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ORGANIC SYNTHESIS BY MEANS OF NOBLE METAL COMPOUNDS–LI[1]

PALLADIUM-CATALYZED ADDITION OF BUTADIENE TO NITROALKANES

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Abstract—Butadiene reacts with nitroalkanes in the presence of triphenylphosphine complexes of palladium. α-Hydrogens of nitroalkanes are displaced with 2,7-octadienyl groups to give nitroolefins. The nitroolefins thus obtained are reduced to give novel long chain amines, which have a primary amino group at the middle of the carbon chain.

Oligomerization of butadiene has been studied extensively by using several transition metal complexes, particularly nickel complexes, as catalysts. Studies of palldium-catalyzed oligomerization and telomerization of butadiene have been initiated only recently, which revealed that the palladium catalyzed reactions of butadiene are different from those catalyzed by nickel. The most interesting and important feature observed in the palladium catalyzed reactions of butadiene is the formation of telomers with various nucleophiles.[2] Butadiene dimerizes with efficient incorporation of nucleophiles mainly at a terminal position to give 1-substituted 2,7-octadienes. Alcohols, carboxylic acids, water, amines, ammonia, enamines are typical nucleophiles which add to butadiene dimer. Also active methylene compounds activated by two electron withdrawing groups such as malonate take part in the reaction.[3]

$$2CH_2{=}CHCH{=}CH_2 + Y{-}H \longrightarrow$$
$$CH_2{=}CHCH_2CH_2CH_2CH{=}CHCH_2{-}Y$$

Y—H: nucleophile

However, active methyl or methylene compounds with one electron-withdrawing group are inert, and simple ketones and esters do not take part in the reaction. We have found that nitroalkanes are exceptional, which react with butadiene smoothly in the presence of a palladium catalyst to give long chain nitroolefins in high yields. Reduction of the nitroolefins gives rise to long chain amines, which are unique in that they have a primary amino group at the middle of the carbon chain. A preliminary account of the work has been given,[4] and details of the reaction is presented in this paper.

RESULTS AND DISCUSSION

It is known that butadiene is converted into 1,3,7-octatriene in the presence of phosphine complexes of palladium in solvents like benzene or secondary alcohols.[5] We have found that the addition of a small amount of nitroalkane to benzene affects the oligomerization reaction, and considerable amounts of trimers and tetramers, in addition to the dimer, were obtained. For example, the oligomerization reaction carried out in benzene in the presence of nitromethane (*ca* 10% of butadiene) gave 1,3,7-octatriene (20%), 1,3,6-octatriene (15%), 1,3,7,11- and 1,3,6,11-dodecatraene (35%) and unidentified tetramers (10%). In the absence of nitromethane, only the dimer was formed.

When the reaction of butadiene in the presence of a considerable amount of nitroalkane was carried out in sec. alcohol such as isopropyl alcohol, the nitralkanes were found to take part in the reaction. The reaction of nitroalkanes with butadiene became the main reaction path when both reactants were used in equimolar amounts, and active hydrogens of nitroalkanes were displaced with 2,7-octadienyl groups, with a minor amount of branched product. Any nitroalkanes which have at least one hydrogen at the α-position undergo this reaction. When there are two or three α-hydrogens, the octadienyl group is introduced successively. It is possible to stop the reaction at certain stages by adjusting the relative amounts of reactants and reaction time. For example, from nitromethane the following products are formed, accompanied by 3-substituted 1,7-octadienes as minor products.

$$CH_2{=}CHCH{=}CH_2 + CH_3NO_2 \longrightarrow$$
$$CH_2{=}CHCH_2CH_2CH_2CH{=}CHCH_2CH_2NO_2$$
$$(CH_2{=}CHCH_2CH_2CH_2CH{=}CHCH_2)_2CHNO_2$$
$$(CH_2{=}CHCH_2CH_2CH_2CH{=}CHCH_2)_3CNO_2.$$

In this study, commercially available nitromethane, nitroethane, 1- and 2-nitropropane and nitrocyclohexane were used.

In this reaction, selection of proper reaction con-

Table 1. Properties of nitroolefins obtained from butadiene and nitroalkanes

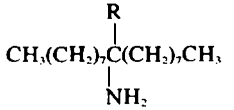
	B.p. °C	C Found (Calcd)	H Found (Calcd)	N Found (Calcd)	Mol. Wt. Found (Calcd)	NMR ppm; J, cps
From nitromethane						
9-nitro-1,6-nonadiene	99°/5 mm	63·97 (63·88)	8·86 (8·94)	8·22 (8·28)	169 (169·22)	1·5(2H), 2·0(4H), 2·67(2H), 4·33 (t, 2H, J = 7), 4·8 – 5·2 (2H), 5·3 – 5·9 (3H).
3-(nitromethyl)-1,7-octadiene	95°/5 mm	63·75 (63·88)	8·90 (8·94)	8·32 (8·28)	169 (169·22)	1·45 (4H), 2·0 (2H), 3·0 (1H), 4·29 (d, 2H, J = 7), 4·8 – 5·2 (4H), 5·4 – 6·0 (2H)
9-nitro-1,6,11,16-heptadecatetraene	120°/0·008 mm	73·51 (73·60)	9·87 (9·81)	5·01 (5·05)	278 (277·39)	1·5 (4H), 2·0 (8H), 2·5 (4H), 4·35 (1H), 4·8 – 5·1 (4H), 5·2 – 5·9 (6H).
9-nitro-9-(2,7-octadienyl)1,6,11,16-heptadecatetraene	177°/0·008 mm	77·94 (77·87)	10·17 (10·20)	3·63 (3·63)	383 (385·57)	1·44(6H), 1·99(12H), 2·46 (d, 6H, J = 7), 4·8 – 5·1 (6H), 5·2 – 5·9 (9H).
9-nitro-10-vinyl-1,6,14-pentadecatriene	114°/0·008 mm	73·48 (73·60)	9·87 (9·81)	5·08 (5·05)	276 (277·39)	1·45 (6H), 2·0 (6H), 2·50 (2H), 3·0 (1H), 4·35 (1H), 4·8 – 5·1 (6H), 5·2 – 5·95 (5H).
From nitroethane						
9-nitro-1,6-decadiene	102°/5 mm	65·78 (65·54)	9·39 (9·35)	7·62 (7·64)	183 (183·24)	1·48 (d, H, J = 7), 1·5 (2H), 1·98(4H), 2·47(t, 2H, J = 6), 4·47 (q, 1H, J = 6·5), 4·8 – 5·15 (2H), 5·25 – 5·85 (3H).
9-methyl-9-nitro-1,6,11,16-heptadecatetraene	125°/0·01 mm	74·21 (74·18)	10·02 (10·03)	4·88 (4·81)	290 (291·42)	1·43(5, 3H), 1·5(4H), 2·0 2·43 (d, J = 7, 2H), 2·53 (d, 2H, J = 7), 4·8 – 5·1 (4H), 5·2 – 5·9 (6H).
From 1-nitropropane						
9-nitro-1,6-undecadiene	115°/5 mm	66·81 (66·97)	9·90 (9·71)	7·13 (7·10)	198 (197·24)	0·95 (t, 3H, J 1·95 (2H), 2·47 (2H), 4·22 (1H), 4·8 – 5·15 (2H), 5·25 – 5·8 (3H).
9-ethyl-9-nitro-1,6,11,16-jeptadecatetraene	130°/0·008 mm	74·68 (74·71)	10·28 (10·23)	4·62 (4·59)	306 (305·45)	0·86 (t, 3H, J = 6), 1·44 (q, J = 6, 2H), 1·99 (10H), 2·52 (d, 4H, J = 7), 4·84 – 5·09 (4H), 5·18 – 5·92 (6H).
From 2-nitropropane						
9-methyl-9-nitro-1,6-decadiene	100°/5 mm	66·36 (66·97)	9·82 (9·71)	7·25 (7·10)	196 (197·27)	1·53 (s, 6H), 1·50 (2H), 1·97 (4H), 2·53 (d, 2H, J = 6), 4·8 – 5·1 (2H), 5·25 – 5·585 (3H).
From nitrocyclohexane						
8-(1-nitrocyclohexyl)-1,6-octadiene	140°/5 mm	70·30 (70·85)	9·70 (9·70)	5·97 (5·90)	237 (237·33)	1·5 (4H), 2·0 (4H), 2·3 (2H), 2·39 (d, 2H, J = 6), 4·8 – 5·1 (2H), 5·18 – 5·9 (3H).

ditions is essential for achieving maximum yields of nitroolefins. Otherwise, oligomerization of butadiene predominates as the competing reaction. Solvents have large influence on the reaction. Benzene and ethyl acetate are not suitable solvents. Secondary and tertiary alcohols were found to be very good solvents.

As the catalyst for this reaction, the presence of palladium and phosphine is essential. Any palladium compounds can be used by combining with phosphines. Palladium acetate and palladium acetylacetonate are used most conveniently. When palladium chloride is used, a base should be added in order to deprive the chloride ion from the coordination sphere of the palladium. Most conveniently, dichlorobis(triphenylphosphine)palladium is used with a base such as potassium hydroxide or sodium phenoxide. Furthermore, the bases have an accelerating effect on the reaction, and usually they are used in a large excess for the palladium. The reaction proceeded faster and gave higher yields when the ratio of potassium hydroxide and palladium was above 100. It seems likely that the formation of an aci-form of the nitro compounds accelerates the reaction. In addition to palladium compounds, the presence of phosphine is essential. The most effective one is triphenylphosphine. Trialkylphosphines or phosphites showed lower activity. The ratio of phosphine and palladium has some influence on the catalytic activity, and higher ratios, such as 10 or larger, tend to increase the life and activity of the palladium catalyst. Presence of an excess of triphenylphosphine seems to protect the palladium catalyst from deactivation by precipitation. One mole of the palladium catalyst easily produces more than 1000 moles of the nitroolefins.

The reaction proceeds even at room temperature. Higher temperature accelerates the reaction, but at the same time the simple dimerization of butadiene to form 1,3,7-octatriene also competes with the telomerization reaction of nitroalkanes. It can be said that favorable reaction temperature is around 50° for high selectivity of the nitroolefin formation. Nitroolefins are obtained in nearly 90% yields based on nitroalkanes by selecting proper reaction conditions as discussed above. Properties of nitroolefins obtained by this reaction are shown in Table 1.

The nitro compounds synthesized by this reaction can be converted into some other compounds. The most simple one is the reduction of both the olefinic bonds and nitro group to give saturated amines. The long chain amines thus produced have a primary amino group at the middle of the molecule as shown below and it is expected that they have properties quite different from usual amines which have amino group at the terminal position.



$$CH_3(CH_2)_7\overset{\overset{R}{|}}{\underset{\underset{NH_2}{|}}{C}}(CH_2)_7CH_3$$

R=H or alkyl

The reduction can be carried out most conveniently by catalytic hydrogenation using Raney nickel as a catalyst. Table 2 shows properties of the amines obtained by the catalytic hydrogenation. Also only the

Table 2. Long chain amines

	B.p. °C	C Found (Calcd)	H Found (Calcd)	N Found (Calcd)	Mol. Wt. Found (Calcd)
1-ethylnonylamine	90°/7 mm	77·06	14·66	8·19	172
		(77·11)	(14·71)	18·14)	(171·3)
1,1-dimethylnonylamine	98°/15 mm	77·03	14·83	8·04	173
		(77·11)	(14·71)	(8·14)	(171·3)
1-methylnonylamine	93°/20 mm	76·36	14·60	8·69	156
		(76·35)	(14·74)	(8·91)	(157·29)
1-octylcyclohexylamine	122°/3 mm	79·25	13·80	6·48	214
		(79·54)	(13·83)	(6·63)	(211·4)
1-methyl-1-octylnonylamine	138°/3 mm	80·33	14·61	5·21	267
		(80·22)	(14·59)	(5·20)	(269·5)
1-ethyl-1-octylnonylamine	154°/3 mm	80·59	14·34	4·80	281
		(80·48)	(14·50)	(4·94)	(283·5)
1,1-dioctylnonylamine	132°/0·004 mm	81·90	14·38	3·89	366
		(81·66)	(14·53)	(3·81)	(367·7)
1-ethyl-3,8-nonadienylamine	106°/14 mm	78·85	12·61	8·12	169
		(78·97)	(12·65)	(8·37)	(167·3)
1-ethyl-1-(2,7-octadienyl)-3,8-nonadienylamine	150°/2 mm	82·67	12·04	5·14	277
		(82·84)	(12·8)	(5·09)	(275·5)
1,1-di(2,7-octadienyl)-3,8-nonadienylamine	129°/0·002 mm	84·28	11·54	4·01	356
		(84·44)	(11·62)	(3·94)	(355)

nitro group can be reduced with the double bond intact by using reducing agents such as lithium aluminum hydride. These amines are useful compounds for preparing various surface active agents.

EXPERIMENTAL

B.ps are uncorrected. All nitroalkanes were commerical products and distilled before use. NMR spectra were measured on a Varian HA 100 spectrometer. Only typical examples of the reactions of butadiene with nitroalkanes and hydrogenation are shown below. Structures of the nitroolefins and amines were determined by molecular weight, elemental analysis, and NMR shown in the tables.

Reaction of nitromethane. In an autoclave (100 ml) was placed a mixture of $PdCl_2(PPh_3)_2$ (0·5 g), sodium phenoxide (1·0 g), nitromethane (6·1 g) and isopropanol (25 ml). Then butadiene (39 g) was charged to the closed autoclave. The reaction was carried out at 25° for 18 h with shaking. The reaction mixture was poured into ether and the solution was washed with water. Distillation of the mixture gave the following products. 3 - (nitromethyl) - 1,7 - octadiene (0·5 g), 9 - nitro - 10 - vinyl - 1,6,14 - pentadecatriene (4·8 g), 9 - nitro - 9 - (2,7 - octadienyl) - 1,6,11,16 - heptadecatetraene (20·5 g); and 9 - nitro - 1,6,11,16 - heptadecatetraene (2·4 g).

Reaction of 2-nitropropane. In an autoclave (500 ml) a mixture of $PdCl_2(PPh_3)_2$ (0·42 g) KOH (1,68g) 2-nitropropane (26·7 g), isopropanol (150 ml) and butadiene (35 g) was charged. The reaction was carried out at 50° for 4 h. After the usual work up, distillation of the product gave the following products. 1,3,7-octatriene (1·9 g), 9 - methyl - 9 - nitro - 1,6 - decadiene (49 g).

Catalytic reduction of 9 - methyl - 9 - nitro - 1,6 - decadiene. The nitroolefin (10 g), methanol (14 ml) and Raney nickel (1 g) were charged in an autoclave and the reduction was carried out at 50° under hydrogen pressure (70 atm) for 3 h. Distillation of the product gave 1,1-dimethylnonylamine in 98% yield.

Reduction with lithium aluminum hydride. In a three-neck flask (200 ml) was placed a mixture of lithium aluminum hydride (1·5 g) and ether (30 ml). A solution of 9 - ethyl - 9 - nitro - 1,6,11,16 - heptadecatetraene in ether (6·1 g in 20 ml) was added dropwise into the flask under reflux. After addition of the solution, the mixture was refluxed for 1 h. After the usual work up, 1 - ethyl - 1 - (2,7 - octadienyl) - 3,8 - nonadienylamine (4·4 g, 80%) was obtained by distillation.

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