NONCATALYTIC SUBSTITUTIVE O-ACYLATION OF OXIRANES WITH TRIFLUOROACETIC ANHYDRIDE

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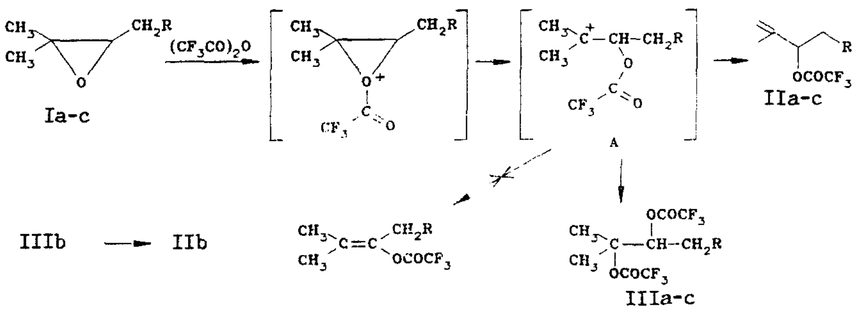
UDC 547.422:542.951

1-R-3-Methyl-2,3-epoxybutanes have been found to react with trifluoroacetic anhydride at 20-40°C in the absence of a catalyst to give mixtures of the difluoroacetate and the product of substitutive O-acylation. The formation of the latter is favored by raising the temperature. The reaction mechanism is discussed.

We have previously shown that some epoxy-compounds react with carboxylic acid anhydrides in the presence of an acidic catalyst on heating to give isomerization products of the oxirane to the allyl alcohol, followed by its acylation (substitutive O-acylation). This reaction, which is carried out at 140-160°C in the presence of an acid (sulfuric, phosphoric, toluene-p-sulfonic, etc.), at lower temperatures gives mainly the diesters of the corresponding glycols. The same unsaturated monoesters of allyl alcohols are formed on decomposition of the glycol diacetates at 120-140°C. The latter reaction is not, however, as regioselective as substitutive O-acylation of the oxiranes themselves [1]. The diacetates give, in addition to allyl esters, substantial amounts of the isomeric vinyl ethers [2]. This excludes the possibility of the formation of allyl monoacetates via intermediate glycol diacetates [1]. However, it remains unclear how the acetoxyl group arises – whether as suggested in [1], or by preliminary isomerization of the epoxides to allyl alcohols [3] followed by acylation by the acid anhydride. The significance of these alternatives resides in the fact that under the conditions of the experiment (120-160°C), these epoxides are capable of isomerizing to the allyl alcohols, either in the presence of a catalyst [3], or thermally [4]. The resulting alcohols could indeed be acylated under the reaction conditions to give esters.

In order to obtain further information on the mechanism of this reaction, we have examined the reaction of trifluoroacetic anhydride with the epoxides (Ia-c). It would be expected that, thanks to the higher electrophilicity of the trifluoroacetyl group and the low nucleophilicity of the trifluoroacetate anion, substitutive O-acylation would occur under milder conditions, thereby excluding the possibility of prior isomerization of the oxiranes to the allyl alcohols.



I—III a R=Cl; b R=Br; c R=OC_6H_5

As expected, trifluoroacetic anhydride reacted exothermically with the oxiranes (Ia-c) even in the absence of a catalyst. This provides a unique opportunity to clarify the behavior of the intermediate carbocationoid species in respect of deprotonation in the presence of the weakly nucleophilic trifluoroacetate group, and to establish whether the latter is trapped by

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 174-176, February, 1990. Original article submitted March 22, 1988; revision submitted May 22, 1989.

TABLE 1. Properties of (IIa-c) and (IIIb)

Compound	Empirical formula	bp, °C (mm)	n_D^{20}	d_4^{20}	PMR spectrum, δ, ppm	Yield, %
IIa	$C_7H_8ClF_3O_2$	44...48 (12)	1,3928	1,2309	1,82 (3H, d.d. J=1 Hz CH_3); 3,75 (2H, d, J=6,4 Hz CH_2Cl); 5,25 (2H, m. $=CH_2$); 5,59 (1H, t, J=6,4 Hz CH)	49
IIb	$C_7H_8BrF_3O_2$	59...62 (12)	1,4140	1,2602	1,85 (3H, d.d. J=1 Hz CH); 3,58 (2H, d, J=6,6 Hz, CH_2Br); 5,28 (2H, m, J=1 Hz, $=CH_2$); 5,62 (1H, t, J=6,6 Hz, CH)	48
IIc	$C_{13}H_{13}F_3O_3$	124...126 (11)	1,4700	1,1614	1,76 (3H, d.d., J=1 Hz, CH_3); 4,08 (2H, d, J=6,6 Hz CH_2); 5,09 (2H, m $=CH_2$); 5,61 (1H, t, J=6,6 Hz, CH); 6,87...7,32 (5H, m, C_6H_5)	40
IIIb	$C_9H_9BrF_6O_4$	96...98 (12)	1,4250	1,5801	1,65 and 1,68 (6H, s, CH_3); 3,46...3,71 (2H, m, CH_2Br); 5,45...5,71 (1H, m, CH)	27

the carbocationoid species as readily as by the more nucleophilic (and basic) acetate group, or whether the reaction gives the unsaturated ester only.

In the case of (Ib), it was found that at 20-40°C a mixture of the mono- (II) and diacetate (III) was formed in a ratio of 3:2. The diagnostic features for measuring this ratio were the signals for the CH_3 and $=CCH_3$ groups in the PMR spectra at 1.65-1.68 and 1.72-1.85 ppm, respectively. At higher temperatures (120-140°C), the proportion of the monoacetate (II) increased slightly, the ratio becoming equal to 7:3. Compounds (IIa-c) and (IIIb) were isolated from the reaction mixtures and characterized [(IIIb) was isolated from the mixture of composition (IIb):(IIIb) = 3:2)].

It is clear that the intermediate carbocationoid species (A) formed during the reaction can coordinate, irrespective of the reaction conditions, with such a weak nucleophile as the trifluoroacetate anion. The decreasing proportion of the diacetate, and the increased proportion of the monoacetate in the reaction products also shows that at elevated temperatures there is either an increase in the rate of deprotonation of the intermediate carbocationoid species, or the glycol ditrifluoroacetate formed decomposes to the monoacetate.

In order to exclude one of these likely pathways for the formation of the monoacetate, we followed the course of the high-temperature decomposition of the ditrifluoroacetate (IIIb). It was found that this ester is stable at temperatures of 100-140°C in the absence of an acid catalyst. Only in the presence of a catalyst (TsOH) at 130°C did cleavage of the diester occur to give (IIb) (PMR), no vinyl isomer being present.

It is therefore evident that substitutive O-acylation of oxiranes does not involve the intermediate formation of allyl alcohols, nor does it occur via the ditrifluoroacetates (III). The likelihood is that the first stage of the reaction is the formation of the carbocationoid species (A), which is then deprotonated to (IIIa-c). It is assumed that substitutive O-acylation of oxiranes by other acid anhydrides follows a similar course.

EXPERIMENTAL

PMR Spectra were recorded in CCl_4 on a Perkin-Elmer R-12B (60 MHz) spectrometer, internal standard HMDS. The gas chromatograph used was an LKhM-8MD, with a catharometer, column (3 m) with 5% OV-17 on Chromaton-Super, carrier gas (helium) flow rate 40-60 ml/min, temperature 120-200°C.

The elemental analyses of (IIa-c) and (IIIb) for C, H, and Hal were in agreement with the calculated values.

Reaction of Oxiranes (Ia-c) with Trifluoroacetic Anhydride. In a three-necked flask, fitted with a thermometer, reflux condenser, and a dropping funnel with a delivery tube reaching to the bottom of the flask, was placed 0.025 mole of the oxirane (Ia-c), heated to 120-140°C, and 3.7 ml (0.025 mole) of trifluoroacetic acid added dropwise over 20 min. As the reaction proceeded, the temperature of the mixture fell to 70-90°C. The reaction was followed by PMR, using the diagnostic signals for the methyl groups of the oxirane at 1.20-1.30 ppm. The reaction was normally complete within 30-40 min, following which the mixture of (II) and

(III) was fractionated to give three fractions: (a) boiling at 46-86°C (12 mm), (b) 59-102°C (12 mm), (c) 124-170°C (12 mm). Fractionation of these fractions gave (IIa-c), the yields and properties of which are given in Table 1.

Reaction of Oxirane (Ib) with Trifluoroacetic Anhydride at 20°C. To 4.13 g (0.025 mole) of the oxirane (Ib) was added dropwise with stirring at 20°C 3.7 ml (0.025 mole) of trifluoroacetic anhydride. An exothermic reaction ensued, the temperature rising to ~40°C. When evolution of heat had ceased, the mixture was stirred for a further 30 min and redistilled to give 7.8 g of a fraction bp 59-102°C (12 mm), which from its PMR spectrum was a mixture of (IIb) and (IIIb) in a ratio of 3:2. Fractionation of this mixture gave 2.5 g (27%) of (IIIb) (Table 1).

Decomposition of 4-Bromo-2-methyl-2,3-ditrifluoroacetoxybutane (IIIb) in the Presence of TsOH. The compound (IIIb) (3.75 g, 0.01 mole) was heated with a few crystals of TsOH at 130°C for 2 h. From its PMR spectrum, the reaction mixture contained 70% of 1-bromo-3-methyl-2-trifluoroacetoxy-3-butene.

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