CONDENSATION OF DIMETHYLVINYLETHYNYLCARBINOL WITH FORMALDEHYDE IN THE PRESENCE OF KU-2 CATALYST

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A study is made of the optimum conditions for condensing dimethylvinylethynylcarbinol with formaldehyde in the presence of KU-2 cation-exchange resin as catalyst, with a view to preparing enyne and dienyne substitution products of 1,3-dioxane.

It was of interest to investigate the optimum conditions for synthesizing 4-methyl-4-vinylethynyl-1, 3-dioxane by condensing dimethylvinylethynylcarbinol with formaldehyde in the presence of KU-2 (the Prins reaction). Such dioxanes were first prepared [1] from divinylacetylene derivatives.

In the present paper a study has been made of the relationship between yield of 4-methyl-4-vinylethynyl-1, 3-dioxane and reaction time, quantity of KU-2 catalyst, and the number of times that it is used. A mixture of 0.3 mole dimethylvinylethynylcarbinol, 0.69 g formaldehyde, (in the form of a 35% formalin solution, or as paraformaldehyde), and the KU-2 catalyst were stirred and refluxed together for 2–7 hours. At the end of reaction the products were extracted with ether, the cationite filtered off, the ether solutions dried over magnesium sulfate, and then vacuum-distilled. Reaction of formaldehyde with tertiary vinylacetylenic alcohols using the H^+ form of KU-2 cationite as catalyst, gives mainly 1, 3-dioxanes, along with a small amount of 1, 3-glycols of the vinylacetylene series [2]. With increase in reaction time (Table 1), the percentage of unreacted dimethylvinylethynylcarbinol falls from 25.5 to 14.6%, and the yield of 4-methyl-4-vinylethynyl-1, 3-dioxane increases, and attains a maximum (50%) with a reaction time of 6 hours. When the reaction time is increased further, the yield of main produce drops, due to formation of 1, 3-glycol, and polymerizing residue.

Using a general reaction time of 6 hours, increase in amount of cationite taken results in decrease in the amount of unreacted dimethylvinylethynylcarbinol from 28.6 to 12.3%, and the yield of 1, 3-dioxane itself reaches a maximum when the cationite amounts to 20% on the mixture of starting materials taken (Tables 2, 3). Further increase in the amount of catalyst leads to increased yield of polymerizing residue.

In some experiments the cationite was used for 42 hours without being regenerated, and the yield of the main product remained unaffected. This is a great advantage of using this catalyst.

The reaction of dimethylvinylethynylcarbinol with formaldehyde gave: 4-methyl-4-vinylethynyl-1, 3-dioxane [bp 59°–61° C (5 mm), d_4^{20} 0.9972, n_D^{20} 1.4830, RM 44.0]. Found: C 71.13, H 8.09%. Calculated for $C_9H_{12}O_2$: C 71.0; H 7.9%. Methylvinylethynyl-1, 3-glycol [bp 80°C (5 mm), d_4^{20} 1.3030, n_D^{20} 1.5010, RM 40.367]. Found C 68.9; H 8.9%. Calculated for $C_8H_{12}O_2$: C 68.5; H 8.58%.

REFERENCES

1. S. G. Matsoyan and A. A. Saakyan, ZhOKh, 33, 3797, 1963.

2. S. A. Vartanyan, Izv. AN Arm. SSR, KhN, 17, 672, 1964.

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Table 1

Relationship between Yields of Products and Reaction Time

Reaction time, hr	Unreacted dimethylvinylethynylcarbinol, %	Yield of 4-methyl-4-vinylethynyl-1, 3-dioxane, %	Yield of methylvinylethynyl-1, 3-glycol, %	Yield of polymer, %
2	25.5	44	7.1	23.4
3	20.6	46.8	7.3	25.3
4	19.0	48.5	7.5	25.0
5	17.0	49.3	7.9	25.8
6	16.2	50.0	8.2	25.6
7	14.6	45.2	8.7	31.5

Table 2

Relationship between Yields of Reaction Products and Amount of Catalyst Used

Amount of catalyst		Dimethylvinyl-ethynylcarbinol recovered, %	Yield of 1, 3-dioxane, %	Yield of 1, 3-glycol, %	Yield of polymer, %
Weight of reactants, %	g, dry				
2	1.02				
10	5	28.6	42.9	4.0	24.5
20	10	16.2	50.0	8.2	25.6
30	15	18.0	47.0	5.4	29.6
40	20	12.3	42.8	4.5	40.4

Table 3

Relationship between Yields of Products and Number of Times Catalyst Used

Hours for which catalyst used	Dimethyl-vinylethynyl-carbinol, %	Yield of dioxane, %	Yield of 1, 3-gylcol, %	Yield of polymer, %
6	16.2	50.0	8.2	25.6
12	18.8	49.5	4.7	27.0
18	18.6	49.6	4.7	27.1
30	19.0	49.2	4.9	26.9
36	25.7	48.5	4.45	21.4
42	15.7	50.6	6.7	27.0