Chemical Utilization of Piperylene

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Abstract. The interaction of aromatic amines with piperylene and its chlorine derivatives was
being studied. Direct alkylation of aniline by piperylene in the presence of Lewis acids results
in its C-substituted derivatives. At reaction of 4-chloro-2-pentene and 3,4-dichloro-2-pentene
with amines in medium of excess aromatic amine, ring-substituted amines are formed
due to proceeding Claisen's amino-rearranging of initially formed N-substituted products. In
medium of triethylamine, the same reaction is completed at the stage of N-alkenylation. The
compounds obtained are of interest as substances with biological activity; at the same time they
are valuable intermediates for the synthesis of nitrogen-containing heterocycles.

1. Introduction

Environmental problems in the Russian Federation have their own characteristics. The chemical and
petrochemical industries of our country until recently were as a rule large-scale productions aimed not
at the manufacture of consumer goods but only of semi-finished products for obtaining consumer
goods. In view of large scale of these productions, their waste is also formed in significant quantities
and creates a serious problem. Despite certain successes in the modernization of technological
processes since the beginning of the XXI century, aimed at creating low-waste technologies and
low-tonnage chemical products, utilization/disposal of chemical and petrochemical wastes remains
relevant.

In the production of isoprene in the Russian Federation, tens of thousands of tons of piperylene
(1,3-pentadiene) are formed as a by-product which unlike other short-chain conjugated dienes does not
find any qualified application. Meanwhile, the diene structure of piperylene provides ample
opportunities for synthesis on its basis of different organic compounds representing practical interest
as well [1]. In our opinion, a very promising direction is the reaction of interaction of piperylene with
aromatic amines which results in alkylated arylamines.

This paper presents the results of introduction of the pentenyl radical into the structure of aromatic
amines molecule by the interaction of the latter with piperylene and its chlorine derivatives, 4-chloro-
2-pentene and 3,4-dichloro-2-pentene. The presence of the allyl type double bond in the alkenyl
moiety of the substituted arylamine allows for further reaction - Claisen's amino-rearranging with
broad synthetic perspectives [2–5]. From N- and C-pentenylarylamines, it is possible to transfer to
nitrogen-containing heterocyclic compounds of various structures, most of which possess biological
activity [6–20].
2. Alkenylation of aromatic amines by piperylene

Direct alkenylation of aniline by piperylene in the presence of Lewis acids results in C-pentenyl arylamines.

Depending on the reaction conditions and the ratio of reagents, either mono- or di- and tri-substituted products predominate, whilst the ortho-isomer 2 always prevails. The most effective catalyst is AlCl₃.

Various aniline derivatives are also involved in the reaction with piperylene. When one of the ortho-positions in the arylamine molecule is occupied, a mixture of three products is formed in comparable quantities.

The reaction of piperylene with meta-toluidine also results in a mixture of three products, and the substitution does not affect the 2-position between the amino- and methyl groups.

If the para-position is occupied, two products are formed.
The reaction proceeds successfully even if both ortho-positions are occupied.

\[
\begin{align*}
&\text{17} \\
&\text{18} \quad 61\%
\end{align*}
\]

2,4-disubstituted anilines naturally give a single product, and in the case of electron-donating methyl groups the yield is much higher.

\[
\begin{align*}
&\text{19a} \quad \text{R=Me} \\
&\text{19b} \quad \text{R=OMe} \\
&\text{20a} \quad 58\% \\
&\text{20b} \quad 37\%
\end{align*}
\]

Also, 2,5-xylidine forms a single product, although in this case there could be other possibilities.

\[
\begin{align*}
&\text{21} \\
&\text{22} \quad 51\%
\end{align*}
\]

3. Interaction of arylamines with chlorine derivatives of piperylene

To increase the selectivity of the process, the reaction of alkylation of aromatic amines is to be carried out not with piperylene itself but with its chlorine derivatives. The reaction of aniline with 4-chloro-2-pentene in medium of triethylamine at 80° C is completed within 3 hours and results in N-substituted product 23a with the yield of 80%. Other primary and secondary arylamines react in the same way. The reaction with 3, 4-dichloro-2-pentene takes place under more severe conditions.
If the reaction of aniline with 4-chloro-2-pentene is carried out not in triethylamine medium, but in an excess of aniline itself as a solvent, it is not N-, but C-substituted products that are formed.

In the first stage of the reaction, N-alkenylation of aniline occurs with the formation of compound 23, followed by Claisen’s amino-rearranging into C-alkenyl derivatives under the action of evolving HCl, which protonates 23a as the strongest base in this reaction system, thereby catalyzing the process.

The conditions for the reaction of Claisen’s amino-rearranging, the composition and the products yield from the reaction of 4-chloro-2-pentene with arylamines are given in Table.

**Table 1.** Reaction conditions and products yield by reacting 4-chloro-2-pentene with aromatic amines.

| Initial arylamine    | Reaction conditions, T, °C / time, h | ortho- | para-  | bis-   |
|----------------------|-------------------------------------|--------|--------|--------|
| Aniline              | 130/4                               | 64 (2) | 9 (3)  | 22 (25) |
| N- Methylaniline      | 130/0.5                             | 70 (26) | -      | -      |
| N- Ethylaniline       | 100/1                               | 76 (27) | -      | -      |
| 2- Methylaniline      | 130/4                               | 56 (7a) | 22 (8a) | 10 (9a) |
| 2- Chloraniline       | 130/5                               | 52 (7b) | 16 (8b) | 12 (9b) |
| 3- Methylaniline      | 130/4                               | 55 (11) | 22 (12) | -      |
| 4- Methylaniline      | 150/6                               | 82 (15) | -      | 8 (16)  |

As follows from the Table, the presence of electron-donating substituents at the nitrogen atom greatly facilitates the rearrangement stage and allows the reaction to take place under milder conditions. The reaction of aniline with 4-chloro-2-pentene at 130° C lasts 4 hours, and that of its N-methyl derivative completes within less than 30 minutes. N-Ethylaniline reacts even easier: already at...
100° C, the reaction comes to an end within 1 hour. In both cases, only ortho-substituted products 26, 27 are found out.

Under similar conditions, 2-methylaniline and 2-chloroaniline form significant amounts of para-(8a, b) and 2, 4-bis- (9a, b) products, respectively.

Unlike the direct alkylation reaction with piperylene, meta-toluidine with 4-chloro-2-pentene does not form a dialkenyl derivative 13; ortho-isomer 11 predominates in the reaction products.

Electron-donating para-substituents significantly slow down the Claisen's amino-rearrangement stage, but at the same time increase the yield of C-alkenylated products.

In all the above reactions, the stereoselective proceeding rearrangement takes note, since the spectral characteristics of the compounds obtained unambiguously confirm the trans-structure of the allylic double bond. As it is known, $\alpha,\gamma$-dimethyl-allyl-phenyl ether [21] rearranges according to Claisen with the similar stereoselectivity.

Amino-rearrangement in the interaction of arylamines with 3,4-dichloro-2-pentene proceeds with exceptional ortho-regioselectivity. Alkyl groups containing nitrogen and having ortho-position accelerate, but ortho-chloro-, para-methyl,2,4-dimethyl groups slow down the process, while the meta-methyl group does not have a significant effect.

![Diagram]

All R=H, 28a (88%); R$_1$=Me, 28b (76%); R$_2$=Me, 28c (75%); R$_3$=Cl, 28d (70%); R$_4$=Me, 28e (70%); R$_5$=Me, 28f (88%)

4. Conclusion

1. The interaction of piperylene with aromatic amines in the presence of Lewis acids leads to C-alkenylation of the latter. Depending on the reaction conditions and the ratio of the reactants, either mono- or di- and tri-substituted arylamines prevail. The most effective catalyst is AlCl$_3$.

2. The reaction of aromatic amines with chlorine derivatives of piperylene – 4-chloro-2-pentene and 3,4-dichloro-2-pentene in triethylamine medium leads to high yield of N-substituted arylamines.

3. In interaction of 4-chloro-2-pentene and 3,4-dichloro-2-pentane with an excess of aromatic amine, directly C-substituted products are formed as a result of the Claisen’s amino-rearrangement of the initially formed N-alkenylationarylamines under the catalytic action of released hydrogen chloride.

5. References

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