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Reaction of Diphenylcyclopropenone with Nitroketeneaminals. Synthesis of 6-Amino-2-pyridones and Their m-Chloroperbenzoic Acid Oxidation to 2,3-Diphenylmaleimides

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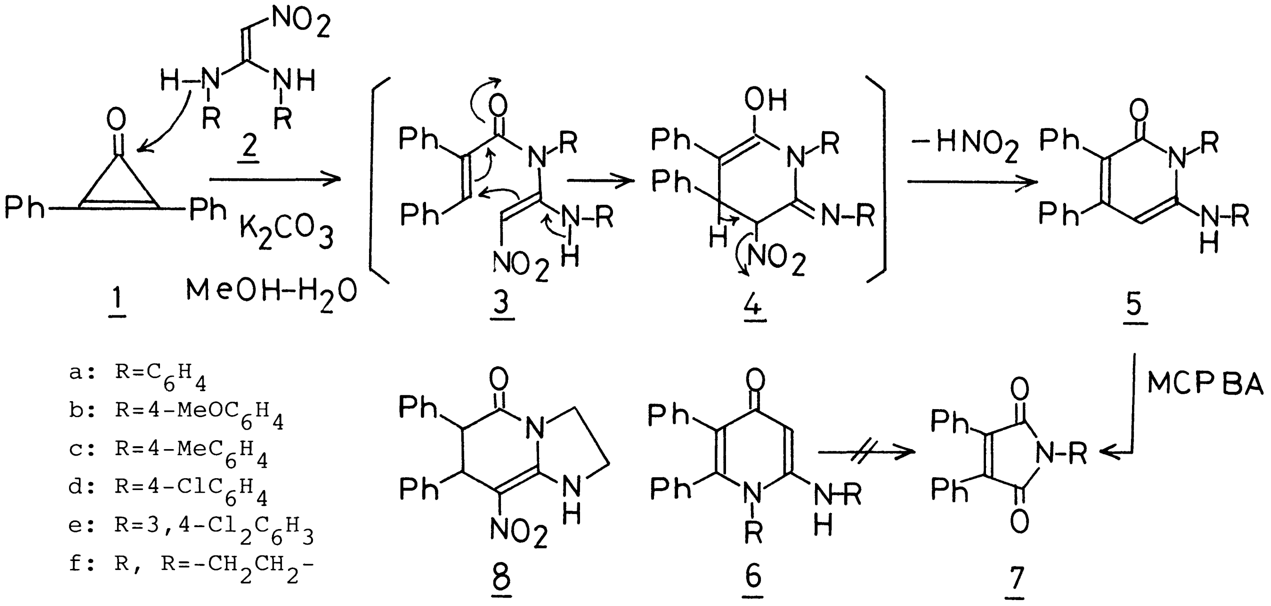
Reaction of diphenylcyclopropenone with nitroketeneaminals gave 6-amino-2-pyridones, which were oxidized by m-chloroperbenzoic acid to 2,3-diphenylmaleimides.

Diphenylcyclopropenone (1) is known as an excellent starting material for organic synthesis.1) In our continuous interest in 1 as a heterocycles synthon2) we noted the reaction of 1 with nitroketeneaminals,3) and have found a simple synthesis of 6-amino-2-pyridones (5), a rare class of pyridine derivatives,4) in moderate yields. Moreover, in the course of establishment of the structure of 5 we have noticed a new oxidative ring contraction of 5 by m-chloroperbenzoic acid (MCPBA) to N-aryl-2,3-diphenylmaleimides (7).

The reaction of 1 with 2a5) in the presence of K_2CO_3 at room temperature gave a cyclized product (56%) with elimination of HNO_2 (Scheme 1). The structure of the product was assigned to be either 6-amino-2-pyridone (5a)6) or isomeric 2-amino-4-pyridone (6a) on the basis of the analytical and spectral data (Table 1). However, the structure was ultimately revealed to be 5a as follows: Treatment of the product (5a or 6a) with MCPBA (3 equiv.) in refluxing CH_2Cl_2 afforded N-phenyl-2,3-diphenylmaleimide (7a), which was identical with the authentic sample.7) The formation of 7a from 5 would be rationalized as shown in Scheme 2. The exocyclic imino group of the initial oxidation product 9a undergoes further oxidation to give spiro-oxaziridine 10a followed by rearrangement to yield 1,3-diazepine 11a as well known in the oxaziridine chemistry.8) Subsequent ring contraction on extrusion of phenyl isocyanate leads to 7a. Treatment of 5a with MCPBA (2 equiv.) gave the stable intermediate 9a9) (15%) and 7a (23%), which was



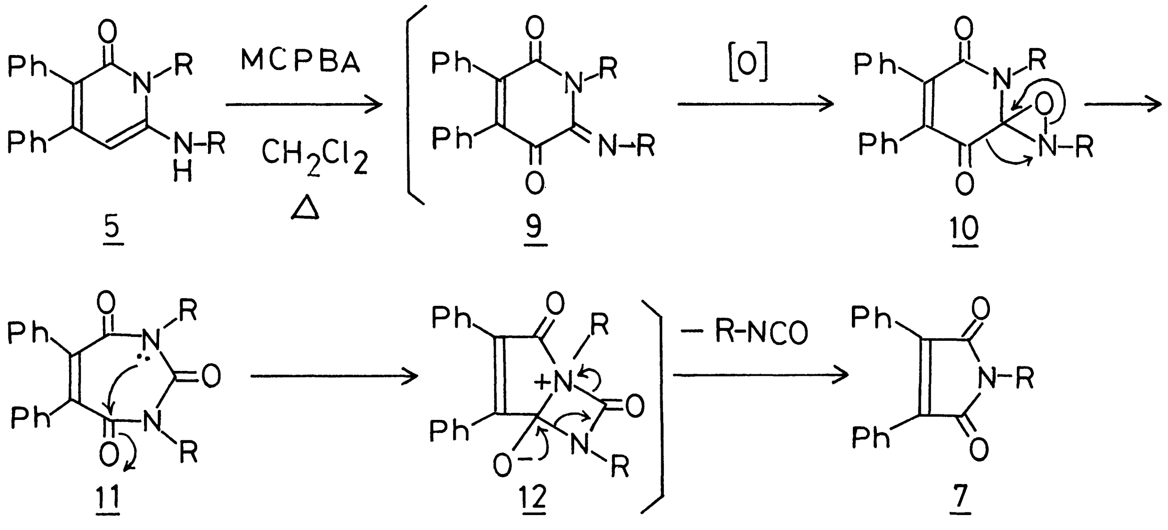
Scheme 1.

a: $R=C_6H_4$
b: $R=4\text{-}MeOC_6H_4$
c: $R=4\text{-}MeC_6H_4$
d: $R=4\text{-}ClC_6H_4$
e: $R=3,4\text{-}Cl_2C_6H_3$
f: R, $R=\text{-}CH_2CH_2\text{-}$

also obtained in 74% yield on oxidation of the former by MCPBA. Although attempted isolation of phenyl isocyanate failed, the IR spectrum of the concentrated reaction mixture showed a band at 2250 cm^{-1} assignable to isocyanate. These observations clearly support the proposed reaction mechanism. The postulated reaction pathway (Scheme 1) from 1 to 5 through the intermediates 3 and 4 was proved by isolation of 8[10)] on treatment with 2f. However, 8 could not be changed to 5f probably because of the presence of a stable hydrogen bond between nitro and amino groups. Other 6-amino-2-pyridones (5b-e) were prepared in 24-50% yields in the similar manner (Table 1) and they were oxidized to the corresponding maleimides 7b-e[11)] in 14-41% yields.

Table 1. 1-Aryl-6-arylamino-3,4-diphenyl-2-pyridones (5a-e)

5	Yield %	Mp t/°C	MS M^+(m/z)	IR (KBr) ν/cm^{-1} NH	IR (KBr) ν/cm^{-1} CO	^{1}H-NMR ($CDCl_3$) δ C=CH	^{1}H-NMR ($CDCl_3$) δ NH
a	56	211-213	414	3390	1640	5.87	5.40
b	28	212-216	474	3400	1635	5.58	5.38
c	24	245-247	442	3380	1640	5.76	5.39
d	39	226-232	483	3400	1640	5.78	5.38
e	50	294-295	552	3400	1635	5.87	5.38



Scheme 2.

A typical procedure is as follows. a) A mixture of 1 (4.0 mmol), 2a (3.9 mmol), and K_2CO_3 (2.5 mmol) in a mixing solvent of water (5 ml) and MeOH (10 ml) was stirred at room temperature for 24 h. The precipitates were collected by filtration and recrystallized from C_6H_6-$CHCl_3$-hexane to give 5a. b) After MCPBA (4.8 mmol) in CH_2Cl_2 (15 ml) was added dropwise to a solution of 5a (1.6 mmol) in CH_2Cl_2 (7 ml) at room temperature, the mixture was refluxed for 13 h. The precipitates were removed by filtration and the filtrate was washed with successive, aq. $NaHSO_3$, aq. $NaHCO_3$, and water, then, dried over $MgSO_4$. Removal of the solvent left a residue, which was purified by column chromatography on silica gel with $CHCl_3$ to afford 7a.

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6) ^{13}C-NMR (CDCl$_3$): δ 89.8 (d), 123.8 (d), 125.4, 126.1, 127.3, 127.5, 127.9, 129.0, 129.1, 129.5, 129.7, 130.4, 131.8 (d), 136.0 (s), 136.3 (s), 138.5 (s), 140.7 (s), 146.7 (s), 151.9 (s), 162.4 (s).

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9) 9a: Dark violet needles; mp 254-256 °C; IR (KBr) 1680, 1610, 1580, 1480 cm^{-1}; MS m/z 428 (M$^+$); ^{13}C-NMR (CDCl$_3$) δ 117.7 (d), 132.2 (d), 127.6, 127.9, 128.4, 128.8, 129.0, 129.2, 130.3, 130.8, 131.7 (s), 133.0 (s), 136.6 (s), 142.8 (s), 144.4 (s), 145.4 (s), 148.6 (s), 161.9 (s).

10) 8: 67% Yield; colorless needles; mp 242-243 °C; IR (KBr) 3380, 1680, 1570 cm^{-1}; ^{1}H-NMR (DMSO-d$_6$) δ 3.27-3.44 (m, 4H), 3.88 (d, J=8 Hz, 1H), 4.87 (d, J=8 Hz, 1H), 7.17-7.27 (m, 10H), 9.25 (s, 1H); ^{13}C-NMR (DMSO-d$_6$) δ 43.3 (t), 48.0 (t), 58.9 (d), 61.9 (d), 113.5 (s), 126.8, 127.1, 128.1, 128.6, 128.7, 137.7 (s), 137.8 (s), 160.2 (s), 179.8 (s); MS m/z 355 (M$^+$).

11) 7b: 24% Yield; mp 193-194 °C. 7c: 32% Yield; mp 195-196 °C. 7d: 41% Yield; mp 197-198 °C. 7e: 14% Yield; mp 115-117 °C.

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