Some Stereoselective Reactions of Norbornene and Norbornane Compounds in Formic Acid

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The reactions of norbornene and a number of norbornenols and norbornanols and their formic esters in formic acid have been studied by performing product analyses and by measuring their rates. Gas chromatography and proton resonance spectroscopy were employed to follow the reactions.

The rearrangements of bicyclic bridge compounds have been extensively studied to expose the role of nonclassical carbonium ions in these reactions. Formic acid seemed to be a suitable medium for these reactions as it is a solvent of moderate acidity and nucleophilicity and for this reason its use as a solvent was expected to contribute experimental data that would supplement the already existing body of data on the formation of bridged carbonium ions.

In an earlier study[1] it was found that the secondary bicyclic alcohols I—IV react in formic acid at 20° at approximately equal rates to give only the unrearranged formates V—VIII. The reactions in question are hence esterifications that proceed by the general mechanism involving acyl carbon-oxygen fission.[2]
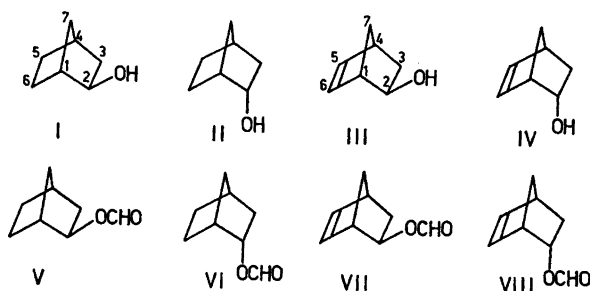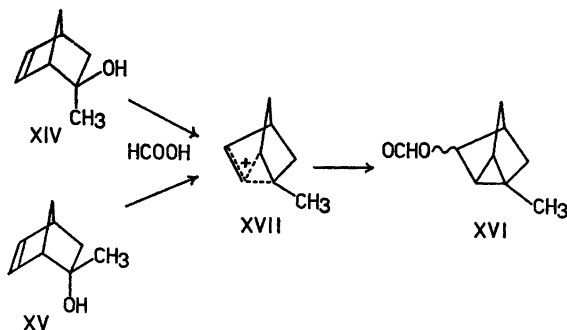
The methyl groups on carbon atom 2 in the bicyclic tertiary alcohols IX, X, XIV and XV have a stabilizing effect on the carbonium ions [3] formed in reactions of these alcohols and hence the reactions of these compounds in formic acid would be expected to differ from the reactions of the bicyclic secondary alcohols in such a way that the formation of the carbonium ions would lead to both unrearranged and rearranged products. The formation of a carbonium ion is also very common in solvolytic reactions and acid-catalysed reactions of secondary bicyclic esters and the corresponding hydrocarbons. The frequently observed large differences in the rates of the exo and endo isomers of these compounds have been attributed to steric,[4] electronic,[5] and torsion [6] effects.

Analysis of the products of the reactions of the saturated tertiary alcohols IX and X in formic acid [1] showed that the intermediates are the unrearranged formates XI and XII. Up to the formation of these intermediates, the reactions appear to be analogous with the reactions of the secondary alcohols I and II, but as the final product is the rearranged ester XIII and the rate of reaction of the exo form IX is much higher than that of the endo isomer ($k_{exo}:k_{endo}=5800$ at 10°C), the reactions evidently proceed by way of the carbonium ions.
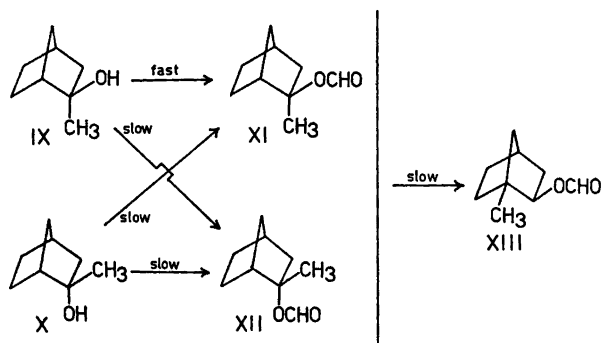

Unsaturated tertiary alcohols XIV and XV differ from the corresponding saturated alcohols in their reactions in formic acid,[7] for both are converted to the same tricyclic formate XVI. The product is a mixture of two stereo-

isomers, α- and β-1-methylnortricyclyl-3 formate. The ratio of the products was the same (ratio of α-form to β-form 2:1) in the reactions of both isomers XIV and XV;[7] this result was confirmed by gas chromatography in the present study. Hence the homoallyl rearrangements of the alcohols XIV and XV in formic acid are without doubt carbonium ion reactions which involve the same intermediate, the symmetric cation XVII, or two asymmetric homoallyl cations that are in dynamic equilibrium.[8]

A point of comparison is provided by the reaction of norbornene (XVIII) in formic acid which gives exclusively exo-norbornyl formate (V).[9] The present author found that, in contrast to the reactions of the alcohols III and IV and the formates VII and VIII in the same conditions, this reaction is fast already at 20°.
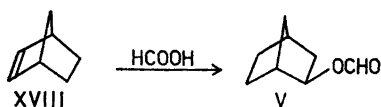
It was obvious from the preceding that much interesting information on the formation of carbonium ions can be obtained by studying the reactions of exo- and endo-norbornenyl formates (VII and VIII) in formic acid at elevated temperatures. The product ratios should reveal whether the reactions are exo-additions to the double bond as in the case of norbornene (XVIII) or homoallyl rearrangements as in the case of the tertiary alcohols XIV and XV. Kinetic studies were expected to clarify the factors that influence the reactions and possibly the nature of the various intermediates.

EXPERIMENTAL

Chemicals

Formic acid (98—100 %, guaranteed reagent from E. Merck AG) was found by Karl Fischer titration to contain about one mole of water per litre.

The preparation and properties of the *alcohols* I—IV, IX, X, XIV and XV and the *formates* VII, VIII, IX and XII have been described earlier.[1,5,7,9—14]

Norbornene (XVIII) was a product from Aldrich Chemical Co., which was purified by sublimation.

Nortricyclyl formate (XXIV), whose study proved necessary as it was formed as an intermediate in the reaction of exo-norbornenyl formate (VII) (see results and discussion below), was isolated by preparative gas chromatography from the products (30 % VII and 70 % XXIV) of the reaction of norbornadiene with formic acid.[15] The gas chromatograph was an AEROGRAPH AUTOPREP A 700, the column a standard SE-30 column 3/8″ in diameter, and the carrier gas helium. The isolated ester had a refraction index n_D^{20} of 1.4740, a density d_4^{20} of 1.1121 and hence a molar refraction R_D of 34.85 (calc. 34.94).

Measurement of reaction rates and product ratio analyses by gas chromatography

Kinetic experiments. In a typical experiment 0.3 mmole of the compound under study (I—IV, VII—XII, XIV, XV, or XXIV) was dissolved in 1 ml of formic acid in a constant temperature bath. After a certain period of time, the reaction was arrested by pouring the mixture into an excess of 10 % potassium carbonate solution and mixing.

The mixture was extracted three times with ether and the combined ether layers were dried with potassium carbonate. The ether layer was filtered, the filtrate evaporated to a small volume and a fraction analysed by gas chromatography. For preparative product studies,[16] the amounts of reactants taken were larger, but their ratios were the same as above. Norbornene (XVIII) dissolved in formic acid so slowly and reacted so rapidly already at room temperature that the preceding method could not be used. The purity of the product, exo-norbornyl formate (V), was, however, confirmed by the same method, employing temperatures up to 100° (boiling water bath) and reaction periods up to 2 days.

Gas chromatographic analyses. Some of the gas chromatographic analyses were performed as described previously [1] at the University of Oulu, but most of the analyses at University of Turku on a Perkin-Elmer model 800 gas chromatograph equipped with a 3-metre-long column (inside diameter 1/8″) filled with Chromosorb W (60/80 mesh) containing 10 % Versamid 900 and employing nitrogen as carrier gas and a two-channel hydrogen flame ionisation detector. Most of the analyses were run isothermally, but for comparison several analyses were run with a programmed linear temperature rise.

The isolation and identification of the intermediates XI, XII, α-XVI and β-XVI have been described earlier.[1,7] Nortricyclyl formate XXIV was isolated from the products of the reaction of exo-norbornenyl formate (VII) by preparative gas chromatography as described above and identified by infrared spectrometry.

In the evaluation of the first-order rate coefficients, it was assumed that the ratio (c) of the area of the peak of the initial reactant to the sum of the areas of the peaks of the initial reactant and the products is directly proportional to the concentration of the initial reactant. The response of the hydrogen flame ionisation detector is not a linear function of the numbers of molecules of the various compounds, but as the products studied were either single compounds or mixtures of isomers, no marked deviations from linearity were expected. This was confirmed by experiment, for a linear plot was obtained, as previously,[1] when the logarithm of the ratio c was plotted against time t. The reactions were hence of pseudo first order. The rate coefficient was calculated from the equation

$$k = 2.303 \times \Delta \log c / \Delta t$$

by the method of least squares; also the standard error of the mean rate coefficient was evaluated (for an example, see Table 1). The results at several temperatures are collected in Tables 3—5. Values of the activation energy (E), frequency factor (log A) and activation entropy (ΔS_{298}^*) at 25°C evaluated by the method of least squares for the reactions

Table 1. Evaluation of the rate coefficient k from peak areas in gas chromatograms recorded during the reaction of endo-norbornenyl formate (VIII) in formic acid at 50°. Calculation of the regression line $y = mx + b$ was performed by the method of least squares.

(x) Time (t) sec × 10⁻³	(c) Relative concentration of ester	(y) log c
0.0	100.0	2.000
1.8	94.3	1.975
6.9	86.8	1.939
9.9	83.9	1.922
13.2	77.7	1.890
18.3	71.2	1.853
23.4	64.3	1.808
28.8	60.8	1.784
88.2	23.0	1.362

$m = -0.0071453 \pm 0.0000855$
$b = 1.988242$
$k = -2.303m \times 10^{-3}$ and hence $k = (1.644 \pm 0.020) \times 10^{-5}$ sec⁻¹.
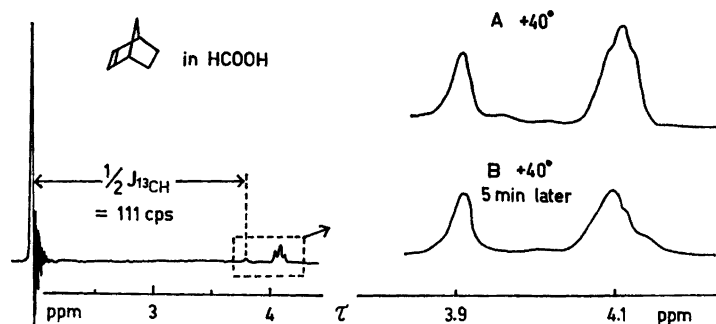
Fig. 1. Part of the proton resonance spectrum of a solution of norbornene in formic acid. The reaction was followed by recording the expanded section of the spectrum at intervals. To facilitate the measurement of the peak areas by planimetry, the resolution was slightly impaired by shifting the y gradient control.

of the compounds are also given in Tables 3—5. The error estimates given are standard errors except when the data related to only three temperatures; in the latter cases the estimates were obtained graphically from straight lines drawn through the data points plus or minus one standard deviation.

The use of proton resonance spectrometry to follow the reactions

The rate of the reaction of norbornene (XVIII) in formic acid was determined by proton resonance spectrometry (Fig. 1). The internal standard was the ^{13}C sideband ($\tau = 3.92$ ppm at 60 Mc) of the solvent CH peak; the coupling constant is exceptionally high in value ($J^{13}_{CH} = 222$ cps, see Ref. 17). Thus the high field ^{13}C sideband of the solvent lies close to the signal ($\tau = 4.07$ ppm) of the double bond protons of norbornene.[10] The concentration of norbornene in the solution can be calculated from the ratio of the signal of double bond protons to the area of the mentioned sideband (which latter thus functions as the internal standard). The same method was employed to measure the rates of the reactions of the formates VII and VIII in formic acid (Fig. 2). Although in these cases the sideband peak of the solvent which was employed as the internal standard
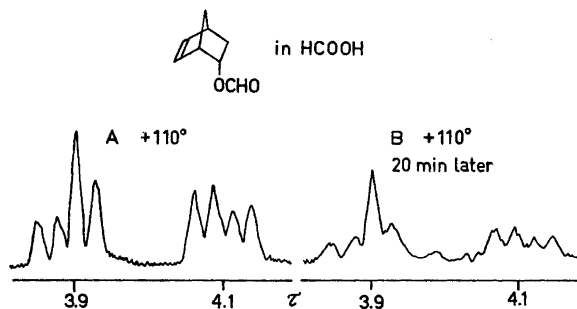

Fig. 2. The progress of the reaction of endo-norbornenyl formate (VIII) in formic acid as revealed by proton resonance spectrometry.

Table 2. Evaluation of the rate coefficient k for the reaction of endo-norbornenyl formate (VIII) in formic acid at 110°C from signal areas in proton resonance spectra recorded at intervals. a6=area of the signal at 3.9 ppm, a5=area of the signal at 4.09 ppm (see Fig. 2), $c=a5/(a6-a5)$.

(x) t, sec.	a6	a5	c	(y) log 10c
0	234	214	10.71	2.030
90	198	177	8.43	1.926
180	190	141	2.88	1.459
300	180	118	1.90	1.280
420	132	113	5.95	1.774
600	110	70	1.75	1.244
780	106	51	0.927	0.967
900	81	44	1.190	1.076

$$y= -(0.00103\pm0.00022)x+1.890521 \quad \text{and hence} \quad k=(232\pm50)\times10^{-5} \text{ sec}^{-1}.$$

overlapped with the signal of the double bond proton attached to carbon 6 ($\tau=3.9$ ppm),[10] a figure proportional to the concentration of the ester was obtained by dividing the area of the signal of the hydrogen atom on carbon 5 ($\tau=4.09$ ppm)[10] by the difference between the areas of the 3.9 and 4.09 signals.

Performance of the kinetic experiments. A 2—5 % solution of each compound (VII, VIII, or XVIII) in formic acid was prepared at +10°C. One millilitre of this solution was transferred to the variable temperature probe of the NMR spectrometer, a high resolution model VARIAN A-60 at the University of Oulu. As judged from the calibration spectra of pure methanol and ethylene glycol samples, the temperature remained constant within one centigrade degree. The part of the spectrum recorded was that between the signals of the ^{13}C sideband (internal reference) and the double bond hydrogen atoms (see Figs. 1 and 2) and the sweep velocity was 4 cps per second. The spectrum was recorded starting from the same point each time. The time between the recordings could be measured to the nearest second. Electronic integration could not be used owing to the low substrate concentration and for this reason the areas of the signals were measured by planimetry. Values of the quantity c proportional to the concentration of the initial reactant were estimated from the areas. The plots of the logarithms of this quantity against time (t) were straight lines. Values of the rate coefficients k were calculated by the method of least squares.

RESULTS AND DISCUSSION

The rate coefficients of the studied reactions and the parameters of the Arrhenius equation derived from these are shown together with their standard errors in Tables 3—5. Analytical data for the products of the reactions of the formates VII and VIII and the deduced structures of these products are presented in another publication.[16]

The reactions of norbornanols and norbornenols. As found previously,[1] the products of the reactions of the secondary alcohols I—IV in formic acid are the unrearranged formates V—VIII and the rate coefficients of the reactions at 20° are approximately equal. To confirm this finding, the author measured the rates of reaction of the norbornenols III and IV in formic acid at several temperatures and calculated the values of the Arrhenius parameters (Table 3).

Table 3. The first-order rate coefficients and Arrhenius parameters of the reactions of norbornanols and norbornenols in formic acid as determined by gas chromatography.

| Reactant	Product	Temp. °C	$k \times 10^5$, sec^{-1}	E kcal/mole	$\log A$	ΔS_{298}^{*} cal/degr.mole
I	V	20	169 ±15			
II	VI	20	219 ±15			
III	VII	10	82.2± 8.3			
		20	143 ±14	11.09±0.57	10.45±0.48	−12.7±2.2
		30	303 ±30			
IV	VIII	10	79.0± 7.9			
		20	152 ±15	11.58±0.59	10.83±0.48	−11.0±2.2
		30	314 ±30			

The similarity of the data shows that a double bond has no influence on the courses of the reactions of either the exo or the endo configurations. This is understandable if the esterification involves acyl-oxygen bond fission following a collision of an alcohol and a formic acid molecule. It can be concluded from molecular models that the various carbon-hydrogen orbitals at carbons 6 and 7 do not appreciably hinder the approach of a formic acid molecule towards the hydroxyl group in alcohols I—IV.

Tertiary norbornanols. On the basis of product ratios [1] (see introduction above) and the kinetic data (Table 4), two alternative mechanisms may be proposed for the reactions of the tertiary norbornanols IX and X in formic acid. The first alternative, which seems more plausible, involves the formation of mesomeric nonclassical cations [5] as intermediates or transition states con-

Table 4. The first-order rate coefficients and Arrhenius parameters of the reactions of tertiary norbornanols and norbornenols and, for comparison, formates XI and XII in formic acid. The rates were determined by gas chromatographic analyses.

| Reactant	Temp. °C	$k \times 10^5$, sec^{-1}	E kcal/mole	$\log A^a$	ΔS_{298}^{*} cal/degr.mole
IX	10	52600 ±3000			
X	10	9.04± 0.8			
	20	28.5 ± 3.0	21.9±0.6	12.85±0.40	−1.7±1.8
	30	113 ± 5			
	40	364 ± 12			
XI	20	14.8 ± 1.1			
XII	20	14.4 ± 1.6			
XIV	10	401 ± 30			
	20	1480 ± 70	18.7±1.0	12.01±0.73	−5.6±3.3
	30	3560 ± 300			
XV	20	7.05± 0.50			
	30	25.5 ± 2.0	20.4±0.8	11.08±0.55	−9.8±2.5
	40	66.2 ± 14			

[a] The erroneous values of $\log A$ and ΔS^{*} given in the earlier paper[1] for X, XIV, and XV are here corrected.
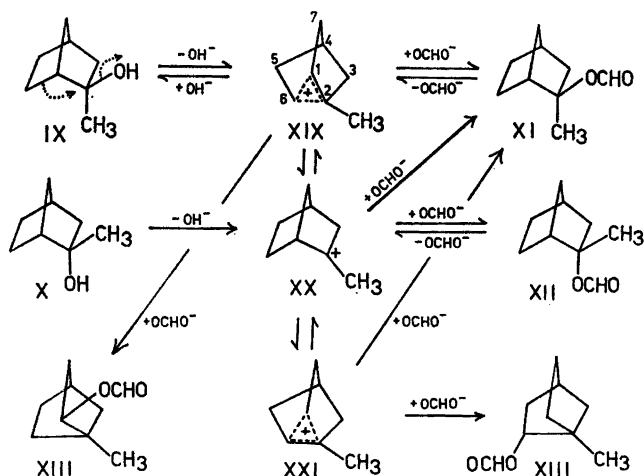
taining "nonclassically" delocalised bonding orbitals (see below). This alternative is visualised below by presenting nonclassical cations XIX and XXI in the scheme; these cations should be considered as parts of ion pair intermediates.[5]

The conversion of the alcohol IX to its formate XI in formic acid and the reverse reaction were so rapid that the rate of the former reaction could be measured only at 10°C. The product ratio (IX:XI) was found to be 0.1. This equilibrium reaction is explained by assuming the formation of the nonclassical intermediate XIX. The displacement of the hydroxyl or formyl group is anchimerically accelerated by the participation of the σ orbital electrons between the carbon atoms 6 and 1: the vacant p orbital of carbon 2 that could be formed by the liberation of the exo-substituent is in a spatially more favourable position so that the mentioned σ orbital overlaps this p orbital without any greater changes in the bond angles.[5,18] This anchimeric participation is indicated by the dotted arrows in the figure. The formation of the cation XIX also explains the stereospecificity of the rapid formation of the product XI; the possible approach of the formate ion to the cation from the endo direction is hindered. The positive charge in such a cation is unevenly distributed with the greater part of the charge on the tertiary carbon 2. Hence the only rapidly formed formate is the tertiary exo ester XI.

The other alternative mechanism is one in which the reaction proceeds solely through a series of classical cations, whereupon the formation of the final product XIII presupposes the transient existence of a classical secondary cation in equilibrium with the tertiary cation XX.
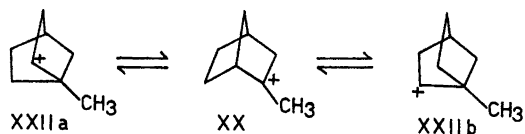
The large differences in the rates of reaction of endo and exo isomers in such cases has been attributed, for example, to the greater steric hindrance offered by the electrons of carbon 6 to the release of the endo-2-substituent compared with the steric hindrance offered by the electrons of carbon 7 to the release of the exo-2-substituent [4] or to the different repulsive actions of these electrons on the methyl group at carbon 2.[18] A third possibility that has recently been proposed [6] is a torsion effect. The stereospecificity of the secondary final product XIII may also be explained by this torsion effect or a so called windshield-wiper effect [4] due to a rapid equilibrium between the cations XXIIa and XXIIb. The author is, however, of the opinion that the formation of classical cations cannot satisfactorily explain the rapid formation of the tertiary exo-formate XI from the exo alcohol XI in formic acid.

The results of the present study do not make it possible to decide conclusively whether nonclassical cationic structures are intermediates in the reactions under discussion. As pointed out by Hückel,[19] collection of more experimental data by determining the total energies of cations of the different types should make it possible to decide whether some nonclassical structure between the classical cations like XX and XXII has a lower energy than the latter. It has been shown by calculations that such a resonance stabilisation is possible in nonclassical norbornyl cations.[18] For this reason, when discussing other reactions below, the author will present only one of the two alternatives, the mesomeric structure, without forgetting that a dynamic equilibrium between classical cations that represent limiting forms of this nonclassical cation may be involved. The Wagner-Meerwein rearrangements and hydride shifts that are discussed are described in a simplified manner (omitting structures of ion pairs, etc.) as taking place by way of certain nonclassical cations analogously as was done recently by Berson et al.[20]

Tertiary norbornenols. The kinetic data in Table 4 confirm the conclusion already drawn from the results of product analyses (see introduction, p. 2201) that 2-methyl-2-norbornenols XIV and XV obviously react in formic acid by a carbonium ion mechanism. The rates of these two isomers, the ratio of which is 210 at 20°, shows that the reaction of the exo form (XIV) is accelerated
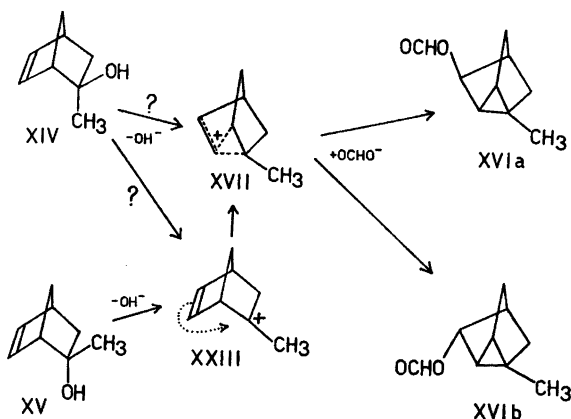
relative to that of the endo form (XV), although the difference in the rates is much smaller than the difference in the rates of the saturated isomers IX and X.

In addition to the homoallyl cation (*e.g.* XVII) discussed in the introduction to this paper, there may also be formed in the reactions of tertiary norbornenols XIV and XV a classical tertiary cation XXIII, either as an intermediate (part of an ion pair) or as the reaction centre of a transition complex. The latter cation is obviously an intermediate in at least the reaction of the endo alcohol XV because the rate of the latter reaction is of the same order of magnitude as the rate of the saturated alcohol X with the same configuration. Evidently the double bond is not involved in the displacement of the hydroxide ion from the alcohol XV and the classical ion XXIII (if not the formate of XIV) is the obvious product of the displacement. The next stage in the reaction of the alcohol XV in formic acid is hence the rearrangement of this first intermediate (*e.g.* XXIII) to the homoallyl cation (*e.g.* XVII).

A more difficult matter is to decide whether the classical cation XXIII is an intermediate in the reaction of the unsaturated tertiary exo alcohol XIV in formic acid. The steric hindrance offered by the double bond to the displacement of the endo hydroxide ion, the repulsion between the double bond and the endo methyl group and possible torsion effects could be responsible for the higher rate of reaction of the exo form and the reaction may then involve the sole formation of the cation XXIII. However, the anchimeric participation of the π electrons in the displacement of the hydroxide ion from the alcohol XIV, which leads directly to the formation of homoallyl cation, offers a simpler course for the reaction.

The high stabilities of homoallyl cations [7,21] and a shift of the positive charge to the carbon 5 are indicated by the conversion of the alcohols XIV and XV to products (monoformates), which do not include unrearranged tertiary esters similar to XI and XII, but exclusively the *trans* (XVI a) and *cis* (XVI b) forms of 1-methylnortricyclyl-3 formate in the same molar ratio (2:1). The identical product ratio in the two cases also confirms that the same intermediate (*e.g.* XVII) is formed in the reactions of the two alcohols.

At higher temperatures, the tricyclic products XVI a and XVI b react further to form diformates, a diol corresponding to one of which was isolated and identified earlier by this author.[7] The proportions and structures of the diformates formed in these reactions are under study.

Norbornene and secondary norbornenyl formates. The participation of a double bond in reactions in formic acid similar to those discussed above became evident when the secondary formates VII and VIII were allowed to react in formic acid at higher temperatures (50—130°). It also became evident, however, in a study of the intermediates formed that the exo and endo forms react by different mechanisms. The intermediate formed from the exo formate VII was nortricyclyl formate (XXIV), but the latter was not found among the products of the reaction of the endo formate VIII.

It has been found [16] that three main products, diformates XXV, XXVI, and XXVII, are formed from the exo formate VII and also from the intermediate XXIV, whereas only two main products, XXVI and XXVII, are formed directly from the endo formate VIII. The corresponding diols and
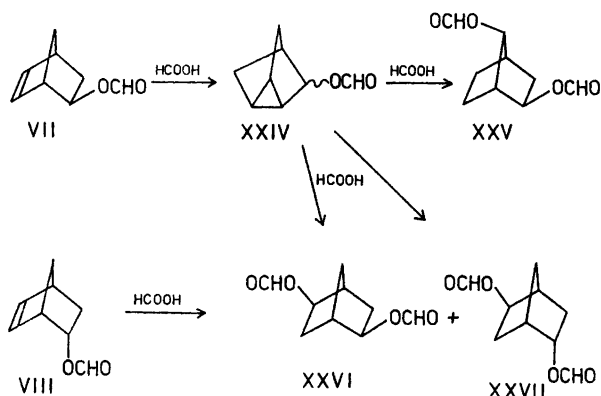
their infrared spectra have been described.[22-24] Thus homoallyl rearrangement does not take place when the endo formate VIII reacts in formic acid. The reaction is hence a simple addition of formic acid to the double bond. An

Table 5. The first-order rate coefficients and Arrhenius parameters of the reactions of norbornene (XVIII), secondary exo- and endo-norbornenyl formates (VII and VIII), and nortricyclyl formate (XXIV) in formic acid. The rates were determined either by gas chromatography (GLC) or by proton resonance spectrometry (NMR).

React- ant	Temp. °C	Meth- od	$k \times 10^5$, sec^{-1}	E kcal/mole	log A	ΔS_{298}* cal/degr.mole
XVIII	2.5	NMR	11.66 ± 2.36			
	20	NMR	46.7 ± 1.9			
	27.5	NMR	64.3 ± 6.5	14.72 ± 0.49	7.66 ± 0.35	−25.5 ± 1.6
	40	NMR	233.0 ± 18.6			
	50	NMR	471.2 ± 21.6			
	60	NMR	1266 ± 42			
VII	50	GLC	1.03 ± 0.11			
	69.5	GLC	15.5 ± 1.6			
	90	NMR	75.9 ± 5.2	20.1 ± 0.59	9.01 ± 0.48	−19.3 ± 2.2
	100	GLC	232 ± 20			
	110	NMR	344 ± 35			
	126	NMR	966 ± 166			
VIII	50	GLC	1.64 ± 0.02			
	69.5	GLC	13.4 ± 1.3			
	90	NMR	40.6 ± 5.9	18.42 ± 0.95	7.73 ± 0.57	−25.1 ± 2.6
	93	NMR	55.0 ± 21.7			
	103	NMR	75.3 ± 28.8			
	110	NMR	237 ± 50			
	126	NMR	427 ± 50			
XXIV	40	GLC	0.362 ± 0.013			
	50	GLC	0.508 ± 0.042	21.87 ± 0.97	9.68 ± 0.96	−16.2 ± 4.4
	60	GLC	1.99 ± 0.25			
	70	GLC	7.12 ± 0.32			

$\log k \times 10^5$ OCHO in HCOOH
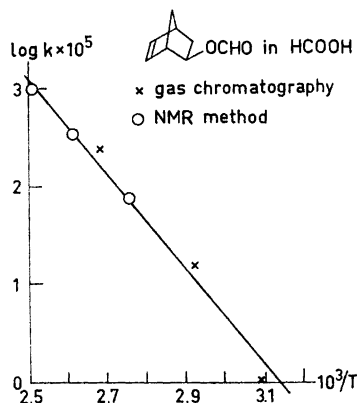
× gas chromatography

○ NMR method

Fig. 3. The temperature dependence of the rate of reaction of exo-norbornenyl formate (VII) in formic acid as determined by NMR (○) and GLC (×). Plot of log $k \times 10^5$ against $10^3/T$ (see Table 5).

analogous reaction is the reaction of norbornene (XVIII) in formic acid (see introduction) which leads to exo-norbornyl formate exclusively.[9]

The rate coefficients determined by gas chromatographic and proton resonance measurements at different temperatures (Table 5) proved to be consistent (Fig. 3). On the basis of these values and the product ratios, a number of comparisons are possible.

The reaction of endo-norbornenyl formate (VIII) with formic acid is much slower than the reaction of norbornene (XVIII). However, the products of both reactions have analogous structures (see below). The kinetic data (Table 5) show that the lower rate of the former reaction is due to a higher activation energy, the frequency factors of the two reactions being nearly equal. It may be concluded that the reaction of the ester VIII is retarded solely by a polar effect,[23] which obviously is the electron-withdrawing effect of the formyl group. As far as the stages leading to the products are concerned, the reactions can be considered identical. The products of the reaction of the ester VIII are analogous with the products found by Krieger [24] to be formed in the reaction of endo-norbornenyl acetate in the Bertram-Walbaum solution, but the product ratio XXVI:XXVII is unity.[16] On this basis the intermediates of the addition reactions of formic acid to the double bonds of XVIII or VIII have analogous structures; they may be, for example, nonclassical carbonium ions XXVIII and XXIX (or a dynamic equilibrium mixture of classical norbornyl ions corresponding to their limiting structures):

XVIII $\xrightarrow{+H^+}$ XXVIII $\xrightarrow[+OCHO^-]{1}$ OCHO   V

$\xrightarrow[+OCHO^-]{2}$ OCHO   V
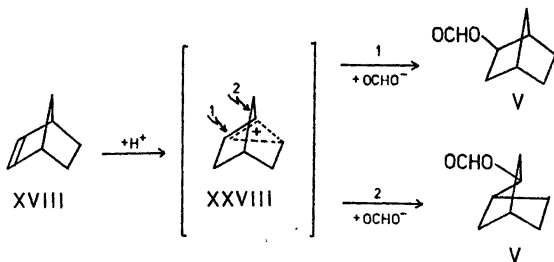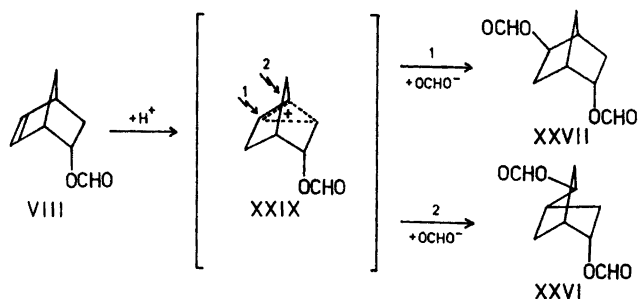
The exo formate VII reacts in formic acid by quite a different mechanism, for it undergoes rearrangement to nortricyclyl formate (XXIV). The intermediate in this homoallyl rearrangement may be taken to be the cation XXX.
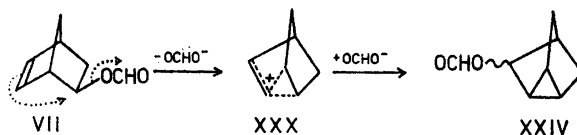
This reaction also involves anchimeric participation (dotted arrows) of the electrons of the double bond which facilitates the liberation of the formate ion with the simultaneous formation of the homoallyl ion (*e.g.* XXX). In this case the kinetic data do not reveal that the exo form is more reactive than the endo form (Table 5). This is understandable because the endo form VIII reacts by a different route; its double bond must take up a proton and no homoallyl ion like XXX can form.

Nortricyclyl formate (XXIV) was found to be an intermediate in the reaction of the ester VII, because the mixture of diformates formed when it reacted with formic acid was identical in composition with the mixture produced [16] from the ester VII.

A similar difference in the courses of reactions of unsaturated exo and endo isomers was observed by Lewis and Whitman [26] in the acetolysis of bicyclo[3.2.0]heptenyl-2-toluenesulfonates. They likewise established that only the exo compound reacts by way of the homoallyl ion.

The further reaction of nortricyclyl formate is, as far as the reaction products are concerned, analogous to the Bertram-Walbaum reaction of nortricyclyl-3 acetate studied by Krieger;[24] only the ratio of the products is different.[16] The overall reaction can in the opinion of this writer be represented by a scheme in which three different nonclassical carbonium ions XXXI— XXXIII (or equilibrium mixtures of classical formyl-norbornyl ions) occur as intermediates.

In this reaction scheme all the diformates produced are considered to have been formed by exo addition of formate ion to carbonium ions, in agreement with other data and the results of earlier studies [16,24,27] of the fission of three-membered rings in nortricyclene compounds in the presence of acids. According to the scheme, only the addition of a formate ion to the cation XXXIII,
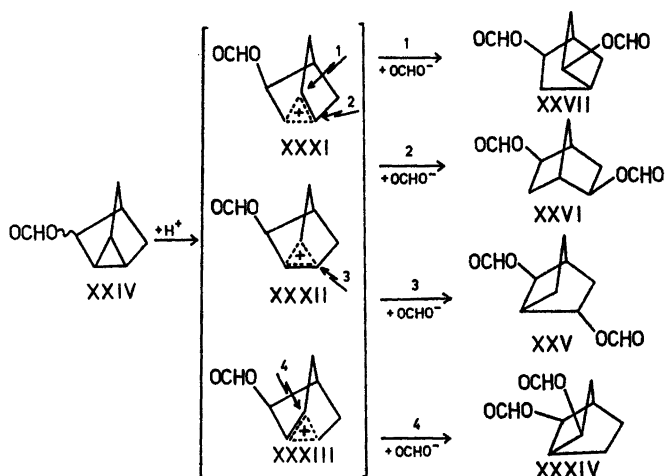
designated by number 4, is sterically hindered by the already existing formyl group. Thus it is readily understandable that exo-2-syn-7-norbornane diformate (XXXIV) does not occur to any appreciable extent among the products of the reactions of esters VII and XXIV.[16] However, XXXIV is formed in appreciable amounts when norbornene (XVIII) is treated with performic acid,[22,23] but in this case the reaction is a different one as the exo-2-syn-7-diester could be formed by way of an epoxide.[24]

To summarize, it may be said that in the case of all the isomer pairs studied a hydroxyl or formate group is much more readily removed when it is in the exo position than when it is in the endo position. With tertiary compounds this is observed as a greater reactivity of the exo isomer. In the case of second-
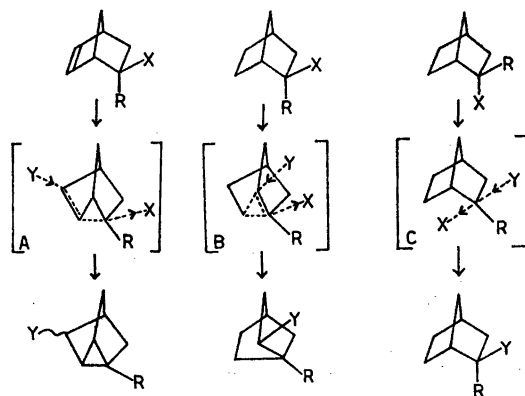

Fig. 4. Bimolecular mechanism as a possible explanation for some products formed in reactions of exo-2-norbornene and exo- and endo-2-norbornane compounds in formic acid. R=H or CH$_3$. X=OH or OCHO. Y=OCHO. X and Y may be protonated. The delocalisation of bonding orbitals is "nonclassical" in the transition states A and B and "classical" in the transition state C.

ary norbornenyl formates the removal takes place only from the exo form (VII) following homoallyl rearrangement, whereas the endo form (VIII) reacts, like norbornene (XVIII), by another mechanism. Several explanations can be proposed for the more facile displacement of the exo-2-substituent.[4–6,18] The formation of all final norbornane diformates can be taken to result from the addition of a formate ion to the formyl-norbornyl cations from the exo direction. These intermediate cations may be either nonclassical [5] (mesomeric) or classical [4,6] structures.

In some cases, a bimolecular mechanism (see Fig. 4) may be presented as another alternative. Then, transition states may contain delocalised bonding orbitals, which could represent nonclassical (A and B) or classical (C) structures. Although the kinetic data presented above are in accordance with unimolecular courses of the reactions, more advanced kinetic methods shall be applied to reach a final decision about their molecularity and mechanism.

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