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Studies on Stable Free Radicals. VI.[1] Synthesis of Substituted 4-Imidazolidinone-1-oxyls

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It was found that the reaction of α-amino nitriles with carbonyl compounds gave the substituted 4-oxoimidazolidines in the presence of basic catalyst. These imidazolidinones were oxidized by hydrogen peroxide: although the imidazolidinones containing an α-hydrogen at the 2- or 5-position gave no radical products, 2,2,5,5-tetrasubstituted imidazolidinones afforded new stable nitroxide radicals. By this method, stable biradicals were also prepared; but, no corresponding stable nitroxide radical was isolated by oxidation of substituted imidazolidine-4-thiones.

Since Rozantsev and Neiman[2] were successful in the preparing of very stable nitroxide radicals, such as 2,2,6,6-tetramethyl-4-oxopiperidine-1-oxyl, interest seems to have increased in the studies of these stable free radicals.[3-6]

We also reported[7] a suitable method for preparing 2,2,6,6-tetramethyl-4-oxopiperidine which afforded a stable nitroxide radical by oxidation.

In present paper, we wish to report that the reaction of α-amino nitriles with aldehydes of ketones in the presence of basic catalyst gave substituted 4-oxoimidazolidines.

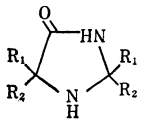
Subsequently, we obtained new, stable nitroxide radicals by oxidation of these imidazolidinones; but the imidazolidinones containing an α-hydrogen at 2- or 5-position gave no radical products.

Attempts to prepare corresponding stable nitroxide radicals from substituted imidazolidine-4-thiones failed.

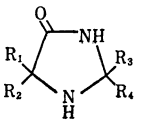
Results and Discussion

Cyclization reaction. Noland *et al.*[8] have reported that cyclohexane-1-spiro-2′-(4′-oxoimidazolidine)-5′-spiro-1″-cyclohexane (IIa) is obtained by self-condensation of 1-amino-1-cyanocyclohexane (IV) catalyzed by sodium ethoxide in ethanol solution containing a small amount of water.

In this method, only two different substituents can be introduced in 2- and 5-positions of the 4-oxoimidazolidine ring (I). In this work, we established a general method for preparing imidazolinones (II) having four different substituents in the 2- and 5-positions.



(I)



(II)

A crystalline solid was obtained on the reaction of 1-amino-1-cyanocyclohexane (IV) with cyclohexanone in the presence of sodium ethoxide in ethanol solution. This product was identified as IIa by comparison of melting point, IR spectrum and elementary analysis with those of an authentic sample of IIa.[8]

Further, the yield of IIa in this reaction was over 100% based on 1-amino-1-cyanocyclohexane (IV). This result was considered to show that cyclohexanone reacted with the α-amino nitrile, IV to give IIa. The

1) Part V: T. Yoshioka, S. Higashide, S. Morimura, and K. Murayama, This Bulletin, **44**, 2207 (1971).

2) E. G. Rozantsev and M. B. Neiman, *Tetrahedron*, **20**, 131 (1964).

3) E. G. Rozantsev, "Free Nitroxyl Raidcals," Plenum Press, New York, N. Y. (1970), Translated from the Russian, references.

4) A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals," Academic Press, New York, N. Y. (1968), pp. 180—238, references.

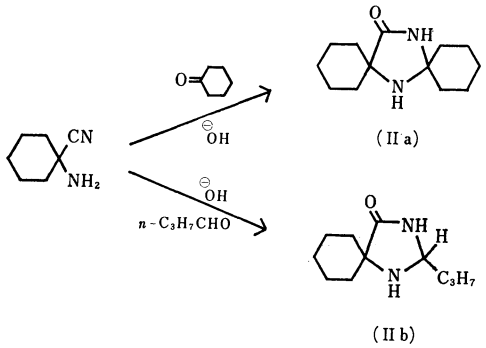
5) K. Murayama, S. Morimura, and T. Yoshioka, This Bulletin, **42**, 1640 (1969).

6) K. Murayama and T. Yoshioka, *ibid.*, **42**, 2307 (1969).

7) K. Murayama, S. Morimura, O. Amakasu, T. Toda, and E. Yamao, *Nippon Kagaku Zasshi*, **90**, 296 (1969).

8) W. E. Noland, R. J. Sundberg, and M. L. Michaelson, *J. Org. Chem.*, **28**, 3576 (1963).

reaction of IV with *n*-butyraldehyde in the presence of a catalytic quantity of aqueous sodium hydroxide afforded similarly the 4-oxoimidazolidine, 1,3-diaza-2-*n*-propyl-4-oxo-spiro[4.5]decane (IIb), as proved by IR spectrum (the presence of carbonyl band at 1691 cm^{-1}) and elementary analysis.



Thus, we confirmed that α-amino nitriles condensed with carbonyl compounds in the presence of a basic catalyst to yield substituted imidazolidinones (II).

The products, IIa—w obtained in this method are listed in Table 1. The structures of these products were confirmed by IR spectra (the presence of carbonyl band at about 1690 cm^{-1}), elementary analysis and the stable nitroxide radicals afforded by oxidation as described in next section.

These imidazolidinones were useful as light stabilizers for synthetic polymers.[9]

Oxidation reaction. Oxidation of the imidazolidinones (II) provided new stable nitroxide radicals (III).

The oxidation[5] of the imidazolidinones were carried out with hydrogen peroxide in the presence of catalytic amount of sodium tungstate and ethylenediaminetetraacetic acid (EDTA) in acetic acid solution.

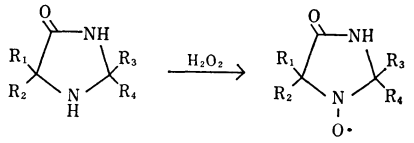
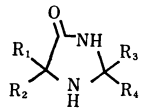


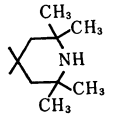
Table 1. Substituted imidazolidinones

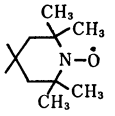


(II)

	Substituents				Yield %	mp °C[B]	Formula	Found %			Calcd %		
	R_1	R_2	R_3	R_4				C	H	N	C	H	N
a	Cyclohexyl		Cyclohexyl		86.6	219—220[a]	$C_{13}H_{22}ON_2$	70.26	9.88	12.57	70.23	9.97	12.60
b	Cyclohexyl		H,	*n*-C_3H_7-	76.4	115—116[b]	$C_{11}H_{20}ON_2$	67.27	10.36	14.16	67.30	10.27	14.27
c	CH_3-	CH_3-	CH_3-	CH_3-	45.9	169—170[c]	$C_7H_{14}ON_2$	58.96	10.11	19.66	59.12	9.92	19.70
d	CH_3-	CH_3-	CH_3-	*i*-C_4H_9-	22.6	126—128[d]	$C_{10}H_{20}ON_2$	65.04	10.88	15.06	65.17	10.94	15.20
e	CH_3-	CH_3-	CH_3-	C_2H_5-	29.5	77— 79[b]	$C_9H_{18}ON_2$	63.43	10.62	16.39	63.49	10.66	16.46
f[A]	CH_3-	CH_3-	Cyclohexyl		90.0	193—194[a]	$C_{10}H_{18}ON_2$	65.77	9.84	15.14	65.89	9.96	15.37
g	Cyclohexyl		Cyclopentyl		70.6	190—191[b]	$C_{12}H_{20}ON_2$	69.25	9.72	13.40	69.19	9.68	13.45
h	Cyclohexyl		H,	*n*-$C_{11}H_{23}$-	23.8	bp170/0.0005	$C_{19}H_{36}ON_2$	73.98	11.55	8.78	73.97	11.76	9.08
i	Cyclohexyl		H,	phenyl	86.2	114.5—115.5[a]	$C_{14}H_{18}ON_2$	72.70	7.88	12.03	73.01	7.88	12.17
j	Cyclohexyl		CH_3-,	3-pyridyl	67.5	147[a]	$C_{14}H_{19}ON_3$	65.77	11.36	16.49	65.83	11.45	16.45
k	Cyclohexyl		TMP[C]		40.5	248.5—249.5[e]	$C_{16}H_{29}ON_3$	68.56	10.47	15.09	68.77	10.46	15.04
l	Cyclohexyl		TMP-oxyl[D]		33.8	198—199[f]	$C_{16}H_{28}O_2N_3$	65.03	9.59	14.08	65.27	9.59	14.27
m	TMP[C]		H,	CCl_3	87.6	190—191[a]	$C_{12}H_{20}ON_3Cl_3$	43.82	6.20	12.62	44.05	6.12	12.85
n	TMP[C]		H,	*p*-Cl-phenyl	68.6	215[d]	$C_{12}H_{24}ON_3Cl$	63.26	7.56	13.20	63.15	7.53	13.28
o	TMP-oxyl[D]		H,	*n*-C_3H_7-	60.6	146—147[a]	$C_{14}H_{26}O_2N_3$	62.49	9.73	15.48	62.65	9.77	15.66
p	TMP-oxyl[D]		Cyclohexyl		44.5	201—202[d]	$C_{16}H_{28}O_2N_3$	65.22	9.57	14.26	65.27	9.59	14.27
q	TMP-oxyl[D]		H,	phenyl	63.5	184—185[a]	$C_{17}H_{24}O_2N_3$	67.46	7.92	13.81	67.52	8.00	13.90
r	TMP-oxyl[D]		H,	*o*-CH-phenyl	88.0	194.5—195.5[d]	$C_{18}H_{26}O_2N_3$	68.40	8.21	13.19	68.32	8.28	13.28
s	TMP-oxyl[D]		H,	*p*-CH_3O-phenyl	81.0	178—179[d]	$C_{18}H_{26}O_3N_3$	64.90	7.81	12.59	65.03	7.88	12.64
t	TMP-oxyl[D]		TMP-oxyl[D]		23.6	261—262[a]	$C_{19}H_{34}O_3N_4$	61.52	9.42	15.14	62.26	9.35	15.29
u	H, phenyl		Cyclohexyl		40.2	176—177[a]	$C_{14}H_{18}ON_2$	72.90	7.91	12.09	73.01	7.88	12.17
v	CH_3-, phenyl		Cyclohexyl		40.0	130—131[b]	$C_{15}H_{20}ON_2$	73.69	8.35	11.21	73.77	8.25	11.21
w	2-CH_3-cyclohexyl		2-CH_3-cyclohexyl		36.0	146—148[a]	$C_{15}H_{26}ON_2$	72.02	10.49	11.22	71.95	10.47	11.19

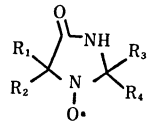
A): Sodium methoxide was used as catalyst. B) The letters indicate the solvent used for recrystallization as follows: a) ethanol; b) petroleum ether; c) water; d) benzene; e) methanol; f) ethyl acetate.

[C]TMP= 

[D]TMP-oxyl= 

9) K. Murayama, S. Morimura, T. Toda, S. Akagi, T. Kurumada, and I. Watanabe, Brit. 1202298 (1970).

TABLE 2. SUBSTITUTED IMIDAZOLIDINONE-1-OXYLS



(III)

	Substituents				Yield %	mp °C[A]	Formula	Found %			Calcd %		
	R_1	R_2	R_3	R_4				C	H	N	C	H	N
a	Cyclohexyl		Cyclohexyl		77.6	227—228[a]	$C_{13}H_{21}O_2N_2$	65.93	8.93	11.87	65.80	8.92	11.81
c	CH_3–,	CH_3–	CH_3–,	CH_3–	63.3	225—226[a]	$C_7H_{13}O_2N_2$	53.03	8.33	17.72	53.48	8.34	17.82
e	CH_3–,	C_2H_5–	CH_3–,	C_2H_5–	68.3	114—115[a]	$C_9H_{17}O_2N_2$	58.25	9.29	15.37	58.35	9.25	15.12
f	CH_3–,	CH_3–	Cyclohexyl		89.0	236—237[b]	$C_{10}H_{17}O_2N_2$	61.18	8.71	14.38	60.89	8.69	14.20
l	Cyclohexyl		TMP-oxyl[B]		16.0	191—192[a]	$C_{16}H_{27}O_3N_3$	61.94	8.83	13.58	62.11	8.80	13.58
p	TMP-oxyl[B]		Cyclohexyl		80.8	219.5—220.5[a]	$C_{16}H_{27}O_3N_3$	62.19	8.83	13.49	62.11	8.80	13.58
w	2-CH_3-cyclohexyl		2-CH_3-cyclohexyl		66.5	174—175[a]	$C_{15}H_{25}O_2N_2$	68.05	9.56	10.70	68.41	8.80	10.64

A) Letters indicate the solvent used for recrystallization: a) benzene; b) methanol.

[B]TMP-oxyl =

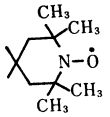
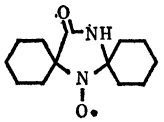
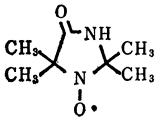
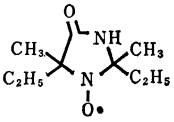
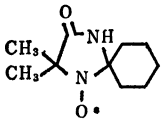
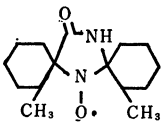
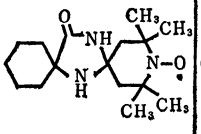
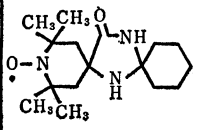
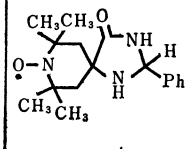
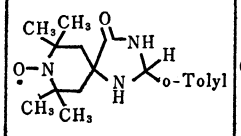
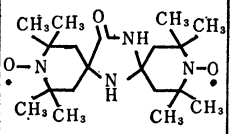


TABLE 3. THE a_N VALUES[a] OF SUBSTITUTED IMIDAZOLIDINONE-1-OXYLS AND PIPERIDINE-1-OXYLS

 (III a) 14.1	 (III c) 14.0	 (III e) 13.6	 (III f) 14.0	 (III w) 14.1
 (II l) 15.3	 (II p) 15.3	 (II q) 15.5	 (II r) 15.0	 (II t) 15.1 (7.5)

a): measured in 10^{-3} mol/l benzene solution at room temperature, are given in gauss and are accurate to within ±0.1G.

The structures of the products (IIIa—g) were assinged by ESR spectra (triplet lines), elementary analysis and IR spectra in which the carbonyl band of corresponding amines at about 1690 cm^{-1} shifted approximately 20 cm^{-1} toward higher frequency. The nitroxide radicals obtained by the oxidation are listed in Table 2.

These radicals are very stable and no change has occurred on standing at room temperature for several years.

The ESR spectra of these radicals exhibited only three lines, which arise through hyperfine interaction with a ^{14}N nucleus, in evacuated benzene solution. The values of the nitrogen hyperfine splitting are shown in Table 3.

Table 3 indicates that the magnitude of the nitrogen hyperfine splitting in the imidazolidinone-1-oxyl radicals, IIIa,c,e,f, and IIIw, are smaller than that of the derivatives of 2,2,6,6-tetramethylpiperidine-1-oxyl radicals, III,p,q,r, and IIt.

It has been reported[10] that the a_N values of the derivatives of 2,2,6,6-tetramethylpiperidine-1-oxyl, measured in the same solvent, decrease as the carbon atom at the 4-position in the piperidine ring becomes more electron deficient.

Therefore, the fact that the a_N values of the imidazolidinone-1-oxyls are smaller than those of the piperidine-1-oxyls could be considered to be due to the difference of dipolar field effect on the radical moiety between the amide group in imidazolidinone-1-oxyl and the substituents at 4-position in piperidine-1-oxyl.

Furthermore, we were interested in the ESR spectra of bi-nitroxide radicals, IIt, IIIl, and IIIp to determine any intramolecular interaction between the two radical part within a single molecule.

10) R. Briere, H. Lamaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, **1966**, 3273.

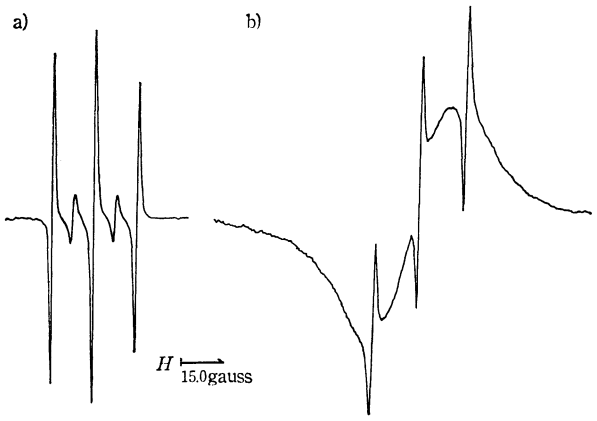


Fig. 1. The ESR spectra of bi-nitroxide radicals.[A)]
A): measured in 10^{-3}mol/l benzene solution at room temperature.
a): 2,2,6,6-tetramethylpiperidine-4-spiro-2′-(4′-oxoimidazolidine)-5′-spiro-4″-(2″,2″,6″,6″-tetramethylpiperidine)-1′,1″-dioxyl (IIt).
b): cyclohexane-1-spiro-2′-(4′-oxoimidazolidine)-5′-spiro-4″-(2″,2″,6″,6″-tetramethylpiperidine)-1′,1″-dioxyl (IIIp).
The ESR spectra of IIIl and IIIp are basically very similar.

As shown in Fig. 1a, IIt gave a quintet lines like the spectrum of the carbonate diester of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl.[11] The spectra of IIIl and IIIp were more complicated than that of IIt (Fig. 1b).

This suggests that the intramolecular interaction between the two nitroxide radical groups was stronger than in IIt. The ESR studies of these bi-nitroxide radicals are currently under detailed investigation.

In the case of imidazolidinones containing an α-hydrogen adjacent to the secondary amino group, the oxidation products were non-radicals.

Treatment of 1,3-diaza-2-phenyl-4-oxo-spiro[4,5]decane (IIi) with hydrogen peroxide in the presence of sodium tungstate in methanol solution gave white crystals. This product was presumed to be 1,3-diaza-2-phenyl-4-oxo-spiro[4.5]-1-decene-1-oxide (V) from its spectral data (the presence of $\nu_{C=N\to O}$ band[12] at 1588 and 1564 cm^{-1} in IR spectrum and a m/e 244 molecular peak in mass spectrum), elementary analysis and the following reaction. The nitroxide, V was converted into 1,3-diaza-2-phenyl-4-oxo-spiro[4.5]decene-1 (VI) on treating with triphenylphosphine. The structure of VI was assigned by IR spectrum (the presence of $\nu_{C=N}$ at 1625 cm^{-1}, mass spectrum (at m/e 228 molecular peak) and elementary analysis.

Similarly, 1,4-diaza-2-phenyl-3-oxo-sprio[4.5]-1-decene-1-oxide (VII) and 1,3-diaza-2-*n*-propyl-4-oxo-spiro[4.5]-1-decene-1-oxide (VIII) were obtained by the oxidation of corresponding amines, IIu and IIb, respectively.

This reaction would proceed as shown in Chart 1.

It seems reasonable that the intermediate, nitroxide radical, IX disproportionates to V and X, since dimethylamino radicals disproportionate into dimethylamine and *N*-methylformaldimine.[13] The hydroxylamine, X would regenerate the nitroxide radical, IX by oxidation with hydrogen peroxide.

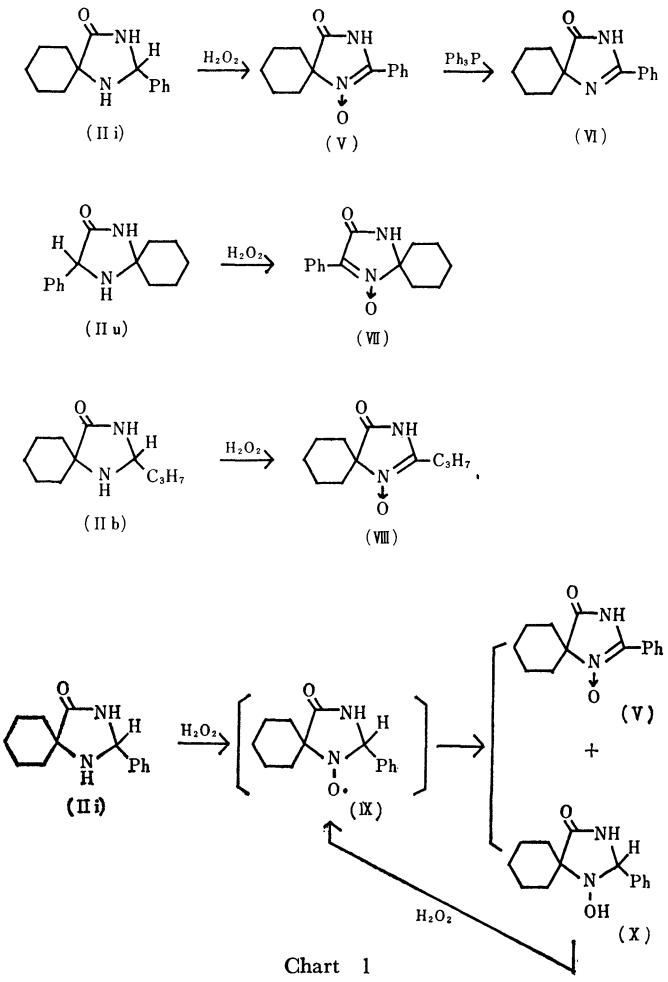


Chart 1

However, it has been reported[14] that norpseudopelletierine containing an α-hydrogen adjacent to a secondary amino group provides a corresponding stable nitroxide radical. In this case, the disproportionation reaction mentioned above, would be hindered by steric factors (Bredt rule).

Oxidation of substituted imidazolidine-4-thiones. We attempted to prepare another stable nitroxide radicals with imidazolidine-4-thione ring.

Rassat *et al.*[15] have suggested the formation of the free radicals of this type in their ESR studies, where they have observed a triplet spectrum on mixing 2,2,5,5-tetramethylimidazolidine-4-thione (XII)[16] and *p*-nitroperbenzoic acid in benzene, but they did not isolate this free radical.

However, we obtained no radical products from the oxidation of imidazolidine-4-thiones.

Treatment of cyclohexane-1-spiro-2′-(imidazolidine-

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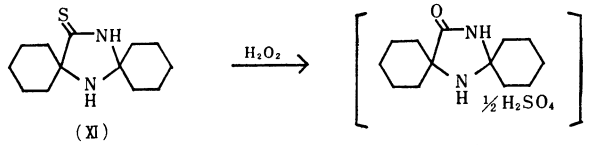
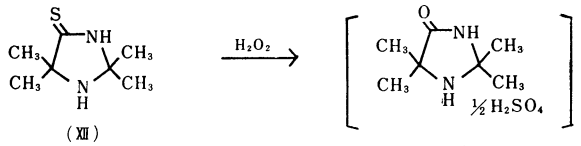
4'-thione)-5'-spiro-1''-cyclohexane (XI)[16] with hydrogen peroxide under similar conditions used in the oxidation of IIa gave white crystals. This product was identified as the sulfate of IIa by direct comparison of IR spectrum with that of an authentic sample prepared from IIa and sulfuric acid.

Treatment of XI with perbenzoic acid or excess hydrogen peroxide gave also the sulfate of IIa. Under similar reaction conditions, XII gave the sulfate of IIc.



(XI) (IIa)



(XII) (IIc)

This reaction would proceed analogously to that in which thiopyrin reacts with hydrogen peroxide in aqueous alkali to give antipyrin and sulfuric acid.[17]

Experimental

Melting points are uncorrected. The IR spectra were determined by means of Nujol mulls and liquid films. The NMR spectra were obtained using a Varian A-60 NMR spectrometer, using tetramethylsilane as the internal standard at 32°C. The mass spectra were obtained using a JEOL-JMS-OIS mass spectrometer. The ESR spectra were recorded on a Hitachi MES 4001 type X-band spectrometer employing 100 kc modulation and the splitting constants were measured relative to aqueous solution of Fremy's salt.

Synthesis of α-Amino Nitriles. α-amino nitriles were prepared from corresponding carbonyl compounds by the Strecker reaction.

4-Amino-4-cyano-2,2,6,6-tetramethylpiperidine. A solution of 2,2,6,6-tetramethyl-4-oxopiperidine[7] (31.0 g, 0.2 mol) in 50 m*l* of methanol saturated with ammonia were added slowly to stirred solution of potassium cyanide (26.0 g) and ammonium chloride (21.5 g) in 200 m*l* of aqueous ammonia (28%) and 60 m*l* of methanol saturated with ammonia at 0—5°C and the solution was stirred at room temperature for 9 hr. The resulting precipitates were removed by filtration and methanolic filtrate was evaporated under reduced pressure at room temperature. The organic layer was extracted with 200 m*l* of methyl ethyl ketone, dried over potassium carbonate and evaporated under reduced pressure to give crude 4-amino-4-cyanotetramethylpiperidine. Recrystallization from petroleum ether gave an analytical sample mp 75—76°C, yield 11.4 g (31.6%). Found: C, 66.45; H, 10.68; N, 23.33%. Calcd for $C_{10}H_{19}N_3$: C, 66.25; H, 10.57; N, 23.18%. IR (cm^{-1}): $\nu_{C\equiv N}$ 2240, ν_{NH} 3470, 3340, 3260, and 3170.

4-Amino-4-cyano-2,2,6,6-tetramethylpiperidine-1-oxyl. In the same manner described above, 34.6 g (0.2 mol) of 2,2,6,6-tetramethyl-4-oxopiperidine-1-oxyl[7] was reacted to give 4-amino-4-cyano-2,2,6,6-tetramethylpiperidine-1-oxyl as a red crystalline solid. Recrystallization from methanol gave an analytically pure sample: mp 129—130°C, yield 15.4 g (40.0%). Found: C, 60.99; H, 9.16; N, 21.42%. Calcd for $C_{10}H_{18}ON_3$: C, 61.19; H, 9.24; N, 21.42%. IR (cm^{-1}): $\nu_{C\equiv N}$ 2200, ν_{NH} 3360, and 3300. ESR (in benzene): a_N= 15.2 gauss.

Cyclization Reactions. In general, the products shown in Table 1 were prepared by the reaction of α-amino nitriles with carbonyl compounds in the presence of catalytic amount of aqueous sodium hydroxide (40%) in ethanol or methanol solution in the manner described below.

Cyclohexane-1-spiro-2'-(4'-oxoimidazolidine)-5'-spiro-1''-cyclohexane (IIa). To a stirred solution of 1-amino-1-cyclohexane (IV) (12.4 g, 0.1 mol) and cyclohexanone (9.8 g, 0.1 mol) in 50 m*l* of methanol was added 1 m*l* of aqueous sodium hydroxide (40%) and the solution was stirred at room temperature for 8 hr. The white product was sepapated (from solution) by filtration, washed with water and ethanol and dried under vacuum. The crude crystals, IIa were recrystallized from ethanol to give an analytically pure sample. IR (cm^{-1}): $\nu_{C=O}$ 1687, ν_{NH} 3300, 3220, and 3020.

Oxidation Reactions. The nitroxide radicals shown in Table II were prepared by oxidation of corresponding substituted imidazolidinones with hydrogen peroxide in a similar way as described previously.[5]

1,3-Diaza-2-phenyl-4-oxo-spiro[4.5]-1-decene-1-oxide (V). To a solution of 9.3 g (40 mmol) of IIi in 50 m*l* of methanol were added 75 mg of EDTA and 50 mg of sodium tungstate and then 20 m*l* of aqueous hydrogen peroxide (30%) with stirring at room temperature. Stirring was continued for 6 days at room temperature. The resulting precipitate was separated by filtration, washed with water and dried *in vacuo* to give 6.0 g (61.5%) of crude crystals, V. The crude crystals, V were recrystallized from methanol to give an analytically pure sample: mp 251—251.5°C. Found: C, 68.35; H, 6.66; N, 11.36%. Calcd for $C_{14}H_{16}O_2N_2$: C, 68.83; H, 6.60; N, 11.47%. IR (cm^{-1}): $\nu_{C=N\to O}$ 1588, 1564, and 1256, $\nu_{C=O}$ 1748. NMR (τ) (in DMF): 7.85—8.35 (10H, broad), 2.34—2.46 (3H, multiplet), 1.27—1.47 (2H, multiplet). Mass spectrum: M^+=244.

1,4-Diaza-2-phenyl-3-oxo-spiro[4.5]-1-decene-1-oxide (VII). From 21.5 g (95 mmol) of IIu, crude crystals, VII were obtained (15.0 g, 65.0%). Recrystallization from methanol gave an analytical sample: mp 259—261°C. Found: C, 68.60; H, 6.60; N, 11.24%. Calcd for $C_{14}H_{16}O_2N_2$: C, 68.83; H, 6.60; N, 11.47%. IR (cm^{-1}): $\nu_{C=N\to O}$ 1555, $\nu_{C=O}$ 1715. NMR (τ) (in DMF): 7.94—8.44 (10H, broad), 2.35—2.47 (3H, multiplet), 1.03—1.23 (2H, multiplet). Mass spectrum: M^+=244.

1,3-Diaza-2-n-propyl-4-oxo-spiro[4.5]-1-decene-1-oxide (VIII). In a similar manner as mentioned above, 6.3 g (32 mmol) of IIb gave 1.8 g (28.6%) of crude crystals, VIII. The crude crystals were recrystallized from cyclohexane to give pure sample: mp 182—183°C. Found: C, 62.99; H, 8.68; N, 13.38%. Calcd for $C_{11}H_{18}O_2N_2$: C, 62.83; H, 8.63; N, 13.32%. IR (cm^{-1}): $\nu_{C=N\to O}$ 1578 and 1242, $\nu_{C=O}$ 1705. Mass spectrum: M^+=210.

1,3-Diaza-2-phenyl-4-oxo-spiro[4.5]decene-1 (VI). A mixture of 3.4 g (14 mmol) of V and 3.7 g (14 mmol) of triphenylphosphine were heated at 270°C for 10 min. The reaction mixture was cooled, dissolved in minimum amount of benzene and chromatographed on a alumina column. Eluting with benzene afforded 2.7 g (87.0%) of VI: mp 178—181°C. Found: C, 74.05; H, 7.63; N, 11.70%. Calcd for $C_{14}H_{16}ON_2$: C, 73.63; H, 7.06; N, 12.27%. IR (cm^{-1}): $\nu_{C=N}$ 1625,

17) R. Kitamura, *Yakugaku Zasshi*, **58**, 676 (1938).

$\nu_{C=O}$ 1714. NMR (τ) (in DMF): 7.95—8.45 (10H, broad), 2.44—2.56 (3H, multiplet), 1.83—2.03 (2H, multiplet). mass spectrum: $M^+=228$. The methanol eluates yielded 1.5 g of triphenylphosphine oxide (mp 156°C) which was confirmed by comparison of IR spectrum with that of an authentic sample.

Sulfate of Cyclohexane-1-spiro-2'-(4'-oxoimidazolidine)-5'-spiro-1''-cyclohexane (IIa). To a solution of 2.4 g (10 mmol) of cyclohexane-1-spiro-2'-(imidazolidine-4'-thione)-5'-spiro-1''-cyclohexane (XI)[15] in 30 m*l* of acetic acid were added 11 mg of EDTA and 9 mg of sodium tungstate and then 30 m*l* of aqueous hydrogen peroxide (30%) at 0—5°C. The solution was stirred at room temperature for additional 1 hr. After the solvent had been evaporated under reduced pressure, a colorless crystalline mass remained. By the recrystallization from ethanol, the sulfate of IIa was obtained as an analytically pure sample: mp 230—231°C, yield 2.4 g (89.0%). Found: C, 57.32; H, 8.54; N, 10.33; S, 5.62%. Calcd for $C_{26}H_{46}O_6N_4S$: C, 57.54; H, 8.85; N, 10.05; S, 5.90%. IR (cm^{-1}): $\nu_{NH_2^+}$ 2000—2600, $\nu_{C=O}$ 1708.

Sulfate of 2,2,5,5-Tetramethyl-4-oxoimidazolidine (IIc). Similarly as described above, 3.2 g (20 mmol) of 2,2,5,5-tetramethylimidazolidine-4-thione (XII)[16] was converted into 2.3 g (60.2%) of sulfate of IIc: mp 236—237°C. IR (cm^{-1}): $\nu_{NH_2^+}$ 2100—2550, $\nu_{C=O}$ 1720.

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