LITERATURE CITED

1. B. Ya. Simkin, S. P. Makarov, N. G. Furmanova, K. Sh. Karaev, and V. I. Minkin, Khim. Geterotsikl. Soedin., No. 6, 747 (1984).
2. B. Ya. Simkin, V. I. Minkin, and L. E. Nivorozhkin, Khim. Geterotsikl. Soedin., No. 9, 1180 (1978).
3. J. Hlubeck, R. Rithie, and W. C. Taylor, Aust. J. Chem., 29, 2347 (1971).
4. A. M. Samat, R. J. Guglielmetti, and G. Martin, J. Org. Magn. Reson., 8, 62 (1976).
5. G. C. Levy and G. L. Nelson, Carbon-13 Nuclear Magnetic Resonance for Organic Chemists, New York (1972).
6. D. Cameron Margaret, US Patent No. 2844590; Ref. Zh. Khim., No. 22, 89742 (1960).
7. N. Donaldson, The Chemistry and Technology of Compounds of the Naphthalene Series [Russian translation], Goskhimizdat, Moscow (1963), p. 317.
8. G. F. Hennion and A. P. Boiselle, J. Org. Chem., 26, 725 (1961).

REGIOSPECIFIC CLEAVAGE OF 1,3-DIOXANES BY ORGANOALUMINUM COMPOUNDS

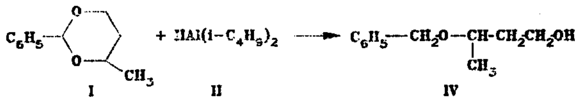
A. A. Volkov, S. S. Zlot-skii, É. Kh. Kravets,
L. V. Spirikhin, and D. L. Rakhmankulov

UDC 541.124:547.841'256.2'214

Organoaluminum compounds react with 4-methyl-2-phenyl-1,3-dioxane with cleavage of the O_1–C_2 bond to give monoethers with a primary alcohol group.

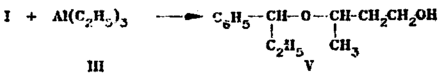
The reduction of cyclic acetals and ketals by alkylaluminum hydrides leads to monoethers of glycols [1], whereas tetrasubstituted 1,3-dioxolanes are selectively reduced to monoethers with a tertiary hydroxy group [2]. Information regarding the specificity of the cleavage of unsymmetrically substituted 1,3-dioxanes is not available.

In the present research we studied the transformations of 2-phenyl-4-methyl-1,3-dioxane (I), which exists in the cis-E, E conformation, under the influence of diisobutylaluminum hydride (II) and triethylaluminum (III). Compound I is reduced to 3-benzyloxy-1-butanol (IV) in virtually quantitative yield under the influence of reagent II. The isomeric 4-benzyloxy-2-butanol is not formed.



In the ^{13}C NMR spectrum of IV the doublet of the $-O-CH(CH_3)-$group is located at weaker field (73.1 ppm) than the signal of the $-CH_2OH$ fragment (59.3 ppm, t).

Under the influence of triethylalumunum (III) acetal I forms only 3-(α-phenylpropoxy)-1-butanol (V):



$$\underset{}{I} + \underset{III}{Al(C_2H_5)_3} \longrightarrow \underset{V}{C_6H_5-\underset{C_2H_5}{CH}-O-\underset{CH_3}{CH}-CH_2CH_2OH}$$

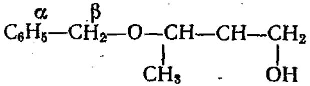
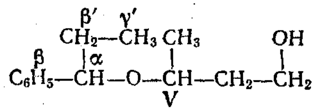
The structure of ether V also follows unambiguously from its ^{13}C NMR spectrum (Table 1).

Steric shielding of the adjacent oxygen atom by the methyl group in acetal molecule I apparently does not make it possible for the aluminum atoms to realize coordination at the

---

Ufa Petroleum Institute, Ufa 450062. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1036-1037, August, 1985. Original article submitted October 22, 1984.

TABLE 1. Characteristics of Glycol Monoethers IV and V

Monoether	bp, deg C (mm)	n_D^{20}	Chemical shift, ppm									Spectrum	Yield, %
			Glycol protons					Side chain protons					
			$>CH-$	$-CH_2-$	CH_2-OH	$-CH_3$	OH	α	β	β′	γ′		
 $\overset{\alpha}{C_6H_5}-\overset{\beta}{CH_2}-O-\underset{CH_3}{CH}-CH-\underset{OH}{CH_2}$ IV	125(10)	1,4992	4,1—4,4,m	1,4—1,7,m	3,49,t	1,05,d	4,28,s	3,72,s	7,15,s			PMR	88
			73,1,d	39,2,t	59,3,t	19,5,q		70,2,t				^{13}C NMR	
 $\overset{\beta}{C_6H_5}-\overset{\overset{\beta'}{CH_2}-\overset{\gamma'}{CH_3}}{\underset{}{\overset{\alpha}{CH}}}-O-\overset{CH_3}{CH}-CH_2-\overset{OH}{CH_2}$ V	130(10)	1,4835	3,4—3,7,m	1,3—1,8,m	3,53,t	0,84,d	3,25,s	4,12,t	7,18,s	1,3—1,7	0,7,t	PMR	85
			72,8,d	38,5,t	59,6,t	20,9,q		82,2,d		31,2,t	10,2,q	^{13}C NMR	

C_2–O_3–C_4 bonds, and, as a result, the ring is cleaved only at the O_1–C_2 bond, which leads to ethers IV and V with a primary alcohol group.

In many respects these data are similar to the results obtained in the cleavage of 1,3-dioxacyclanes by organomagnesium compounds [3]. It is interesting that the homogeneous catalytic oxidation of substrate I by tert-butyl hydroperoxide in the presence of Pd(II) salts leads to a mixture of 1,3-butanediol monobenzoates; ring opening at the C_2–O_3 bond is dominant [4].

EXPERIMENTAL

The organoaluminum compounds were used in the form of 50% solution in hexane. The experiments were carried out in an inert atmosphere in a three-necked flask equipped with a reflux condenser, a stirrer, and a dropping funnel, into which diisobutylaluminum hydride (II) or triethylaluminum (III) and reagent I in stoichiometric ratios (0.03 mole each) were introduced successively. The reaction mixture was maintained at 70°C for 10 min, after which it was cooled, and excess water was added. The precipitated aluminum hydroxide was removed by filtration, the organic layer was dried, and the amounts of products IV and V were determined chromatographically; IV and V were then isolated by distillation (Table 1).

LITERATURE CITED

1. L. N. Zakharkin and I. M. Khorina, Izv. Akad. Nauk SSSR, Ser. Khim., 6, 2255 (1959).
2. W. Zajac and K. Byrne, J. Org. Chem., 38, 384 (1973).
3. B. A. Trofimov and S. E. Korostova, Usp. Khim., 44, 75 (1975).
4. Takahiro Kosokawa, Chem. Commun., 1245 (1983).