To obtain flash photolysis kinetics, the spectrograph was operated as a monochromator with a 1P21 photomultiplier at the exit slit. The photomultiplier signal was fed through a logarithmic amplifier to an oscilloscope in order to record intensity changes in units of absorbance.

Thermal π-Route Rearrangement of 4-Cycloheptene-1-methyl Acetate

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Abstract: Pyrolysis of 4-cycloheptene-1-methyl acetate under flow conditions gives only rearranged acetates and rearranged hydrocarbons whereas static conditions lead only to a simple elimination product and its Cope rearrangement isomer. The rearranged bicyclic acetates formed under flow conditions are strikingly similar to those of π-route solvolysis of the corresponding brosylate. The reaction rates under flow conditions were sensitive to conditioning of the reactor with allyl bromide.
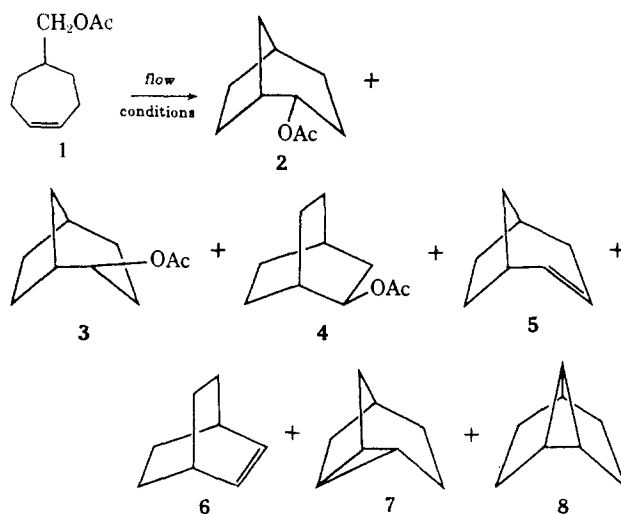
E ster pyrolysis is a well-established method for generating olefins, normally without rearrangement.[1] Considerable data indicate a concerted loss of carboxylic acid through a transition state that is somewhat polar, but less so than in halide pyrolyses.[1] When carried out in well-conditioned reactors, many such eliminations have been shown to be well-behaved homogeneous gas phase reactions. A few cases are known that give carbonium ion like rearrangements.[2-4] Only one of these has been shown to be a homogeneous gas phase reaction.[2a] The other systems[3,4] show evidence for surface catalysis.[1a]

The system studied here, 4-cycloheptene-1-methyl acetate (1), is one that has been studied solvolytically as the brosylate[5,6] and gives "π-route" entry[7] to the bicyclo[3.2.1]octyl system. Thus it is a system with a different type of potential carbonium ion like rearrangement than esters pyrolyzed previously.

Results

4-Cycloheptene-1-methanol was prepared by the method outlined previously[6,8] and then converted to the acetate (1). Pyrolysis of 1 under various flow conditions, including those normally used for preparative ester pyrolysis (slowly dripping 1 through a column of glass beads at 350° under a nitrogen flow), gave only rearranged products. The products that result are three bicyclic acetates 2, 3, and 4, two bicyclic olefins 5

(1) For recent reviews of ester and halide pyrolyses, see (a) G. G. Smith and F. W. Kelly, *Progr. Phys. Org. Chem.*, **8**, 75 (1971); (b) A. Maccoll, *Chem. Rev.*, **69**, 33 (1969).

(2) (a) E. U. Emonov, *J. Chem. Soc.*, B, 588 (1968); (b) T. Sato, K. Marata, A. Misimura, T. Tsuchiya, and N. Wasada, *Tetrahedron*, **23**, 1791 (1967).

(3) M. Hanack, H. J. Schneider, and H. S. Schneider-Berlohr, *Tetrahedron*, 23, 2195 (1967).

(4) E. S. Lewis and E. R. Newman, *J. Amer. Chem. Soc.*, **91**, 7455 (1969).

(5) G. Le Ny, *C. R. Acad. Sci.*, 251, 1526 (1960).

(6) H. L. Goering and G. N. Fickes, *J. Amer. Chem. Soc.*, **90**, 2848, 2856, 2862 (1968).

(7) S. Winstein and P. Carter, *J. Amer. Chem. Soc.*, 83, 4485 (1961).

(8) G. Stork and H. K. Landesman, *J. Amer. Chem. Soc.*, 78, 5129 (1956).

and 6, and two tricyclic hydrocarbons 7 and 8. The

structural assignments of the products were made by spectral and glc retention time comparison with authentic samples.[9]

The reaction was examined in a stirred flow reactor[10] to determine whether surface effects are important and to study to what extent products 5–8 arise from acetates 2–4. The reactor design was tested by measuring values for the cracking of norbornene.[11] The rate constants for that system were reproducible, invariant with changes in flow rate over the range used in the acetate study, and gave activation parameters (E_a = 45.9 kcal/mol, log A = 14.86) in reasonable agreement with literature values[11] (E_a = 42.8 kcal/mol, log A = 13.78).

Rate measurements for 1 in the stirred flow reactor were not reproducible although the measured values

(9) We thank Dr. H. L. Goering for samples of alcohols corresponding to 3 and 4, Dr. G. J. Gleicher for samples of 5 and 6, and Dr. G. N. Fickes for samples of 7 and 8. Compound 2 was prepared as described earlier.[6]

(10) W. C. Herndon, *J. Chem. Educ.*, 41, 425 (1964).

(11) W. C. Herndon, W. B. Cooper, Jr., and M. J. Chambers, *J. Phys. Chem.*, 68, 2016 (1964).

were reasonably constant over a few days time. Non-reproducibility usually results from surface catalysis, an effect that is decreased by conditioning the reaction vessel. In the case of **1**, conditioning the reactor with allyl bromide steadily decreased the rate of rearrangement. The rate was slowed about 100-fold before the conditioning was discontinued. After conditioning, the overall rate was not sensitive to a twofold change in flow rate but the ratio of acetate to olefins changed appreciably (Table I) indicating consecutive reactions.

Table I. Flow Pyrolysis[a] of **1** at 285°

Contact time, min	% acetates 2, 3, and 4	% hydro-carbons[b] 5, 6, 7, and 8	10^5k, sec^{-1}
10.5	1.70	1.86	5.56
10.5	1.54	1.94	5.45
10.6	1.74	3.16	7.66
23.9	2.24	7.65	7.62
18.9	1.90	7.68	9.21
27.2	2.46	10.82	9.46
24.5	2.58	6.31	6.69
24.5	2.79	6.51	6.98

[a] The reactor is described in the Experimental Section. Each pair of reactions was run on the same day. [b] The ratio of hydrocarbons is constant within the limits of error in measurement. The relative amounts of **5, 6, 7,** and **8** with average deviations are 52 ± 2, 11 ± 1, 15 ± 1, and 22 ± 2. For the α-dideuterated compound (**1-**d_2), the 5:6:7:8 ratio is 48:5:26:21.

The pyrolysis of **1** and of the three acetate products is shown in Table II. The data were collected over a 2-

Table II. Pyrolysis of 4-Cycloheptene-1-methyl Acetate (**1**) and Its Rearrangement Products under Flow Conditions[a]

| Compd	% re-arranged acetate	Rearranged acetate compd[b] 2	3	4	% hydro-carbon	Hydrocarbon composition[c,d] 5	6	7	8
1	1.75	76	10	14	3.2	50	11	15	24
2	0	100			33	62	9	24	5
3	4		92	8	46	69	13	18	
4	7		9.5	90.5	31	57	21	22	

[a] 285°, contact time 19 min; the four runs were made over a 2-day time period. [b] Analyzed as the alcohols by capillary glc on a 150-ft TCEP column. [c] Analyzed by glc on a 1/8 in. × 32 ft 5% Carbowax 20M-0.5% XF-1150 on Firebrick column. [d] The hydrocarbons are stable to the reaction conditions and do not form acetates when pyrolyzed with a fivefold excess of acetic acid.

day period to minimize differences in reactor conditions. It is evident that **3** and **4** interconvert and that **2, 3,** and **4** all eliminate acetic acid, giving a mixture of hydrocarbons similar to that obtained from **1** except that **8** is minor or absent in the pyrolyses of **2–4**. Pyrolysis of α dideuterated **1** (**1-**d_2) changed the hydrocarbon product ratio but the relative amount of **8** only decreased slightly (see Table I, footnote b). Pyrolyses of the hydrocarbons **5–8**, by themselves or in a stream containing a fivefold excess of acetic acid, showed that they are stable to the reaction conditions. All the products were shown to be stable to standing in acetic acid.

A search for possible radical products revealed no dimers or carbon dioxide that might arise from decarbonylation of acetoxy radical.

The rearrangement of **1** in sealed ampoules gives strikingly different results. Under conditions similar

to those used in the stirred flow reactor, no reaction took place. Even heating the ampoules for much longer times (up to 4.5 hr at 285°) gave no measurable reaction. At higher temperatures (350°), no rearrangement products (**2–8**) were formed but instead simple elimination gave methylenecyclohept-4-ene (**9**) along with a Cope rearrangement isomer **10** in a ratio of
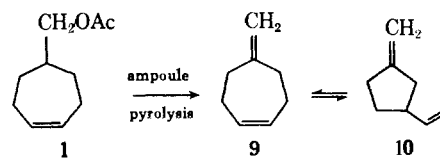
1:8. It was shown that **9** is not stable to the reaction conditions but rapidly rearranges to a 1:8 mixture of **9** and **10**. The structures of **9** and **10** were assigned by comparison of the spectra with those reported.[12,13] Compound **9** was also prepared by elimination of the p-bromobenzensulfonate with potassium $tert$-butoxide.

Measurement of the rate of elimination of **1** in unconditioned sealed ampoules gave a linear plot ($10^5k =$ 6.4 ± 0.3 sec^{-1} at 350°). A later measurement duplicated the rate within 8%.

Attempts to induce the formation of the products observed under flow conditions were not successful in the ampoule. Higher temperatures gave other unidentified products but no **2–8**. At 350°, changes in pressure, concentration, added acetic acid, and added crushed glass gave none of the **2–8** products.

Pyrolysis of the endo bicyclic acetate **2** in ampoules at 330° gave the simple 1,2 elimination product **5** (>97%). The rate of elimination in the ampoule at 330° is comparable to that in the flow system at 285°, i.e., at the same temperature elimination in the ampoule is several orders of magnitude slower than in the flow system.

Discussion

The erratic rates of reaction of **1** in the stirred flow reactor suggest surface catalysis. The considerable decrease in the rate caused by allyl bromide conditioning of the flow reactor is strong evidence for the importance of the surface effects.

In earlier work, certain types of rearranged products have been cited as evidence for ionic intermediates.[2–4] A similar argument can be made here for the reactions in the flow reactor but it should be kept in mind that such ionic species are probably associated with the glass surface. As noted earlier,[4] glass surfaces should favor polar interactions. The ratio of acetate products **2, 3,** and **4** produced by pyrolysis (76:10:14)[14] is strikingly similar to the ratio of the same products produced by acetolysis at 100° of the corresponding brosylate (83: 10:8).[6] This strongly suggests that **2, 3,** and **4** are formed via ion-pair intermediates by a scheme similar to that proposed for solvolysis[6] (Scheme I). The geometry of **1** dictates that the acetate anion would be generated on the exo face in the first formed ion pair, **11**. Movement of the anion to the endo face, **12,** then

(12) P. G. Gassman and E. A. Armour, $Tetrahedron Lett.$, 1431 (1971); note that the band reported at 4.28 (s, 2) should have been 5.28 (private communication).

(13) P. Dowd, G. Sengupta, and K. Sachdev, $J. Amer. Chem. Soc.$, 92, 5726 (1970).

(14) Because the acetates **2, 3,** and **4** form hydrocarbons at different rates the observed ratio will be different than the ratio in which they are formed. The relative rates shown in Table II suggest that the distortion should be small at this low conversion.

Scheme I

CH₂OAc
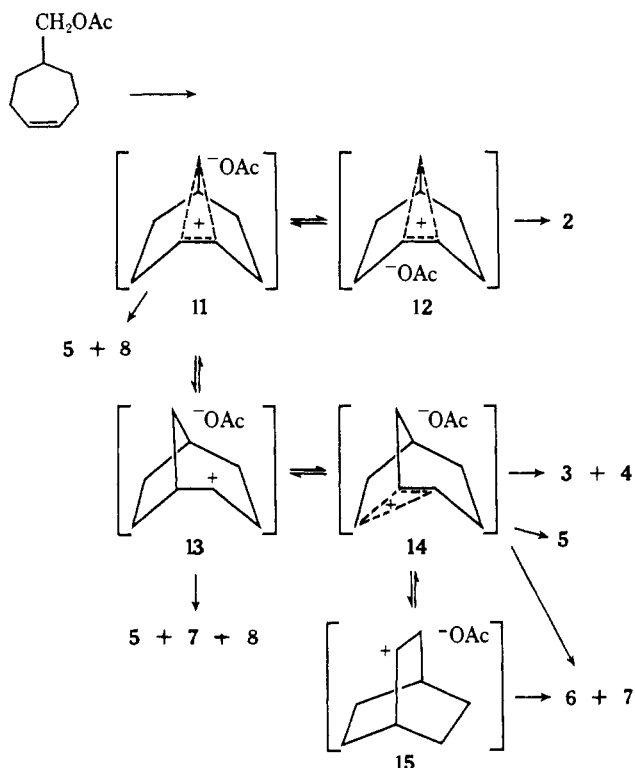
would allow recombination to endo acetate **2**. Leakage to the energetically similar ion pair, **14**, presumably *via* the classical species, **13**, would then yield exo acetate **3** and the [2.2.2] acetate **4**. Nonclassical species seem necessary since it is difficult to see why a classical ion pair, generated with the anion on the exo face, would give predominant endo product. However, since these rearrangements are surface catalyzed, the selectivity could possibly be due to the surface interaction.

As in solvolysis,[6] the exo-[3.3.1], and -[2.2.2] isomers, **3** and **4**, are interconverted; however, no endo-[3.2.1] acetate, **2**, is formed from either **3** or **4**. This is plausible since the anion would be generated on the correct side to interconvert **3** and **4** but on the wrong side to give **2**. An alternative mechanism, concerted rearrangement of **3** and **4**, is not ruled out by the present results.

Other mechanisms for the rearrangement of **1** seem less likely. A concerted rearrangement to the endo acetate **2** is sterically precluded. A tight radical pair would be generated with the acetoxy radical on the exo face and should give predominantly exo products. A radical process could also lead to dimers or carbon dioxide from decarbonylation of acetoxy radical,[15] neither of which were found.

The hydrocarbon products **5–8** could arise by 1,2 or 1,3 elimination from **13** or **15** (see Scheme I) or from their nonclassical counterparts. The data in Table II suggest that not all the hydrocarbons arise in that way because the acetates **2–4** eliminate under the reaction conditions at rates that are comparable to their rates of formation. If the eliminations were all homogeneous, rates calculated[10] from the data in Table II would indicate that about half of the hydrocarbons arise from the

rearranged acetates and the other half from other intermediates (*e.g.*, ion pairs or possibly directly from **1**). Unfortunately, the heterogeneous character of the reactions invalidates such rate analysis so that it is uncertain how much of the hydrocarbons arise from the reranged acetates. The eliminations of the rearranged acetates (**2** and **3**) are also surface catalyzed and presumably pass through the same type of intermediates as **1**.

One of the hydrocarbon products, **8**, clearly does not arise only from the rearranged acetates since **3** and **4** give no **8** while **2** gives a much smaller relative amount of **8** than **1**. Thus **8** must arise directly from **1** or from an unstable intermediate generated from **1**. The structure of **8** suggests that it could arise by α elimination leading to a carbene intermediate[16] or from the ionic species in Scheme I.[6,17] The ratio of hydrocarbons formed from 1-d_2 shows little change in the relative amount of **8**. This would seem to rule out an α elimination pathway which should show a primary isotope effect;[16a] however, caution is warranted since the magnitude of isotope effects for such surface catalyzed reactions is not known. Somewhat the same arguments hold with regard to **8** arising from the ionic intermediates in Scheme I.

The products formed from **1** in the ampoule method correspond to 1,2 elimination of acetic acid (**9**) and subsequent Cope rearrangement of **9** to give **10**. The reproducibility and linearity of the rate plots suggest that surface catalysis plays little or no role in the ampoule reaction of **1**. The higher temperatures required to induce **1** to react (or **2**) in the ampoule also indicates catalysis in the flow case and not the ampoules. That **1** eliminates much more slowly than **2**, **3**, and **4** is not surprising since primary esters are normally slower than secondary ones.[1]

It is not clear why the catalyzed reaction will not take place in the ampoules or whether this result is general. For this system, the flow conditions apparently enhance the surface catalyzed rearrangements leading to π-route products at the expense of the simple elimination pathway.

Experimental Section

General. Infrared spectra were measured on a Beckman IR 8 infrared spectrometer. Nmr spectra were measured on Varian Associates A-60 or HA-100 instruments. Mass spectra were obtained on an Atlas CH7 mass spectrometer equipped with a gas chromatograph inlet system. Elemental analyses were performed by Galbraith Laboratories. Analytical gas liquid chromatography (glc) utilized a Varian Aerograph Model 1200 instrument with flame ionization detector and the following columns: (A) 0.01 in. × 150 ft TCEP capillary; (B) 0.125 in. × 7 ft 5% UCON Polar LB550X on 110–120 Anachrom; (C) 0.125 in. × 32 ft 10% Carbowax 20M 1% XF 1150 on 60–80 firebrick; (D) 0.125 in. × 7 ft 2.5% KOH–2.5% Carbowax 4000 on 80–100 Chromosorb W; (E) 0.125 in. × 7 ft 4.7% TCEP on 80–100 Chromosorb W. Preparative glc was done with an Aerograph A-90-P instrument with columns (F) 0.25 in. × 10 ft 5% UCON Polar LB550X on 70–80 Chromosorb G and (G) 0.25 in. × 10 ft 5% TCEP on 70–80 Chromosorb G.

4-Cycloheptene-1-methanol was prepared by methods described previously[6,8] (a single glc peak on column D).

4-Cycloheptene-1-methyl acetate (**1**) was prepared from the

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(15) R. Louw and E. C. Kooyman, *Recl. Trav. Chim. Pays-Bas*, 86, 147 (1967); 84, 1151 (1965).

(16) (a) H. Kwart and H. G. Ling, *Chem. Commun.*, 302 (1969); (b) E. S. Lewis and W. C. Herndon, *J. Amer. Chem. Soc.*, 83, 1961 (1961).

(17) S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *J. Amer. Chem. Soc.*, 87, 376 (1965).

Table III. Mass Spectra of Hydrocarbons from Flow Pyrolysis of 4-Cycloheptene-1-methyl Acetate (1)

Compd	108	93	91	81	80	79	78	77	67	66	65	54	53	52	51	50
6	15.4	5.4	6.4	10	100	44	12	16.4	12.7	8.2	7.3	6.4	8.2	7.3	17.3	6.4
Authentic 6	12	3	6	10	100	41	5	15	11	3	6	6	6	6	9	4
5	27	23	11	3.2	37	100	20	25	37.1	61.2	11.3	21	10.5	9	13.7	6.5
7	29	22	15	4.1	45	100	22	31	52	82	13.3	36	12	10	15	7
Authentic 7	18	16	10	9.5	36	100	17	28	49	90	13.5	47	15	9.5	15	6.5
8	10.5	10.5	8.2	4.3	54	45	9	15.2	100	19	9.7	8.9	7	6.2	9.3	4.3
Authentic 8	5.7	7	6.4	4.7	59	47	7.7	17.4	100	13	11.5	8.5	11	8.5	15.3	6.4

Table IV. Mass Spectra[a] of Reduced Esters from Flow Pyrolysis of 4-Cycloheptene-1-methyl Acetate (1)

Compd	126	108	95	93	91	82	80	79	77	69	68	67	66	65	58	57	55	54	53	41
2	12	30	12.5	25	5.7	37	97	45	11	17	18	100	25	8	28.5	44	29	22	20	66
Authentic 2	15	30	10	31	8.2	36	97	53	11	23	23	100	20	11.5	26	43	26	25	18	80
4	7	52	9	31	6	22	78	69	9	11	11	100	35	6	16	30	32	42	22	72
Authentic 4	5	81	10	40	7	20	77	100	13	8	10	100	40	8	23	27	47	100	20	70
3	12	30	11	26	6	30	96	35	10	17	18	100	20	7.6	20	40	22	20	17	50
Authentic 3	13	27	8	25	4	32	97	32	8.7	16	20	100	22.5	7.6	26	42	19	15	14	53

[a] The mass spectra were obtained with a glc–mass spectrometer combination. The compounds are listed in order of retention time. The peaks for 3 and 4 were not completely resolved under the conditions required to obtain spectra so that the smaller component (4) probably contained some 3. A 5:1 mixture of authentic 3 and 4 analyzed in the same way as the pyrolysis mixture gave a much closer fit for the mass spectra of 4.

alcohol by refluxing for 3 hr with pyridine and acetic anhydride. After the normal work-up, the acetate was purified by column chromatography on SilicAR (Mallinckrodt) followed by vacuum transfer. This gave an 80% yield of 1 that gave one peak on glc (column E) and one spot on thin layer chromatography: ir (neat) 3030, 2935, 1725, 1435, 1385, 1359, 1233, 1058, 1040, 1027, and 703 cm⁻¹; nmr (CCl₄, δ) 5.70 (m, 2), 3.83 (d, J = 6 Hz, 2), 0.85–2.30 (m, 12).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.34; H, 9.51.

α,α-d_2-4-Cycloheptene-1-methyl acetate (1-d_2) was prepared as above except that lithium aluminum deuteride was used for reduction of 4-cycloheptene-1-carboxylic acid.

endo-Bicyclo[3.2.1]octan-2-yl acetate (2). The corresponding alcohol was synthesized as described earlier[6] and then converted to the acetate and purified as above. This gave 97% pure 2 contaminated with 2% of 3 and 1% of 4. The spectra checked with those of authentic samples.[18]

exo-Bicyclo[3.2.1]octan-2-yl acetate (3) and bicyclo[2.2.2]octan-2-yl acetate (4) were prepared from authentic samples of the alcohols[9] as above (the samples of 3 and 4 showed one glc peak on column E). The spectra agreed with those for authentic acetate samples.

Bicyclo[3.2.1]octan-2-ene (5), Bicyclo[2.2.2]oct-2-ene (6), Tricyclo[3.2.1.0²,⁷]octane (7), and Tricyclo[3.3.0.0²,⁸]octane (8). Authentic samples were obtained from Dr. G. J. Gleicher and Dr. G. N. Fickes.[9]

Methylenecyclohept-4-ene (9). 4-Cycloheptene-1-methyl brosylate was prepared as described previously.[6] A solution of 3.76 g (10.6 mmol) of the brosylate in 10 ml of dry dimethyl sulfoxide was stirred under nitrogen, and a solution of 2.4 g (11.2 mmol) of potassium tert-butoxide in 100 ml of dry dimethyl sulfoxide was added over 3 hr. After the mixture was stirred at room temperature for 6 hr, 50 ml of water was added and the mixture was extracted four times with 50-ml portions of pentane. The pentane extracts were washed five times with 75 ml of water and then dried over magnesium sulfate. The pentane was removed by distillation through a Vigreux column which left 3.7 g of liquid. Two isomers were detected by glc (column B) in a 93:7 ratio which were subsequently isolated using column F. The major fraction was assigned as 9 on the basis of its spectral properties: ir (neat) 3010, 2954, 2890, 1616, 1449, 1418, 1370, 1341, 1234, 1217, 1183, 1085, 1069, 1007, 973, 877, 753, and 698 cm⁻¹; nmr (CCl₄, δ) 5.75 (m, 2), 4.64 (s, 2), 2.0–2.4 (m, 8). This agrees with the nmr spectral data of Gassman and Armour.[12] The minor isomer was assigned as 1-methylcyclohepta-1,4-diene on the basis of its nmr spectrum:

(18) We thank H. L. Goering for spectra of 2, 3, and 4.

(CCl₄, δ) 5.5–5.6 (m, 2), 5.2–5.5 (m, 1), 2.6–3.0 (m, 2), 2.1–2.5 (m, 4), 1.6–2.0 (m, 3).

Pyrolysis Conditions. General. Pyrex glass was used in all apparatus and ampoules.

(A) The Stirred Flow Reactor. Acetate samples were placed in a glass bulb vaporizer (25–75°) with a nitrogen inlet tube directed toward the sample and a side outlet. The outlet was connected by 8-mm tubing to the bottom of a 576-ml glass sphere in which two glass baskets were magnetically spun (ca. 1400 rpm). A short length of 8-mm tubing which was maintained at about 75° led out of the top of the stirred sphere into a Dry Ice–acetone cold trap. The flow of prepurified nitrogen was passed through hot copper turnings, Ascarite, and Drierite before it passed into the vaporizer. The flow was regulated by a restrictor and a calibrated fine metering valve. The flow was measured at the outlet by means of a 50-ml bubble flow meter, correcting for the temperature difference between the reactor and the outlet stream. The stirred reactor was maintained at a given temperature by means of a potassium nitrate–sodium nitrite fused salt bath regulated by a Bailey Model 124 temperature controller. The glass surfaces were conditioned by passing allyl bromide through the apparatus.

(B) Open Tube Systems. Several systems were tried in which a flow of vapor was passed through a long tube or an unstirred sphere using flow and temperature conditions similar to Table I. The products were the same as from the reactor described in (A).

(C) Packed Tube Pyrolysis. Acetate was slowly dripped down a vertical 13 in. × 12 mm Pyrex tube packed with no. 3 Pyrex beads heated to 350 ± 20°. A stream of nitrogen (10 ml/40 sec) was passed through the system. The products were collected in a Dry Ice–acetone cold trap and were the same as seen in the systems described above.

(D) Ampoules. Most pyrolyses were run in evacuated ampoules (10 mg of acetate per 10-ml ampoule) which were not specially treated. No difference was noted when the ampoules were washed with water, acetone, and ammonia and then dried before use. Changes in sample concentration (0.2–40 mg per 10-ml ampoule), pressure (1 atm nitrogen), added crushed glass, or added acetic acid did not affect the nature of the products.

Product Analysis. The hydrocarbons were analyzed on column C at 50° which gave the following retention times: 10, 7.0; 6, 14.0; 5, 15.2; 9, 16.0; 7, 18.7; 8, 20.0 min. The acetates were only partially resolvable so that they were normally reduced to the alcohols (LiAlH₄) and analyzed on column A at 110° which gave the following retention times: 3, 35.6; 4, 38.5; 2, 41.6; 1, ca. 70 min.

The major flow pyrolysis products 2 and 5 were purified on column G and assigned structures by comparison of infrared, nmr, and mass spectra with authentic samples. Products 6, 7, and 8

were assigned by comparing retention times (coinjection with authentic samples on column C) and mass spectra with those for authentic samples (Table III). In addition, the nmr spectra of a mixture of **5** and **6** clearly showed the characteristic vinyl triplet and the bridgehead protons for bicyclo[2.2.2]octene (**6**). The nmr spectrum of a mixture of **7** and **8** clearly showed the spectra of the individual components since the spectra only overlap in one small area. The spectra agreed with those for authentic samples. The nmr spectra for **6**, **7**, and **8** are as follows: **6** (δ, CCl$_4$) 6.20 (t, J = 3 Hz, 2), 2.47 (br s, 2), 1.47 (d, J = 8 Hz, 4), 1.20 (d, J = 8 Hz, 4); **7** (δ, CCl$_4$) 1.65 (m, 9), 1.25 (d, J = 8 Hz, 2), 0.70 (m, 1); **8** (δ, CCl$_4$) 2.50 (m, 1), 1.7–2.0 (m, 5), 1.2–1.5 (m, 6).

The minor acetate products **3** and **4** were identified by comparison of retention times (coinjection with authentic samples on column

C) and by their mass spectra which were superimpossable with those of authentic samples (Table IV). Further spectral identification was thwarted by the extremely small quantities involved and by the fact that efficient separation was only attainable on capillary glc columns.

The ampoule pyrolysis products **9** and **10** were separated on column F. The nmr spectra agreed with those reported.[12,13]

Claisen Rearrangement of Cinnamyl Phenyl Ether in Isotropic and Nematic Solvents and in a Clathrate[1]

Michael J. S. Dewar* and Boris D. Nahlovsky

Contribution from the Department of Chemistry, the University of Texas at Austin, Austin, Texas 78712. Received February 24, 1973

Abstract: Claisen rearrangement of cinnamyl phenyl ether yields both ortho and para products, contrary to previous reports. In basic solvents the ortho product predominates while in acidic or neutral solvents more para product is formed. Allyl phenyl ether, on the other hand, gives exclusively *o*-allylphenol in solvents of all kinds. The rate of rearrangement of cinnamyl phenyl ether was measured in a variety of solvents including one forming a nematic phase (hydroquinone di-*p*-*n*-hexyloxybenzoate). The rate in this showed no discontinuity on passing from nematic to isotropic liquids, the activation parameters remaining unchanged ($\Delta E^{\pm}$ = 30.4 $\pm$ 0.85 kcal mol^{-1}; $\Delta H^{\pm}$ = 29.5 $\pm$ 0.85 kcal mol^{-1}; $\Delta S^{\pm}$ = -15.0 $\pm$ 1.8 cal deg^{-1} mol^{-1}). A clathrate of cinnamyl phenyl ether in 4,4'-dinitrobiphenyl was prepared. In the clathrate rearrangement of the ether was strongly inhibited.

The majority of nematic liquid crystals involve rod-shaped molecules which tend to orient themselves with their long axes parallel. If an anisotropic molecule is dissolved in such a nematic phase, it will tend to be oriented by the surrounding molecules of solvent. If then the nematic liquid crystal is oriented by, e.g., a strong magnetic field, the solute molecules will adopt a corresponding and known orientation. This phenomenon has proved of practical value in several branches of spectroscopy.[2]

Consider a bimolecular reaction between two anisotropic solvents in a nematic solvent. In a "normal" solvent, three degrees of rotational freedom are lost on forming the transition state with a consequent negative contribution to the entropy of activation. The hindered rotation of solute molecules in a nematic solution should lead to a smaller loss of entropy when they combine. The entropy of activation should therefore be greater, and the rate likewise greater, for the reaction in a nematic solvent. Similar though smaller differences should be observed in the case of unimolecular reactions if the moment of inertia of the transition state differs significantly from that of the reactant.

While effects of this kind must in theory exist, no one

knows how large they are likely to be. If they were large, the use of nematic solvents could well influence polymerization reactions in a useful way.[3]

Several authors have reported effects of orientation when reactions are carried out in nematic liquid crystals instead of normal liquids, e.g., the thermal decomposition of picric acid[5] and the pyrolysis of xanthates.[6] Recently it was claimed[7] that the Claisen rearrangement of allyl *p*-tolyl ether (**1a**) proceeds faster in nematic solvents; however, subsequent work[8] showed this not to be the case and similar negative results have been reported[9] for the rearrangement of 2,4,6-trimethoxy-1,3,5-triazine.

While the effects of orientation should be greater in the case of bimolecular reactions than unimolecular ones, we decided first to study a unimolecular process, the Claisen rearrangement, in view of claims[5,7] in the literature at the time this work was started. If these claims could be substantiated, one would expect rather large effects in the case of bimolecular reactions.

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(2) See, e.g., L. C. Snyder and E. W. Anderson, *J. Amer. Chem. Soc.*, **86**, 5023 (1964); E. Sackmann, *ibid.*, **90**, 3569 (1968); A. Carrington and G. R. Luckhurst, *Mol. Phys.*, **8**, 401 (1964).

(3) Some very recent papers[4] report studies of polymerization reactions in nematic solvents. The results at present seem somewhat equivocal.

(4) (a) Yu. B. Amerik, I. I. Konstantinov, and B. A. Krentsel, *J. Polym. Sci., Part C*, **23**, 231 (1968); (b) C. M. Paleos and M. M. Labes, *Mol. Crystallogr.*, **11**, 385 (1970); (c) A. Blumstein, N. Kitagawa, and R. Blumstein, *ibid.*, **12**, 215 (1971).

(5) T. Svedberg, *Kolloid-Z. Z. Polym.*, **18**, 54 (1916).

(6) W. E. Barnett and W. H. Sohn, *Chem. Commun.*, 1002 (1971).

(7) W. E. Bacon and G. H. Brown, *Mol. Crystallogr.*, **6**, 155 (1969).

(8) W. E. Bacon and G. H. Brown, *Mol. Crystallogr.*, **12**, 229 (1971).

(9) W. E. Bacon and G. H. Brown, Abstracts, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, p 208.