The Reactions of 1,2-Diphenyl-1-azaspiro[2.2]pentane and 2-Phenyl-1-azaspiro[2.2]pent-1-ene with *C,N*-Diarylnitrilimines[1]

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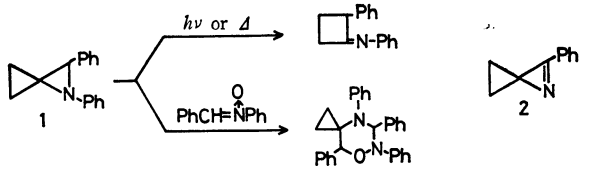
(Received June 20, 1979)

The reactions of highly strained 1,2-diphenyl-1-azaspiro[2.2]pentane (**1**) and 2-phenyl-1-azaspiro[2.2]pent-1-ene (**2**) with *C,N*-diarylnitrilimines (**3**) were described. The reaction of **1** with **3** gave the corresponding 4,5,7,8-tetraphenyl-4,6,7-triazaspiro[2.5]oct-5-ene, 1,5,7,8-tetraphenyl-5,6,8-triazaspiro[3.4]oct-6-ene, 1,3,5-triphenyl-2-pyrazoline, 1,3,4-triphenyl-1,2,4-triazolin-5-one, and/or 1,3,4,6,8-pentaphenyl-1,2,4,6,7-pentaazaspiro[4.4]nona-2,7-diene, whose yields depended on the reaction conditions. The pathways for the formation of products are also postulated. The azaspiropentene **2** readily reacted with **3** to give the corresponding 1,2,4-triphenyl-2,3,5-triazabicyclo[4.2.0]octa-3,5-diene arising from the rearrangement of initial 1,3-cycloadduct.

It has been reported that highly strained 1,2-diphenyl-1-azaspiro[2.2]pentane (**1**) is susceptible to rupture of the peripheral C–N bond. Upon photolysis or pyrolysis the azaspiropentane **1** isomerizes to the (phenylimino)-cyclobutane,[2] whereas the [3+3] cycloadduct is formed from the reaction in the presence of α,*N*-diphenylnitrone.[3] On the other hand, 2-phenyl-1-azaspiro-[2.2]pent-1-ene (**2**) exhibited high reactivity toward 1,3-dipoles such as nitrile ylide and nitrone.[4]

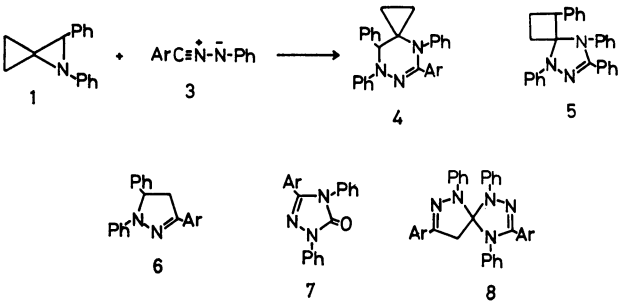


In the present paper we wish to report on the reactions of these highly strained heterocycles, **1** and **2**, with *C,N*-diarylnitrilimines, generated *in situ* from the corresponding *N*-(α-chlorobenzylidene)-*N'*-phenylhydrazines and triethylamine.

Reaction of 1,2-Diphenyl-1-azaspiro[2.2]pentane (1). When the azaspiropentane **1** was allowed to react with 1 equivalent of *C,N*-diphenylnitrilimine (**3a**) in chloroform at room temperature for 60 h, a 1:1 adduct **4a** was obtained in 19.5% yield, together with small amounts of 1,3,5-triphenyl-2-pyrazoline (**6a**)[5] and 1,3,4-triphenyl-1,2,4-triazolin-5-one (**7a**).[6] However, the reaction employed 2 equivalents of **3a** in boiling chloroform for 1 h afforded a new 1:1 adduct **5a** and pyrazoline **6a** in 54 and 23% yields respectively.

Although purification of the 1:1 adduct **4a** was difficult, **4a** was deduced to be the expected [3+3] cycloadduct, 4,5,7,8-tetraphenyl-4,6,7-triazaspiro[2.5]-oct-5-ene, on the basis of its ^{1}H-NMR spectrum displaying signals at δ 0.50—1.85 (m, 4H) and 4.69 ppm (s, 1H) besides aromatic protons. On the other hand, the ^{1}H-NMR spectrum of the 1:1 adduct **5a** showed signals at δ 1.81—2.40 (m, 3H), 2.72—3.20 (m, 1H), and 4.54 ppm (t, 1H, J=12 Hz) besides aromatic protons. The adduct **5a** was thus assigned to be the 1,3-cycloadduct of **3a** to 1-phenyl-2-(phenylimino)-cyclobutane, 1,5,7,8-tetraphenyl-5,6,8-triazaspiro[3.4]-oct-6-ene[7] (Scheme 1).

Next, the reaction of **1** with *C*-(*p*-chlorophenyl)-*N*-phenylnitrilimine (**3b**) was investigated in chloroform under various conditions. The results are summarized in Table 1. As shown in Table 1, the kinds and yields



a: Ar=Ph; **b**: Ar=p-ClC$_6$H$_4$

Scheme 1.

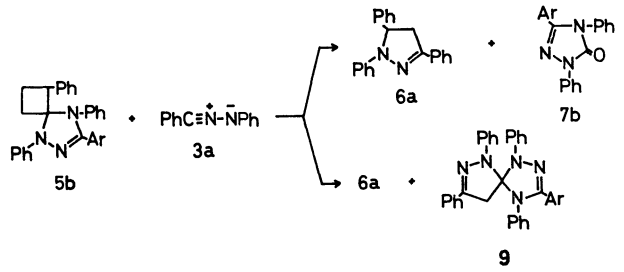
of products greatly depended on the reaction conditions. The reaction at room temperature gave the expected [3+3] cycloadduct **4b** as the major product, whereas the isomeric 1:1 adduct **5b** was formed as the sole product in the reaction under reflux. When excess of **3b** was employed, 3-(*p*-chlorophenyl)-1,5-diphenyl-2-pyrazoline (**6b**), 3-(*p*-chlorophenyl)-1,4-diphenyl-1,2,4-triazolin-5-one (**7b**), and/or a new product **8b** were formed together with 1:1 cycloadducts **4b** and/or **5b**. The structures of **6b** and **7b** were confirmed by the identification with authentic samples prepared from the 1,3-dipolar cycloadditions of **3b** to styrene and phenyl isocyanate respectively.

The molecular formula of **8b** agreed with that of the compound derived from a 1:2 adduct of **1** to **3b** with the elimination of styrene. The ^{1}H-NMR spectrum

Table 1. Reaction of azaspiropentane **1** with nitrilimine **3b** in chloroform

1/**3b** (mol/mol)	Reaction temp	Reaction time/h	Product yield/%				
			4b	**5b**	**6b**	**7b**	**8b**
1	r.t.	60	43	trace	—	—	—
1	reflux	1	—	21	—	—	—
1	reflux	4	—	38	—	—	—
1/2	reflux	2	29	17	3	7	—
1/3	reflux	6	10	—	60	—	8

of **8b** displayed two doublets (each 1H, J=20 Hz) at δ 3.20 and 3.78 ppm besides aromatic protons. On the basis of the above facts and of a consideration of the mode of formation, **8b** was deduced to be 3,8-bis(*p*-chlorophenyl)-1,4,6-triphenyl-1,2,4,6,7-pentaazaspiro-[4.4]nona-2,7-diene.

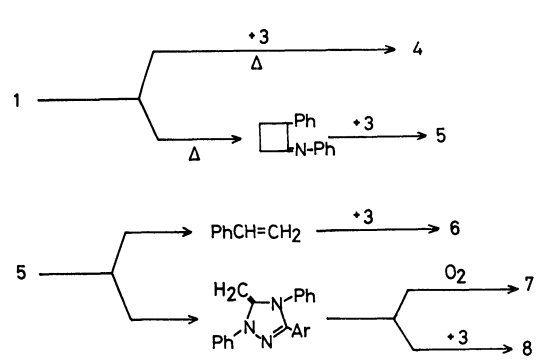


Ar=*p*-ClC$_6$H$_4$

Scheme 2.

The above results suggest that the products, **6**, **7**, and **8** might be arisen from the 1 : 1 adduct **5**. In fact, when a chloroform solution of the 1 : 1 adduct **5b** was heated with 1 equivalent of the nitrilimine **3a** for 4 h, the pyrazoline **6a** was formed in 23% yield along with a trace amount of the triazolinone **7b**. In the same reaction in degassed chloroform under nitrogen, however, **6a** and the pentaazaspiro[4.4]nonadiene **9** were obtained in 23 and 30% yields respectively (Scheme 2).

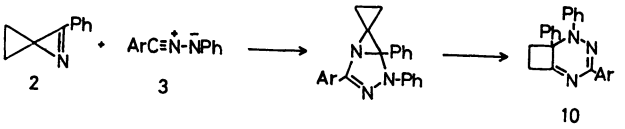
On the basis of the above facts, the pathways for the formation of products are outlined as depicted in Scheme 3. A species generated by the rupture of the peripheral C–N bond of the azaspiropentane **1** reacts with the nitrilimine **3** to give the [3+3] cycloadduct **4**, and/or isomerizes to the (phenylimino)cyclobutane. The nitrilimine **3** undergoes 1,3-dipolar cycloaddition to the (phenylimino)cyclobutane to yield the isomeric 1 : 1 adduct **5**, which partially decomposes to styrene and methylenetriazoline. The 1,3-cycloaddition of **3** to styrene or methylenetriazoline gives the pyrazoline **6** or pentaazaspirononadiene **8** respectively. On the other hand, oxidation of the methylenetriazoline intermediate with oxygen leads to the formation of the triazolinone **7**. A similar oxidation of methylene group with oxygene has been reported by Woerner *et al.*[8]



Scheme 3.

Reaction of 2-Phenyl-1-azaspiro[2.2]pent-1-ene (2). Several 1,3-dipolar cycloadditions to 1-azirines have been investigated.[9] However, no studies on the cycloadditions of nitrilimine to 1-azirines seem to have been reported, although it is known that nitrilimines undergo cycloadditions to C=N bonds.[6]

The azaspiropentene **2** readily reacted with *C,N*-diarylnitrilimines, **3a** and **3b**, in benzene at room temperature, giving the corresponding 1 : 1 adducts, **10a** and **10b**, in excellent yields respectively. On the basis of spectral data as well as of the chemical conversions, the 1 : 1 adducts **10** were assigned to be the corresponding 1,2,4-triphenyl-2,3,5-triazabicyclo[4.2.0]octa-3,5-dienes which corresponded to the rearranged compounds of initial 1,3-cycloadducts (Scheme 4).



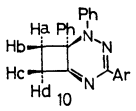
a: Ar=Ph; b: Ar=*p*-ClC$_6$H$_4$

Scheme 4

The ^{1}H-NMR spectra of **10a** and **10b** displayed four double double doublets (each 1H) indicating the presence of a cyclobutane ring. An inspection of the Dreiding models of **10** indicated that the fused cyclobutane ring in **10** is substantially fixed. On the basis of values of chemical shifts and coupling constants,[10] the protons of cyclobutane ring in **10** are assigned as shown in Table 2.

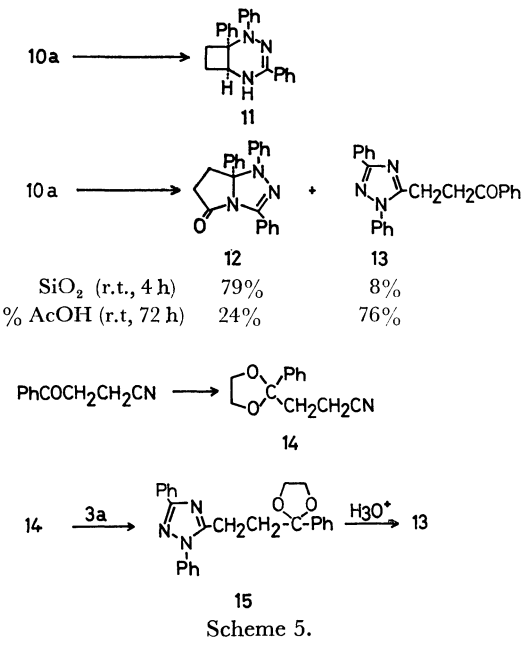
Reduction of **10a** with sodium borohydride in tetrahydrofuran gave the dihydro compound **11** in good yield. Structural elucidation of **11** was accomplished on the basis of spectral data. In addition, it was found that **10a** was converted to 2,4,5-triphenyl-1,3,4-triazabicyclo[3.3.0]oct-2-en-8-one (**12**) and 5-(2-benzoylethyl)-1,3-diphenyl-1,2,4-triazole (**13**) on treatment with silica gel or 1% aqueous acetic acid in benzene (Scheme 5).[11]

Table 2. ^{1}H-NMR spectral data of **10**[a]



	Chemical shift, δ/ppm				Coupling const/Hz					
	H_a	H_b	H_c	H_d	J_{ab}	J_{ac}	J_{ad}	J_{bc}	J_{bd}	J_{cd}
10a	2.85	3.16	3.80	3.36	11.0	9.8	8.5	10.0	3.2	16.2
10b	2.88	3.22	3.84	3.36	10.5	10.0	8.5	10.4	3.3	16.3

a) Measured in $CDCl_3$.



Scheme 5.

The structure of **12** was assigned on the basis of the spectral data, and **13** was confirmed by the identification with an authentic sample prepared by the route shown in Scheme 5.

Experimental

All melting points are uncorrected. IR, NMR, and mass spectra were obtained on a JASCO IRA-1 spectrometer, Hitachi R-40, JEOL SX-100 spectrometers, and a Hitachi RMS-4 spectrometer, respectively.

Reaction of Azaspiropentane ***1*** *with* C,N-*Diphenylnitrilimine (**3a**).* A solution of *N*-(α-chlorobenzylidene)-*N'*-phenylhydrazine[6] (1.0 g, 4.34 mmol) in $CHCl_3$ (10 ml) was added, drop by drop, to a stirred solution of the azaspiropentane **1**[2] (0.89 g, 4.02 mmol) and NEt_3 (2.1 g, 20.8 mmol) in $CHCl_3$ (30 ml), under nitrogen, at room temperature. The reaction mixture was stirred at room temperature for 60 h, and then filtered to remove the formed triethylammonium chloride. The filtrate was concentrated *in vacuo*, and the residue was chromatographed on silica gel. From the fraction using hexane–benzene (1:2) as eluent, 0.325 g (19.5%) of the [3+3] cycloadduct **4a**, mp *ca.* 100 °C, as yellow crystals, and 3 mg of 1,3,5-triphenyl-2-pyrazoline (**6a**), mp 137—138 °C (lit,[5] mp 137—138 °C), as colorless needles were obtained. The fraction using $CHCl_3$ as eluent gave 5 mg of 1,3,4-triphenyl-1,2,4-triazolin-5-one (**7a**), mp 224—225 °C (lit,[6] mp 223—224 °C), as colorless needles.

Recrystallization of **4a** was difficult. IR (KBr) 1560 cm^{-1} (C=N). ^{1}H-NMR ($CDCl_3$) δ 0.50—1.85 (m, 4H), 4.69 (s, 1H), 6.25—7.75 ppm (m, 20H). MS *m/e* 415 (M^+).

The azaspiropentane **1** (0.89 g) reacted with the nitrilimine **3a**, generated from the chloride (2.0 g, 8.68 mmol) and NEt_3 (4.2 g, 41.6 mmol), in $CHCl_3$ (40 ml) under reflux for 1 h, giving 0.90 g (54%) of the isomeric 1:1 adduct **5a** and 0.276 g (23%) of **6a**.

Recrystallization of **5a** from EtOH afforded yellow plates, mp 128—130 °C. IR (KBr) 1555 cm^{-1} (C=N). ^{1}H-NMR ($CDCl_3$) δ 1.81—2.40 (m, 3H), 2.72—3.20 (m, 1H), 4.54 (t, 1H, J=12 Hz), 6.60—7.64 ppm (m, 20H). MS *m/e* 415 (M^+). Found: C, 83.82; H, 6.06; N, 10.11%. Calcd for $C_{29}H_{25}N_3$: C, 83.55; H, 6.04; N, 9.99%.

Reaction of Azaspiropentane ***1*** *with* C-(p-*Chlorophenyl)*-N-*phenylnitrilimine (**3b**).* The reaction of **1** with **3b**, generated from *N*-(α,*p*-dichlorobenzylidene)-*N'*-phenylhydrazine[12] and NEt_3, was carried out under various conditions. The reaction mixture was worked up in a similar manner as above. From the fraction using hexane–benzene (1:2) as eluent the [3+3] cycloadduct **4b** and 3-(*p*-chlorophenyl)-1,5-diphenyl-2-pyrazoline (**6b**) were obtained. The second and third fractions using benzene and $CHCl_3$ as eluents afforded the isomeric 1:1 adduct **5b**, and 3-(*p*-chlorophenyl)-1,4-diphenyl-1,2,4-triazolin-5-one (**7b**) and the pentaazaspirononadiene **8b** respectively. The results are summarized in Table 1.

The 1:1 Cycloadduct ***4b***: Mp 203—204 °C as colorless prisms (from hexane). IR (KBr) 1560 cm^{-1} (C=N). ^{1}H-NMR ($CDCl_3$) δ 0.50—2.05 (m, 4H), 4.69 (s, 1H), 6.21—7.52 ppm (m, 19H). MS *m/e* 451, 449 (M^+). Found: C, 77.70; H, 5.40; N, 9.32%. Calcd for $C_{29}H_{24}N_3Cl$: C, 77.40; H, 5.38; N, 9.34%.

The 1:1 Adduct ***5b***: Mp 134—135 °C as yellow plates (from MeOH). IR (KBr) 1560 cm^{-1} (C=N). ^{1}H-NMR ($CDCl_3$) δ 1.51—2.49 (m, 3H), 2.52 (m, 1H), 4.48 (m, 1H), 6.52—7.76 ppm (m, 19H). MS *m/e* 451, 449 (M^+), 347, 345 (M^+—PhCH=CH_2, base peak). Found: C, 77.36; H, 5.47; N, 9.41%. Calcd for $C_{29}H_{24}N_3Cl$: C, 77.40; H, 5.38; N, 9.34%.

The Pyrazoline ***6b***: Mp 150—151 °C as pale greenish needles (from EtOH). This compound was identical with an authetic sample prepared from the following method. A solution of styrene (1.0 g, 9.62 mmol) and *N*-(α,*p*-dichlorobenzylidene)-*N'*-phenylhydrazine (2.6 g, 9.81 mmol) in benzene (10 ml) was stirred with NEt_3 (4.3 g, 42.5 mmol) at 60 °C for 2 h. The reaction mixture was filtered to remove the formed triethylammonium chloride, and the filtrate was concentrated *in vacuo* to leave the residue. Recrystallization from MeOH gave 0.83 g (63%) of **6b**, mp 150—151 °C. IR (KBr) 1550 cm^{-1} (C=N). ^{1}H-NMR ($CDCl_3$) δ 3.06, 3.78, 5.25 (each dd, 1H, J=7.5, 12.5, 17 Hz), 6.64—7.68 ppm (m, 14H). Found: C, 75.83; H, 5.05; N, 8.62%. Calcd for $C_{21}H_{17}N_2Cl$: C, 75.79; H, 5.11; N, 8.42%.

The Triazolinone ***7b***: Mp 185—186 °C as colorless needles (from EtOH). This compound was identical with an authentic sample prepared from the reaction of *N*-(α,*p*-dichlorobenzylidene)-*N'*-phenylhydrazine (1.0 g, 3.77 mmol) with phenyl isocyanate (0.5 g, 4.20 mmol) in the presence of aluminum oxide (0.3 g) according to the Huisgen's method.[6] IR (KBr) 1720 (C=O), 1580 cm^{-1} (C=N). ^{1}H-NMR ($CDCl_3$) δ 7.08—7.58 (m, 12H), 7.90—8.16 ppm (m, 2H). Found: C, 68.89; H, 4.25; N, 12.13%. Calcd for $C_{20}H_{14}N_3OCl$: C, 69.06; H, 4.03; N, 12.08%.

The Pentaazaspirononadiene ***8b***: Mp 174—175 °C (dec) as colorless needles (from EtOH). IR (KBr) 1595 cm^{-1} (C=N). ^{1}H-NMR ($CDCl_3$) δ 3.20, 3.78 (each d, 1H, J=20 Hz), 6.61—7.75 ppm (m, 23H). MS *m/e* 577, 575, 573 (M^+), 347, 345, 343 (M^+—ArC≡$\overset{+}{N}$–$\overset{-}{N}$Ph). Found: C, 70.86; H, 4.37; N, 11.99%. Calcd for $C_{34}H_{25}N_5Cl_2$: C, 71.08; H, 4.39; N, 12.19%.

Reaction of the 1:1 Adduct ***5b*** *with the Nitrilimine* ***3a***. *i*): A solution of NEt_3 (0.1 ml, 0.69 mmol) in $CHCl_3$ (5 ml) was added, drop by drop, to a stirred solution of **5b** (0.3 g, 0.67 mmol) and *N*-(α-chlorobenzylidene)-*N'*-phenylhydrazine (0.16 g, 0.69 mmol) in $CHCl_3$ (10 ml) at room temperature. The reaction mixture was then refluxed for 4 h, and concentrated *in vacuo* to leave the residue. Benzene was added to the residue, and the resultant mixture was filtered to remove the formed triethylammonium chloride. The filtrate was concentrated *in vacuo* and the residue was chromatographed on silica

gel using hexane–benzene (1: 1) and benzene as eluents, giving 46.3 mg (23%) of **6b** and 7 mg of **7b**.

ii): The same reaction was carried out in degassed $CHCl_3$ under nitrogen. After removal of triethylammonium chloride, the residue was triturated with EtOH to give 0.108 g (30%) of the pentaazaspirononadiene **9**. The EtOH solution was chromatographed on silica gel to give 31.9 mg (23%) of **6a**.

The Pentaazaspirononadiene ***9***: Mp 184—186 °C as colorless needles (from cyclohexane). IR (KBr) 1560 cm^{-1} (C=N). ^{1}H-NMR ($CDCl_3$) δ 3.35, 3.86 (each d, 1H, J=20 Hz), 6.73—7.04 (m, 4H), 7.08—7.48 (m, 18H), 7.54—7.80 ppm (m, 2H). MS *m/e* 541, 539 (M^+), 347, 345 (M^+—PhC≡$\overset{+}{N}$–$\overset{-}{N}$Ph). Found: C, 75.53; H, 4.89; N, 13.03%. Calcd for $C_{34}H_{26}N_5Cl$: C, 75.64; H, 4.82; N, 12.97%.

Reaction of Azaspiropentane ***2*** *with* C,N-*Diphenylnitrilimine (****3a****).* A solution of *N*-(α-chlorobenzylidene)-*N'*-phenylhydrazine (1.37 g, 5.94 mmol) in benzene (40 ml) was added, drop by drop, to a stirred solution of the azaspiropentene **2**[13] (0.85 g, 5.94 mmol) and NEt_3 (2.88 g, 28.4 mmol) in benzene (15 ml) under nitrogen at room temperature. The reaction mixture was then stirred for 24 h, and filtered to remove the formed triethylammonium chloride. The filtrate was concentrated *in vacuo* to leave the residue, which on recrystallization from hexane afforded 1.13 g (97%) of the triazabicyclooctadiene **10a**, mp 153—154 °C, as yellow needles. IR (KBr) 1675 cm^{-1} (C=N). ^{13}C-NMR ($CDCl_3$) δ 36.2, 38.5, 66.7, 116.2, 121.7, 125.5, 126.0, 127.9, 128.2, 128.5, 128.8, 129.0, 134.9, 136.3, 142.6, 146.0, 165.1. MS *m/e* 337 (M^+). Found: C, 81.85; H, 5.64; N, 12.46%. Calcd for $C_{23}H_{19}N_3$: C, 81.87; H, 5.18; N, 12.45%.

A similar reaction of **2** (0.37 g, 2.6 mmol) with the nitrilimine **3b**, generated from the corresponding chloride (0.68 g, 2.6 mmol) and NEt_3 (1.26 g, 13 mmol), in benzene (35 ml) afforded 0.89 g (94%) of the triazabicyclooctadiene **10b**, mp 178—180 °C (dec), as yellow needles. IR (KBr) 1673 cm^{-1}. ^{13}C-NMR ($CDCl_3$) δ 36.2, 38.5, 66.6, 116.3, 121.9, 125.9, 126.7, 127.9, 128.4, 128.8, 129.0, 133.4, 134.3, 136.1, 142.3, 145.1, 165.2. MS *m/e* 373, 371 (M^+). Found: C, 74.31; H, 4.83; N, 11.16%. Calcd for $C_{23}H_{18}N_3Cl$: C, 74.28; H, 4.88; N, 11.30%.

Reduction of ***10a****.* After a solution of **10a** (0.1 g) in THF (2 ml) was stirred with $NaBH_4$ (26 mg) at room temperature for 5 h, water (5 ml) was added to the reaction mixture. The mixture was acidified with 1.8% HCl to give a solid, which on recrystallization from cyclohexane gave 96 mg (95%) of the dihydro compound **11**, mp 181—182 °C, as colorless needles. IR (KBr) 3470 (NH), 1630 cm^{-1} (C=N). ^{1}H-NMR ($CDCl_3$) δ 1.4—2.75 (m, 4H), 3.85 (broad, 1H, after exchange with D_2O, the signal changed to a double doublet, J=7.0, 8.8 Hz), 4.95 (broad, 1H, exchanged with D_2O), 6.50—7.50 (m, 13H), 7.60—7.85 (m, 2H). ^{13}C-NMR ($CDCl_3$) δ 23.1, 29.2, 54.5, 61.8, 115.8, 118.3, 124.8, 125.6, 126.7, 128.1, 128.6, 134.9, 138.1, 142.7, 144.6. MS *m/e* 339 (M^+), 311 (base peak), 235, 219, 207, 180, 207, 180, 144, 104, 91. Found: C, 81.36; H, 6.33; N, 12.50%. Calcd for $C_{23}H_{21}N_3$: C, 81.38; H, 6.24; N, 12.38%.

Treatment of ***10a*** *with Silica Gel.* A solution of **10a** (0.1 g) in benzene (2 ml) was stirred with silica gel (Wako-gel C-200, 0.5 g) at room temperature for 4 h. The mixture was filtered and the filtrate was concentrated *in vacuo* to leave a residue. The residue was chromatographed on silica gel using benzene as eluent to give 82.7 mg (79%) of the triazabicyclooctenone **12** and 8.4 mg (8%) of the 1,2,4-triazole **13**.

The Triazabicyclooctenone ***12***: Mp 96—97 °C as colorless prisms (from benzene). IR (KBr) 1735 cm^{-1} (C=O). ^{1}H-NMR ($CDCl_3$) δ 2.60—3.40 (m, 4H), 6.70—7.40 (m, 14H), 7.70—7.90 (m, 1H). ^{13}C-NMR ($CDCl_3$) δ 34.3, 35.4, 90.4, 114.4, 120.3, 125.5, 127.2, 127.8, 128.1, 128.2, 129.0, 129.7, 139.3, 140.9, 142.0, 174.5. MS *m/e* 353 (M^+), 298, 276, 194, 165, 103, 91. Found: C, 78.24; H, 5.43; N, 11.67%. Calcd for $C_{23}H_{19}N_3O$: C, 78.16; H, 5.42; N, 11.89%.

The 1,2,4-Triazole ***13***: Mp 115—116 °C as colorless needles (from EtOH). IR (KBr) 1682 cm^{-1} (C=O). ^{1}H-NMR ($CDCl_3$) δ 3.10—3.35 (m, 2H), 3.50—3.75 (m, 2H), 7.20—7.65 (m, 11H), 7.90—8.20 (m, 4H). ^{13}C-NMR ($CDCl_3$) δ 21.1, 36.1, 125.2, 126.4, 128.0, 128.5, 128.6, 128.9, 129.1, 130.8, 133.2, 136.5, 137.4, 155.8, 198.0. MS *m/e* 353 (M^+), 248 (M^+—PhCO, base peak), 105, 91. Found: C, 78.19; H, 5.34; N, 11.88%. Calcd for $C_{23}H_{19}N_3O$: C, 78.16; H, 5.42; N, 11.89%.

Treatment of ***10a*** *with 1% Aqueous AcOH.* A solution of **10a** (40 mg) in benzene (2 ml) was stirred with 1% aqueous AcOH (1 ml) at room temperature for 4 days. The benzene solution was concentrated *in vacuo* to leave a residue. Chromatography of the residue on silica gel (benzene) afforded 10 mg (24%) of **12** and 32 mg (76%) of **13**.

*Preparation of 5-(β-Benzoylethyl)-1,3-diphenyl-1,2,4-triazole (****13****).* A mixture of β-benzoylpropionitrile[14] (4.0 g), ethylene glycol (6.0 g), and a catalytic amount of *p*-toluenesulfonic acid in benzene (70 ml) was boiled with azeotropic removal of water. After being boiled for 50 h, the reaction mixture was concentrated *in vacuo* to give 5.3 g (100%) of 2-(2-cyanoethyl)-2-phenyl-1,3-dioxolane (**14**) which on recrystallization from hexane afforded colorless needles, mp 62.5—63.5 °C. Found: C, 70.88; H, 6.54; N, 6.77%. Calcd $C_{12}H_{13}NO_2$: C, 70.91; H, 6.45; N, 6.89%.

A solution of *N*-(α-chlorobenzylidene)-*N'*-phenylhydrazine (1.9 g, 8.24 mmol) in benzene (30 ml) was added, drop by drop, to a stirred solution of the above dioxolane **14** (1.7 g, 8.37 mmol) and NEt_3 (5.9 g, 83.4 mmol) in benzene (20 ml), under nitrigen, at room temperature. After being refluxed for 65 h, the reaction mixture was filtered, and the filtrate was concentrated *in vacuo* to leave a residue. The residue was chromatographed on silica gel using benzene as eluent to give 0.329 g (10%) of 2-[2-(1,3-diphenyl-1,2,4-triazol-5-yl)-ethyl]-2-phenyl-1,3-dioxolane (**15**), along with recovery of 1.5 g (88%) of **14**.

The Triazole ***15***: Mp 104—105 °C as colorless needles (from hexane). Found: C, 75.64; H, 5.87; N, 10.61%. Calcd for $C_{25}O_{23}N_3O_2$: C, 75.54; H, 5.83; N, 10.57%.

A suspension of the triazole **15** (50 mg) in 5% aqueous HCl (5 ml) was stirred at room temperature for 22 h. Filtration gave crystals which were washed with NH_4OH and water, and then recrystallized from EtOH to give 42.3 mg (95.5%) of **13**, mp 115—116 °C.

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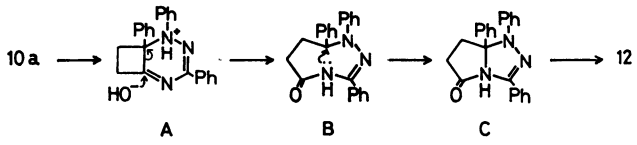
C,N-diphenylnitrilimine added to the *exo*-*N*-phenylimino groups of 2,4-diphenyl-5-phenylimino-1,3,4-oxazoline-2 and 5-phenylimino-1,3,4-triphenyl-1,2,4-triazoline-2 to give the corresponding 1,2,4-triazoline derivatives as the sole products.[15]



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