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TELOMERIZATION OF ALLENE WITH WATER CATALYZED BY PALLADIUM COMPLEXES

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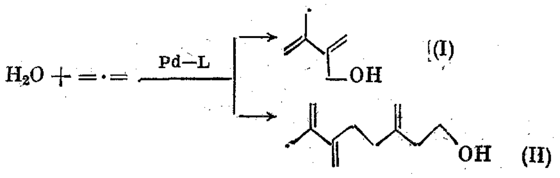
The homo- and cotelomerization of 1,3-dienes with water by the action of palladium complex catalysts leads to mixtures of unsaturated C_8–C_{10} alcohols which arise, as a rule, from two diene molecules and one water molecule [1-3]. There have been no reports of the telomerization of H_2O with 1,2-dienes. We studied the reaction of water with allene catalyzed by palladium complexes in order to obtain C_6–C_{12} alcohols containing methylenic double bonds in the hydrocarbon chain.

Upon the action of the complex obtained by mixing $Pd(acac)_2$ with PPh_3 [$Pd(acac)_2:PPh_3$ = 1:1] in DMF solution in the presence of excess CO_2 [3, 4], the reaction of H_2O with allene in 2:1 ratio in this medium (P_{CO_2} = 50 atm) at 70°C for 6 h leads to a mixture of unsaturated alcohols (I) and (II) in 10% yield relative to the allene taken. Alcohols (I) and (II) were isolated as pure compounds by vacuum distillation and identified by IR, UV, ^1H NMR, ^{13}C NMR, and mass spectroscopy.

These results indicate that (I) is 3-methyl-2-methylene-3-buten-1-ol, while (II) was identified as 2,3,6,7-tetramethylene-1-octanol.



In order to increase the yield of the mixture of alcohols (I) and (II), we studied the effect of the reaction conditions and ratio of the catalyst components on the direction and yield of the products of the telomerization of allene with water. Table 1 shows that an increase in the reaction temperature to 90°C and in the reaction time to 20 h leads to an increase in the overall yield of alcohols (I) and (II) to 73%. The content of (I) in the reac-

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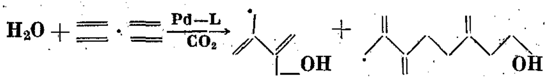
TABLE 1. Effect of the Reaction Conditions on the Yield and Composition of the Products of the Telomerization of Allene with Water



$[Pd(acac)_2]$:$[H_2O]$ mole ratio	Reaction time τ, h	Alcohol yield relative to allene, %	Composition of the reaction products, %	
			(I)	(II)
1 : 1000	6	10	61	39
1 : 1000	10	24,3	71,2	28,8
1 : 1000	20	43,3	89,5	10,5
1 : 500	20	73	65,2	34,8
1 : 250	20	84,5	77,1	22,9

Reaction conditions: 0.001 mole $Pd(acac)_2$:PPh_3, 0.3 mole allene, 0.5 mole H_2O in 25 ml DMF, $P_{CO_2} = 50$ atm at 90°C.

tion mass is 65.2%. An increase in the catalyst concentration from 1:1000 to 1:250 leads to an increase in the yield of (I) and (II) to 84.5%. C_6 alcohols are mainly formed under these conditions. The high yields of (I) and (II) were obtained on a catalyst consisting of 1:1 $Pd(acac)_2$:PPh_3. An increase in the PPh_3 fraction has virtually no effect on the catalyst activity and direction of the reaction of allene with water.

EXPERIMENTAL

The study was carried out with 60% allene flegmatized with propane. The products were analyzed on a Chrom-47 chromatograph on a 1.2-m column packed with SE-30, using helium as the carrier gas. The ^1H NMR spectra were carried out on Tesla BS-487B and Tesla BS-467B spectrometers in $CDCl_3$ relative to TMS. The ^{13}C NMR spectra were taken on a Jeol FX-90Q spectrometer with broad band proton suppression in the homoresonance mode relative to TMS. The IR spectra were taken neat on a UR-20 spectrophotometer. The UV spectra were taken on a Specord UV-VIS spectrometer. The mass spectra were taken on an MKh-1306 mass spectrometer at 70 eV and 200°C ionization chamber temperature.

Telomerization of Allene with Water. A sample of 0.26 PPh_3 was added to a solution of 0.31 g $Pd(acac)_2$ in 25 ml abs. DMF and stirred for 10-15 min in an argon atmosphere at 20°C. Then, the catalyst was transferred to a 100-ml steel autoclave cooled to −20°C and then 20 g (0.5 mole) allene and 9 ml (0.5 mole) H_2O were added. Carbon dioxide was introduced to a pressure of 50 atm. The autoclave contents were heated for 20 h at 90°C. After cooling, the reaction mass was diluted with 50 ml benzene, washed two or three times with water to remove DMF, and the benzene solution was dried over Na_2SO_4. The solvent was distilled off at a water pump to yield 25.7 g (73% relative to allene taken) of a 65:35 mixture of alcohols (I) and (II). This mixture was distilled in vacuum.

3-Methyl-2-methylene-3-buten-1-ol (I), bp 30°C (1 mm), n_D^{20} 1.461. IR spectrum (ν, cm^{-1}) 900, 1600, 1670, 3095 ($>C{=}CH_2$), 3200-3600 (OH). ^1H NMR spectrum (δ, ppm): 2.08 s (3H, $CH_3{-}C{=}$), 4.8 s (2H, $CH_2{-}O$), 5.6-6.0 ($={CH_2}$). ^{13}C NMR spectrum (δ, ppm): 63.15 t (C^1), 140.87 s (C^2), 146.87 s (C^3), 111.98 t (C^4), 21.12 q (C^5), 112.37 t (C^6). UV spectrum (λ, nm): 225 (ε 17,000) in EtOH. m/z 98.

2,3,6,7-Tetramethylene-1-octanol (II), bp 80°C (1 mm), n_D^{20} 1.512. IR spectrum (ν, cm^{-1}): 900, 1600, 1640, 3095 ($>C{=}CH_2$), 3200-3600 (OH). ^1H NMR spectrum (δ, ppm): 2.0 s (3H, $CH_3{-}C{=}$), 4.7 s (2H^1, CH_2O), 4.0 m (1H, OH), 4.8 and 5.7 m (8H, $={CH_2}$). ^{13}C NMR spectrum (δ, ppm): 64.2 t (C^1), 142.53 s (C^2), 145.31 s (C^3), 32.90 t (C^4), 33.72 t (C^5), 146.22 s (C^6), 147.59 s (C^7), 110.45 t (C^8), 21.18 q, (C^9), 112.11 t (C^{10}, C^{11}, C^{12}). UV spectrum (λ, nm): 226 (ε 58,344); m/z 178.

CONCLUSIONS

The telomerization of allene with water catalyzed by palladium complexes leads to the preparation of 3-methyl-2-methylene-3-buten-1-ol and 2,3,6,7-tetramethylene-1-octanol in high yields.

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REACTION OF THE TETRAETHYLAMMONIUM SALT OF N-METHYL-N-NITROSOHYDROXYLAMINE WITH ALLYL BROMIDE

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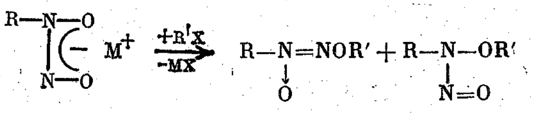
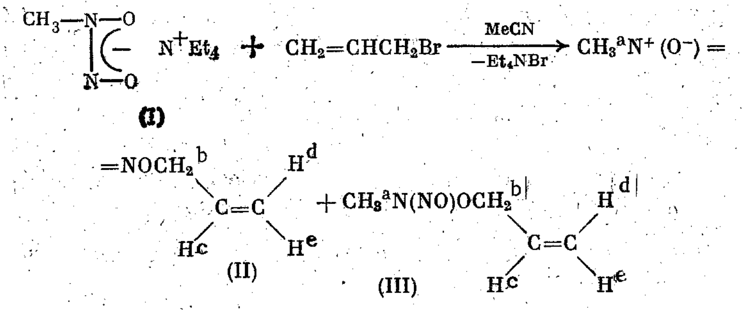
N-Alkyl-N-nitrosohydroxylamines (NHA) and their salts are alkylated at both oxygen atoms, although there is no information available on the ratio of the alkylation products since the desired product of this reaction is, as a rule, an N-alkyl-N'-alkoxydiazene N-oxide, while alkylalkoxynitrosoamines decompose under the synthesis and separation conditions [1]:



In this work, we have shown that the reaction of the tetraethylammonium salt of N-methyl-N-nitrosohydroxylamine (I) with allyl bromide proceeds exothermally at 20°C to form N-methyl-N'-allyloxydiazene N-oxide (II) and methylallyloxynitrosamine (III) in 1:1.6 ratio with a total yield of 89%:



The structures of (II) and (III) were supported by their elemental analysis, molecular refraction indices, and IR, UV, and PMR spectra. The purity of (II) and (III) were checked by gas–liquid chromatography. The amount of the impurity of (III) in (II) was monitored by UV spectroscopy relative to the $n-\pi^*$ transition (λ_{max} 373 nm in heptane). A shift in the $n-\pi^*$ transition toward longer wavelengths and the appearance of fine structure are noted in the UV spectrum of (II), as in the case of dialkylnitrosamines [2], in going from water to hydrocarbon solution. As a result, this band is better resolved from the strong $\pi-\pi^*$ transition band in (II), which reduces the limit for the observation of an impurity of (III) in (II) by almost an order of magnitude. Oxide (II) is a colorless liquid, while (III) is a yellow liquid which de-

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