BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2192—2194 (1970)

The Hydroformylation of Nitroalkenes with Rhodium Carbonyl

Masahiko TAKESADA and Hachiro WAKAMATSU

Central Research Laboratories, AJINOMOTO CO., INC., Kawasaki

(Received January 7, 1970)

The hydroformylation of butenes in nitrobenzene or nitroethane gives C_5-aldehydes in an excellent yield in the presence of tetrarhodium dodecarbonyl, but in only a poor yield in the presence of dicobalt octacarbonyl. Under hydroformylation conditions, nitrobenzene is hydrogenated to aniline above 150°C with rhodium carbonyl and at 125°C with cobalt carbonyl. The hydroformylation of nitroalkenes with rhodium carbonyl is described. 4-Nitrostyrene gives isomeric (4-nitrophenyl)-propionaldehydes in a 96% yield. 3-Nitropropene-1 gives C_4-nitroaldehydes, mostly 2-methyl-3-nitropropionaldehyde, in a 96% yield. However, no reaction of nitroethylene occurred below 140°C.

It has been already established that nitrobenzene is hydrogenated to give aniline under hydroformylation conditions at an elevated temperature and in the presence of cobalt carbonyl.[1,2] However, no study has been reported on the hydroformylation of nitroalkenes. In this paper, the hydroformylation of butenes in a solvent of nitro compounds will be described, together with the hydrogenation of nitrobenzene under hydroformylation conditions in the presence of cobalt and rhodium carbonyl. The hydroformylations of nitroethylene, 3-nitropropene-1, and 4-nitrostyrene will also be described.

Results and Discussion

Hydroformylation of Butenes. The results of the hydroformylation of butenes in a solvent of various nitro compounds are shown in Table 1. In the reaction of butene-1 with a mixture of carbon monoxide and hydrogen in nitrobenzene in the presence of dicobalt octacarbonyl, the absorption of the gas started at 120°C and more than 2 moles of the gas were consumed per mole of butene-1. However, the yield of C_5-aldehydes was only 37% and the ratio of 2-methylbutyraldehyde to *n*-valeraldehyde was 1.0 to 1.40. The yield and the isomeric ratio of the products in this system are different from those of the hydroformylation of butene-1 in benzene, where the yield of the aldehydes and the isomeric ratio were reported to be 89% and 0.23 respectively.[3] The poor yield of the aldehydes in nitrobenzene is probably due to further reactions of the aldehydes with the aniline formed from nitrobenzene under hydroformylation conditions.

TABLE 1. HYDROFORMYLATION OF BUTENES

Reaction conditions[a)]					Product	
Olefin	Catalyst	Solvent	Temp. °C	Time min	Yield of aldehydes %	Ratio of isomers[c)] B/N
Butene-1	Co	Nitrobenzene	120	170	37	1.40
	Rh	Nitrobenzene	60	41	95	1.19
	Rh	Nitroethane	60	42	94	1.24
	Rh	Benzene	60	33	94	1.26
trans-Butene-2	Rh[b)]	Nitrobenzene	60	100	93	100
	Rh[3)]	Benzene	60	120	91.4	∞

a) Other reaction conditions:
Butenes: 100 mmol, solvent: 45 ml, pressure: 200 kg/cm², $[Rh(CO)_3]_4$: 50 mg or $[Co(CO)_4]_2$: 145 mg.
b) $[Rh(CO)_3]_4$: 80 mg.
c) B: 2-methyl-butyraldehyde. N: *n*-valeraldehyde.

---

[1] I. Wender, H. Greenfield, S. Meltin and M. Orchin, *J. Amer. Chem. Soc.*, **74**, 4079 (1952).

[2] S. Murahashi, S. Horiie and T. Joh, *Nippon Kagaku Zasshi*, **79**, 68 (1958).

[3] H. Wakamatsu, *ibid.*, **85**, 227(1964).

In the presence of tetrarhodium dodecacarbonyl in place of dicobalt octacarbonyl, the hydroformylation of butenes gave C_5-aldehydes in an excellent yield even in nitrobenzene or nitroethane, and the amount of gas consumed was almost the theoretical value for hydroformylation. On the hydroformylation of butene-1 or *trans*-butene-2 with rhodium carbonyl under milder conditions, there are no significant differences in the yield and isomeric distribution of the aldehydes between the benzene and the nitrobenzene used as solvents.

Hydrogenation of Nitrobenzene. In order to elucidate the catalytic activity of cobalt and rhodium carbonyl for the hydrogenation of nitro compounds to amino derivatives under hydroformylation conditions, the hydrogenation of nitrobenzene was studied. The results are shown in Table 2.

TABLE 2. HYDROGENATION OF NITROBENZENE

Reaction conditions				Yield of aniline %
Catalyst	Solvent	Temp. °C	Time min	
Co[a]	Benzene	125	30	100
Rh[a]	Benzene	180	140	94
Rh[b]	—	150—154	105	96

Other reaction conditions:

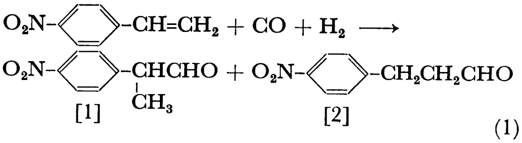
a) Nitrobenzene (80 mmol)+benzene: 40 m*l*, pressure: 250 kg/cm^2 ($CO+H_2$), $[Rh(CO)_3]_4$: 73 mg or $[Co(CO)_4]_2$: 465 mg.

b) Nitrobenzene: 30 m*l*, pressure: 182 kg/cm^2 ($CO+H_2$), $[Rh(CO)_3]_4$: 80 mg.

Nitrobenzene is hydrogenated to aniline under hydroformylation conditions at 125°C with cobalt carbonyl as shown in Table 2. Rhodium carbonyl also catalyzed the hydrogenation of nitrobenzene above 150°C without a solvent or at 180°C in benzene, but at lower temperatures no reaction took place. A higher temperature is required for the hydrogenation of nitro groups with rhodium carbonyl than with cobalt carbonyl.

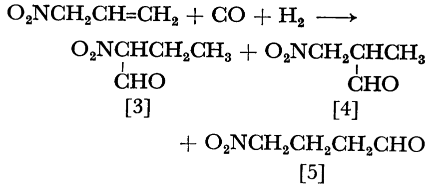
Hydroformylation of Nitroalkenes with Rhodium Carbonyl. In view of the above results, it may be expected that the hydroformylation of nitroalkenes to nitroaldehydes proceeds without hydrogenating the nitro group below 150°C with rhodium carbonyl. The hydroformylation of nitroalkenes was carried out with tetrarhodium dodecacarbonyl as a catalyst.

The hydroformylation of 4-nitrostyrene in benzene gave (4-nitrophenyl)-propionaldehydes in a 96% yield. By means of PMR study, the (4-nitrophenyl)-propionaldehydes thus produced were found to be a mixture of two isomers, [1] and [2]. The ratio of [1] to [2] was determined to be 7.3. This ratio is somewhat smaller than those of the 2-phenyl-propionaldehyde to the 3-phenyl-propionaldehyde produced by the hydroformylation of styrene, of which ratios are 11.9 at 60°C and 13.8 at 70°C.[4] Thus, the nitro substitution on styrene is observed to induce a change in the isomeric distribution of the products, probably because of the electron-withdrawing effect of the substituent.[5]


(1)

$[1]/[2] = 7.3$

The hydroformylation of 3-nitropropene-1 proceeded smoothly at 60°C and gave C_4-nitroaldehydes in a 96% yield. Although the formation of three isomeric aldehydes was anticipated, it was found by PMR that 2-methyl-3-nitropropionaldehyde, [4], was the predominant product and that the amounts of the other isomers were very small. On the hydroformylation of propene with rhodium carbonyl at 40°C, the ratio of the isobutyraldehyde to the *n*-butyraldehyde produced is 1.0 to 1.25.[3] There is a great difference in the isomeric distribution of the reaction products between 3-nitropropene-1 and propene. It is clear that a nitro-group on the olefin has a great effect on the isomeric distribution. This effect may be explained in terms of the interaction of the nitro group with rhodium in the intermediate step of the reaction, although further work on the intermediate is required to clarify this interesting observation.


(2)

$$O_2NCH_2CH{=}CH_2 + CO + H_2 \longrightarrow \underset{[3]}{O_2N\underset{\displaystyle CHO}{CH}CH_2CH_3} + \underset{[4]}{O_2NCH_2\underset{\displaystyle CHO}{CH}CH_3} + \underset{[5]}{O_2NCH_2CH_2CH_2CHO} \qquad (2)$$

Similarly, when nitroethylene was treated with a mixture of carbon monoxide and hydrogen, no absorption of the gas was observed below 140°C. When this is compared with the reaction of 3-nitropropene-1, it seems reasonable to consider that the inactiveness of nitroethylene to hydroformylation is to be ascribed to the possible deviation of the nature of the carbon-carbon double bond in nitroethylene, which may originate from the conjugation with a nitro group.

Experimental

All the melting points were uncorrected. The PMR spectra were obtained at room temperature on a Varian A-60 spectrometer, using tetramethylsilane as an internal standard. The IR spectra were recorded on a Perkin Elmer 21 spectrometer. Gas-liquid chromatographic

---

[4] M. Takesada and H. Wakamatsu, to be published.

[5] M. Kainosho, M. Takesada and H. Wakamatsu, the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1967.

analyses were carried out with a Shimadzu GC-2B apparatus.

Materials. The nitrobenzene and nitroethane were obtained commercially and were rectified before use. The nitroethylene[6] and 4-nitrostyrene[7] were prepared in the manner as described in the literature. The 3-nitropropene-1 was synthesized according to the method of Askennasy[8] and was purified by fractional distillation using diphenyl ether as a diluent.

Quantitative Analyses of Aldehydes. The amount of aldehydes produced was determined by the method described previously.[3]

Hydroformylation of Butenes. The reaction and the determination of the ratio of the isomeric aldehydes were carried out in the manner described previously.[3]

Hydrogenation of Nitrobenzene. The hydrogenation was carried out similarly to the hydroformylation of butenes. The quantitative analyses of aniline were carried out by gas-liquid chromatography.

Hydroformylation of 4-Nitrostyrene. A solution (50 m*l*) of 4.7 g of 4-nitrostyrene in benzene, 88 mg of tetrarhodium dodecacarbonyl, and a small amount of hydroquinone were put into an 100 m*l*-autoclave. The mixture was then shaken for 30 min at 60—70°C under the pressure (203 kg/cm^2) of an equimolar mixture of carbon monoxide and hydrogen. A part of the reaction mixture (36.6 m*l*) was concentrated to give a crystalline residue. By the fractional distillation of the residue, 3.3 g of [1] was obtained; bp 142.5—144°C/1 mmHg, mp 42—43°C recrystallized from ether (lit,[9] mp 43°C).

Found: C, 59.96; H, 5.19; N, 7.61%. Calcd for $C_9H_9NO_3$: C, 60.32; H, 5.06; N, 7.82%.

IR: 2822, 2722 ($\underline{CH}$O), 1724 (C=O), 1519, 1352 (NO_2) cm^{-1}.

PMR (in CCl_4): 8.50 τ (doublet) for CH_3, 6.19 τ (broad quartet) for CH, 2.20 τ (multiplet) for the aromatic protons, 0.20 τ (doublet) for CHO.

The PMR spectra of the reaction mixture were obtained and the ratio of the isomeric aldehydes was calculated according to Eq. 3:

$$[1]/[2] = 4A/C = 4B/3C \tag{3}$$

A : relative intensity of the CH proton in [1], 7.02 τ.
B : relative intensity of the CH_3 protons in [1], 8.92 τ.
C : relative intensity of the CH_2 protons in [2], 7.4—8.2 τ (multiplet).

Hydroformylation of 3-Nitropropene-1. A solution (25 m*l*) of 4.4 g of 3-nitropropene-1 in benzene, 50 mg of tetrarhodium dodecacarbonyl, and a small amount of hydroquinone were put into a 50 m*l*-autoclave and then the mixture was shaken for 20 min at 60°C under the pressure (200 kg/cm^2) of an equimolar mixture of carbon monoxide and hydrogen. A part of the reaction mixture (17 m*l*) was concentrated, and the residue was fractionally distilled to give 2.8 g of [4]; bp 74—75.5°C/1 mmHg, $n_D^{21.5}$ 1.4428.

Found: C, 41.19; H, 6.26; N, 12.04%. Calcd for $C_4H_7NO_3$: C, 41.02; H, 6.03; N, 11.96%.

IR: 2846, 2746 ($\underline{CH}$O), 1723 (C=O), 1555, 1384 (NO_2) cm^{-1}.

PMR (in benzene): 9.27 τ (doublet) for CH_3, 7.42 τ (multiplet) for CH, 5.92 τ (multiplet) for CH_2, 0.78 τ (singlet) for CHO.

2,4-Dinitrophenylhydrazone: yellow needles, mp 138—139°C recrystallized from ethanol.

Found: C, 40.44; H, 4.46; N, 23.77%. Calcd for $C_{10}H_{11}N_5O_6$: C, 40.40; H, 3.73; N, 23.57%.

The PMR spectrum of the reaction mixture was virtually identical with that of [4].

The encouragement and support of Dr. Toichi Yoshida are gratefully acknowledged. The authors wish also to thank Dr. Asao Nakamura for his helpful discussion of the PMR studies, and Mrs. Keiko Terao and Mr. Nobuyoshi Kitamura for their technical assistance.

---

6) G. D. Buckly, *J. Chem. Soc.*, **1947**, 1471.

7) R. H. Wiley and R. Smith, "Organic Syntheses," Coll. Vol. IV, p. 731 (1963).

8) P. Askennasy and V. Meyer, *Ber.*, **25**, 1701 (1892).

9) F. Nerdel and H. Winter, *J. Prakt. Chem.*, **12**, 110 (1960).