Neocryptomerin (V)——The MeOH–pyridine filtrate separated from isocryptomerin was allowed to stand a few days in an ice box after addition of MeOH to give yellow prisms (21 mg), which were recrystallized once from a mixture of MeOH and a small portion of pyridine to yield pale yellow prisms, mp >299—300° (decomp., uncorr.). One spot by TLC (*Rf*: 0.37). IR (KBr) cm^{-1}: 1655, 1606, 1500, 1440, 1365, 1299, 1255, 1230, 1198, 1175, 1158, 1110, 1096, 835. The above prisms (7 mg) were acetylated in the same way as described above in the case of hinokiflavone–7,7″–dimethyl ether and washed with a large amount of water to give white powder (6 mg). The NMR signals of methyl protons of this compound were shown in Table I.

Hinokiflavone (III)——The precipitates (211 mg) obtained from fraction 3 were crystallized from MeOH–pyridine to give pale yellowish brown prisms (141 mg), mp>300°, which gave the same *Rf* value (0.26) by TLC and the same IR spectrum with hinokiflavone.

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Chemistry of Sodium Borohydride and Diborane. V.[1] Reduction of Nitrobenzenes with Sodium Borohydride in Pyridine

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Few examples of the reduction of nitro compounds with borohydrides are found in the literature, and it is generally reported that nitro group is reduced only in exceptional cases.[3]

Nitrobenzene was reduced to azoxybenzene on heating with sodium borohydride at 90—100° in diglyme for 6 hours.[4] Nitrobenzene was also reduced to aniline with lithium borohydride after 18 hours' reflux in tetrahydrofurane.[5] On the reduction of N,N–dimethyl–4–nitrobenzamide with $NaBH_4$–LiCl in refluxing tetrahydrofurane the corresponding azoxybenzene was obtained.[6]

An interesting result was obtained from the reduction of *m*– and *p*–substituted nitrobenzenes with KBH_4 in boiling ethanol and in pyridine at 90°.[7] Under these conditions it was found that some *m*– and *p*–substituted nitrobenzenes carrying a substituent with a positive value of the Hammett sigma constant were reduced to the azoxy compounds but those with a negative sigma constant were not reduced.

No report for converting a nitro compound to the corresponding azo or hydrazo compound with sodium borohydride has been published except as a patent[8] claiming the preparation of azobenzene by treating nitrobenzene with $NaBH_4$–NaOH–$KNi(CN)_4$.

As part of an investigation of the reaction with sodium borohydride in pyridine the reduction of *p*–substituted nitrobenzenes was studied. In the previous paper[9] we reported the reduc-

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6) M. Davis, *J. Chem. Soc.*, **1956**, 3981.
7) H.J. Shine and H.E. Mallory, *J. Org. Chem.*, **27**, 2390 (1962).
8) Dutch Patent 6409225 (1965); *Chem. Abstr.*, **65** 5399*g* (1966).
9) S. Yamada, Y. Kikugawa, and S. Ikegami, *Chem. Pharm. Bull.* (Tokyo), **13**, 394 (1965).

tion of tertiary amides to the corresponding tertiary amines with sodium borohydride in refluxing pyridine. We considered that sodium borohydride in pyridine has a different reactivity than in alcohol. We applied this procedure to the reduction of *p*–substituted nitrobenzenes and found that *p*–cyanonitrobenzene carrying a cyano group with a large positive sigma constant could be reduced to 4,4′–dicyanohydrazobenzene, *p*–chloronitrobenzene with a medium positive sigma constant and nitrobenzene to the corresponding azobenzene and *p*–nitroanisole with a negative sigma constant to 4,4′–dimethoxyazoxybenzene. The results are summerized in Table I.

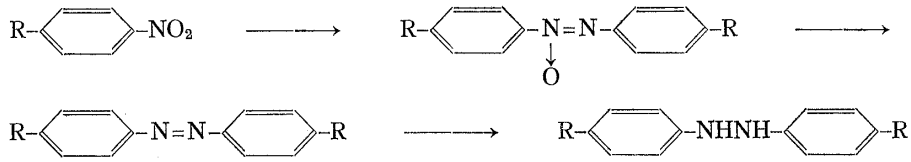

Table I. Reduction with Sodium Borohydride in Pyridine

Substrate	Sigma value[a]	Mole of $NaBH_4$[b]	Temp.	Time hr	Product	Yield (%)	mp (°C) (mp, lit.)
p–Methoxynitrobenzene	−0.268	0.75	reflux	1	azoxyanisole	84.5	117—126 (118—136[d])
		1.0	reflux	5	azoxyanisole	86	
Nitrobenzene	0	1.0	reflux	1	azoxybenzene	91	33—35 (36[e])
		1.0	reflux	10	azoxybenzene	9	
					azobenzene	76	65—68
p–Chloronitrobenzene	+0.227	0.75	reflux	1	4,4′–dichloro-azoxybenzene[f]	91	151—153 (155—156[d])
		1.0	reflux	4	4,4′–dichloro-azobenzene[g]	72	182—185
p–Cyanonitrobenzene	+0.628	0.75	room temp.	1	4,4′–dicyano-azobenzene[h]	41[c]	250
		1	room temp.	16	4,4′–dicyano-azobenzene	90.5	
4,4′–Dicyanoazobenzene		1	reflux	2	4,4′–dicyano-hydrazobenzene[i]	76.3	197—200

a) H.H. Jaffe, *Chem. Rev.*, **53**, 191 (1953)
b) molar ratio to substrate
c) 47.6% of starting material was recovered.
d) P.H. Gore and O.H. Wheeler, *J. Am. Chem. Soc.*, **78**, 2160 (1956)
e) G.H. Badger and R.G. Buttery, *J. Chem. Soc.*, **1953**, 2156
f) *Anal.* Calcd. for $C_{12}H_8ON_2Cl_2$: C, 53.95; H, 3.02; N, 10.49. Found: C, 54.22; H, 3.02; N, 10.49.
g) *Anal.* Calcd. for $C_{12}H_8N_2Cl_2$: C, 57.39; H, 3.21; N, 11.16. Found: C, 57.05; H, 3,28; N, 10.94.
h) *Anal.* Calcd. for $C_{14}H_8N_4$: C, 72.40; H, 3.47; N, 24.13. Found: C, 72.34; H, 3.54; N, 24.41.
i) *Anal.* Calcd. for $C_{14}H_{10}N_4$: C, 71.78; H, 4.30; N, 23.92. Found: C, 71.83; H, 4.25; N, 23.88.

p–Nitroanisole gave only azoxyanisole under a prolonged heating and no detectable azoanisole. Both nitrobenzene and *p*–chrolonitrobenzene gave corresponding azoxy compounds under mild heating and corresponding azo compounds under longer heating. *p*–cyanonitrobenzene gave only the azo compound at room temperature and no recognizable amount of azoxy compound was obtained. The 4,4′–dicyanoazobenzene obtained was reduced to the hydrazo compound with sodium borohydride in boiling pyridine.

Experimental

All materials were obtained commercially and purified as usual. The melting points are not corrected.

Method——A mixture of *p*–substituted nitrobenzene and sodium borohydride in pyridine was treated under the conditions listed in Table I. The solvent was then removed under reduced pressure and the cooled residue was poured over ice. The precipitated product was filtered, washed with water, dried and recrystallized. In the case of nitrobenzene the precipitated product was extracted with benzene and was chromatographed over silica gel.