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Reaction of Six-Membered Azaaromatics with Allyltributyltin

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Pyridazines were reacted with allyltributyltin in the presence of chloroformate to give 1-alkoxycarbonyl-6-allyl and 1-alkoxycarbonyl-4-allyldihydropyridazines as major and minor products, respectively. The reaction system was applied to other diazines and pyrimidine and pyrazine were shown to afford diallyltetrahydroadducts. Benzodiazines also gave allylation products in good yields. The reaction seems to be applicable to most six-membered azaaromatics.

Keywords pyridazine; pyrimidine; pyrazine; benzodiazine; 1,2,3-triazine; allyltributyltin; alkyl chloroformate

Nucleophilic introduction of substituents into π-electron-deficient azines has been one of the most important research fields in heterocyclic chemistry.[2] In particular, *N*-quaternizations have been widely used for nucleophilic reactions of azaaromatics. Although the reactions of pyridines, as the *N*-alkoxycarbonyl quaternary salts with various nucleophilic reagents have been reported,[3] there are few papers dealing with the reactivities of *N*-alkoxycarbonyl salts of other azaaromatics, because these salts are unstable and inseparable. This instability prompted us to attempt to trap them *in situ*. Although alkyl quaternary salts are convenient as substrates of nucleophilic reactions since they are stable and isolable for many azines, the reactions of *N*-alkoxycarbonylazinium salts also seem to be of interest because they must be more reactive to nucleophiles than alkylazinium salts. The candidates for the trapping reagents must be unreactive to alkyl chloroformates, and so organosilane and organotin reagents, which do not react with carbonyl groups in the absence of Lewis acid,[4] were considered. The use of organosilane reagents, however, afforded only low yields of the products when allyltrimethylsilane and pyridazine were reacted in the presence of ethyl chloroformate.

In this paper, we describe the reaction of allyltributyltin with π-deficient azaaromatics, including polyazaaromatics.[5] First, pyridazines **1** were adopted as the substrates. The introduction of substituents into pyridazines has been performed mainly using chloropyridazines or pyridazine *N*-oxides as substrates,[6] and only a few reports have described direct nucleophilic addition followed by oxidation.[7] Ring activation through the quaternary salts ordinarily resulted in ring opening,[8] and some reactions of *N*-alkoxycarbonyl salts of pyridazines **2** have been reported.[9] In fact, compound **2** could not be readily isolated, in contrast to the case of pyridines.[10] When readily isolable *N*-methylpyridazinium salts **3** were allowed to react with allyltributyltin, the products **4a** and **4b** were obtained only from substrates with an electron-withdrawing group (Chart 1).

When each of **1a**—**d** was treated with ethyl chloroformate in CH_2Cl_2, the solution turned brown and a complicated mixture of products was obtained. Simultaneous addition of allyltributyltin controlled the reaction to afford the corresponding **5a**—**d** and **6a**—**d** in good yields (Chart 2 and Table I). That is, pyridazine **1a** and allyltributyltin were allowed to react in the presence of ethyl chloroformate in CH_2Cl_2 at 0 °C, giving 6-allyl-1-

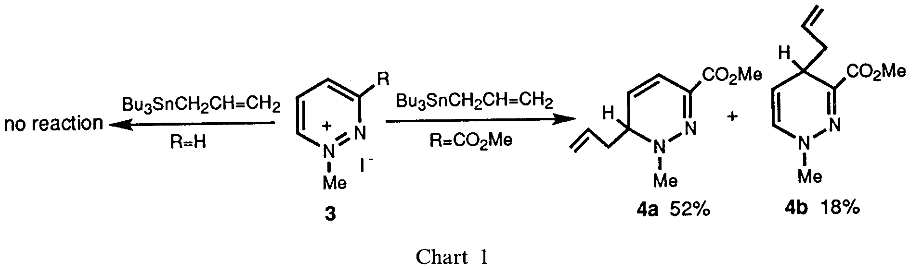


Chart 1

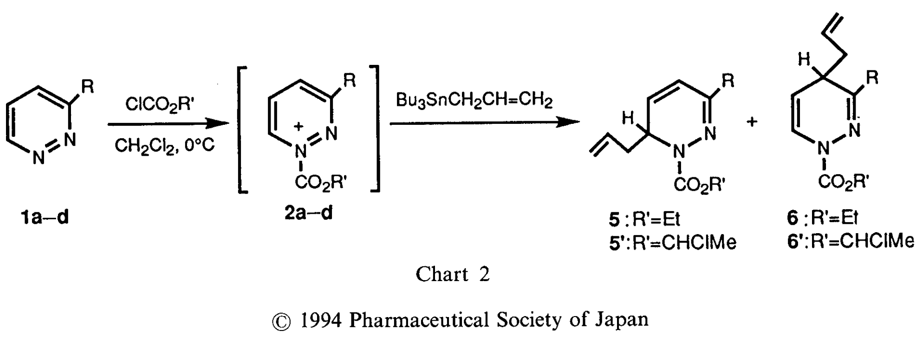


Chart 2

ethoxycarbonyl-1,6-dihydropyridazine **5a** and 4-allyl-1-ethoxycarbonyl-1,4-dihydropyridazine **6a** in 63% and 14% yields, respectively. Other 3-substituted pyridazines were also adopted as substrates and the results are summarized in Table I.

1,6-Dihydroderivatives **5** were dominant products in all cases.[11] Increase of the electron deficiency of the ring favored α-attack.

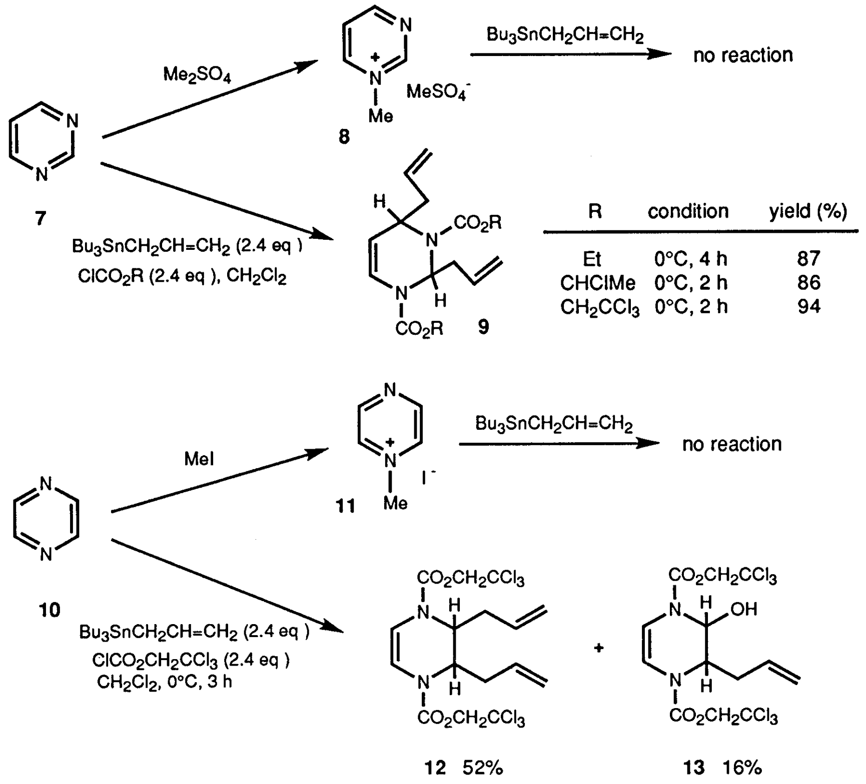
Next, pyrimidine **7** and pyrazine **10** were applied to the reaction. These compounds were easily transformed to the corresponding *N*-methyl quaternary salts **8** and **11**, but they are unreactive to allyltributyltin. When ethyl chloroformate was added dropwise to a mixture of pyrimidine and allyltributyltin, 2,4-diallyl-1,3-diethoxycarbonyl-1,2,3,4-tetrahydropyrimidine **9** was obtained in 87% yield (Chart 3). In these cases, dihydro adducts were not obtained even by the use of 0.5 eq of alkyl chloroformate and allyltributyltin. Moreover, the regulation of the reaction to dihydro adducts failed even when bulky chloroformates such as 9-fluorenylmethyl chloroformate and menthyl chloroformate were used. These facts suggest that the second addition was much faster than the first. Though the first reaction site of the tin reagent remained unclear, we think that the first attack might occur at the C-4 position on the basis of the experimental results with quinazoline. Pyrazine **10** afforded a tetrahydro adduct **12** under the same conditions, accompanied with 2-allyl-3-hydroxy-1,2,3,4-tetrahydropyrazine **13** (Chart 3). The formation of **13** was probably due to steric hindrance, inhibiting the second attack of allyltributyltin, and H_2O might add instead to an intermediary iminium salt during the work-up procedure.

TABLE I. Reaction of Pyridazines **1** with Allyltributyltin in the Presence of Chloroformate

Substrate	R	R′	Yield of **5** (%)	Yield of **6** (%)	Ratio of **5**/**6**
1a	H	Et	63	14	4.50
		CHClMe	77	12	6.42
1b	Me	Et	67	18	3.72
		CHClMe	59	13	4.54
1c	Ph	Et	65	8	8.13
		CHClMe	80	8	10.00
1d	CO_2Me	Et	79	7	11.29
		CHClMe	80	4	20.00

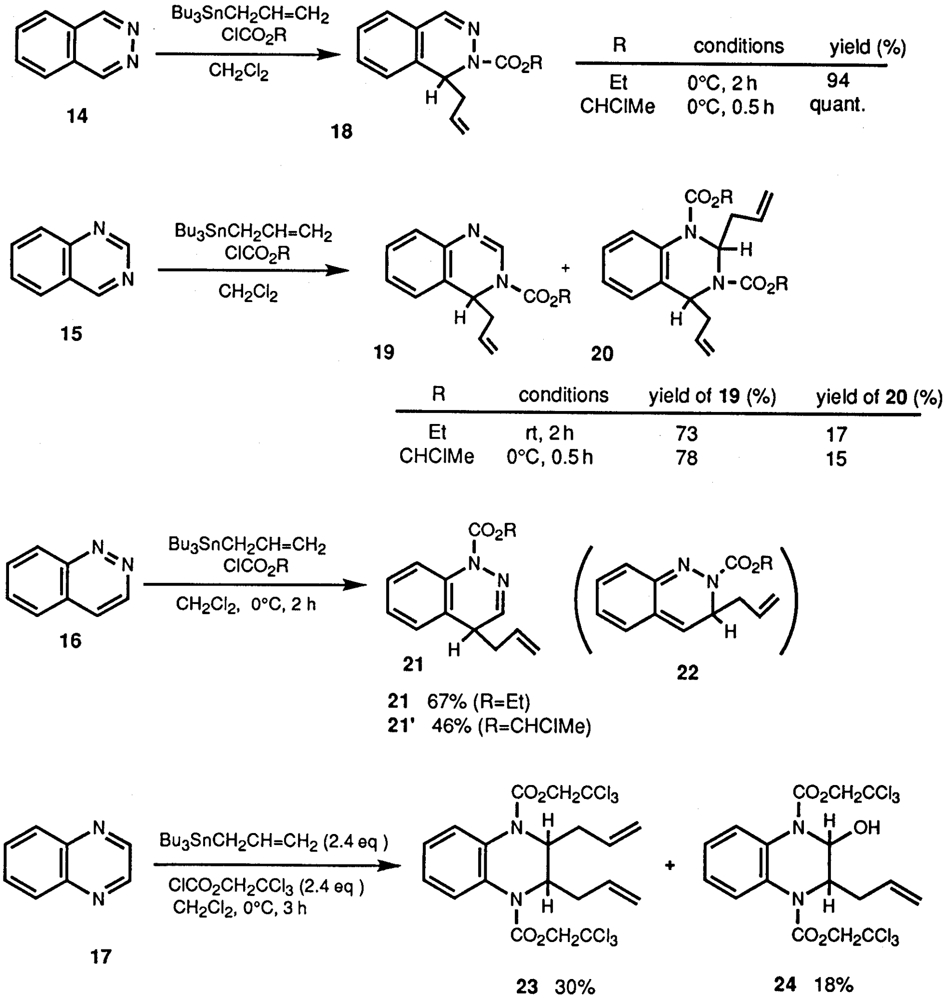
The above reaction system was next applied to the benzodiazines, and the results are summarized in Chart 4. Phthalazine (**14**) and quinazoline (**15**) were easily attacked under the same conditions to afford the 1,2-dihydro adducts **18** and **19**, respectively, accompanied with the tetrahydro adduct **20** from **15**. Selective dihydro addition of pyridazines **1** and phthalazine (**14**) was supposed to be a consequence of the difficulty of the second quaternization process. In the case of cinnoline (**16**), the reaction was slow and the products included the 1,4-adduct **21**, showing a different regioselectivity from the other cases. This was probably because the supposed product **22** was less stable than **21** owing to loss of the aromaticity of the benzo-ring. When quinoxaline (**17**) was used, the products obtained were analogous to those from pyrazine.

Finally, the scope and the limitations of the reactivity of allyltributyltin were investigated using *N*-methylazinium salts (Chart 5). The parent *N*-methylpyridinium salt **25a** did not react with allyltributyltin, as was the same case with the parent pyridazinium salt. In the case of 3-



R	condition	yield (%)
Et	0°C, 4 h	87
CHClMe	0°C, 2 h	86
CH_2CCl_3	0°C, 2 h	94

Chart 3

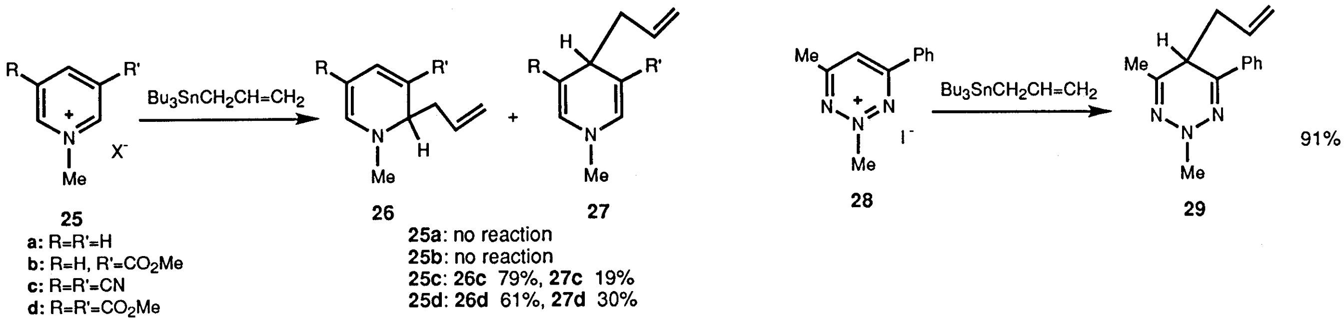


R	conditions	yield (%)
Et	0°C, 2 h	94
CHClMe	0°C, 0.5 h	quant.

R	conditions	yield of **19** (%)	yield of **20** (%)
Et	rt, 2h	73	17
CHClMe	0°C, 0.5h	78	15

21 67% (R=Et)
21' 46% (R=CHClMe)

Chart 4



25
a: R=R'=H
b: R=H, R'=CO$_2$Me
c: R=R'=CN
d: R=R'=CO$_2$Me

25a: no reaction
25b: no reaction
25c: **26c** 79%, **27c** 19%
25d: **26d** 61%, **27d** 30%

Chart 5

methoxycarbonylpyridine too, the starting material was recovered. The introduction of two electron-withdrawing substituents made the addition possible, affording 2-allyl-1-methyl-1,2-dihydropyridines **26** and the 4-allyl isomers **27** in good yields. The 2-methyl-1,2,3-triazinium salt **28** readily reacted with allyltributyltin in the absence of any electron-withdrawing group to give the adduct **29**.

The above results indicate that allyltributyltin is reactive to *N*-alkoxycarbonylazinium salts, and to *N*-methylazinium salts which have one and two electron-withdrawing group(s) in the case of pyridazine and pyridine, respectively. Since our previous reports[12)] revealed that allyltributyltin reacted with various azoles in the presence of alkyl chloroformate, the reaction system seems to be applicable to most of azaaromatics.

Experimental

All melting points were taken on a Büchi 535 micro melting point apparatus and are uncorrected. The mass spectra were recorded on JEOL JMS-D300 and JMS-SX102A instruments. The nuclear magnetic resonance (NMR) spectra were measured with JEOL JNM-FX100 and GX400 spectrometers using tetramethylsilane as an internal standard. The abbreviations used are as follows: s, singlet; d, doublet; dd, double doublet; t, triplet; q, quartet; m, multiplet.

Reaction of 1-Methylpyridazinium Iodides with Allyltributyltin The 1-

methyl-pyridazinum salt **3** (R$=$CO$_2$Me, 0.5 mmol) was dissolved in MeCN (8 ml) and allyltributyltin (0.55 mmol) was added to the solution at 0 °C. The solution was stirred at 0 °C for 5 h, then diluted with diethyl ether (20 ml) and treated with 1 M aqueous KF solution (3 ml). The precipitate was taken off by filtration, and the filtrate was dried over MgSO$_4$ and evaporated. The residue was chromatographed on alumina to afford **4a** and **4b**.

6-Allyl-3-methoxycarbonyl-1-methyl-1,6-dihydropyridazine (4a) Yield 52%. Colorless oil. ^{1}H-NMR (CDCl$_3$) δ: 2.30 (2H, t, $J=6.1$ Hz), 3.34 (3H, s), 3.81 (3H, s), 4.14 (1H, q, $J=6.1$ Hz), 4.92—5.18 (2H, m), 5.45—5.80 (2H, m), 6.48 (1H, d, $J=9.8$ Hz). The positions of the substituents were confirmed by the observation of nuclear Overhauser effect (NOE). The NOE was observed between the signals of 1-CH$_3$ and 6-H. HRMS m/z (M$^+$$-$allyl): Calcd for C$_7H_9N_2O_2$: 153.0664. Found: 153.0658.

4-Allyl-3-methoxycarbonyl-1-methyl-1,4-dihydropyridazine (4b) Yield 18%. Colorless oil. ^{1}H-NMR (CDCl$_3$) δ: 2.07 (2H, t, $J=6.6$ Hz), 3.34 (3H, s), 3.56 (1H, q, $J=6.6$ Hz), 3.82 (3H, s), 4.83—5.06 (2H, m), 5.40—5.80 (2H, m), 6.15 (1H, d, $J=7.3$ Hz). HRMS m/z (M$^+$$-$allyl): Calcd for C$_7H_9N_2O_2$: 153.0664. Found: 153.0668.

Reactions of Pyridazines 1 with Allyltributyltin in the Presence of Chloroformate Pyridazine (1 mmol) and allyltributylin (1.2 mmol) were dissolved in CH$_2$Cl$_2$ (5 ml), and the mixture was cooled to 0 °C. Alkyl chloroformate (1.2 mmol) was added dropwise and the mixture was allowed to stand at 0 °C for several hours. Then it was diluted with diethyl ether (15 ml) and treated with 1 M aqueous KF solution (3 ml) to precipitate tributyltin fluoride. The solid was filtered off, and the filtrate was dried over MgSO$_4$ and evaporated to leave a residue, which was chromatographed on alumina to afford **5** and **6**.

6-Allyl-1-ethoxycarbonyl-1,6-dihydropyridazine (5a) Yield 63%. Colorless oil. ^{1}H-NMR (CDCl$_3$) δ: 1.36 (3H, t, $J=7.3$ Hz), 2.25—2.43 (2H, m), 4.33 (2H, q, $J=7.3$ Hz), 4.91—5.15 (3H, m), 5.57—5.97 (2H, m), 6.16 (1H, ddd, $J=19$, 6.1, 9.4 Hz), 7.09—7.14 (1H, m). ^{13}C-NMR (CDCl$_3$) δ: 14.42 (CH$_3$), 37.96 (CH$_2$), 50.08 (CH), 62.59 (CH$_2$), 117.0 (CH), 118.74 (CH$_2$), 131.86 (CH), 131.92 (CH), 140.41 (CH), 154.22 (CO). HRMS m/z (M$^+$$-$allyl): Calcd for C$_7H_9N_2O_2$: 153.0664. Found: 153.0675.

6-Allyl-1-(1-chloroethoxycarbonyl)-1,6-dihydropyridazine (5a′) Yield 77%. Colorless oil. ^{1}H-NMR (CDCl$_3$) δ: 1.90 (3H, d, $J=5.9$ Hz), 2.26—2.45 (2H, m), 4.98—5.17 (3H, m), 5.57—6.01 (2H, m), 6.21 (1H, dd, $J=9.8$, 5.9 Hz), 6.68 (1H, q, $J=5.9$ Hz), 7.18 (1H, br s). ^{13}C-NMR (CDCl$_3$) δ: 24.59 (CH$_3$) 37.27 (CH$_2$), 50.00 (CH), 82.71 (CH), 116.41 (CH), 118.56 (CH$_2$), 131.03 (CH), 131.81 (CH), 140.83 (CH), 151.10 (CO). HRMS m/z (M$^+$$-$allyl): Calcd for C$_7H_8^{35}ClN_2O_2$: 187.0271. Found: 187.0266.

4-Allyl-1-ethoxycarbonyl-1,4-dihydropyridazine (6a) Yield 14%. Colorless oil. ^{1}H-NMR (CDCl$_3$) δ: 1.30 (3H, t, $J=7.3$ Hz), 2.13—2.27 (2H, m), 2.88 (1H, br s), 4.28 (2H, q, $J=7.3$ Hz), 4.76—5.12 (3H, m), 5.57—6.00 (1H, m), 6.77 (1H, br s), 6.96 (1H, d, $J=8.8$ Hz). ^{13}C-NMR (CDCl$_3$) δ: 13.68 (CH$_3$), 31.94 (CH$_2$), 39.49 (CH), 63.15 (CH$_2$), 104.56 (CH), 118.14 (CH$_2$), 123.13 (CH), 133.62 (CH), 138.16 (CH), 145.73 (CO). HRMS m/z (M$^+$$-$allyl): Calcd for C$_7H_9N_2O_2$: 153.0664. Found: 153.0658.

4-Allyl-1-(1-chloroethoxycarbonyl)-1,4-dihydropyridazine (6a′) Yield 12%. Colorless oil. ^{1}H-NMR (CDCl$_3$) δ: 1.83 (3H, d, $J=5.9$ Hz), 2.22 (2H, t, $J=6.9$ Hz), 2.86—2.95 (1H, m), 4.85—5.12 (3H, m), 5.49—5.82 (1H, m), 6.59 (1H, q, $J=5.9$ Hz), 6.83—6.98 (2H, m). ^{13}C-NMR (CDCl$_3$) δ: 24.66 (CH$_3$), 31.94 (CH$_2$), 39.25 (CH), 83.44 (CH), 106.20 (CH), 118.41 (CH$_2$), 122.70 (CH), 133.36 (CH), 133.39 (CH), 147.27 (CO). HRMS m/z (M$^+$$-$allyl): Calcd for C$_7H_8^{35}ClN_2O_2$: 187.0275. Found: 187.0287.

6-Allyl-1-ethoxycarbonyl-3-methyl-1,6-dihydropyridazine (5b) Yield 67%. Colorless oil. ^{1}H-NMR (CDCl$_3$) δ: 1.36 (3H, t, $J=7.3$ Hz), 2.08 (3H, s), 2.21—2.37 (2H, m), 4.31 (2H, q, $J=7.3$ Hz), 4.85—5.14 (3H, m), 5.55—5.90 (1H, m), 5.91 (1H, d, $J=10$ Hz), 6.20 (1H, dd, $J=6.3$, 10.0 Hz). ^{13}C-NMR (CDCl$_3$) δ: 14.24 (CH$_3$), 21.31 (CH$_3$), 37.60 (CH$_2$), 49.11 (CH), 62.12 (CH$_2$), 118.23 (CH$_2$), 119.40 (CH), 131.96 (CH), 132.31 (CH), 148.55 (C), 153.99 (CO). HRMS m/z (M$^+$$-$allyl): Calcd for C$_8H_{11}N_2O_2$: 167.0819. Found: 167.0819.

6-Allyl-1-(1-chloroethoxycarbonyl)-3-methyl-1,6-dihydropyridazine (5b′) Yield 59%. Colorless oil. ^{1}H-NMR (CDCl$_3$) δ: 1.89 (3H, d, $J=5.9$ Hz), 2.09 (3H, s), 2.24—2.36 (2H, m), 4.78—5.31 (3H, m), 5.50—5.85 (1H, m), 5.92 (1H, d, $J=9.8$ Hz), 6.24 (1H, dd, $J=5.9$, 9.8 Hz), 6.67 (1H, q, $J=5.9$ Hz). ^{13}C-NMR (CDCl$_3$) δ: 21.53 (CH$_3$), 25.14 (CH$_3$), 37.75 (CH$_2$), 49.68 (CH), 83.22 (CH), 118.89 (CH$_2$), 119.55 (CH), 131.73 (CH), 132.83 (CH), 149.73 (C), 151.70 (CO). HRMS m/z (M$^+$$-$allyl): Calcd for C$_8H_{10}^{35}ClN_2O_2$: 201.0432. Found: 201.0442.

4-Allyl-1-ethoxycarbonyl-3-methyl-1,4-dihydropyridazine (6b) Yield 18%. Colorless oil. ^{1}H-NMR (CDCl$_3$) δ: 1.37 (3H, t, $J=7.3$ Hz), 2.06 (3H, s), 2.26 (2H, t, $J=6.8$ Hz), 2.90—3.12 (1H, m), 4.35 (2H, q, $J=7.3$ Hz), 4.87—5.15 (3H, m), 5.57—5.95 (1H, m), 7.09 (1H d, $J=7.8$ Hz). ^{13}C-NMR (CDCl$_3$) δ: 14.49 (CH$_3$), 22.30 (CH$_3$), 35.68 (CH$_2$), 38.13 (CH), 62.99 (CH$_2$), 104.26 (CH), 117.97 (CH$_2$), 123.10 (CH), 133.82 (CH), 149.96 (C), 152.79 (CO). HRMS m/z (M$^+$$-$allyl): Calcd for C$_8H_{11}N_2O_2$: 167.0821. Found: 167.0837.

4-Allyl-1-(1-chloroethoxycarbonyl)-3-methyl-1,4-dihydropyridazine (6b′) Yield 13%. Colorless oil. ^{1}H-NMR (CDCl$_3$) δ: 1.90 (3H, d, $J=5.9$ Hz), 2.06 (3H, s), 2.22—2.36 (2H, m), 2.87—3.04 (1H, m), 4.95—5.15 (3H, m), 5.50—5.94 (1H, m), 6.67 (1H, q, $J=5.9$ Hz), 7.04 (1H, d, $J=8.3$ Hz). ^{13}C-NMR (CDCl$_3$) δ: 22.23 (CH$_3$), 25.34 (CH$_3$), 35.60 (CH$_2$), 38.00 (CH), 83.41 (CH), 105.95 (CH), 118.23 (CH$_2$), 122.68 (CH), 133.55 (CH), 149.95 (C), 151.68 (CO). HRMS m/z (M$^+$$-$allyl): Calcd for C$_8H_{10}^{35}ClN_2O_2$: 201.0428. Found: 201.0428.

6-Allyl-1-ethoxycarbonyl-3-phenyl-1,6-dihydropyridazine (5c) Yield 65%. Colorless oil. ^{1}H-NMR (CDCl$_3$) δ: 1.39 (3H, t, $J=7.3$ Hz), 2.18—2.40 (2H, m), 4.35 (2H, q, $J=7.3$ Hz), 4.90—5.22 (3H, m), 5.52—5.96 (1H, m), 6.37 (1H, dd, $J=5.4$ Hz, 9.0 Hz), 6.52 (1H, d, $J=9.0$ Hz), 7.20—7.45 (3H, m), 7.59—7.81 (2H, m). ^{13}C-NMR (CDCl$_3$) δ: 14.39 (CH$_3$), 37.92 (CH$_2$), 49.75 (CH), 62.51 (CH$_2$), 117.00 (CH), 118.62 (CH$_2$), 125.69 (2CH), 128.40 (2CH), 129.24 (CH), 132.00 (CH), 132.37 (CH), 135.47 (C), 147.54 (C), 154.43 (CO). HRMS m/z (M$^+$$-$allyl): Calcd for C$_{13}H_{13}N_2O_2$: 229.0975. Found: 229.0965.

6-Allyl-1-(1-chloroethoxycarbonyl)-3-phenyl-1,6-dihydropyridazine (5c′) Yield 80%. Colorless oil. ^{1}H-NMR (CDCl$_3$) δ: 1.91 (3H, d, $J=5.9$ Hz), 2.33—2.50 (2H, m), 5.02—5.17 (3H, m), 5.58—5.97 (1H, m), 6.40 (1H, dd, $J=5.4$, 9.8 Hz), 6.53 (1H, d, $J=9.8$ Hz), 6.69 (1H, q, $J=5.9$ Hz), 7.30—7.52 (3H, m), 7.61—7.88 (2H, m). The ^{13}C-NMR spectrum was obtained as that of a mixture of two isomers. ^{13}C-NMR (CDCl$_3$) δ: 25.28, 25.38 (CH$_3$), 37.97 (CH$_2$), 50.22 (CH), 83.40 (CH), 116.99 (CH), 119.17 (CH$_2$), 125.90 (2CH), 128.50, 128.52 (2CH), 129.65, 129.68) (CH), 131.66 (CH), 132.81, 132.94 (CH), 135.15 (C), 148.00 (C), 152.20 (CO). HRMS m/z (M$^+$$-$allyl): Calcd for C$_{13}H_{12}^{35}ClN_2O_2$: 263.0585. Found: 263.0585.

4-Allyl-1-ethoxycarbonyl-3-phenyl-1,4-dihydropyridazine (6c) Yield 8%. Colorless oil. ^{1}H-NMR (CDCl$_3$) δ: 1.41 (3H, t, $J=7.3$ Hz), 2.20—2.33 (2H, m), 3.67—3.74 (1H, m), 4.38 (2H, q, $J=7.3$ Hz), 4.92—5.25 (3H, m), 5.50—5.91 (1H, m), 7.21 (1H, d, $J=7.8$ Hz), 7.28—7.48 (3H, m), 7.68—7.88 (2H, m). ^{13}C-NMR (CDCl$_3$) δ: 14.49 (CH$_3$), 32.05 (CH$_2$), 39.17 (CH), 63.14 (CH$_3$), 105.29 (CH), 117.92 (CH$_2$), 123.47 (CH), 126.39 (2CH), 128.53 (2CH), 129.68 (CH), 133.67 (CH), 135.62 (C), 149.70 (C), 152.63 (CO). HRMS m/z (M$^+$$-$allyl): Calcd for C$_{13}H_{13}N_2O_2$: 229.0977. Found: 229.0982.

4-Allyl-1-(1-chloroethoxycarbonyl)-3-phenyl-1,4-dihydropyridazine (6c′) Yield 8%. Colorless oil. ^{1}H-NMR (CDCl$_3$) δ: 1.94 (3H, d, $J=5.9$ Hz), 2.20—2.35 (2H, m), 3.63—3.80 (1H, m), 4.93—5.10 (2H, m), 5.26 (1H, dd, $J=4.4$, 7.8 Hz), 5.58—5.98 (1H, m), 6.69 (1H, q, $J=5.9$ Hz), 7.17 (1H, d, $J=7.8$ Hz), 7.38—7.45 (3H, m), 7.79—7.90 (2H, m). The ^{13}C-NMR spectrum was obtained as that of a mixture of two isomers. ^{13}C-NMR (CDCl$_3$) δ: 25.36 (CH$_3$), 31.94, 31.97 (CH$_2$), 39.06, 39.11 (CH), 83.53 (CH), 106.90 (CH), 118.17, 118.19 (CH$_2$), 122.95, 122.98 (CH), 126.45 (2CH), 128.57 (2CH), 130.01 (CH), 133.34 (CH), 135.18 (C), 150.59 (C), 150.79 (CO). HRMS m/z (M$^+$$-$allyl): Calcd for C$_{13}H_{12}^{35}ClN_2O_2$: 263.0585. Found: 263.0569.

6-Allyl-1-ethoxycarbonyl-3-methoxycarbonyl-1,6-dihydropyridazine (5d) Yield 79%. Colorless oil. ^{1}H-NMR (CDCl$_3$) δ: 1.39 (3H, t, $J=7.3$ Hz), 2.31—2.43 (2H, m), 3.88 (3H, s), 4.37 (2H, q, $J=7.3$ Hz), 4.97—5.15 (3H, m), 5.54—5.95 (1H, m), 6.19 (1H, dd, $J=5.9$, 9.8 Hz), 6.55 (1H, d, $J=9.8$ Hz). The ^{13}C-NMR spectrum was obtained as that of a mixture of two isomers. ^{13}C-NMR (CDCl$_3$) δ: 14.02 (CH$_3$), 38.30 (CH$_2$), 50.37 (CH), 52.39 (CH$_3$), 63.33 (CH$_2$), 115.72 (CH), 119.22 (CH$_2$), 130.51 (CH), 130.95 (CH), 139.14 (C), 153.47 (CO), 163.13 (CO). HRMS m/z (M$^+$$-$allyl): Calcd for C$_9H_{11}N_2O_4$: 211.0717. Found: 211.0707.

6-Allyl-1-(1-chloroethoxycarbonyl)-3-methoxycarbonyl-1,6-dihydropyridazine (5d′) Yield 80%. Colorless oil. ^{1}H-NMR (CDCl$_3$) δ: 1.92 (3H, d, $J=5.9$ Hz), 2.19—2.45 (2H, m), 3.89 (3H, s), 5.02—5.18 (3H, m), 5.53—5.90 (1H, m), 6.25 (1H, dd, $J=5.9$, 10.0 Hz), 6.53—6.72 (2H, m). The ^{13}C-NMR spectrum was obtained as that of a mixture of two isomers. ^{13}C-NMR ($CDCl_3$) δ: 24.87, 24.97 (CH_3), 38.28 (CH_2) 50.72, 50.79 (CH), 52.47, 52.49 (CH_3), 83.46 (CH), 115.65 (CH), 119.59, 119.63 (CH_2), 130.64 (CH), 131.19, 131.36 (CH), 140.47 (C), 151.20, (CO), 162.85, 162.95 (CO). HRMS *m/z* (M^+ − allyl): Calcd for $C_9H_{10}{}^{35}ClN_2O_4$: 245.0329. Found: 245.0341.

4-Allyl-1-ethoxycarbonyl-3-methoxycarbonyl-1,4-dihydropyridazine (6d) Yield 7%. Colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 1.39 (3H, t, J = 7.3 Hz), 2.26 (2H, t, J = 6.4 Hz), 3.46—3.70 (1H, m), 3.87 (3H, s), 4.38 (2H, q, J = 7.3 Hz), 4.96—5.23 (3H, m), 5.53—5.91 (1H, m), 7.09 (1H, d, J = 8.3 Hz). ^{13}C-NMR ($CDCl_3$) δ: 14.32 (CH_3), 31.10 (CH_2), 39.56 (CH), 52.84 (CH_3), 64.03 (CH_2), 107.07 (CH), 118.48 (CH_2), 122.76 (CH), 133.09 (CH), 142.19 (C), 151.73 (CO), 164.23 (CO). HRMS *m/z* (M^+ − allyl): Calcd for $C_9H_{11}N_2O_4$: 211.0719. Found: 211.0730.

4-Allyl-1-(1-chloroethoxycarbonyl)-3-methoxycarbonyl-1,4-dihydropyridazine (6d′) Yield 4%. Colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 1.94 (3H, d, J = 5.9 Hz), 2.20—2.35 (2H, m), 3.51—3.71 (1H, m), 3.89 (3H, s), 4.99—5.31 (3H, m), 5.50—5.89 (1H, m), 6.65 (1H, q, J = 5.9 Hz), 7.09 (1H, d, J = 7.8 Hz). The ^{13}C-NMR spectrum was obtained as that of a mixture of two isomers. ^{13}C-NMR ($CDCl_3$) δ: 25.19, 25.25 (CH_3), 31.22, 31.27 (CH_2), 39.40, 39.44 (CH), 52.88, 52.91 (CH_3), 83.80, 83.85 (CH), 108.3 (CH), 118.73 (CH_2), 122.31, 122.41 (CH), 132.85, 132.89 (CH), 143.95 (C), 149.20 (CO), 163.97 (CO). HRMS *m/z* (M^+ − allyl): Calcd for $C_9H_{10}{}^{35}ClN_2O_4$: 245.0330. Found: 245.0345.

The Reaction of Pyrimidine, Pyrazine, and Benzodiazines with Allyltributyltin At first, the same procedure as described for pyridazines was applied to pyrimidine and pyrazine to give a mixture of diallyl adducts and the starting materials. Therefore 2.4 eq of allyltributyltin and alkyl chloroformate were used for the complete reactions of pyrimidine, pyrazine, and quinoxaline. In the cases of phthalazine, quinazoline, and cinnoline, the same conditions as the case of pyridazines were adopted.

2,4-Diallyl-1,3-bis(ethoxycarbonyl)-1,2,3,4-tetrahydropyrimidine (9) Yield 87%. Colorless oil. ^{1}H-NMR (DMSO-d_6, 80 °C) δ: 1.20 (3H, t, J = 7.3 Hz), 1.22 (3H, t, J = 7.3 Hz), 2.30—2.63 (4H, m), 4.07—4.18 (4H, m), 4.31—4.37 (1H, m), 4.96—5.14 (4H, m), 5.23 (1H, dd, J = 3.9 Hz, 8.3 Hz), 5.57—5.89 (2H, m), 6.01—6.28 (1H, m), 6.27—6.72 (1H, m). The ^{13}C-NMR spectrum was obtained as that of a mixture of two isomers. ^{13}C-NMR (DMSO-d_6, 80 °C) δ: 14.21 (CH_3), 14.27 (CH_3), 36.05, 36.65 (CH_2), 38.00, 40.25 (CH_2), 49.91, 50.02 (CH), 61.01, 61.43 (CH_2), 61.25, 63.48 (CH), 61.81 (CH_2), 107.26, 111.89 (CH), 117.35, 117.41 (CH_2), 118.01, 118.09 (CH_2), 121.56, 122.37 (CH), 132.79, 133.10 (CH), 133.37, 134.75 (CH), 151.44, 151.72 (CO), 154.12, 154.24 (CO). HRMS *m/z*: (M^+, 3%) Calcd for $C_{16}H_{24}N_2O_4$: 308.1733. Found: 308.1732. (M^+ − allyl, 100%) Calcd for $C_{13}H_{19}N_2O_4$: 267.1342. Found: 267.1317.

2,4-Diallyl-1,3-bis(1-chloroethoxycarbonyl)-1,2,3,4-tetrahydropyrimidine (9′) Yield 86%. Colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 1.84 (3H, t, J = 5.9 Hz), 1.85 (3H, t, J = 5.9 Hz), 2.29—2.73 (4H, m), 4.19—4.46 (1H, m), 5.04—5.38 (5H, m), 5.60—5.89 (2H, m), 6.04—6.82 (4H, m). The ^{13}C-NMR spectrum was obtained as that of a mixture of four isomers. ^{13}C-NMR ($CDCl_3$) δ: 25.27, 25.44 ($2CH_3$), 36.81, 36.98 (CH_2), 40.12, 41.13 (CH_2), 50.64, 50.82 (CH), 62.05, 64.14 (CH), 82.97, 83.08, 83.19 (2CH), 108.45, 113.04 (CH), 118.45, 118.69, 119.06, 119.34 ($2CH_2$), 120.77, 121.62, 122.02 (CH), 132.04, 132.31, 133.69, 133.74 (2CH), 149.82 (CO), 151.63 (CO). HRMS *m/z*: (M^+ − allyl) Calcd for $C_{13}H_{17}Cl_2N_2O_4$: 335.0566. Found: 335.0573.

2,4-Diallyl-1,3-bis(2,2,2-trichloroethoxycarbonyl)-1,2,3,4-tetrahydropyrimidine (9″) Yield 94%. Colorless oil. ^{1}H-NMR (DMSO-d_6, 80 °C) δ: 2.38—2.80 (4H, m), 4.24—4.48 (1H, m), 4.88—5.19 (8H, m), 5.29—5.48 (1H, m), 5.59—5.93 (2H, m), 6.18—6.41 (1H, m), 6.71—6.81 (1H, m). The ^{13}C-NMR spectrum was obtained as that of a mixture of two isomers. ^{13}C-NMR (DMSO-d_6, 80 °C) δ: 36.14, 36.54 (CH_2), 37.36, 37.73 (CH_2), 50.49, 50.55 (CH), 62.03, 64.14 (CH), 74.49, 74.78, 74.82, 75.55 ($2CH_2$), 95.39 (CCl_3), 95.63 (CCl_3), 108.63, 113.93 (CH), 117.96, 118.09 (CH_2), 118.82 (CH_2), 120.92, 121.96 (CH), 132.13, 132.33 (CH), 132.64, 134.16 (CH), 149.76 (CO), 152.03 (CO). HRMS *m/z*: (M^+) Calcd for $C_{16}H_{18}{}^{35}Cl_6N_2O_4$: 511.9396. Found: 511.9391. (M^+ − allyl) Calcd for $C_{13}H_{13}{}^{35}Cl_6N_2O_4$: 470.9005. Found: 470.9005.

2,3-Diallyl-1,4-bis(2,2,2-trichloroethoxycarbonyl)-1,2,3,4-tetrahydropyrazine (12) Yield 52%. Colorless oil. ^{1}H-NMR (DMSO-d_6, 80 °C) δ: 2.18 (4H, br s), 4.35 (2H, t, J = 7.3 Hz), 4.93 (4H, s), 5.05 (4H, d, J = 12.7 Hz), 5.77 (2H, dd, J = 7.3, 12.7 Hz), 6.31 (2H, br s) ^{13}C-NMR (DMSO-d_6, 80 °C) δ: 34.93 ($2CH_2$), 52.12 (2CH), 74.74 ($2CH_2$), 95.52 ($2CCl_3$), 106.78 (2CH), 118.34 ($2CH_2$), 133.21 (2CH), 150.55 (2CO). HRMS *m/z*: (M^+, 100%) Calcd for $C_{16}H_{18}{}^{35}Cl_6N_2O_4$: 511.9397. Found 511.9415. (M^+ − allyl, 44%) Calcd for $C_{13}H_{13}{}^{35}Cl_6N_2O_4$: 470.9003. Found: 470.8985.

2-Allyl-3-hydroxy-1,4-bis(2,2,2-trichloroethoxycarbonyl)-1,2,3,4-tetrahydropyrazine (13) Yield 16%. Colorless oil. ^{1}H-NMR (DMSO-d_6, 80 °C) δ: 2.05—2.11 (2H, m), 4.33 (1H, t, J = 7.3 Hz), 4.85—5.06 (6H, m), 5.67 (1H, d, J = 2.9 Hz), 5.71—5.80 (1H, m), 6.24—6.29 (2H, m), 6.39 (1H, br). The ^{13}C-NMR spectrum was obtained as that of a mixture of two isomers. ^{13}C-NMR (DMSO-d_6, 80 °C) δ: 33.45, 33.98 (CH_2), 54.96, 55.80 (CH), 73.19, 73.61 (CH), 74.73 (CH_2), 74.76 (CH_2), 95.52 (CCl_3), 95.66 (CCl_3), 106.73 (2CH), 118.08, 118.40 (CH_2), 133.06 (CH), 150.33 (CO), 150.88 (CO). HRMS *m/z*: (M^+, 100%) Calcd for $C_{13}H_{14}{}^{35}Cl_6N_2O_5$: 487.9033. Found: 487.9053. (M^+ − allyl, 72%) Calcd for $C_{10}H_9{}^{35}Cl_6N_2O_5$: 446.8640. Found: 446.8620.

1-Allyl-2-ethoxycarbonyl-1,2-dihydrophthalazine (18) Yield 94%. Colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 1.38 (3H, t, J = 7.3 Hz), 2.39 (2H, t, J = 7.1 Hz), 4.37 (2H, q, J = 7.3 Hz), 4.97 (1H, dd, J = 1.2, 16.6 Hz), 5.01 (1H, dd, J = 1.2, 9.3 Hz), 5.55 (1H, br s), 5.64—5.75 (1H, m), 7.13 (1H, d, J = 7.3 Hz) 7.27 (1H, d, J = 6.8 Hz), 7.33—7.37 (1H, m), 7.41—7.45 (1H, m), 7.67 (1H, br s). ^{13}C-NMR ($CDCl_3$) δ: 14.63 (CH_3), 39.47 (CH_2), 53.42 (CH), 62.84 (CH_2), 118.82 (CH_2), 123.87 (C), 125.68 (CH), 126.37 (CH), 128.22 (CH), 131.31 (CH), 132.81 (CH), 133.34 (C). 142.85 (CH), 154.19 (CO). HRMS *m/z*: (M^+ − allyl) Calcd for $C_{11}H_{11}N_2O_2$: 203.0821. Found: 203.0827.

1-Allyl-2-(1-chloroethoxycarbonyl)-1,2-dihydrophthalazine (18′) Yield 100%. Colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 1.91 (3H, d, J = 5.9 Hz), 2.41 (2H, t, J = 6.8 Hz), 4.87—5.08 (2H, m), 5.50—5.92 (2H, m), 6.71 (1H, q, J = 5.9 Hz), 7.05—7.55 (4H, m), 7.72 (1H, br s). The ^{13}C-NMR spectrum was obtained as that of a mixture of two isomers. ^{13}C-NMR ($CDCl_3$) δ: 25.16, 25.29 (CH_3), 39.33, 39.45 (CH_2), 53.35, 53.62 (CH), 83.36, 83.44 (CH), 119.20 (CH_2), 123.31, 123.33 (C), 125.86, 125.88 (CH), 126.12, 126.22 (CH), 128.25 (CH), 131.58 (CH), 132.16, 132.34 (CH), 133.07 (C), 143.87, 144.01 (CH), 151.61 (CO). HRMS *m/z* (M^+ − allyl): Calcd for $C_{11}H_{10}{}^{35}ClN_2O_2$: 237.0429. Found: 237.0424.

4-Allyl-3-ethoxycarbonyl-3,4-dihydroquinazoline (19) Yield 73%. Colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 1.37 (3H, t, J = 7.3 Hz), 2.33—2.52 (2H, m), 4.34 (2H, q, J = 7.3 Hz), 4.98 (1H, dd, J = 1.5, 17.1 Hz), 5.04 (1H, dd, J = 1.5, 9.8 Hz), 5.25—5.29 (1H, m), 5.62—5.72 (1H, m), 7.03 (1H, d, J = 7.3 Hz), 7.17—7.21 (1H, m), 7.28—7.31 (2H, m), 8.04 (1H, s). ^{13}C-NMR ($CDCl_3$) δ: 14.32 (CH_3), 41.75 (CH_2), 53.27 (CH), 63.19 (CH_2), 119.20 (CH_2), 125.66 (CH), 125.80 (C), 126.11 (CH), 126.94 (CH), 128.56 (CH), 132.31 (CH), 139.48 (C), 142.21 (CH), 152.49 (CO). HRMS *m/z*: (M^+, 1%) Calcd for $C_{14}H_{16}N_2O_2$: 244.1209. Found: 244.1194. (M^+ − allyl, 100%) Calcd for $C_{11}H_{11}N_2O_2$: 203.0819. Found: 203.0819.

2,4-Diallyl-1,3-bis(ethoxycarbonyl)-1,2,3,4-tetrahydroquinazoline (20) Yield 17%. Colorless oil. ^{1}H-NMR (DMSO-d_6, 80 °C) δ: 1.20 (3H, t, J = 7.3 Hz), 1.26 (3H, t, J = 7.3 Hz), 1.78—2.31 (2H, m) 2.39—2.42 (2H, m), 4.16—4.21 (4H, m), 4.75—4.88 (4H, m), 4.97—4.99 (1H, m), 5.42—5.52 (1H, m), 5.54—5.61 (1H, m), 6.16 (1H, dd, J = 4.1 Hz, 10 Hz), 7.19—7.34 (4H, m). ^{13}C-NMR ($CDCl_3$) δ: 14.23 (CH_3), 14.39 (CH_3), 37.38 (CH_2), 41.35 (CH_2), 54.63 (CH), 60.99 (CH_2), 61.83 (CH_2), 64.56 (CH), 117.70 (CH_2), 117.85 (CH_2), 125.60 (CH), 126.10 (CH), 127.23 (CH), 127.56 (CH), 131.91 (C), 132.39 (CH), 132.99 (CH), 134.67 (C), 153.11 (CO), 153.20 (CO). HRMS *m/z*: (M^+ − allyl) Calcd for $C_{17}H_{21}N_2O_4$: 317.1498. Found: 317.1470.

4-Allyl-3-(1-chloroethoxycarbonyl)-3,4-dihydroquinazoline (19′) Yield 78%. Colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 1.91 (3H, d, J = 5.9 Hz), 2.36—2.60 (2H, m), 4.90—5.32 (3H, m), 5.41—5.89 (1H, m), 6.66 (1H, q, J = 5.9 Hz), 6.95—7.34 (4H, m), 8.00 (1H, br s). The ^{13}C-NMR spectrum was obtained as that of a mixture of two isomers. ^{13}C-NMR ($CDCl_3$) δ: 24.98 (CH_3), 41.34 (CH_2), 53.51 (CH), 83.05 (CH), 119.55 (CH_2), 125.38, 125.52 (CH), 125.81, 125.85 (C), 125.94, 125.97 (CH), 127.24, 127.27 (CH), 128.62 (CH), 131.76 (CH), 138.88 (C), 140.74 (CH), 150.01 (CO). HRMS *m/z*: (M^+ − allyl) Calcd for $C_{11}H_{10}{}^{35}ClN_2O_2$: 237.0428. Found: 237.0416.

2,4-Diallyl-1,3-bis(1-chloroethoxycarbonyl)-1,2,3,4-tetrahydroquinazoline (20′) Yield 15%. Colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 1.89 (6H, d, J = 5.9 Hz), 2.40—2.58 (4H, m), 4.68—5.10 (5H, m), 5.38—5.76 (2H, m), 6.18—6.36 (1H, m), 6.50—6.79 (2H, m) 7.08—7.40 (4H, m). The ^{13}C-NMR spectrum was obtained as that of mixture of six isomers. ^{13}C-NMR ($CDCl_3$) δ: 24.61, 24.90 (CH_3), 25.24, 25.32, 25.42,, 25.45, 25.54 (CH_3), 36.56, 37.22 (CH_2), 40.65, 40.75, 42.13, 42.35 (CH_2), 55.77, 55.89 (CH), 64.84, 65.00, 65.68 (CH), 82.68, 82.81, 83.01, 83.06, 83.17, 83.41 (2CH), 118.91, 119.01, 119.14, 119.18, 119.52 ($2CH_2$), 126.33, 126.39, 126.45, 126.48, 126.63 (2CH), 127.40, 127.66, 127.80, 127.94 (2CH), 131.22, 131.26 (C), 131.48, 131.67, 131.74 (CH), 132.05, 132.29, 132.38 (CH), 133.38, 133.82 (C), 150.68, 150.72, 150.80 (CO), 151.23, 151.47 (CO). HRMS *m*/*z*: (M^+ − allyl) Calcd for $C_{17}H_{19}{}^{35}Cl_2N_2O_4$: 385.0722. Found: 385.0753.

4-Allyl-1-ethoxycarbonyl-1,4-dihydrocinnoline (21) Yield 67%. Colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 1.44 (3H, t, $J=7.3$ Hz), 2.40—2.44 (2H, m), 3.44—3.48 (1H, m), 4.45 (2H, q, $J=7.3$ Hz), 5.05—5.12 (2H, m), 5.70—5.81 (1H, m), 7.06—7.12 (1H, m), 7.16—7.20 (1H, m), 7.27—7.31 (2H, m), 8.05 (1H, d, $J=8.3$ Hz). ^{13}C-NMR ($CDCl_3$) δ: 14.61 (CH_3), 37.42 (CH_2), 38.06 (CH), 62.98 (CH_2), 118.38 (CH_2), 119.44 (CH), 124.80 (C), 125.51 (CH), 126.90 (CH), 127.21 (CH), 133.58 (CH), 134.97 (C), 149.16 (CH), 152.91 (CO). HRMS *m*/*z*: (M^+) Calcd for $C_{14}H_{16}N_2O_2$: 244.1209. Found: 244.1182. (M^+ − allyl) Calcd for $C_{11}H_{11}N_2O_2$: 203.0818. Found: 203.0801.

4-Allyl-1-(1-chloroethoxycarbonyl)-1,4-dihydrocinnoline (21′) Yield 46%. Colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 1.95 (3H, d, $J=5.9$ Hz), 2.35—2.49 (2H, m), 3.40—3.52 (1H, m), 5.00—5.13 (2H, m), 5.53—5.98 (1H, m), 6.77 (1H, q, $J=5.9$ Hz), 6.95—7.38 (4H, m), 8.01 (1H, d, $J=7.3$ Hz). The ^{13}C-NMR spectrum was obtained as that of a mixture of two isomers. ^{13}C-NMR ($CDCl_3$) δ: 25.24, 25.28 (CH_3), 37.12, 37.39 (CH_2), 37.78, 38.03 (CH), 83.35, 83.37 (CH), 118.49, 118.61 (CH_2), 119.61, 119.64 (CH), 125.09, 125.16 (C), 126.02 (CH), 126.76, 126.91 (CH), 127.26 (CH), 133.04, 133.23 (CH), 134.26, 134.31 (C), 150.31, 150.35 (CO), 150.74, 150.85 (CH). HRMS *m*/*z*: (M^+ − allyl) Calcd for $C_{11}H_{10}{}^{35}ClN_2O_2$: 237.0428. Found: 237.0425.

2,3-Diallyl-1,4-bis(2,2,2-trichloroethoxycarbonyl)-1,2,3,4-tetrahydroquinoxaline (23) Yield 30%. Colorless oil. ^{1}H-NMR (DMSO-d_6, 80 °C) δ: 2.13—2.25 (4H, m), 4.67 (2H, t, $J=6.4$ Hz), 4.93—5.08 (8H, m), 5.77—5.89 (2H, m), 7.12 (2H, dd, $J=3.4$, 6.4 Hz), 8.02 (2H, dd, $J=3.4$, 6.4 Hz). ^{13}C-NMR (DMSO-d_6, 80 °C) δ: 35.22 ($2CH_2$), 53.51 (2CH), 74.94 ($2CH_2$), 95.41 ($2CCl_3$), 118.20 ($2CH_2$), 122.71 (2CH), 123.76 (2CH), 125.68 (2C), 133.25 (2CH), 151.72 (2CO). Compound **23** gave an inadequate HRMS because the peak intensities of (M^+) and (M^+ − allyl) were extremely low.

2-Allyl-3-hydroxy-1,4-bis(2,2,2-trichloroethoxycarbonyl)-1,2,3,4-tetrahydroquinoxaline (24) Yield 18%. Colorless oil. ^{1}H-NMR (DMSO-d_6, 80 °C) δ: 1.94—2.17 (2H, m), 4.68 (1H, m), 4.84—5.16 (6H, m), 5.76—5.84 (1H, m), 5.95 (1H, dd, $J=2.4$, 4.4 Hz), 6.54 (1H, d, $J=4.4$ Hz), 7.07—7.15 (2H, m), 7.80—7.83 (1H, m), 8.07—8.09 (1H, m). ^{13}C-NMR (DMSO-d_6, 80 °C) δ: 33.16 (CH_2), 55.87 (CH), 74.85 (CH_2), 74.89 (CH_2), 75.77 (CH), 95.37 (CCl_3), 95.52 (CCl_3), 117.94 (CH_2), 121.52 (CH), 123.21 (CH), 123.97 (CH), 124.03 (CH), 125.60 (C), 126.86 (C), 133.06 (CH), 151.43 (CO), 152.41 (CO). HRMS *m*/*z*: (M^+, 84%) Calcd for $C_{17}H_{16}{}^{35}Cl_6N_2O_5$: 537.9190. Found: 537.9182. (M^+ − allyl, 100%) Calcd for $C_{14}H_{11}{}^{35}Cl_6N_2O_5$: 496. 8799. Found: 496.8830.

Reactions of *N*-Methylpyridinium and 2-Methyl-1,2,3-triazinium Salts with Allyltributyltin The reaction was carried out according to the same procedure as in the case of the *N*-methylpyridazinium salt **3**.

2-Allyl-3,5-dicyano-1-methyl-1,2-dihydropyridine (26c) Yield 79%. Pale yellow needles from isopropyl ether, mp 86.5—87 °C. *Anal.* Calcd for $C_{11}H_{11}N_3$: C, 71.33; H, 5.99; N, 22.69. Found: C, 71.16; H, 5.92; N, 22.64. ^{1}H-NMR ($CDCl_3$) δ: 2.36—2.52 (2H, m), 3.15 (3H, s), 4.27—4.30 (1H, m), 5.22—5.26 (2H, m), 5.82—5.93 (1H, m), 6.74 (1H, d, $J=1.0$ Hz), 7.01 (1H, s). ^{13}C-NMR ($CDCl_3$) δ: 37.27 (CH_2), 42.90 (CH_3), 59.03 (CH), 78.18 (C), 91.28 (C), 117.96 (C), 118.65 (C), 120.96 (CH_2), 130.76 (CH), 136.74 (CH), 150.84 (CH).

4-Allyl-3,5-dicyano-1-methyl-1,4-dihydropyridine (27c) Yield 19%. Pale yellow needles from acetone–isopropyl ether, mp 98—99 °C. *Anal.* Calcd for $C_{11}H_{11}N_3$: C, 71.33; H, 5.99; N, 22.69. Found: C, 71.58; H, 6.00; N, 22.82. ^{1}H-NMR ($CDCl_3$) δ: 2.39—2.42 (2H, m), 3.08 (3H, s), 3.49 (1H, t, $J=4.9$ Hz), 5.22—5.27 (2H, m), 5.79—5.90 (1H, m), 6.53 (2H, s). ^{13}C-NMR ($CDCl_3$) δ: 33.98 (CH), 39.43 (CH_2), 41.42 (CH_3), 87.00 (2C), 118.43 (2C), 120.02 (CH_2), 132.26 (CH), 141.60 (2CH).

2-Allyl-3,5-bis(ethoxycarbonyl)-1-methyl-1,2-dihydropyridine (26d) Yield 61%. Pale yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 2.26—2.40 (2H, m), 3.19 (3H, s), 3.73 (3H, s), 3.74 (3H, s), 4.62—4.65 (1H, m), 5.05—5.10 (2H, m), 5.79—5.89 (1H, m), 7.52 (1H, s), 7.63 (1H, d, $J=1.5$ Hz). ^{13}C-NMR ($CDCl_3$) δ: 37.66 (CH_2), 43.11 (CH_3), 50.95 (CH_3), 51.43 (CH_3), 58.36 (CH), 97.82 (C), 108.81 (C), 118.71 (CH_2), 133.23 (CH), 133.41 (CH), 150.51 (CH), 166.28 (CO), 166.46 (CO). HRMS *m*/*z*: (M^+, 3%) Calcd for $C_{13}H_{17}NO_4$: 251.1158. Found: 251.1156. (M^+ − allyl, 100%) Calcd for $C_{10}H_{12}NO_4$: 210.0766. Found: 210.0767.

4-Allyl-3,5-bis(ethoxycarbonyl)-1-methyl-1,4-dihydropyridine (27d) Yield 30%. Pale yellow needles from isopropyl ether, mp 84.5—85 °C. *Anal.* Calcd for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57. Found: C, 62.16; H, 6.86; N, 5.53. ^{1}H-NMR ($CDCl_3$) δ: 2.15—2.18 (2H, m), 3.14 (3H, s), 3.72 (6H, s), 3.95 (1H, t, $J=4.9$ Hz), 4.88—4.96 (2H, m), 5.64—5.76 (1H, m), 7.10 (2H, s). ^{13}C-NMR ($CDCl_3$) δ: 30.72 (CH), 40.44 (CH_2), 41.35 (CH_3), 51.23 ($2CH_3$), 106.29 (2C), 116.90 (CH_2), 134.98 (CH), 139.85 (2CH), 167.56 (2CO).

5-Allyl-2,4-dimethyl-6-phenyl-2,5-dihydro-1,2,3-triazine (29) Yield 91%. Yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 2.10 (3H, s), 2.11—2.17 (2H, m), 3.55 (3H, s), 3.65 (1H, dd, $J=6.2$, 8.5 Hz), 5.02—5.10 (2H, m), 5.72—5.80 (1H, m), 7.31—7.40 (3H, m), 7.74—7.77 (2H, m). ^{13}C-NMR ($CDCl_3$) δ: 22.00 (CH_3), 30.21 (CH), 35.65 (CH_2), 47.08 (CH_3), 117.69 (CH_2), 125.77 (2CH), 128.43 (2CH), 128.72 (CH), 134.92 (CH), 135.03 (C), 138.23 (C), 142.72 (C). HRMS *m*/*z*: (M^+) Calcd for $C_{14}H_{17}N_3$: 227.1422. Found: 227.1425. (M^+ − allyl) Calcd for $C_{11}H_{12}N_3$: 186.1031. Found: 186.1030.

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References and Notes

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