FORMATION OF 1,2,3,5-TETRASUBSTITUTED 2-PYRROLIN-4-ONES AND 1,2,3-TRISUBSTITUTED PYRROLES FROM DIPHENYLCYCLOPROPENONE AND 1,4-DIAZABUTADIENES

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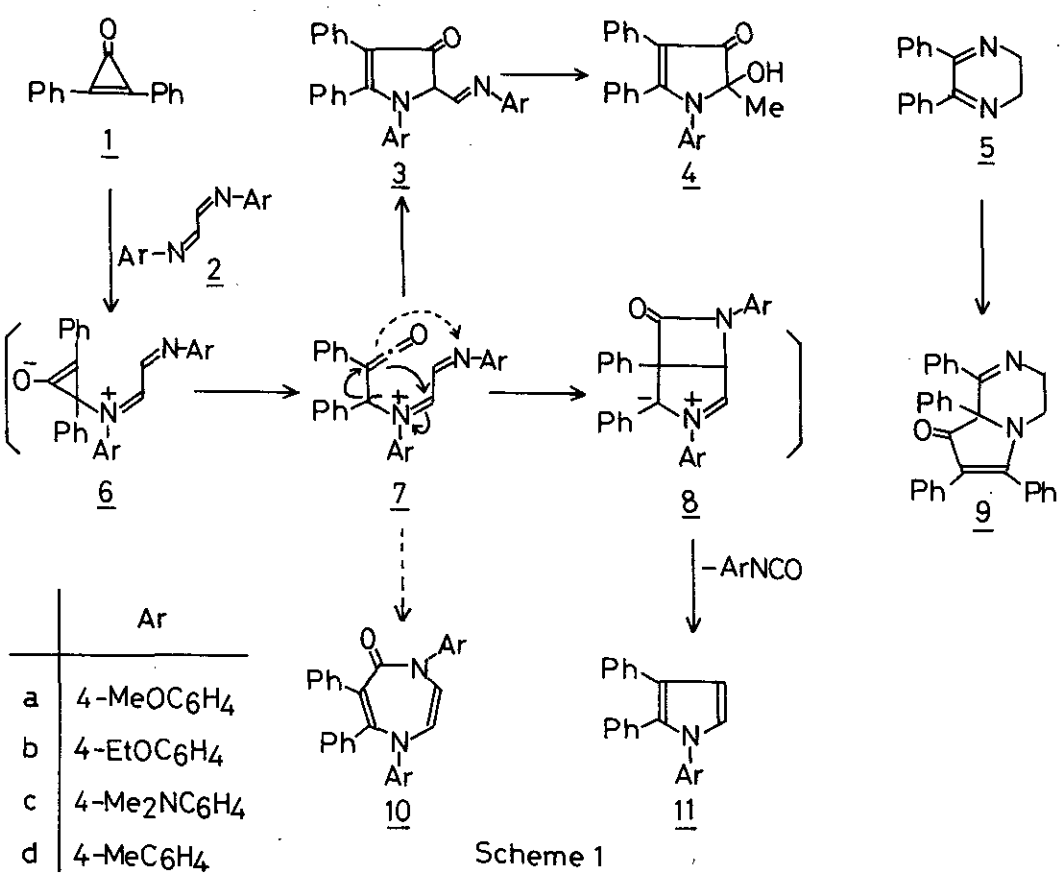
Abstract---The reaction of diphenylcyclopropenone (1) with 1,4-diaryl-1,4-diazabutadienes (2) afforded 1-aryl-5-(N-aryl) iminomethyl-2,3-diphenyl-2-pyrrolin-4-ones (3) as major products and 1-aryl-2,3-diphenylpyrroles (11) as minor products.

Although the reaction of diphenylcyclopropenone (1) with imines has been established by Eicher et al.,[1] those with conjugated compounds containing C=N double bonds have not been studied extensively.[2] We have tried previously the reaction of 1 with 1,4-diaryl-2,3-diazabutadienes (arylaldazines) and reported the formation of 5-aryl-2,3-diphenyl-2-pyrrolin-4-ones,[3] whose structures were later corrected to be 5,5'-dimeric structure.[4] These unexpected results prompted us to examine the reaction of 1 with other diazabutadienes, and we now report the formation of 2-pyrrolin-4-ones (3) and pyrroles (11) from 1 and 1,4-diaryl-1,4-diazabutadienes (2).

Treatment of 1 (5.0 mmol) with 2[5] (5.0 mmol) in refluxing toluene (25 ml) for 24 h followed by column chromatography (silica gel, $CHCl_3$) gave two products (Scheme 1). The major products obtained in 20-79% yields as orange crystals, which were solely produced in 31-74% yields on refluxing in EtOH for 24 h, were confirmed to be 1:1 adducts on the basis of the microanalyses and the mass spectra (Table 1). The IR spectra showed carbonyl absorptions at 1650-1660 cm^{-1}, and the NMR spectra suggested the presence of CH=N groups at



	Ar
a	4-$MeOC_6H_4$
b	4-$EtOC_6H_4$
c	4-$Me_2NC_6H_4$
d	4-MeC_6H_4

Scheme 1

δ 9.6-10.6 as broad singlets (Table 2). The characteristic absorptions of methine or olefinic protons, however, were not observed in the spectra and seemed to be overlapped by aromatic protons. In order to prove the structure 3 and rule out the alternative diazepine 10, the orange compounds 3a and 3b (1.0 mmol) were subjected to hydrogenation over 5% Pd-C (200 mg) in MeOH (50 ml) for 24 h. The filtrate after removal of Pd-C was stirred at room temperature on exposure to air to complete the air oxidation. The products isolated by column chromatography (silica gel, $CHCl_3$) were revealed to be 5-hydroxy-5-methyl-2-pyrrolin-4-ones (4a and 4b) on the basis of the spectral data (Table 1 and 2). The reaction would proceed via hydrogenolysis of C=N double bond of 3 followed by air oxidation of C-5 position to give 4. The similar rapid autoxidation of C-5 position of 2-pyrrolin-4-ones has been reported in some cases.[6] Thus, it was confirmed that the major products were not the diazepines but 1-aryl-5-(N-aryl)iminomethyl-2,3-diphenyl-2-pyrrolin-4-ones (3). A cyclic 1,4-diaza-

TABLE 1. Yields, physical constants, and spectral data of 3, 4, 9, and 11

Compound	Yield %	Mp °C	Formula[a]	MS M^+, m/e	IR KBr, cm^{-1}
3a	79 (74[b])	200-203[c]	$C_{31}H_{26}O_3N_2$	474	1650, 1510, 1240
3b	52 (57[b])	196-199[c]	$C_{33}H_{30}O_3N_2$	502	1660, 1510, 1240
3c	24 (31[b])	281-283[d]	$C_{33}H_{32}ON_4$	500	1650, 1520, 1265
3d	20 (61[b])	215-217[d]	$C_{31}H_{26}ON_2$	442	1650, 1510, 1260
4a	51	215-221[e]	$C_{24}H_{21}O_3N$	371	3150, 1640, 1505
4b	51	207-210[e]	$C_{25}H_{23}O_3N$	383	3200, 1645, 1510
9	92	212-232[c]	$C_{31}H_{24}ON_2$	440	1660, 1550, 1325
11a	17	195-196[f]	$C_{23}H_{19}ON$	325	1600, 1510, 1240
11b	5.1	159-160[f]	$C_{24}H_{21}ON$	339	1595, 1505, 1240
11c	5.9	157-159[f]	$C_{24}H_{22}N_2$	338	1610, 1510, 1330
11d	15	180-181[f,g]	$C_{23}H_{19}N$	309	1595, 1515, 1360

[a]Satisfactory microanalyses were obtained. [b]Refluxing in EtOH. [c]From EtOH. [d]From benzene. [e]From MeOH. [f]From cyclohexane. [g]Lit.,[8] mp 181°C.

Table 2. NMR spectra of 3, 4, 9, and 11 (δ)

3a[a] 3.89 (s, 6H), 6.82-7.40 (m, 19H), 10.60 (broad s, 1H)

3b[a] 1.35 (t, J=6.8 Hz, 6H), 3.97 (q, J=6.8 Hz, 4H), 6.65-7.23 (m, 19H), 9.63 (broad s, 1H)

3c[a] 2.96 (s, 6H), 3.01 (s, 6H), 6.54-7.40 (m, 19H), 9.85 (broad s, 1H)

3d[a] 2.25 (s, 3H), 2.30 (s, 3H), 6.77-7.28 (m, 19H), 10.33 (broad s, 1H)

4a[b] 1.20 (s, 3H), 3.63 (s, 3H), 6.66-7.21 (m, 15H), 6.74 (s, 1H)[c]

4b[b] 1.22 (t, J=7.0 Hz, 3H), 3.85 (q, J=7.0 Hz, 2H), 6.62-7.25 (m, 15H) 6.72 (s, 1H)[c]

9[a] 3.45-4.00 (m, 4H), 7.08-7.82 (m, 20H)

11a[a] 3.73 (s, 3H), 6.47-7.17 (m, 16H)

11b[a] 1.37 (t, J=7.2 Hz, 3H), 3.96 (q, J=7.2 Hz, 2H), 6.47-7.17(m, 16H)

11c[a] 2.88 (s, 6H), 6.46-7.14 (m, 16H)

11d[a] 2.29 (s, 3H), 6.48-7.16 (m, 16H)

[a]In $CDCl_3$. [b]In DMSO-d_6. [c]OH, exchangeable with D_2O.

butadiene 5[7] reacted similarly to give 9.

The minor products were isolated in 5.1-17% yields as white crystalline compounds, and their structures were established unambiguously as 1-aryl-2,3-diphenylpyrroles (11) (Table 1 and 2).

While the formation of 3 is a usual reaction as anticipated from the publication,[1] pyrroles 11 were unexpected products. The plausible pathway for this reaction is shown as outlined in Scheme 1. Initial nucleophilic addition of 2 to 1 occurs to give 6, followed by ring opening to afford the ketene intermediate 7. Subsequent cyclization by nucleophilic attack of ketene on iminium group leads to the major product 3. On the other hand, intramolecular [2+2] cycloaddition between ketene and imino groups of 7 forms azetidinone 8, which extrudes aryl isocyanate to give the minor product 11.

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