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THE SYNTHESIS OF CIS- AND TRANS-1,2-DIBROMOCYCLOPROPANE

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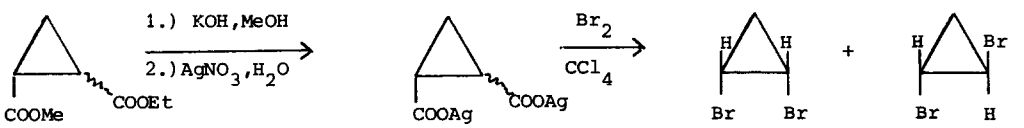
Abstract: A preparative route to cis- and trans-1,2-dibromocyclopropane (1) was developed via the Hunsdiecker reaction of silver cyclopropane-1,2-dicarboxylate (2). Cis- and trans-2 gave the same ratio of cis- and trans-1 (1:3.2). The mechanism of this reaction is briefly discussed.

In connection with our investigations of organometallic derivates of cyclopropane[1], we needed cis- and trans-1,2-dibromocyclopropane (cis- and trans-1). Trans-1 has been obtained as the exclusive product by bromination of cyclopropene[2]; this approach was not very satisfactory in our hands, mainly because of the low yields (<1%) obtained in the cyclopropene synthesis[3]. Both trans-1 and cis-1 were obtained[4] by Hunsdiecker reaction[5] of the mercuric salt of trans-cyclopropane-1,2-carboxylic acid, and separated by glc. We decided to investigate the Hunsdiecker reaction of silver cyclopropane-1,2-dicarboxylate (2). 2 was prepared as a mixture of stereoisomers from the mixture of esters (represented by 3) obtained according to McCoy[6].



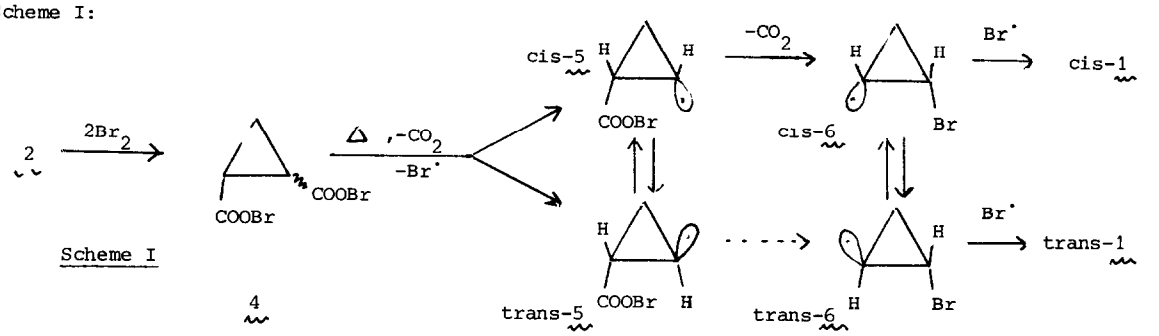
3 2 cis-1 trans-1

The Hunsdiecker reaction was performed as follows. 25g (65.8 mmol) of 2 (dried over P_2O_5) was added during 3 hours to a refluxing solution of 60 g Br_2 (dried on P_2O_5) in 300 ml dry CCl_4; after the addition, reflux was continued for one hour. AgBr was filtered off and the filtrate was washed with aqueous Na_2SO_3 and Na_2CO_3 and dried on $MgSO_4$. Careful distillation yielded 4.0 g (32%) pure trans-1[7], and 1.25 g (10%) pure cis-1[7]. This approach constitutes a rather satisfactory preparative route to both stereoisomers of 1.

In order to clarify the stereochemical relationship between educts and products, the reaction was repeated under identical conditions with pure cis-2 or trans-2[8]; identical yields and ratios of cis-1 and trans-1 were obtained. From the observation that under the reaction conditions, cis- and trans-1 are stable and do not isomerize, it is concluded that the reaction is kinetically controlled.

It is generally agreed[5] that the Hunsdiecker reaction proceeds via the acyl hypobromites (such as 4, Scheme I) which decompose by radical pathways. Applequist and Werner[9] have demonstrated that in the case of a vicinal dicarboxylate, i.e. silver trans-1,2-cyclohexanedicarboxy-

late (7), two of the many a priori reasonable pathways are important: one proceeding via cyclohexene, and another one involving an intramolecular bromine transfer step, analogous to the conversion of cis-5 to cis-6. The former pathway cannot be important in our case because cyclopropene in an unlikely intermediate (high strain energy!); moreover, it would be converted exclusively to trans-1[2]. Therefore, the main course of our reaction is probably best represented by Scheme I:



Scheme I

Contrary to the reaction of 7, which stereospecifically yields trans-1,2-dibromocyclohexane[9], the reaction of 2 is not stereospecific. The stereochemistry of 2 may be lost at the stage of either 5 (preferential reaction of cis-5 via the intramolecular pathway[9]) of 6; the stereochemistry of 1 is very likely determined in the last step (6 → 1). If one considers the generally high rate of inversion of α-hydrogen cyclopropyl radicals[10], which has in particular been demonstrated in the Hunsdiecker reaction[11], and assumes a comparable rate of reaction for cis-6 and trans-6, the cis/trans ratio of 1 reflects the (thermodynamically determined) cis/trans ratio of 6. The preference for trans-6 might be caused by an unfavourable interaction between the unpaired electron and the C-Br dipole in cis-6 (cf. ref. 1)

References and Notes

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7. Trans-1: b.p. (120°C/300 mbar) and ^{1}H NMR spectrum were in agreement with the literature[2]; cis-1: m.p. 8°C; b.p. 120°C/100 mbar; ^{1}H NMR spectrum ($CDCl_3$, 250 Mhz): δ = 3.10 ppm (dd, J = 8.2 and 5.8 Hz, 2H, CHBr), 1.74 ppm (dt, J = 8.3 and 8.2 Hz, 1H, CH_2-proton trans to Br), 1.12 ppm (dt, J = 8.3 and 5.8 Hz, 1H); ^{13}C NMR spectrum ($CDCl_3$, 62.89 MHz): δ = 26.0 ppm (d, $^1J_{CH}$ = 191.0 Hz), 17.9 ppm (t, $^1J_{CH}$ = 165.8 Hz).
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