N-Phenylaminomethylation: A One-Step Route to N-Substituted Anilines From Unsaturated Fatty Derivatives and Olefins[1]

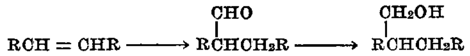
ROBERT A. GRIMM, Ashland Chemical Company, Bloomington, Minnesota 55420

Abstract

Unsaturated fatty materials, such as ethyl oleate and oleonitrile, are found to react with carbon monoxide, hydrogen and aniline at 150 C to give N-monoalkylanilines. The alkyl group is derived from the unsaturated fatty material plus the group H-CH_2 added across the double bond. Similarly 1-decene, in a rapid reaction, gives N,N-di-*n*-undecylaniline and N-undecylaniline as major and minor products respectively. 1,2,3-Tris-(triphenylphosphine)trichlorohodium is an excellent catalyst for this reaction.

Introduction

The hydroformylation of olefins is a well-studied reaction and involves the addition of carbon monoxide and hydrogen to an olefin in the presence of a catalyst. Aldehydes are the usual reaction products but alcohols are formed under more vigorous conditions. Catalysts for this reaction are



$$RCH{=}CHR \longrightarrow R\overset{\displaystyle CHO}{\overset{|}{C}}HCH_2R \longrightarrow R\overset{\displaystyle CH_2OH}{\overset{|}{C}}HCH_2R$$

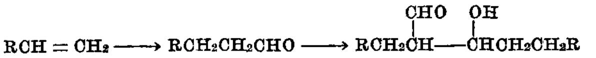
usually cobalt, iron, nickel and platinum carbonyl (1,12,17) but more recently compounds of rhodium (13,20) and ruthenium (2,5) have been used.

If ammonia or simple amines are incorporated into the reaction mixture, more highly substituted amines result. In work on ethylene for example, Reppe (15,16) found that propylamine, carbon monoxide and water react with large amounts of iron carbonyl to give a mixture of dipropylamine. Ethylene has also been reported to react with aniline under oxo conditions to give N-propyl and N,N-dipropylanilines (8) but no details were given. Higher olefins have been studied more recently (3) by workers who found that by using phosphine-complexed cobalt carbonyls, catalytic hydroformylation in the presence of aliphatic amines does occur and the product is a mixture of higher amines and the oxo alcohol. Smoothest results were obtained when the amines were secondary.

$$RCH{=}CH_2 + R_2NH \xrightarrow{H_2,\ CO} RCH_2CH_2CH_2NR_2 + RCH_2CH_2CH_2OH$$

High conversions were obtained and the product contained approximately equal amounts of the amine and alcohol. The process is stated to yield mostly *n*-alkylamines as shown in the above reaction.

In a related patent (4) hydroformylation in the presence of bases was claimed to give, in one step, the aldol product shown below. A variety of bases,



$$RCH{=}CH_2 \longrightarrow RCH_2CH_2CHO \longrightarrow RCH_2\overset{\displaystyle CHO}{\overset{|}{C}}H{-}{-}\overset{\displaystyle OH}{\overset{|}{C}}HCH_2CH_2R$$

including amines and aniline, were suggested for this reaction but, in general, strong bases such as hydroxides seemed to perform best.

This paper describes some studies of the hydroformylation of unsaturated fatty materials and longer-chain α-olefins in the presence of excess aniline. 1,2,3-Tris-(triphenylphosphine)trichlorohodium (III) was commonly used as catalyst. These results show that this reaction provides a one step route to a variety of substituted anilines.

Experimental Procedures

The autoclave used in this work was a 300 ml magnetically-stirred unit made of 316 stainless steel. The gases, carbon monoxide and hydrogen, were admitted to the autoclave from separate cylinders. This arrangement made it difficult to measure the amounts of the gases used but in general the hydrogen carbon monoxide ratio in the autoclave was held around two, in accordance with the stoichiometry of the reaction.

Most of the experiments were run on the ethyl esters of commercially available monoenoic acid (Ashland Chemical, 95% $C_{18:1}$, 35% *trans*) in which the double bonds are located mainly in the C_7 to C_{13} part of the chain. The methyl oleate (98% $C_{18:1}$, 6% *trans*) was prepared by fractionation of commercial methyl oleate on a 40-plate spinning band column. Ethyl linoleate was prepared from a sample of linoleic acid (>95%) supplied by the USDA Northern Regional Laboratory. Commercial samples of oleylnitrile (6% $C_{16:1}$, 80% $C_{18:1}$), soybean oil and tallow (acidless) were used without further purification.

The rhodium catalyst used in this work was prepared by mixing a hot solution of rhodium trichloride trihydrate (3 g) in 95% ethanol (200 ml) with a hot solution of triphenylphosphine (15 g) in 95% ethanol (200 ml) and allowing the mixture to cool. An orange precipitate (10.8 g), mp around 270 C, formed. Malerbi (11) reports that this compound is 1,2,3-tris-(triphenylphosphine)trichlororhodium (III) while others (14) report similar conditions give tris-(triphenylphosphine)chlororhodium (I). The melting point of our material suggests that it is mainly the trichloride but it may contain smaller amounts of the monochloride complex. In our experiments we will refer to it as the trichloride.

The cobalt-phosphine catalyst was prepared by mixing, in the autoclave containing the ester and aniline, dicobalt octacarbonyl (1.0 g, 2.9 × 10^{-3} moles) and triphenylphosphine (1.5 g, 5.7 × 10^{-3} moles). Some gas was evolved. The autoclave was sealed and the run started.

Aliphatic amino nitrogen determinations, such as total amino nitrogen (TAN), were run according to the AOCS Official Method Tf 3a-64. Aromatic amino nitrogen was determined by the method described by Siggia (18).

In the experiments below we have used x to designate a position of a fatty chain since several double bond isomers are present in the starting

---

[1] Presented at the AOCS Meeting, San Francisco, April 1969.

material or may be formed during the reaction (6,20). In these cases the products are isomeric and differ in the point of attachment to the fatty chain.

Anil of Ethyl x-Formyloctadecanoate

Into the autoclave was charged ethyl octadecenoate (130 g, 0.42 moles), aniline (76.5 g, 0.82 moles) and 1,2,3-tris-(triphenylphosphine)trichlororhodium (III) (0.3 g, 3.10^{-4} mole). The autoclave was then sealed, the stirrer was started and carbon monoxide (0–700 psig) and hydrogen (700–1400 psig) were added. The heater brought the autoclave to reaction temperature (103 C) within 15 min and reaction, as indicated by pressure drops, occurred smoothly. Typically with internally unsaturated esters, the pressure drop per unit time was around 100 psig/min. After 2 hr the reaction mixture was removed from the autoclave and distilled. After the excess aniline was removed, the head temperature quickly rose to 200 C/0.5 mm, and the product a yellow oil (141 g, 82% of theory) was collected from 200–240 C (most 228 C) at 0.5 mm. The distillation residue (17 g) was found by TLC (benzene) to be similar to the distillate. Thin layer chromatography (TLC) of this reaction product showed a spot due to aniline and another spot indicating another aromatic amine upon spraying with developer (ceric ammonium sulfate-sulfuric acid). Heating of the chromatogram showed an additional spot. That this anil contained some of the N-phenylaminomethylated product was indicated by the TLC behavior and by the infrared spectrum which had absorptions at 3400 cm^{-1} (N–H), 1735 cm^{-1} (COOEt), 1660 cm^{-1} (–N = CH–), 1600 cm^{-1} and 1500 cm^{-1} (phenyl).

Analysis: TAN (aromatic), calculated 3.35%, MW 417.5 g/mole; TAN, found 3.16%; MW 406 g/mole.

Steam distillation of this material and subsequent vacuum distillation gave a main fraction bp 158 C/0.02 mm that was free of aniline. This sample formed a 2,4-dinitrophenylhydrazone (19) that was recrystallized from cold ethanol, mp 45–46 C.

Methyl x-(N-Phenylaminomethyl)Stearate (Methyl N-PAM Stearate)

Into the autoclave were placed methyl oleate (98.5 g, 0.33 moles), aniline (34 g, 0.37 moles) and 1,2,3-tris-(triphenylphosphine)trichlororhodium (III) (0.3 g, 3×10^{-4} moles). The autoclave was then sealed and the stirrer started before carbon monoxide (0–750 psig) and hydrogen (750–1500 psig) were added. The reaction mixture was then heated at 125 C for 165 min during which time additional hydrogen and carbon monoxide were added. When the run was over the contents were removed and concentrated on a rotary evaporator. On standing overnight, part of the crude reaction mixture (3 g) crystallized. This solid was removed by filtration and was recrystallized twice from acetone to give shiny, white plates, mp 74.5–75.5 C.

Analysis: Calculated for $C_{26}H_{45}NO_2$: C, 77.36; H, 11.25; N, 3.47; TAN (aromatic) 3.47; TAN (aliphatic) 0.0. Found: C, 77.23; H, 11.26; N, 3.53; TAN (aromatic) 3.45; TAN (aliphatic) 0.0.

The rest of the reaction mixture was fractionally distilled to give a lower boiling fraction (19.4 g) of methyl oleate. The main fraction (76 g) then distilled from 206–218 C/0.05 mm (most 211–212 C/0.05 mm) and a center cut was taken for analysis. The distillation residue (8 g) was shown by TLC analysis.

Analysis: Found: C, 77.61; H, 11.42; N, 3.57; TAN (aromatic), 3.52; TAN (aliphatic), 0.0 (benzene) to contain some of the main reaction product. All of the high boiling fraction gave only a single spot by TLC (benzene).

The NMR spectrum of the main fraction shows absorptions at δ 0.8–2.5 ppm (several overlapping absorptions, 34.2, $C_{17}H_{34}$), 3.0 ppm (doublet, J_{AB} = 5Hz, 2.0, H–C–CH_2–N), 3.64 ppm (two singlets, partially superimposed, 4.0, –NH– and –OCH_3) and 6.4–7.4 ppm (complex multiplet, 4.8, C_6H_5).

Similar procedures were used for the experiments described in Table I.

x-(N-Phenylaminomethyl)Stearic Acid

Methyl x-(N-phenylaminomethyl)stearate (41 g, 0.10 moles) was mixed with a solution of potassium hydroxide (14 g, 0.25 moles) in 50% methanol (200 ml) and the resulting emulsion stirred at 50 C until a clear solution formed. After an additional hour the solution was acidified with acetic acid and the resulting oil was extracted into ether. The ether extracts were washed with water, dried and concentrated under vacuum (0.06 mm at 50 C for 6 hr) to give a yellow oil (37 g, 92% of theory).

Analysis: Calculated for $C_{25}H_{43}NO_2$: neutralization equivalent, 389.5 g/mole; TAN (aromatic) 3.59%. Found: neutralization equivalent, 389 g/mole; TAN (aromatic), 3.25%.

TABLE I

Hydroformylation of Unsaturated Fatty Materials and Longer-Chain α-Olefins in the Presence of Excess Aniline

Expt.	Substrate	Ratio aniline-substrate	Reaction time, hr	Temp.	Products (yields)
1	Ethyl octadecenoate	1.9	1.6 0.3	122 C 150 C	Ethyl x-(N-PAM) stearate (78%)
2	Ethyl[a] octadecenoate	2.0	2.0	125	Ethyl x-(N-PAM) stearate (70%)
3	Ethyl[b] octadecenoate	2.0	1.5	120–150 C	Ethyl x-(N-PAM) stearate (55%)
4	Ethyl[c] octadecenoate	2.0	1.5	120–150 C	Schiff base + N-PAM product (28%); Undistillable residue
5	Ethyl[a] linoleate	4.0	2.0	100–160 C	Schiff base of monoaldehyde (18%); TAN 3.08%
6	Oleonitrile	1.7	2.5	122 C	Schiff base + N-PAM stearonitrile (67%)
7	Tallow[d]	4	2.0 1.5	135 C 160 C	Solid triglyceride TAN 0.9%
8	Oleic acid[d]	1.5	4.5	122 C	Viscous glass TAN = 3.1%; Eq Wt = 605 g/mole

[a] Ethanol solvent.

[b] Dicobalt octacarbonyl (0.5% w/w) as catalyst.

[c] Dicobalt hexacarbonyl-bis (triphenyl phosphine) complex (1.3% w/w) as catalyst.

[d] Sample is aniline free by TLC.

Ethyl x-(N-Cyclohexylaminomethyl) Stearate

Ethyl x-(N-phenylaminomethyl)stearate (117 g, 0.28 mole), ethanol (75 ml) and 5% Rh/C catalyst (4 g) were placed in a 300 ml autoclave and the mixture was vigorously stirred at 110 C under a hydrogen pressure of 1400 psig. After 7 hr, more 5% Rh/C (4 g) was added and the above conditions repeated for 3 hr. Upon cooling, the reaction mixture was removed from the autoclave, filtered and concentrated under vacuum. A portion of the residue (100 g) was then vacuum-distilled to give a water-white mobile oil (78 g), bp 221–223 C/0.4 mm. The infrared spectrum of this oil was free of aromatic absorptions at 1500 cm^{-1} and 1600 cm^{-1}.

Analysis: Calculated for $C_{27}H_{53}NO_2$: TAN (aliphatic) 3.30; TAN (aromatic) 0.0; tertiary amino nitrogen, 0.00; primary amino nitrogen 0.00. Found: TAN (aliphatic), 3.2; TAN (aromatic) 0.1; tertiary amino nitrogen, <0.25; primary amino nitrogen, <0.21.

x-(N-Phenylaminomethyl) Stearylamine

The oleonitrile derivative containing both the Schiff base and the N-phenylaminomethylated material (71 g, 0.19 moles) was mixed with a 5.4 M solution of ammonia in ethanol (100 ml) and Raney nickel (1 tsp) in an autoclave. The reaction mixture was heated to 38 C for 5 hr under a hydrogen pressure of 1000 psig. The autoclave was then emptied and the contents filtered, concentrated and distilled under vacuum to give a main fraction (28 g), bp 204–224 C/0.1 mm as nearly colorless oil. Analysis of the main fraction by TLC (benzene-ether-ammonium hydroxide, 50:29:1) showed one spot.

Analysis: Calculated for $C_{25}H_{46}N_2$: TAN (aliphatic), 3.74; TAN (aromatic), 3.74. Found: TAN (aliphatic), 3.72; TAN (aromatic), 3.72.

N-Phenylaminomethylated Soybean Oil

Soybean oil (125 g) aniline (60 g, 0.65 mole) and 1,2,3-tris-(triphenylphosphine)trichlororhodium (III) (0.4 g, 4×10^{-4} mole) were sealed into the autoclave, the stirrer was started and carbon monoxide (0–600 psig) and hydrogen (600–1200 psig) were added. Reaction was run at 107 C for 1.5 hr and then at 125 C for 4.5 hr.

The reaction mixture was then steam distilled until the distillate was free of aniline. The residue was dissolved in benzene and passed over a column of alumina (Alcoa F-20) to remove the catalyst. The resulting product was then concentrated to a cloudy oil (103 g) with a total amino nitrogen value of 1.4%. TLC of this sample (benzene) showed one spot different from aniline. The tallow derivative was treated similarly.

N-Undecyl and N,N-Diundecylaniline

1-Decene (111 g, 0.79 mole), aniline (50 g, 0.54 mole), ethanol (25 ml) and 1,2,3-tris-(triphenylphosphine)trichlororhodium (III) (0.3 g, 3×10^{-4} mole) were charged to the autoclave. After sealing, the stirrer was started and carbon monoxide (0–500 psig) and hydrogen (500–1250 psig) were added. Gas absorption became noticeable around 75 C and in the following reaction gases were absorbed at rates around 1000 psig/min and the temperature rose to 120 C. During this time the gas pressure was maintained between 500 and 1250 psig by alternate addition of carbon monoxide and hydrogen. When the reaction slowed, more hydrogen was added and the mixture heated to 150 C for 30 min.

After concentration on a rotary evaporator, the product was distilled rapidly. An early fraction, bp 130 C/0.05 mm distilled smoothly. Decomposition then started and the remainder of the product was removed at temperatures up to 280 C/4 mm (total 115 g) until only a small amount of pot residue remained. This product was redistilled to give the lower-boiling fraction bp 118 C/0.015 mm (34 g). The distillation temperature then rose rapidly.

Analysis: Calculated for $C_{17}H_{29}N$: TAN (aromatic), 5.67. Found: TAN (aromatic), 5.77.

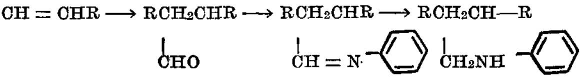
A second fraction, bp 193 C/0.015 mm (66 g) was collected. Both products were mobile yellow oils.

Analysis: Calculated for $C_{28}H_{51}N$: TAN (aromatic), 3.49. Found: TAN (aromatic), 3.51.

The NMR spectrum of the major product had absorptions at δ 0.9 ppm (one main peak, 6.05, CH_3–), 1.3 ppm [one main peak, 34.2, –$(CH_2)_9$–], 2.5–3.2 ppm (multiplet, 4.0, –CH_2–N) and 7.2–8.2 ppm (multiplet, 5.00, C_6H_5). The NMR spectrum of the minor component indicated this material still contained some of the anil. It also showed at least four peaks in the methyl region compared to one peak for the dialkyl aniline.

Results and Discussion

The results show that hindered internal olefins undergo hydroformylation in the presence of aniline and that the hydroformylated product forms an anil which can be hydrogenated to a monoalkylaniline. This reaction is summarized below for a symmetrical olefin. Internal olefins such as those found in oleates react smoothly to give good yields of x-(N-phenylaminomethyl)stearates, the monoalkylaniline.



α-Olefins react more rapidly than the internal olefins and two products, the monoalkyl and the di-*n*-alkylaniline, are formed but the latter predominates.

Diolefins such as linoleate and 1,5-cyclooctadiene react but yields are low and, at least for the latter case, several hard to separate products are formed. This behavior of the diolefins parallels that reported (20) in the hydroxymethylation of soy and other oils in which the oxo reaction occurs at only one site and the other double bond is hydrogenated.

Of the functional groups examined, Table I shows that esters and nitriles do not interfere seriously with the reaction. Triglycerides react more slowly then simple monoesters but the low nitrogen analysis found with soybean oil undoubtedly reflects the failure of the linoleate residues to undergo reaction. The carboxyl group does interfere with the reaction. Attempted N-phenylaminomethylation of oleic acid results in a stiff glass that resists purification. However, N-phenylaminomethylstearic acid prepared by saponification of the methyl ester is a light yellow, mobile oil.

1,2,3-Tris-(triphenylphosphine)trichlororhodium (III) was used as catalyst for most of this work since it gives good results and is easy to work with. Experiments 1, 3 and 4 compare the three catalysts used in this study. The rhodium catalyst is the best (78%) followed by cobalt octacarbonyl (55–60%) and the cobalt octacarbonyl-triphenylphosphine complex (27–29%). In the last case a considerable amount of black undistillable tar was formed. A similarity between the rhodium and cobalt catalysts is their failure to catalyze (1) the reaction when the partial pressure of carbon monoxide is much greater than the partial pressure of hydrogen. These stalled reactions could be started by venting part of the gas charge and repressuring the autoclave with hydrogen. Apparently the high partial pressures of carbon monoxide cause the equilibrium formation of a new metal species that is inactive as a hydroformylation catalyst.

The suggestion of an anil intermediate in the monoaddition reactions is based on the observation that at temperatures around 100 C we are consistently able to form the anil in a rapid (approx. 30 min) reaction. Subsequent heating of the reaction mixture to 150 C with hydrogen then gives the N-phenylaminomethylated product.

REFERENCES

1. Bird, C. W., Chem. Rev. *62*, 283 (1962).
2. Evans, D., J. A. Osborn, F. H. Jardine and G. Wilkenson, Nature *208*, 1203 (1965).
3. Finch, H., and R. E. Meeker, U.S. Patent 3,234,283 (1966).
4. Green, C. R., U.S. Patent 3,287,612 (1966).
5. Halpern, J., Chem. Eng. News *44*(45), 68 (1966).
6. Harrod, J. F., and A. J. Chalk, J. Am. Chem. Soc. *86*, 1776 (1964).
7. Heck, R. F., and D. S. Breslow, Ibid. *85*, 2779 (1963).
8. Kindler, H., and L. Schlecht, German Patent 1,124,931 (1962).
9. Kodama, S., I. Taniguchi, S. Yuasa, A. Watanabe and I. Yoshida, J. Chem. Soc. Japan Ind. Chem. Sect. *57*, 395 (1954); Chemical Abstracts *49*, 5005 (1955).
10. Macho, V., Chem. Zvesti *16*, 73–81 (1962); Chemical Abstracts *58*, 8883 (1963).
11. Malerbi, B. W., Plantimum Metals Rev. *9*, 47–50 (1965).
12. Orchin, M., Advan. *Catalysis* *16*, 1–47 (1966).
13. Osborn, J. A., G. Wilkenson and F. J. Young, Chem. Comml. *17* (1965).
14. Osborn, J. A., F. H. Jardine, J. F. Young and G. Wilkenson, J. Chem. Soc. (*A*), 1711 (1966).
15. Reppe, W., German Patent 839,800 (1952).
16. Reppe, W., N. Jutepow and M. Heintzeler, German Patent 909,937 (1954).
17. Schrauzer, G. N., *Adv. Organometallic Chem.* *2*, 1 (1964).
18. Siggia, S., "Quantitative Organic Analysis via Functional Groups," 3rd Edition, John Wiley & Sons, Inc., New York, 1967, p. 433.
19. Vogel, A. I., "Practical Organic Chemistry" 3rd Edition, Longmans Green and Co., New York, 1961, p. 344.
20. Wakamatsu, H., Nippon Kagaku Zasshi *85*, 227 (1964); Chemical Abstract. *61*, 13173 (1964).

[Received May 6, 1969]