

Reactions of 1,3-Dioxacyclanes with Acid Halides A New Synthesis for ω -Halohydrine Esters

Short Communication

Stefan Kwiatkowski* and Andrzej Wolinski

Faculty of Chemistry, Technical University (Politechnika),
 PL-00-662 Warszawa, Poland

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Reaction of 1,3-dioxolanes and 1,3-dioxanes with aliphatic acid chlorides and bromides yields 2- or 3-halohydrine esters.

(Keywords: 1,3-Dioxolanes and 1,3-dioxanes, ring opening of)

Reaktionen von 1,3-Dioxacyclanen mit Säurehalogeniden. Eine neue Synthese für ω -Halogenhydrinester (Kurze Mitteilung)

Die Reaktion von 1,3-Dioxolanen und 1,3-Dioxanen mit aliphatischen Säurechloriden ergab 2- bzw. 3-Halogenhydrinester.

Searching for nonhydrolytic conditions of cleaving acetals we have found that aliphatic acid halides react readily with 1,3-dioxanes and 1,3-dioxolanes to give a mixture of the corresponding halohydrine esters and carbonyl compounds in good yields.

Recently similar results were described using *Lewis* acids as catalysts^{1,2}. Our method seems to be interesting not only for deprotecting ketones but mainly for the synthesis of halohydrine esters. In the case of 4-substituted 1,3-dioxolanes one of the two possible bromohydrine acetates with a secondary acetate group was formed exclusively (Scheme 1). The results are presented in the Table 1.

Scheme 1

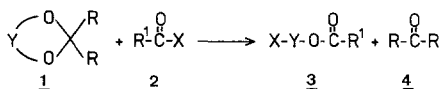


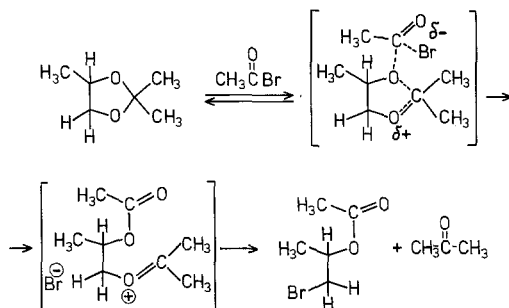
Table 1. Reactions of dioxacyclanes (1) with acid halides (2)

1,3-Dioxacyclane Y	R	Acid halide ^a 2	Solvent ^b	Temp. (°C)	Time (h)	Halohydrine ester (3) (for Y see 1)	b.p. (°C/Torr)	Yield of 3 %	Yield of 4 %	Ref.
						X R'				
—(CH ₂) ₂ —		2a	A	40	72	Br CH ₃	145/760	69	88	7
—(CH ₂) ₂ —		2b	B	20	48	Br CH ₂ Cl	117/30	67	70	7
CH ₃ ...CH—										
CH ₃ ▲CH—		2a	B	20	48	Br CH ₃	65/30	53	65	7
CH ₂ —										
CH ₃ —CH—		2a	B	20	24	Br CH ₃	160—162/760	72	83	7
—(CH ₂) ₂ —		2a	C	20	48	Br CH ₃	144—145/760	85	92	7
—(CH ₂) ₃ —		2a	A	40	72	Br CH ₃	162—163/760	75	90	7
—(CH ₂) ₃ —		2c	A	40	168	Cl CH ₂ Cl	104—105/15	40	53	8
—(CH ₂) ₃ —		2b	B	20	48	Br CH ₂ Cl	120/10	52	71	5
CH ₂ —										
n—C ₅ H ₁₁ —CH—		2a	B	20	20	Br CH ₃	72/16	69	75	6

^a 2a: CH₃COBr; 2b: ClCH₂COBr; 2c: ClCH₂COCl.^b A: benzene; B: CCl₄; C: CHCl₃.

They indicate that the reaction starts by the attack of the acid halide on the oxygen atom with higher electron density. That attack weakens the bond between oxygen and tertiary carbon, giving finally a cationic species with a good leaving group which then can be easily substituted by halogen anion (Scheme 2).

Scheme 2



The substitution seems to be an S_N2 -reaction with full retention of configuration, because *trans*-2,2,4,5-tetramethyl-1,3-dioxolane in the reaction with acetyl bromide gives 2-acetoxy-3-bromobutane which on treatment with sodium benzyloxylate afforded pure *trans*-2,3-dimethyl oxetane with 92% yield³. Further investigations concerning the mechanism and applicability of this reaction are in progress.

Experimental

All reactions were carried out with equimolar amounts (0.1 mol) of reactants. Products were purified by distillation. The course of the reaction and the purities of the products were analyzed by gas chromatography⁴. Structures of the products were established by IR and ¹H-NMR spectroscopy and by comparison with literature data (see Table 1).

References and Notes

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- ³ Golding B. T., Hall D. R., Sakrikar S., *J. Chem. Soc., Perkin I* **1973**, 1216, 1219.
- ⁴ 2.5 m-column packed with OV-101 10% on Chromosorb W.
- ⁵ Chloroacetic acid-3-bromopropylester, ¹H-NMR (100 MHz; CCl₄; δ): ppm, 4.35 (t, 2 H, $J = 6.5$, —CH₂—O—), 4.10 (s, 2 H, Cl—CH₂—CO—), 3.52 (t, 2 H, $J = 6.5$, —CH₂—Br), 2.20 (m, 2 H, —CH₂—).

⁶ (*R,S*)-1-bromo-2-acetoxyheptane, ¹H-NMR (100 MHz; CCl₄; δ): ppm, 4.91 [1 H, *J* = 6.5, —C(OAc)H—], 3.41 (d, 2 H, *J* = 6.5, Br—CH₂—), 2.00 (s, 3 H, —COCH₃), 1.64 [m, 2 H, —C(OAc)H—CH₂—], 1.31 [m, 6 H, —(CH₂)₃—], 0.89 (t, 3 H, *J* = 7, —CH₃).

⁷ Beilsteins Handbook, Vol. 2.

⁸ Dittmer D. C., Hertler W. R., Winicov H., J. Amer. Chem. Soc. **79**, 4431 (1957).