The Ring Transformation of 1,2,3-Triazines

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Monocyclic 1,2,3-triazines reacted with electron rich dienophiles to give pyridines and pyridazines. 4,6-Disubstituted 1,2,3-triazine was denitrogenated to the azete intermediate, which afforded isomeric pyridines. 2,5-Dihydrotriazines were oxidized by *m*-chloroperbenzoic acid to give 1,2,3-triazoles. Ring transformations of other triazine derivatives are also reported.

Keywords 1,2,3-triazine; ring transformation; azacyclobutadiene (azete); 1,2,3-triazine 2-imine; 2-methyl-1,2,3-triazinium iodide; *N*,*N*-diethyl-1-propynylamine; oxidation; 2,5-dihydro-1,2,3-triazine

Monocyclic 1,2,3-triazines **1** are six-membered heteroaromatics,[1] which are so π-deficient as to react with nucleophiles.[2] The reaction site is mainly the C-4 position, and sequential N_2 elimination occurrs to give ring opened products (Chart 1).

These compounds also have a tendency to fragment to acetylene, nitrile, and nitrogen when heated or on electron impact.[3] These results indicate that the resonance energy of **1** is smaller than those of other heteroaromatics such as pyridine or pyridazine. Thus **1** might be able to react as a diene or an ene (dienophile).[4] This paper describes the reactions of various 1,2,3-triazine derivatives with electron-rich dienophiles. In addition, the oxidation of 2,5-dihydro-1,2,3-triazine is reported.

Reaction of 1,2,3-Triazines 1a—c with an Ynamine 2 First, the parent and 4-substituted triazines **1a—c** were allowed to react with *N*,*N*-diethyl-1-propynylamine **2** under reflux in chloroform to afford pyridines **3** and pyridazines **4** (Chart 2 and Table I).

Compound **1c** reacted slowly and 36% of **1c** was recovered even after 92 h. Compounds **3** and **4** were supposed to be produced *via* the Diels–Alder adducts **5** and **6**, respectively (Chart 3). Molecular orbital calculation[5] indicated that the lowest unoccupied molecular orbital (LUMO) coefficients were large at the N-2 and C-5 positions of **1a**, whereas C-4 (and N-1) were electron deficient, so the formation of **5** seemed to involve an unconcerted ionic reaction and that of **6**, an orbital-controlled reaction. In the case of **1c**, the steric repulsion between phenyl and diethylamino groups in adduct **5** made its formation disadvantageous enough for adduct **6** to become relatively significant.

Reaction of 4,6-Dimethyl-1,2,3-triazine 1d with Dienophiles[6] Compound **1d** did not react with **2** under reflux in xylene. In the absence of dienophile, **1d** was decomposed and the evolution of nitrogen gas was observed at 180 °C. When **1d** was heated with an electron-rich dienophile in a sealed tube at 180 °C, pyridines **7** and **8** were obtained (Chart 4 and Table II).

Although 2,4-dimethylpyridines **7** are the normal Diels–Alder products of the reaction, 2,6-dimethylpyridines **8** were also obtained unexpectedly. In particular, when **1d**

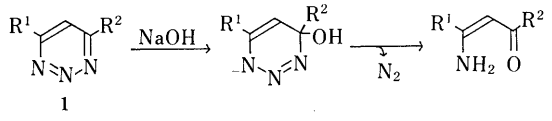

Chart 1

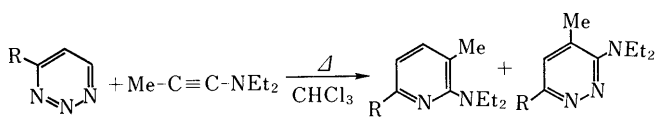

Chart 2

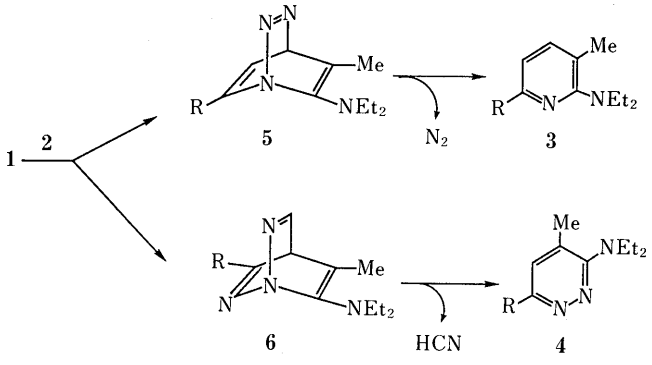

Chart 3

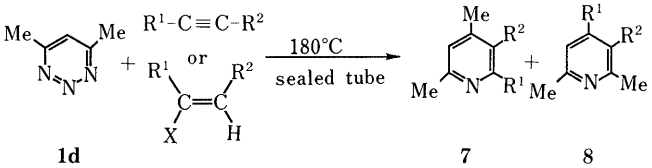

Chart 4

TABLE I. Reaction of 1,2,3-Triazines **1** with **2**

Substrate	R of **1**	Reaction time (h)	Yield (%)	
			3	**4**
1a	H	5	52	Trace
1b	Me	7	31	3
1c	Ph	92	21	24

TABLE II. Reaction of **1d** with Dienophiles

Entry	Dienophile	R^1	R^2	X	Yield (%)	
					7	**8**
a	Me–C≡C–NEt_2	NEt_2	Me	—	50	—
b	Ph–C≡C–H	Ph	H	—	38	—
c	CH_2=CHSOPh	H	H	SOPh	35	Trace
d	CH_2=$C(OEt)_2$	OEt	H	OEt	4	31

was heated with ketene diethyl acetal, the 2,6-dimethylpyridine derivative was the major product (Table II, entry d). The formation of both the 2,4- and 2,6-dimethylpyridine derivatives might be explained by the involvement of the azacyclobutadiene (azete) intermediate **9** (Chart 5); the formation of the latter cannot be explained by direct Diels–Alder type addition between **1d** and the dienophile. Thus the intermediary formation of an azacyclobutadiene by denitrogenation of **1**, followed by the addition of dienophile from the (A) or (B) side (Chart 5) might produce 2,4- or 2,6-dimethylpyridine, respectively. Since very little is known about the properties of monocyclic azacyclobutadiene,[7] this reaction system may be useful to research its chemical reactivities.

Reaction of 1,2,3-Triazine 2-Imines 10a—c with 2 We have already reported the reaction of **10** with electron-deficient dienophiles to produce pyrazolo[2,3-*b*][1,2,4]triazine rings.[8] The mechanism of the ring formation was considered to be 1,3-dipolar cycloaddition followed by ring transformation. This time **10** was allowed to react with an electron-rich dienophile **2** to form a different ring system; that is, 1,2,3-triazolo[1,5-*a*]pyrimidine derivatives **11a—c** were obtained as shown in Chart 6 and Table III. The structure of **11b** was confirmed by X-ray crystallographic analysis (Fig. 1, Table IV). The reaction was supposed to start with 1,3-dipolar cycloaddition of **10** with **2**, and then ring expansion and ring closure would afford **11** (Chart 6).

Oxidation of 2,5-Dihydro-1,2,3-triazine 12a—c by *m*-Chloroperbenzoic Acid (*m*CPBA)[9] Triazines and their 2-methylated quaternary salts were readily reduced by sodium borohydride to form corresponding 2,5-dihydro-derivatives.[10] 2-Methyl-2,5-dihydrotriazines **12** thus obtained were allowed to react with 2 molar eq of *m*CPBA in methylene chloride to give 2-methyltriazoles **13** and 5-oxo-2,5-dihydrotriazines **14**. When R^1 and R^2 were phenyl, benzoic acid was also produced in 23% yield[11] (Chart 7 and Table V).

The reaction mechanism is summarized in Chart 8. 2-Methyltriazinium iodide **15** was treated with potassium

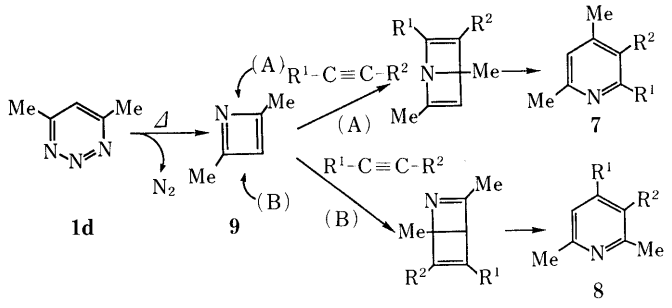

Chart 5

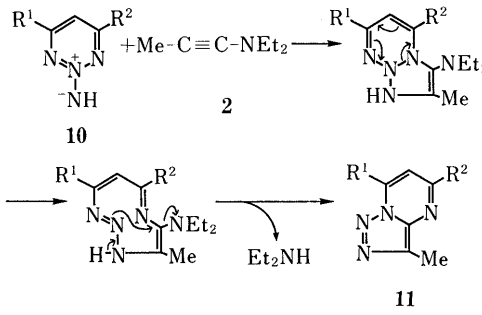

Chart 6

TABLE III. Reaction of **10** with **2**

Substrate	R^1	R^2	Yield of **11** (%)
10a	Me	Me	31
10b	Me	Ph	56
10c	Ph	Ph	20

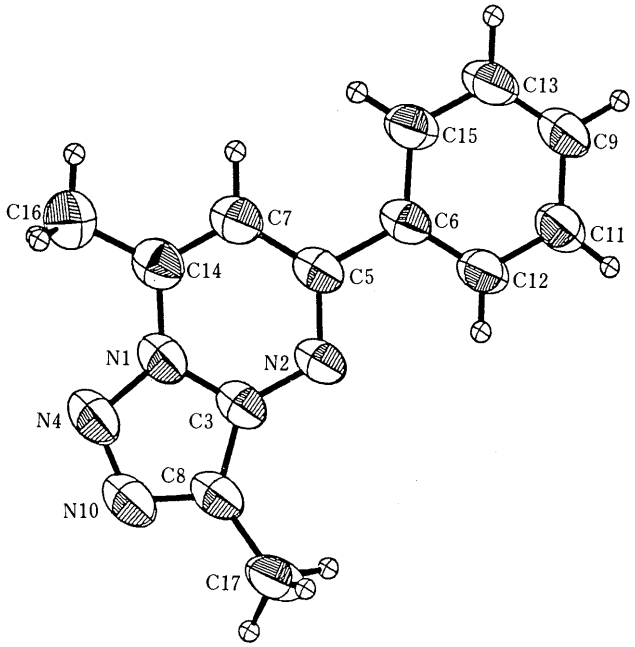

Fig. 1. ORTEP Drawing of **11b**

TABLE IV. Fractional Atomic Coordinates and Isotropic Thermal Parameters of **11b**

Atom	*X*	*Y*	*Z*	B_{eq}
N(1)	0.3327 (1)	0.7731 (1)	0.2517 (2)	4.63 (15)
N(2)	0.3914 (1)	0.8732 (1)	0.5573 (2)	4.41 (15)
C(3)	0.3749 (1)	0.7749 (1)	0.4516 (3)	4.36 (15)
N(4)	0.3242 (1)	0.6645 (1)	0.1799 (3)	5.61 (16)
C(5)	0.3641 (1)	0.9691 (1)	0.4604 (3)	4.20 (15)
C(6)	0.3840 (1)	1.0775 (1)	0.5745 (3)	4.21 (16)
C(7)	0.3187 (1)	0.9694 (2)	0.2533 (3)	4.72 (16)
C(8)	0.3919 (1)	0.6611 (2)	0.4997 (3)	4.90 (16)
C(9)	0.4256 (1)	1.2801 (2)	0.7906 (4)	5.20 (16)
N(10)	0.3613 (1)	0.5981 (1)	0.3343 (3)	5.65 (16)
C(11)	0.4487 (1)	1.1756 (2)	0.8814 (4)	5.55 (16)
C(12)	0.4278 (1)	1.0757 (2)	0.7746 (3)	5.07 (16)
C(13)	0.3811 (1)	1.2833 (2)	0.5932 (4)	5.64 (16)
C(14)	0.3026 (1)	0.8714 (2)	0.1467 (3)	4.75 (16)
C(15)	0.3601 (1)	1.1831 (2)	0.4869 (4)	5.31 (16)
C(16)	0.2567 (2)	0.8603 (2)	−0.0674 (4)	6.06 (17)
C(17)	0.4366 (2)	0.6101 (2)	0.6956 (5)	6.46 (17)

$B_{eq} = 1/3\sum_i\sum_j B_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$.

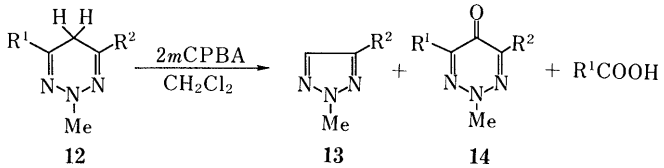

Chart 7

TABLE V. Oxidation of **12** by *m*CPBA

Substrate	R^1	R^2	Yield (%)		R^1COOH
			13	**14**	
12a	Me	Me	Trace	30	—
12b	Me	Ph	68	9	—
12c	Ph	Ph	69	0	23%

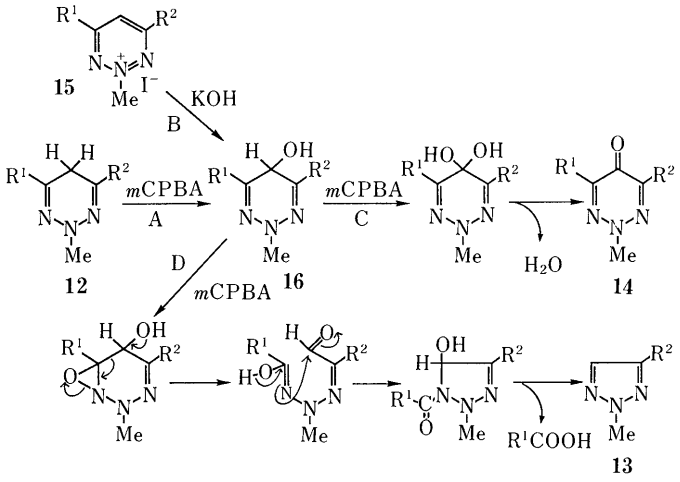

Chart 8

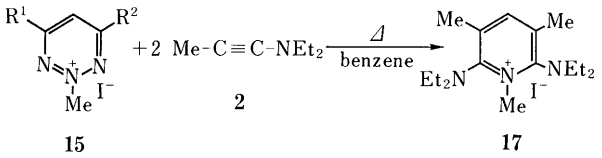

Chart 9

hydroxide in methylene chloride/water for 5 min under a nitrogen atmosphere followed by rapid separation of the methylene chloride layer. Then 1.2 eq of *m*CPBA was added to this solution, which resulted in the formation of **13** and **14**. It was therefore suggested that 5-hydroxy-2,5-dihydrotriazine **16** was the common intermediate of both reactions (Chart 8, paths A and B). When R^1 and R^2 are sterically small, path C proceeds preferentially. The second attack of *m*CPBA also occurred at the C-5 position followed by dehydration to produce **14**. On the other hand, path D was preferred to path C when R^1 or R^2 was a phenyl group. The second attack of *m*CPBA at C-5 was inhibited because of steric hindrance, so the second oxidant reacted at N-1 and the subsequent ring opening and ring closure afforded **13**, accompanied with the elimination of carboxylic acid.

The Reaction of 2-Methyltriazinium Salts 15a—c with 2 The reaction of **15**[10] with various nucleophiles occurred at the C-5 position to form dihydro compounds (*e.g.*, Chart 8, **16**) and oxidation by air then proceeded spontaneously to give the degradation products.[12] However, **15a—c** reacted with **2** under reflux in benzene to give a single product quantitatively. The spectral data indicated its structure as 2,6-bis(diethylamino)-1,3,5-trimethylpyridinium iodide **17** (Chart 9), which was supposed to be formed by the double Diels–Alder type additions of **2** to **15**, representing a unique reactivity of **15**.

In this paper we have described a variety of ring transformations of 1,2,3-triazine derivatives, revealing characteristic reactivities of the 1,2,3-triazine ring system.

Experimental

All melting points were taken on a Yanaco micro melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded with a JASCO A-102 spectrometer. The mass spectra (MS) were measured with a JEOL JMS-D300 instrument. The proton (^{1}H-) and carbon (^{13}C-) nuclear magnetic resonance (NMR) spectra were taken on 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.

The Reaction of 1a with 2 Compounds **1a** (2.55 mmol) and **2** (3.32 mmol) were dissolved in $CHCl_3$ and the solution was refluxed for 5 h. Then the solvent was evaporated off and the residue was subjected to alumina column chromatography to give 2-(diethylamino)-3-methylpyridine **3a** in 52% yield. **3a**: Yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 1.06 (6H, t, J=7 Hz), 2.24 (3H, s), 3.18 (4H, q, J=7 Hz), 6.77 (1H, dd, J=5, 8 Hz), 7.35 (1H, dd, J=1.5, 8 Hz), 8.15 (1H, dd, J=1.5, 5 Hz). The positions of the substituents were confirmed by the nuclear Overhauser effect (NOE) difference spectrum. Irradiation at the resonance due to CH_3 (δ 2.24) produced NOEs for γ-H (δ 7.35) and ethyl groups. Exact MS m/z (M^+) Calcd for $C_{10}H_{16}N_2$: 164.132. Found: 164.132. **4a** was detected by examination of the gas chromatography-mass spectrum (GC-MS) of the reaction mixture.

The Reaction of 1b with 2 A chloroform solution of **1b** (6 mmol) and **2** (7.8 mmol) was refluxed for 7 h. The solvent was evaporated off and the residue was chromatographed on alumina (hexane–CH_2Cl_2). Compound **3b** was obtained in 31% yield. **3b**: Yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 1.04 (6H, t, J=7 Hz), 2.16 (3H, s), 2.36 (3H, s), 3.17 (4H, q, J=7 Hz), 6.55 (1H, d, J=8 Hz), 7.17 (1H, d, J=8 Hz). The assignment of the substituent positions was achieved by analysis of the NOE difference spectrum in a same manner as **3a**. Exact MS m/z (M^+) Calcd for $C_{11}H_{18}N_2$: 178.145. Found: 178.146. The existence of **4b** was confirmed by GC-MS.

The Reaction of 1c with 2 Compounds **1c** (3 mmol) and **2** (4.3 mmol) were dissolved in $CHCl_3$ and the solution was heated at reflux for 92 h. Separation was done by alumina chromatography (hexane–CH_2Cl_2) to give **3c** and **4c** in 21% and 24% yields, respectively. **3c**: Yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 1.12 (6H, t, J=7 Hz), 2.23 (3H, s), 3.27 (4H, q, J=7 Hz), 7.12—7.46 (5H, m), 7.79—8.01 (2H, m). Exact MS m/z (M^+) Calcd for $C_{16}H_{20}N_2$: 240.167. Found: 240.165. **4c**: Yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 1.15 (6H, t, J=7 Hz), 2.29 (3H, s), 3.35 (4H, q, J=7 Hz), 7.28—7.45 (4H, m), 7.90—8.02 (2H, m). The nuclear Overhauser effect spectroscopy (NOESY) spectrum of **4c** was measured, and a large NOESY effect was observed between CH_3 (δ 2.29) and the pyridazine ring proton (δ *ca.* 7.45). Exact MS m/z (M^+) Calcd for $C_{15}H_{19}N_3$: 241.152. Found: 241.155. The starting material **1c** was recovered in 36% yield.

General Procedure for the Reaction of 4,6-Dimethyltriazine 1d with Dienophiles Compound **1d** (1 mmol) and 4 mmol of a dienophile were heated under a nitrogen atmosphere in a sealed tube at 180 °C for 1—2.5 h. After cooling, the residue was separated by alumina chromatography. **7a**: Yellow oil. Yield 50%. ^{1}H-NMR ($CDCl_3$) δ: 1.03 (6H, t, J=7 Hz), 2.14 (3H, s), 2.19 (3H, s), 2.37 (3H, s), 3.12 (4H, q, J=7 Hz), 6.58 (1H, s). Exact MS m/z (M^+) Calcd for $C_{12}H_{20}N_2$: 192.162. Found; 192.162. **8a** was not obtained; instead an isomer, 3-diethylamino-2,4,6-collidine **8a'**, was formed. **8a'**: Yellow oil. Yield 3%. ^{1}H-NMR ($CDCk_3$) δ: 1.02 (6H, t, J=8 Hz), 1.99 (3H, s), 2.19 (3H, s), 2.32 (3H, s), 3.06 (4H, q, J=8 Hz), 6.37 (1H, s). Exact MS m/z (M^+) Calcd for $C_{12}H_{20}N_2$: 192.162. Found; 192.162. The positions of the substituents of **7a** and **8a'** have been investigated by measuring the NOE difference spectra. In the case of **8a'**, irradiation at the resonance due to a ring proton (δ 6.37) produced NOEs for methyl groups (δ 1.99 and 2.32). **7b**: Colorless oil. Yield 38%. ^{1}H-NMR ($CDCl_3$) δ: 2.34 (3H, s), 2.57 (3H, s), 6.92 (1H, s), 7.32 (1H, s), 7.33—7.05 (3H, m), 7.87—8.00 (2H, m). Exact MS m/z (M^+) Calcd for $C_{13}H_{13}N$: 183.103. Found: 183.104. **8b**: Although an isomer was detected by GC-MS, the positions of the substituents were not determined. The structures of **7c** and **8c** were determined by comparing the spectral data with those of standard samples. **7d**: Colorless oil. Yield 4%. ^{1}H-NMR ($CDCl_3$) δ: 1.32 (3H, t, J=8 Hz), 2.31 (3H, s), 2.42 (3H, s), 3.99 (2H, q, J=8 Hz), 6.24 (1H, s), 6.43 (1H, s). MS m/z: 151 (M^+). **8d**: Colorless oil. Yield 31%. ^{1}H-NMR ($CDCl_3$) δ: 1.41 (3H, t, J=7 Hz), 2.47 (6H, s), 4.03 (2H, q, J=7 Hz), 6.48 (2H, s). Exact MS m/z (M^+) Calcd for $C_9H_{13}NO$: 151.105. Found: 151.102.

General Procedure for the Reaction of 1,2,3-Triazine 2-Imine 10 with 2 Compound **10** (0.6 mmol) and **2** (1.2 mmol) were dissolved in benzene and the solution was refluxed for 1.2 h. The benzene was evaporated off *in vacuo* and the residue was chromatographed on a silica gel column (CH_2Cl_2: Et_2O = 1 : 1) to give **11** in 20—56% yield. **11a**: Colorless needles from Et_2O–AcOEt; mp 145°C. *Anal.* Calcd for $C_8H_{10}N_4$: C, 59.24; H, 6.21; N, 34.55. Found: C, 58.56; H, 6.08; N, 34.22. Exact MS *m/z* (M^+) Calcd for $C_8H_{10}N_4$: 162.086. Found: 162.091. ^{1}H-NMR ($CDCl_3$) δ: 2.63 (3H, s), 2.68 (3H, s), 2.87 (3H, s), 6.64 (1H, s). ^{13}C-NMR ($CDCl_3$) δ: 9.92, 16.54, 24.71, 110.64, 133.40, 142.82, 154.52, 159.61. **11b**: Colorless needles from Et_2O–AcOEt; mp 173 °C. *Anal.* Calcd for $C_{13}H_{12}N_4$: C, 69.62; H, 5.39; N, 24.99. Found: C, 69.50; H, 5.34; N, 25.12. ^{1}H-NMR ($CDCl_3$) δ: 2.73 (3H, s), 2.95 (3H, s), 7.23 (1H, s), 7.45—8.16 (5H, m). ^{13}C-NMR ($CDCl_3$) δ: 10.3, 17.3, 107.0, 127.1, 128.7, 130.5, 134.7, 136.5, 140.8, 143.1, 156.4. **11c**: Colorless needles from Et_2O–AcOEt; mp 191 °C. *Anal.* Calcd for $C_{18}H_{14}N_4$: C, 75.50; H, 4.93; N, 19.57. Found; C, 75.54; H, 4.88; N, 19.59. ^{1}H-NMR ($CDCl_3$) δ: 2.74 (3H, s), 7.40 (1H, s), 7.40—8.20 (10H, m).

X-Ray Crystallography of 11b The observed cell parameters for a crystal of **11b** (0.40 × 0.30 × 0.50 mm) obtained from a CH_3OH solution are as follows: molecular formula $C_{13}H_{12}N_4$, molecular weight 224.27, space group $P2_1/a$ (monoclinic), $Z=4$, $a=14.283$ (1), $b=11.678$ (1), $c=6.835$ (4) Å, $\beta=101.57$ (1)°, $V=1116.9(2)$Å^3, $D_c=1.334$ g·cm^{-3}. Data were collected on a Rigaku AFC-5 diffractometer using graphite monochromated Cu$K\alpha_1$ radiation by the θ–2θ scan method. The scan speed was 16° min^{-1}. The data were corrected for Lorentz and polarization factors, but no absorption correction was applied. A total of 1969 reflections were measured within the 2θ angle of 120°. The crystal structure was determined by the direct method and refined by the full-matrix least-squares procedure. The final *R* value was 0.055 for 1421 reflections above 3σ (*F*) including anisotropic thermal factors for nonhydrogen atoms and isotropic ones for hydrogen atoms. The final atomic coordinates for nonhydrogen atoms are listed in Table IV.

General Procedure for the Oxidation of 2,5-Dihydrotriazine 12 The starting materials **12** were synthesized by the reduction of the corresponding 2-methyltriazinium iodide. Compound **12** (1 mmol) was dissolved in CH_2Cl_2 under a nitrogen atmosphere in order to avoid air oxidation, and was stirred with 2 mmol of *m*CPBA at 0 °C for 12 h. After purification by alumina column chromatography, products were obtained as follows. 2-Methyl-4-phenyl-1,2,3-triazole **13** was identified by comparison of the spectral data with those of a standard sample.[13] **14a**: Colorless oil. IR ν_{max}^{KBr} 1610 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.28 (6H, s), 4.09 (3H, s). Exact MS *m/z* (M^+) Calcd for $C_6H_9N_3O$: 139.075. Found: 139.077. **14b**: Colorless needles from hexane; mp 94 °C. *Anal.* Calcd for $C_{11}H_{11}N_3O$: C, 65.67; H, 5.51; N, 20.88. Found: C, 65.88; H, 5.51; N, 20.91. ^{1}H-NMR ($CDCl_3$) δ: 2.37 (3H, s), 4.17 (3H, s), 7.39—7.46 (3H, m), 8.24—8.30 (2H, m).

Reaction of 2-Methyltriazinium Iodide 15 with 2 One of **15a—c** (1 mmol) and 2.4 mmol of **2** were dissolved in 20 ml of benzene and the solution was refluxed for 3 h. The solvent was evaporated off and the residue was chromatographed on an alumina column (CH_2Cl_2). Compound **17** was obtained quantitatively in all cases. **17**: Pale yellow needles from benzene; mp 201 °C. *Anal.* Calcd for $C_{16}H_{30}IN_3$: C, 49.10; H. 7.67; N, 10.74. Found: C, 49.37; H, 7.89; N, 10.95. ^{1}H-NMR ($CDCl_3$) δ: 1.20 (12H, t, $J=7$ Hz), 2.35 (6H, s), 3.40 (8H, q, $J=7$ Hz), 4.06 (3H, s), 7.79 (1H, s). ^{13}C-NMR ($CDCl_3$) δ: 13.9, 18.4, 42.2, 46.1, 129.5, 150.6, 154.8.

References and Notes

1) A. Ohsawa, H. Arai, H. Ohnishi, T. Itoh, T. Kaihoh, M. Okada, and H. Igeta, *J. Org. Chem.*, **50**, 5520 (1985).
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