Rearrangements of Pinane Derivatives. Part V.[1] The Influence on Rearrangements of a Neutral Nucleophile associated with the Carbonium Ion

By **Harvey Indyk** and **David Whittaker,*** The Robert Robinson Laboratories, University of Liverpool, P.O. Box 147, Liverpool L69 3BX

Comparison of the products of acid-catalysed rearrangements of the pinan-2-ols in aqueous dioxan and acetic acid has shown that in the latter solvent the water molecule generated in the alcohol heterolysis reaction has a strong influence on the products of rearrangement. The acid involved in the reaction is also important, perchloric acid being able to displace the water molecule and give rise to products typical of an intimate ion pair.

EARLY studies of carbonium ion rearrangements generally restricted consideration of ion pairing to internal return of the ions produced in ester ionisation, which yielded rearranged esters. More recently, ion pairing has been shown to play a more important role in solvolysis reactions than had been previously realised, and kinetic evidence of involvement of ion pairs in solvolyses reactions has been presented.[2] Consideration of the effects of ion pairing on products of rearrangement have, however, been largely neglected.

We have chosen the pinane system as a convenient vehicle to investigate the effects of ion pairing on the products of carbonium ion rearrangements. The pinanes show a wide range of possible rearrangement pathways, the general outlines of which are known from earlier work [3,4] and it has been shown in both these papers that solvolysis reactions of the system are affected by internal return. The effect of the counterion in solvolysis reactions is, however, sufficient to obscure lesser effects, so we have chosen to generate the ions by acid-catalysed olefin addition and alcohol heterolysis reactions. Previous studies of the former have shown ion pairing to have a strong influence on products.

Recent work by Shiner [5] has shown that in poor ionising solvents, addition of an unionised acid to an olefin gives rise to an intimate ion pair; reaction of an unionised acid with an alcohol gives an ion pair in which ion and counterion are separated by the water molecule produced in the heterolysis step. In a good ionising solvent, however, both reactions should proceed with ionised acid to yield similar, solvent separated ion pairs. We have used these observations to rationalise product variations.

EXPERIMENTAL

Materials were prepared, and reactions followed by the techniques described in earlier papers.[4,6] 2β,3,3-Trimethylnorbornan-2α-ol (methyl camphenilol) was prepared by the method of Hückel.[7]

RESULTS AND DISCUSSION

The acid-catalysed hydrations of pin-2-ene and pin-2(10)-ene follow first-order kinetics over at least two half lives of the reaction.

From the data in Table 1 we calculate: for pin-2-ene hydration, $\Delta H^* = 25{\cdot}9$ kcal mol^{-1} and $\Delta S^* = -3{\cdot}6$ cal mol^{-1} K^{-1}; for pin-2(10)-ene hydration, $\Delta H^* = 24{\cdot}8$ kcal mol^{-1} and $\Delta S^* = -2{\cdot}9$ cal mol^{-1} K^{-1}.

The effect of replacing water in the solvent by deuterium oxide has also been studied: for pin-2-ene, $k_H/k_D = 1{\cdot}48$ and for pin-2(10)-ene, $k_H/k_D = 1{\cdot}60$. These values are similar to the value of 1·45 for acid catalysed

---

[1] Part IV, P. I. Meikle, J. R. Salmon, and D. Whittaker, *J.C.S. Perkin II*, 1972, 23.

[2] R. A. Sneen and J. W. Larsen, *J. Amer. Chem. Soc.*, 1969, **91**, 362.

[3] E. C. Friedrich and S. Winstein, *J. Amer. Chem. Soc.*, 1964, **86**, 2721.

[4] J. R. Salmon and D. Whittaker, *J. Chem. Soc.* (*B*), 1971, 1249.

[5] V. J. Shiner, jun., and W. Dowd, *J. Amer. Chem. Soc.*, 1969, **91**, 6528.

[6] C. M. Williams and D. Whittaker, *J. Chem. Soc.* (*B*), 1971, 668.

[7] W. Huckel, W. Doll, S. Eskala, and H. Weidenev, *Annalen*, 1941, **549**, 186.

hydration of but-2-ene,[8] consistent with a reaction mechanism involving a rate-determining protonation step.

TABLE 1

First-order rate constants for the perchloric acid catalysed hydration of pin-2-ene and pin-2(10)-ene in dioxan–water (4 : 1, v/v)

Substrate	[Acid]/ M	$10^5k_1/s^{-1}$ at 40°	50°	60°	70°	80°
Pine-2-ene	0·050		0·82	2·24. 2·10 1·49 * 1·48 *	6·82	20·4
	0·097			5·63		
Pine-2(10)-ene	0·050	1·51, 1·56 0·90 *, 0·97 *	5·48	1·65		
	0·097	4·09		3·76		
	0·28	19·3				

* Reactions carried out in deuterium oxide–dioxan (1 : 4).

The products of hydration of the two olefins, listed in Table 2, are almost identical, suggesting that the ions involved in the reaction are identical except for minor differences in the solvation shells.

TABLE 2

Products of hydration of pin-2-ene and pin-2(10)-ene in dioxan–water (4 : 1, v/v) containing 0·0495M-perchloric acid at 60·0°

			Composition of products											
Substrate	Time (h)	Unchanged substrate (%)	Pin-2-ene	7,7-Dimethyl-2-methylenenorbornane	2,2-Dimethyl-3-methylenenorbornane	*p*-Mentha-1,3-diene	*p*-Mentha-1,8-diene	*p*-Mentha-1,4-diene	*p*-Mentha-1,4(8)-diene	1,3,3-Trimethylnorbornan-2α-ol	*p*-Menth-1-en-4-ol	*p*-Menth-1-en-8-ol	Bornan-2α-ol
Pin-2-ene	4	68		2	8	1	11	1	12	5	2	52	5
	6	60		1	7	1	11	1	11	6	3	50	7
	8	54		2	8	1	10	1	12	6	3	55	4
	10	42		2	6	1	11	1	12	6	2	55	5
	13	35		3	7	1	9	1	12	6	3	54	4
	15·5	30		2	7	1	10	1	11	7	2	55	4
	18	21		2	6	1	11	1	12	7	2	53	5
	24	17		2	6	1	11	1	12	7	2	54	5
Pin-2(10)-ene	0·5	66	2	2	5	1	9	1	8	6	8	44	6
	1	56	2	2	3	1	10	1	11	7	8	48	6
	1·5	38	2	2	3	1	11	1	11	8	6	49	5
	2	30	2	2	3	1	10	1	11	7	5	50	5
	2·5	21	2	2	4	1	10	1	11	8	4	52	5
	3	17	2	2	4	1	11	1	11	7	4	52	5

The rates of acid catalysed rearrangement of the pinan-2-ols have been measured, together with the rates of rearrangement of 2β,3,3-trimethylnorbornan-2α-ol, and *p*-menth-1-en-8-ol (α-terpineol). 2β,3,3-Trimethylnorbornan-2α-ol is considered to show little or no electronic assistance to ionisation, and is known not to undergo oxygen exchange in acid solution, making its rate of rearrangement a suitable standard for comparison of the rates of rearrangement of the pinanols.

From the data in Table 3, we see that, at 25°, k_1 (pinan-2α-ol)/k_1(2β,3,3-trimethylnorbornan-2α-ol) = $8{\cdot}3 \times 10^4$ and k_1(pinan-2β-ol)/k_1(2β,3,3-trimethylnorbornan-2α-ol) = $5{\cdot}8 \times 10^3$.† Thus, the 2α-alcohol reacts more rapidly than the 2β by a factor of 14 in contrast to solvolysis of the *p*-nitrobenzoates,[4] where the factor involved is 60, and the acid catalysed decomposition of the 6,6-dimethylnorpinan-2-ols (nopinols) where the β-isomer reacts faster by a factor of 11. A possible rationalisation of these data is that the *gem*-dimethyl substituent reduces the rate of reaction of the α-isomer relative to the β,[9] but this electronic effect is offset by steric repulsion between the 2-methyl group and the *gem*-dimethyl group. In a fairly flexible system such as pinane,[10] steric effects are difficult to predict accurately, but adoption of a con-

---

† In using the αβ notation for pinenes, the isopropylidene bridge is considered to have the β-configuration. Note, however, that Winstein's [3] ' β-nopinol ' is thus named 6,6-dimethylnorpinan-2α-ol.

[8] V. Gold and M. A. Kessick, *J. Chem. Soc.*, 1965, 6718.

[9] P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Amer. Chem. Soc.*, 1965, **87**, 375.

[10] R. J. Abraham, F. H. Bottom, M. A. Cooper, J. R. Salmon, and D. Whittaker, *Org. Magnetic Resonance*, 1969, **1**, 51.

formation to place the ester group equatorial would increase methyl–methyl repulsion in the 2α-isomer.

The acceleration of the alcohol reaction by electronic effects is thus of the order of 10^4, contrasting with acceleration by a factor of *ca.* 10^2, in the rate of hydration of pin-2-ene over the corresponding double bond of *p*-mentha-1,8-diene (limonene).[6] Since both reactions give ions which show only small differences, probably in solvation, our rate data provide support for the suggestion of Cristol[11] that the transition states for acid additions attain less positive charge on carbon than do those for solvolysis.

TABLE 3

Rate constants for the perchloric acid catalysed rearrangement of tertiary alcohols in dioxan–water (4 : 1, v/v)

Alcohol	[Acid]/M	Temp. (°C)	10^5k_1(s^{-1})	ΔH^*(kcal mol^{-1})
Pinan-2α-ol	0·025	0·0	2·07	25·5
Pinan-2α-ol	0·025	25·0	92	
Pinan-2β-ol	0·025	10·0	0·75	24·5
Pinan-2β-ol	0·025	25·0	6·40	
2β,3,3-Trimethylnorbornan-2α-ol	0·049	75·0	1·28	33·0
2β,3,3-Trimethylnorbornan-2α-ol	0·049	95·2	16·6	
p-Menth-1-en-8-ol	0·097	85·0	0·73	

TABLE 4

Products of rearrangement of the pinan-2-ols in dioxan–water (4 : 1 v/v) containing 0·025M-perchloric acid

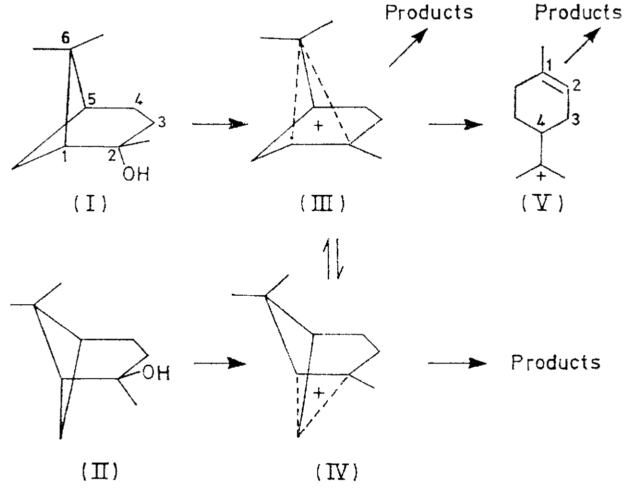
		Composition of reaction products									
Time (min)	Unchanged substrate	Pin-2-ene	7,7-Dimethyl-2-methylenenorbornane	2,2-Dimethyl-3-methylenenorbornane	Pin-2(10)-ene	*p*-Mentha-1,8-diene	*p*-Mentha-1,4(8)-diene	Pinan-2α-ol	1,3,3-Trimethylnorbornan-2β-ol	*p*-Menth-1-en-8-ol	Bornan-2α-ol
Pinan-2α-ol at 20·5°											
0	88										
5	74	5	1	3	2	7	6	4	10	43	11
10	69	4	1	2	1	9	9	6	11	49	8
15	60	4	1	2	1	8	10	5	10	49	8
20	53	4	1	2	1	8	8	6	10	51	8
30	41	3	1	2	1	8	9	6	10	52	8
45	33	3	1	2	1	7	9	6	9	50	8
Pinan-2β-ol at 25·0°											
0	96										
120	62	1	1	1		7	8		24	48	4
180	50	1	1	1		8	9		25	50	4
240	38	1	1	1		7	8		26	52	4
360	23	1	1	1		7	9		24	48	4
480	14	1	1	1		7	9		25	49	4

The products of rearrangement of the pinan-2α- and -2β-ols in acid are listed in Table 4.

The products from the two alcohols show unexpected differences. The α-isomer (I) yields more 1,3,3-trimethylnorbornan-2α-ol (α-fenchol) and bornan-2α-ol (borneol) and less camphene, *p*-mentha-1,4(8)-diene (terpinolene), and *p*-menth-1-en-8-ol (α-terpineol) than do the olefins; the β-isomer (II) gives a high yield of 1,3,3-trimethylnorbornan-2α-ol at the expense of several minor products. Formation of 1,3,3-trimethylnorbornan-2α-ol from pinan-2β-ol is consistent with (II) forming (IV), which reacts at a rate close to the rate of rearrangement to (III); similarly (I) forms (III) which yields borneol and (IV) at roughly similar rates. That ions (III) and (IV), formed from the pinanols do interconvert is shown by formation of β-alcohol from (I), and *p*-menth-1-en-8-ol from (II). The olefins must form a mixture of (III) and (IV) directly depending on the direction of protonation, so

[11] S. J. Cristol, quoted by T. G. Traylor, *Accounts Chem. Res.*, 1969, **2**, 1952.

that their reactions are less stereoselective than those of the alcohols.



This simple picture would, however, predict that pinan-2α-ol (I) would yield less 1,3,3-trimethylnorbornan-2α-ol than the olefins, whereas it in fact yields significantly more. The ions from the alcohols must, in some way, differ from those formed from the olefins. Since the β-alcohol (II) gives a very high yield of 1,3,3-trimethylnorbornan-2α-ol, it seems probably that the water molecule produced in the alcohol heterolysis may be affecting the reaction. We therefore repeated the alcohol studies in acetic acid; in anhydrous acetic acid, we should expect[5] the reactions outlined in the Scheme. The results are recorded in Table 5.

$$\begin{tikzcd} \mathrm{ROH} + \mathrm{HX} \arrow[r, shift left] & \mathrm{R}^+\,\mathrm{H_2O}\,\mathrm{X}^- \arrow[l, shift left] \arrow[r] \arrow[d] & \mathrm{R}^+ \arrow[d] \\ & \text{Products} & \text{Products} \end{tikzcd}$$

SCHEME

The results in Table 5 do not list bornan-2α-ol among the products. It was generally found in an amount of 1—2%, showing little variation in yield from pinan-2α- or -2β-ol, but as the g.l.c. peak came between those from *p*-menth-1-en-8-ol and *p*-menth-1-en-8-yl acetate it was difficult to measure quantitatively. In anhydrous acetic acid, both alcohols give rise to both 1,3,3-trimethylnorbornan-2α-ol and *p*-menth-1-en-8-ol, these amounting to 7% of the products from the α- and 18% from the β-alcohol. These cannot arise from traces of water in the solvent, since the solvent acetic acid was dried and 0·25% acetic anhydride added; it must, therefore, have come from the alcohol.

TABLE 5

Products of acid catalysed rearrangement of the pinan-2-ols at 25°. Sulphuric acid was used as catalyst except when indicated by an asterisk, where perchloric acid was used

				Composition of products														
Solvent	Substrate	[Acid]/M	Reaction time (min)	Pin-2-ene	7,7-Dimethyl-2-methylenenorbornane	2,2-Dimethyl-3-methylenenorbornane	*p*-Mentha-1,3-diene	*p*-Mentha-1,8-diene	*p*-Mentha-1,4-diene	*p*-Mentha-1,4(8)-diene	*p*-Mentha-2,4(8)-diene	1,3,3-Trimethylnorbornan-2α-yl acetate	Unknown	1,3,3-Trimethylnorbornan-2α-ol	Bornan-2α-yl acetate	Unknown	*p*-Menth-1-en-8-ol	*p*-Menth-1-en-8-yl acetate
Anhydrous acetic acid	Pinan-2α-ol	0·097	2		2	2	1	9	1	14		3	1	2	3	3	5	44
	Pinan-2β-ol	0·097	1		3	3		12	1	13		4		14	3		4	42
	Pinan-2α-ol	0·10*	1		3	6	21	14	12	28	2	2		2	2		1	3
	Pinan-2β-ol	0·10*	1		5	5	19	12	12	23	3	3		11	1			1
95% Acetic acid, 5% water	Pinan-2α-ol	0·10	1	1	1	1		6		12		2	2	1	4	2	18	44
	Pinan-2β-ol	0·10	1		2	2		7		11		3		14	3		14	44
90% Acetic acid, 10% water	Pinan-2α-ol	0·10	2	1		1		3		10		2	1	3	4	4	25	43
	Pinan-2β-ol	0·10	2		1	1		6		9		3		13	3		24	40
80% Acetic acid, 20% water	Pinan-2α-ol	0·10	2	1		1		3		10		1	2	3	3		35	34
	Pinan-2β-ol	0·10	2	1	1	1		5		10		2		13	3		32	33
	Pin-2-ene	0·10	60		1	3		5		10		1	2	1	3	2	34	39
	Pin-2(10)-ene	0·10	6	2		1		7		10		1		1	2	11	33	32
	Pinan-2α-ol	0·10*	1	1	1	2		13		14		1		3	3		34	29
	Pinan-2β-ol	0·10*	1		1	1		6		9		2		12	3		32	28

Since pinan-2α-ol (I) gives rise to both 1,3,3-trimethylnorbornan-2α-ol and *p*-menth-1-en-8-ol, it is clear that the water molecule produced in this reaction must remain close to the carbonium ion centre throughout the sequence of rearrangements (III) ⟶ (IV) or (V).

This is in contrast to the behaviour of the *p*-nitrobenzoate ion in the ion pairs produced by heterolysis of the pinan-2-yl *p*-nitrobenzoates.[4] In these reactions, ion pair collapse was stereospecific, and ion pairing blocked ion interconversion. This may be expected from the greater stabilising effect of a negatively charged *p*-nitrobenzoate ion as compared to a neutral water molecule.

Replacement of sulphuric acid as catalyst by toluene-*p*-sulphonic acid produced only small changes in the reaction products, but replacement by perchloric acid produced a substantial change in the products of reaction of both alcohols. Yields of *p*-menth-1-en-2-yl acetate fell, and those of monocyclic olefins rose; the olefins now included greater amounts of *p*-mentha-1,3-diene (α-terpinene), *p*-mentha-1,4-diene (γ-terpinene), and *p*-mentha-2,4(8)-diene (isoterpinolene). Although these are known rearrangement products of *p*-mentha-1,8-diene and *p*-mentha-1,4(8)-diene, the rates of rearrangement are insufficient [12] for *p*-mentha-1,8-diene and *p*-mentha-1,4(8)-diene to be regarded as their precursors, nor do they arise from *p*-menth-1-en-2-yl, since it is slowly formed from these olefins in acid conditions.[12] They must arise from stabilisation of the ion (V) by the perchlorate counterion, thus permitting the hydride shift needed to move the carbonium ion centre to C-4. Reaction of this type has been observed when perchloric acid reacts with pin-2-ene and pin-2(10)-ene,[12] and attributed to the effects of intimate ion pair formation.[12] In this case, a water separated ion pair is formed, so that the above reactions must be considered as resulting from either collapse of the water separated ion pair, or separation of a solvent solvated ion, which is subsequently captured by a perchlorate ion.

To distinguish between the two, the reaction was repeated in acetic acid containing 20% water, where the perchloric acid would be expected to be fully ionised. Reaction was then found to be almost identical with that using sulphuric acid as catalyst. We conclude, then, that the reaction is between alcohol and un-ionised or ion-paired acid, giving a water separated ion pair, which can react with the water molecule, separate to a solvent solvated ion, or collapse to an intimate ion pair. The latter reaction is detected only with perchlorate ion; this ion is, however, known to modify reaction paths by prolonging the lifetime of carbonium ions.[13]

Collapse of a water separated ion pair produced by treatment of an alcohol with an acid can be detected only when reaction in an anhydrous solvent produces a rearranged alcohol. There exist, therefore, a very limited number of reactions in which the phenomenon can be detected, even if the reaction was general. One possible system in which collapse of a water separated ion pair may be detected is the rearrangement of 2β,3,3-trimethylnorbornan-2α-ol with mineral acid in acetic acid: in aqueous dioxan,[14] the reaction gives 2α,3,3-trimethylnorbornan-2β-ol (camphene hydrate) which would not be stable in the conditions for the first step of the reaction, and bornan-2β-ol (isoborneol), which would be stable. Rearrangement in acetic acid, however, gave only bornan-2β-yl acetate. In this case, ionisation of the water separated ion pair proved faster than collapse, suggesting that the latter reaction may be detectable only when facilitated by the substrate.

An unexpected feature of the results recorded in Table 5 was the yield of 1,3,3-trimethylnorbornan-2α-ol from pinan-2β-ol remaining at 13—14% while the solvent changed from anhydrous acetic acid to acetic acid–water (4 : 1, v/v). Ion pairing would be expected to be relatively unimportant in the more aqueous solvent, and a fortuitous balance between the products of ion pair collapse and solvent attack seems unlikely, though the yield of 1,3,3-trimethylnorbornan-2α-ol from pinan-2α-ol varies only from 1—3% over the solvent range studied. A possible explanation is that the water molecule produced in the alcohol heterolysis remains close to the carbonium ion even in a good ionising solvent because it is restrained by steric interaction with the ion. The structure of (III) suggests that the methyl hydrogens and ring hydrogens could effectively restrain a water molecule. Absence of a proximate *gem*-dimethyl group would limit the restraining influence extended on the water molecule by (IV).

Formation of an ion such as (IV) with a water molecule trapped close to the ion centre would result in rapid but reversible formation of pinan-2β-ol, and slower but irreversible formation of 1,3,3-trimethylnorbornan-2α-ol. That 1,3,3-trimethylnorbornan-2α-ol is not the sole reaction product is due to competition between collapse of (IV) to 1,3,3-trimethylnorbornan-2α-ol and rearrangement of (IV) to (III), a reaction which would facilitate separation of a water molecule, and, being electronic in nature and intramolecular, would show limited dependence on solvent.

We conclude then, that the water molecule produced during acid catalysed heterolysis of an alcohol remains close to the carbonium ion in a poor ionising solvent, and may undergo reaction with the carbonium ion, but that in a moderately good ionising solvent, it is less important. The high yields of 1,3,3-trimethylnorbornan-2α-ol from pinan-2α-ol must be attributed to the structure of the substrate, and therefore are exceptional. Minor differences between the products of reaction of the β-alcohol and the olefins may be attributable to the same cause, so that we do not consider our data to contradict the view that in general, reaction of an alcohol with an acid in aqueous solvent produces a water molecule which equilibrates rapidly with the solvation shell.[14]

[3/1254 *Received*, 15*th June*, 1973]

---

[12] C. M. Williams and D. Whittaker, *J. Chem. Soc.* (*B*), 1971, 672.

[13] C. A. Bunton, J. P. Leresche, and D. Hachey, *Tetrahedron Letters*, 1972, 2431.

[14] C. A. Bunton, K. Khaleeluddin, and D. Whittaker, *J.C.S. Perkin II*, 1972, 1154.