Amidrazones and Related Compounds. V.[1] The Formation of Pyrazole, 1*H*-1,2,4-Triazepine, and 4*H*,11*H*-[1,5]Diazocino-[2,3-*e*: 6,7-*e*']di[1*H*-1,2,4]triazepine Derivatives

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(Received September 30, 1976)

Amidrazones $RC(NH_2)=NNH_2$ (**1a**, **b**) (R=2-pyridyl, phenyl) reacted with $EtOCH=CR^1R^2$ (**2a—d**) (R^1,R^2=CN, $CO_2C_2H_5$, $COCO_2C_2H_5$) to give $RC(NH_2)=NNHCH=CR^1R^2$ (**3a—g**). 3,4-Disubstituted pyrazoles (**4a**, **b**) were obtained on the heating of **3a**, **b**, **e**, and **f** (R=2-pyridyl, phenyl, R^1=CN, R^2=CN, $CO_2C_2H_5$) in toluene. However, the heating of **3c** (R=2-pyridyl, $R^1=R^2=CO_2C_2H_5$) gave a dimer, the 2,3,7,9,10-pentaazadodeca-1,4,8,11-tetraene derivative (**9**), instead of **4**. 5-Amino-6-ethoxycarbonyl-3-(2-pyridyl)-1*H*-1,2,4-triazepine (**10**) was obtained by the reaction of **3a** (R=2-pyridyl, R^1=CN, $R^2=CO_2C_2H_5$) with ethanolic hydrogen chloride. The treatment of **10** with alkaline gave 2,9-di-2-pyridyl-6,7,13,14-tetrahydro-4*H*,11*H*-[1,5]diazocino-[2,3-*e*: 6,7-*e*']di[1*H*-1,2,4]triazepine-6,13-dione (**11**). Triazepine (**10**) reacted with hydrazines to give 5-hydrazino-1*H*-1,2,4-triazepine derivatives (**13a**, **b**).

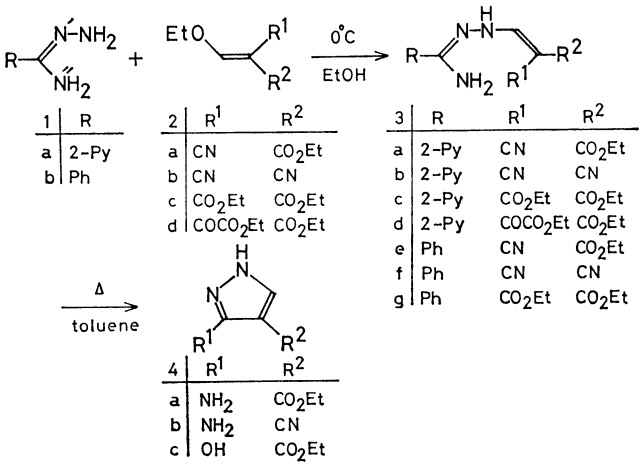
Amidrazones[2] show a strong nucleophilicity similar to hydrazine and are known as versatile reagents in the synthesis of some nitrogen heterocycles. However, the synthesis of monocyclic 1,2,4-triazepine derivatives by the use of amidrazone has not been reported. The fully or partially saturated monocyclic 1,2,4-triazepine derivatives have been synthesized by the reactions of thiosemicarbazides with malonyl dichloride,[3a,b] β-keto esters,[4,5] β-diketo compounds,[4] and 1,1,3,3-tetraethoxypropane.[6] On the other hand, the synthesis of fully unsaturated monocyclic 1,2,4-triazepine derivatives has been reported recently; 2*H*-1,2,4-triazepines were prepared by the cycloaddition reaction of 1,2,4,5-tetrazines with 1-azirines,[7a—d] and 4*H*-1,2,4-triazepines were formed photochemically from 3,4,7-triaza-2,4-norcaradienes.[8]

In the present paper we wish to report the results of the attempted synthesis of the 1*H*-1,2,4-triazepine derivative from amidrazones and ethoxymethylenic compounds.

Results and Discussion

When picolinamidrazone (**1a**) was treated with ethoxymethylenic compounds (**2a—d**) in EtOH at 0 °C, the products isolated were *N*-(2,2-disubstituted vinyl)-picolinamidrazones (**3a—d**). Similarly, the treatment of benzamidrazone (**1b**), which was generated *in situ* by the reaction of ethyl benzimidate with hydrazine hydrate, with **2a—c** gave **3e—g**. The physical properties and spectral data, shown in Table 1, are consistent with the assigned structure.

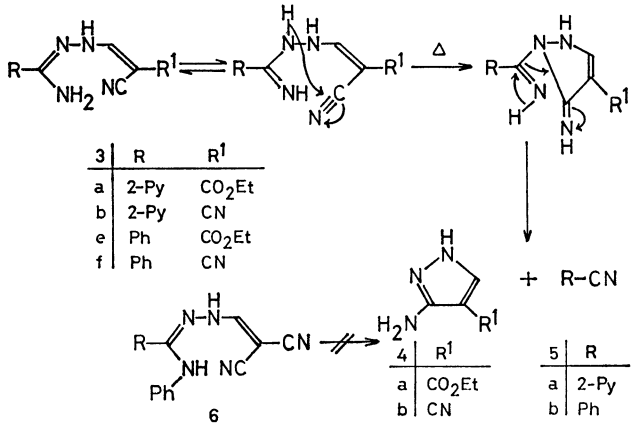
Next, the thermal and acid- or base-catalyzed cyclizations of **3** to 1,2,4-triazepine derivatives were attempted. When a toluene solution of **3a** was heated for 4 h, a product was obtained in an 87% yield as white needles. Its mp and IR spectrum were consistent with those of ethyl 3-amino-4-pyrazolecarboxylate (**4a**).[9] Similarly, the heating of a toluene solution of **3b** gave a white crystalline product (91% yield) which was identical with 3-amino-4-cyanopyrazole (**4b**).[10] In a similar manner, **4a** and **4b** were obtained from **3e** and **3f** respectively. It can be assumed that the formation of **4a** and **4b** has occurred by mean of the intramolecular nucleophilic attack of the N′ atom on the cyano group,



Scheme 1.

followed by the elimination of arylnitrile, as is shown in Scheme 2. In fact, when a toluene solution of *N*-(2,2-dicyanovinyl)-*N*″-phenylbenzamidrazone (**6**) was heated for 24 h, the pyrazole derivative was not obtained as expected, and the starting material was recovered.

However, on the treatment of **3c** in a similar manner, the pyrazole derivative was not obtained, rather yellow needles were obtained in a 45% yield. The IR spectrum showed the absorption band of the amide NH at 3440



Scheme 2.

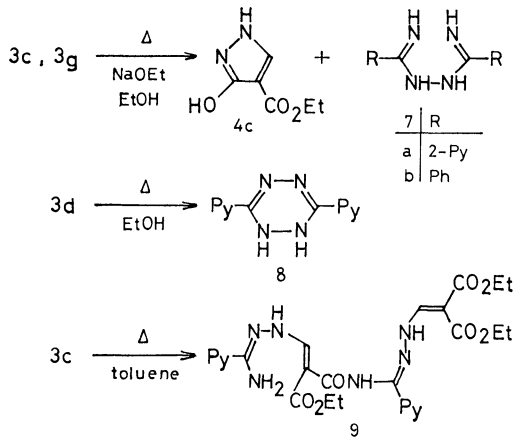
TABLE 1. THE PHYSICAL PROPERTIES AND THE SPECTRAL DATA OF **3**

Compd	Yield (%)	Mp (°C) (Solvent)	Molecular formula	Found (Calcd) C%	Found (Calcd) H%	IR (KBr) cm^{-1}	NMR δ, ppm
3a[a]	92	126—129 (MeOH)	$C_{12}H_{13}N_5O_2$	55.84 (55.59	5.08 5.05)	3300, 3200, 2200, 1685	10.85 (s, =NH), 7.63 (s, =CH–), 7.88—8.60 (m, aromatic H), 7.03 (s, $-NH_2$), 4.14 (q, J= 6.8 Hz, $-CH_2-$), 1.20 (t, J=6.8 Hz, $-CH_3$)
3b[b]	97	129—132 (MeOH)	$C_{10}H_8N_6$	56.81 (56.59	4.05 3.80)	3390, 3310, 2200	10.10 (s, =NH), 7.56 (s,=CH–), 7.59—8.71 (m, aromatic H), 6.99 (s, $-NH_2$)
3c[b]	71	131—132 (MeOH)	$C_{14}H_{18}N_4O_4$	55.06 (55.38	5.84 5.65)	3480, 3340, 3200, 1680	11.58 (d, J=11.4 Hz, =NH), 8.47 (d, J= 11.4 Hz,=CH–), 7.29—8.52 (m, aromatic H), 5.80 (s, $-NH_2$), 4.26 (q, J=6.8 Hz, $-CH_2-$), 4.20 (q, J=6.8 Hz, $-CH_2-$), 1.36 (t, J=6.8 Hz, $-CH_3$), 1.30 (t, J=6.8 Hz, $-CH_3$)
3d[b]	80	123—125 (MeOH)	$C_{15}H_{18}N_4O_5$	54.08 (53.88	5.43 5.43)	3440, 3340, 1720, 1695	8.51 (d, J=11.4 Hz, =CH–), 7.36—8.58 (m, aromatic H), 6.21 (s, $-NH_2$), 4.23 (q, J=6.8 Hz, $-CH_2-$), 4.33 (q, J=6.8 Hz, $-CH_2-$), 1.34 (t, J=6.8 Hz, $-CH_3$), 1.27 (t, J=6.8 Hz, $-CH_3$)
3e[a]	61	129—131 (EtOH)	$C_{13}H_{14}N_4O_2$	60.16 (60.45	5.37 5.46)	3340, 3240, 2200, 1675	10.48 (s, =NH), 7.58 (s, =CH–), 7.19—8.07 (m, aromatic H), 6.90 (s, $-NH_2$), 4.20 (q, J=6.8 Hz, $-CH_2-$), 1.25 (t, J=6.8 Hz, $-CH_3$)
3f	94	150—155 (benzene-MeOH)	$C_{11}H_9N_5$	62.48 (62.55	4.30 4.30)	3400, 3280, 2200	
3g[a]	78	140—142 (EtOH)	$C_{15}H_{19}N_3O_4$	58.69 (59.00	6.12 6.27)	3310, 3220, 1674, 1653	11.28 (d, J=10.8 Hz, =NH), 8.26 (d, J= 10.8 Hz, =CH–), 7.35—8.15 (m, aromatic H), 6.81 (s, $-NH_2$), 4.08 (q, J=6.8 Hz, $-CH_2-$), 1.22 (t, J=6.8 Hz, $-CH_3$)

a) The NMR spectrum was measured in DMSO-d_6. b) The NMR spectrum was measured in $CDCl_3$.

cm^{-1} and those of the carbonyl groups at 1645—1695 cm^{-1}. The mass spectrum showed the parent peak at *m/e* 566. From the above data and the results of the elemental analysis, the product was confirmed to be a dimer,triethyl 1-amino-6-oxo-1,8-di-2-pyridyl-2,3,7,9,10-pentaazadodeca-1,4,8,11-tetraene-5,12,12-tricarboxylate (**9**). The treatment of **3c** in EtOH in the presence of sodium ethoxide gave **4c**[11] and 1,2-bis(2-pyridylcarbonimidoyl)hydrazine (**7a**).[12a,b] Similarly, **4c** was obtained from **3g** in the same manner, but the method failed to isolate the corresponding product (**7b**). On the heating of an ethanol solution of **3d**, an orange product was obtained and revealed to be 1,2-dihydro-3,6-di-2-pyridyl-1,2,4,5-tetrazine (**8**).[13a,b]

When **3a** was treated with an ethanolic hydrogen chloride, followed by neutrallization with sodium hydrogen carbonate, a product was obtained in a 57% yield as white needles. The IR spectrum indicated the presence of ester (1700 cm^{-1}) and amino (3320—3110 cm^{-1}) groups, but it did not show the absorption band of the cyano group at *ca.* 2200 cm^{-1}. The ester group was confirmed by the signals at δ 3.96 and δ 1.15 ppm due to the ethyl group. Considering the above data and the parent peak at *m/e* 259, the structure of the product can clearly be assigned to the desired compound, 5-amino-6-ethoxycarbonyl-3-(2-pyridyl)-1*H*-1,2,-4-triazepine (**10**). However, all attempts at the cyclization of **3b**—**g** to 1*H*-1,2,4-triazepine derivatives were unsuccessful. Then the reactivity of **10** was studied. When an aqueous sodium hydroxide solution of **10** was

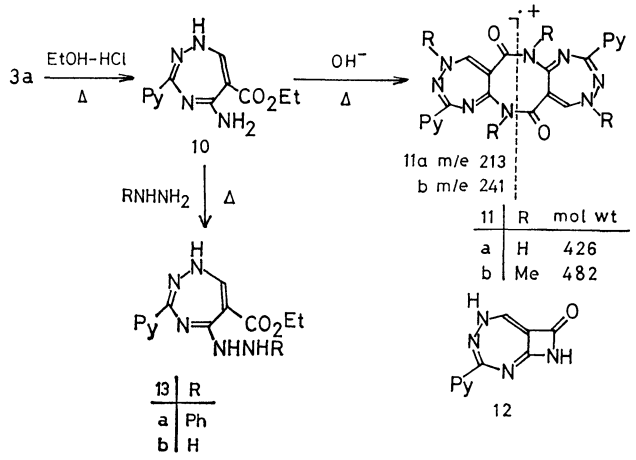


Scheme 3.

heated, a product was obtained in a 74% yield as white powder. According to the emperical formula, $C_{10}H_7N_5O$, and the mass spectral parent peak at *m/e* 213, the product seems to be [2,3-*e*][1*H*-1,2,4]triazepine (**12**). However, the carbonyl absorption observed at the comparably low frequency (1680 cm^{-1}) is in conflict with the strained β-lactam structure, **12**. Consequently, the only possible structure which satisfies both the analytical and mass spectral results is the dimeric and symmetric one, 2,9-di-2-pyridyl-6,7,13,14-tetrahydro-4*H*,11*H*-[1,5]diazocino[2,3-*e*: 6,7-*e'*]di[1*H*-1,2,4]triazepine-6,13-dione (**11a**), which belongs to a new ring system. A similar condensation, followed by a dimeriza-

tion reaction, that is the conversion of 4-amino-5-ethoxycarbonyl-pyrimidine to 5,6,11,12-tetrahydro[1,5]-diazocino[2,3-*d*: 6,7-*d'*]dipyrimidine-5,11-dione, has been reported by Bredreck *et al.*[14] Additional support for the structure of **11a** was provided by its methylation with methyl iodide. The IR spectrum of the product showed the absorption band of the carbonyl at 1705 cm^{-1} and none of the imino group in the NH region. The NMR spectrum showed the two singlet signals at δ 4.20 and δ 3.82 ppm due to two pairs of four methyl groups, although the mass spectrum showed the parent peak at *m/e* 241 corresponding to half the molecular weight. These data show the structure to be a tetramethyl derivative (**11a**).

The treatment of **10** with phenylhydrazine gave a substituted product, 6-ethoxycarbonyl-5-(2-phenylhydrazino)-3-(2-pyridyl)-1*H*-1,2,4-triazepine (**13a**), whose structure was clarified on the basis of the spectral and analytical measurements. Similarly, the treatment of **10** with hydrazine hydrate gave corresponding product (**13b**).



Scheme 4.

Experimental

All the melting points are uncorrected. The IR, UV, and NMR spectra were measured with a JASCO Model IRA-2 spectrometer, a Shimadzu Model MPS-501 spectrometer, and a Hitachi Model R-20 spectrometer respectively. A Shimadzu Model UM-3B apparatus was used for the elemental analysis.

Materials. The compounds **1a**,[15] **2a**,[16] **2b**,[16] and **2d**[17] were prepared by the reported methods. The **2c** was commercially available.

N-(2-Cyano-2-ethoxycarbonylvinyl)picolinamidrazone (3a). To a stirred solution of **2a** (1.01 g, 6.0 mmol) in EtOH (15 ml), was added **1a** (0.82 g, 6.0 mmol) at 0 °C. After the stirring had continued for 30 min, the resulting precipitates were filtered and dried to give **3a** (1.43 g, 92%). Recrystallization from MeOH afforded yellow plates; mp 126—129 °C. **3b—d** were prepared by the same procedure.

N-(2-Cyano-2-ethoxycarbonylvinyl)benzamidrazone (3e). Ethyl benzimidate hydrochloride[18] (1.91 g, 10.2 mmol) was added to an aq solution (10 ml) containing potassium hydroxide (10.2 mmol). The resulting oil was extracted twice with ethyl acetate (10 ml), and the organic phase was concentrated *in vacuo*. The oily residue was dissolved into EtOH (10 ml), and hydrazine hydrate (532 mg, 10.5 mmol) was stirred into this solution in portions at 0 °C. After the stirring had continued for 2 h, at 0 °C, **2a** (1.74 g, 10.3 mmol) was added to the EtOH solution with stirring at 0 °C. After the stirring had continued for 30 min, the precipitates were filtered and dried to give **3e** (1.63 g, 61% based on the hydrochloride). Recrystallization from EtOH afforded yellow needles; mp 129—131 °C. **3e** and **g** were prepared by the same procedure.

Ethyl 3-Amino-4-pyrazolecarboxylate (4a). A toluene solution (20 ml) of **3a** (520 mg, 2.0 mmol) was refluxed for 4 h. After cooling at 0 °C, the precipitates were filtered and dried to give **4a** (270 mg, 87%). Recrystallization from benzene afforded white needles; mp 100—101 °C. Its mp, TLC, and IR spectrum were identical with those of the authentic sample.[9] **4a** was also obtained from **3e** by the same procedure (84%).

3-Amino-4-cyanopyrazole (4b). A toluene solution (10 ml) of **3b** (420 mg, 2.0 mmol) was refluxed for 8 h. After cooling, the precipitates were filtered and dried to give **4b** (200 mg, 91%). Recrystallization from benzene–THF afforded white needles; mp 171—174 °C. Its mp TLC, and IR spectrum were identical with those of the authentic sample.[10] **4b** was also obtained from **3f** by the same procedure (71%).

N-(2,2-Dicyanovinyl)-N″-phenylbenzamidrazone (6). To a stirred solution of **2b** (122 mg, 1.0 mmol) in EtOH (5 ml) was added *N″*-phenylbenzamidrazone[19] (211 mg, 1.0 mmol) at room temperature. After 30 min, the resulting precipitates were filtered and dried to give **6** (159 mg, 55%). Recrystallization from EtOH afforded white needles; mp 223—226 °C. Found: C, 71.26; H, 4.47%. Calcd for $C_{17}H_{13}N_5$: C, 71.06; H, 4.56%. IR (KBr): 3360, 3250, 2200, 1640, 1618, 1550 cm^{-1}.

Ethyl 3-Hydroxy-4-pyrazolecarboxylate (4c) and 1,2-Bis(2-pyridylcarbonimidoyl)hydrazine (7a). To a solution of sodium ethoxide (3.0 mmol) in EtOH (10 ml) was added **3c** (569 mg, 1.9 mmol), after which the solution was refluxed for 2 h. The resulting sodium salts were filtered, dissolved in water (10 ml), and neutralized with dil hydrochloric acid. After cooling, white crystals were filtered out and dried to give **4c** (86 mg, 30%). Recrystallization from MeOH–H_2O afforded white needles; mp 182—183 °C. Its mp, TLC, and IR spectrum were identical with those of the authentic sample.[11] Then the filtrate was concentrated *in vacuo*, and a small amount of water was added to the residue. The resulting yellow crystals were filtered and dried to give **7a** (15 mg, 8%). Recrystallization from MeOH afforded yellow needles; mp 208—210 °C. Its mp, TLC, and IR spectrum were identical with those of the authentic sample.[12a,b] **4c** was also obtained from **3g** by the same procedure (30%).

1,2-Dihydro-3,6-di-2-pyridyl-1,2,4,5-tetrazine (8). An EtOH solution (10 ml) of **3d** (337 mg, 1.0 mmol) was refluxed for 24 h. After cooling, the precipitates were filtered and dried to give **8** (23 mg, 29%). Recrystallization from EtOH afforded orange needles; mp 198—202 °C. Its mp, TLC, and IR spectrum were identical with those of the authentic sample.[13a,b]

Triethyl 1-Amino-6-oxo-1,8-di-2-pyridyl-2,3,7,9,10-pentaaza-1,4,8,11-tetraene-5,12,12-tricarboxylate (9). A toluene solution (15 ml) of **3c** (461 mg, 1.5 mmol) was refluxed for 9 h. After cooling, the toluene was evaporated *in vacuo*, and a small amount of MeOH was added to the residue. Crystallization was induced by scratching the flask, and the resulting precipitates were filtered and dried to give **9** (194 mg, 45%). Recrystallization from MeOH–benzene afforded yellow needles; mp 196—198 °C. Found: C, 55.50; H, 5.35%. Calcd for $C_{26}H_{30}N_8O_7$: C, 55.12; H, 5.30%. IR (KBr):

3440, 3140, 2960, 1695, 1670, 1645, 1615, 1500 cm^{-1}. MS *m/e* (%): 566 (M^+, 0.4), 359 (3), 332 (5), 260 (7), 162 (10), 147 (40), 110 (20), 105 (100), 79 (26), 78 (30). UV (MeOH, nm (log ε)): 223 (4.50), 328 (sh, 4.70), 341 (4.80), 370 (sh, 4.40).

5-Amino-6-ethoxycarbonyl-3-(2-pyridyl)-1H-1,2,4-triazepine (10). A solution of **3a** (1.58 g, 6.1 mmol) in ethanolic hydrogen chloride (0.2 M, 46 ml) was refluxed for 1 h. The solvent was then evaporated *in vacuo*, and the water (10 ml) was added to the residue. The acidic solution was neutrallized with sodium hydrogen carbonate. After cooling, the resulting precipitates were filtered and dried to give **10** (901 mg, 57%). Recrystallization from MeOH–DMF afforded white needles; mp 200 °C (dec). Found: C, 55.63; H, 5.12%. Calcd for $C_{12}H_{13}N_5O_2$: C, 55.59; H, 5.05%. IR (KBr): 3320, 3250, 3110, 1700 cm^{-1}. NMR of **10**·HCl (D_2O): δ 7.97 (s, 1H, =CH–), 7.45—8.38 (m, 4H, aromatic H), 3.96 (q, J= 6.8 Hz, 2H, $-CH_2-$), 1.15 (t, J=6.8 Hz, 3H, $-CH_3$). MS *m/e* (%): 259 (M^+, 69), 214 (14), 186 (100), 155 (95), 109 (86), 105 (53), 78 (44). UV (MeOH, nm, (log ε)): 221 (4.29), 278 (3.96), 300 (3.98).

2,9-Di-2-pyridyl-6,7,13,14-tetrahydro-4H,11H-[1,5]diazocino-[2,3-e:6,7-e']di[1H-1,2,4]triazepine-6,13-dione (11a). A solution of **10** (266 mg, 1.0 mmol) in aq NaOH (0.2 M, 10 ml) was refluxed for 1 h. After cooling, the solution was neutrallized with dil hydrochloric acid, and the resulting precipitates were filtered and dried to give **11a** (162 mg, 74%). Recrystallization from DMF–MeOH afforded white powder; mp>300 °C. Found: C, 56.17; H, 3.43%. Calcd for $C_{20}H_{14}N_{10}O_2$: C, 56.33; H, 3.31%. IR (KBr): 3200, 1680, 1550 cm^{-1}. NMR (CF_3COOH): δ 8.20—9.20 (m, 10H, aromatic H and =CH–). MS *m/e* (%): 213 (93), 157 (3), 135 (9), 109 (100), 105 (20), 89 (14), 88 (24), 78 (5). UV (MeOH, nm (log ε)): 228 (4.61), 301 (4.43).

2,9-Di-2-pyridyl-4,7,11,14-tetramethyl-6,7,13,14-tetrahydro-4H,11H-[1,5]diazocino[2,3-e:6,7-e']di[1H-1,2,4]triazepine-6,13-dione (11b). To a suspension of NaH (41 mg, about 50% in oil, 0.85 mmol) in *N,N*-dimethylacetamide (5 ml) added **11a** (113 mg, 0.27 mmol) in portions. After the evolution of hydrogen had ceased, methyl iodide (0.5 ml) was added, and the mixture was stirred at room temperature for 1 day. The reaction mixture was poured into water (20 ml), the resulting precipitates were filtered off, and then the filtrate was extracted three times with ethyl acetate (20 ml). The organic phase was evaporated *in vacuo*, and a small amount of ether was added to the residue. The resulting precipitates were filtered and dried to give **11b** (60 mg, 46%). Recrystallization from MeOH afforded white needles; mp 266—227 °C. Found: C, 59.71; H, 4.62%. Calcd for $C_{24}H_{22}N_{10}O_2$: C, 59.74; H, 4.60%. IR (KBr): 3100, 2960, 1705, 1560, 1550 cm^{-1}. NMR (CF_3COOH): δ 8.25—9.30 (m, 10H, aromatic H and =CH–), 4.20 (s, 6H, $-CH_3$), 3.82 (s, 6H, $-CH_3$). MS *m/e* (%): 241 (100), 240 (72), 213 (6), 212 (13), 171 (7), 105 (4), 82 (16), 79 (24). UV (MeOH, nm (log ε)): 213 (4.66), 261 (sh, 4.18), 282 (4.23).

6-Ethoxycarbonyl-5-(2-phenylhydrazino)-3-(2-pyridyl)-1H-1,2,4-triazepine (13a). A mixture of **10** (132 mg, 0.5 mmol) and phenylhydrazine (117 mg, 1.1 mmol) in EtOH (10 ml) was refluxed. After 3 h, additional phenylhydrazine (113 mg, 1.0 mmol) was added to the reactoin mixture and it was refluxed for 4 h again. After cooling, the precipitates were filtered off and the filtrate was concentated *in vacuo*. A small amount of ether was added to the residue, and crystallization was induced by scratching the flask. The resulting precipitates were filtered and dried to give **13a** (77 mg, 44%). Recrystallization from MeOH–H_2O afforded yellow plates; mp 181—183° °C. Found: C, 61.69; H, 5.11%. Calcd for $C_{18}H_{18}N_6O_2$: C, 61.70; H, 5.18%. IR (KBr): 3320, 3240, 3020, 2980, 1670, 1570, 1550 cm^{-1}. NMR (DMSO-d_6): δ 9.72 (br, 1H, =NH), 8.12 (s, 1H, =CH–), 7.60—8.58 (m, 4H, aromatic H), 7.03—7.55 (m, 5H, aromatic H), 6.75 (br, 1H, =NH), 4.34 (q, J=7.0 Hz, 2H, $-CH_2-$), 1.40 (t, J= 7.0 Hz, 3H, $-CH_3$).

6-Ethoxycarbonyl-5-hydrazino-3-(2-pyridyl)-1H-1,2,4-triazepine (13b). A mixture of **10** (529 mg, 2.0 mmol) and 100% hydrazine hydrate (213 mg, 4.0 mmol) was refluxed, with stirring, for 1 h, After cooling, the resulting precipitates were filtered and dried to give **13b** (161 mg, 29%). Recrystallization from benzene–THF afforded pale yellow particles; mp 163—166 °C. Found: C, 52.50; H, 5.18%. Calcd for $C_{12}H_{14}N_6O_2$: C, 52.54; H, 5.15%. IR (KBr): 3380, 3120, 1700, 1580, 1535 cm^{-1}.

The authors wish to express their thanks to Professor Masaki Ohta for his encouragement, to Dr. Masatoshi Hirayama and Mr. Mamoru Sekine for the NMR measurements, and to Sankyo Co., Ltd., for the mass measurements.

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