Stereoselective Cyclopropane Ring Opening Reactions of Nortricyclene Hydrocarbons in Formic Acid. II. Reactions of Cyclofenchene and α-Fenchene

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Addition of formic acid to nortricyclene or tricyclene produced only one formate in both cases, exo-2-norbornyl or isobornyl formate.[1] We have studied the analogous treatment of cyclofenchene (I), and found it to lead to a very complicated mixture of initial, intermediate and final products. α-Fenchene (II) was the most important early intermediate of the reaction of I. A closer study was made of the rates and product ratios at different temperatures of the reactions of I and II in a formic acid-methylene chloride 1:1 mixture. The initial hydrocarbons I and II were purified by preparative gas chromatography. Gas chromatography, IR, mass and NMR-spectrometry were used for product analysis All products except one formate X were identified by comparing the spectra with the authentic samples of the Department of Chemistry, University of Helsinki.

The kinetic measurements were done from the start until 50 % of the initial hydrocarbon had reacted. The consumption of I and II during the reactions followed first order kinetics. The experimental rate constants and Arrhenius parameters together with the values of apparent entropy and free energy of activation at 25 and 105°C are collected in Table 1. The free energy difference of cyclofenchene (I) and α-fenchene (II) was determined at 105°C by equilibrating the mixture without formic acid using silica gel as catalyst. Other fenchenes appeared in the mixture,[2] but the molar ratio II:I approached 17.5:1. Thus $\Delta G° = -RT \ln K = -2.15$ kcal/mol; α-fenchene (II) being thermodynamically more stable than cyclofenchene (I). From the apparent free energies of activation at 105° (Table 1), the calculated free energy of the apparent transition state for the reaction of cyclofenchene (I) is 3 kcal/mol higher than for the reaction of α-fenchene (II). This indicates different mechanisms for the reactions of I and II. The Arrhenius parameters and apparent entropies of activation (Table 1) also show differences in the reaction mechanisms: the reaction of α-

Table 1. The first order rate constants (k), Arrhenius parameters and the apparent values of the entropies and free energies of activation of the reactions of cyclofenchene (I) and α-fenchene (II) in a formic acid-methylene chloride 1:1 mixture.

Com- pound	Temp. °C	$k \times 10^5$ sec^{-1}	E kcal/mol	log A	Corr. factor	$\Delta S*$ [a] cal/degr. mol	$\Delta G*$ [a] kcal/mol
I	0.	0.294					
	13.8	2.975					
	26.2	16.54	23.18 ± 1.62	13.06 ± 1.22	-0.9952		
	32.0	23.24					
	25.0	13.7 [b]				-0.726	22.81
	105					-1.20	22.88
II	0.	2.107					
	15.4	12.31	17.27 ± 0.58	9.15 ± 0.44	-0.9995		
	25.4	31.01					
	25.0	30.2 [b]				-18.62	22.23
	105					-19.10	23.74

[a] Calculated from E and log A according to the theory of absolute reaction rates.
[b] Interpolated from the experimental values at different temperatures.

fenchene (II) is electronically favored over the reaction of cyclofenchene (I), as is demonstrated by the lower energy of activation of II.[3] From the apparent entropies of activation it could be concluded that the transition state of the reaction of II has a definite structure, while conversely, the reaction of I proceeds via random collisions of protonated-I with surrounding (mainly solvent) molecules.
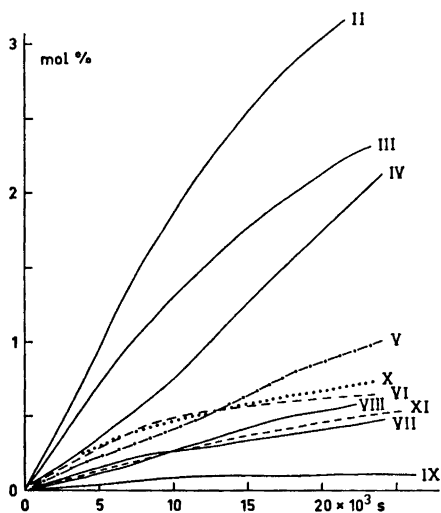

Fig. 1. Product composition (mol % of the sum I + products) in the reaction of cyclofenchene (I) in a formic acid-methylene chloride 1:1 mixture at 0°C. Notation as in the text.
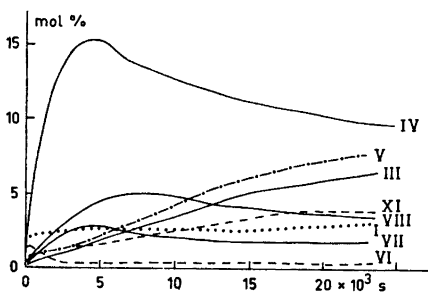

Fig. 2. Product composition (mol % of the sum II + products) in the reaction of α-fenchene (II) in a formic acid-methylene chloride 1:1 mixture at 0°C. Notation as in the text.

The product ratios (see Figs. 1 and 2) also show differences in the reactions of I and II. Exo-α-fenchene hydrate formate (IV) seems to be the only first intermediate product formed from α-fenchene (II). Cyclofenchene (I), however, appears to react via three main routes: α-fenchene (II), exo-β-fenchene hydrate formate (III) and exo-α-fenchene hydrate formate (IV) all appear to be direct reaction products from I. Tertiary endo-isomers of III and IV, endo-β-fenchene hydrate formate (VII) and endo-α-fenchene hydrate formate (VIII), appeared as the next intermediates, and the secondary exo-formates α-isofenchyl formate (V) and β-fenchyl formate (VI) as the final products on the main reaction routes. α-Fenchyl formate (IX), ε-fenchene (XI), β-fenchene (XII), and an unknown formate X appeared as minor side products of the reaction of cyclofenchene (I). Only ε-fenchene (XI) and cyclofenchene (I), however, were observed as side products in the reaction of α-fenchene (II) (see Fig. 2). The progress of the reactions of I and II can be presented as follows (most reverse reactions are unmarked; the main reactions are shown by solid arrows): Scheme 1.

The results of the product analysis show that no Wagner-Meerwein rearrangement occurs in the additions of formic acid to cyclofenchene (I) or α-fenchene (II) with the conditions employed. Such rearrangements are, however, involved in the formation of the final products V and VI from the adducts III and IV or their (Walden inversion products) epimers VII and VIII. This behavior is completely different from the reaction of nortricyclene, norbornene, and tricyclene under corresponding conditions, in which only secondary exo-products were formed.[1] In the present reactions, the final product ratio V:VI was 4:1, quite the same as the corresponding ratio of the final product acetates from the reaction of cyclofenchene (I) in Bertram-Walbaum solution (acetic acid containing a little 50 % sulfuric acid).[2,4,5]

Both kinetic and product ratio data indicate different reaction mechanims for the consumption of I and II, with no Wagner-Meerwein rearrangement occurring in the first phases. Thus, intermediate cation structures, if any, other than "asymmetrically bridged" (see Ref. 1), following the protonation of I or II, should be considered. The opening of the cyclopropane ring of cyclofenchene (I) to give III and IV can be considered as normal Markowni-
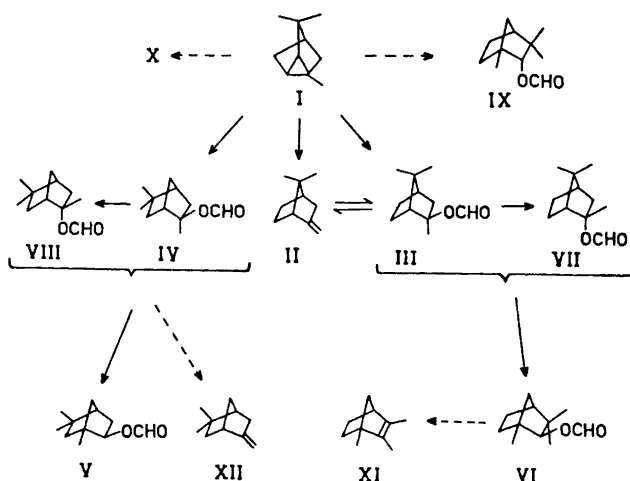
Scheme 1.

kov-addition reactions. Reasonable first structures formed from I might be the edge-protonated cyclopropanes,[6] "C-cyclofenchonium ions",[7] XIII and XIV. These ions closely resemble intermediate (S_N1 type) structures, which form the products II, III, and IV by random collisions with formic acid molecules through "disorganized transition states". Addition of formic acid to α-fenchene (II) seems to be more synchronous; perhaps an ion-pair transition state with a fixed structure is formed. The considerable exo-preference of the product (IV as sole or major product) gives some justification for a partially σ-bond-delocalised structure XV as the cation part of the transition state. This structure is analogous to the partially delocalised 2-methylnorbornonium ion (XVI), experimentally deduced by Paasivirta[8] and by Olah et al.[7,9,10]
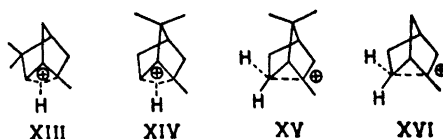
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