

Classical Carbonium Ions. Part 14.¹ The Lifetime of Secondary Carbocations in Acetic Acid

By Margaret Monitz, Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY
 Mark C. Whiting,* Department of Organic Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS

Oct-1-ene and *cis*- and *trans*-oct-4-enes were treated with *p*-nitrobenzenesulphonic acid in acetic acid (0.1M) at 25°, when addition of the sulphonic acid and of acetic acid and the direct formation of isomeric octenes were all observed. At a greater rate, the covalent ester underwent acetolysis. The kinetically controlled mixture of products from the olefins was deduced from analyses at varying small degrees of reaction, extrapolating to zero conversion, and correcting for the products known to have been formed *via* covalent arenesulphonate. The results for *cis*-oct-4-ene proved that the lifetime of the 4-octyl cation in acetic acid is short compared with the time for rotation around a $C_3H_7\overset{\oplus}{C}H-CH_2C_3H_7$ bond.

THE lifetime of a carbonium-ion intermediate is difficult to establish; it can best be estimated by comparing it with some other rapid process, such as hydride shift or conformational change.² Here we discuss the products obtained when simple hydrocarbons (oct-1-ene, *cis*- and *trans*-oct-4-enes) are treated with *p*-nitrobenzenesulphonic ('nosylic') acid in acetic acid at room temperature. They consist of (a) covalent arenesulphonate, (b) octyl acetates, and (c) isomeric octenes; and it is the last group that provides most information.

Redistillation of commercial oct-1-ene gave material of 99.1% purity; catalytic hydrogenation of oct-4-yne gave *cis*-oct-4-ene of 99.25% purity; and sodium-ammonia reduction of the same acetylene gave *trans*-oct-4-ene of 95.0% purity. In all cases, other octenes constituted the remainder of the material, the *trans*-4-isomer being heavily contaminated with *trans*-oct-3-ene, and all analyses of products had to be corrected for these initial impurities. These preparations and the analytical methods used in this paper have been described.³ We first measured, by g.l.c., the initial rates of disappearance of the three isomers in a solution (0.1M) of *p*-nitrobenzenesulphonic acid in anhydrous acetic acid at 25°, as 1.2×10^{-7} , 6.4×10^{-8} , and $<3 \times 10^{-8}$ s⁻¹, respectively. Because of its slow reaction rate and poor initial purity, we did little further work on *trans*-oct-

usual equation (1) for the concentration at time *t* of an intermediate (B) formed during consecutive irreversible unimolecular reactions, (A) → (B) → (C) of rate constants *k*₁ and *k*₂.

$$[(B)]_t = [(A)]_0 k_1 (k_2 - k_1)^{-1} (e^{-k_1 t} - e^{-k_2 t}) \quad (1)$$

It was easy to calculate the percentage of covalent nosylate to be expected if the reaction had passed entirely through this intermediate, and hence that 22.5% (oct-1-ene) and 36% (*cis*-oct-4-ene) actually did so. Only when this addition was known to be a minor side-reaction was it clear that study of the other reaction products would be profitable. This is because two corrections would be needed. As it proved difficult to remove covalent ester before g.l.c. analysis without the possibility of introducing reaction products from it, we injected samples containing the trace of these esters directly, and subtracted the (small) amounts of octenes formed by thermolysis of authentic esters under similar conditions. We also calculated the distribution of products expected from the acetolysis of the small amounts of octyl arenesulphonates formed as intermediates in the reaction, having analysed the reaction products of the authentic 2- and 4-esters, and subtracted these from the extrapolated composition of the initial

solvolysis and nosylic acid addition give 'cool' carbonium ions.

When a similar set of mixtures (18 days, seven mixtures, up to 9% reaction) from *cis*-oct-4-ene were analysed, and the results extrapolated, a more interesting result emerged. No *trans*-oct-4-ene or *cis*-oct-3-ene

formation than to the positioning of the counterion, since no similar differences could be seen in the oct-1-ene-2-octyl nosylate comparison.

All that could be deduced about *trans*-oct-4-ene was that it reacted very slowly and gave substantially more (probably >2.5 times as much) *cis*-oct-3-ene than *cis*-

TABLE 1

Initial products from octenes and octyl *p*-nitrobenzenesulphonates

Starting material	2-ac	3-ac	4-ac	1	<i>t</i> -2	<i>c</i> -2	<i>t</i> -3	<i>c</i> -3	<i>t</i> -4	<i>c</i> -4
2-O-nos	70.4	1.7	0.1	2.2	14.7	10.1	0.6	0.1		
2-O-nos ^a	72.0	1.7	0.1	<i>a</i>	15.0	10.3	0.6	0.1		
1-ene (uncorr.)	56.2	1.7	0.2		20.9	20.9		0.1		
1-ene	51.6	1.7	0.2		23.8	22.5		0.1		
4-O-nos	0.1	1.7	58.7		0.5	0.2	16.0	5.3	14.0	5.5
4-O-nos ^a	0.1	1.8	62.1		0.5	0.2	16.9	5.6	14.8	<i>a</i>
<i>c</i> -4-ene (uncorr.)	0.2	1.5	78.2				19.2		1.0	
<i>c</i> -4-ene	0.2	1.2	79.9				18.8			

^a Renormalised with the exclusion of oct-1-ene and *cis*-oct-4-ene, for comparison with the products from isomerisation of these olefins. All reactions in 0.1M-nitrobenzenesulphonic acid in acetic acid at 25°. 2-O-nos = 2-octyl *p*-nitrobenzenesulphonate; *c*-4-ene = *cis*-oct-4-ene; 2-ac = 2-octyl acetate; uncorr. = Products not corrected for reaction *via* covalent nosylates.

could be identified in the initial product, the olefinic fraction of which consisted almost entirely of *trans*-oct-3-ene; whilst it is difficult to estimate experimental errors, the two former olefins are most unlikely to amount to as much as 10% of the proportion of the reaction product as did the last isomer. The acetates were unremarkable, again showing no great difference from the nosylate-derived mixture, though the reduced amount of rearrangement is certainly significant. The substitution/elimination ratio this time was higher than for the nosylate solvolysis. Evidently the 4-octyl⁺ cation, which must of course be formed in a 4-*cisoid* conformation, reacts, by addition of nosylate anion or acetic acid or by deprotonation to an isomeric olefine, before it undergoes significant equilibration with its more stable *transoid* conformer. This in itself explains the absence of *trans*-oct-4-ene; if we remember that *cis,cisoid* conformations are high in enthalpy,⁵ we can see that the cation must be 3-*transoid*, and the oct-3-ene formed must be almost entirely *trans*, as observed.

oct-4-ene, a result in keeping with our conclusions drawn from the two more tractable isomers.

It had been hoped that this work could have been repeated with new analytical methods, probably based on efficient capillary g.l.c. columns, which would have afforded results of greater precision; but the importance of the essential conclusion, reported briefly in 1966,⁶ now justifies the provision of experimental details. Plainly the lifetime of the cation with respect to deprotonation (*ca.* 20% of reaction) is at least 10 times smaller than that of rotation about a R $\dot{C}H-CH_2R$ bond. The energy barrier for this should be about the same as for methyl torsion in propene, *ca.* 8.5 kJ⁻¹ mol⁻¹; thus $e^{-E/RT}$ is *ca.* 0.1, and the rate constant for rotation is *ca.* 10¹⁰ s⁻¹, taking log *A* in the Arrhenius equation as 11. If the rate constant for deprotonation is ten times larger, and for all the possible reactions of the cation taken together 50 times larger, we have a maximum half-life for the 4-octyl cation in acetic acid of the order of 10⁻¹² s. It is, obviously, dependent on the value assumed for log *A*, but the implication is that such intermediates react in acetic acid at a diffusion-controlled rate, and stand on the



analysed well for the dihydrate ($C_6H_9NO_7S$ requires C, 30.15; H, 3.8%; equivalent, 239.2. Found: C, 30.5; H, 3.9%; equivalent, 240.2, 239.3). Solutions in acetic acid, fractionally distilled from acetic anhydride, were prepared by direct weighing and adding the calculated quantity of anhydride to react with two molecules of water.

The preparation and purification of oct-1-ene and the two oct-4-enes have been described, as has the analytical method used (method B with fore-column).³ The two octyl *p*-nitrobenzenesulphonates were prepared by the literature method,⁴ but their rates of solvolysis were re-determined by i.r. spectroscopy, in case the presence of nitrobenzenesulphonic acid significantly changed the rate of reaction.

Kinetic Experiments.—Solutions of each of the n-octenes (560 mg) in acetic acid (100 cm³) containing *p*-nitrobenzenesulphonic acid (0.1M), n-octane and (*cis* + *trans*) decalin (*ca.* 50 mg each) were prepared and used to fill a number of sealed ampoules, each containing 3 cm³. One was opened at once, the others were held at $25.0 \pm 0.1^\circ$ in a thermostatically controlled bath. Similar ampoules (2 cm³) were prepared containing 2-octyl nosylate (16.8 mg per 15 cm³) and 4-octyl nosylate (7.8 mg per 15 cm³), without addition of internal standards. Rates of acetolysis of the nosylates were obtained by opening ampoules, adding light petroleum (b.p. 30–40°; freed from aromatic contaminants by passing through silica-gel), washing repeatedly with water, evaporating to dryness, and dissolving in tetrachloroethylene (1 cm³ for early fractions, 0.5 cm³ for later ampoules). I.r. spectra were determined in the region 1500–1600 cm⁻¹ under standard conditions (cells, slit-widths, etc.), and optical densities were calculated using the N–O stretching band at 1550 cm⁻¹, $\Delta\epsilon$ 990, corrected for baseline at 1540 cm⁻¹, determined on crystalline 4-octyl nosylate. First-order plots were satisfactorily linear, with least-squares lines corresponding to 2.5×10^{-6} s⁻¹ (2-ester) and 7.4×10^{-6} s⁻¹ (4-ester); seven ampoules were used in each case, covering 2 and 2.5 half-lives respectively. A similar estimation of covalent nosylate was carried out using ampoules originally containing oct-1-ene, which after 14 days was made up to 3 cm³ with tetrachloroethylene

and now contained a 1.0% yield of covalent ester, and of *cis*-oct-4-ene, which after 18 days, made up to 0.5 cm³, contained a 0.3% yield of ester. Rates of reaction for the two hydrocarbons were obtained from the g.l.c. analyses of products. Using these and the nosylate solvolysis rates, it was calculated that *ca.* 22.5% (oct-1-ene) and 36% (*cis*-oct-4-ene) of the reaction was taking place *via* covalent esters. This method of treating the results ignores any reaction (*e.g.* polymerisation) of the octenes that does not involve the products analysed.

TABLE 2
Analyses required for corrections

	1	<i>c</i> -4	<i>t</i> -4	2-nos	4-nos
1	99.08			17.84	
<i>c</i> -2	0.44			16.40	6.05
<i>t</i> -2	0.27			32.78	11.36
<i>c</i> -3	0.18			7.72	20.11
<i>t</i> -3	0.19	0.06	5	15.50	29.57
<i>c</i> -4		98.25		2.62	10.82
<i>t</i> -4	0.05	1.67	95	7.12	21.93

2-nos and 4-nos are the products obtained from authentic nosylates, thermolysed under standard conditions.

For each ampoule, in each of the two cases, the yield of each product was expressed as a percentage of the principle product, unrearranged acetate. These figures (Tables 5 and 6) were plotted as ordinate against the total conversion as abscissa, and least-squares lines plotted. The intercepts at (conversion = zero) approximate to the initial kinetic-product composition, still relative to the main product (column c). These were now converted into percentage composition, equating all small negative yields to zero (column b). Corrections were now made in each case for the amounts of each product expected to have been formed *via* covalent arenesulphonate, and these were subtracted, small negative percentages again being ignored, and renormalised to 100% (column a). This is certainly the correct procedure for *cis*-oct-4-ene, where in the products analysed the covalent nosylate had reached a steady state concentration, but in the oct-1-ene case it overcorrects for this complication (Table 2).

In reporting the analyses of reaction products (Tables 3

TABLE 3
Products from oct-1-ene

<i>c</i> -2	0.56	0.78				3.22	3.38
<i>t</i> -2	0.49	0.86				3.07	3.39
<i>c</i> -3	-0.01					-0.02	0.05
<i>t</i> -3	-0.08	-0.07				0.20	0.33
<i>t</i> -4	-0.05	-0.08				-0.08	-0.01
2-ac	1.40	2.41	3.53	4.83	6.77	7.97	9.56
3-ac	0.04	0.08	0.12	0.17	0.24	0.29	0.38
4-ac			0.01	0.01	0.02	0.01	0.02
Time (h)	70.5	118.5	166.5	219.3	287	360.25	430.75
2-Nosylate	0.52	0.71	0.84	0.91	0.95	0.97	0.96 (uncorr.)

cis-Oct-4-ene could not be detected; residual starting-material was estimated by difference.

TABLE 4
Products from *cis*-oct-4-ene

<i>c</i> -3	-0.02	0.01	0.03	0.05	0.07	0.11	0.12	0.18
<i>t</i> -3	0.31	0.54	0.80	0.83	1.14	1.24	1.43	1.52
<i>t</i> -4	0.04	0.04	0.16	0.17	0.25	0.35	0.42	0.48
2-ac			0.01	0.01	0.01	0.02	0.02	0.02
3-ac	0.03	0.05	0.07	0.09	0.12	0.14	0.18	0.18
4-ac	1.43	2.29	2.95	3.67	4.56	5.51	6.81	6.81
Time (h)	93	141	188.4	240.1	288.6	325.3	425.5	425.5
4-nosylate	0.28	0.30	0.30	0.30	0.29	0.29	0.28	(uncorr.)

Oct-1-ene and the two oct-2-enes could not be detected; residual *cis*-oct-4-ene was estimated by difference.

TABLE 5

Kinetically controlled products from oct-1-ene										
Reaction (%)	0(a)	0(b)	0(c)	2.77	4.54	7.06	9.25	12.09	14.74	17.1
2-ac	51.6	56.22	100	100	100	100	100	100	100	100
3-ac	1.7	1.71	3.04	3.02	3.43	3.42	3.49	3.59	3.62	3.94
4-ac	0.2	0.19	0.33	0.00	0.29	0.28	0.23	0.24	0.18	0.20
<i>t</i> -2	22.5	20.90	37.17	35.14	35.81	38.22	33.86	32.81	33.98	32.14
<i>c</i> -2	22.8	20.87	37.12	39.71	32.16	43.33	41.24	30.97	37.93	33.72
<i>t</i> -3			-5.46	-5.71	-2.78	-0.82	0.04	1.20	0.95	1.93
<i>c</i> -3	0.1	0.12	0.20	-0.50			1.45		-0.34	-0.25

TABLE 6

Kinetically controlled products from <i>cis</i> -oct-4-ene										
Reaction (%)	0(a)	0(b)	0(c)	2.29	3.13	4.25	5.02	6.35	7.57	9.16
2-ac	0.2	0.17	0.22				0.29	0.21	0.26	0.30
3-ac	1.2	1.45	1.85	2.00	1.98	2.48	2.36	2.59	2.64	2.59
4-ac	79.9	78.18	100	100	100	100	100	100	100	100
<i>t</i> -3	18.8	19.16	24.51	21.72	23.37	27.13	22.45	25.09	22.45	21.06
<i>c</i> -3			-1.24	-1.54	0.57	0.92	1.25	1.51	2.05	1.75
<i>t</i> -4		1.04	1.33	2.73	1.66	5.38	4.60	5.37	6.43	6.10

and 4), two corrections are applied; the amounts of the isomeric octenes present in the starting-materials are first subtracted. We then calculate the amount of covalent nosylate, assumed to be 2- when derived from oct-1-ene and 4- when derived from *cis*-oct-4-ene, that ought to be present in each ampoule; assume that its thermolysis products are as given above; and subtract the proper amount from each isomer. To illustrate how small this undeniably rough correction is, for the final ampoules we give the analysis corrected only for impurities in the starting material, and also after applying the correction for thermolysis of the nosylate.

It will be appreciated that although the proper corrections have been made, many are small relative to experimental imprecision, and it is quite unimportant that they themselves are only approximate. The main conclusions emphasised in the text are directly evident in the crude data of Tables 3 and 4.

Reactions of trans-Oct-4-ene.—Only *cis*-oct-3-ene and *cis*-oct-4-ene were analysed; yields after 1, 2, 3, 4, 5, 6, and 7 weeks were, in percent of starting material, 0.21, 0.17; 0.52, 0.37; 0.42, 0.36; 0.41, 0.09; 0.49, 0.10; 0.62, 0.23; 0.91, 0.34. Plainly, more of the oct-3-ene than of the oct-4-ene is formed, but the poor purity of the starting

material would in this case make a full treatment of complete analyses quite difficult.

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