

A NEW ROUTE TO 3,4-DIHYDRO-2-PYRIDONES FROM
A DIOXOPYRROLINE DERIVATIVE¹

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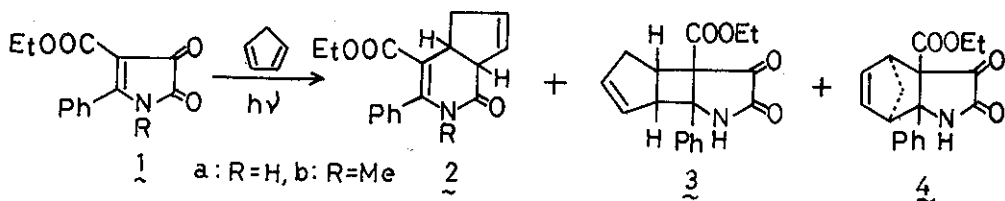
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In photocycloaddition of 2-phenyl-3-ethoxycarbonyl- Δ^2 -pyrrolone-4,5-dione to olefins, the formation of dihydropyridones were observed although the yields were variable depending on the structure of olefins.

In the preceding paper² we described that photocycloaddition of cyclopentadiene to 2-phenyl-3-ethoxycarbonyl- Δ^2 -pyrrolone-4,5-dione (1a) yielded the dihydropyridone (2), together with the cyclobutane (3) and the bicycloheptane derivative (4).



The formation of 2 prompted us to check the generality of this reaction. We show here that in photocycloaddition of 1 to olefins dihydropyridones are usually formed though the yields are variable depending on the structures of olefins.

Irradiation of cyclopentene with 1a in dimethoxyethane with high pressure Hg lamp (100 W, quartz) for 2 hr at 0°C afforded a dihydropyridone (5a), m.p. 143-144°. Cycloolefins, such as 1-trimethylsilyloxycyclopent-1-ene, indene, and cyclohexadiene similarly gave the dihydropyridones (6, 9a and 10), in the yields respectively as shown in Table I. They were easily characterized

Table I. *Photocycloaddition of Dioxopyrrolines with Olefins*

Dioxo- pyrroline	Olefin	Reaction Condition		Dihydropyridone	
		Temp. (°C)	Time (hr)	m.p.	Yield (%)
<u>1a</u>	cyclopentadiene	-30°	1.5	<u>2a</u> 119-120°	30 ^{a)}
"	cyclopentene	0°	2	<u>5a</u> 143-144°	10 ^{b)}
"	1-trimethylsilyl- oxycyclopentene	0°	2	<u>6</u> 125-126°	9 ^{c)}
"	indene	0°	3	<u>9a</u> 194-195°	40 ^{b)}
"	cyclohexadiene	0°	1.5	<u>10</u> 144-146°	1.5 ^{d)}
"	styrene	0°	2	<u>13a</u> 134-136°	6 ^{e)}
"	ethyl vinyl ether	0°	2	<u>14</u> 112-113°	4 ^{e)}
<u>1b</u>	cyclopentadiene	-30°	1	<u>2b</u> 89-91°	11 ^{a, b)}

a) ref. 2

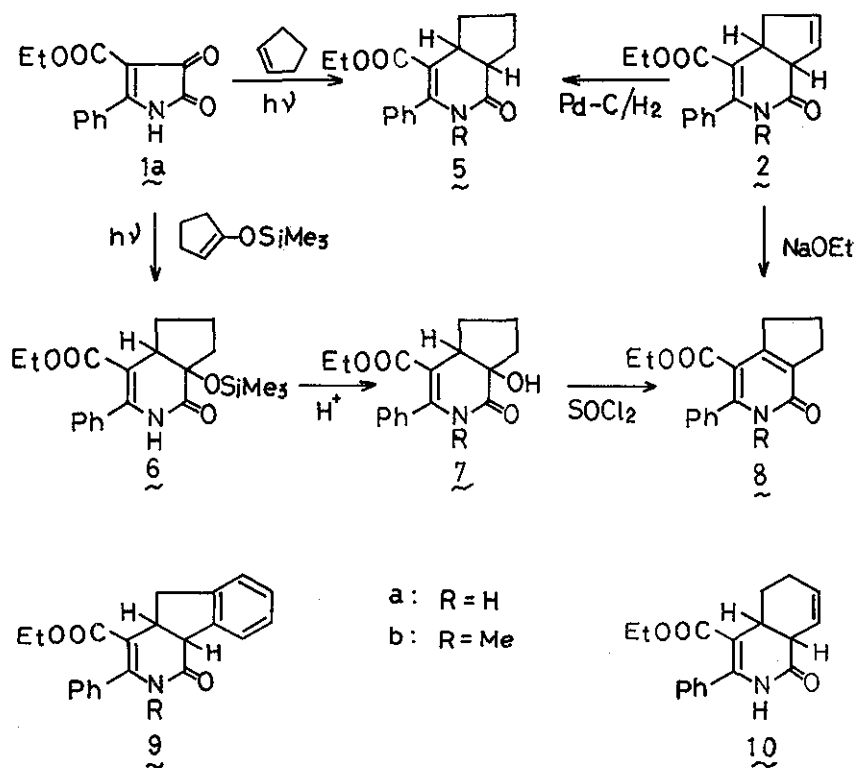
b) The only isolable crystalline product.

c) Isolated as a major product with several crystalline minor products.

d) Isolated as a minor product with two other products (30%).

e) Isolated as a minor product with formation of cyclobutane derivative (ref. 5).

by their UV and IR spectra which were very similar with those of the dihydropyridone (2)². The dihydropyridones (5a, 7a and 9a) were methylated on treatment with dimethyl sulfate in CH₃CN to the corresponding N-methyl derivatives: (5b) m.p. 95-97°, (7b)³ m.p. 80-83°, (9b) m.p. 117-118°.



Structural elucidations of these compounds were made as follows. Hydrogenation of 2a over 5% Pd-C in ethanol gave the dihydro-derivative identical with 5a. Hydrolysis of 6 with dilute hydrochloric acid followed by treatment of the resulting hydroxy-compound (7a), m.p. 187-189°, with thionyl chloride in pyridine afforded the pyridone (8a), m.p. 182-184°. The α -pyridone character

of 8a was demonstrated by its characteristic UV spectrum [λ_{\max} 273 ($\epsilon=9,900$) and 304 nm ($\epsilon=7,800$)] and by the increase of acidity (pK_a 9.18)⁴ compared with that of 2a ($pK_a \sim 14$). In agreement with this evidence, 8a was smoothly methylated with diazomethane to the N-methyl derivative (8b), m.p. 117-119°, λ_{\max} 273 ($\epsilon=10,400$) and 305 nm ($\epsilon=7,200$). The same pyridones 8a and 8b were obtained from 2a and 2b respectively, on treatment with sodium ethoxide.

Table II. IR and UV Spectra of the dihydropyridones

dihydropyridones (R=H)	ν_{\max} cm ⁻¹ (Nujol)	λ_{\max} (ϵ)	
		in EtOH	in EtOH-KOH
<u>2a</u>	1695, 1670, 1640	285(9,000)	328(9,060)
<u>5a</u>	1670, 1630	286(11,000)	323(10,000)
<u>6</u>	1695, 1675, 1645	285(10,300)	325(9,650)
<u>7a</u>	1695, 1670, 1640	282(9,900)	321(8,800)
<u>9a</u>	1700, 1680, 1640	287(9,400)	330(9,100)
<u>10</u>	1700, 1680, 1645	287(10,000)	330(8,300)
<u>13a</u>	1695, 1670, 1640	285(9,300)	325(9,700)
<u>14</u>	1700, 1620	284(10,400)	325(10,600)
dihydropyridones (R=Me)			
<u>2b</u>	1670, 1630	286(11,000)	unchanged
<u>5b</u>	1690, 1630	286(11,000)	"
<u>7b</u>	1700, 1670	284(9,400)	"
<u>9b</u>	1690, 1680, 1630	287(9,500)	"
<u>13b</u>	1710, 1680, 1620	286(10,500)	"

To the minor products in photocycloaddition of 1a to acyclic olefins, styrene and ethyl vinyl ether, dihydroazatropolone

structures (11) and (12) have been tentatively suggested⁵. It was now revealed that their UV and IR spectra were characteristic of the dihydropyridones. Actually they had the compositions less than those for dihydroazatropolones by CO unit, and now are proved to be 13a and 14, respectively. 13a gave the N-methyl derivative (13b), m.p. 95-97°. Dehydrogenation of 13a and 14 with DDQ in refluxing benzene afforded the pyridones (15a) and (16): 15a, m.p. 219-221° (80% yield) [λ_{\max} 280 ($\epsilon=9,000$) and 328 nm (13,200)] and 16, m.p. 194-196° (~30% yield) [λ_{\max} 290 nm (16,000)], respectively. 15a was methylated with diazomethane to the mixture of N-methyl-(15b), m.p. 122-123° [IR: 1690 and 1647 cm^{-1} ; λ_{\max} 284(14,000) and 324 nm (18,000)] and the O-methyl-derivative (17), m.p. 113-114° [IR: 1720 cm^{-1} ; λ_{\max} 297 nm ($\epsilon=17,800$)] in the ratio of 3:1.

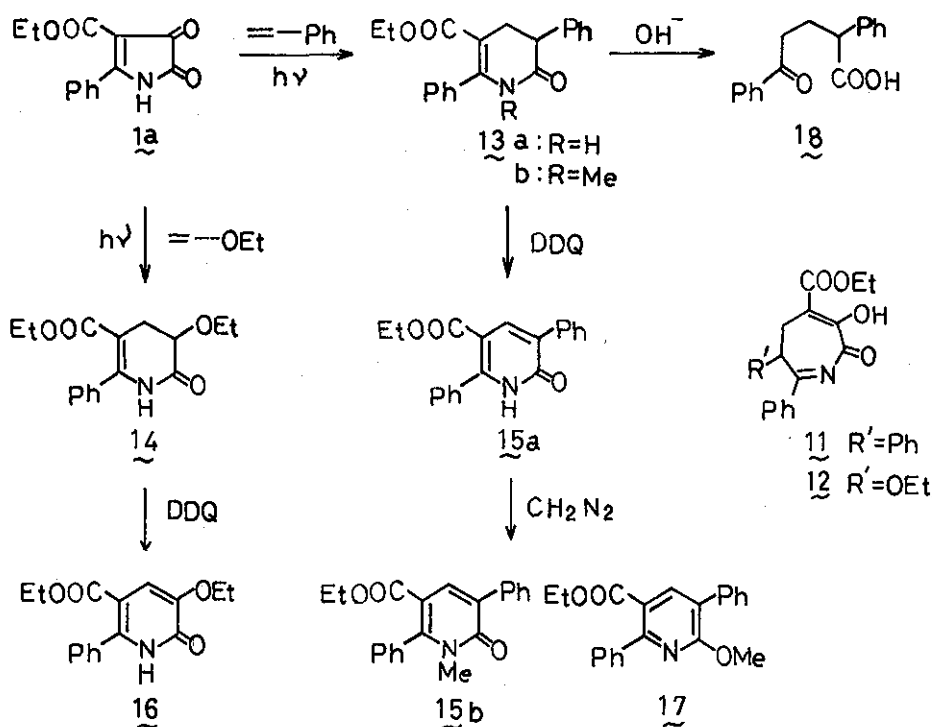
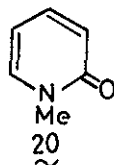
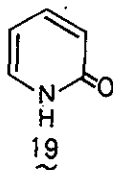
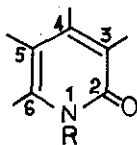
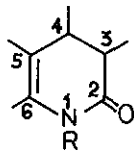


Table III.

Assignment of ^{13}C -NMR shifts of dihydropyridones and pyridones
(δ ppm in CDCl_3 from TMS)



Dihydropyridone	2	3	4	5	6
<u>2a</u>	166.6	48.0	37.3	107.9	142.9
<u>2b</u>	167.5	36.9	32.3	111.1	146.9
<u>5a</u>	167.2	43.0	40.0	108.6	143.7
<u>6</u>	167.0	80.6	48.2	109.3	142.8
<u>7b</u>	165.5	78.9	32.5	114.4	142.8
<u>9a</u>	167.0	48.4	39.7	107.8	144.2
<u>9b</u>	167.3	48.9	39.0	110.7	147.6
<u>10</u>	166.9	40.1	34.3	109.4	144.8
<u>13a</u>	166.6	45.9	30.0	105.5	145.9
<u>14</u>	166.6	73.2	29.4	104.2	145.3
Pyridones					
<u>8a</u>	166.2	131.5	148.5	109.9	156.2
<u>19</u> ⁷	165.3	120.1	134.8	106.7	141.6
<u>15a</u>	166.2	128.4	139.7	109.9	150.7
<u>15b</u>	165.1	129.1	137.4	110.2	150.0
<u>20</u> ⁸⁾	161.8	119.1	139.5	104.8	139.5

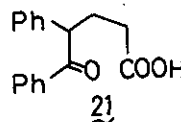
Hydrolysis of 13a with methanolic sodium hydroxide yielded, accompanied by decarboxylation, a keto-acid (18)⁶, m.p. 144-145°, [λ_{\max} 240 nm ($\epsilon=11,600$) and 278 nm ($\epsilon=760$) for PhCO- ; δ 2.88 (2H, t, J=7.2Hz), 2.40 (2H, m), and 3.78 ppm (1H, t, J=7.2 Hz) for -CH₂-CH₂-CH], thus establishing the structure.

The CMR spectra (Table III) of dihydropyridones and of pyridones also supported our structural assignments: for example, C-3 of 15 showed no ¹³C-H coupling but C-4 appeared as a doublet in the off-resonance spectra.

The above results show that the reactions of cycloolefins, particularly cyclopentene derivatives, with the dioxopyrroline (1) yield dihydropyridones as major product (up to 40%), whereas acyclic olefins gave dihydropyridones only in a minute amount. This difference should be attributable to stability of the intermediate cyclobutane derivatives². However, there may be still another factor to be clarified, since the reaction of 1a with norbornadiene gave only a cyclobutane derivative, m.p. 205-208°, and reaction of cyclopentene with 1-methyldioxopyrroline derivative (1b) did not give any characterizable product.

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