# Syntheses of Long-chain Amines by Palladium-catalysed Telomerisation of Butadiene

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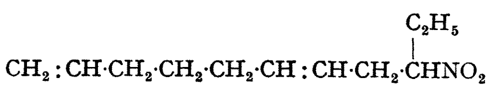
*Summary* Novel syntheses of long-chain amines by the palladium-catalysed telomerisation of butadiene with ammonia and nitroalkanes, followed by hydrogenation, are reported.

RECENTLY several reports have appeared concerning the reactions of butadiene with nucleophiles catalysed by palladium complexes.[1] We now report palladium-catalysed telomerisation of butadiene with ammonia and nitroalkanes as novel synthetic methods for long-chain amines.

Direct reaction of olefinic compounds with ammonia would be an attractive method of amine synthesis, but so far there has been no report on smooth addition of ammonia to olefinic bonds, except Michael-type addition to activated olefins. Now we have found that ammonia reacts smoothly with butadiene under appropriate conditions. Typically, a mixture of aqueous ammonia (28%, 5 g) and butadiene (32 g) in acetonitrile (60 ml) was allowed to react in the presence of palladium acetate (63 mg) and triphenylphosphine (261 mg) at 80° for 10 h. Distillation of the reaction mixture gave a small amount of diocta-2,7-dienylamine (1·2 g) at 105—107°/0·25 mm, and then triocta-2,7-dienylamine (I) (29 g) at 139—142°/0·05 mm. The structure of (I) was supported by the following data. Correct analysis and molecular weight (mass spectrum, 341) for $C_{24}H_{39}N$; i.r. spectrum ($cm^{-1}$), 910, 990 (terminal olefin); n.m.r. spectrum ($\tau$), 8·35 (q, 6H, $CH_2$), 7·85—8·15 (m, 12H, allylic), 6·9—7·1 (d, 6H, $N$-$CH_2$) 4·8—5·2 (m, 6H, terminal olefin), 3·9—4·5 (m, 9H, olefinic). Also (I) absorbed 6 moles of hydrogen to give the known trioctylamine over a Raney nickel catalyst.

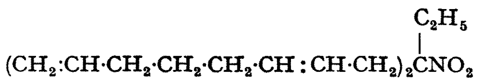
We have also found that hydrogens at the $\alpha$-carbon of nitroalkanes are replaced by octa-2,7-dienyl groups. Thus, a mixture of 1-nitropropane (9g), butadiene (25 g), dichlorobis(triphenylphosphine)palladium (500 mg), and sodium phenoxide (950 mg) in n-butanol (25 ml) was allowed to react at room temperature for 20 h. Distillation of the reaction mixture gave 9-nitroundeca-1,6-diene (II) (10·7 g) at 115°/5 mm and 9-ethyl-9-nitro-1,6,11,16-heptadecatetraene (III) (12·8 g) at 130°/0·008 mm. The structures assigned are consistent with the n.m.r. spectra, and analyses and molecular weight (198 and 306) for $C_{11}H_{19}NO_2$ and $C_{19}H_{31}NO_2$ provide further evidence. Compounds (II) and (III) were easily reduced to 1-ethylnonylamine (b.p. 90°/7 mm) and 1-ethyl-1-octylnonylamine (b.p. 154°/3 mm), respectively, over Raney nickel catalyst.

$$CH_3{\cdot}CH_2{\cdot}CH_2NO_2 + CH_2{:}CH{\cdot}CH{:}CH_2 \rightarrow$$



$$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}\overset{\overset{\displaystyle C_2H_5}{|}}{C}HNO_2$$

(II)



$$(CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2)_2\overset{\overset{\displaystyle C_2H_5}{|}}{C}NO_2$$

(III)

The reaction may be applied to other nitroalkanes such as nitromethane, nitroethane, and nitrocyclohexane. The amines produced by this method are novel in that they have a primary amino-group at the middle of the carbon chain, rather than at a terminal position.

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[1] S. Takahashi, T. Shibano, and N. Hagihara, *Tetrahedron Letters*, 1967, 2451; *Bull. Chem. Soc. Japan*, 1968, **41**, 454; E. J. Smutny, *J. Amer. Chem. Soc.*, 1967, **89**, 6793; G. Hata, K. Takahashi, and A. Miyake, *Chem. and Ind.*, 1969, 1826.