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Palladium Catalyzed Telomerization of Butadiene with Sucrose: A Highly Efficient Approach to Novel Sucrose Ethers

Karlheinz Hill,* Bert Gruber, and Kenneth J. Weese

Henkel KGaA, D-40191 Düsseldorf, F.R.G.

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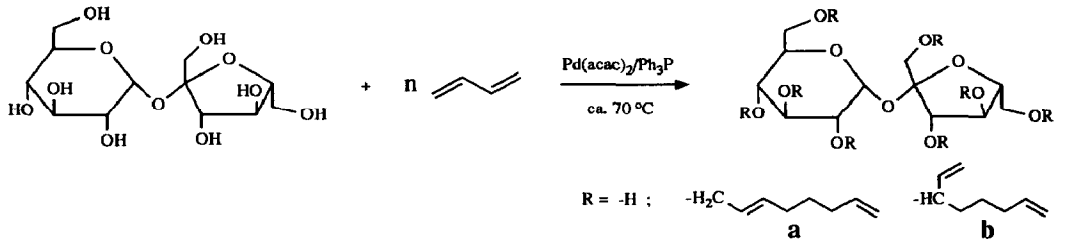
Abstract: *The novel telomerization of butadiene with sucrose, catalyzed by $Pd(acac)_2$ and phosphine ligand, yielding the corresponding sucrose octadienyl ethers at high turn over numbers of 40000 is described.*

The telomerization reaction of dienes with nucleophiles provides an elegant method for the synthesis of various useful compounds.[1] For example, octadienyl ethers can be obtained by the telomerization of butadiene with the respective alcohols, diols, and polyols without producing a byproduct during the formation of the ether linkage.[1] In spite of the increasing importance of carbohydrates as cheap and renewable polyfunctional starting materials for industrial use,[2] there is only one example describing the use of a carbohydrate derivative, namely 1,2,3,4-diisopropylidene-α-D-galactopyranose, as the nucleophile in the telomerization reaction.[3]

In this paper we report a direct route for the telomerization of butadiene with sucrose as outlined in Scheme 1. Sucrose was reacted with butadiene in 2-propanol / water in the presence of palladium(II)-2,4-pentanedionate and triphenylphosphine as the catalyst system. In view of a potential technical process no protective groups and only selected solvents were used. High catalyst turn over numbers (conversion of mol butadiene / mol $Pd(acac)_2$) and high yields of sucrose octadienyl ethers were achieved by using an appropriate



Scheme 1.

solvent system. It was found that a mixture of 2-propanol and water (80:20 by weight) at an amount of ca. 30 weight % relative to the total reaction mixture gave the highest conversions of butadiene and sucrose (Table 1, entries 1 and 5). Very low conversions of sucrose (< 10 %) were obtained in acetone, acetonitrile, and 2-propanol. Furthermore, a significant increase of catalyst activity and product yield with catalyst turn over numbers up to 40000 was observed when the butadiene was added continuously to the reaction mixture at

constant pressure. Varying the amount of triphenylphosphine had a minor effect (Table 1, entries 2-4). Depending on the ratio of sucrose and butadiene, an average number of hydroxyl groups was derivatized to give a mixture of mono-, di-, tri-, etc., octadienyl ethers **a** and **b**, where the 2,7-octadienyl ether derivatives **a** being formed predominantly (>90% according to ^{1}H-NMR). The average degree of substitution was determined by ^{1}H-NMR. Groups of isomers with a distinct degree of substitution were characterized by HPLC/MS or isolated by preparative HPLC and characterized by MS.[4] Applying the conditions given in Table 1, entries 2 and 4, sucrose octadienyl ethers were obtained with an average degree of substitution of 4.7 - 5.3. The products were clear, almost colorless liquids with a viscosity of 1500 - 2000 mPas at 25 °C and practically insoluble in water. With regard to their properties, the products are potential emulsifiers and defoaming agents. Further optimization of the process and the use of other carbohydrates is in progress.

Table 1. Reaction Conditions and Yield for the Synthesis of Sucrose Octadienyl Ethers[a]

Entry	SUC[b]	BUT[b]	PPh_3[b]	Method[c]	SUC-Cv.[d]	Yield[e]	POE[f]	Pressure[g]
(1)	1460	19900	2	B	60-70	42	11	7.5
(2)	1460	19900	2	C	>98	57	5	2.5-3.5
(3)	2935	40000	2	C	88	53	4	2.5-3.5
(4)	2935	40000	10	C	97	63	4	2.5-3.5
(5)	2935	40000	10	B	28	33	9	7.5

[a]Reaction conditions: 68°C, 12 hours, 30 weight % solvent (2-propanol/H_2O) rel. to total reaction mixture.
[b]Molar ratio relative to $Pd(acac)_2$ = 1, SUC = sucrose, BUT = butadiene.
[c]Method "B" is batch (entire charge at once) addition, method "C" is continuous addition of butadiene at a constant pressure.
[d]Conversion of sucrose (SUC-Cv.) in weight %, unreacted sucrose is recovered by filtration.
[e]Weight % of product in the final reaction mixture.
[f]Weight % of 2-propyl octadienyl ether (POE) in crude product.
[g]Maximum pressure during the reaction in atm.

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