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Transformation of *o*-Nitrobenzenes to Quinolines with Tetracarbonylhydridoferrate

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Synopsis. Condensates of *o*-nitrobenzaldehyde with carbonyl compounds are reduced with tetracarbonylhydridoferrate under mild conditions to give quinolines in good yields.

Derivatives of tetracarbonylferrate such as hydrido-,[1] acyl-,[2] alkyl-,[3] and carbamoyl-[4] are powerful reducing reagents for the conversion of nitro compounds into the corresponding amines, amides and ureas. The present study deals with the applicability of tetracarbonylhydridoferrate to the synthesis of *N*-heterocycles from condensates of *o*-nitrobenzaldehyde and *o*-nitroaniline with carbonyl compounds and/or primary amines.

Experimental

Infrared spectra were measured with a 215 Hitachi Model spectrophotometer. Nuclear magnetic resonance spectra were measured with a JEOL-JNM-PM-60 NMR spectrometer in deuteriochloroform with Me_4Si as an internal standard. Melting points were uncorrected.

Materials. *o*-Nitrocinnamaldehyde, *o*-nitrobenzaldehyde, *o*-nitroaniline, 1-naphthylamine, acetophenone, iron pentacarbonyl and solvents were all commercial products and were used without further purification. *N*-(*o*-Nitrobenzylidene)-1-naphthylamine(**3a**), *N*-(*o*-nitrobenzylidene)-*p*-anisidine(**3b**) and *p*-chloro-*N*-(*o*-nitrobenzylidene)aniline (**3c**) were prepared from *o*-nitrobenzaldehyde and 1-naphthylamine, *p*-anisidine and *p*-chloroaniline, respectively. *o*-Nitro-*N*-benzylideneaniline(**6a**) and *o*-nitro-*N*-(*p*-chlorobenzylidene)aniline(**6b**) were prepared from *o*-nitroaniline and benzaldehyde and *p*-chlorobenzaldehyde, respectively. Potassium tetracarbonylhydridoferrate was prepared according to the method described in a previous paper.[5]

General Reaction Procedure. To the ferrate(11 mmol) in moist ethanol (50—100 ml), a nitro compound(11 mmol) was added and the mixture stirred under an argon atmosphere at room temperature for 1 h. Reaction products, quinoline, quinaldine and 2-phenylquinoline were analyzed by GLC using internal standards: a column(0.3 cm ϕ, 3 m) packed with 10% Versamid on Neopak 60—80 mesh. Other products were detected by chromatography on alumina, silica gel or florisil, IR and PMR spectroscopy and elemnetal analysis.

Condensates of *o*-nitrobenzaldehyde with acetaldehyde, acetone or acetophenone were prepared *in situ* and submitted for further reaction: a mixture of *o*-nitrobenzaldehyde(11 mmol) and a carbonyl compound(13 mmol) in ethanol (20 ml) was stirred in the presence of a certain amount of potassium hydroxide under an argon atmosphere at room temperature for 3—23 h and then to this mixture were added iron pentacarbonyl(11 mmol) and 1 M potassium hydroxide(30—33 mmol) solution in ethanol.

Reaction of o-*Nitro*-N-*benzylideneaniline(**6a**) with* $KHFe(CO)_4$. The brown reaction mixture obtained was filtered and evaporation of the filtrate gave a brown residue which was chromatographed on florisil (3×30 cm) using dichloromethane as an eluant. A yellow orange band fraction gave 2-phenylbenzimidazole(**7a**) as yellow crystals in 10% yield. The reaction of *o*-nitro-*N*-(*p*-chlorobenzylidene)aniline(**6b**) gave 2-(*p*-chlorophenyl)benzimidazole(**7b**) as yellow orange crystals in 16% yield.

Preparation of N-*(o-Nitrobenzylidene) Amines (**3**).* A mixture of *o*-nitrobenzaldehyde(20 mmol), a primary amine (20 mmol) and ethanol(15 ml) was stirred at room temperature for 5 h to give yellow or orange precipitates, which were separated by filtration and recrystallized from chloroform-ethanol. *N*-(*o*-Nitrobenzylidene)-1-naphthylamine(**3a**), yield 45%, yellow crystals. PMR($CDCl_3$): δ 9.0(s, 1, –C<u>H</u>=N–), 7—8.5(m, 11, Ar). IR(KBr): $\nu_{C=N}$ 1620 cm^{-1}. *N*-(*o*-Nitrobenzylidene)-*p*-anisidine(**3b**), 85%, orange crystals. PMR($CDCl_3$): δ 8.9(s, 1, –C<u>H</u>=N–), 6.8—8.4(m, 8, Ar), 3.8(s, 3, –OC<u>H</u>$_3$). IR(KBr): $\nu_{C=N}$ 1620 cm^{-1}. *p*-Chloro-*N*-(*o*-nitrobenzylidene)aniline(**3c**), 75%, yellow crystals. PMR($CDCl_3$): δ 8.9(s, 1, –C<u>H</u>=N–), 7—8.4(m, 8, Ar). IR(KBr): $\nu_{C=N}$ 1610 cm^{-1}.

Reaction of N-*(o-Nitrobenzylidene)amines (**3**) with* $KHFe(CO)_4$. A mixture of **3**, the ferrate and moist ethanol (100 ml) was stirred under argon at room temperature for 3 h. The reaction products, *N*-(*o*-aminobenzylidene) amines (**4**) were isolated by evaporating the filtered solution to dryness and purified by recrystallization from chloroform-ethanol.

N-(*o*-Aminobenzylidene)-1-naphthylamine(**4a**), yield 50%, yellow crystals mp 80.5—81.5 °C. PMR($CDCl_3$): δ 8.5 (s, 1, –C<u>H</u>=N–), 6.3—8.4(m, 13, Ar and –N<u>H</u>$_2$). IR (KBr): ν_{NH_2} 3370, $\nu_{C=N}$ 1620 cm^{-1}. Found: C, 83.04; H, 5.66; N, 11.08%. Calcd for $C_{17}H_{14}N_2$: C, 82.90; H, 5.73; N, 11.37%.

N-(*o*-Aminobenzylidene)-*p*-anisidine(**4b**), 8%, yellow crystals, mp 122.0—123.5 °C. PMR($CDCl_3$): δ 8.5 (s, 1, –C<u>H</u>=N–), 6.2—7.7(m, Ar and –N<u>H</u>$_2$), 3.8(s, 3, –OC<u>H</u>$_3$). IR(KBr): ν_{NH_2} 3470, $\nu_{C=N}$ 1620 cm^{-1}. Found: C, 73.96; H, 6.09; N, 12.30; O, 7.62%. Calcd for $C_{14}H_{14}N_2O$: C, 74.31; H, 6.24; N, 12.38; O, 7.07%.

p-Chloro-*N*-(*o*-aminobenzylidene)aniline(**4c**), 9%, white yellow crystals, mp 108.5—110.0 °C. PMR($CDCl_3$): δ 8.4(s, 1, –C<u>H</u>=H–), 6.1—7.9 (m, 10, Ar and –N<u>H</u>$_2$). IR (KBr): ν_{NH_2} 3460, $\nu_{C=N}$ 1620 cm^{-1}. Found: C, 67.99; H, 4.69; N, 12.13; Cl, 15.38%. Calcd for $C_{13}H_{11}N_2Cl$: C, 67.68; H, 4.81; N, 12.14; Cl, 15.37%.

Results and Discussion

Alcoholic tetracarbonylhydridoferrate has high reactivity for the conversion of condensates of *o*-nitrobenzaldehyde with carbonyl compounds into the corresponding 2-alkylquinolines under mild conditions. The results are summarized in Table 1.

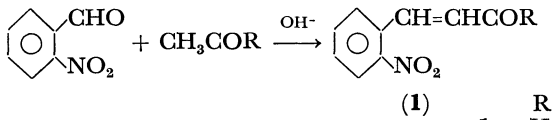
o-Nitrocinnamaldehyde readily reacted with the ferrate to give quinoline quantitatively which appeared to be formed by an intramolecular cyclization of

Table 1. The reduction of *o*-nitrobenzenes to quinolines with $KHFe(CO)_4$[a]

Run	Nitro compound	Carbonyl compound	Condensation[b] KOH[c]	Condensation[b] Time (h)	Product	Yield %
1	*o*-Nitrocinnamaldehyde	—	—	—	Quinoline	100
2	*o*-Nitrobenzaldehyde	Acetaldehyde	0.49	10	Quinoline	33
3	*o*-Nitrobenzaldehyde	Acetone	0.06	3	Quinaldine	55
4	*o*-Nitrobenzaldehyde	Acetone	0.06	23	Quinaldine	45
5	*o*-Nitrobenzaldehyde	Acetophenone	0.06	23	2-Phenylquinoline	17

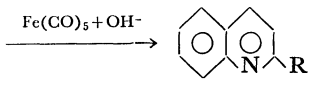
a) At room temperature under argon for 1—3 h. b) *o*-Nitrobenzaldehyde was treated with carbonyl compounds at room temperature and then the condensates obtained *in situ* were reduced. c) Molar ratio, potassium hydroxide/carbonyl compound.

o-aminocinnamaldehyde. *o*-Nitrocinnamaldehyde is a condensate of *o*-nitrobenzaldehyde with acetaldehyde. Two succesive treatments of *o*-nitrobenzaldehyde with such carbonyl compounds as acetaldehyde, acetone or acetophenone in the presence of potassium hydroxide and then with the ferrate gave quinoline(**2a**), quinaldine(**2b**) and 2-phenylquinoline(**2c**) in good yields, respectively. The potassium hydroxide used appears to play two roles, a catalyst for the aldol condensation of *o*-nitrobenzaldehyde with the carbonyl compounds and a reagent for the formation of the ferrate.



(**1**)

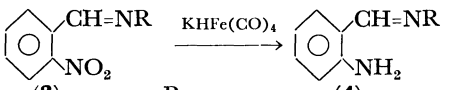
	R
1a	H
1b	CH_3
1c	Ph



(**2**)

These results show that *o*-nitrobenzaldehyde combined with carbonyl compounds and with the ferrate as a reducing reagent can provide a simple route to a variety of 2-alkylquinolines.

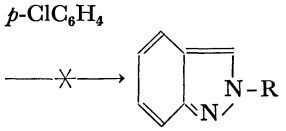
N-(*o*-Nitrobenzylidene)amines(**3**), condensates of *o*-nitrobenzaldehyde with 1-naphthylamine, *p*-anisidine and *p*-chloroaniline, gave only the corresponding *N*-(*o*-aminobenzylidene)amines(**4**) in good to poor yields. The expected *N*-heterocycles, 2-alkylbenzopyrazoles(**5**), could not be detected.



(**3**)

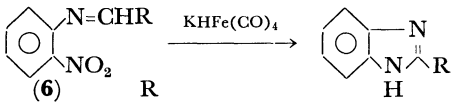
	R
3a	1-naphthyl
3b	*p*-$CH_3OC_6H_4$
3c	*p*-ClC_6H_4

(**4**)



(**5**)

On the other hand, *o*-nitro-*N*-benzylideneaniline(**6**), condensates of *o*-nitroaniline with benzaldehyde or *p*-chlorobenzaldehyde, gave benzimidazoles(**7**) but in poor yields.



(**6**)

	R
6a	Ph
6b	*p*-ClC_6H_4

(**7**)

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