CONVENIENT METHOD FOR THE SYNTHESIS OF 2-(α-BROMOALKYL)-1,3-DIOXACYCLANES

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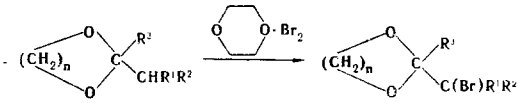
Cyclic acetals (ketals) of α-bromo aldehydes and ketones are usually obtained by reaction of these carbonyl compounds or their acyclic acetals (ketals) with the corresponding diols; however, the starting α-bromo carbonyl compounds are usually lachrymators, and the processes themselves are two- or three-step reactions.

We have developed a convenient method for the synthesis of 2-(α-bromoalkyl)-1,3-dioxacyclanes (II) by the action of an equimolar amount of dioxane dibromide on 2-alkyl-1,3-dioxacyclanes (I).



Ia-f IIa-f

I, IIa n=2; b n=3; c-f n=4; a-c $R^1=R^2=R^3=H$; d $R^1=CH_3$, $R^2=R^3=H$; e $R^1=R^2=CH_3$, $R^3=H$; f $R^1=R^2=H$, $R^3=CH_3$

Thus a solution of 0.2 mole of dioxane dibromide in 150 ml of dioxane was added to 0.2 mole of dioxacyclane I in 75 ml of purified (to remove peroxides) 1,4-dioxane in such a way that the temperature of the mixture did not rise above 15-20°C. At the end of the reaction (2-2.5 h), the liberated HBr was neutralized with diethylamine, and the precipitate was removed by filtration and washed twice with 25 ml of dioxane. The solvent was removed by distillation at reduced pressure, and the residue was fractionated in vacuo. The properties of IIa-c, which were obtained in 72-90% yields, were in agreement with the properties described in the literature [1-3]. The following compounds were also obtained: IId (76%), bp 78-79°C (6 mm), d_4^{20} 1.3798, and n_D^{20} 1.4834; IIe (71%); bp 65-66°C (1 mm); d_4^{20} 1.3376, and n_D^{20} 1.4828; IIf (66%), bp 62-63°C (1 mm), d_4^{20} 1.3822, and n_D^{20} 1.4824. Good results of elementary analysis were obtained for them. The individuality of the compounds was monitored by gas-liquid chromatography and IR spectroscopy.

LITERATURE CITED

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