The Addition of Acetic Acid and Allylalcohol to Dicyclopentadiene

Chemistry and sensory evaluation

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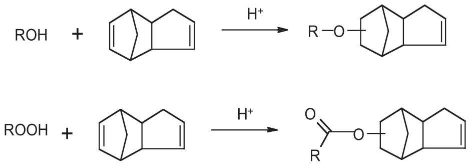
Leitmannová et al. investigated the effect of reaction conditions on addition of carboxylic acids (acetic and propionic) and alcohols (allylalcohol) to dicyclopentadiene. The effect of temperature, an excess of carboxylic acid or alcohol and the catalyst amount, as well as the effect of the presence of water in the case of the addition of carboxylic acids were monitored. The catalyst applied in the case of the addition of acids to dicyclopentadiene was sulfuric acid, and methanesulphonic acid in the case of the allylalcohol addition. Acquired optimal conditions were verified via preparative experiments with yields around 88 percent. The products of carboxylic acid additions to dicyclopentadiene were further hydrogenated. During hydrogenation, the effect of temperature and the catalyst amount (Ni/Al_2O_3) was monitored. All acquired products have use in the perfume industry.

Introduction

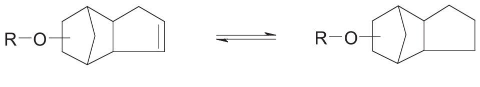
The addition of alcohols and carboxylic acids to dicyclopentadiene (DCPD) proceeds in the presence of acidic catalysts and produces relevant ethers and esters of dicyclopentadiene:



Two different ways of preparation of the given compounds are known.[1] During the first, carboxylic acid reacts with hydroxydihydrodicyclopentadiene or alcoholate of an alkali metal with dicyclopentadienyl halide. The second method consists in an electrophilic addition of an alcohol or acid to DCPD in the presence of an acid catalyst (a different reactivity of double bonds in DCPD is beneficially utilized).

The following acid catalysts may be used: mineral acids (H_2SO_4, $HClO_4$), BF_3 in a complex of an organic oxygen acid, organic acid containing sulfo-group and ion-exchanges containing $-SO_3$ group.[2-12] Some esters can be prepared even without the presence of any catalyst (under an increased temperature and pressure).[13,14]

In this work, sulfuric acid was selected as the catalyst for the addition of carboxylic acids to DCPD and methanesulfonic acid for the addition of allylalcohol. Produced ethers and esters could be further hydrogenated. This hydrogenation would likely lead to significant alterations in the fragrant properties of substances. It proceeds according to the following schema:



R = alkyl, acyl

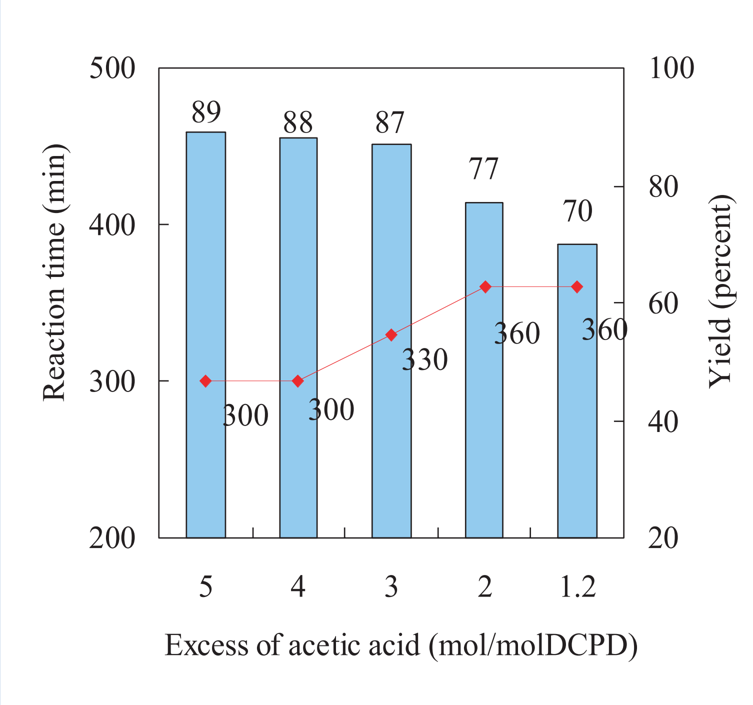
The chemical literature describes hydrogenation of these substances using various catalysts based on nickel, platinum and even palladium.[9,15-18] These hydrogenations reactions proceed with a high selectivity. In this work, Ni/Al_2O_3 was selected as the catalyst for hydrogenation of products of the addition of carboxylic acids to DCPD.

Experimental

The experiments were carried out in the range of temperature of 60°-120°C with a homogenous catalyst — in the case of addition acids, it was sulfuric acid; in case of allylalcohol, it was methanesulfonic acid. The experiments with organic acids were carried out in a batch; the experiments with allylalcohol were necessarily carried out in a semi-continuous process (gradual addition of the catalyst and DCPD by drops to the alcohol). Hydrogenations were carried out in a labora-

Excess of acetic acid effect on reaction time and yield during addition of acetic acid to DCPD (temperature 100°C, 3.25 percent wt of catalyst; water content 1.5 times higher than of the catalyst)

F-1



tory autoclave under a constant hydrogen pressure (7-7.5 MPa). The catalyst used (Ni/Al_2O_3, Leuna Werke contact no. 6524) contained 50 percent Ni. Experiments on a preparative scale were carried out in a three-necked flask placed in a heating mantle. After the reaction was terminated, Na_2CO_3 was introduced to the flask (during addition of acids); in other cases, CH_3ONa was introduced (during addition of allylalcohol) to carry out neutralization; later, the product was vacuum-distilled. Samples acquired from both of the synthetic steps were analyzed on a Varian 3800 gas chromatograph with a flame-ionization detection using a temperature program from 80°-220°C in a constant column flow 1 mL/min (N_2). Acquired chromatograms were assessed by use of the method of internal standard (dodecane). Chromatographic analyses revealed the presence of more isomers of the products. Molecular modeling was used for identification of these isomers. The molecular modeling of each individual isomer was based on PM3 parameterization, i.e. a semi-empiric SCF method. The parameterization of atoms was outsourced from the software HyperChem 6.0. Molecules were calculated as the molecules in their basic state. Systemic scanning of the conformational space by a unit step of 10° was used to find the global minimum.

Results and Discussion

Addition of carboxylic acids to DCPD: This part of the work involved a searching for suitable reaction conditions during addition of acetic acid to DCPD in the presence of sulfuric acid (used as the catalyst). The effect of temperature, composition of the reaction mixture, the catalyst amount and the presence of water on the reaction course was studied. During additions of organic acids to DCPD, the desired product started consecutive changes after reaching the maximal yield. These changes proceeded under all conditions. In the curve of concentration dependences on time, it was possible to determine the maximum, i.e. during addition of acetic acid to DCPD; the existence of an optimal reaction time was observed.

Experiments were carried out under the temperature range of 60°-118°C. During temperatures ranging between 60°C and 100°C, the yields differed only within the extent of the determination error. Having increased the temperature to the reflux temperature of acetic acid, the yield decreased, probably as a result of decomposition of initial substance DCPD and undesirable polymerization reactions. From the practical point of view, the temperature of 100°C appeared to be the most appropriate.

The starting reaction rate (mol/l*min) of the individual changes was calculated from the dependence of the product concentration on time and the reaction activation energy, which equaled to 21.8 kJ/mol, from the reaction rate dependence on temperature using the Arrhenius Equation.

Optimal molar excess of acetic acid was searched in the range of 1.2 mol/mol$_{DCPD}$ to 5 mol/mol$_{DCPD}$. It appears that the most beneficial is to work with the molar ratio of 1 mol of DCPD:4 mol of acetic acid (F-1). With a decrease of the excess, a yield decrease occurred, probably owing to the proceeding polymerization reactions. The excess of 3 mol/mol$_{DCPD}$ did not demonstrate a difference in the yield, but in a lower reaction rate.

The effect of the presence of water was monitored in the range of weight ratios of water and sulfuric acid of 0.5-2.5:1 (i.e. the weight concentration of sulfuric acid was 64 percent to 27 percent). The reaction yield ranged within the extent of the measurement error, i.e. around 87 percent (F-2). The optimal weight ratio of sulfuric acid:water appeared to be 1:1.5 (concentration: 39 percent). When the ratio decreased, the reaction period increased. The same effect had an increasing ratio (F-2). Having used a concentrated acid, the reaction period became double.

The amount of sulfuric acid was monitored in the range of 0.6-12.5 percent wt per the weight of DCPD to determine the effect of the catalyst amount. An increase of the catalyst amount caused an increase in the reaction rate, but also a yield decrease (F-3). Having decreased the amount of sulfuric acid, the reaction rate was significantly decreased. The optimal catalyst amount was determined as 3 percent wt of sulfuric acid (F-3) per the weight of DCPD.

The following conditions were selected from the above-mentioned experiments as optimal for the addition reaction of acetic acid to DCPD:

Molar ratio of DCPD:acetic acid	1:4
Catalyst amount (sulfuric acid) per weight of DCPD	3 percent wt
Weight ratio of sulfuric acid:water	1:1.5
Temperature	100°C

The addition of acetic acid to DCPD was performed in a preparation scale under optimal conditions described in the above-mentioned sections with a resultant yield of 86 percent of acetoxydihydrodicyclopentadiene with a purity of 96 percent (the boiling point 118°C at 1.33 kPa).

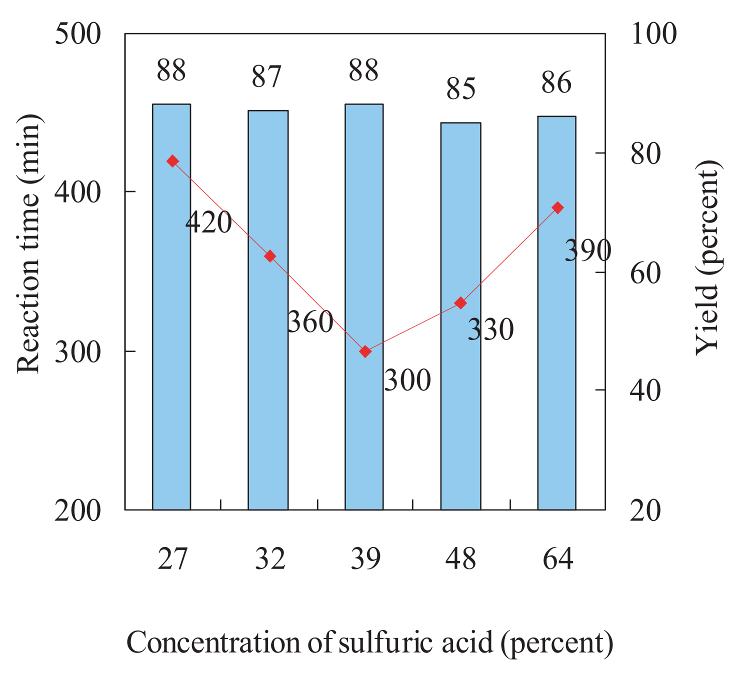
To verify the applicability of the presented optimal conditions with another from the series of organic acids, addition of propionic acid to DCPD was carried out. The reaction yield was 84 percent of propionyloxydihydrodicyclopentadiene with its purity of 97 percent (the boiling point 110°C at 0.66 kPa).

Molecular modeling: The presence of four isomers of the desired product was found in the individual chromatographic analyses. It is probable that a chromatographic column is not capable of separating all the theoretically possible isomers, and displays each with its own retention time. Furthermore, it is possible that some isomers are significantly unstable and are not at all present in the product. The literature provides that from the sensory point of view, the isomers do not necessarily need to be separated.[19]

An experiment was performed to distinguish all isomers by use of molecular modeling, during which energetic content of individual molecules, i.e. the extent of their stability, was calculated. In general, it can be stated that *exo*-isomers with the

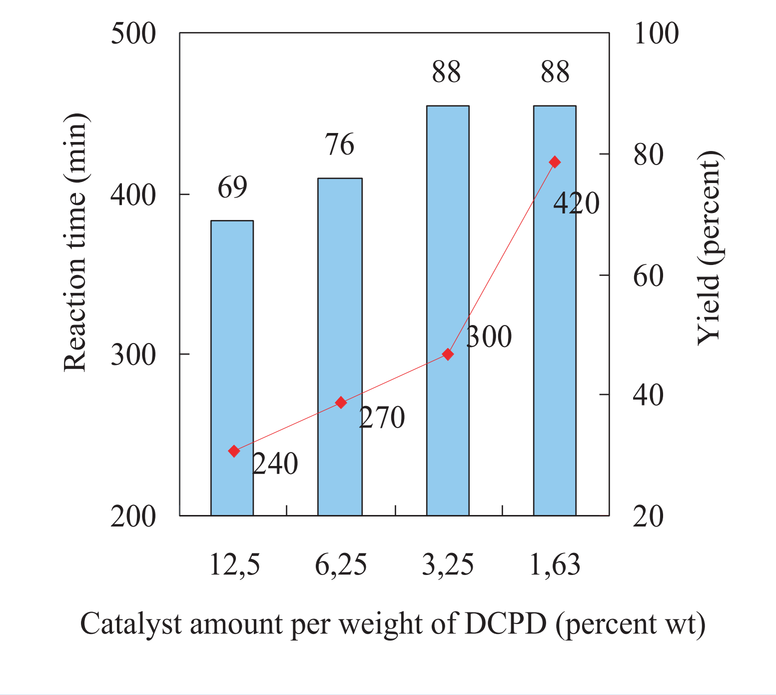
Concentration effect of sulfuric acid on reaction time and yield during addition of acetic acid to DCPD (temperature 100°C, excess of acetic acid 4mol/mol$_{DCPD}$, 3.25 percent wt of H_2SO_4 to DCPD)

F-2



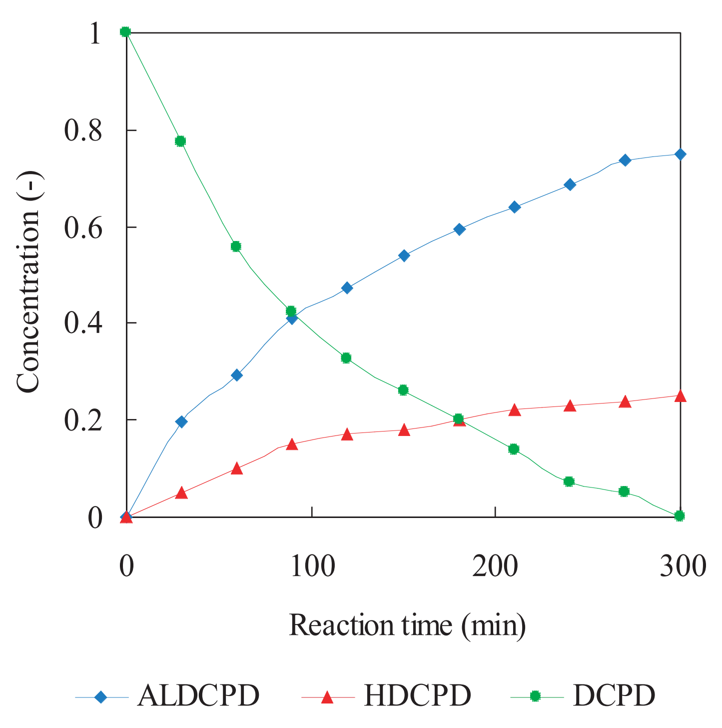
Effect of catalyst amount (sulfuric acid) on reaction time and yield during addition of acetic acid to DCPD (temperature 100°C, excess of acetic acid 4mol/mol$_{DCPD}$, water content 1.5 times higher than of the catalyst)

F-3



Reaction course during addition of allylalcohol to DCPD (catalyst sulfuric acid, temperature 97°C) (DCPD: dicyclopentadiene; ALDCPD: allyloxydihydrodicyclopentadiene; HDCPD: hydroxydihydrodicyclopentadiene; concentration (-): dimensionless concentration related to theoretical concentration)

F-4



acylic group placed in position 9-, in axial position in a hexagonal (norbornenic) ring, are more stable. The energy of individual isomers did not significantly differ and thus the product mixture probably contained all of them.

Hydrogenation of addition products of DCPD and carboxylic acids: Products prepared on a laboratory scale were hydrogenated. Optimal conditions for hydrogenation of the addition products were determined:

Catalyst	Ni/Al_2O_3(1 percent wt)
Temperature	140°C
Pressure	7.5 MPa

Hydrogenation proceeded with 100 percent selectivity; the total conversion was achieved in 60 min. Hydrogenations of acetoxydihydrodicyclopentadiene were carried out with temperatures 130°C, 140°C and 155°C. The reaction rate in its equilibrium state (mol/min*g_{kat}) was calculated from the dependence of the concentration course on time, and the apparent activation energy of this hydrogenation, which equaled to 85.1 kJ/mol, from the reaction rate dependence on temperature using the Arrhenius Equation. Acetoxytetrahydrodicyclopentadiene was purified by rectification (the boiling point 109°C/0.66 kPa, the purity 99 percent). Hydrogenation of propionyloxydihydro-dicyclopentadiene was carried out in a solvent (n-heptane). The acquired propionyloxytetrahydrodicyclopentadiene was purified by rectification (the boiling point 105°C at 0.66 kPa, the purity 98.9 percent).

Addition of allylalcohol to DCPD: In this part, an apposite catalyst was sought; the effect of temperature, the composition of the starting reaction mixture and the catalyst amount were monitored. During the addition of allylalcohol to DCPD, the desired product started consecutive changes after reaching the maximal yield. These changes proceeded under all conditions. In the curve of concentration dependences on time, it was possible to determine the maximum, i.e. during addition of acetic acid to DCPD; the existence of an optimal reaction time was observed. A catalyst suitable for the addition of allylalcohol to dicyclopentadiene was sought. Suitable catalysts were methanesulfonic acid and p-toluenesulfonic acid. Other catalysts, such as sulfuric acid, metaphosphoric acid, hydrochloric acid, and zeolite β**,** were not suitable owing to their low activity or undesired reactions; see F-4 (addition of water, released from the reaction of two molecules of allylalcohol to DCPD).

It was found that from the point of view of polymer production, it is necessary in the case of allylalcohol addition, to first slowly add the catalyst to a stirred alcohol and than introduce DCPD by drops to the alcoholic reaction mixture with the catalyst. Next, methanesulfonic acid was selected as the catalyst for the addition of allylalcohol.

Experiments were carried out under the temperature range of 60°-97°C. In this temperature range, the yields differed only within the extent of the determination error and were around 86 percent. The shortest reaction period was observed under the temperature 97°C (the reflux of allylalcohol). Simultaneously, under this temperature, no significant decrease of the yield occurred.

The starting reaction rate (mol/l*min) was calculated from the dependence course of the product concentration on time and the total reaction activation energy, which equaled 21.8 kJ/mol, from the reaction rate dependence on temperature using the Arrhenius Equation.

Optimal molar excess of allylalcohol was sought in the range of 1.2 mol/mol_{DCPD} to 5 mol/mol_{DCPD}. It seems that the most beneficial is to work with the molar ratio of 3 mol/mol_{DCPD}. With decreasing of the molar excess (F-5), an increase in the reaction rate occurred, but the yield significantly decreased, probably owing to the undesired polymerization reactions. An increase of the excess did not demonstrate any significant difference in the yield (F-5).

The optimal catalyst amount (methanesulfonic acid) was sought in the range of 3-50 mol percent per weight of DCPD. The reaction period and the yield significantly depended on the catalyst amount used. With an increased catalyst amount, an increase of the reaction rate occurred, but also a significant decrease of the yield (F-6), probably owing to the undesired polymerization reactions. A decrease of methanesulfonic acid amount showed little effect on the yield, but the reaction period was markedly extended. Apparently, the optimal is to work with 10 percent wt of methanesulfonic acid per the weight of DCPD.

The following conditions were selected as optimal for the addition of allylalcohol to DCPD:

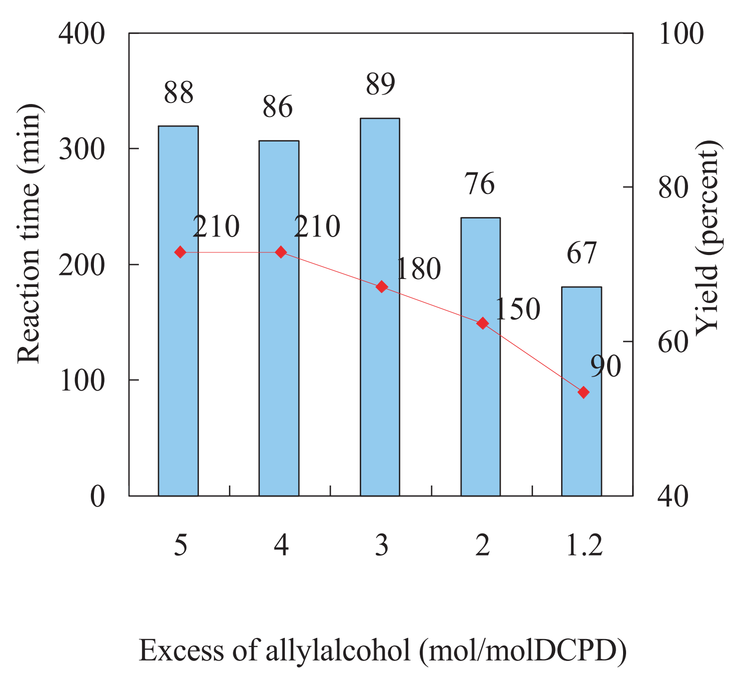
Molar ratio DCPD: allylalcohol	1:3
Catalyst amount (methanesulfonic acid) to the weight of DCPD	10 percent
Temperature	97°C

These conditions were utilized in a preparative experiment yielding 84 percent of allyloxydihydrodicyclopentadiene (the boiling point 95°C at 0.5 kPa) with the purity at 96 percent.

Sensory evaluation: Aroma Co. performed sensory evaluation of the products acquired from the preparative experiments (which were purified by rectification). According to the reviewers, acetoxydihydrodicyclopentadiene (jasmacyclene) and propionyloxydihydrodicyclopentadiene (florocyclene) have similar fragrant characteristics compared to those described in the chemical literature.[9,13] Acetoxytetrahydrodicyclopentadiene possesses a flowery to fruity undertone and a gently flowery to fruity upper tone; the material resembles florocyclene. Propionyloxytetrahydrodicyclopentadiene possesses a flowery to fruity, chocolate undertone, and a flowery to fruity upper tone. Allyloxydihydrodicyclopentadiene imparts a fatty undertone, and fruity to flowery,

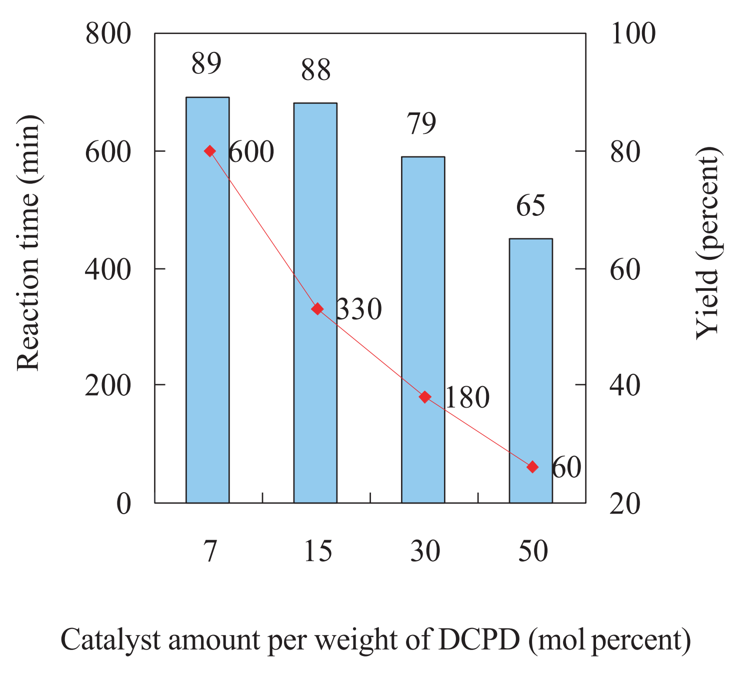
F-5

Excces of allylalcohol effect on reaction time and yield during addition of allylalcohol to DCPD (temperature 97°C, mol 10 percent of catalyst)



F-6

Effect of catalyst amount (methanesulfonic acid) on reaction time and yield during addition of allylalcohol to DCPD (temperature 97°C, excess of allylalcohol 3 mol/mol_{DCDPD})



mushroomy upper tone; it resembles jasmacyclene.

Conclusion

Optimal conditions were found for the addition of carboxylic acids and allylalcohol to DCPD. The addition of carboxylic acids (acetic acid) was carried out with sulfuric acid used as the catalyst. Optimal temperature was found (100°C — above this temperature, DCPD most probably undergoes a decomposition), as well as optimal excess of carboxylic acids (4 mol/mol_{DCPD}), concentration of sulfuric acid (39 percent) and the catalyst amount (3 percent wt per weight of the DCPD substrate). Under these conditions, the yields of the preparative experiments were 88 percent (adduct with acetic acid) and 86 percent (adduct with propionic acid). Hydrogenation of addition products was carried out at the temperature of 140°C; pressure: 7.5 MPa. The addition of allylalcohol was carried out with methanesulfonic acid as the catalyst. Optimal temperature (97°C — reflux of allylalcohol), optimal excess of allylalcohol (3 mol/mol_{DCPD}) and the optimal catalyst amount (10 percent wt per the weight of DCPD) were found. The optimal conditions were verified by a preparative experiment resulting in the yield of 86 percent. The fragrant characteristics of all the prepared substances are promising in the sense of their industrial utilization.

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