CATALYTIC SYNTHESIS OF UNSATURATED TERTIARY AMINES

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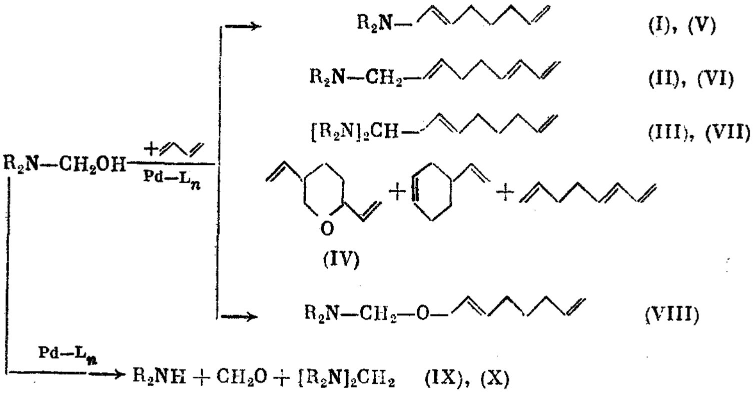
We have previously shown that palladium complexes efficiently catalyze the formation of formaldehyde and 1,3-dienes or derivatives of 2,5-divinylpiperidine from primary amines [1, 2]. In this connection it seemed of interest to investigate the telomerization of N-hydroxymethylamines, which were obtained from secondary amines and formaldehyde [3], with butadiene, as well as of secondary amines with formaldehyde and butadiene, in the presence of homogeneous Pd catalysts.

The telomerization of N-hydroxymethylpiperidine with butadiene taken in a 1 : 2 ratio on a catalyst prepared by reducing $Pd(acac)_2$ with triethylaluminum in the presence of PPh_3 results in the formation of a mixture of oligomers consisting of butadiene dimers (4-vinylcyclohexene and 1,3,7-octatriene), N-2,7-octadienylpiperidine (I), N-2,6,8-nonatrienylpiperidine (II), 1,1'-piperidyl-3,8-nonadiene (III), and 2,5-divinyltetrahydropyran (IV) in a 54 : 15 : 15 : 15 : 1 ratio with a total yield of ~50%.

The structures of amines II and III were confirmed by spectral methods, and those of compounds I and IV and the butadiene homodimers were proved by comparison with known preparations [4-6]. In addition, the hydrogenation of amines II and III on Pd/C in ethyl acetate occurs with the absorption of 3 and 2 moles of H_2, respectively.

N-Hydroxymethyldiethylamine reacts similarly with butadiene on the catalyst indicated, yielding 4-vinylcyclohexene, N-2,7-octadienyldiethylamine (V), N-2,6,8-nonatrienyldiethylamine (VI), 1,1-diethylamino-3,8-nonadiene (VII), and a mixed cooligomer (VIII) with a total yield of ~40%.

The only product of a new type in experiments with N-hydroxymethyldiethylamine is the cooligomer (VIII), which is found in the reaction mixture in an amount ≤3%. All of our attempts to increase the yield of VIII by changing the nature and structure of the catalyst components, as well as the ratio between the original monomers, were unsuccessful.



R_2=—$(CH_2)_5$—(I), (II), (III) (IX); R=Et (V), (VI), (VII), (VIII), (X)

In order to account for the paths for the formation of unsaturated amines I-III and V-VII we postulated that under the conditions of our experiments N-hydroxymethylpiperidine or N-hydroxymethyldiethylamine disproportionates under the action of the palladium complexes into formaldehyde, the corresponding secondary amines, and bisamines IX and X. The subsequent reaction of the decomposition products with butadiene produces unsaturated amines I-III and V-VII, as well as 2,5-divinyltetrahydropyran [7].

In reality, the heating of N-hydroxymethylpiperidine or N-hydroxymethyldiethylamine in the presence of butadiene on the $Pd(acac)_2-PPh_3-Al(C_2H_5)_3$ (100°C, 5 h) results in the synthesis of formaldehyde, diethylamine, or piperidine, as well as bisamines IX and X.

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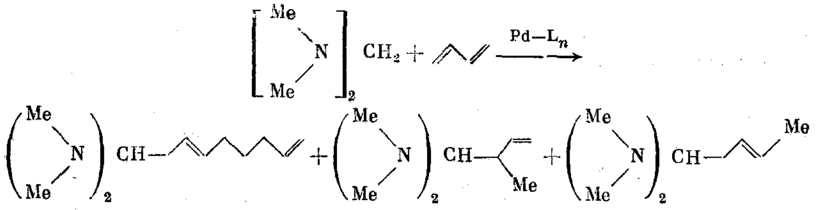
Unsaturated bisamines III and VII are obviously formed by the telomerization of butadiene with amines IX and X in the presence of Pd catalysts, and trienes II and VI form as a result of the reaction of the N-hydroxymethylamines with 1,3,7-octatriene according to the scheme

In order to confirm the hypothesis advanced, we investigated the reaction of butadiene with tetramethylmethylenediamine on the aforementioned catalytic system in a solution of absolute toluene. 1,1-Dimethylamino-3,8-nonadiene (XI) was isolated. Along with the latter the catalysate contained insignificant amounts of butenyl derivatives XII and XIII:

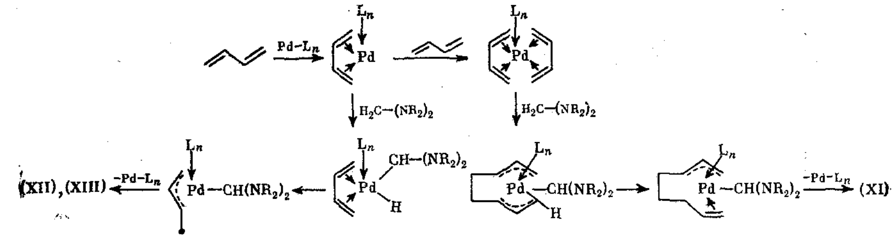


(XI) (XII) (XIII)

Under similar conditions N-hydroxymethylpiperidine or N-hydroxymethyldiethylamine reacts with 1,3,7-octatriene, yielding trienes II and VI, and octadienylamines I and V form from diethylamine or piperidine and butadiene [4, 5].

Somewhat different results were obtained as a result of the simultaneous reaction of butadiene with CH_2O and piperidine or diethylamine. In this case, the main reaction products are IV, the butadiene dimers, and amines I and V. It must be assumed that the formation of the corresponding N-hydroxymethylamines and bisamines IX and X, which are responsible for the formation of the molecules of unsaturated amines II and VI or III and VII, is not observed in these experiments.

On the basis of the results obtained it may be concluded that in the first step the N-hydroxymethylamines split into formaldehyde, secondary amines, and bisamines under the action of the palladium complexes under the conditions of our experiments. The addition of the amines cited, which contain mobile hydrogen atoms, to butadiene occurs in the second stage with a step involving oxidative addition to the central atom of the catalyst with cleavage of C—H or N—H bonds. The further combining of the activated molecules yields amines I-III and V-VII [8]. The following most probable scheme for the formation of amines III and VIII was proposed in the example case of the telomerization of butadiene with bisamines IX and X:



The reaction indicated permits the synthesis of relatively unaccessible and reactive unsaturated Mannich bases in one step from 1,3-dienes and bisamines.

EXPERIMENTAL

Monomers with a purity ≥ 99% were used in the work. The mixtures of oligomers were analyzed on a Tsvet-102 chromatograph, the detector was of the flame-ionization type, the column had a length of 2 m and contained 15% Apiezon L on Celite 545, and the carrier gas was nitrogen. The IR spectra were recorded on a UR-20 spectrophotometer (films), and the PMR spectra were recorded on a Tesla BS-480B instrument in CCl_4, the internal reference being HMDS. The mass spectra were recorded on an MX-1306 instrument with an energy of the ionizing electrons equal to 70 eV and a temperature of the ionization chamber equal to 200°C.

Telomerization of N-Hydroxymethylamines with Butadiene (General Procedure). A solution of 1 g of $Pd(acac)_2$, 3.6 g of PPh_3, and 5 ml of butadiene in 20 ml of absolute toluene was given an addition of 2.5 g of $AlEt_3$ in 10 ml of toluene at 0°C in a stream of argon, and the mixture was stirred for 10 min and transferred to a 300 ml steel autoclave containing 2 moles of butadiene and 1 mole of the N-hydroxymethylamine. The autoclave was heated for 10 h at 120°C. The catalyst was cooled, and the organic layer was washed with 5% $NaHCO_3$ and water to a neutral reaction and dried over $MgSO_4$. The solvent was evaporated, and the residue was vacuum distilled. This yielded 110 g of a mixture of oligomers from N-hydroxymethylpiperidine and 80 g of a mixture from N-hydroxymethyldiethylamine.

The oligomers, which were recovered by rectification in a column, as well as by preparative GLC, had the following constants.

N-2,6,8-Nonatrienylpiperidine (II), bp 77°C (2 mm), n_D^{20} 1.4900. UV spectrum (λ_{max}, ethanol): 227 nm, ε= 35,600. IR spectrum (ν, cm^{-1}): 920, 100, 3085 ($CH=CH_2$), 975, 1030 (trans-$CH=CH$). PMR spectrum (δ, ppm): 1.35 (m, 6 H, CH_2), 2.11 (m, 4 H, $=\underline{CH_2CH_2}C=$), 2.22 (m, 4 H, NCH_2), 2.77 (d, 2 H, $N\underline{CH_2}C=$), 4.87 (t, 2 H, $C=\underline{CH_2}$), 5.37 (m, 2 H, $CH=CH$), 5.84 (m, 3 H, $\underline{CH}=\underline{CH}-\underline{CH}=CH_2$), M^+ 205.

The hydrogenation of 1 g of II on Pd/C in ethyl acetate proceeds with the absorption of 3 moles of H_2 and the formation of the saturated amine, bp 80°C (2 mm), n_D^{20} 1.4560, M^+ 211. Found: C, 79.8; H, 13.7; N, 6.5%. Calculated for $C_{14}H_{29}N$: C, 79.6; H, 13.8; N, 6.6%.

1,1'-Piperidyl-3,8-nonadiene (III), bp 153-154°C (1.5 mm), n_D^{60} 1.4970. IR spectrum (ν, cm^{-1}): 920, 1000, 3085 ($C=CH_2$), 980, 3020 (trans-$CH=CH$). PMR spectrum (δ, ppm): 1.45 (m, 14 H, CH_2), 2.1 (t, 6 H, $CH_2C=$), 2.22 (8 H, NCH_2), 2.7 (d, 1 H, NCHN), 4.94 (t, 2 H, $C=CH_2$), 5.33 (m, 3 H, $CH=CH$, $CH=C$), M^+ 290.

The hydrogenation of 2 g of III under the conditions described above proceeds with the absorption of 2 moles of H_2 and results in the synthesis of bispiperidyloctylmethane, bp 167-168°C (2 mm), n_D^{20} 1.4560, M^+ 294. Found: C, 77.7; H, 12.8; H, 9.5%. Calculated for $C_{19}H_{38}N_2$: C, 77.6; H, 12.9; N, 9.5%.

N-2,6,8-Nonatrienyldiethylamine (VI), bp 110-112°C (10 mm), n_D^{20} 1.4780. UV spectrum (λ_{max}, ethanol): 227 nm, ε=33,800. IR spectrum (ν, cm^{-1}): 920, 1000, 3085 ($CH=CH_2$), 978, 3030 (trans-$CH=CH$). PMR spectrum (δ, ppm): 1.06 (m, 6 H, CH_3), 2.04 (m, 4 H, CH_2), 2.10 (m, 4 H, $=CCH_2CH_2C=$), 2.76 (d, 2 H, $NCH_2C=$), 4.89 (t, 2 H, $C=\underline{CH_2}$), 5.38 (m, 2 H, $CH=CH$), 5.84 (m, 3 H, $CH=CH-CH=C$), M^+ 193.

1,1'-Diethylamino-3,8-nonadiene (VII), bp 123-124°C (3 mm), n_D^{20} 1.4460. IR spectrum (ν, cm^{-1}): 920, 1000, 3081 ($CH=CH_2$), 976, 3030 (trans-$CH=CH$). PMR spectrum (δ, ppm): 0.95 (t, 12 H, CH_3), 1.5 (m, 2 H, CH_2), 2.12 (m, 6 H, $CH_2C=$), 2.25 (m, 8 H, CH_2N), 2.87 (d, 1 H, NCHN), 4.95 (t, 2 H, $C=CH_2$), 5.36 (m, 3 H, $HC=CH$, $\underline{CH}=CH_2$), M^+ 266.

The hydrogenation of 1 g of VI or VII under the aforementioned conditions yields the corresponding saturated amines with quantitative yields.

Diethylnonylamine, bp 115-117°C (10 mm), n_D^{20} 1.4430, M^+ 199. Found: C, 78.3; H, 14.6; N, 7.0%. Calculated for $C_{13}H_{29}N$: C, 78.4; H, 14.5; N, 7.1%.

Bis(diethylamino)octylmethane, bp 90°C (2 mm), n_D^{20} 1.4520, M^+ 270. Found: C, 75.5; H, 14.1; N, 10.3%. Calculated for $C_{13}H_{30}N_2$: C, 75.6; H, 14.0; N, 10.4%.

Splitting of N-Hydroxymethylamines under the Action of Palladium Complexes. A solution of 10 g of N-hydroxymethylpiperidine in absolute toluene and a catalytic system consisting of 0.1 g of $Pd(acac)_2$, 0.36 g of PPh_3, and 0.25 g of $AlEt_3$ was heated for 4 h at 100°C. This resulted in the formation of ~50% and 20% bis(piperidyl)methane, bp 110°C (22 mm), n_D^{15} 1.4880 (compare [9]), and 30% of the original amine was recovered. The catalysate also contained an insoluble precipitate (25%), which was essentially polyhydroxymethylene.

Under similar conditions 5 g of N-hydroxymethyldiethylamine yielded 2 g of diethylamine and 1 g of bis(diethylamino)methane, bp 165-167°C, n_D^{18} 0.8103 (compare [10]) with conversion of 3.9 g of the original amine.

Telomerization of N-Hydroxymethylamines with 1,3,7-Octatriene. A solution of 5 g of N-hydroxymethylpiperidine in 30 ml of absolute toluene was heated for 6 h with an equimolar amount of 1,3,7-octatriene in an argon current at 120°C in the presence of a Pd catalyst prepared as described above.

Treatment of the catalysate yielded a mixture of products consisting of 20% piperidine, 15% bis(piperidyl)methane, 50% N-2,6,8-nonatrienylpiperidine, and ~15% polyhydroxymethylene. The extent of conversion of the original monomers did not exceed 20%.

Similar results were obtained in the experiments with N-hydroxymethyldiethylamine (the extent of conversion was ~25%).

Telomerization of Butadiene with Tetramethylmethylenediamine. A solution of the catalyst prepared according to the procedure described above was transferred to a 300-ml steel autoclave containing 162 g of butadiene and 102 g of tetramethylmethylenediamine. The autoclave was heated for 10 h at 120°C and then cooled. The product was filtered through 200 g of Al_2O_3 (third activity level) and washed with toluene, and the combined eluates were evaporated in a vacuum. Removal of the solvent yielded 80 g of a mixture of oligomers consisting of XI, a mixture of XII+XIII, and dimers of butadiene (vinylcyclohexene and 1,3,7-octatriene), whose total quantity in the mixture amounted to ~15%.

The unsaturated amines recovered by rectification in a Widmer column had the following constants.

XI, 90%, bp 79-80°C (1.5 mm), n_D^{20} 1.4630. IR spectrum (ν, cm^{-1}): 920, 1000, 3085 ($CH=CH_2$), 976, 3030 (trans-$CH=CH$). PMR spectrum (δ, ppm): 2.07 (m, 12 H, CH_3N; 2 H, CH_2; 6 H, $CH_2C=$), 2.7 (d, 1 H, NCHN), 4.9 (m, $C=CH_2$), 5.37 (t, $CH=CH$), M^+ 210.

XII+XIII, 10%, bp 30-32°C (1.5 mm), n_D^{20} 1.4520. IR spectrum (ν, cm^{-1}): 918, 1000, 3084 ($CH-CH$), 975, 3030 (trans-$CH=CH$), M^+ 156. Found: C, 69.0; H, 12.9; N, 18.1%. Calculated for $C_9H_{20}N_2$: C, 69.2; H, 12.8; N, 18.0%.

Telomerization of Butadiene with Formaldehyde and Piperidine or Diethylamine. A mixture of 10 g of piperidine, 11 g of butadiene, and 10 ml of formaldehyde in a solution of absolute toluene on a $Pd(acac)_2$ (0.1 g)$-PPh_3$ (0.36 g)$-AlEt_3$ (0.25 g) catalyst under the aforementioned conditions yielded 18.9 g of a mixture of oligomers consisting of 30% IV [4], 30% N-2,7-octadienylpiperidine (I) [5], and 40% butadiene dimers [6].

A mixture of 7.5 g of diethylamine, 10 ml of formaldehyde, and 10.9 g of butadiene yielded 19 g of a mixture of IV (~25%), V (~30%), and butadiene dimers (~45%).

CONCLUSIONS

1. The possibility of synthesizing unsaturated mono- and bisamines by the telomerization of butadiene with N-hydroxymethylpiperidine and N-hydroxymethyldiethylamine in the presence of homogeneous Pd catalysts has been demonstrated.

Under the conditions of this reaction the N-hydroxymethylamines indicated decompose into formaldehyde, methylenebisamine, and a secondary amine.

2. The mixed telomerization of butadiene with formaldehyde and secondary amines in the presence of Pd catalysts results in the synthesis of 2,5-divinyltetrahydropyran, the corresponding N-2,7-octadienylamines, and homodimers of butadiene (vinylcyclohexene and 1,3,7-octatriene).

3. The telomerization of tetramethylmethylenediamine with butadiene, which results in the synthesis of unsaturated 1,1-dimethylamino-3,8-nonadiene, 1,1-dimethylamino-2-pentene, and 1,2-dimethylamino-3-methyl-1-butene, has been studied for the first time.

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