Reactions of Azomethine Derivatives. IV.[1] The Synthesis of 2,3,5-Trisubstituted 2-Pyrrolin-4-ones and Their Oxidation to 2,4,5-Trisubstituted 1,3-Oxazin-6-ones

Masahiko TAKAHASHI,* Nobuyuki INABA, Hiroji KIRIHARA, and Shin-ichi WATANABE

Department of Industrial Chemistry, Faculty of Engineering, Ibaraki University, Hitachi, Ibaraki 316

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The reaction of aromatic azines with diphenylcyclopropenone in refluxing toluene gave 5-aryl-2,3-diphenyl-2-pyrrolin-4-ones (**4**) in moderate yields *via* initial [2+3] 1:1 cycloaddition and subsequent elimination of an aromatic nitrile from the adducts. Treatment with phosphorus pentasulfide deoxygenated the compounds **4** to 5-aryl-2,3-diphenyl-pyrroles. The same compounds **4** were oxidized to 2-aryl-4,5-diphenyl-1,3-oxazin-6-ones (**11**) by refluxing the pyridine solution in a stream of oxygen, by treatment with hydrogen peroxide, or by irradiation of the chloroform solution in a stream of oxygen. Treatment with alkali in aqueous pyridine converted **4** into 3-aroylamino-2,3-diphenylacrylic acids. These were also obtained from the hydrolysis of **11**. When *p*-dimethylaminobenzaldehyde azine reacted with diethyl azodicarboxylate in refluxing toluene, a 1:2 conjugated adduct, 3,6-bis(*p*-dimethylaminophenyl)-1,2,7,8-tetrakis(ethoxycarbonyl)-1,2,4,5,7,8-hexaaza-3,5-octadiene, and a 1:1 conjugate adduct, 3,6-bis(*p*-dimethylaminophenyl)-1,2-bis(ethoxycarbonyl)-1,2,4,5-tetraaza-3,5-hexadiene, were obtained.

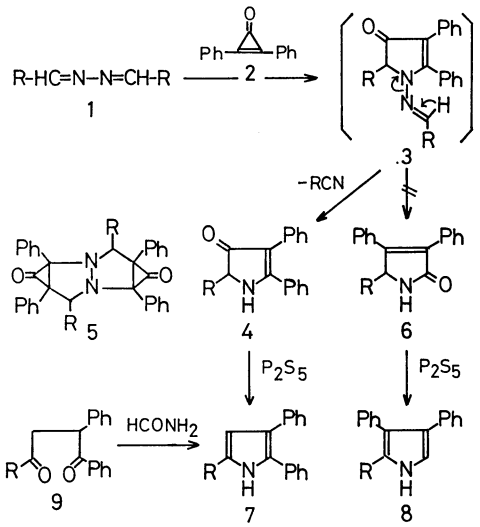
The cycloaddition reactions of azines with various dipolarophiles generally give criss-cross 1:2 adducts.[2] Eicher *et al.* have reported [2+3] cycloaddition reactions of aldimines,[3] ketimines,[4] guanidines,[5] and benzamidines[5] with diphenylcyclopropenone to give 2,3-diphenyl-2-pyrrolin-4-ones as reaction intermediates or products. When appropriately substituted amidines and guanidines were used for the reaction, 5,6-dihydropyrimidin-4-ones were produced.[6]

In the course of our study of cycloaddition reactions of heterodienes containing azomethine groups,[1] these publications prompted us to investigate the reaction of azines **1** with diphenylcyclopropenone (**2**); we obtained 5-aryl-2,3-diphenyl-2-pyrrolin-4-ones (**4**).[7] These pyrrolinones **4** were found to be oxidized by oxygen, by hydrogen peroxide, or by irradiation in a stream of oxygen to 2-aryl-4,5-diphenyl-1,3-oxazin-6-ones (**11**). Although many oxidation reactions of pyrroles have been reported,[8] little is known concerning the oxidation reactions of 2-pyrrolin-4-ones: 2,5-dimethyl-1-phenyl-2-pyrrolin-4-one was reported to be oxidized to 5-hydroxy derivative,[9] and 2,3-dimethyl-2-pyrrolin-4-one was found to be oxidized to tetramethylpyrrole indigo[10] or 3-pyrrolin-5-one derivative.[11] To the best of our knowledge the oxidative ring-enlargement of 2-pyrrolin-4-ones has not been reported. Moreover, the resulting oxadinones **11** belong to relatively rare derivatives of 1,3-oxazines.[12]

When azines **1** reacted with diethyl azodicarboxylate, similar cycloaddition reactions were not observed; the 1:2 and 1:1 conjugate addition products (**13** and **14**, respectively) were obtained in the case of **1e**.

Results and Discussion

When a mixture of *p*-methoxybenzaldehyde azine (**1a**) and diphenylcyclopropenone (**2**) in toluene was refluxed, a yellow crystalline product was obtained in 55% yield. The molecular formula $C_{23}H_{19}O_2N$ was confirmed on the basis of the elemental analysis and the mass spectrum (M^+, 341). The IR spectrum showed NH and CO absorptions at 3200 and 1640 cm^{-1}, respectively. These data suggest that the product is not an expected product such as a criss-cross 1:2 adduct **5a** or a [2+3] 1:1 adduct **3a**, but an addition-elimination product **4a** or **6a** (Scheme 1).



a: R=*p*-$MeOC_6H_4$ **b**: R=*p*-MeC_6H_4
c: R=*p*-$Me_2CHC_6H_4$ **d**: R=C_6H_5
e: R=*p*-$Me_2NC_6H_4$

Scheme 1.

In order to distinguish between two regioisomers, **4a** and **6a**, conversion of the product into the known pyrrole derivative was attempted. Thus, treatment of the product with phosphorus pentasulfide in refluxing benzene gave a deoxygenated product, which seemed to be (*p*-methoxyphenyl)diphenylpyrrole (**7a**) or (**8a**). An authentic specimen **7a**[13] prepared from **9a** was identical with the deoxygenated product; this proved that the addition-elimination product was not **6a** but 5-(*p*-methoxyphenyl)-2,3-diphenyl-2-pyrrolin-4-one (**4a**).

Other 2-pyrrolin-4-ones (**4b**—**e**) were also obtained in a similar manner from **1b**—**e** in moderate yields (35—87%). The compounds **4b** and **4d** were converted

into the corresponding pyrroles **7b** and **7d**, whose structures were identified by comparison with the authentic samples prepared from **9b** and **9d**, respectively.

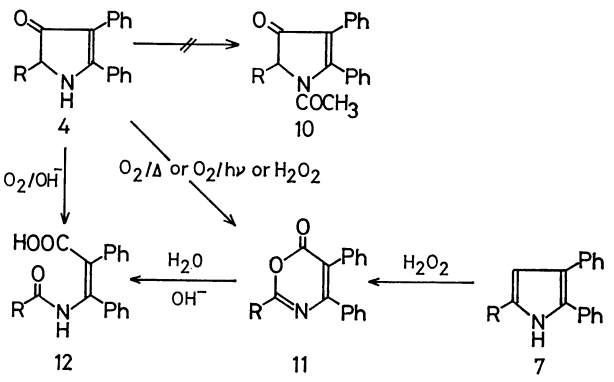
As shown in Scheme 1, the reaction is considered to proceed *via* the formation of a [2+3] cycloadduct **3**, followed by elimination of RCN. A similar process involving the initial cycloaddition to azomethine group of azine followed by elimination of RCN has been reported in the case of the reaction of azines with diphenylketene.[14]

In the course of the structure elucidation of **4a**, a mixture of **4a** in acetic acid and acetic anhydride was heated for acetylation. A product was separated in 23% yield by column chromatography. This compound showed no NH absorption and a new carbonyl absorption at 1738 cm^{-1} in the IR spectrum, but the absorption at 1640 cm^{-1} present in **4a** disappeared. These data imply that the product is not the desired acetate **10** but an auto-oxidation product, 2-(*p*-methoxyphenyl)-4,5-diphenyl-1,3-oxazin-6-one (**11a**) (Scheme 2). The compound **11a** was identical with the authentic sample prepared from **7a** by oxidation with hydrogen peroxide, according to the literature method.[15] These results suggest the possibility that **4** are generally oxidized by oxygen to 1,3-oxazin-6-ones (**11**). In fact, when the solutions of **4a—d** in pyridine were refluxed in a stream of oxygen, **11a—d** were obtained in 38—50% yields. The structures of **11b—d** were established by spectral data or by comparison with the samples derived from **7**.

Oxidations of **4** to **11** in different manners were further examined. When the solutions of **4** in chloroform were irradiated by a mercury lamp in a stream of oxygen, photooxidation products **11a** (21%), **11b** (14%), and **11c** (16%) could be isolated by column chromatography, but pure products were not obtained from **4d** and **4e**. Oxidation of **4** by hydrogen peroxide in acetic acid proceeded smoothly only in the cases of **4a** and **4c** to yield **11a** (85%) and **11c** (32%), respectively.

When a solution of **4a** in aqueous pyridine containing potassium hydroxide was stirred at room temperature, an acidic product (36%) was produced, accompanied by a mixture of neutral products, whose structures could not be determined because of low yields and difficulties in purification. The IR spectrum of the acidic product showed carboxyl absorptions at 3020 and 1688 cm^{-1} and an amide absorption at 1640 cm^{-1}. Consideration of the mass and the NMR spectra suggested that the acidic products was 3-(*p*-methoxybenzamido)-2,3-diphenylacrylic acid (**12a**). The structure of **12a** was further confirmed by comparing the samples obtained by the alkaline hydrolysis of **11a** under the same conditions. The compounds **12b** (25%), **12c** (26%), and **12d** (41%) were similarly obtained, and their structures were assigned by the spectral data or by comparison with the samples derived from **11**.

To explain the formation of 3-aroylamino-2,3-diphenylacrylic acids and indenone derivatives from aldimines and diphenylcyclopropenone, Eicher *et al.*[3] proposed a mechanism where the initially formed

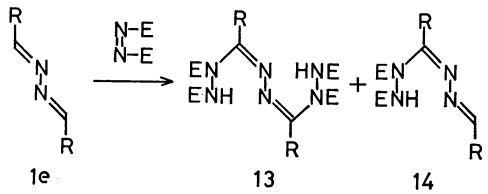


a: R=*p*-$MeOC_6H_4$ **b**: R=*p*-MeC_6H_4
c: R=*p*-$Me_2CHC_6H_4$ **d**: R=C_6H_5

Scheme 2.

2-pyrrolin-4-ones were oxidized by air to 1,3-oxazin-6-ones, which subsequently underwent hydrolysis to acrylic acids or ring-opening, followed by cyclization to indenones. Taking into account this explanation and our experiments on the hydrolysis of **11** to **12**, the oxidative cleavage of **4** to **12** appears to proceed *via* **11**. On the other hand, for the formation of **11**, the following pathway seems plausible: 2-pyrrolin-4-ones (**4**) are first cleaved to acrylic acids **12**, which are subsequently dehydrated to **11**. This pathway, however, may not be possible, since treatment of **12d** under the same conditions as the oxidation of **4** to **11**, that is, heating of **12d** in pyridine in a stream of oxygen, yielded **11d**, but the corresponding **11a—c** were not formed in the cases of **12a—c**, which gave unidentified products. To clarify the oxidation mechanism more detailed experiments will be needed.

During further studies of the reaction of azines, diethyl azodicarboxylate was found to add to *p*-dimethylaminobenzaldehyde azine (**1e**) in refluxing toluene, although no reaction occurred in the cases of **1b—d** and purification of the products from **1a** was difficult. Chromatographic separation of the reaction mixture from **1e** afforded two products. The first and the second eluated products proved to be a 1:2 adduct and a 1:1 adduct, respectively, on the basis of the elemental analyses and the mass spectra. The NMR spectrum of the 1:2 adduct **13** showed a singlet peak at δ 3.08 ppm due to two equivalent dimethylamino groups, suggesting a symmetrical structure. On the other hand, the NMR spectrum of the 1:1 adduct **14** showed two singlet peaks at δ 3.00 and 3.07 ppm due to two non-equivalent dimethylamino groups, suggesting an unsymmetrical structure. Moreover, the UV spectra of both **13** and **14** were very similar



R=*p*-$Me_2NC_6H_4$ E=$CO_2C_2H_5$

Scheme 3.

to those of the starting azine **1e**. From the above observations it was concluded that both **13** and **14** were not the anticipated cycloadducts, but 1,4-conjugate adducts. Although Marchetti *et al.*[16] reported the reactions of ketazines with diethyl azodicarboxylate, that is, the formation of 2-[*N*,*N'*-bis(ethoxycarbonyl)-hydrazino]cyclohexanone azines from cyclohexanone azines by conjugate addition, no reactions of aldazines have appeared in the literature.[2]

Experimental

The measurements of IR, UV, and NMR spectra and the elemental analyses were performed with the same instruments as previously described.[1b]

*Preparation of 5-Aryl-2,3-diphenyl-2-pyrrolin-4-ones (**4**).* *General Procedure*: A mixture of **1** (1.0 mmol) and **2** (1.2 mmol) in toluene (10 ml) was refluxed for 18—48 h. After cooling the precipitates were collected by filtration and recrystallized to give yellow needles **4**.

*Compound **4a***: Reaction time 18 h. Yield 55%. Mp 282—285 °C (C_6H_6). IR (KBr): 3200, 1640, 1600, 1580, 1540, 1507 cm^{-1}. UV (MeOH) nm (log ε): 243 (4.35), 383 (3.88), 250 sh (4.34). MS *m/e* (%): 341 (M^+, 42), 339 (M^+-H_2, 28), 326 (M^+ —NH, 28), 298 (326—CO, 5.1), 178 (PhC≡CPh, 100). Found: C, 81.30; H, 5.23%. Calcd for $C_{23}H_{19}O_2N$: C, 80.91; H, 5.61%.

*Compound **4b***: Reaction time 48 h. Yield 49%. Mp 269—271 °C (C_6H_6). IR (KBr): 3230, 1640, 1605, 1582, 1540, 1508 cm^{-1}. UV (MeOH) nm (log ε): 254 (4.33), 383 (3.84). Found: C, 85.01; H, 5.64%. Calcd for $C_{23}H_{19}ON$: C, 84.89; H, 5.89%.

*Compound **4c***: Reaction time 48 h. Yield 42%. Mp 274—275 °C (THF–MeOH). IR (KBr): 3240, 2960, 1640, 1605, 1582, 1542, 1510 cm^{-1}. UV (MeOH) nm (log ε): 255 (4.32), 378 (3.81). Found: C, 85.00; H, 6.23%. Calcd for $C_{25}H_{23}ON$: C, 84.95; H, 6.56%.

*Compound **4d***: Reaction time 24 h. Yield 35%. Mp 279—284 °C (sublimation) (DMF). IR (KBr): 3230, 1640, 1605, 1580, 1540, 1512 cm^{-1}. UV (MeOH) nm (log ε): 254 (4.31), 385 (3.84). Found: C, 84.81; H, 5.26%. Calcd for $C_{22}H_{17}ON$: C, 84.86; H, 5.50%.

*Compound **4e***: Reaction time 18 h. Yield 87%. Mp 244—247 °C (C_6H_6). IR (KBr): 3200, 3040, 2880, 2800, 1633, 1600, 1580, 1540, 1510 cm^{-1}. UV (MeOH) nm (log ε): 261 (4.35), 400 (4.09). Found: C, 81.47; H, 5.84%. Calcd for $C_{24}H_{22}ON_2$: C, 81.32; H, 6.26%.

*Preparation of 5-Aryl-2,3-diphenylpyrroles (**7**).* *General Procedure*: A mixture of **4** (0.50 mmol) and powdered phosphorus pentasulfide (1.0 mmol) in C_6H_6 (10 ml) was refluxed for 3 h. After cooling the undissolved materials were removed from the mixture by decantation, and the solvent was removed under reduced pressure. The resulting residue was washed with a small amount of MeOH and recrystallized once to give **7**. In the case of **7d** the residue was purified by column chromatography on silica gel with $CHCl_3$.

*Compound **7a***: Yield 70%. White prisms; mp 180—182 °C (MeOH) (lit,[13] 180 °C). IR (KBr): 3370, 3050, 1605, 1530 cm^{-1}. MS *m/e* (%): 325 (M^+, 100). NMR ($CDCl_3$): δ 3.80 (s, 3H, OMe), 6.5—7.6 (m, 15H, ArH), 8.32 (braod s, 1H, NH).

*Compound **7b***: Yield 26%. White needles; mp 116—118 °C (MeOH). IR (KBr): 3460, 3020, 2920, 1603, 1493 cm^{-1}. NMR ($CDCl_3$): δ 2.35 (s, 3H, Me), 6.6—7.5 (m, 15H, ArH), 8.35 (broad s, 1H, NH). Found: C, 89.14; H. 6.11%. Calcd for $C_{23}H_{19}N$: C, 89.28; H, 6.19%.

*Compound **7d***: Yield 31%. Pale yellow plates; mp 137—138 °C (C_6H_6-petroleum ether) (lit,[17] 140 °C).

*Preparation of **7** from **9**.* Compounds **7a** (73%), **7b** (26%), and **7d** (24%) were prepared from the corresponding **9a**, **9b**, and **9d**, respectively, according to the literature method,[13] and showed the same mps and IR spectra as those of **7** prepared from **4**.

*Treatment of **4a** with a Mixture of AcOH and Ac_2O.* A solution of **4a** (300 mg) in a mixture of AcOH (30 ml) and Ac_2O (0.3 ml) was refluxed for 10 h. The solvent was removed under reduced pressure and the resulting residue was purified by column chromatography on silica gel with $CHCl_3$ to give 2-(*p*-methoxyphenyl)-4,5-diphenyl-1,3-oxazin-6-one (**11a**) (93 mg, 23%). Recrystallization from MeOH–THF afforded yellow needles; mp 204—205 °C. IR (KBr): 1738, 1598, 1570, 1535, 1510 cm^{-1}. NMR (CF_3COOH): δ 4.03 (s, 3H, OMe), 7.1—8.5 (m, 14H, ArH). MS *m/e* (%): 355 (M^+, 53), 327 (M^+ —CO, 53), 135 (100). Found: C, 77.88; H, 4.88%. Calcd for $C_{23}H_{17}O_3N$: C, 77.73; H, 4.82%.

*Oxidation of **4** by Oxygen.* *General Procedure*: A solution of **4** (1.0 mmol) in pyridine (10 ml) was refluxed for 6—11 h in a stream of oxygen. After removal of the solvent under reduced pressure, the resulting residue was washed with a small amount of MeOH and recrystallized to give 2-aryl-4,5-diphenyl-1,3-oxazin-6-ones (**11**).

*Compound **11a***: Reaction time 6 h. Yield 46%. The mp and the IR spectrum were identical with those described above.

*Compound **11b***: Reaction time 9 h. Yield 38%. Yellow needles; mp 203—204 °C (MeOH). IR (KBr): 1730, 1610, 1600, 1570, 1545, 1505 cm^{-1}. NMR ($CDCl_3$): δ 2.45 (s, 3H, Me), 7.3—8.4 (m, 14H, ArH). Found: C, 81.17; H, 5.01%. Calcd for $C_{23}H_{17}O_2N$: C, 81.39; H, 5.05%.

*Compound **11c***: Reaction time 11 h. Compound **11c** was separated from the residue by column chromatography on silica gel with $CHCl_3$. Yield 50%. White needles; mp 131—134 °C (MeOH–THF). IR (KBr): 2960, 1732, 1610, 1600, 1565, 1548 cm^{-1}. NMR ($CDCl_3$): δ 1.28 (d, J=6.8 Hz, 6H, 2Me), 2.99 (m, 1H, CH), 7.2—8.3 (m, 14H, ArH). Found: C, 81.75; H, 5.77%. Calcd for $C_{25}H_{21}O_2N$: C, 81.72; H, 5.76%.

*Compound **11d***: Reaction time 9 h. Yield 45%. Yellow needles; mp 206—207 °C (MeOH–THF). The mp and the IR spectrum were identical with those of an authentic specimen prepared according to the literature.[15]

*Preparation of **11** from **7**.* Compounds **11a** (36%), **11b** (30%), and **11d**(14%) were prepared from the correponding **7a**, **7b**, and **7d**, respectively, according to the literature method.[15] The mps and the IR spectra were identical with those described above.

*Photooxidation of **4**.* *General Procedure*: A solution of **4** (0.50 mmol) in $CHCl_3$ (200 ml) was irradiated by means of a 100W high-pressure mercury arc lamp with stirring in a stream of oxygen for 4 h. Removal of the solvent followed by column chromatography on silica gel with $CHCl_3$ gave the products **11**. Compounds **11a** (21%), **11b** (14%), and **11c** (16%) were obtained. The mps and the IR spectra were identical with those described above.

*Oxidation of **4** by Hydrogen Peroxide.* To a suspension of **4a** (340 mg, 1.0 mmol) in AcOH (10 ml) was added 30% H_2O_2 (0.45 g, 4.0 mmol) and the mixture was stirred at room temperature. After one day another equal amount of 30% H_2O_2 (0.45 g) was added and the reaction mixture was stirred for an additional day. The precipitates were

collected by filtration, washed with a small amount of MeOH, and recrystallized to give **11a** (290 mg, 85%). In the case of **4c** the reaction mixture was evaporated to dryness and the residue was chromatographed on silica gel with $CHCl_3$ to give **11c** (32%). The mps and the IR spectra were identical to those described above.

*Alkali Treatment of **4**.* General procedure: A solution of **4** (1.0 mmol) in a mixture of 1.0 M KOH (4.0 ml) and pyridine (16 ml) was stirred at room temperature for 2—3 h. The reaction mixture was poured into water (200 ml) and the precipitates were filtered off. The filtrate was acidified with dil HCl and allowed to stand. The separated precipitates were collected by filtration and once recrystallized to give 3-aroylamino-2,3-diphenylacrylic acids (**12**).

*Compound **12a***: Reaction time 2 h. Yield 36%. White prisms; mp 189—192 °C (MeOH). IR (KBr): 3020 (broad), 1688, 1640, 1600, 1584, 1560 cm^{-1}. NMR (DMSO-d_6) : δ 3.86 (s, 3H, OMe), 7.0—8.1 (m, 14H, ArH). MS *m/e* (%): 373 (M^+, 8.1), 355 ($M^+ - H_2O$, 4.2), 329 ($M^+ - CO_2$, 41), 222 (7.8), 135 (100). Found: C, 73.68; H, 5.25%. Calcd for $C_{23}H_{19}O_4N$: C, 73.98; H, 5.13%.

*Compound **12b***: Reaction time 2 h. Yield 25%. White needles; mp 190—191 °C (MeOH). IR (KBr): 3180, 1655, 1610, 1595, 1575 cm^{-1}. NMR (DMSO-d_6): δ 2.38 (s, 3H, Me), 7.1—9.1 (m, 14H, ArH). Found: C, 77.49: H, 5.67%. Calcd for $C_{23}H_{19}O_3N$: C, 77.29; H, 5.36%.

*Compound **12c***: Reaction time 3 h. Yield 26%. White needles; mp 197—198 °C (MeOH). IR (KBr): 3160, 2960, 1670, 1605, 1595, 1575 cm^{-1}. NMR (DMSO-d_6): δ 1.23 (d, J=6.8 Hz, 6H, 2Me), 2.95 (m, 1H, CH), 7.8—8.0 (m, 14H, ArH). Found: C, 77.79; H, 6.22%. Calcd for $C_{25}H_{23}O_3N$: C, 77.90; H, 6.01%.

*Compound **12d***: Reaction time 2 h. Yield 41%. White needles; mp 151—152 °C (EtOH). IR (KBr): 3060, 2860, 1690, 1650, 1615, 1593 cm^{-1}. Found: C, 73.01; H, 5.19%. Calcd for $C_{22}H_{17}O_3N \cdot H_2O$: C, 73.11; H, 5.30%.

*Alkali Treatment of **11***. Compounds **11** were treated with alkali in the same manner as described in the case of **4**. Compounds **12a** (65%), **12b** (63%), and **12d** (20%) were obtained and their mps and IR spectra were identical to those described above.

*Reaction of **1e** with Diethyl Azodicarboxylate.* A mixture of **1e** (1.30 g, 4.5 mmol) and diethyl azodicarboxylate (1.58 g, 9.1 mmol) in toluene (30 ml) was refluxed for 5 h. After removal of the solvent the resulting residue was subjected to column chromatography on silica gel with $CHCl_3$–AcOEt (1:1). Both the first and the second eluated fractions gave oils **13** (1.1 g, 77%) and **14** (430 mg, 42%), respectively, which crystallized upon adding a small amount of MeOH.

*3,6-Bis(p-dimethylaminophenyl)-1,2,7,8-tetrakis(ethoxycarbonyl)-1,2,4,5,7,8-hexaaza-3,5-octadiene (**13**).* Yellow powders; mp 188—189 °C (MeOH–H_2O). IR (KBr) : 3180, 2960, 1735, 1705, 1585, 1518 cm^{-1}. NMR (DMSO-d_6) : δ 0.92—1.35 (m, 12H, 4Me), 3.08 (s, 12H, 2NMe_2), 3.83—4.15 (m, 8H, 4CH_2), 8.58 (s, 2H, 2NH), 6.95 (d, J=9.0 Hz, 4H, 4*m*-H of ArH), 7.72 (d, J=9.0 Hz, 4H, 4*o*-H of ArH). UV (MeOH) nm (log ε): 241 (4.22), 320 sh (4.25), 382 (4.65).[18] MS *m/e* (%): 642 (M^+, 9.4), 467 (42), 454 (23), 351 (13), 294 (22), 280 (100), 266 (21), 175 (42). Found: C, 56.07; H, 6.54%. Calcd for $C_{30}H_{42}O_8N_8$: C, 56.06; H, 6.59%.

*3,6-Bis(p-dimethylaminophenyl)-1,2-bis(ethoxycarbonyl)-1,2,4,5-tetraaza,-3,5-hexadiene (**14**).* Yellow powders; mp 120—122 °C (MeOH–H_2O). IR (KBr): 3280, 2980, 2920, 1735, 1710, 1680, 1600, 1557, 1520 cm^{-1}. NMR ($CDCl_3$): δ 1.20 (t, J=7.5 Hz, 3H, Me), 1.27 (t, J=7.5 Hz, 3H, Me), 3.00 (s, 6H, NMe_2), 3.07 (s, 6H, NMe_2), 4.14 (q, J=7.5 Hz, 2H, CH_2), 4.22 (q, J=7.5 Hz, 2H, CH_2), 5.17 (s, 1H, CH), 6.70 (d, J=9.0 Hz, 2H, 2*m*-H of ArH), 6.85 (d, J=9.0 Hz, 2H, 2*o*-H of ArH), 7.70 (d, J=9.0 Hz, 4H, 2*o*- and 2*m*-H of ArH), 8.56 (s, 1H, NH). UV (MeOH) nm (log ε): 243 (4.26), 325 sh (4.28), 388 (4.61). Found: C, 61.31; H, 6.94%. Calcd for $C_{24}H_{32}O_4N_6$: C, 61.52; H, 6.88%.

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