a** = **19a**). However, for a general discussion, a superior, new numbering is introduced.

– 100°. 3-Phenyltriazine **31a** and 6-phenyltriazine **31c** also form zwitterions at low temperatures, both by attack at the 5-position. The fragmentation of the zwitterion **34a** back to **31a** can be observed at *ca.* 100°. It is hard to imagine, that two isomeric zwitterions, *e.g.*, **33b** and **34a**, that should be comparable in energy, would show such differences in fragmentation rates.

Overall, it seems reasonable to assume that the three types of zwitterions **32** – **34** are formed in all reactions of triazines with **1** (*Scheme 6*). While **34** is trapped in a dead-end equilibrium, the other two isomers can react further to the cycloadducts **35** and **36**, respectively, and finally, after loss of N_2, to the dihydropyridines **37** and **38**. Whether the zwitterions can be detected, or even isolated, is partly a question of their relative and absolute stabilities, but also depends on the activation barriers of the following reaction steps. For a deeper understanding of the deciding factors of these multi-step reactions, we decided to carry out calculations for conceivable intermediates in the reactions of the monophenyl-substituted triazines **31a**, **31b**, and **31c**.

4. Calculations. – As anticipated in *Scheme 6*, the first step of the overall cycloaddition reactions of triazines **31** proceeds through the zwitterionic structures **32**, **33**, and **34**. All of these zwitterions can be identified as true minima on the Becke3LYP/SB potential-energy surface for all three triazines. The relative enthalpies of these intermediates, calculated at the Becke3LYP/LB//Becke3LYP/SB level, strongly depend on the substitution pattern of the parent triazines. For 3-phenyltriazine (**31a**), addition to C(6) and C(5) is energetically comparable, while addition to the (substituted!) C(3) position is less-favorable by more than 40 kJ/mol (*Table 4*). Similarly, reaction of 5-phenyl-1,2,4-triazine (**31b**) is least favorable at the substituted C(5)-atom, while addition to C(6) and, in particular, to C(3) are more favorable. Finally, the reaction of **1** with the 6-phenyl congener **31c** yields the C(3)-adduct **33c** as the most-stable zwitterion, closely followed by the C(5)-adduct **34c**. Both of these zwitterions are much more stable than the C(6)-adduct **32c**.

The formation of all zwitterions is calculated to be accompanied by a substantial increase in the molecular dipole moment (*Table 4*). This is a consequence of the charge separation indicated in the *Lewis* structures (see *Scheme 6*). Taking the reaction of **31a** as an example, the overall NPA charge of the triazine moiety amounts to 0.0 in reactant **31a**, – 0.71 in **32a**, – 0.68 in **33a**, and – 0.77 in **34a** (gas-phase values). The absolute and relative energetics of the formation of these species are, therefore, substantially influenced by solvent effects, even in a medium of intermediate polarity such as CH_2Cl_2. Relative to the two reactants **1** and **31**, the reaction enthalpies become more favorable on inclusion of solvent effects. However, even after consideration of such effects through CPCM single-point calculations, all reaction enthalpies for the formation of zwitterionic intermediates **32** – **34** remain positive[3]) (*Table 4*).

The conformational space available to the zwitterions is quite significant due to rotation about the newly formed C–C bond. On reaction with **1**, the former triazine ring deforms into a boat-like structure, providing a pseudo-axial and pseudo-equatorial

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[3]) Full geometry optimization in the presence of the solvent reaction field was explored for zwitterion **32a**. For this system the solvation free energy calculated for the solution-optimized geometry is 1 kJ/mol larger as compared to the free energy of solvation using the gas-phase structure.

Table 4. *Energies and Structural Characteristics for Stationary Points in the Reaction of Triazines* **31a–c** *with* **1** *at 298.15 K* (in the gas phase or in solution). All values were calculated at the Becke3LYP/LB//Becke3LYP/SB level of theory. The gas-phase dipole moment μ was obtained at the Becke3LYP/SB level. For conformations, see *Figs. 2* and *3*.

Stationary point	ΔH_{298} (gas) [kJ/mol]	ΔH_{298} (CH_2Cl_2) [kJ/mol]	μ [D]	Conformer	r(C–C) [pm]
3-Phenyl:					
31a + **1**	0.0	0.0	–	–	–
32a	+44.3	+39.0	9.2	**E**	159.6
33a	+88.1	+79.0	9.3	**A**	163.8
34a	+47.1	+33.4	11.1	**C**	162.9
35a	+72.5	+93.0	4.7	–	153.8
36a	+60.6	+75.8	3.3	–	156.5
37a	−129.9	−105.4	2.5	–	147.6
38a	−140.2	−117.1	2.1	–	150.3
39a	+63.5	+83.8	2.2	–	154.9
5-Phenyl:					
31b + **1**	0.0	0.0	–	–	–
32b	+47.1	+39.9	8.9	**E**	159.9
33b	+29.6	+21.5	11.2	**B**	153.6
34b	+87.9	+59.6	13.3	**C**	167.9
35b	+35.7	+57.6	3.1	–	154.2
36b	+29.6	+50.0	3.6	–	154.0
37b	−157.3	−135.8	3.0	–	147.8
38b	−162.4	−139.7	2.8	–	147.9
39b	+101.4	+119.6	2.5	–	158.4
6-Phenyl:					
31c + **1**	0.0	0.0	–	–	–
32c	+115.1	+92.7	12.3	**E**	172.3
33c	+19.2	+5.4	11.7	**B**	153.5
34c	+26.3	+13.5	9.3	**C**	160.4
35c	+57.9	+74.7	2.4	–	156.9
36c	+61.8	+82.3	3.8	–	153.4
37c	−140.0	−118.3	2.6	–	155.5
38c	−145.1	−121.2	2.8	–	147.8
39c	+62.6	+80.5	2.5	–	155.2

position at the reaction center. The zwitterionic intermediates **33** obtained through addition to C(3) of the triazine ring can, thus, be classified as being either of the axial (**A**) or equatorial (**B**) type (*Fig. 2*). The conformers of intermediates **32** and **34** can be classified accordingly. Reviewing the results described in *Table 4*, we note that the most-favorable conformers of the zwitterions **32a–c** are all of type **E**. Similarly, the most-stable conformers of the zwitterions obtained through addition at C(5), **34**, are all of type **C**. For zwitterions **33**, the conformational preference (**A** *vs.* **B**) depends on the substitution pattern, and no general rule can be formulated. The structures of the most-stable conformers of each type are shown in *Fig. 3*. One notable feature of the structures of type **B** for **33b** and **33c** are the much smaller distances of the newly formed C–C bonds of 153.6 and 153.5 pm, respectively. In all other structures in which the newly formed C–C bond occupies the pseudo-axial position, significantly larger bond distances ($\geq$159.6 pm) are obtained (*Table 4*).

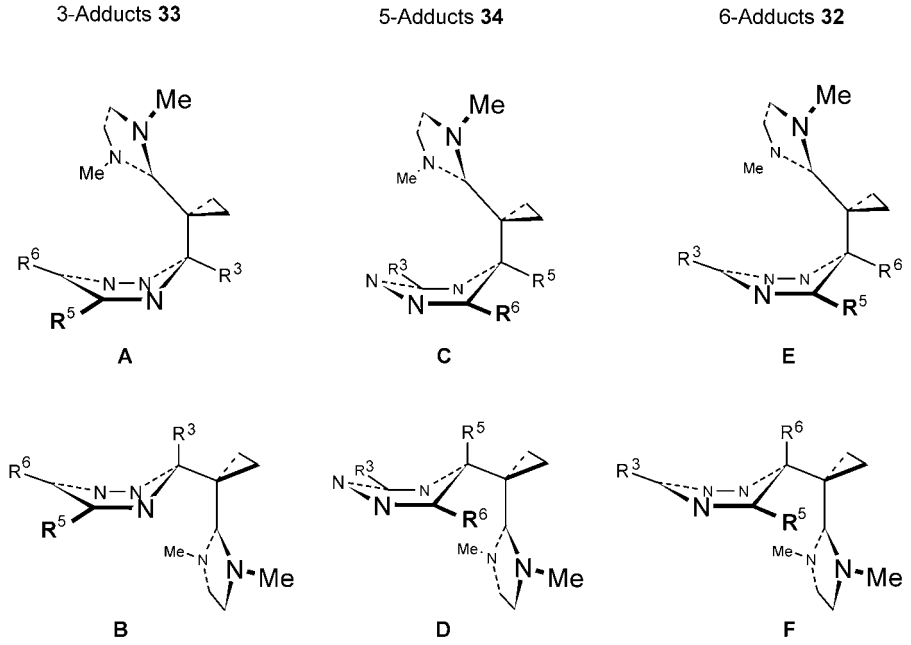

Fig. 2. *Principal conformations of zwitterions* **32**–**34**

Cyclization of the zwitterionic intermediates to the fully cyclized adducts **35**, **36**, and **39** is an endothermic process in all cases, and adducts of type **39** (see *Scheme 6*) are not dramatically less stable than either **35** or **36**. The energetically least-favorable mode of cyclization always occurs onto a phenyl-substituted center, as in the conversion of **32a** to **35a**, or in the conversion of **33c** to **36c**. Due to the charge-neutralizing character of these cyclization reactions, the consideration of solvent effects now leads to much less-favorable reaction energetics widening the energy difference to the preceding zwitterionic intermediates. The final elimination of N_2 is strongly exothermic in all cases. The most-stable products formed in the reactions of triazines **31a**–**c** are **38a**–**c**. However, the energy differences between the products **37b**/**38b** and **37c**/**38c** are rather small, and product mixtures would have to be expected in case the reaction outcome is based on product stability. This is clearly not the case due to the strongly exothermic nature of the final reaction step. The outcome of the reaction is, thus, most likely determined by the relative heights of the N_2 elimination barriers.

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Experimental Part

1. *General.* Abbreviations: Ar, aryl, Ph, phenyl; Tol, tolyl; cPr, cyclopropyl; Im, imidazole or imidazolium based moieties. 3,5-Diphenyl-1,2,4-triazine (**5a**) [18][19], 5-(2-methylphenyl)-3-phenyl-1,2,4-triazine (**5b**) [20], 3-(4-methylphenyl)-6-phenyl-1,2,4-triazine (**2d**) [8], 3-(4-methoxyphenyl)-6-phenyl-1,2,4-triazine (**2h**) [8], 6-phenyl-1,2,4-triazine (**3a**) [18], 5-phenyl-1,2,4-triazine (**4a**) [19], 3-phenyl-1,2,4-triazine (**19a**) [19], 3,5,6-

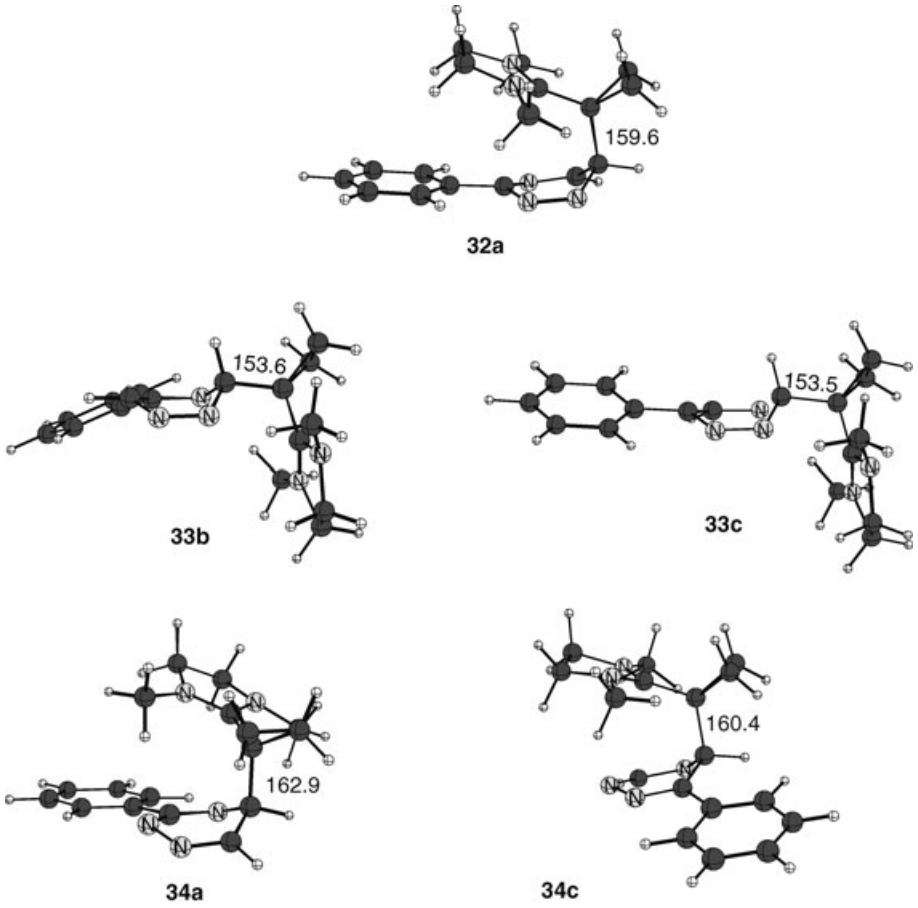

Fig. 3. *Three-dimensional structures of the most-stable zwitterions* **32** – **34**

triphenyl-1,2,4-triazine (**6a**) [18][19], and 5,6-diphenyl-1,2,4-triazine (**6b**) [21] were prepared according to literature procedures. All cycloaddition reactions were performed in oven-dried glassware with anh. solvents under Ar gas. For all distillations, a *Kugelrohr* apparatus was used. UV Spectra: *Perkin-Elmer Lambda-3* and *Zeiss PMQ II*; λ_{max} (log ε) in nm. IR Spectra: *Perkin-Elmer 1420* and *IFS 45*; in cm^{-1}. NMR Spectra: *Varian VXR 400S* or *Bruker WP 80*; if not specified otherwise, ^1H- and ^{13}C-NMR chemical shifts δ (in ppm) of Ph groups are listed in the order (*ipso*), *ortho*, *meta*, *para*. EI-MS: *Finnigan MAT 90*; in *m*/*z* (rel. %)

2. *Synthesis of Triazines. General Procedure A* (*GP A*). The appropriate arylcarboxylic hydrazide (*n* g, 2*m* mmol) was heated in a mixture of EtOH (3*m* ml) and glacial AcOH (*m* ml) to 60°, until a clear soln. resulted. AcONa (1.1*m* mmol) and 2-bromo-1-phenylethanone (*p* g, *m* mmol) were added, and the mixture was heated at reflux for 3 h. Crystalline precipitates were collected by filtration, solns. were poured on ice/H_2O and neutralized with $NaHCO_3$. After extraction with Et_2O (3×20 ml) and drying ($MgSO_4$), the solvent was removed, and the residue was crystallized from EtOH or glacial AcOH.

General Procedure B (*GP B*). To a pre-cooled mixture of formamidine acetate (*r* g, *s* mmol) in anh. MeOH (20 ml), anh. hydrazine (*t* g, *u* mmol) was added at $-10°$ under Ar gas, and the mixture was stirred for 5 min. Slowly, a soln. of freshly distilled 2-aryl-2-oxoethanal (*v* g, *s* mmol) in anh. MeOH (10 ml), and, after 10 min, Et_3N (*w* g, *s* mmol) were added. After stirring at 20° for 24 h, the solvent was removed *in vacuo*, the residue was

extracted with Et_2O (3×20 ml), the combined org layers were washed with brine, dried ($MgSO_4$), and concentrated. The resulting residue was separated by column chromatography (CC).

5-(4-Methoxyphenyl)-3-phenyl-1,2,4-triazine (**5c**). To a pre-cooled slurry of benzenecarboxamidine hydrochloride · 1.8 H_2O (1.55 g, 9.89 mmol) and Na_2SO_4 (1.42 g, 10.0 mmol) in anh. MeOH (50 ml), anh. hydrazine (0.475 g, 14.8 mmol) was added at 0°, and the mixture was stirred for 2 h, until NH_3 evolution ceased. Slowly, a soln. of freshly distilled 2-(4-methoxyphenyl)-2-oxoethanal (1.09 g, 6.72 mmol) in anh. MeOH (10 ml) and, after 10 min, Et_3N (1.00 g, 9.9 mmol) were added. After stirring at 20° for 24 h, the solvent was removed *in vacuo*, and the residue was extracted with Et_2O (3×50 ml). The org. layer was washed with brine, dried ($MgSO_4$), and evaporated. The resulting solid, according to ^{1}H-NMR analysis made of 10% of **3b**, 18% of 3,6-bis(4-methoxyphenyl)tetrazine, and 72% of **5c**, was separated by CC (SiO_2; toluene/AcOEt 20 : 1; R_f 0.14). Orange-yellow platelets. Yield of **5c**: 0.960 g (54%). M.p. 118–120° (EtOH). UV ($CHCl_3$): 332 (1.24). ^{1}H-NMR ($CDCl_3$, 400 MHz): 3.90 (MeO); 7.07 ($J = 9.0$, H–C(3,5) of 5-Ar); 7.56 (H–C(3,4,5) of 3-Ph); 8.26 (H–C(2,6) of 5-Ar); 8.64 (H–C(2,6) of 3-Ph); 9.52 (H–C(6)). ^{13}C-NMR ($CDCl_3$, 100 MHz): 55.5 (MeO); 114.9 (C(3,5) of 5-Ar); 125.9 (C(1) of 5-Ar); 128.3 (C(3,5) of 3-Ph); 128.8 (C(2,6 of 3-Ph); 129.4 (C(2,6) of 5-Ar); 131.5 (C(1) of 3-Ph); 135.5 (C(4) of 3-Ph); 143.7 (C(6)); 154.6 (C(5)); 163.3 (C(4) of 6-Ar); 163.2 (C(3)). EI-MS: 263 (23, M^+). Anal. calc. for $C_{16}H_{13}N_3O$ (263.3): C 72.99, H 4.98, N 15.96; found: C 72.84, H 4.92, N 16.11.

6-(2-Methylphenyl)-3-phenyl-1,2,4-triazine (**2b**). *GP A* ($n = 0.980$, $m = 7.18$, $p = 0.770$). Yield: 0.772 g (63%). M.p. 96° (EtOH). UV ($CHCl_3$): 275 (1.80). IR: 3052, 2964, 2924, 1602,1581,1495, 1439, 1403, 767, 726, 695. ^{1}H-NMR ($CDCl_3$, 400 MHz): 2.51 (Me); 7.40 (H–C(3,4,5) of 6-Ar); 7.53 (H–C(6)); 7.57 (H–C(3,4,5) of 3-Ph); 8.61 (H–C(2,6) of 3-Ph); 8.79 (H–C(5)). ^{13}C-NMR ($CDCl_3$, 100 MHz): 20.5 (Me); 126.5 (C(6) of 6-Ar); 128.2 (C(3,5) of 3-Ph); 128.9 (C(2,6) of 3-Ph); 129.8 (C(3) of 6-Ar); 130.0 (C(5) of 6-Ar); 131.5 (C(4) of 6-Ar); 131.7 (C(4) of 3-Ph); 133.6 (C(1) of 3-Ph); 136.8 (C(2) of 6-Ar); 134.7 (C(1) of 6-Ar); 149.1 (C(5)); 158.2 (C(6)); 161.9 (C(3)). EI-MS: 247 (44, M^+). Anal. calc. for $C_{16}H_{13}N_3$ (247.3): C 77.71, H 5.30, N 16.99; found: C 77.56, H 5.26, N 16.72.

6-(4-Methoxyphenyl)-3-phenyl-1,2,4-triazine (**2c**) [8b]. *GP A* ($n = 1.50$, $m = 11.0$, $p = 1.26$). Yield: 0.610 g (42%). M.p. 161–164° (AcOH). UV ($CHCl_3$): 447 (1.91). ^{1}H-NMR (CF_3COOD, 400 MHz): 4.07 (MeO); 7.31 ($J = 8.3$, H–C(3,5) of 6-Ar); 7.77 (H–C(3,5 of 3-Ph); 7.91 (H–C(4) of 3-Ph); 8.26 (H–C(2,6) of 6-Ar); 8.50 (H–C(2,6) of 3-Ph); 9.96 (H–C(5)). ^{13}C-NMR (CF_3COOD, 100 MHz): 54.9 (MeO); 118.1 (C(3,5) of 6-Ar); 130.0 (C(1) of 6-Ar); 131.1 (C(3,5) of 3-Ph); 132.0 (C(2,6) of 3-Ph); 132.3 (C(2,6) of 6-Ar); 132.4 (C(1) of 3-Ph); 138.8 (C(4) of 3-Ph); 155.8 (C(5)); 159.7 (C(4) of 6-Ar); 162.4 (C(6)); 167.2 (C(3)). EI-MS (130°, 70 eV): 263 (17, M^+). Anal. calc. for $C_{16}H_{13}N_3O$ (263.3): C 72.99, H 4.98, N 15.96; found: C 73.00, H 5.07, N 15.83.

3-(2-Methylpenyl)-6-phenyl-1,2,4-triazine (**2e**). *GP A* ($n = 17.8$, $m = 11.9$, $p = 10.1$; 18 h reflux). Yield: 3.66 g (25%). M.p. 118–120° (EtOH). IR: 3052, 2964, 2924, 1602,1581,1495, 1439, 1403, 767, 726, 695. UV ($CHCl_3$): 278 (1.40). ^{1}H-NMR ($CDCl_3$, 400 MHz): 2.68 (Me); 7.37–7.41 (H–C(3,4,5) of 3-Ar); 7.57 (H–C(3,4,5) of 6-Ph); 8.03 (H–C(6) of 3-Ar); 8.19 (H–C(2,6) of 6-Ph); 9.09 (H–C(5)). ^{13}C-NMR ($CDCl_3$, 100 MHz): 21.6 (Me); 126.2 (C(4) of 6-Ph); 126.8 (C(3,5) of 6-Ph); 129.4 (C(2,6) of 6-Ph); 134.8 (C(1) of 6-Ph); 130.4 (C(3) of 3-Ar); 130.9 (C(4) of 3-Ar); 130.9 (C(5) of 3-Ar); 131.7 (C(6) of 3-Ar); 133.3 (C(2) of 3-Ar); 138.3 (C(1) of 3-Ar); 145.9 (C(5)); 154.3 (C(6)); 165.3 (C(3)). EI-MS (90°, 70 eV): 247 (54, M^+). Anal. calc. for $C_{16}H_{13}N_3$ (247.3): C 77.71, H 5.30, N 16.99; found: C 77.57, H 5.27, N 17.02.

6-Phenyl-3-[4-(trifluoromethyl)phenyl]-1,2,4-triazine (**2f**). *GP A* ($n = 0.200$, $m = 0.41$, $p = 0.160$). Yield: 0.110 g (37%). M.p. 194–197° (AcOH). UV ($CHCl_3$): 320 (1.20). ^{1}H-NMR (CF_3COOD, 400 MHz): 7.78 (H–C(3,5) of 6-Ph); 8.04 ($J = 8.3$, H–C(2,6) of 3-Ar); 8.25 (H–C(2,6) of 6-Ph); 7.89 (H–C(4) of 6-Ph); 8.70 (H–C(3,5) of 3-Ar); 10.10 (H–C(5)). ^{13}C-NMR (CF_3COOD, 100 MHz): 125.3 (J(C,F) = 273.1, F_3C); 128.5 (C(1) of 3-Ar); 129.1 (J(C,F) = 3.8, C(3,5) of 3-Ar); 130.1 (C(3,5) of 6-Ph); 131.8 (C(2,6) of 6-Ph); 132.6 (C(2,6) of 3-Ar); 132.9 (C(1) of 6-Ph); 137.1 (C(4) of 6-Ph); 140.1 (J(C,F) = 32.3, C(4) of 3-Ar); 156.2 (C(5)); 160.6 (C(6)). EI-MS (130°, 70 eV): 301 (10, M^+). Anal. calc. for $C_{16}H_{10}F_3N_3$ (301.3): C 64.74, H 3.62, N 13.94; found: C 65.07, H 3.56, N 13.73.

3-(4-Nitrophenyl)-6-phenyl-1,2,4-triazine (**2g**). *GP A* ($n = 3.71$, $m = 21.0$, $p = 2.04$). Yield: 0.852 g (29%). M.p. >220° (AcOH). UV ($CHCl_3$): 316 (0.45). ^{1}H-NMR (CF_3COOD, 400 MHz): 7.84 (H–C(3,5) of 6-Ph); 7.95 (H–C(4) of 6-Ph); 8.26 (H–C(2,6) of 6-Ph); 8.61 ($J = 9.1$, H–C(3,5) of 3-Ar); 8.82 (H–C(2,6) of 3-Ar); 10.20 (H–C(5)). ^{13}C-NMR (CF_3COOD, 100 MHz): 126.8 (C(3,5) of 3-Ar); 127.4 (C(1) of 6-Ph); 130.6 (C(2,6) of 3-Ar); 132.5 (C(2,6) of 6-Ph); 132.9 (C(3,5) of 6-Ph); 137.4 (C(1) of 3-Ar); 138.3 (C(4) of 6-Ph); 153.6 (C(6)); 154.9 (C(4) of 3-Ar); 160.8 (C(5)); 164.4 (C(3). EI-MS (200°, 70 eV): 278 (29, M^+). Anal. calc. for $C_{15}H_{10}N_4O_2$ (278.2): C 64.74, H 3.62, N 20.14; found: C 65.07, H 3.56, N 20.16.

3-[4-(Dimethylamino)phenyl]-6-phenyl-1,2,4-triazine (**2i**). *GP A* ($n = 2.68$, $m = 15.0$, $p = 1.16$). Yield: 0.781 g (38%). M.p. 208–210° (EtOH). UV ($CHCl_3$): 368 (0.45). ^{1}H-NMR ($CDCl_3$, 400 MHz): 3.07 (MeN);

6.81 (J = 8.1, H–C(3,5) of 3-Ar); 7.54 (H–C(3,5) of 6-Ph); 7.54 (H–C(4) of 6-Ph); 8.11 (H–C(2,6) of 6-Ph); 8.46 (H–C(2,6) of 3-Ar); 8.91 (H–C(5)). ^{13}C-NMR (CF_3COOD, 100 MHz): 40.1 (MeN); 111.8 (C(3,5) of 3-Ar); 121.9 (C(1) of 3-Ar); 126.3 (C(2,6) of 3-Ar); 129.2 (C(3,5) of 6-Ph); 129.6 (C(2,6) of 6-Ph); 130.3 (C(4) of 6-Ph); 133.8 (C(1) of 6-Ph); 146.2 (C(5)); 152.7 (C(6)); 153.5 (C(4) of 3-Ar); 162.7 (C(3)). EI-MS (130°, 70 eV): 276 (26, M^+). Anal. calc. for $C_{17}H_{16}N_4$ (276.3): C 73.89, H 5.84, N 20.28; found: C 74.04, H 5.82, N 20.21.

6-(4-Methoxyphenyl)-3-[4-(trifluoromethyl)phenyl]-1,2,4-triazine (**2j**). *GP A* (n = 0.300, m = 1.47, p = 0.161). Yield: 0.090 g (39%). M.p. 192° (AcOH). UV ($CHCl_3$): 417 (2.70). ^{1}H-NMR (CF_3COOD, 400 MHz): 4.08 (MeO); 7.35 (J = 8.6, H–C(3,5) of 6-Ar); 7.99 (J = 8.1, H–C(2,6) of 3-Ar); 8.27 (H–C(2,6) of 6-Ar); 8.66 (H–C(3,5) of 3-Ar); 10.09 (H–C(5)). ^{13}C-NMR (CF_3COOD, 100 MHz): 57.4 (MeO); 118.7 (C(3,5) of 6-Ar); 125.4 (J(C,F) = 272.4, F_3C); 128.8 (J(C,F) = 3.8, C(3,5) of 3-Ar); 131.3 (C(2,6) of 3-Ar); 132.8 (C(2,6) of 6-Ar); 132.8 (C(1) of 6-Ar); 133.9 (C(1) of 3-Ar), 139.5 (J(C,F) = 32.3, C(4) of 3-Ar); 153.6 (C(5)); 160.2 (C(4) of 6-Ar); 163.1 (C(6)); 168.7 (C(3). EI-MS (130°, 70 eV): 331 (18, M^+). Anal. calc. for $C_{17}H_{12}F_3N_3O$ (331.3): C 61.63, H 3.65, N 12.68; found: C 61.66, H 3.41, N 12.71.

6-(4-Methoxyphenyl)-3-(4-nitrophenyl)-1,2,4-triazine (**2k**). *GP A* (n = 3.62, m = 20.0, p = 2.29). Yield: 1.26 g (44%). M.p. 239° (AcOH). UV ($CHCl_3$): 439 (2.37). ^{1}H-NMR (CF_3COOD, 400 MHz): 4.09 (MeO); 7.38 (J = 8.3, H–C(3,5) of 6-Ar); 8.30 (H–C(2,6) of 6-Ar); 8.56 (J = 8.1, H–C(2,6) of 3-Ar); 8.76 (H–C(3,5) of 3-Ar); 10.12 (H–C(5)). ^{13}C-NMR (CF_3OOD, 100 MHz): 57.5 (MeO); 118.3 (C(3,5) of 6-Ar); 126.7 (C(3,5) of 3-Ar); 132.0 (C(2,6) of 3-Ar); 133.3 (C(2,6) of 6-Ar); 132.0 (C(1) of 6-Ar); 138.2 (C(1) of 3-Ar); 152.1 (C(4) of 3-Ar); 153.2 (C(5)); 160.6 (C(4) of 6-Ar); 163.6 (C(6)); 169.8 (C(3)). EI-MS (150°, 70 eV): 308 (18, M^+). Anal. calc. for $C_{16}H_{12}N_4O_3$ (308.3): C 62.33, H 3.92, N 18.17; found: C 62.11, H 4.05, N 18.10.

3-(4-Methoxyphenyl)-6-(4-nitrophenyl)-1,2,4-triazine (**2l**). *GP A* (n = 1.66, m = 10.0, p = 1.01). Yield: 0.550 g (36%). M.p. >235° (dec.). UV ($CHCl_3$): 350 (1.30). ^{1}H-NMR (CF_3COOD, 400 MHz): 4.05 (MeO); 7.30 (J = 9.2, H–C(3,5) of 3-Ar); 7.98 (H–C(2,6) of 3-Ar); 8.30 (J = 8.8, H–C(3,5) of 6-Ar); 8.48 (H–C(2,6) of 6-Ar); 9.93 (H–C(5)). ^{13}C-NMR (CF_3COOD, 100 MHz): 54.3 (MeO); 116.4 (C(3,5) of 3-Ar); 126.5 (C(3,5) of 6-Ar); 130.6 (C(2,6) of 3-Ar); 132.5 (C(2,6) of 6-Ar); 134.9 (C(1) of 3-Ar); 139.0 (C(1) of 6-Ar); 162.6 (C(4) of 3-Ar); 160.6 (C(4) of 6-Ar); 163.1 (C(6)); 170.9 (C(3). EI-MS (175°, 70 eV): 308 (13, M^+, $C_{16}H_{12}N_4O_3^+$).

3-[4-(Dimethylamino)phenyl]-6-(4-nitrophenyl)-1,2,4-triazine (**2m**). *GP A* (n = 0.500, m = 2.78, p = 0.280). Yield: 0.440 g (95%). M.p. >195° (dec.). UV ($CHCl_3$): 313 (1.65). ^{1}H-NMR (CF_3COOD, 400 MHz): 3.55 (MeN); 7.85 (J = 8.8, H–C(3,5) of 3-Ar); 8.05 (H–C(2,6) of 3-Ar); 8.19 (J = 9.0, H–C(3,5) of 6-Ar); 8.48 (H–C(2,6) of 6-Ar); 9.65 (H–C(5)). EI-MS (210°, 70 eV): 321 (22, M^+, $C_{17}H_{15}N_5O_2^+$).

6-(4-Nitrophenyl)-3-phenyl-1,2,4-triazine (**2n**). *GP A* (n = 0.68, m = 5.00, p = 0.230). Yield: 0.300 g (43%). M.p. >210° (dec.). UV ($CHCl_3$): 320 (1.20). ^{1}H-NMR (CF_3COOD, 400 MHz): 7.83 (H–C(3,5) of 3-Ph); 8.02 (H–C(4) of 3-Ph); 8.30 (H–C(3,5) of 6-Ar); 8.51 (H–C(2,6) of 6-Ar); 8.64 (H–C(2,6) of 3-Ph); 10.10 (H–C(5)). ^{13}C-NMR (CF_3COOD, 100 MHz): 126.5 (C(3,5) of 3-Ph); 131.0 (C(1) of 6-Ar); 132.5 (C(2,6) of 3-Ph); 132.7 (C(2,6) of 6-Ar); 130.8 (C(3,5) of 6-Ar), 138.9 (C(1) of 3-Ph); 138.9 (C(4) of 6-Ar); 157.3 (C(6)); 152.0 (C(5)). EI-MS (160°, 70 eV): 278 (15, M^+, $C_{15}H_{10}N_4O_2^+$).

6-(4-Methoxyphenyl)-1,2,4-triazine (**3b**). *GP B* (r = 1.08, s = 10.4, t = 0.340, u = 10.4, v = 1.71, w = 1.05). Purification by CC (cyclohexane/1,4-dioxane 95 : 5; R_f 0.05). Yield: 0.063 g (3%). M.p. 139–140°. UV ($CHCl_3$): 278 (0.82). ^{1}H-NMR ($CDCl_3$, 400 MHz): 3.76 (MeO); 6.93 (J = 8.8, H–C(3,5) of 6-Ar); 7.94 (H–C(2,6) of 6-Ar); 8.84 (H–C(5)); 9.43 (H–C(3)). ^{13}C-NMR ($CDCl_3$, 100 MHz): 54.4 (MeO); 113.8 (C(3,5) of 6-Ar); 124.3 (C(1) of 6-Ar); 127.3 (C(2,6) of 6-Ar); 145.0 (C(5)); 156.2 (C(3)); 156.2 (C(6)); 161.1 (C(4) of 6-Ar). EI-MS: 187 (64, M^+). Anal. calc. for $C_{10}H_9N_3O$ (187.1): C 64.16, H 4.85, N 22.45; found: C 63.88, H 5.02, N 20.61.

6-(4-Nitrophenyl)-1,2,4-triazine (**3c**) [22b]. *GP B* (r = 0.590, s = 5.67, t = 0.284, u = 8.87, v = 1.02, w = 0.573). Mixture: **3c**/**4d** 24 : 76. Total yield: 0.680 g (59%). ^{1}H-NMR ($CDCl_3$, 400 MHz): 8.34 (J = 8.7, H–C(2,6) of 6-Ar); 8.45 (H–C(2,6) of 6-Ar); 9.13 (H–C(5)); 9.77 (H–C(3)). ^{13}C-NMR ($CDCl_3$, 100 MHz): 124.6 (C(3,5) of 6-Ar); 127.7 (C(2,6) of 6-Ar); 138.9 (C(1) of 6-Ar); 146.8 (C(5)); 149.5 (C(4) of 6-Ar); 156.1 (C(6)); 156.9 (C(3)).

5-(4-Methylphenyl)-1,2,4-triazine (**4b**). *GP B* (r = 1.54, s = 14.8, t = 0.470, u = 14.8, v = 2.19, w = 1.50). Purified by CC (cyclohexane/1,4-dioxane 90 : 10; R_f 0.07). Yield: 0.401 g (16%). Glassy solid. *B.p.* 120°/0.1 mbar. UV ($CHCl_3$): 286 (1.26). ^{1}H-NMR ($CDCl_3$, 400 MHz): 2.52 (Me); 7.38 (H–C(3,5) of 5-Ar); 7.46 (H–C(4) of 5-Ar); 7.56 (H–C(6) of 5-Ar); 9.45 (J = 2.0, H–C(6)); 9.71 (H–C(3)). ^{13}C-NMR ($CDCl_3$, 100 MHz): 20.5 (Me); 126.6 (C(5) of 5-Ar); 130.0 (C(6) of 5-Ar); 131.0 (C(3) of 5-Ar); 131.8 (C(4) of 5-Ar); 133.6 (C(1) of 5-Ar); 137.2 (C(2) of 5-Ar); 150.0 (C(6)); 156.9 (C(3)); 158.9 (C(5)). EI-MS: 171 (12, M^+). Anal. calc. for $C_{10}H_9N_3$ (171.2): C 70.16, H 5.30, N 24.54; found: C 70.23, H 5.26, N 24.15.

5-(2,4,6-Trimethylphenyl)-1,2,4-triazine (**4c**). *GP B* (r = 1.29, s = 12.4, t = 0.411, u = 12.3, v = 2.20, w = 1.26). Purified by CC (cyclohexane/1,4-dioxane 95 : 5; R_f 0.17). Yield: 0.185 g (7%). Glassy solid. B.p. 140°/0.01 mbar.

^{1}H-NMR (C_6D_6, 400 MHz): 1.81 (2 Me); 2.10 (Me); 6.68 (H–C(3,5) of 5-Ar); 8.7 (J = 2.1, H–C(6)); 9.53 (H–C(3)). ^{13}C-NMR (C_6D_6, 100 MHz): 19.9 (2 Me); 21.0 (Me); 129.1 (C(3,5) of 5-Ar); 132.0 (C(1) of 5-Ar); 135.9 (C(2,6) of 5-Ar); 139.4 (C(4) of 5-Ar); 157.8 (C(3)); 159.8 (C(5)). EI-MS: 199 (17, M^+). Anal. calc. for $C_{12}H_{13}N_3$ (199.2): C 72.34, H 6.57, N 21.09; found: C 71.92, H 6.57, N 20.27.

5-(4-Nitrophenyl)-1,2,4-triazine (**4d**). *GP B* (r = 0.590, s = 5.67, t = 0.284, u = 8.87, v = 1.02, w = 0.573). Mixture: **3c**/**4d** 24 : 76. Total yield: 0.680 g (59%). ^{1}H-NMR ($CDCl_3$, 400 MHz): 8.37 (J = 9.0, H–C(2,6) of 5-Ar); 8.44 (H–C(2,6) of 5-Ar); 9.82 (J = 2.0, H–C(6)); 9.83 (H–C(3)). ^{13}C-NMR ($CDCl_3$, 100 MHz): 124.6 (C(3,5) of 5-Ar); 128.7 (C(2,6) of 5-Ar); 139.1 (C(1) of 5-Ar); 146.7 (C(6)); 150.3 (C(4) of 5-Ar); 153.2 (C(5)); 157.6 (C(3)). EI-MS: 202 (36, M^+). Anal. calc. for $C_9H_6N_4O_2$ (202.1): C 53.46, H 2.99, N 27.71; found: C 53.33, H 2.98, N 27.13.

5-(4-Methoxyphenyl)-1,2,4-triazine (**4e**). *GP B* (r = 1.08, s = 10.4, t = 0.340, u = 10.4, v = 1.71, w = 1.05). Purified by CC (cyclohexane/1,4-dioxane 95 : 5; R_f 0.01). Yield: 0.080 g (4%). M.p. 134–135°. UV ($CHCl_3$): 278 (0.82). ^{1}H-NMR ($CDCl_3$, 400 MHz): 3.77 (MeO); 6.91 (J = 8.9, H–C(3,5) of 5-Ar); 8.02 (H–C(2,6) of 5-Ar); 9.43 (J = 1.9, H–C(6)); 9.51 (H–C(3)). ^{13}C-NMR ($CDCl_3$, 100 MHz): 54.5 (MeO); 113.9 (C(3,5) of 5-Ar); 127.3 (C(1) of 5-Ar); 128.3 (C(2,6) of 5-Ar); 145.2 (C(6)); 153.8 (C(5)); 156.3 (C(3)); 162.4 (C(4)) of 5-Ar). EI-MS: 187 (100, M^+). Anal. calc. for $C_{10}H_9N_3O$ (187.1): C 64.16, H 4.85, N 22.45; found: C 63.85, H 4.87, N 21.93.

3-(4-Nitrophenyl)-1,2,4-triazine (**19b**). To a pre-cooled mixture of 4-nitrobenzenecarboxamidine hydrochloride (1.14 g, 5.66 mmol) in anh. MeOH (50 ml), anh. hydrazine (0.270 g, 8.49 mmol) was added at −10° under Ar gas, and the mixture was stirred for 4 h, until NH_3 evolution ceased. Slowly, a soln. of freshly distilled 2-(4-methoxyphenyl)-2-oxoethanal (0.370 g, 6.38 mmol) in anh. MeOH (10 ml) and, after 10 min, Et_3N (0.740 g, 7.33 mmol) were added. After stirring at 20° for 24 h, the solvent was removed *in vacuo*, and the residue was extracted with Et_2O (3 × 50 ml). After washing with brine and drying ($MgSO_4$), the solvent was removed, and the resulting solid was crystallized from AcOH. Yellow platelets. Yield: 0.970 g (85%). M.p. 161° (lit. 176–178° [19]). UV ($CHCl_3$): 284 (0.43). ^{1}H-NMR ($CDCl_3$, 400 MHz): 8.40 (J = 9.1, H–C(2,6) of 3-Ar); 8.76 (H–C(3,5) of 3-Ar); 8.77 (J = 2.5, H–C(5)); 9.28 (H–C(6)). ^{13}C-NMR ($CDCl_3$, 100 MHz): 124.0 (C(3,5) of 3-Ar); 129.3 (C(2,6) of 3-Ar); 140.4 (C(1) of 3-Ar); 148.4 (C(5)); 148.5 (C(6)); 150.1 (C(4) of 3-Ar); 162.6 (C(3)). EI-MS (95°, 70 eV): 202 (26, M^+). Anal. calc. for $C_9H_6N_4O_2$ (202.1): C 53.46, H 2.99, N 27.71; found: C 53.53, H 2.96, N 27.36.

3. *Addition Reactions to 3,5,6-Triphenyl-1,2,4-triazine* (**6a**). *5,8-Dimethyl-9,10,12-triphenyl-5,8,11-triazadispiro[2.0.4.4]dodeca-9,11-diene* (**8a**) [12]. Compound **1** (24 mg, 0.174 mmol) was added to a soln. of **6a** (50.0 mg, 0.161 mmol) in C_6D_6 (1 ml). Vigorous gas evolution set in, which was finished after a few minutes. By NMR, 74% of **8a** were identified. ^{1}H-NMR (C_6D_6, 400 MHz): 1.05 (2 H of cPr); 1.19 (2 H of cPr); 2.27 (2 MeN); 2.76 (2 NCH_2); 7.03–7.66 (3 Ph). ^{13}C-NMR (C_6D_6, 100 MHz): 11.3 (C(1,2)); 26.9 (C(3)); 36.5 (2 MeN); 52.5 (C(6,7)); 81.5 (C(4)); 125.6 (C(9)); 144.8 (C(10)); 173.1 (C(12); 141.2, 132.7, 127.42, 126.9 (9-Ph); 141.2, 130.8, 127.44, 126.6 (10-Ph); 139.5, 129.4, 127.9, 126.8 (12-Ph).

*2,3-Dihydro-1-methyl-4,6,7-triphenyl-1*H*-pyrrolo[3,2-*c*]pyridine* (**9a**). To **6a** (100 mg, 0.323 mmol) in CD_2Cl_2 (1 ml) under Ar gas, compound **1** (53.0 mg, 0.383 mmol) was added slowly *via* syringe at −60°. The orange-brown soln. was allowed to slowly warm up, and at *ca.* −25°, vigorous gas evolution started. After 14 h at r.t., the solvent was removed *in vacuo*, and the residue was purified by prep. TLC (Al_2O_3; petroleum ether/AcOEt 30 : 1; R_f 0.16). Yellow solid. Yield 119 mg (42%). M.p. >200° (dec.). ^{1}H-NMR ($CDCl_3$, 400 MHz): 2.24 (MeN); 3.20 (H–C(3)); 3.44 (H–C(2)); 7.00–7.83 (3 Ph). ^{13}C-NMR (CD_2Cl_2, 100 MHz): 27.5 (C(3)); 37.7 (MeN); 57.0 (C(2)); 116.3 (C(7)); 122.4 (C(3a)); 150.8 (C(7a)); 157.4 (C(6)); 158.1 (C(4)); 137.1, 128.4, 128.1, 127.9 (4-Ph); 139.9, 129.9, 127.2, 126.9 (6-Ph); 141.1, 131.6, 127.7, 126.7 (7-Ph).

*3-[1-(4,5-Dihydro-1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)cyclopropyl]-3,5,6-triphenyl-3*H*-1,2,4-triazin-2-ide* (**10a**)[4]. To a soln. of **6a** (71 mg, 0.23 mmol) in CD_2Cl_2 (1 ml) under Ar gas, compound **1** (38 mg, 0.28 mmol) was carefully added at −40°. NMR Spectra were then recorded at −40, −20, 0, and +25°. The following product distribution was found: *a*) T = −40°, 1.5 h: **6a**/**1**/**8**/**9**/**10** 53 : 41 : 18 : 0 : 29; *b*) T = −30°, 1 h: 57 : 44 : 33 : 0 : 10; *c*) T = 0°, 1 h: 25 : 6 : 75 : 0 : 0; *d*) T = 25°, 48 h: 25 : 0 : 0 : 75 : 0.

Data of **10a**. ^{1}H-NMR (CD_2Cl_2, 400 MHz, T = −40°): 0.70–0.95 (4 H of cPr); 2.52 (MeN); 2.73 (MeN); 3.55 (m_c, 2 NCH_2); 6.70–7.30 (3 Ph). ^{13}C-NMR (CD_2Cl_2, 100 MHz): 10.8 (2 CH_2 of cPr); 24.8 (cPr); 35.5 (MeN); 35.7 (MeN); 52.4 (NCH_2); 52.9 (NCH_2); 81.5 (C(3)); 146.8 (C(5)); 148.6 (C(6)); 168.6 (C(2) of Im); 137.9, 127.0, 126.8, 121.7 (3-Ph); 139.6, 127.1, 126.9, 126.3 (5-Ph); 140.9, 130.3, 127.1, 128.3 (6-Ph).

4. *Addition Reactions to 5,6-Diphenyl-1,2,4-triazine* (**6b**). *5,8-Dimethyl-9,10-diphenyl-5,8,11-triazadispiro-[2.0.4.4]dodeca-9,11-diene* (**8b**) [12]. Compound **1** (36 mg, 0.251 mmol) was added to a soln. of **6a** (75.0 mg,

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[4]) Systematic name of one single resonance structure out of several possible ones.

0.241 mmol) in C_6D_6 (1 ml). Vigorous gas evolution set in, which was finished after a few minutes. By NMR, 93% of **8b** was identified. ^{1}H-NMR (C_6D_6, 400 MHz): 0.62 (2 H of cPr); 1.10 (2 H of cPr); 2.15 (2 MeN); 2.60, 2.67 (2 NCH_2); 7.08 (H–C(12)); 6.93–7.53 (2 Ph). ^{13}C-NMR (C_6D_6, 100 MHz): 12.1 (C(1,2)); 26.4 (C(3)); 35.1 (2 MeN); 52.4 (C(6,7)); 80.2 (C(4)); 126.5 (C(9)); 145.0 (C(10)); 167.4 (C(12)); 141.3, 132.8, 127.36, 126.9 (9-Ph); 141.9, 130.7, 127.42, 126.5 (10-Ph).

*2,3-Dihydro-1-methyl-6,7-diphenyl-1*H*-pyrrolo[3,2-*c*]pyridine* (**9b**). To compound **6b** (143 mg, 0.610 mmol) in CH_2Cl_2 (2 ml) under Ar gas, compound **1** (93.0 mg, 0.67 mmol) was slowly added *via* syringe at $-65°$. The orange soln. was allowed to warm up, and at *ca.* $-50°$, gas evolution started. After 24 h at r.t., the solvent was removed *in vacuo*, and the residue was purified by prep. TLC (Al_2O_3; petroleum ether/AcOEt 6:1; R_f 0.1). Colorless solid. Yield: 108 mg (38%). M.p. 175°. UV ($CHCl_3$): 245 (1.40). ^{1}H-NMR ($CDCl_3$, 400 MHz): 2.24 (MeN); 3.05 (^4J = 0.9, H–C(3)); 3.48 (H–C(2)); 7.09–7.22 (2 Ph); 8.16 (H–C(4)). ^{13}C-NMR ($CDCl_3$, 100 MHz): 25.3 (C(3)); 37.1 (MeN); 56.7 (C(2)); 117.1 (C(7)); 125.2 (C(3a)); 142.3 (C(4)); 156.3 (C(7a)); 158.2 (C(6)); 141.0, 127.7, 131.6, 126.9 (6-Ph); 136.9, 127.3, 129.6, 126.7 (7-Ph). EI-MS: 286 (68, M^+, $C_{20}H_{18}N_2^+$).

*3-[1-(4,5-Dihydro-1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)cyclopropyl]-5,6-diphenyl-3*H*-1,2,4-triazin-2-ide* (**10b**)[4]). To a soln. of **6b** (75 mg, 0.321 mmol) in CD_2Cl_2 (1 ml) under Ar gas, compound **1** (43.0 mg, 0.311 mmol) was carefully added at $-40°$. Then, NMR spectra were recorded at -40, -20, and $+25°$, giving rise to the following product distributions: *a*) $T = -40°$, 1 h: **6b**/**8b**/**9b**/**10b** 33:5:62:0; *b*) $T = -20°$, 7 h: 20:10:70:0; *c*) $T = 25°$, 1 h: 20:0:80:0; *d*) $T = 25°$, 168 h: 20:0:0:80.

Data of **10b**. ^{1}H-NMR (CD_2Cl_2, 400 MHz; $T = -20°$): 1.07 (2 H of cPr); 1.46 (H of cPr); 1.58 (H of cPr); 2.08 (H–C(3)); 3.42 (MeN); 3.45 (MeN); 3.65 (m_c, 2 NCH_2); 6.83–7.42 (2 Ph). ^{13}C-NMR (CD_2Cl_2, 100 MHz): 9.8 (CH_2 of cPr); 10.8 (CH_2 of cPr); 19.6 (cPr); 34.9 (MeN); 35.3 (MeN); 49.4 (NCH_2); 49.5 (NCH_2); 89.2 (C(3)); 136.2 (C(5)); 147.9 (C(6)); 168.9 (C(2) of Im); 134.0, 130.4, 127.4, 127.0 (5-Ph); 136.7, 123.9, 127.3, 121.8 (6-Ph).

5. *Additions to 3,5-Diaryl-1,2,4-triazines* **5**. *5,8-Dimethyl-9,11-diphenyl-5,8,10-triazadispiro[2.0.4.4]dodeca-9,11-diene* (**11a**). Compound **1** (61 mg, 0.44 mmol) was slowly added to a soln. of **5a** (86.0 mg, 0.365 mmol) in toluene (3 ml). A vigorous gas evolution set in, and the initially formed precipitate dissolved again. After 20 min, the solvent was removed *in vacuo*, and the residue was distilled at 250°/0.01 mbar. Yellow glass. Yield: 126 mg (99%). ^{1}H-NMR (C_6D_6, 400 MHz): 0.58 (2 H of cPr); 1.12 (2 H of cPr); 2.16 (2 MeN); 2.70, 2.82 (2 NCH_2); 5.58 (H–C(12)); 7.26–7.30, 8.02–8.08 (2 Ph). ^{13}C-NMR (C_6D_6, 100 MHz): 13.3 (C(1)); C(2)), 22.0 (C(3)), 35.4 (2 MeN); 52.3 (C(6,7)); 78.6 (C(4)); 120.5 (C(12)); 144.1 (C(11)); 164.8 (C(9)); 140.3, 129.6, 128.1, 128.2 (9-Ph); 138.9, 127.3, 125.1, 126.9 (11-Ph). EI-MS: 343 (100, M^+). Anal. calc. for $C_{23}H_{25}N_3$ (343.4): C 80.43, H 7.34, N 12.23; found: C 80.07, H 7.21, N 12.35.

5,8-Dimethyl-11-(2-methylphenyl)-9-phenyl-5,8,10-triazadispiro[2.0.4.4]dodeca-9,11-diene (**11b**). Compound **1** (44 mg, 0.32 mmol) was slowly added to a soln. of **5b** (76.0 mg, 0.307 mmol) in toluene (3 ml). A vigorous gas evolution set in. After 20 min, the solvent was removed *in vacuo*, and the residue was distilled at 250°/0.01 mbar. Yellow glass. Yield: 103 mg (92%). ^{1}H-NMR (C_6D_6, 400 MHz): 0.51 (2 H of cPr); 1.07 (2 H of cPr); 2.18 (2 MeN); 2.52 (Me of Tol); 2.67, 2.80 (2 NCH_2); 5.11 (H–C(12); 7.13 (H–C(3,4,5) of Tol); 7.19 (H–C(3,4,5) of Ph); 7.51 (H–C(6) of Tol); 7.97 (H–C(2,6) of Ph). ^{13}C-NMR (C_6D_6, 100 MHz): 13.4 (C(1,2)); 21.4 (Me of Tol); 22.2 (C(3)); 35.9 (2 MeN); 52.7 (C(6,7)); 78.5 (C(4)); 124.9 (C(12)); 143.5 (C(11)); 164.3 (C(9)); 144.3, 129.9, 127.7, 128.5 (9-Ph); 140.6 (C(1) of Tol); 136.5 (C(2) of Tol); 130.9 (C(3) of Tol); 127.4 (C(4) of Tol); 125.8 (C(5) of Tol); 129.3 (C(5) of Tol); 129.3 (C(6) of Tol). EI-MS: 357 (92, M^+). Anal. calc. for $C_{24}H_{27}N_3$ (358.5): C 80.63, H 7.61, N 11.75; found: C 79.69, H 7.41, N 11.67.

11-(4-Methoxyphenyl)-5,8-dimethyl-9-phenyl-5,8,10-triazadispiro[2.0.4.4]dodeca-9,11-diene (**11c**). Compound **1** (27 mg, 0.11 mmol) was slowly added to a soln. of **5c** (27.0 mg, 0.103 mmol) in C_6D_6 (1 ml). A vigorous gas evolution set in. After 20 min, the solvent was removed *in vacuo*, and the residue was distilled at 250°/0.01 mbar. Yellow glass. Yield 35.1 mg (91%). ^{1}H-NMR (C_6D_6, 400 MHz): 0.56 (2 H of cPr); 1.20 (2 H of cPr); 2.14 (2 MeN); 2.68, 2.80 (2 NCH_2); 3.33 (MeO); 5.73 (H–C(12)); 6.90 (J = 9.0, H–C(2,6)) of 11-Ar); 7.30–7.45 (H–C(3,4,5) of 9-Ph); 7.99 (H–C(3,5) of 11-Ar); 8.05 (H–C(2,6) of 9-Ph). ^{13}C-NMR (C_6D_6, 100 MHz): 13.6 (C(1,2)); 22.4 (C(3)); 35.9 (2 MeN); 52.7 (C(6,7)); 54.8 (MeO); 79.2 (C(4)); 118.8 (C(12)); 144.7 (C(11)); 164.3 (C(9)); 140.4, 130.0, 127.7, 128.5 (9-Ph); 132.0, 126.7, 114.0, 159.8 (11-Ar). EI-MS: 373 (100, M^+). Anal. calc. for $C_{24}H_{27}N_3O$ (373.5): C 77.18, H 7.29, N 11.25; found: C 76.74, H 6.98, N 11.37.

*4,5-Dihydro-2-[1-(1,6-dihydro-3,5-diphenyl-1,2,4-triazin-6-yl)cyclopropyl]-1,3-dimethyl-1*H*-imidazolium Acetate* (**13a**). To compound **5a** (79 mg, 0.34 mmol) in toluene (2 ml) under Ar gas, compound **1** (56 mg, 0.41 mmol) was slowly added *via* syringe at $-75°$ with stirring. After 15 min, AcOH (21 mg, 0.35 mmol) was added to the suspension, and the orange soln. was allowed to warm to r.t. After removal of the solvent *in vacuo*, the residue (97% of **13a**) was analyzed by NMR. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.86 (2 H of cPr); 1.15 (H of

cPr); 2.86 (MeN); 3.20 (MeN); 3.54, 3.78 (m_c, 2 NCH_2); 5.09 (H–C(6) of triazine); 7.37 (H–C(3,4,5 of 3-Ph); 7.49 (H–C(3,4,5) of 5-Ph); 8.03 (H–C(2,6) of 3-Ph); 8.16 (H–C(2,6) of 5-Ph). ^{13}C-NMR ($CDCl_3$, 100 MHz): 10.7 (CH_2 of cPr); 11.9 (CH_2 of cPr); 16.8 (C of cPr); 34.6 (MeN); 34.9 (MeN); 49.2 (C(6) of triazine); 49.6 (NCH_2); 49.8 (NCH_2); 147.1 (C(3) of triazine); 147.6 (C(5) of triazine); 165.8 (C(2) of Im); 135.2, 124.2, 128.7, 128.7 (3-Ph); 135.3, 127.5, 129.3, 131.8 (5-Ph).

*4,5-Dihydro-2-[1-[1,6-dihydro-5-(4-methoxyphenyl)-3-phenyl-[1-^{2}H]-1,2,4-triazin-6-yl]cyclopropyl]-1,3-dimethyl-1*H*-imidazolium [2,2,2-$^2H_3$]Acetate* (**13c**). To **5c** (88 mg, 0.33 mmol) in CD_2Cl_2 (1 ml) under Ar gas, compound **1** (51 mg, 0.37 mmol) was slowly added *via* syringe at $-40°$. After 15 min, CD_3COOD (30 mg, 0.49 mmol) was added to the suspension, and the orange soln. (61% of **13c**) was analyzed by NMR ^{1}H-NMR (CD_2Cl_2, 400 MHz; $T = -30°$): 0.77 (2 H of cPr); 1.15 (H of cPr); 2.74 (MeN); 3.16 (MeN); 3.72 (MeO); 3.83 (m_c, 2 NCH_2); 4.80 (H–C(6) of triazine); 6.97 ($J = 9.0$, H–C(3,5) of 5-Ar); 7.40 (H–C(3,4,5) of 3-Ph); 8.06 (H–C(2,6) of 3-Ph); 8.14 (H–C(2,6) of 5-Ar). ^{13}C-NMR ($CDCl_3$, 100 MHz; $T = -30°$): 9.7 (2 CH_2 of cPr); 16.5 (cPr); 34.3 (MeN); 34.8 (MeN); 49.1(C(6) of triazine); 49.2 (NCH_2); 49.3 (NCH_2); 149.7 (C(3) of triazine); 147.0 (C(5) of triazine); 165.5 (C(2) of Im); 134.9, 129.2, 128.7, 129.3 (3-Ph); 126.7, 128.6, 129,3, 131.8 (5-Ar).

6. *Additions to 3,6-Diaryl-1,2,4-triazines* **2**. *General Procedure C* (*GP C*). To compound **2** (*n* mg, *m* μmol) in either C_6D_6 or (D_8)toluene (0.6 ml), compound **1** (*q* mg, *p* mmol) was added *via* syringe under Ar gas. The orange suspension was heated to 108° in a sealed tube for 19 h, and the resulting yellow-brown soln. was investigated by NMR. For yields and ratios of regioisomers, see *Table 2*; for characteristic ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) shifts, see *Tables 5–7*.

5,8-Dimethyl-9,12-diphenyl-5,8,11-triazadispiro[2.0.4.4]dodeca-9,11-diene (**14a**) *and 5,8-Dimethyl-9,12-diphenyl-5,8,10-triazadispiro[2.0.4.4]dodeca-9,11-diene* (**15a**). *GP C* ($n = 28$, $m = 120$, $q = 23$, $p = 166$).

Data of **14a**. ^{1}H-NMR ((D_8)toluene): 7.14–7.72 (2 Ph). ^{13}C-NMR ((D_8)toluene): 141.9, 128.7, 126.7, 126.8 (9-Ph); 138.7, 129.3, 129.1, 128.3 (12-Ph).

Data of **15a**. ^{1}H-NMR ((D_8)toluene): 7.14–8.00 (2 Ph). ^{13}C-NMR ((D_8)toluene): 144.0, 129.9, 129.6, 128.2 (9-Ph); 137.3, 128.0, 127.3, 127.1 (12-Ph).

Table 5. *Selected ^{1}H-NMR Chemical Shifts of Compounds* **14** *and* **15**

	Solvent	**14**				**15**			
		cPr[a])	MeN	CH_2N	H–C(11)	cPr	MeN	CH_2N	H–C(11)
a	(D_8)toluene	0.93, 1.16	2.26	2.80	7.38	0.73, 0.99	2.27	2.86	7.03
b	C_6D_6	1.04, 1.18	2.44	2.78	7.28	0.62, 0.95	2.44	2.78	7.02
c	C_6D_6	0.96, 1.17	2.30	2.80	7.49	0.80, 1.03	2.29	2.80	7.30
d	(D_8)toluene	0.98, 1.18	2.28	2.82	7.39	0,74, 1.00	2.29	2.82	7.03
e	C_6D_6	1.02, 1.16	2.24	2.78	7.42	0.78, 1.02	2.30	2.78	7.06
f	C_6D_6	0.73, 1.13	2.22	2.77	7.42	0.74, 0.95	2.15	2.77	7.06
g	(D_8)toluene	0.68, 1.15	2.20	2.79	7.31	0.72, 0.94	2.14	2.70	6.97
h	(D_8)toluene	1.00, 1.20	2.28	2.84	7.40	0.75, 1.01	2.31	2.84	7.04
i	(D_8)toluene	1.09, 1.23	2.31	2.87	7.44	0.74, 1.02	2.36	2.86	7.05
j	C_6D_6	0.75, 1.15	2.26	2.80	7.44	0.91, 0.98	2.18	2.71	7.12
k	C_6D_6	0.66, 1.14	2.23	2.78	7.42	0.79, 0.96	2.13	2.67	7.10

[a]) cPr = Cyclopropyl.

5,8-Dimethyl-9-(2-methylphenyl)-12-phenyl-5,8,11-triazadispiro[2.0.4.4]dodeca-9,11-diene (**14b**) *and 5,8-Dimethyl-12-(2-methylphenyl)-9-phenyl-5,8,10-triazadispiro[2.0.4.4]dodeca-9,11-diene* (**15b**). *GP C* ($n = 29$, $m = 117$, $q = 20$, $p = 144$).

Data of **14b**. ^{1}H-NMR (C_6D_6): 2.23 (Me of Tol); 7.02–7.53 (9-Ar, 12-Ph). ^{13}C-NMR (C_6D_6): 20.5 (Me of 9-Ar); 134.3, 137.1, 131.5, 130.1, 165.5, 125.0 (9-Ar); 126.1, 129.5, 129.1, 128.6 (12-Ph).

Data of **15b**. ^{1}H-NMR (C_6D_6): 7.04–8.00 (12-Ar, 9-Ph). ^{13}C-NMR (C_6D_6): 20.3 (Me of Tol); 144.0, 129.9, 129.6, 128.2 (9-Ph); 144.4, 136.6, 132.0, 128.1, 127.6, 125.1 (12-Ar).

Table 6. *Selected ^{13}C-NMR Chemical Shifts of Compounds* **14**

	Solvent	C(1,2)	C(3)	C(4)	C(6,7)	C(9)	C(10)	C(12)	MeN
14a	(D_8)toluene	10.4	26.4	80.7	52.7	137.1	138.5	173.3	36.4
14b	C_6D_6	10.3	26.8	80.7	53.0	139.3	140.1	173.6	35.6
14c	C_6D_6	10.8	26.7	80.8	53.0	129.8	138.3	173.2	36.7
14d	(D_8)toluene	10.4	26.5	80.7	52.7	137.1	138.7	173.1	36.4
14e	C_6D_6	11.4	28.1	80.5	52.8	129.4	138.3	173.1	36.6
14f	C_6D_6	10.9	26.6	80.8	52.9	128.0	138.5	172.3	36.6
14g	(D_8)toluene	10.6	26.1	80.8	52.6	136.8	138.0	171.2	36.2
14h	(D_8)toluene	10.3	26.6	80.8	52.7	131.0	138.8	173.0	36.5
14i	(D_8)toluene	10.5	26.9	81.5	53.1	128.2	139.6	173.7	37.1
14j	C_6D_6	10.9	26.3	80.6	52.9	129.4	137.9	171.7	36.6
14k	C_6D_6	10.9	26.3	80.5	52.9	129.2	137.7	171.0	36.6

9-(4-Methoxyphenyl)-5,8-dimethyl-12-phenyl-5,8,11-triazadispiro[2.0.4.4]dodeca-9,11-diene (**14c**) *and 12-(4-Methoxyphenyl)-5,8-dimethyl-9-phenyl-5,8,10-triazadispiro[2.0.4.4]dodeca-9,11-diene* (**15c**). *GP C* ($n = 43$, $m = 163$, $q = 23$, $p = 166$).

Data of **14c**. ^{1}H-NMR (C_6D_6): 3.36 (MeO of 9-Ar); 6.81, 7.69 ($J = 8.9$, 9-Ar); 7.10–7.69 (12-Ph). ^{13}C-NMR (C_6D_6): 54.7 (MeO of 9-Ar); 134.4, 130.7, 113.7, 159.5 (9-Ar); 139.3, 129.5, 127.9, 128.4 (12-Ph).

Data of **15c**. ^{1}H-NMR (C_6D_6): 3.32 (MeO of 12-Ar); 7.20–7.32 (9-Ph); 6.72, 8.09 ($J = 7.9$, 12-Ar) . ^{13}C-NMR (C_6D_6): 54.8 (MeO of 12-Ar); 144.3, 131.4, 129.8 128.5 (9-Ph); 135.5, 131.3, 113.7, 159.5 (12-Ar).

Table 7. *Selected ^{13}C-NMR Chemical Shifts of Compounds* **15**

	Solvent	C(1,2)	C(3)	C(4)	C(6,7)	C(9)	C(11)	C(12)	MeN
15a	(D_8)toluene	10.0	23.6	79.5	52.7	164.1	133.1	135.3	36.4
15b	C_6D_6	10.2	24.8	79.6	53.0	164.1	133.1	136.9	35.6
15c	C_6D_6	10.3	24.1	79.9	52.9	164.2	132.8	135.9	36.8
15d	(D_8)toluene	10.0	23.5	79.3	52.7	164.0	132.6	137.3	36.4
15e	C_6D_6	10.3	23.5	79.1	52.9	164.2	132.3	135.9	36.6
15f	C_6D_6	10.5	23.8	79.6	52.7	163.2	132.6	[a])	36.6
15g	(D_8)toluene	10.2	23.6	79.4	52.4	162.1	132.2	136.7	36.6
15h	(D_8)toluene	10.0	23.5	79.2	52.6	162.7	132.5	136.5	36.4
15i	(D_8)toluene	10.3	24.0	79.8	53.0	164.3	133.1	134.5	36.9
15j	C_6D_6	10.4	24.1	79.8	52.8	162.9	132.5	136.4	36.6
15k	C_6D_6	10.5	24.2	79.8	52.7	162.3	132.5	133.8	36.6

[a]) Signal masked.

5,8-Dimethyl-12-(4-methylphenyl)-9-phenyl-5,8,11-triazadispiro[2.0.4.4]dodeca-9,11-diene (**14d**) *and 5,8-Dimethyl-9-(4-methylphenyl)-12-phenyl-5,8,10-triazadispiro[2.0.4.4]dodeca-9,11-diene* (**15d**). *GP C* ($n = 31$, $m = 125$, $q = 21$, $p = 152$).

Data of **14d**. ^{1}H-NMR ((D_8)toluene): 2.13 (Me of 12-Ar); 7.17–7.74 (9-Ph); 6.96, 7.46 ($J = 8.1$, 12-Ar). ^{13}C-NMR ((D_8)toluene): 20.8 (Me of 12-Ar); 142.0, 128.2, 127.8, 126.7 (9-Ph); 137.9, 129.2, 129.3, 136.1 (12-Ar).

Data of **15d**. ^{1}H-NMR ((D_8)toluene): 2.19 (Me of 9-Ar); 7.14–7.74 (9-Ar, 12-Ph). ^{13}C-NMR ((D_8)toluene): 20.8 (Me of 9-Ar); 141.0, 129.5, 130.0, 136.8 (9-Ar); 137.8, 129.0, 128.0, 127.0 (12-Ph).

5,8-Dimethyl-12-(2-methylphenyl)-9-phenyl-5,8,11-triazadispiro[2.0.4.4]dodeca-9,11-diene (**14e**) and *5,8-Dimethyl-9-(2-methylphenyl)-12-phenyl-5,8,10-triazadispiro[2.0.4.4]dodeca-9,11-diene* (**15e**). *GP C* ($n = 30$, $m = 121$, $q = 19$, $p = 137$).

Data of **14e**. ^{1}H-NMR (C_6D_6): 2.40 (Me of 12-Ar); 7.02–7.90 (12-Ar, 9-Ph). ^{13}C-NMR (C_6D_6): 19.8 (Me of 12-Ar); 142.3, 129.9, 128.0, 127.2, (9-Ph); 136.9, 138.1, 130.2, 131.0, 124.7, 129.3 (12-Ar).

Data of **15e**. ^{1}H-NMR (C_6D_6): 2.58 (Me of 9-Ar); 7.04–8.20 (9-Ar, 12-Ph). ^{13}C-NMR (C_6D_6): 23.5 (Me of 9-Ar); 141.3, 137.4, 129.8, 130.3, 124.6, 128.7 (9-Ar); 137.7, 130.6, 129.1, 127.1 (12-Ph).

5,8-Dimethyl-9-phenyl-12-[4-(trifluoromethyl)phenyl]-5,8,11-triazadispiro[2.0.4.4]dodeca-9,11-diene (**14f**) *and 5,8-Dimethyl-12-phenyl-9-(4-(trifluoromethyl)phenyl]-5,8,10-triazadispiro[2.0.4.4]dodeca-9,11-diene* (**15f**). *GP C* ($n = 24$, $m = 80$, $q = 11$, $p = 80$).

Data of **14f**. ^{1}H-NMR (C_6D_6): 7.09–7.24, 7.75 (9-Ph); 7.31, 7.35 ($J = 8.4$, 12-Ar). ^{13}C-NMR (C_6D_6): 137.3, 129.6, 128.2, 127.4 (9-Ph); 141.9, 129.8, 124.9, 130.3 (12-Ar).

Data of **15f**. ^{1}H-NMR (C_6D_6): 7.31, 7.41 ($J = 8.2$, 9-Ar); 7.09–7.24, 7.94 (12-Ph). ^{13}C-NMR (C_6D_6): 142.4, 127.4, 124.7, 130.5 (9-Ar); 144.0, 130.1, 130.1, 127.9 (12-Ph).

5,8-Dimethyl-12-(4-nitrophenyl)-9-phenyl-5,8,11-triazadispiro[2.0.4.4]dodeca-9,11-diene (**14g**) *and 5,8-Dimethyl-9-(4-nitrophenyl)-12-phenyl-5,8,10-triazadispiro[2.0.4.4]dodeca-9,11-diene* (**15g**). *GP C* ($n = 26$, $m = 94$, $q = 14$, $p = 102$).

Data of **14g**. ^{1}H-NMR ((D_8)toluene): 7.12–7.19 (9-Ph); 7.82, 7.91 ($J = 9.0$, 12-Ar). ^{13}C-NMR ((D_8)toluene): 145.5, 129.6, 127.6, 127.1 (9-Ph); 144.0, 129.3, 122.7, 147.9 (12-Ar).

Data of **15g**. ^{1}H-NMR ((D_8)toluene): 7.21, 7.78 ($J = 9.0$, 9-Ar); 7.12, 7.68 (12-Ph). ^{13}C-NMR ((D_8)toluene): 141.4, 129.7, 122.5, 147.7 (9-Ar); 149.6, 129.7, 127.6, 127.5 (12-Ph).

12-(4-Methoxyphenyl)-5,8-dimethyl-9-phenyl-5,8,11-triazadispiro[2.0.4.4]dodeca-9,11-diene (**14h**) *and 9-(4-Methoxyphenyl)-5,8-dimethyl-12-phenyl-5,8,10-triazadispiro[2.0.4.4]dodeca-9,11-diene* (**15h**). *GP C* ($n = 40$, $m = 152$, $q = 21$, $p = 152$).

Data of **14h**. ^{1}H-NMR ((D_8)toluene): 3.34 (MeO of 12-Ar); 7.19, 7.75 (9-Ph); 6.72, 7.50 ($J = 8.9$, 12-Ar). ^{13}C-NMR ((D_8)toluene): 54.4 (MeO of 12-Ar); 142.1, 129.2, 127.9,126.7 (9-Ph); 129.5, 130.6, 112.9, 160.2 (12-Ar).

Data of **15h**. ^{1}H-NMR ((D_8)toluene): 3.38 (MeO of 9-Ar); 6.86, 7.95 ($J = 8.7$, 9-Ar); 7.15, 7.87 (12-Ph). ^{13}C-NMR ((D_8)toluene): 54.5 (MeO of 9-Ar); 137.5, 130.1, 112.8, 160.7 (9-Ar); 135.0, 130.0, 129.0, 126.5 (12-Ph).

12-(4-(Dimethylamino)phenyl]-5,8-dimethyl-9-phenyl-5,8,11-triazadispiro[2.0.4.4]dodeca-9,11-diene (**14i**) *and 9-[4-(Dimethylamino)phenyl]-5,8-dimethyl-12-phenyl-5,8,10-triazadispiro[2.0.4.4]dodeca-9,11-diene* (**15i**). *GP C* ($n = 32$, $m = 116$, $q = 21$, $p = 152$).

Data of **14i**. ^{1}H-NMR (C_6D_6): 2.53 (Me_2N of 12-Ar); 7.18, 7.77 (9-Ph) ; 6.47, 7.59 ($J = 8.9$, 12-Ar). ^{13}C-NMR (C_6D_6): 39.8 (Me_2N of 12-Ar); 142.7, 129.4, 128.1, 126.8 (9-Ph); 127.0, 130.8, 111.4, 150.9 (12-Ar).

Data of **15i**. ^{1}H-NMR (C_6D_6): 2.53 (Me_2N of 9-Ar); 6.56, 7.18 ($J = 8.8$, 9-Ar); 7.12, 7.98 (12-Ph). ^{13}C-NMR (C_6D_6): 39.9 (Me_2N of 9-Ar); 138.0, 130.3, 111.5, 149.0 (9-Ar); 138.0, 130.8, 128.0, 127.3 (12-Ph).

9-(4-Methoxyphenyl)-5,8-dimethyl-12-[4-(trifluoromethyl)phenyl]-5,8,11-triazadispiro[2.0.4.4]dodeca-9,11-diene (**14j**) *and 12-(4-Methoxyphenyl)-5,8-dimethyl-9-[4-(trifluoromethyl)phenyl]-5,8,10-triazadispiro[2.0.4.4]dodeca-9,11-diene* (**15j**). *GP C* ($n = 23$, $m = 69$, $q = 10$, $p = 73$).

Data of **14j**. ^{1}H-NMR (C_6D_6): 3.37 (MeO of 9-Ar); 6.80, 7.67 ($J = 8.6$, 9-Ar); 7.32, 7.36 ($J = 8.4$, 12-Ar). ^{13}C-NMR (C_6D_6): 54.8 (MeO of 9-Ar); 124.9 (F_3C of 12-Ar); 134.0, 130.7, 113.8, 159.8 (9-Ar); 142.5, 129.8, 124.9 (J(C,F) = 3.8), 130.3 (J(C,F) = 32.0) (12-Ar).

Data of **15j**. ^{1}H-NMR (C_6D_6): 3.32 (MeO); 7.42, 7.92 ($J = 8.3$, 9-Ar); 6.73, 7.10 ($J = 8.6$, 12-Ar). ^{13}C-NMR (C_6D_6): 54.8 (MeO of 12-Ar); 125.0 (F_3C of 9-Ar); 147.8, 130.1, 124.8 (J(C,F) = 3.8), 130.1 (J(C,F) = 32.0) (9-Ar); 142.5, 131.2, 113.8, 159.8 (12-Ar).

9-(4-Methoxyphenyl)-5,8-dimethyl-12-(4-nitrophenyl)-5,8,11-triazadispiro[2.0.4.4]dodeca-9,11-diene (**14k**) *and 12-(4-Methoxyphenyl)-5,8-dimethyl-9-(4-nitrophenyl)-5,8,10-triazadispiro[2.0.4.4]dodeca-9,11-diene* (**15k**). *GP C* ($n = 24$, $m = 78$, $q = 11$, $p = 80$).

Data of **14k**. ^{1}H-NMR (C_6D_6): 3.37 (MeO of 9-Ar); 6.82, 7.66 ($J = 9.0$, 9-Ar); 7.21, 7.79 ($J = 8.8$, 12-Ar). ^{13}C-NMR (C_6D_6): 54.8 (MeO of 9-Ar); 133.8, 130.7, 113.8, 159.8 (9-Ar); 145.3, 130.3, 123.1, 148.2 (12-Ar).

Data of **15k**. ^{1}H-NMR (C_6D_6): 3.33 (MeO); 7.87, 7.93 ($J = 9.0$, 9-Ar); 6.73, 7.08 ($J = 8.9$, 12-Ar). ^{13}C-NMR (C_6D_6): 54.8 (MeO of 12-Ar); 144.4, 129.9, 122.9, 148.0 (9-Ar); 137.0, 131.2, 113.8, 159.8 (12-Ar).

*4,5-Dihydro-2-[1-(2,5-dihydro-3,6-diphenyl-[2-^{2}H]-1,2,4-triazin-5-yl)cyclopropyl]-1,3-dimethyl-1*H*-imidazolium [2,2,2-$^2H_3$]Acetate* (**17a**). To compound **2a** (51 mg, 0.22 mmol) in THF (10 ml) under Ar gas, compound **1** (30 mg, 0.22 mmol) was slowly added *via* syringe at $-40°$ with stirring. After 1 h, the orange precipitate was collected by filtration at $-40°$ under Ar gas, and washed with pentane. After removal of the last traces of solvent at $-20°$/0.1 mbar, the remaining solid (75%) was dissolved in $CDCl_3$ (0.6 ml) containing CD_3COOD (0.6 mmol). ^{1}H-NMR ($CDCl_3$, 400 MHz; $T = 25°$): 1.06, 1.08, 1.26, 1.28 (cPr); 3.08 (2 MeN); 3.72 (m_c, 2 NCH_2); 5.62 (H–C(5) of triazine); 7.96, 7.50, 7.63 (3-Ph); 7.78, 7.55, 7.50 (6-Ph). ^{13}C-NMR ($CDCl_3$, 100 MHz; $T = 25°$): 10.2 (CH_2 of cPr); 10.8 (CH_2 of cPr); 18.2 (C of cPr); 34.8 (MeN); 35.0 (MeN); 50.0 (NCH_2); 50.1 (NCH_2); 51.5

(C(5) of triazine); 144.8 (C(6) of triazine); 156.4 (C(3) of triazine); 164.5 (C(2) of Im); 128.5, 127.8, 129.4, 133.2 (3-Ph); 133.5, 126.2, 129.5, 131.2 (6-Ph).

*2,5-Dihydro-2-{1-[1,6-Dihydro-3-(2-methylphenyl)-6-phenyl-1,2,4-triazin-5-yl]cyclopropyl}-1,3-dimethyl-1*H*-imidazolium Acetate* (**17e**). To compound **2e** (143 mg, 0.58 mmol) in toluene (10 ml) under Ar gas, compound **1** (95 mg, 0.69 mmol) was slowly added *via* syringe at −40° with stirring. After 1 h, AcOH (1.2 mmol) was added to the orange precipitate, which dissolved within 30 min. The solvent was removed at 0.1 mbar, the residue (76%) was dissolved in $CDCl_3$ (0.6 ml), and investigated by NMR. ^{1}H-NMR ($CDCl_3$, 400 MHz; T = 25°): 1.05, 1.10, 1.30, 1.42 (cPr); 2.38 (Me of 3-Ar); 2.99 (MeN); 3.14 (MeN); 3.78 (m_c, 2 NCH_2); 5.42 (H−C(5) of triazine); 7.20–7.60 (3-Ar); 7.76, 7.15, 7.45 (6-Ph). ^{13}C-NMR ($CDCl_3$, 100 MHz; T = 25°): 8.3 (CH_2 of cPr); 10.2 (CH_2 of cPr); 18.5 (C of cPr); 19.9 (Me of 3-Ar); 34.7 (MeN); 34.9 (MeN); 49.4 (NCH_2); 49.7 (NCH_2); 51.3 (C(5) of triazine); 137.9 (C(6) of triazine); 157.7 (C(3) of triazine); 165.5 (C(2) of Im); 128.3, 131.8 130.2, 131.2 (3-Ar); 141.5, 125.3, 129.0, 129.1 (6-Ph).

*2,5-Dihydro-2-{1-[1,6-dihydro-3-(4-methylphenyl)-6-phenyl-1,2,4-triazin-5-yl]cyclopropyl}-1,3-dimethyl-1*H*-imidazolium Acetate* (**17d**). To compound **2d** (100 mg, 0.41 mmol) in toluene (10 ml) under Ar gas, compound **1** (67 mg, 0.48 mmol) was slowly added *via* syringe at 25° with stirring. After 1 h, AcOH (1.2 mmol) was added to the orange precipitate, which dissolved within 30 min. The solvent was removed at 0.1 mbar, the residue (75%) was dissolved in $CDCl_3$ (0.6 ml), and investigated by NMR. ^{1}H-NMR ($CDCl_3$, 400 MHz; T = 25°): 0.96, 0.99, 1.32, 1.33 (cPr); 2.36 (Me of 3-Ar); 2.96 (MeN); 2.99 (MeN); 3.68 (m_c, 2 NCH_2); 5.08 (H−C(5) of triazine); 7.97, 7.23 (J = 8.3, 3-Ar); 7.77, 7.40, 7.40 (6-Ph). ^{13}C-NMR ($CDCl_3$, 100 MHz; T = 25°): 10.1 (CH_2 of cPr); 11.1 (CH_2 of cPr); 18.6 (C of cPr); 21.4 (Me of 3-Ar); 34.7 (MeN); 34.9 (MeN); 49.7 (NCH_2); 49.8 (NCH_2); 53.7 (C(5) of triazine); 146.5 (C(6) of triazine); 154.8 (C(3) of triazine); 165.2 (C(2) of Im); 135.0, 125.6, 129.0, 141.5 (3-Ar); 141.9, 129.5, 126.9, 129.7 (6-Ph).

*4,5-Dihydro-2-{1-[2,5-dihydro-3-(4-nitrophenyl)-6-phenyl-[2-^{2}H]-1,2,4-triazin-5-yl]cyclopropyl}-1,3-dimethyl-1*H*-imidazolium [2,2,2-$^2H_3$]Acetate* (**17g**). To compound **2g** (220 mg, 0.79 mmol) in THF (10 ml) under Ar gas, compound **1** (181 mg, 1.31 mmol) was slowly added *via* syringe at −40° with stirring. After 1 h, the orange precipitate was collected by filtration under Ar gas, and washed with pentane. After removal of last traces of solvent at 0.1 mbar, the resulting solid (66%) was dissolved in $CDCl_3$ (0.6 ml) containing CD_3COOD (3.9 mmol). ^{1}H-NMR ($CDCl_3$, 400 MHz; T = 25°): 1.15, 1.15, 1.45, 1.60 (cPr); 3.12 (MeN); 3.13 (MeN); 3.40, 3.70 (2 NCH_2); 5.93 (H−C(5) of triazine); 7.98, 7.44 (J = 8.4, 3-Ar); 7.98, 7.56, 7.56 (6-Ph). ^{13}C-NMR ($CDCl_3$, 100 MHz; T = 25°): 10.3 (CH_2 of cPr); 10.5 (CH_2 of cPr); 18.1 (C of cPr); 34.8 (MeN); 35.0 (MeN); 48.2 (C(5) of triazine); 49.8 (2 NCH_2); 147.8 (C(6) of triazine); 155.5 (C(3) of triazine); 163.6 (C(2) of Im); 130.7, 129.2 126.7 146.8 (3-Ar); 132.3, 129.7, 130.7, 132.1 (6-Ph).

*4,5-Dihydro-2-{1-[2,5-dihydro-3-(4-methoxyphenyl)-6-phenyl-[2-^{2}H]-1,2,4-triazin-5-yl]cyclopropyl}-1,3-dimethyl-1*H*-imidazolium [2,2,2-$^2H_3$]Acetate* (**17h**). To compound **2h** (202 mg, 0.77 mmol) in THF (10 ml) under Ar gas, compound **1** (129 mg, 0.93 mmol) was slowly added *via* syringe at −40° with stirring. After 1 h, the orange precipitate was collected by filtration under Ar gas, and washed with pentane. After removal of last traces of solvent at 0.1 mbar, the resulting solid (67%) was dissolved in $CDCl_3$ (0.6 ml) containing CD_3COOD (2.8 mmol). ^{1}H-NMR ($CDCl_3$, 400 MHz; T = 25°): 1.14, 1.14, 1.40, 1.54 (cPr); 3.07 (2 MeN); 3.40, 3.70 (2 NCH_2); 3.78 (MeO of 3-Ar); 5.97 (H−C(5) of triazine); 8.08, 7.10 (J = 8.1, 3-Ar); 7.98, 7.54, 7.54 (6-Ph). ^{13}C-NMR ($CDCl_3$, 100 MHz; T = 25°): 10.4 (CH_2 of cPr); 10.7 (CH_2 of cPr); 18.5 (C of cPr); 34.9 (MeN); 35.1 (MeN); 49.4 (C(5) of triazine); 50.0 (NCH_2); 50.1 (NCH_2); 55.8 (MeO of 3-Ar); 147.4 (C(6) of triazine); 155.7 (C(3) of triazine); 165.3 (C(2) of Im); 133.3, 131.4, 115.5, 164.2 (3-Ar); 130.4, 129.8, 126.8, 132.1 (6-Ph).

*4,5-Dihydro-2-(1-{2,5-dihydro-3-[4-(dimethylamino)phenyl]-6-phenyl-[2-^{2}H]-1,2,4-triazin-5-yl}cyclopropyl)-1,3-dimethyl-1*H*-imidazolium [2,2,2-$^2H_3$]Acetate* (**17i**). To compound **2i** (95 mg, 0.34 mmol) in toluene (10 ml) under Ar gas, compound **1** (57 mg, 0.41 mmol) was slowly added *via* syringe at −40° with stirring. After 1 h, CD_3COOD (1.2 mmol) was added to the orange precipitate, which dissolved within 30 min. The solvent was removed at 0.1 mbar, and the residue (25%) was dissolved in $CDCl_3$ (0.6 ml), and investigated by NMR. ^{1}H-NMR ($CDCl_3$, 400 MHz; T = 25°): 1.00, 1.00, 1.35, 1.45 (cPr); 3.17 (2 MeN); 3.19 (Me_2N of 3-Ar); 3.75 (m_c, 2 NCH_2); 5.16 (H−C(5) of triazine); 7.97, 6.70 (J = 9.0, 3-Ar); 7.82 ,7.40, 7.40 (6-Ph). ^{13}C-NMR ($CDCl_3$, 100 MHz; T = 25°): 10.4 (CH_2 of cPr); 11.3 (CH_2 of cPr); 18.5 (C of cPr); 34.8 (MeN); 35.1 (MeN); 49.4 (C(5) of triazine); 49.8 (NCH_2); 49.9 (NCH_2); 53.3 (Me_2N of 3-Ar); 142.5 (C(6) of triazine); 154.9 (C(3) of triazine); 165.1 (C(2) of Im); 116.5, 125.7, 111.6, 152.7 (3-Ar); 134.8, 128.2, 129.0, 129.9 (6-Ph).

*5-[1-(4,5-Dihydro-1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)cyclopropyl]-3,6-diphenyl-5*H*-1,2,4-triazin-2-ide* (**16a**)[4]). To a yellow soln. of compound **2a** (273 mg, 1.17 mmol) in toluene (10 ml), compound **1** (193 mg, 1.40 mmol) was slowly added at −40°. After 1 h, the orange precipitate was collected by filtration at −40° under Ar gas. After washing with pentane and removal of last traces of solvent at −20°/0.1 mbar, the solid

(100% of **16a**) was dissolved in CD_2Cl_2 (0.6 ml), and analyzed by NMR. ^{1}H-NMR (CD_2Cl_2, 400 MHz; $T=-20°$): 0.56, 0.64, 1.26, 1.34 (cPr); 2.94 (MeN); 2.98 (MeN); 3.45 (m_c, 2 NCH_2); 4.86 (H–C(5)); 7.87, 7.29, 7.17 (3-Ph); 8.29, 7.29, 7.29 (6-Ph). ^{13}C-NMR (CD_2Cl_2, 100 MHz; $T=-20°$): 9.4 (CH_2 of cPr); 11.0 (CH_2 of cPr); 19.8 (C of cPr); 35.1 (MeN); 35.2 (MeN); 49.7 (2 NCH_2); 56.9 (C(5) of triazine); 140.1 (C(6) of triazine); 160.3 (C(3) of triazine); 166.9 (C(2) of Im); 134.7, 124.3, 129.7, 126.7 (3-Ph); 139.7, 127.2, 128.9, 127.8 (6-Ph).

*5-[1-(4,5-Dihydro-1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)cyclopropyl]-3-(4-methoxyphenyl)-6-phenyl-5*H*-1,2,4-triazin-2-ide* (**16h**)[4]. To a yellow soln. of compound **2h** (0.186 g, 0.710 mmol) in THF (10 ml), compound **1** (0.980 g, 710 mmol) was added at $-40°$. After 1 h, the orange precipitate was collected by filtration at $-40°$ under Ar gas. After removal of last traces of solvent at $-20°$/0.1 mbar, the solid (79% of **16h**) was dissolved in CD_2Cl_2 (0.6 ml) and analyzed by NMR. ^{1}H-NMR (CD_2Cl_2, 400 MHz; $T=-30°$): 0.7–1.3 (4 H of cPr); 2.91 (MeN); 2.93 (MeN); 3.43 (m_c, 2 NCH_2); 3.75 (MeO); 4.81 (H–C(5)); 8.14, 6.80 ($J=8.1$, 3-Ph); 7.78, 7.29, 7.15 (6-Ph). ^{13}C-NMR (CD_2Cl_2, 100 MHz; $T=-30°$): 8.2 (CH_2 of cPr); 9.8 (CH_2 of cPr); 18.4 (C of cPr); 33.9 (MeN); 34.1 (MeN); 48.5 (NCH_2); 48.9 (NCH_2); 53.8 (C(5) of triazine); 54.4 (MeO of 3-Ar); 165.6 (C(2) of Im); 134.1, 127.6, 111.7, 158.9 (3-Ph); 125.7, 123.2, 127.7, 125.6 (6-Ph).

7. *Addition Reactions to 3-Aryl-1,2,4-triazines* **19**. *5,8-Dimethyl-9-phenyl-5,8,10-triazadispiro[2.0.4.4]dodeca-9,11-diene* (**20a**). Compound **1** (48 mg, 0.35 mmol) was slowly added to a soln. of **19a** (45 mg, 0.29 mmol) in C_6D_6 (0.6 ml). The resulting suspension (yellow precipitate) was heated in a sealed tube at 105° for 2 h. A clear yellow-brown soln resulted (90% of **20a**), which was analyzed by NMR. ^{1}H-NMR (C_6D_6, 400 MHz): 0.43, 1.01 (4 H of cPr); 2.13 (2 MeN); 2.63, 2.77 (2 NCH_2); 4.88 ($J=6.7$, H–C(12)); 7.00 (H–C(11)); 7.96, 7.18, 7.18 (9-Ph). ^{13}C-NMR (C_6D_6, 100 MHz): 13.2 (2 CH_2 of cPr); 21.8 (C(3)); 35.7 (2 MeN); 52.7 (2 NCH_2); 79.4 (C(4)); 126.6 (C(12)); 132.7 (C(11)); 165.2 (C(9)); 144.4, 129.9, 127.6, 128.4 (9-Ph).

5,8-Dimethyl-9-(4-nitrophenyl)-5,8,10-triazadispiro[2.0.4.4]dodeca-9,11-diene (**20b**). Compound **1** (46 mg, 0.33 mmol) was slowly added to a soln. of **19b** (56 mg, 0.28 mmol) in C_6D_6 (0.6 ml). The suspension (brown precipitate) was heated in a sealed tube at 105° for 2 h. A clear yellow-brown soln. resulted (40% of **20a**), which was analyzed by NMR. ^{1}H-NMR (C_6D_6, 400 MHz): 0.42, 0.95 (4 H of cPr); 1.98 (2 MeN); 2.54 (2 NCH_2); 4.85 ($J=6.8$, H–C(12)); 6.95 (H–C(11)); 7.72, 7.91 (9-Ar). ^{13}C-NMR (C_6D_6, 100 MHz): 13.4 (2 CH_2 of cPr); 21.9 (C(3)); 36.0 (2 MeN); 53.5 (2 NCH_2); 79.5 (C(4)); 127.4 (C(12)); 132.4 (C(11)); 163.3 (C(9)); 140.5, 130.6, 122.7, 150.2 (9-Ar).

*4,5-Dihydro-2-[1-(2,5-dihydro-3-phenyl-[2-^{2}H]-1,2,4-triazin-5-yl)cyclopropyl]-1,3-dimethyl-1*H*-imidazolium [2,2,2-$^2H_3$]Acetate* (**22a**). To compound **19a** (53 mg, 0.34 mmol) in CD_2Cl_2 (1 ml) under Ar gas, compound **1** (56 mg, 0.41 mmol) was slowly added *via* syringe at $-70°$. After addition of CD_3COOD (30 mg, 0.49 mmol) to the orange precipitate, a clear soln. resulted, which was analyzed by NMR at temps. between $-70°$ and $+25°$. At all temps., 85–88% of **22a** were identified. ^{1}H-NMR (CD_2Cl_2, 400 MHz; $T=25°$): 1.15, 1.40 (4 H of cPr); 3.14 (MeN); 3.16 (MeN); 3.84 (m_c, 2 NCH_2); 3.94 ($J=2.7$, H–C(5) of triazine); 6.78 (H–C(6) of triazine); 7.97, 7.43, 7.43 (3-Ph). ^{13}C-NMR (CD_2Cl_2, 100 MHz; $T=25°$): 9.8 (CH_2 of cPr); 9.9 (CH_2 of cPr); 19.4 (C of cPr); 33.2 (MeN); 34.4 (MeN); 50.3 (NCH_2); 50.4 (NCH_2); 56.7 (C(5) of triazine); 134.5 (C(6) of triazine); 154.6 (C(3) of triazine); 165.9 (C(2) of Im); 132.1, 127.1, 129.0, 131.5 (3-Ph).

*4,5-Dihydro-2-{1-[2,5-dihydro-3-(4-nitrophenyl)-[2-^{2}H]-1,2,4-triazin-5-yl]cyclopropyl}-1,3-dimethyl-1*H*-imidazolium [2,2,2-$^2H_3$]Acetate* (**22b**). To compound **19b** (30 mg, 0.15 mmol) in toluene (4 ml) under Ar gas, compound **1** (21 mg, 0.15 mmol) was slowly added *via* syringe at $-20°$. After 30 min, the dark-brown precipitate was collected at $-20°$, and washed with pentane. After removal of the solvent at $-20°$/0.01 mbar, the solid (90% of **22b**) was dissolved in CD_2Cl_2 (1 ml) containing CD_3COOD (16 mg, 0.27 mmol), and analyzed by NMR at $-30°$. ^{1}H-NMR (CD_2Cl_2, 400 MHz; $T=-30°$): 1.04, 1.44 (4 H of cPr); 3.05 (MeN); 3.14 (MeN); 3.75 (m_c, 2 NCH_2); 3.93 ($J=2.5$, H–C(5) of triazine); 6.84 (H–C(6) of triazine); 8.15 ($J=8.3$, C(2,6) of 3-Ar); 8.24 (C(3,5) of 3-Ar). ^{13}C-NMR (CD_2Cl_2, 100 MHz; $T=-30°$): 9.8 (CH_2 of cPr); 10.8 (CH_2 of cPr); 18.6 (C of cPr); 34.7 (MeN); 35.2 (MeN); 49.6 (NCH_2); 49.8 (NCH_2); 56.6 (C(5) of triazine); 134.3 (C(6) of triazine); 153.3 (C(3) of triazine); 164.5 (C(2) of Im); 137.1, 128.1, 123.8, 149.0 (3-Ar).

8. *Addition Reactions to 5-Aryl-1,2,4-triazines* (**4**). *5,8-Dimethyl-10-phenyl-5,8,11-triazadispiro[2.0.4.4]dodeca-9,11-diene* (**23a**) *and 5,8-Dimethyl-11-phenyl-5,8,10-triazadispiro[2.0.4.4]dodeca-9,11-diene* (**24a**). *Method 1*. Compound **1** (26 mg, 0.19 mmol) was added to a soln. of **4a** (30 mg, 0.19 mmol) in C_6D_6 (0.6 ml). The vigorous gas evolution was finished after a short time, and a clear soln. resulted, which was analyzed by NMR: **23a/24a** 83 :17 (total yield: 58%).

Method 2. Compound **1** (57 mg, 0.41 mmol) was slowly added to a soln. of **4a** (59 mg, 0.38 mmol) in toluene (15 ml) at $-78°$. After a few minutes, gas evolution ceased, and after 30 min, the soln. was allowed to warm to r.t. Distillation at 210°/0.01 mbar yielded a yellow oil (70 mg, 70%).

Data of **23a**. ^{1}H-NMR (C_6D_6, 400 MHz): 0.65, 1.57 (4 H-cPr), 2.14 (2 MeN), 2.55, 2.86 (2 NCH_2), 5.77 (H−C(9)), 6.97 (H−C(12); 8.15, 7.28, 7.10 (10-Ph). ^{13}C-NMR (C_6D_6, 100 MHz): 12.8 (2 CH_2 of cPr); 24.7 (C(3)); 35.4 (2 MeN); 50.9 (2 NCH_2); 77.6 (C(4)); 107.0 (C(9)); 146.8 (C(10)); 170.2 (C(12)); 139.6, 126.3, 128.3, 128.0 (10-Ph).

Data of **24a**. UV ($CHCl_3$): 255 (0.80). ^{1}H-NMR (C_6D_6, 400 MHz): 0.55, 1.35 (4 H of cPr); 2.24 (2 MeN); 2.62, 2.87 (2 NCH_2); 5.39 (H−C(12)); 7.52 (H−C(9); 8.02, 7.16, 7.15 (10-Ph). ^{13}C-NMR (C_6D_6, 100 MHz): 13.7 (2 CH_2 of cPr); 20.7 (C(3)); 35.3 (2 MeN); 51.8 (2 NCH_2); 76.1 (C(4)); 122.0 (C(12)); 140.8 (C(11)); 156.1 (C(9)); 139.3, 125.5, 128.3, 127.3 (9-Ph). EI-MS: 267 (100, M^+). Anal. calc. for $C_{17}H_{21}N_3$ (267.3): C 76.37, H 7.92, N 15.71; found: C 76.13, H 7.60, N 15.25.

5,8-Dimethyl-10-(4-methylphenyl)-5,8,11-triazadispiro[2.0.4.4]dodeca-9,11-diene (**23b**) *and 5,8-Dimethyl-11-(4-methylphenyl)-5,8,10-triazadispiro[2.0.4.4]dodeca-9,11-diene* (**24b**). Compound **1** (36 mg, 0.26 mmol) was added to a soln. of **4b** (40 mg, 0.23 mmol) in C_6D_6 (0.6 ml). After a short time, the vigorous gas evolution was finished, and a clear soln. resulted, which was analyzed by NMR: **23b**/**24b** 92 :8 (total yield: 100%). ^{1}H-NMR (C_6D_6, 400 MHz): 0.65, 1.58 (4 H of cPr); 2.19 (2 MeN); 2.44, 2.86 (2 NCH_2); 2.50 (Me of 10-Ar); 5.16 (J = 0.9, H−C(9)); 6.78 (H−C(12); 7.08 (C(3,4,5) of 10-Ar); 7.48 (C(6) of 10-Ar). ^{13}C-NMR (C_6D_6, 100 MHz): 12.7 (2 CH_2 of cPr); 21.1 (Me of 10-Ar); 24.4 (C(3)); 35.4 (2 MeN); 50.7 (2 NCH_2); 77.6 (C(4)); 110.3 (C(9)); 150.0 (C(10)); 169.1 (C(12)); 141.4, 136.4, 129.5, 130.6 (10-Ar).

Data of **24b**. UV ($CHCl_3$): 264 (0.85). ^{1}H-NMR (C_6D_6, 400 MHz): 0.57, 1.37 (4 H of cPr); 2.35 (2 MeN); 2.49 (Me of 9-Ar); 2.64, 2.82 (2 NCH_2); 4.97 (J = 1.1, H−C(12)); 7.45 (H−C(9); 7.20 (C(3,4,5) of 9-Ar); 7.52 (C(6) of 9-Ar). ^{13}C-NMR (C_6D_6, 100 MHz): 12.9 (2 CH_2 of cPr); 19.2 (C(3)); 20.8 (Me of 9-Ar); 35.0 (2 MeN); 51.4 (2 NCH_2); 75.8 (C(4)); 125.6 (C(12)); 143.2 (C(11)); 154.8 (C(9)); 140.3, 136.0, 128.9, 130.4, 125.5, 127.2 (9-Ar). EI-MS: 281 (31, M^+, $C_{18}H_{23}N_3^+$).

5,8-Dimethyl-10-(2,4,6-trimethylphenyl)-5,8,11-triazadispiro[2.0.4.4]dodeca-9,11-diene (**23c**). Compound **1** (43 mg, 0.31 mmol) was added to a soln. of **4c** (61 mg, 0.31 mmol) in C_6D_6 (0.6 ml). After a short time, the vigorous gas evolution was finished, and a clear soln. resulted, which was analyzed by NMR: **23c/24c** 100 :0 (total yield: 100%). ^{1}H-NMR (C_6D_6, 400 MHz): 0.64, 1.63 (4 H of cPr); 2.22 (4-Me of 10-Ar); 2.24 (2 MeN); 2.38, 2.82 (2 NCH_2); 2.43 (2,6-Me_2 of 10-Ar); 5.01 (J = 1.0, H−C(9)); 6.85 (H−C(12)); 6.90 (H−C(3,5) of 10-Ar). ^{13}C-NMR (C_6D_6, 100 MHz): 12.5 (2 CH_2 of cPr); 20.7 ((2,6-Me_2 of 10-Ar); 20.8 (4-Me of 10-Ar); 24.1 (C(3)); 35.4 (2 MeN); 50.4 (2 NCH_2); 77.1 (C(4)); 111.1 (C(9)); 147.4 (C(10)); 169.6 (C(12)); 136.0, 135.7, 128.2, 138.4 (10-Ar).

5,8-Dimethyl-10-(4-nitrophenyl)-5,8,11-triazadispiro[2.0.4.4]dodeca-9,11-diene (**23d**) *and 5,8-Dimethyl-11-(4-nitrophenyl)-5,8,10-triazadispiro[2.0.4.4]dodeca-9,11-diene* (**24d**). Compound **1** (7 mg, 0.05 mmol) was added to a soln. of **4d** (19 mg, 0.10 mmol) in C_6D_6 (0.6 ml). A brown precipitate formed immediately, and dissolved again under vigorous gas evolution, which was finished after a few minutes. The resulting clear soln. was analyzed by NMR: **23d/24d** 73 :27 (total yield 95%).

Data of **23d**. ^{1}H-NMR (C_6D_6, 400 MHz): 0.64, 1.53 (4 H of cPr); 2.11 (2 MeN); 2.56, 2.85 (2 NCH_2); 5.75 (J = 0.9, H−C(9)); 7.35 (H−C(12)); 8.04 (J = 9.0, 10-Ar); 7.86 (10-Ar). ^{13}C-NMR (C_6D_6, 100 MHz): 12.5 (2 CH_2 of cPr); 24.3 (C(3)); 34.8 (2 MeN); 50.6 (2 NCH_2); 76.9 (C(4)); 110.6 (C(9)); 144.2 (C(10)); 170.3 (C(12)); 144.4, 126.1, 123.4 147.4 (10-Ar).

Data of **24d**. ^{1}H-NMR (C_6D_6, 400 MHz): 0.59, 1.40 (4 H of cPr); 2.20 (2 MeN); 2.61, 2.76 (2 NCH_2); 5.35 (J = 0.9, H−C(12)); 7.46 (H−C(9)); 8.07 (J = 8.9, 11-Ar); 7.74 (11-Ar). ^{13}C-NMR (C_6D_6, 100 MHz): 0.59, 1.40 (4 H- of cPr); 2.20 (2 MeN); 2.61, 2.76 (2 NCH_2); 5.35 (J = 0.9, H−C(12)); 7.46 (H−C(9); 8.07 (J = 8.9, 11-Ar); 7.74 (11-Ar). ^{13}C-NMR (C_6D_6, 100 MHz): 13.9 (2 CH_2, cPr), 19.9 (C(3)), 34.7 (2 NMe), 51.4 (2 NCH_2), 75.5 (C(4)), 123.4 (C(12)), 138.7 (C(11)), 156.3 (C(9)); 146.3, 124.9, 127.9, 146.8 (9-Ar).

10-(4-Methoxyphenyl)-5,8-dimethyl-5,8,11-triazadispiro[2.0.4.4]dodeca-9,11-diene (**23e**) *and 11-(4-Methoxyphenyl)-5,8-dimethyl-5,8,10-triazadispiro[2.0.4.4]dodeca-9,11-diene* (**24e**).Compound **1** (17 mg, 0.14 mmol) was added to a soln. of **4e** (19 mg, 0.10 mmol) in C_6D_6 (0.6 ml). The vigorous gas evolution was finished after a short time, and a clear soln. resulted, which was analyzed by NMR: **23e/24e** 86 :14 (total yield: 100%).

Data of **23e**. ^{1}H-NMR (C_6D_6, 400 MHz): 0.67, 1.62 (4 H of cPr); 2.20 (2 MeN); 2.60, 2.91 (2 NCH_2); 3.37 (MeO of 10-Ar); 5.74 (J = 0.8, H−C(9)); 7.03 (H−C(12); 8.16 (J = 8.9, 10-Ar); 6.96 (10-Ar). ^{13}C-NMR (C_6D_6, 100 MHz):12.4 (2 CH_2 of cPr); 24.4 (C(3)); 35.1 (2 MeN); 50.6 (2 NCH_2); 54.4 (MeO); 77.4 (C(4)); 104.5 (C(9)); 146.0 (C(10)); 169.6 (C(12)); 131.9, 127.2, 113.7, 159.8 (10-Ar).

Data of **24e**. ^{1}H-NMR (C_6D_6, 400 MHz): 0.60, 1.39 (4 H of cPr); 2.30 (2 MeN); 2.65, 2.82 (2 NCH_2); 3.38 (MeO of 11-Ar); 5.35 (J = 1.1, H−C(12)); 7.59 (H−C(9)); 8.03 (J = 8.9, 11-Ar); 6.94 (11-Ar). ^{13}C-NMR (C_6D_6, 100 MHz):13.2 (2 CH_2 of cPr); 19.2 (C(3)); 35.0 (2 MeN); 51.5 (2 NCH_2); 54.1 (MeO); 75.8 (C(4)); 119.6 (C(12)); 140.0 (C(11)); 155.7 (C(9)); 131.9, 126.1, 127.9, 159.5 (11-Ar).

9. *Addition Reactions to 6-Aryl-1,2,4-triazines* **3**. *5,8-Dimethyl-9-phenyl-5,8,11-triazadispiro[2.0.4.4]dodeca-9,11-diene* (**25a**). Compound **1** (94 mg, 0.68 mmol) was slowly added to a soln. of **3a** (90.0 mg, 0.57 mmol) in toluene (3 ml). A dark-red precipitate formed, which dissolved again under gas evolution. After 15 min, the solvent was removed *in vacuo*, and full conversion was verified by NMR. Distillation at 250°/0.01 mbar afforded **25a** as an oil (115 mg, 76%). UV ($CHCl_3$): 280 (0.22). ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.92, 1.30 (4 H of cPr); 2.19 (2 MeN); 2.90 (m_c, 2 NCH_2); 6.85 (H–C(12)); 7.05 (H–C(10)); 7.60, 7.25, 7.25 (9-Ph). ^{13}C-NMR ($CDCl_3$, 100 MHz): 12.0 (2 CH_2 of cPr); 26.4 (C(3)); 35.0 (MeN); 52.5 (NCH_2); 79.1 (C(4)); 130.8 (C(9)); 137.3 (C(10)); 168.9 (C(12)); 141.3, 129.7, 127.6, 127.0 (9-Ph). EI-MS: 267 (50, M^+, $C_{17}H_{21}N_3^+$).

9-(4-Methoxyphenyl)-5,8-dimethyl-5,8,11-triazadispiro[2.0.4.4]dodeca-9,11-diene (**25b**). Compound **1** (19 mg, 0.14 mmol) was added slowly to a soln. of **3b** (25 mg, 0.13 mmol) in C_6D_6 (0.6 ml). A slow gas evolution started, which was finished after 15 min. By NMR, 55% of **25b** were identified. ^{1}H-NMR (C_6D_6, 400 MHz): 0.54, 1.10 (4 H of cPr); 2.16 (2 MeN); 2.62 (NCH_2); 2.73 (NCH_2); 3.35 (MeO of 9-Ar); 6.78 (J = 7.7, H–C(3,5) of 9-Ar); 6.94 (H–C(12)); 7.25 (H–C(10)); 7.57 (H–C(2,6) of 9-Ar). ^{13}C-NMR (C_6D_6, 100 MHz): 11.8 (2 CH_2 of cPr); 26.3 (C(3)); 35.2 (2 MeN); 52.6 (2 NCH_2); 54.6 (MeO of 9-Ar); 79.4(C(4)); 130.0 (C(9)); 138.0 (C(10)); 167.6 (C(12)); 141.8, 130.6, 113.5, 159.6 (9-Ar).

*1,2,3,4,5,6-Hexahydro-1,4-dimethyl-10-phenylpyrido[4,3-*e*][1,4]diazocine* (**26a**), *5-[1-(4,5-Dihydro-1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)cyclopropyl]-6-phenyl-5*H*-1,2,4-triazin-2-ide* (**27a**), *and 3-[1-(4,5-Dihydro-1,3-dimethyl-1*H*-imidazol-3-ium-2-yl)cyclopropyl]-6-phenyl-5*H*-1,2,4-triazin-2-ide* (**28a**). To a soln. of compound **3a** (40 mg, 0.25 mmol) in CD_2Cl_2 (1 ml) under Ar gas, compound **1** (42 mg, 0.31 mmol) was carefully added at –40°. Both at –40° and, after 30 min, at 25°, NMR spectra were recorded. Product distribution: at T = –40°: **3a**/**27a**/**28a**/**25a**/**26a** 5 : 87 : 8 : 0 : 0; at T = 25°: 33 : 33 : 0 : 0 : 34. The experiment was repeated with mixing, and taking the first NMR spectrum at –15°. Here, the following distributions were found: at T = –15°: **3a**/**27a**/**28a**/**25a**/**26a** 0 : 85 : 15 : 0 : 0; at T = +25°: 30 : 30 : 0 : 16 : 24.

Data of **26a**. ^{1}H-NMR (CD_2Cl_2, 400 MHz; T = 25°): 2.37 (MeN); 2.41 (MeN); 2.65, 2.77, 3.45, 3.58 (4 CH_2); 7.66 (m_c 10-Ph); 8.21 (C(7)); 8.65 (C(9)). ^{13}C-NMR (CD_2Cl_2, 400 MHz; T = 25°): 36.7, 36.8 (2 MeN); 47.8, 49.9, 50.3, 51.7 (4 CH_2); 89.1 (C(3)); 128.6, 129.0 (2 CH); 156.1 (C(9)); 157.8 (C(7)).

Data of **27a**. ^{1}H-NMR (CD_2Cl_2, 400 MHz; T = –40°): 0.60, 0.67, 1.15, 1.28 (4 H of cPr); 2.88 (MeN); 3.08 (MeN); 3.33 (NCH_2); 3.48 (NCH_2); 4.61 (H–C(5)); 7.36 (H–C(3); 7.75, 7.32, 7.24 (6-Ph). ^{13}C-NMR (CD_2Cl_2, 100 MHz; T = –40°): 9.8 (CH_2 of cPr); 10.8 (CH_2 of cPr); 19.3 (C of cPr); 35.1 (MeN); 35.2 (MeN); 49.5 (NCH_2); 49.6 (NCH_2); 54.8 (C(5)); 139.1 (C(6); 155.1 (C(3); 166.2 (C(2) of Im); 135.1, 124.3, 128.9, 127.4 (6-Ph).

Data of **28a**. ^{1}H-NMR (CD_2Cl_2, 400 MHz; T = –40°): 1.77, 1.85 (4 H of cPr); 2.91 (MeN); 3.16 (MeN); 3.45 (2 NCH_2); 5.72 (H–C(3)); 7.28 (H–C(5)); 7.61, 7.46, 7.46 (6-Ph). ^{13}C-NMR (CD_2Cl_2, 100 MHz; T = –40°): 11.0 (CH_2 of cPr); 11.2 (CH_2 of cPr); 22.0 (C of cPr); 34.5 (MeN); 36.2 (MeN); 47.8 (2 NCH_2); 89.1 (C(3)); 129.1 (C(5)); 155.7 (C(3)); 164.7 (C(2) of Im); 137.6, 126.8, 128.6, 128.2 (6-Ph).

10. *Computations.* All structures were optimized at the Becke3LYP/6-31G(d) level of theory. Enthalpies at 298.15 K were calculated for each conformer based on its harmonic vibrational frequencies. Single-point-energy calculations were also performed at the Becke3LYP/6-311 + G(d,p) level of theory. Combination of these single-point energies with the enthalpy values calculated at the Becke3LYP/6-31G(d) level allows the calculation of Becke3LYP/6-311 + G(d,p)//Becke3LYP/6-31G(d) reaction enthalpies at 298.15 K. Solvent effects in CH_2Cl_2 were estimated through single-point calculations with the CPCM continuum solvation model at the Becke3LYP/6-31G(d) level of theory using UAKS radii, and the gas phase Becke3LYP/6-31G(d) geometries [22]. Atomic charges were calculated with the Natural Population Analysis (NPA) scheme at the Becke3LYP/6-31G(d) level of theory [23]. Throughout the manuscript, the 6-31G(d) basis is abbreviated as 'SB' (small basis), and the 6-311 + G(d,p) basis set as 'LB' (large basis). All calculations were performed with the Gaussian 03 software [24].

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