N. V. Shidkova, L. N. Turovskaya, V. M. Kobryanskii, G. M. Trofimova, and D. D. Novikov

Spiroorthoesters (SOE) are used for the preparation of nonshrinking polymers [1-3]. The classical means for their preparation involves the reaction of γ -butyrolactone (BL) with epoxides in the presence of Lewis acids with the formation of an intermediate complex of BL with the catalyst [4]:

 $\begin{array}{c|c}
CH_2-CH_2 & CH_2 & CH_2 & CH_2 & O-CH_2 \\
CH_2-O & CH & CH_2-O & O-CH \\
(BL) & R & (SOE) & R
\end{array}$ (1)

UDC 542.91:547-314:547.431.2

In this case, the product yields are relatively low (30-60%) and depend significantly on the type of R.

In the present work, we elucidated the reasons for the low yield of SOE in the reactions of BL with epichlorohydrin (ECH) and the diglycidyl ether of 3-hydroxyphenol (DGEH) in the presence of Lewis acids.

Gel permeation chromatography was used to show that there are virtually no high-molecular-weight compounds below 20°C in the products of the reaction of BL with the epoxides studied in the presence of BF_3 etherate. Only BL, epoxide and SOE were identified in the reaction mixture. The material balance calculated relative to BL and SOE during the synthesis showed that the consumption of BL entirely corresponds to the amount of SOE formed. Thus, the reason for the low yield of the desired product cannot be the polymerization of the epoxides and SOE.

The kinetics of the reaction of BL with epoxides was studied by IR spectroscopy relative to the consumption of BL (\forall C=0 1770 cm⁻¹) and accumulation of SOE (1330 cm⁻¹). The 1330 cm⁻¹ band is found in the spectra of all the SOE obtained and is lacking in the spectra of the starting compounds. The optical density of the band at 1330 cm⁻¹ linearly correlates with the SOE concentration. Two steps are clearly evident in the reactions of BL with epoxides in the presence of BF₃ etherate. The conversion relative to BL is 33% in the first, rapid step, which is complete in 0.5 h, while 20% BL is consumed in the second, slow step over 4.5 h (Figs. 1 and 2). The nature of the kinetic curves shows that there is apparent self-inhibition, i.e., the product formed hinders the major reaction. The probable reason for this effect is competition for the catalyst between BL and SOE. A rather strong complex is formed upon mixing BL with BF₃ etherate [4], which is detected in the IR spectrum by the finding of a band at 1725 cm⁻¹. The rapid disappearance of this band is observed upon the addition of SOE to the complex of BL with BF₃ as a result of the formation of a stronger complex of BF₃ with SOE



(2)

Hence, most of the catalyst at the onset of the reaction is bound in a complex with BL, which forms SOE with epoxides. As the reaction proceeds, some of the catalyst is bound with SOE and gives a complex which is inactive in this reaction and, thus, the concentration of the active complex of the catalyst with BL steadily drops. Virtually all the catalyst in the presence of BF_3 etherate upon reaching 60% conversion of BL is bound to SOE and the reaction almost stops.

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 199-202, January, 1987. Original article submitted February 21, 1986.

178



Fig. 1. Kinetic curves for the consumption of BL (1) and accumulation of SOE (2) in the reaction of BL with ECH in CH_2Cl_2 catalyzed by $Et_2O \cdot BF_3$ at $10^{\circ}C$. [BL]₀ = 1.63, [ECH]₀ = 1.63, [Et_2O \cdot BF_3]₀ = 1.63 \cdot 10^{-2} mole/liter.

Fig. 2. Kinetic curves for the consumption of BL (1) and accumulation of SOE (2) upon the reaction of BL and DGEH in CH₂Cl₂ catalyzed by $Et_20 \cdot BF_3$. [BL]₀ = 1.42, [DGEH]₀ = 0.71, [$Et_20 \cdot BF_3$] = 2.56 $\cdot 10^{-2}$ mole/liter.



Fig. 3. Kinetic curves for the accumulation of SOE upon the reaction of BL with ECH in CH₂Cl₂ in the presence of SnCl₄ (1), Et₂O·BF₃ (2), SbCl₅ (3) at 10°C. [ECH]₀ = 1.63, [BL]₀ = 1.63, [SnCl₄] = $1.63 \cdot 10^{-2}$, [Et₂O·BF₃] = $1.63 \cdot 10^{-2}$, [SbCl₅] = $1.63 \cdot 10^{-2}$ mole/liter.

Thus, the low yields of SOE in the reactions of BL with epoxides may be attributed to inhibition of the reaction due to binding of the catalyst by the SOE formed. An increase in the yield of the desired product would require a shift in equilibrium (2) toward the active complex due to an excess of BL, elevation of the temperature or selection of a suitable catalyst.

In the case of the reaction of BL with ECH, a two-fold excess of BL leads to an increase in the yield of SOE by about 5%. However, this method for improving the yield is difficult to realize since a significant amount of the SOE is lost upon the removal of highboiling BL (bp 206°C). Carrying out the reaction at elevated temperatures does not lead to an increase in the product yield since the products begin to polymerize above 30-40°C.

Comparison of the strength of the complexes of BL and SOE (2-chloromethyl-1,4,6-trioxaspiro[4,4]nonane) with Lewis acids TiCl₄, SnCl₄, BF₃, and SbCl₅ relative to the free BL band at 1770 cm⁻¹ and the band for the BL complex at 1725 cm⁻¹ shows that SnCl₄, BF₃, and SbCl₅ form nonequilibrium complexes both with BL and SOE. For these catalysts, equilibrium (2) is shifted toward the SOE complex. TiCl₄ forms a weak equilibrium complex both with BL and SOE. SOE is formed in only slight amounts in the reaction of BL with ECH in the presence of TiCl₄ since this catalyst causes the polymerization of ECH. The greatest yield in the reactions of BL with ECH in the presence of SnCl₄, BF₃, and SbCl₅ is found for the weakest acid, SnCl₄ (Fig. 3). Carrying out this reaction in the presence of SnCl₄ for 48 h at 20°C permits an increase in the yield of SOE from ECH to 90% and in the yield of SOE from DGEH to 85%.

EXPERIMENTAL

The spiroorthoesters were prepared in methylene chloride at $10-20^{\circ}$ C in a dry argon atmosphere. A sample of γ -butyrolactone was dried over granulated KOH and distilled in vacuum with added 0.3% 2,4-toluidenediisocyanate. A sample of epichlorohydrin was dried and distilled over CaH₂, bp 116°C. The diglycidyl ether of 3-hydroxyphenol was distilled in vacuum, bp 170°C (0.04 mm). The catalysts were dried and distilled over P₂O₃ and then placed into ampuls in a stream of dry argon. A sample of methylene chloride was dried and distilled over P₂O₅. The gel permeation chromatography of the reaction mixture was carried out on a Waters 200 chromatograph in THF.

CONCLUSIONS

1. The yield of spiroorthoesters in the reaction of γ -butyrolactone with epichlorohydrin depends significantly on the type of catalyst employed.

2. An increase in the spiroorthoester yield requires the formation of nonequilibrium complexes between the catalyst and lactone. This excludes the polymerization of the epoxy compounds. On the other hand, the equilibrium between the complexes of the catalyst with the lactone and spiroorthoester should not be completely shifted toward the latter since this would lead to inhibition of the reaction.

LITERATURE CITED

1. W. J. Bailey, J. Macromol. Sci., <u>A9</u>, No. 5, 849 (1975).

2. T. Endo and W. J. Bailey, J. Polymer Sci., Polym. Lett. Ed., <u>18</u>, 25 (1980).

3. W. J. Bailey and K. L. Sun, J. Am. Chem. Soc., Div. Polymer Chem., Preprints, <u>13</u>, 400 (1972).

4. K. Bodenbenner, Liebigs Ann. Chem., 623, 183 (1959).

DIRECT ¹³C-¹H COUPLING CONSTANTS IN THE VINYL GROUP OF 1-VINYLPYRAZOLES

UDC 543.422.25:547.772.2

A. V. Afonin, V. K. Voronov,

L. A. Es'kova, E. S. Domnina,

E. V. Petrova, and O. V. Zasyad'ko

In a continuation of a study of the rotational isomerism of 1-vinylpyrazoles [1], we studied the direct 13 C-H coupling constants in the vinyl group of 1-vinylpyrazole (I), 1-vinyl-4-bromopyrazole (II), 1-vinyl-3-methylpyrazole (III), 1-vinyl-5-methylpyrazole (IV), 1-vinyl-3,5-dimethylpyrazole (V), and 1-vinyl-4-nitro-3,5-dimethylpyrazole (VI) (Table 1). Only limited experimental data have appeared related to the steric specificity of 13 C-H coupling constants [2-4]. Table 1 shows that the magnitude of the 13 C-H coupling constants in 1-vinylpyrazoles (I)-(VI) depends on the nature and position of the ring substituent. Electron-withdrawing bromine and nitro substituents at C⁴ in the ring ((II) and (VI)) increase the 1 C_{GHA} and 1 JC_{GHB} coupling constants by from 0.3 to 1.7 Hz and the 1 JC_{GHX} coupling constants than the Br group. The introduction of an electron-donor methyl group at C³ of the pyrazole ring ((III) and (V)) leads to a decrease in the 1 JC_{GHA} and 1 JC_{GHA} and 1 JC_{GHA} coupling constants by 0.3-0.4 Hz and 1 JC_{GHX} coupling constants by 1.0-1.2 Hz. This type of substituent effect on 1 JC_H coupling constants is in general accord with literature data and was theoretically analyzed by Sergeev [5] and Wehrli [6].

A methyl group at C⁵ in the ring ((IV) and (V)) also reduces the ¹JCBHA and ¹JCaHX constants by 1.0-1.1 and 2.8-3.0 Hz, respectively. However, the effect of a methyl group at C⁵ in the ring on the ¹JCBHB coupling constant is anomalous since it causes an increase by 2.0 and 2.3 Hz relative to compounds unsubstituted at C⁵. According to our previous conclusions [1], 1-vinylpyrazoles (I)-(III) unsubstituted at C⁵ in the ring shifts the equilibrium

Irkutsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 202-204, January, 1987. Original article submitted March 5, 1986.