Acylation of linalool in the presence of polymeric pyrrolidinopyridines

E. D. Alieva, N. I. Truhmanova, and N. A. Platé*

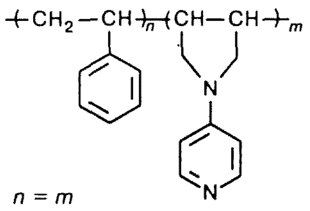
A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences,
29 Leninsky prosp., 117912 Moscow, Russian Federation.
Fax: +7 (095) 230 2224

The effect of a number of factors on the efficiency of polymers containing immobilized pyrrolidinopyridine groups as polymeric activating reagents for the acylation of weakly reactive sterically hindered alcohols was studied. The conditions of the acylation of linalool with acetic anhydride in the presence of polymeric pyrrolidinopyridines were selected in such a way that the activity of polymeric systems under study was close to that of their low-molecular-weight analog, pyrrolidinopyridine (in a homogeneous medium).

Key words: linalool, acylation; polymeric pyrrolidinopyridines, polymeric activating reagent.

Previously[1] it was demonstrated for the first time that polymers containing immobilized 4-*N*-pyrrolidinopyridine groups can be used as macromolecular "transferring reagents" or activating reagents in the acylation of sterically hindered alcohols. We have applied our approach to the development of polymeric reagents activating various organic reactions to the acylation of a relatively inert alcohol, linalool, with acetic anhydride.

In this paper we present new data on the acylation of linalool in the presence of polymeric pyrrolidinopyridines (poly-S-PP).



Characteristic features and some specific features of the occurrence of reactions of this type in the presence of polymers have been established, which allowed this process to be substantially optimized.

Experimental

GLC analysis was carried out using a Tsvet-100 chromatograph (a combined column with 10 % PEG (M = 20000) and with 10 % Apieson L on Chromosorb W-AW; nitrogen as the carrier gas, the rate of gas flow was 30 mL min^{-1}).

Acylation of linalool with acetic anhydride was carried out with stirring in an argon flow. Poly-S-PP (0.2 mol.-equiv. with respect to the starting alcohol) with various contents of the functional PP groups, linalool (10 mmol), triethylamine (TEA, 15 mmol), and benzene or toluene (20 mL) were placed in a reactor. Acetic anhydride (15 mmol) was added at 24 °C or at 60 °C at the beginning of the reaction (t = 0) and samples (0.1 mL) withdrawn from the reaction mixture at regular intervals were analyzed by GLC.

Prior to the reaction, poly-S-PP samples of various compositions were subjected to "swelling," which was carried out by keeping the polymers in benzene or toluene for 3—10 h with stirring in an argon flow at a controlled temperature (24 °C or 60 °C), and after that, the above amounts of linalool and TEA were added to the reactor. The instant at which acetic anhydride was added was taken as the beginning of the reaction (t = 0). Analyses of the reaction products and of the degree of conversion of linalool into the corresponding ester were carried out as described above.

Polymeric pyrrolidinopyridines (poly-S-PP) with PP-groups in the backbone and with various contents of the functional groups were synthesized[1] by the condensation of the alternating copolymer of styrene and maleic anhydride (M = 70000) with appropriate amounts of 4-aminopyridine followed by the reduction of the carbonyl groups in the pyridylmaleimide rings. The degree of functionalization of the polystyrene matrix with PP-groups (as a percentage of the maximum possible content of PP-groups in poly-S-PP) was determined on the basis of quantification of the content of nitrogen in the resulting copolymers.

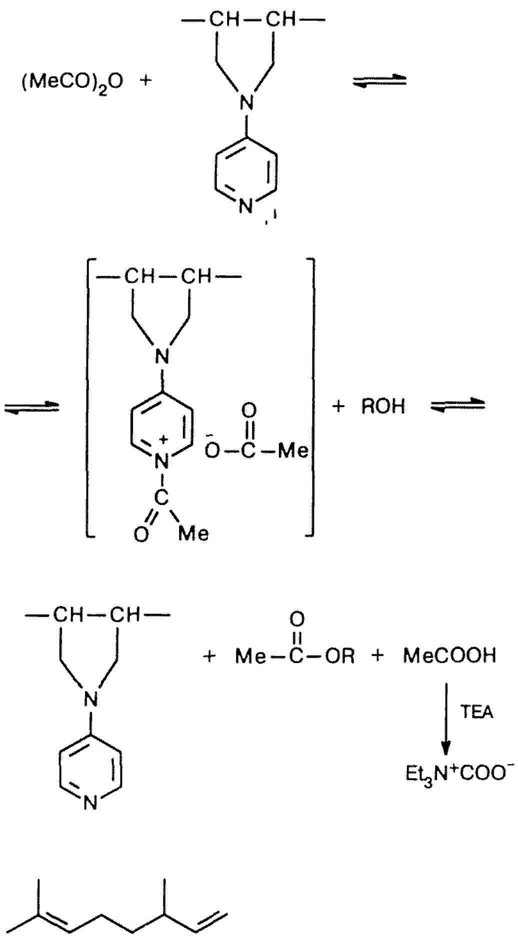
Results and Discussion

It has been shown previously[1,2] that the degree of conversion and the rate of the acylation of linalool with acetic anhydride increase both with an increase in the

---

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 1287—1290, May, 1996.

Scheme 1



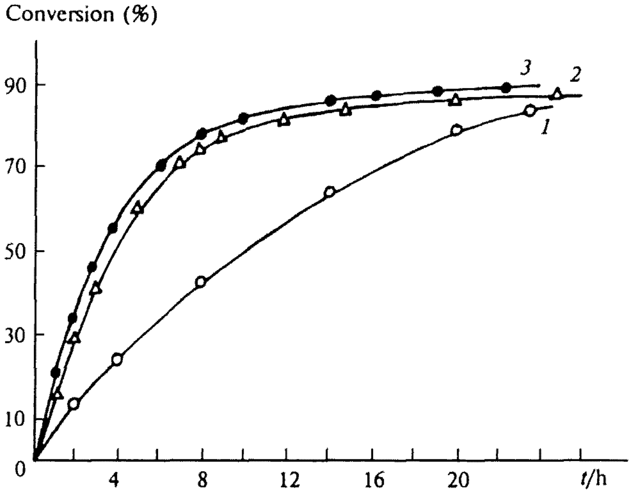


Fig. 1. Time dependence of the degree of conversion of linalool during its acylation with acetic anhydride at 60 °C in the presence of poly-S-PP in the medium of the reactants (*1*), in benzene (*2*), and in toluene (*3*).

temperature of the reaction and upon the addition of the sterically hindered TEA, which shifts the equilibrium toward the formation of the final product by binding the acetic acid liberated in the reaction (Scheme 1).

Further it has been shown that the increase in the reaction rate and in the degree of conversion of linalool in the presence of poly-S-PP is largely caused by the decrease in the polarity of the medium. Figure 1 presents the time dependence of the degree of conversion of linalool for the processes carried out in the medium of the reactants (curve *1*), in benzene (curve *2*), and in toluene (curve *3*).

We suggested that the increase in the degree of conversion of the alcohol into the corresponding ester will be also favored by "swelling" of the polymeric matrix in nonpolar media, because "swelling" should lead to an increase in the number of "activating sites" accessible to the reactants. It was shown that when the polymeric activating reagent is kept in benzene (Fig. 2, *a*) or in toluene (Fig. 2, *b*) for 3 h prior to the addition of acetic anhydride into the reactor, the yield of the final product is further increased, irrespective of the temperature at which the process is carried out.

We have also studied the dependence of the degree of conversion of the alcohol on the duration of the preliminary keeping of the polymeric activating reagent in benzene. The optimal time of the preliminary "swelling" of poly-S-PP was found to be 10 h. In this case, the degree of conversion of linalool (at 60 °C in C_6H_6) increased to 90—95 %.

Thus, the maximum possible "swelling" of poly-S-PP in a nonpolar medium, which makes the active sites of the polymer more accessible to the components of the reaction, is one of the important factors affecting the activity of the polymeric system under study.

Previously[3,4] acylation of linalool with acetic anhydride has been studied in the presence of another heterogeneous polymeric system, *viz.*, 4-*N*-benzyl(*N*-methylamino)pyridine immobilized on crosslinked polystyrene. This polymeric system is a macromolecular analog of dimethylaminopyridine (DMAP). The macromolecular activator of the reaction, poly-S-PP, synthesized by us is a polymeric analog of pyrrolidinopyridine, the activating capacity of which both in acylation and in other processes is much higher than that of DMAP.[2,5] Therefore, in the development of the optimal conditions for the interaction of the heterogeneous polymeric system with the components of the reaction, one should have expected that the catalytic activity of poly-S-PP may not only be higher in some cases than that of the polymeric analog of DMAP, which has been found by us previously,[1] but may also approach that of pyrrolidinopyridine,

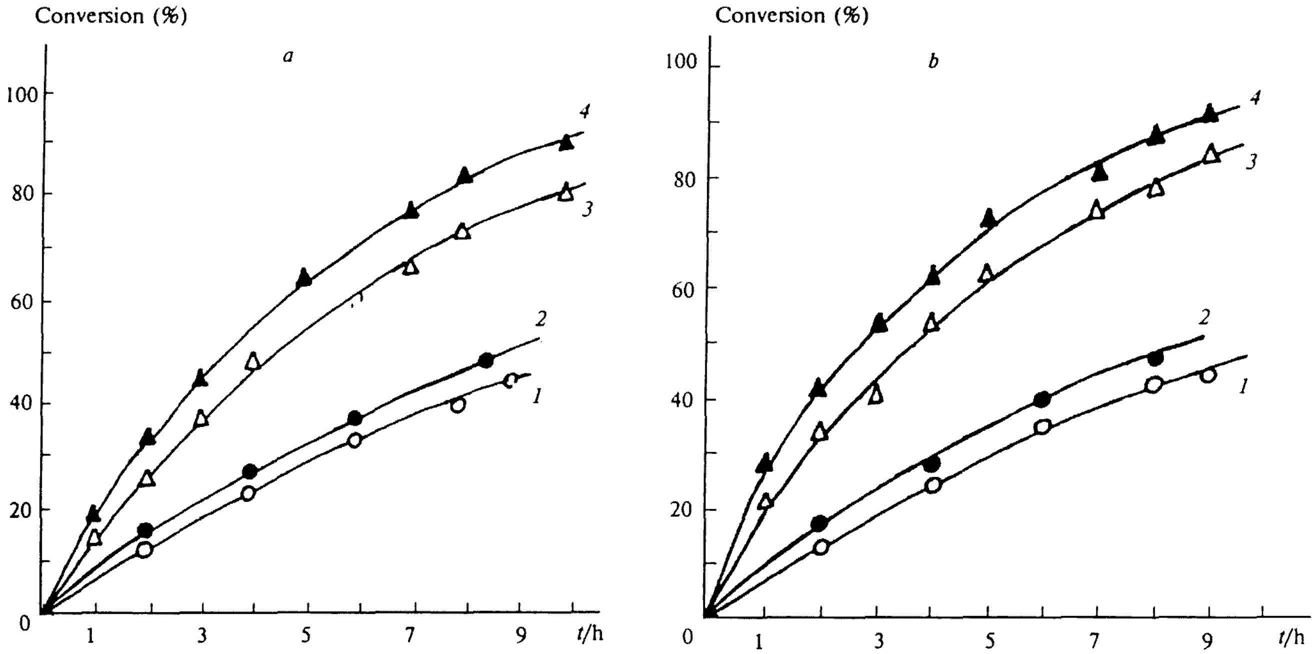


Fig. 2. Time dependence of the degree of conversion of linalool during its acylation with acetic anhydride in the presence of poly-S-PP in benzene (*a*) and in toluene (*b*) with preliminary "swelling" for 3 h (*2, 4*) and without "swelling" (*1, 3*); *T*/°C = 24 (*1, 2*) and 60 (*3, 4*).

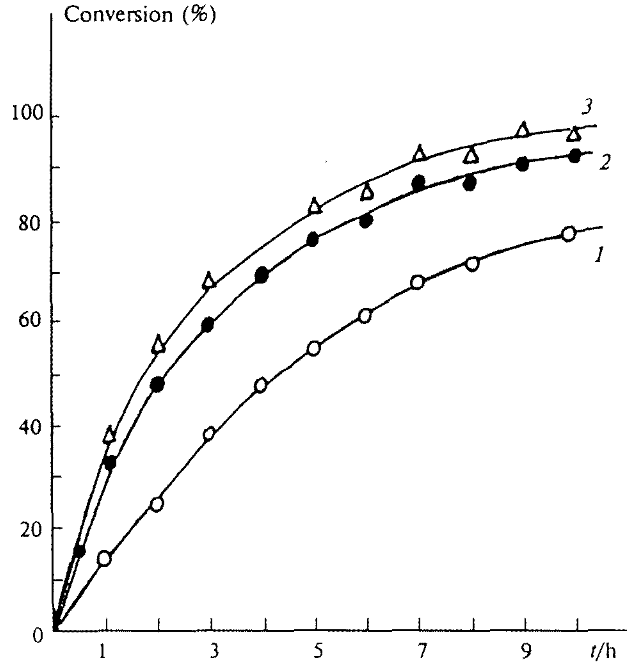


Fig. 3. Time dependence of the degree of conversion of linalool during its acylation with acetic anhydride at 60 °C in the presence of poly-S-PP (*1, 2*) in benzene without "swelling" (*1*), with preliminary "swelling" for 10 h (*2*), and in the presence of 0.2 equiv. (with respect to linalool) of pyrrolidinopyridine (*3*).

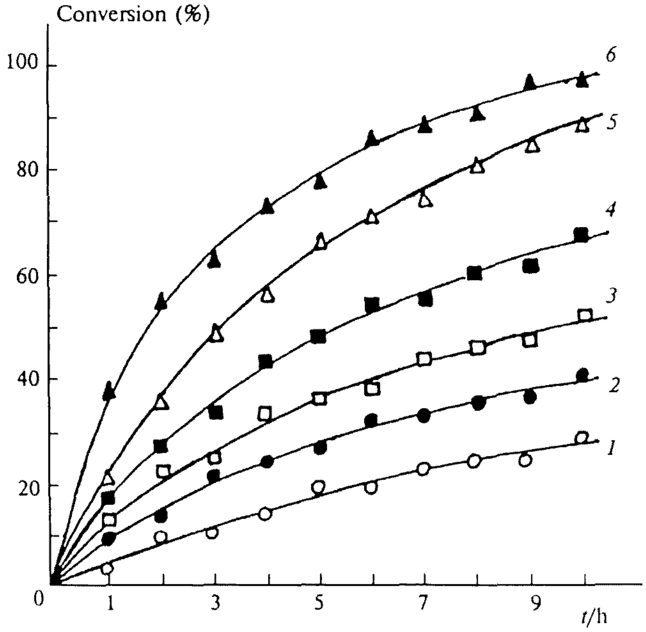


Fig. 4. Time dependence of the degree of conversion of linalool during its acylation with acetic anhydride at 60 °C in the presence of polymeric pyrrolidinopyridines with various contents of the PP-groups: 10 % (*1, 2*), 50 % (*3, 4*), and 100 % (*5, 6*); the reaction was carried out in benzene without "swelling" (*1, 3, 5*) and with preliminary "swelling" for 10 h (*2, 4, 6*).

the advantages provided by the heterogeneous character of the activating reagent under study in the acylation being retained in this case.

In the present paper we showed that, when the acylation of linalool is carried out under the optimal conditions combining all the factors listed above, the activity of poly-S-PP in this reaction is higher than that of the polymer used without the preliminary "swelling" (Fig. 3, curves *2* and *1*) and is close to that of its low-molecular-weight analog, pyrrolidinopyridine (see Fig. 3, curve *3*).

It has also been of interest to find out whether the degree of functionalization of the polymer has an effect on its activity in the acylation. For this purpose, we synthesized polymers with various proportions of pyrrolidinopyridine groups and studied the acylation of linalool with acetic anhydride in the presence of these polymers. It is seen from Fig. 4 that the most efficient polymeric samples are those with the maximum content of the PP-groups both when the reaction is carried out without the preliminary "swelling" of the heterogeneous polymeric activators (see Fig. 4, curves *1*, *3*, and *5*) and when it is carried out with polymers that were kept in benzene for 10 h before the interaction (see Fig. 4, curves *2*, *4*, and *6*).

Thus, we managed to optimize the conditions of the acylation of linalool with acetic anhydride in the presence of poly-S-PP and to bring the efficiency of the polymeric systems in this process close to the efficiency of their low-molecular-weight analog, pyrrolidinopyridine, in a homogeneous medium, all the advantages of the heterogeneous system being retained. The latter include the possibility of conducting these transformations in an automatic "column" mode and of using the polymeric reagent repeatedly.

References

1. E. D. Alieva, N. I. Trukhmanova, S. A. Shuvalova, and N. A. Platé, *Dokl. Akad. Nauk SSSR*, 1990, **314**, 1147 [*Dokl. Chem.*, 1990, **314** (Engl. Transl.)].
2. G. Höfle, W. Steglich, and H. Vorbrüggen, *Angew. Chem.*, 1978, **90**, 602.
3. M. Tomoi, Y. Akada, and H. Kakiuchi, *Makromol. Chem. Rapid Commun.*, 1982, **3**, 537.
4. M. Tomoi, M. Goto, and H. Kakiuchi, *J. Pol. Sci.*, *A*, 1987, **25**, 77.
5. E. F. V. Scriven, *Chem. Soc. Rev.*, 1983, **13**, 129.

Received September 14, 1995;
in revised form December 17, 1995