ARYLOLEFINS IN MODIFIED PRINS REACTION

M. G. Safarov, N. G. Nigmatullin,
U. G. Ibatullin, and S. R. Rafikov

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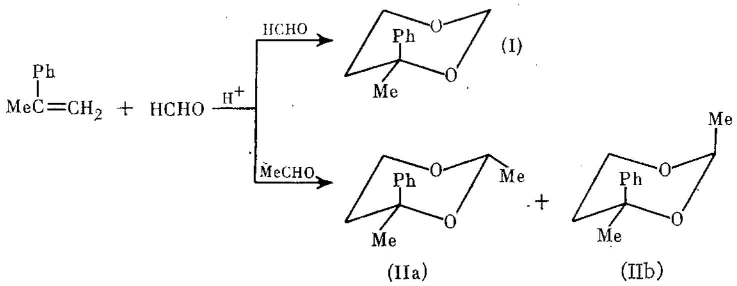
It is known [1] that in acid-catalyzed reactions 2-R-1,3-dioxanes (acetals) exhibit a higher reactivity than 2-H-1,3-dioxanes (formals), and therefore are more promising starting materials in the synthesis of various 1,3-bifunctional compounds. Acetals can be obtained by the modified Prins reaction, a simultaneous reaction of an unsaturated compound with formaldehyde and alkanal [2]. In this reaction, the acetals are usually accompanied by the corresponding cyclic formals.

In the present work, to study the influence of various conditions on the yield of the acetal and formal, we investigated cocondensation of formaldehyde and acetaldehyde with α-methylstyrene.



By using GLC, we found that 2,4-dimethyl-4-phenyl-1,3-dioxane forms as difficulty soluble isomers (IIa) and (IIb) in a ratio of 3:1. To confirm the structure of these isomers, we prepared (IIa) by alternative synthesis from acetaldehyde and 3-phenyl-1,3-butanediol by the method of [3]. The PMR spectrum of the mixture of (IIa) and (IIb) shows two quartets in the 4.5 ($2H_a$) and 5.0 ppm ($2H_e$) regions, while for pure (IIa), the signal in the 5.0 ppm region is absent. Hence, in (IIa), the CH_3 group is situated equatorially (the lower-boiling isomer), and in (IIb), axially [4].

The kinetic curves of the accumulation of (I) and (II) during the cocondensation are characteristic of consecutive-parallel reactions (Fig. 1a). The possibility of transacetylation of the acetal into the formal was confirmed by independent experiments. At a >30 min duration of the experiment, the concentration of the formal remains practically unchanged and that of the acetal decreases, which is apparently due to the hydrolysis of the acetal into 3-phenyl-1,3-butanediol or its intamolecular dehydration into 2-methyl-4-phenyl-5,6-dihydropyran [5]. This assumption makes it possible to explain the regularities obtained when the temperature (Fig. 1b) and the catalyst concentration (Fig. 1c) were varied. In comparison with (I), the yield maxima of (II) are situated in the region of less rigid conditions, which agrees with data on their relative reactivity in acid-catalyzed reactions [1]. From the results obtained it follows that high selectivity with respect to the acetal can be attained by carrying out the cocondensation at 70-80°C with $[H_2SO_4] < 10\%$ and molar ratio $[RCHO]/[HCHO] > 1$ (Fig. 1d).

It should be noted that in all experiments, the products of the crotonic condensation, acrolein and crotonaldehyde, were, in general, not formed, or were formed in an inappreciable amount (<5%).

We studied the modified Prins reaction in the case of C_2-C_5 alkanals, styrene, and α-methylstyrene. According to the GLC data and PMR spectra, 2-R-4-phenyl-1,3-dioxanes are formed only as a single isomer with an equatorial orientation of the substituents in the 2-position, while all the synthesized 4-methyl-2-R-4-phenyl-1,3-dioxanes are obtained as two isomers with a similar (II) orientation of the substituents.

Institute of Chemistry, Bashkir Branch, Academy of Sciences of the USSR, Ufa. Bashkir State University, Ufa. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 899-902, April, 1982. Original article submitted July 13, 1981.

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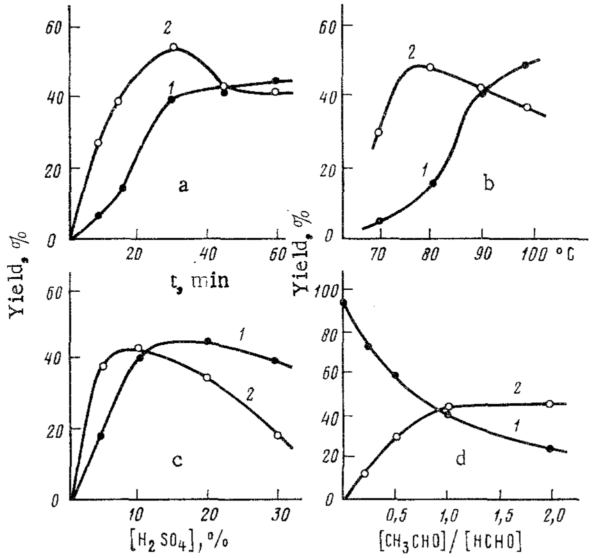

Fig. 1. Dependences on reaction time (a), temperature (b), H_2SO_4 concentration (c), and molar ratio of aldehydes (d) of dioxane yields during condensation of formaldehyde and acetaldehyde with α-methylstyrene: 1) 4-methyl-4-phenyl-1,3-dioxane; 2) 2,4-dimethyl-4-phenyl-1,3-dioxane [a) 90°C, $[H_2SO_4]$ = 10%, [RCHO]/[HCHO] = 1; b) $[H_2SO_4]$ = 10%, 45 min, [RCHO]/[HCHO] = 1; c) 90°C, 45 min, [RCHO]/[HCHO] = 1; d) 90°C, $[H_2SO_4]$ = 10%, 45 min].

TABLE 1. Cocondensation of Formaldehyde and Alkanals RCHO with Styrene and α-Methylstyrene (90°C, $[H_2SO_4]$ = 10%, [olefin]:[HCHO]:[RCHO] = 1:1.5:1.5)

R	Time, min	Yield, % per olefin used		R	Time, min	Yield, % per olefin used	
		formal	acetal			formal	acetal
Styrene				α-Methylstyrene			
CH_3	60	5,6	52,0	CH_3	30	37,0	58,5
C_2H_5	60	–	28,8	C_2H_5	20	10,5	60,2
n-C_3H_7	60	–	35,2	n-C_3H_7	60	26,3	38,5
i-C_3H_7	60	3,1	25,2	i-C_3H_7	45	18,9	17,8
				i-C_4H_9	45	25,2	14,8

With increasing molecular weight and branching of the alkanals, the yield of acetals during the cocondensation decreases (Table 1). This is apparently due to the lower solubility of the formaldehyde homologs in the aqueous phase of the reaction mixture.

EXPERIMENTAL

The GLC analysis was carried out on the "Viruchrom" apparatus on a 2 m × 3 mm column with 8% Se-30 on AW-HMDS Chezasorb, with helium as gas carrier, and temperature programming (4 deg/min) from 100 to 140°C.

The PMR spectra were taken in CCl_4, the chemical shifts are given as δ, ppm.

The experiments were carried out in sealed ampules (25 ml), each containing 20-60 mmoles of HCHO as paraform, 5 ml of 5-30% aqueous H_2SO_4, 2-40 mmoles of RCHO, and 20 mmoles of olefin. During the first 5 min, the contents of the ampule were heated without mixing, and then with vigorous mixing to ensure carrying out the reaction in the kinetic region. At the end of the experiment, the ampule was cooled, opened, and the organic phase was separated, treated with 15% NH_4OH, dried over Na_2SO_4, and analyzed by GLC. The acetals were isolated from the organic phase of a series of experiments by vacuum rectification.

2-Methyl-4-phenyl-1,3-dioxane: bp 108-110°C (9 mm), d_4^{20} 1.065, n_D^{20} 1.5182. PMR spectrum: 1.2 d ($2CH_3$), 1.6 m ($5H_{a,e}$), 3.7 m ($6H_{a,e}$), 4.4 m ($4H_a$), 4.6 q ($2H_a$), 7.1 s (C_6H_5).

2-Ethyl-4-phenyl-1,3-dioxane: bp 117-118°C (9 mm), d_4^{20} 1.058, n_D^{20} 1.5148. PMR spectrum: 0.9 t ($2'CH_3$), 1.5 m ($5H_{a,e}$ $2'CH_2$), 3.7 m ($6H_{a,e}$), 4.5 m ($2H_a$, $4H_a$), 7.1 s (C_6H_5).

2-Propyl-4-phenyl-1,3-dioxane: bp 126-128°C (9 mm), d_4^{20} 1.036, n_D^{20} 1.5089. PMR spectrum: 0.9 t ($2'CH_3$), 1.6 m ($5H_{a,e}$, $2'CH_2CH_2$), 3.7 m ($6H_{a.e}$), 4.4 m ($2H_{a,e}$, $4H_a$), 7.1 s (C_6H_5).

2-Isopropyl-4-phenyl-1,3-dioxane: bp 114-116°C (9 mm), d_4^{20} 1.048, n_D^{20} 1.5076. PMR spectrum: 0.9 d ($2'CH_3$), 1.6 m ($5H_{a,e}$, 2'CH), 3.7 m ($6H_{a,e}$), 4.4 m ($2H_a$, $4H_a$), 7.1 s (C_6H_5).

2,4-Dimethyl-4-phenyl-1,3-dioxane: bp 88-95°C (6 mm). PMR spectrum: 1.3 m ($2'CH_{3a,e}$, $4CH_3$), 1.8 m ($5H_{a,e}$), 3.7 m ($6H_{a,e}$), 4.5 q ($2H_a$), 5.0 q ($2H_e$), 7.1 m (C_6H_5).

4-Methyl-2-ethyl-4-phenyl-1,3-dioxane: bp 110-114°C (6 mm). PMR spectrum: 0.9 m ($2'CH_3$), 1.4 s ($4CH_3$), 1.8 m ($5H_{a,e}$, $2'CH_2$), 3.7 m ($6H_{a,e}$), 4.6 m ($2H_{a,e}$), 7.1 m (C_6H_5).

4-Methyl-2-propyl-4-phenyl-1,3-dioxane: bp 122-126°C (6 mm). PMR spectrum: 0.9 m ($2'CH_3$), 1.3 s ($4CH_3$), 1.8 m ($5H_{a,e}$, $2'CH_2CH_2$), 3.7 m ($6H_{a,e}$), 4.6 m ($2H_{a,e}$), 7.1 m (C_6H_5).

4-Methyl-2-isopropyl-4-phenyl-1,3-dioxane: bp 121-125°C (6 mm). PMR spectrum: 0.9 m ($2'CH_3$), 1.3 s ($4CH_3$), 1.8 m ($5H_{a,e}$, 2'CH), 3.7 m ($6H_{a,e}$), 4.4 m ($2H_{a,e}$), 7.1 m (C_6H_5).

4-Methyl-2-isobutyl-4-phenyl-1,3-dioxane: bp 124-130°C (6 mm). PMR spectrum: 0.9 m ($2'CH_3$), 1.3 s ($4CH_3$), 1.8 m ($5H_{a,e}$ $2'CH_2CH$), 3.7 m ($6H_{a,e}$), 4.5 m($2H_{a,e}$), 7.1m (C_6H_5).

The IR spectra of acetals, obtained by the modified Prins reaction and synthesized by the method described in [3], are identical.

CONCLUSIONS

Acid-catalyzed cocondensation of formaldehyde and alkanals RCHO with styrene leads to 2-R-4-phenyl-1,3-dioxanes with equatorial orientation of substituent R in the 2-position, and with α-methylstyrene to a mixture of 4-methyl-2-R-4-phenyl-1,3-dioxanes with axial and equatorial orientation of substituent R.

The yield of the cocondensation products in this reaction reaches 60%.

LITERATURE CITED

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