of direct methods using the weighted phase-sum formula.[7] Several cycles of full-matrix least-squares refinement (only isotropic non-hydrogen atoms included) gave an R-value of 0.136. The molecular structure is shown in Fig. 1. Intramolecular distances and angles are listed in Table 1. Full details

Table 1. Intramolecular distances and angles. Estimated standard deviations in parentheses.

C(1)−C(2)	1.50(3) Å	C(1)−C(2)−C(3)	108(2)°
C(2)−C(3)	1.57(3)	C(2)−C(3)−C(4)	118(2)
C(3)−C(4)	1.41(4)	C(3)−C(4)−C(5)	100(2)
C(4)−C(5)	1.56(3)	C(4)−C(5)−O(5)	109(2)
C(5)−C(6)	1.53(4)	C(5)−O(5)−C(1)	116(2)
C(1)−O(1)	1.38(2)	O(5)−C(1)−C(2)	116(2)
C(2)−O(2)	1.50(2)	C(1)−O(1)−C(7)	115(2)
C(3)−O(3)	1.50(3)	O(1)−C(1)−C(2)	108(2)
C(4)−O(4)	1.46(3)	O(1)−C(1)−O(5)	108(2)
C(5)−O(5)	1.49(2)	C(1)−C(2)−O(2)	108(2)
C(1)−O(5)	1.40(3)	O(2)−C(2)−C(3)	103(2)
C(6)−O(3)	1.44(3)	C(2)−C(3)−O(3)	104(2)
C(7)−O(1)	1.47(3)	C(3)−C(3)−C(4)	104(2)
		C(3)−C(4)−O(4)	120(2)
		O(4)−C(4)−C(5)	111(2)
		C(4)−C(5)−C(6)	97(2)
		C(6)−C(5)−O(5)	111(2)
		C(3)−O(3)−C(6)	105(2)
		O(3)−C(6)−C(5)	107(2)

of the X-ray diffraction investigation wil be published elsewhere.

As expected, the distance between O-2 and O-4 is short, 2.76 Å, in accordance with the observed chemical properties. Furthermore, although the hydrogens have not been located, the packing of the molecules would suggest an intramolecular hydrogen bond between O-2 and O-4 in the crystalline state.

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Stereoselective Cyclopropane Ring Opening Reactions of Nortricyclene Hydrocarbons in Formic Acid I. Reactions of Nortricyclene, Norbornene and Tricyclene

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During the study of the stereochemistry of the nortricyclene compounds and their cyclopropane ring opening products in our laboratory, the course of the reactions of nortricyclene hydrocarbons in formic acid has been examined.[1,2] The protonation of the cyclopropane ring in this system apparently leads to the same cationic intermediates as are found in the SN_1 solvolyses and E_1 eliminations of 2-norbornyl derivatives.[3,4] The aim in the present series is to connect kinetic data with the intermediate and final product analysis.

The addition of formic acid to nortricyclene (I) or norbornene (III) has nor-bornyl-2-*exo*-formate (II) as the sole main product.[5,6] This was confirmed in the present study. The hydrocarbon III from I, or I from III, occurred as a minor side product of the reaction, leading to the following overall picture:
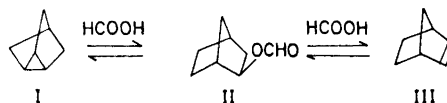

Only one ester product, isobornyl formate (V), was found from tricyclene (IV); the only hydrocarbon byproduct present

Table 1. The first-order rate coefficients and Arrhenius parameters of the reactions of nortricyclene (I), norbornene (III), and tricyclene (IV) in formic acid-methylene chloride 1:1 mixture.

Compound	Temp. °C	$k \times 10^5$ sec^{-1}	E kcal/mol	log A	Corr. factor R
I	0.	0.330			
	14.9	1.936			
	22.8	3.229	18.10 ± 1.20	8.98 ± 0.90	-0.9957
	40.0	24.99			
III	14.9	0.791			
	22.8	2.100			
	30.0	3.714	21.44 ± 1.59	11.13 ± 1.15	-0.9918
	35.5[a]	8.908			
	40.0	17.32			
IV	0.	0.594			
	26.0	7.281	15.93 ± 0.31	7.52 ± 0.23	-0.9998
	37.2	20.34			

[a] Rate determination by NMR.[1] The other measurements were made by gas chromatography.

was bornylene (VI). The absence of camphene (IX) and the camphene hydrate formates (VII and VIII) in the reactions mixture was confirmed by gas chromatography using authentic reference samples. The formation of tertiary intermediate products was prevented possibly because of steric repulsions hindering the attack of the nucleophile (HCOO⁻ or HCOOH).
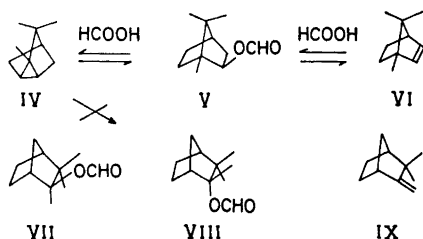
The reaction rates were difficult to determine in pure formic acid owing to the slow solubility of the hydrocarbons I, III, and IV. However, the hydrocarbons dissolved quickly when a formic acid-methylene chloride 1:1 (w/w) mixture was used. Methylene chloride retarded the reaction rates, but did not influence the product ratios. The mixture was taken for general use in this series. The reactions were followed

mainly by gas chromatography, and in some cases also with NMR spectrometry.[1]

The rate coefficients and Arrhenius parameters obtained are collected in Table 1. The termodynamic data of activation at 25 and 105°C were calculated using the theory of absolute reaction rates and are collected in Table 2.
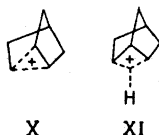
The free energy difference between nortricyclene (I) and norbornene (III) is small; 0.9 kcal/mol at 105°C according to Schleyer.[7] The closely similar values of the free energies of activation for the reactions of I and III (see Table 2) thus indicate that both reactions proceed through equivalent transition states to the same product, II. Such a transition state is formed from an intermediate carbonium ion, the structure of which could also be presented as being the same from both I and III. This interpretation is supported by the distribution of deuterium in the products of DX additions to I and III,[8,9] and in the products of different electrophilic additions to 5,6-dideuterionorbornenes.[10] The intermediate is to be "asymmetrically bridged": either the nonclassical 6-norbornonium ion (X) [1,11,12] or an equilibrium mixture of classical 2-norbornyl cations.[13,14] This intermediate involves the Wagner-Meerwein rearrangement. The nonclassical structure X has additionally been supported by spectral studies from superacid solutions at low tempera-

Table 2. Thermodynamic parameters for the reactions of nortricyclene (I), norbornene (III), and tricyclene (IV) with formic acid calculated from the results of the kinetic measurements.

Reaction	Temp. °C	ΔH^* kcal/mol	ΔS^* cal/degr. mol	ΔG^* kcal/mol
I in formic acid-CH_2Cl_2	25	17.51	-19.41	23.30
III in formic acid-CH_2Cl_2	105	17.35	-19.89	24.87
	25	20.84	-9.57	23.70
III in pure formic acid [a]	105	20.68	-10.04	24.48
	25	14.17	-25.35	21.73
IV in formic acid-CH_2Cl_2	105	14.01	-25.82	23.78
	25	15.34	-26.11	23.13
	105	15.18	-26.58	25.23

[a] Calculated from the data in Table 5 of Ref. 1. The other results are calculated from the data in Table 1 of the present paper.

tures.[15,16] Another intermediate, C-nortricyclonium ion (XI),[12] which is somewhat less stable than X, might be the route of 1,2,6-hydrogen shifts during the reactions if the conditions allow the cations a longer lifetime. The cyclopropane ring opening, of I and IV could also, at least partly, proceed via this XI-type of edge-protonated nortricyclene structure.

X   XI

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