irradiated by light, 4-nitropyridine 1-oxide (I) is formed exclusively, which is in turn subjected to further photoisomerization as described above. In a higher concentration of II (ca. $10^{-2}M$), both dark and light reactions result in the formation of IX. These facts can be understood if the rate of the dark reaction to form IX is dependent on the concentration and it becomes faster as the concentration of II increases, and thus, the following reaction mechanism*8 in which the rate is second-order to II could be postulated :

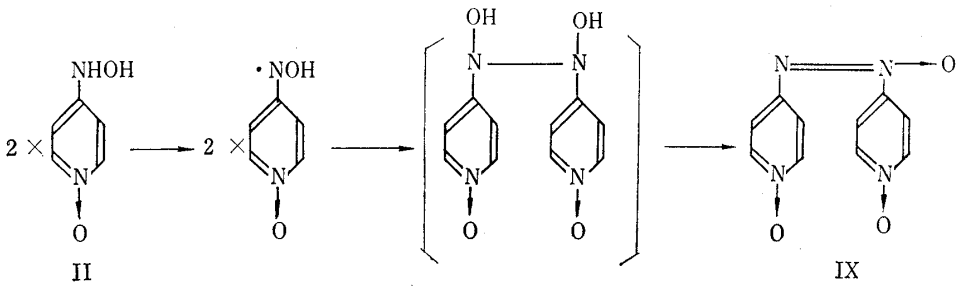

Chart 2.

Though the exact photochemical process from II to I is unknown, its rate should be first-order to II and is very slow compared to that of I to II, which is confirmed in the comparative experiment under exactly the same condition. 4-Nitrosopyridine 1-oxide[3] (IV), m.p. 139°; UV λ_{max}^{EtOH} mμ (log ε) : 250 (3.81), 370 (4.12), on the contrary, is reduced to II by its light reaction, either in the presence or absence of oxygen. However, this process also proceeds with much slower rate than that of I to II, and in this case, the concentration of IV has no effect on the product formation (10^{-5}~$10^{-2}M$). These experiments on IV rationally exclude the possibility that the photochemical reaction of 4-nitropyridine 1-oxide (*e.g.* I to II) involves IV as an intermediate.

The mechanisms shown in this paper are at present without direct proof, however, and more experimental data will have to be obtained before the obviously complex mechanisms of the photolysis of I and its related N-oxides (II and IV) can be understood.

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*8 Stable radical formation from 4-hydroxyaminoquinoline 1-oxide by molecular oxygen was reported by C. Nagata, N. Kataoka, A. Imamura, Y. Kawazoe, G. Chihara (GANN, **57**, 323 (1966)).

3) E. Ochiai, H. Mitarashi : Ann. Rept. ITSUU Lab., **14**, 17 (1965). See also F. Parisi, P. Bovina, A. Quilico : Gaz. chim. ital., **90**, 903 (1960); *Idem* : *Ibid.*, **92**, 1138 (1962).

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Structure of Leucomycin A_1

Evidences have been presented that leucomycins[1] are composed of six components, leucomycin A_1, A_2, B_1, B_2, B_3 and B_4,[2] and the major component A_1 having the highest

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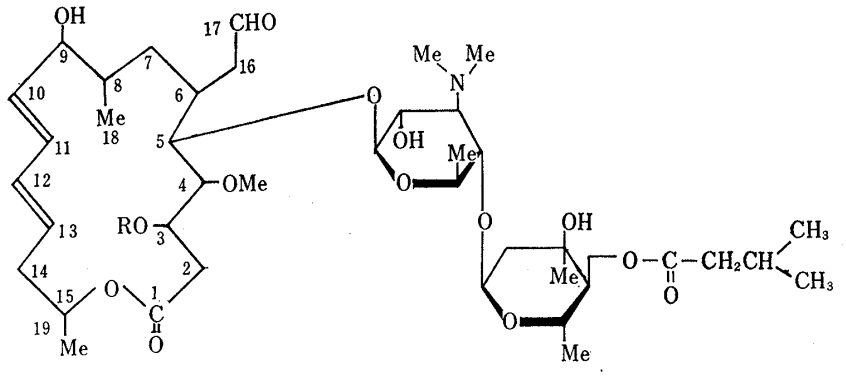
2) T. Watanabe : Bull. Chem. Soc. Japan, **33**, 1101, 1105 (1960), *Ibid.*, **34**, 15 (1961).

antibacterial activity is specified as one of the macrolide antibiotics and is 4-O-(4-O-iso-valerylmycaropyranosyl)mycaminopyranoside of large membered lactone.[3]

Leucomycin A_1, ($[\alpha]_D^{25}$ −66.0°(c=1.0, $CHCl_3$), UV λ_{max}^{MeOH} mμ ($E_{1cm}^{1\%}$) : 232 (400), pKa′ 6.69 (50% EtOH), *Anal.* Calcd. for $C_{40}H_{67}O_{14}N$: C, 61.11; H, 8.60; N, 1.78. Found: C, 60.56; H, 8.50; N, 1.70) is quite similar to leucomycin A_3 (Ib)[4] (m.p. 120~121°, $[\alpha]_D^{25}$ −55.4°(c=1.0, $CHCl_3$), UV λ_{max}^{MeOH} mμ ($E_{1cm}^{1\%}$) 231.5 (351), pKa′ 6.70 (50% EtOH), *Anal.* Calcd. for $C_{42}H_{69}O_{15}N$: C, 60.92; H, 8.40; N, 1.69. Found : C, 60.57; H, 8.19; N, 1.75) which was found as a new component of leucomycins on chemical and physico-chemical properties.[4] Leucomycin A_1 is converted to crystalline triacetate (m.p. 125~126°, $[\alpha]_D^{25}$ −82.5°(c=1.3, $CHCl_3$), pKa′ 5.69 (50% EtOH), *Anal.* Calcd. for $C_{46}H_{73}O_{17}N$: C, 60.57; H, 8.07; N, 1.54. Found : C, 60.73; H, 7.93; N, 1.56). On the other hand, leucomycin A_3 is converted to diacetate (m.p. 125~126°, $[\alpha]_D^{25}$ −81.0°(c=1.0, $CHCl_3$), pKa′ 5.72 (50% EtOH), *Anal.* Calcd. for $C_{46}H_{73}O_{17}N$: C, 60.57; H, 8.07; N, 1.54. Found: C, 60.53; H, 8.10; N, 1.60). Comparing leucomycin A_1 triacetate with leucomycin A_3 diacetate in the NMR (100 Mc), IR spectra and behavior on thin-layer chromatography, complete coincidence is found between both components. Thus, it is concluded that the structure of leucomyin A_1 corresponds with the structure which eliminates one acetyl group from leucomycin A_3 as Ia. Furthermore, this structure is confirmed by mixing melting point of leucomycin A_1 triacetate with leucomycin A_3 diacetate.



Ia : R=—H
Ib : R=—CO—CH_3

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