cps CH–OMs), 6.65 (3H, s, CH_3SO_3). XVI was demesylated by refluxing in collidine to XVIII, $C_{20}H_{26}O_3$, mp 201—203°. IR ν_{max}^{KBr}: 1745 cm^{-1}. NMR ($CDCl_3$) τ: 4.42 and 4.55 (each 1H, br., s, C_9–H and O–CH–O), 6.21 and 6.45 (2H, AB, q, J=12.5 cps), 8.30 (3H, d, J=1 cps, C=C–CH_3).

Because of the difficulty and no necessity of separation, further reactions were carried out with the mixture of XII and XIII, which was reduced, mesylated, and demesylated as mentioned above, and its NMR spectrum showed the presence of products consisting of 1:1 mixture of XVIII and XIX, and also a small amount of exo double bond isomers. The mixtire, treated with KOH in abs. diethlene glycol under refluxing, gave a mixture of the acids (XX and XXI). The NMR spectra of the acid mixture and also of its methyl esters showed signals for 2:1 mixture of XX and XXI. Among them the spectrum of XXI was identical with that of natural gibberellin-A_{15}.[4] From the acid mixture, XXI separated out from acetone–hexane as crystals and was recrystallized from acetone to prisms, mp 262—264°.

Characteristic fluorescence, thin-layer chromatogram with 10% $AgNO_3$-silica gel, ORD curve, and IR spectrum of XXI were identical with those of natural gibberellin-A_{15}, and showed no depression of mp on admixture.

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[4] J.R. Hanson, *Tetrahedron*, **23**, 733 (1967).

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The Reactions of 4-Nitroquinoline 1-Oxide Derivatives with Nucleophiles in the Presence of Potassium Cyanide

During an investigation of reaction of 4-nitroquinoline 1-oxide derivatives,[1] it happened to be found that treatment with some nucleophiles in the presence of potassium cyanide led to formation of 4-substituted quinoline-3-carbonitrile derivatives.

When potassium cyanide (0.7 g, 0.01 mole) was added with stirring to a solution of 4-nitroquinoline 1-oxide (0.95 g, 0.005 mole) and ethyl cyanoacetate (2.2 g, 0.019 mole) in dimethyl sulfoxide (30 ml) and the whole was stirred for 6 hours at room temperature, ethyl α-(3-cyano-4-quinolyl)-cyanoacetate (I) was obtained in 27.3% yield after treatment with ice–water and 10% hydrochloric acid. Recrystallization from methanol–chloroform gave orange-red powder of mp 218° (decomp.), IR ν_{max}^{KBr} cm^{-1}: 2230, 2176 (CN), 1654 (C=O). *Anal.* Calcd. for $C_{15}H_{11}O_2N_3$: C, 67.91; H, 4.18; N, 15.84. Found: C, 67.64; H, 4.13; N, 16.03.

The structure of I was confirmed by direct comparison with an authentic sample prepared from 4-chloroquinoline-3-carbonitrile and ethyl cyanoacetate.

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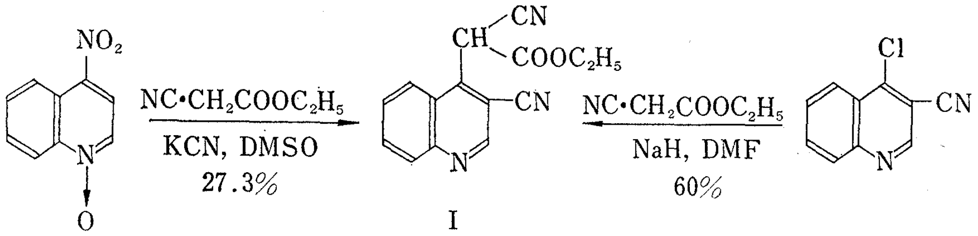
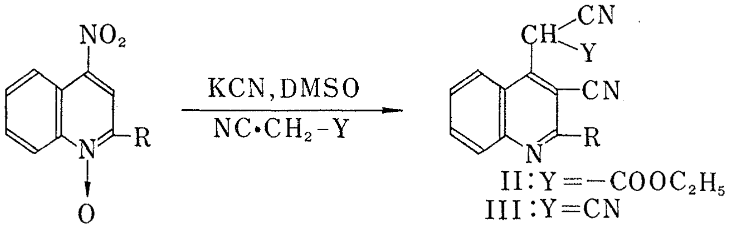
[1] M. Yamazaki, K. Noda, J. Onoyama, and M. Hamana, *Yakugaku Zasshi*, **88**, 656 (1968).



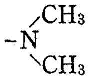
I

Some 2-substituted 4-nitroquinoline 1-oxides also underwent the same reaction with ethyl cyanoacetate or malononitrile under the same condition, the results of which are given in Table I.

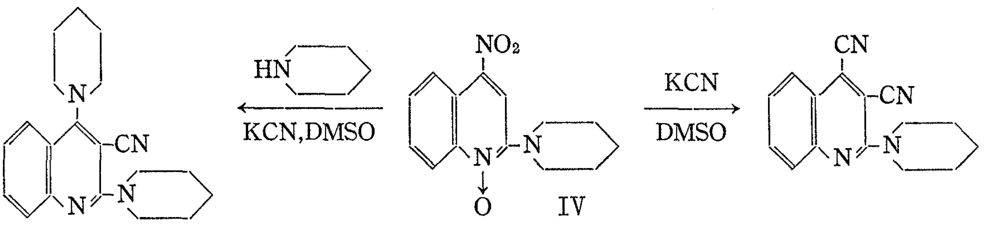
TABLE I. Reactions of 4-Nitroquinoline 1-Oxides with Active Methylene Compounds in the Presence of Potassium Cyanide



II: Y = $-COOC_2H_5$
III: Y = CN

R	II mp (°C)	II Yield (%)	III mp (°C)	III Yield (%)
	222	61.9	309	56.8
	230	35.0	311	32.0
	210	35.7	316	30.8
 $-N(CH_3)_2$	229	53.1	311	41.5
$-CH_3$	211—213	21.1	254—256	30.3

It was further found that 4-nitro-2-piperidinoquinoline 1-oxide (IV) reacted with piperidine as a nucleophile under similar condition to give 2,4-dipiperidinoquinoline-3-carbonitrile in 51.4% yield. On the other hand, the reaction of IV (0.7 g, 0.0025 mole) with potassium cyanide (0.8 g, 0.005 mole) in dimethyl sulfoxide (30 ml) and water (3 ml) without other nucleophile resulted in formation of 2-piperidinoquinoline-3,4-dicarbonitrile in 44% yield.



IV

These results are apparently significant for two implication; *i.e.*, a new nucleophilic displacement of 4-nitro group of quinoline 1-oxides, especially with carbanions, and an extension of the von Richter reaction. Further studies are in progress to explore the scope of the reaction and also to elucidate the reaction mechanism. Details of these studies will be published in the near future.

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