Only secondary amide tested, N-methylhydrocinnamamide was not reduced by the present procedure and the recovery of the starting material was quantitative.

Surprisingly, in case of primary amide, the reduction of hydrocinnamamide did not occur, instead, the amide underwent dehydration to give hydrocinnamonitrile. In previous reports, acidic dehydrating agents[15,16] such as phosphoryl chloride and thionyl chloride, are ordinary employed to obtain nitriles from primary amides. Therefore, it should be mentioned that dehydration with sodium borohydride, the basic agent, is of great interest.

General procedure : A mixture of 0.01 mole of acid amide and 0.03 moles of sodium borohydride in 20 ml. of pyridine was gently refluxed for 10~20 hours, the solvent was removed under reduced pressure, 10% of hydrochloric acid was added, the acidic solution was warmed on a water bath for 20~30 minutes and then extracted with ether to remove the starting material or to obtain a nitrile. The aqueous layer was made alkaline with 10% potassium hydroxide and extracted with ether, the ether extract was washed with water and dried over anhydrous sodium sulfate, ether was evaporated and the residual amine was distilled. In case of obtaining a nitrile, the ether extract from acidic layer was treated as usual. The actual yields given in Table I are probably not the highest values.

As mentioned above, the marked difference observed in the reaction of primary, secondary and tertiary amides with sodium borohydride in refluxing pyridine is noteworthy.

Investigations are now continuing on the scope and mechanism of these new type reactions.

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Study on N^{15}-H Spin-Spin Coupling of 4-Nitroquinoline 1-Oxides Containing Deuterium and/or Nitrogen-15

Not so many studies have been reported on the nitrogen-proton spin-spin interactions in a system of $N-CH_{\alpha}-CH_{\beta}$. A fairly strong spin-spin coupling was recently observed[1] between quaternary nitrogen-14 nucleus and β-hydrogen (CH_3) but not between nitrogen and α-hydrogen (CH_2) of tetraethylammonium halogenides. No such coupling has been clearly observed for any N^{14} compounds other than the above quaternary amines and isonitriles,[2] so far.

Now, we wish to report on the spin-spin interactions of aromatic ring protons with the nitrogen contained in an aromatic ring or a nitro group, using N^{15} substituted quinoline 1-oxide and 4-nitroquinoline 1-oxides, I, Ⅲ, Ⅳ, and Ⅴ. The syntheses of N^{15}

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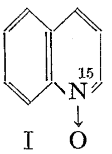
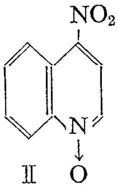
[1] E. Bullock, D. G. Tuck, E. J. Woodhouse : J. Chem. Phys., 38, 2318 (1963).

[2] I. D. Kuntz, P. von R. Schleyer, A. Allerhand : *Ibid.*, 35, 1533 (1961).


I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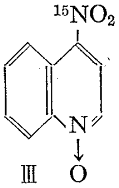
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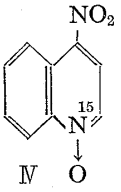
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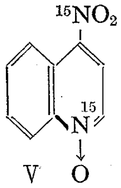
V

compounds were carried out in authentic preparative ways, started with nitration of benzene (for 1-N^{15} compounds) or quinoline 1-oxide (for 4-$N^{15}O_2$ compounds) with potassium nitrate-N^{15} (97 atom %). The assignment of the signals was done by comparison of the spectra of deuterated quinoline 1-oxides and deuterated 4-nitroquinoline 1-oxide in which deuterium was substituted at various positions and in different numbers.[*1] The results are given below, which shows that $J_{N^{15}, 3\text{-}H}$ is larger than $J_{N^{15}, 2\text{-}H}$ and that $J_{N^{15}, 8\text{-}H}$ is clearly observable.

$J_{1\text{-}N^{15}, 3\text{-}H}=5.1\pm0.15$ c.p.s.

$J_{N^{15}O_2, 3\text{-}H}=2.5\pm0.15$ c.p.s.

$J_{1\text{-}N^{15}, 8\text{-}H}=$a few c.p.s.

$J_{1\text{-}N^{15}, 2\text{-}H}=$less than a c.p.s. (a little broadened)

It is of worth to note that observable coupling seems to appear with the protons on β-carbons but not those on α-carbons directly attached to the nitrogen concerned and, furthermore, that the coupling constant between 1-N^{15} and 3-H is twice larger than that between $N^{15}O_2$ and 3-H. This difference in magnitude might be explained by the fact that the 1-N^{15} and 3-H are situated in *trans* configuration with respect to the 2-C and 3-C bond, while 4-$N^{15}O_2$ and 3-H are of *cis* configuration to the 3-C and 4-C bond and 1-N^{15} and 8-H are of also *cis* to the 9-C and 8-C bond. Alternatively, it might be merely due to the difference in the electronic structure between a nitro and an aromatic basic nitrogens.

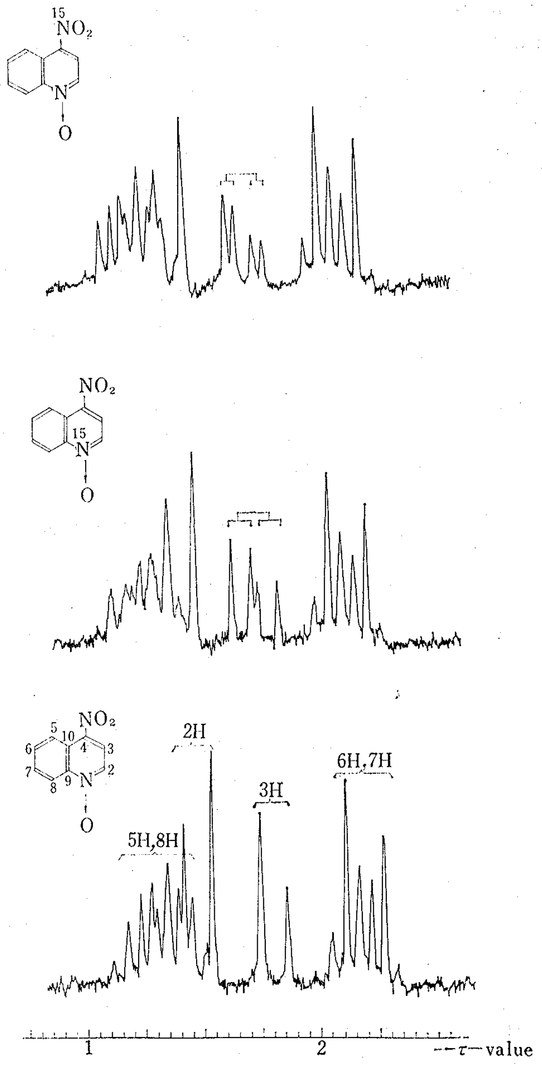

Fig. 1. Nuclear Magnetic Resonance Spectra of 4-Nitroquinoline 1-Oxides measured in Dioxane at 60 Mc.p.s.

The same observation of $J_{N^{15}, H\beta} > J_{N^{15}, H\alpha}$ was recently obtained by Dudek, *et al.*[3] with N^{15} substituted aliphatic amine molecules.

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[*1] Syntheses of these deuterated compounds will be described in the forthcoming full paper.

3) G. O. Dudek, E. P. Dudek: J. Am. Chem. Soc., **86**, 4283 (1964).