1192m, 1111m, 1041m, 1035m, 1022m, 983w, 929w, 775m, 767w, 750m, 691m] in high yields, together with small amounts of deoxygenated products. Similarity in the UV spectra of I, II, and III strongly suggested the existence of a common chromophore in these three compounds. The NMR spectra of II and III together with the assignments are shown in Table I, and these are consistent with the proposed structures, II and III.

Table I. Nuclear Magnetic Resonance Spectra*[7,a] of Oxaziranes

Compounds	$-CH_3$	Aromatic protons	Olefinic protons	Ratio
I	8.05[b] J=3	2.65~2.84[c]	3.89[d] J=3	3:4:1
II	—	2.75~3.15[c]	4.07,[b] 4.28[b] J=6 J=6	4:1:1
III	—	1.8~2.03,[c] 2.5~3.0[c]	3.72,[b] 4.03[b] J=6 J=6	2:7:1:1

a) Coupling constants are given in c.p.s.
b) Center of doublet.
c) Multiplet.
d) Center of quartet.

Preliminary studies on these oxazirane compounds (I~III) indicated that these compounds are quite stable either in their solid state or in non-polar solvents, even at elevated temperature. Strong contrast of these oxaziranes derived from aromatic N-oxides with those[8] derived from aliphatic nitrones is the lack of oxidizing ability of the former compounds. Thus, I to III do not liberate iodine from potassium iodide. Another feature of these compounds is their susceptibility to cationic reagents. So far we have found many interesting reactions of these compounds using a variety of cationic reagents. A detailed study of the chemical reactions of these novel heterocyclic compounds will be reported in near future.

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Autoxidation of Quinoline N-Oxide

In this paper the authors wish to report a new type of reaction that quinoline 1-oxide (I) is autoxidized in the presence of potassium *tert*-butoxide to afford 1-hydroxycarbostyril (II) and 2,2′-biquinoline (III), accompanied with a mono N-oxide (IV) of III.

When quinoline 1-oxide (I) was heated with an equimolar amount of potassium *tert*-butoxide in *tert*-butanol at 70° for 9 hr. with bubbling of oxygen, three kinds of compounds (II, m.p. 190°, III, m.p. 193° and IV, m.p. 170°) were obtained as the main reaction products in 41%, 34% and 10% yields respectively. In addition to these, carbostyril (V) was detected in a very poor yield (0.6%), accompanied by the recovery (5%) of the starting material (I). III, IV, V, and recovery of I were separated by column chromatography of the basic fraction on alumina, while the acidic fraction mainly consisted of II.

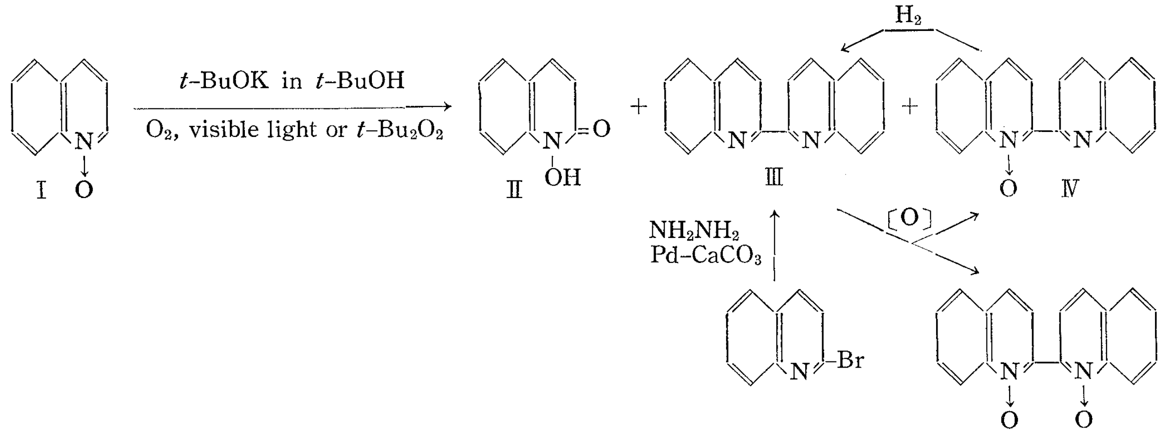

Chart 1.

III was considered to be biquinoline from its analytical values (*Anal.* Calcd. for $C_{18}H_{12}N_2$: C, 84.35; H, 4.72; N, 10.93. Found : C, 84.42; H, 4.79; N, 11.07), and the identity of III with 2,2′-biquinoline was confirmed by comparison of the ultraviolet[1,2] and infrared absorption spectra and also on admixture with the authentic sample prepared[2] by the reductive condensation of 2-bromoquinoline in the presence of hydrazine over palladium on calcium carbonate.

IV gave the analytical data corresponding to a mono oxide of III (*Anal.* Calcd. for $C_{18}H_{12}ON_2$: C, 79.39; H, 4.44; N, 10.29. Found: C, 79.42; H, 4.70; N, 10.42) and showed no carbonyl or hydroxyl band in its infrared region. Accordingly, either phenolic or pyridone type of compound was ruled out and in view of its ultraviolet spectral data (λ_{max}^{EtOH} mμ : 266, 334~336, shoulder 304; $\lambda_{max}^{dioxane}$ mμ : 249, 273.5, 300~302, 331~333) IV was unlikely to be a biquinolyl ether type of compound. The structure of IV was elucidated to be a mono N-oxide of III by the following reactions : i) IV was quantitatively transformed to III after an absorption of an equimolar amount of hydrogen by catalytic hydrogenation, and ii) it was derived from III by partial oxidation with an equimolar amount of monoperphthalic acid, accompanied with the simultaneous formation of 1,1′-dioxide of III (VI, m.p. 248~250°[3]).

II gave an intense red coloration with ferric chloride and was proved to be 1-hydroxycarbostyril on admixture and by comparison of the infrared absorption spectra. Comparison of the ethylated compound (m.p. 71°) of II with authentic 1-ethoxycarbostyril (VII)[4] also confirmed their identity.

The reaction was very sensitive to either the presence of oxygen or the irradiation of visible light. When the reaction was carried out under the sunlight or the irradiation of 600 W sun lamp, a fairly smooth reaction occurred, even without bubbling of oxygen (Table I, reaction number 3), whereas in the dark, and without oxygen, no reaction took place and 98% of the starting material was recovered (No. 4). Moreover, when oxygen was bubbled under irradiation of sun lamp, II was found to be the reaction product (52%) except the recovery of the starting material (41%), while under nitrogen atmosphere free from oxygen by passage through Fieser's solution, no reaction took place even with irradiation (No. 2 and No. 5). It has to be emphasized that irradiation

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[2] S. Nakano : Yakugaku Zasshi, **79**, 310 (1959).
[3] *Idem* : *Ibid.*, **82**, 498 (1962).
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of ultraviolet light of wave length 2537 A showed no appreciable effect on this reaction (No. 6 and No. 7), and the reaction was sufficiently inhibited by addition of hydroquinone (No. 8 and No. 9).

The reaction proceeds less successfully both in the systems of ethanolic sodium ethoxide and of methanolic sodium methoxide, while in benzene or tetrahydrofuran solution in the presence of dry potassium *tert*-butoxide, an exclusive formation of II was observed (No. 11 and No. 12). As a whole, the reaction condition 1 in Table I was found to be most satisfactory for obtaining 2,2′-biquinoline (III), the chelating reagent for cuprous ion; on the other hand, for synthesizing 1-hydroxycarbostril (II) in a high yield was effective the reaction condition 12.

TABLE I. Reaction of Quinoline 1-Oxide

Reaction No.	Reagent[a]	Conditions[b]	Products (%)				Recovery of I (%)
			II	III	IV	V	
1	*t*-BuOK-*t*-BuOH	O_2, 70°, 9 hr.	41	34	10	0.6	5
2	〃	O_2, 80°, 5 hr., 600 W lamp	52	—	—	—	41
3	〃	air, 80°, 6 hr., 600 W lamp	26	23	16	—	5
4	〃	air, 80°, 6 hr., in the dark	trace[d]	—	—	—	98
5	〃	N_2, 70~80°, 5 hr.,600 W lamp	trace[d]	—	—	—	96
6	〃	air, 30°, 58 hr., UV lamp	7	0.3	trace	7	74
7	〃	air, 80°, 6 hr., UV lamp	14	—	2	0.7	64
8	〃	air, 80°, 5.5 hr., 600 W lamp 0.1 mole of HQ was added	—	—	—	—	99
9	〃	O_2, 60~65°, 10.5 hr. 0.5 mole of HQ was added	—	—	—	—	98
10	〃	N_2, 60~70°, 7.5 hr. Bu_2O_2 was added	23	25	18	—	8
11	dry *t*-BuOK-C_6H_6[c]	O_2, 60~70°, 9 hr.	73	trace	—	—	7
12	dry *t*-BuOK-THF[c]	O_2, 40°, 4 hr.	92	trace	trace	—	trace

HQ: Hydroquinone. Bu_2O_2: Di-*tert*-butyl peroxide. THF: Tetrahydrofuran.

[a] One molar equivalent of potassium *tert*-butoxide(*t*-BuOK) was used.

[b] Under the diffused light except where otherwise indicated.

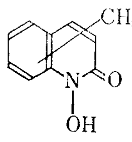
[c] 2.4 molar equivalents of dry potassium *tert*-butoxide was used.

[d] A trace of crude acidic substance positive to $FeCl_3$ test.

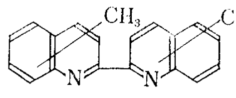
TABLE II. Reaction of Some Methylquinoline N-Oxides

Methylquinoline N-oxide	Products % (m.p.)					Others	Recovery (%)
	VIII	IX	X	XI	XII		
2-methyl	—	—	—	—	4 (169~171°)[5]	acidic resinous substances	63
4-methyl	1[a]	1 (275°)[2]	—	—	5 (259°)[7]	lepidine and acidic resinous substances	43
6-methyl	3 (200°)[6]	9 (259°)[8]	1 (278°)	1 (230°)	—		50

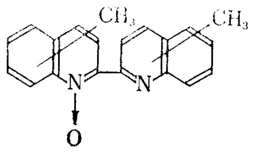
[a] The ethylated product, m.p. 91~92°, was identical with the authentic specimen derived from 4-methyl carbostyril 1-oxide[6].



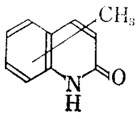
VIII



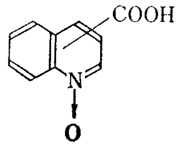
IX



X



XI



XII

Reactions of some methyl derivatives of quinoline 1-oxide were examined under the similar condition to reaction number 1 in Table I, and it was found that much amounts of the starting materials were recovered as well as the oxidation of the active methyl group to the carboxylic acid took place (Table II). Pyridine 1-oxide did not react in any way.

The investigation of the reaction mechanism is under way, but the above experimental results indicate that the reaction involves some radical intermediate rather than ionic. In fact, when di-*tert*-butyl peroxide was added to the reaction mixture under the nitrogen atmosphere, quinoline 1-oxide (I) gave the same products, II, III, IV (reaction No. 10 in Table I). Quinoline, 2,2′-biquinoline (III), 2,2′-biquinoline 1,1′-dioxide (VI), carbostyril (V) and its N-oxide (II) were all recovered nearly quantitatively under the reaction condition 1, and thus, all of them were unlikely to be possible intermediates.

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