Rearrangement of Esters in the Gas Phase. III. Heterogeneity in the Rearrangements of Norbornyl and Cyclopropylcarbinyl Trifluoroacetates[1]

Edward S. Lewis and Edward R. Newman[2]

Contribution from the Department of Chemistry, Rice University, Houston, Texas 77001. *Received May 1, 1969*

Abstract: In a diffusively stirred flow system, *exo*-norbornyl trifluoroacetate racemizes, but the reaction is largely and possibly totally heterogeneous. Cyclopropylcarbinyl trifluoroacetate also rearranges with the characteristics of a surface reaction. Upper limits to the rates of any homogeneous rearrangement in both cases are significantly slower than the previously studied rates of rearrangement of isotopically labelled allyl trifluoroacetate, suggesting that the latter does not involve a gas-phase ion pair. It is suggested that earlier examples of carbonium ion rearrangements in the gas phase may also have been heterogeneous.

In connection with our interest in gas phase reactions with highly polar transition states, we have been concerned with the extent of the parallel between ionization reactions in solution and some rearrangements of esters in the gas phase.[3] We have previously shown[4] that substituent effects indicate a transition state for the rearrangement of allylic esters with a substantial carbonium carboxylate contributing structure. We can then ask if a gas phase ion pair is a true intermediate or if there are transition states so similar to the ion pair that typical carbonium ion rearrangements might be found. The existence of rearrangements[5] has in fact been used as an argument for such highly polar transition states, possibly leading to an ion pair. In the accompanying paper,[6] it is shown that an ^{18}O tracer in crotyl trifluoroacetate rearranges predominantly in the direction expected for a Cope rearrangement. A significant amount of a different course was observed and could be described as a random shuffling. It was not shown that this shuffling reaction was necessarily homogeneous. This experiment excludes an ion pair with nearly free rotation of the ions with respect to each other, but a planar ion pair with substantial barrier is not excluded.[7]

An alternative way to search for an ion-pair intermediate is to find an ester with the possibility of rearrangement through the ion but for which the concerted Cope rearrangement is excluded. Thus, gas phase rearrangement of such an ester which is selected to ionize at least as rapidly as the allyl ester would support a similar ionic pathway for both. We here present a study of the racemization of *exo*-norbornyl trifluoroacetate and the rearrangement of cyclopropylcarbinyl trifluoroacetate. In both cases it is, of course, possible to formulate a one-step concerted rearrangement process, but there is little analogy for this, nor, as it turns out, need for it.

Results

The thermal reaction of optically active *exo*-norbornyl trifluoroacetate produced bicycloheptene (norbornene), nortricyclene, cyclopentadiene, ethylene, presumably trifluoroacetic acid (to which the flame ionization detector is insensitive), and unreacted norbornyl ester, which had a lower rotation than the starting material. Flow rates in the diffusively stirred flow system were adjusted so there was at least 25% recovery of the ester. All rates of racemization are based upon at least 10% loss of original rotation. Table I shows the results of these experiments calculated as rate constants for racemization, k_α elimination to norbornene, k_{el}, and elimination to nortricyclene, k_Δ. It was assumed that cyclopentadiene and ethylene were derived from the reverse Diels–Alder reaction of norbornene,[8] and the conclusion that nortricyclene is not produced from norbornene[8] was confirmed by our observation that the ratio of nortricyclene to norbornene (+ cyclopentadiene) was not flow-rate dependent, which shows that they are derived from the same substance. Control experiments showed that loss of rotation of *exo*-norbornyl trifluoroacetate did not arise from readdition of trifluoroacetic acid to norbornene in the trap. Low rotations were also not due to contamination, since the ester was purified by preparative scale gas chromatography both before and after reaction. We made no attempt to measure rate constants for the norbornene decomposition because the extra complexities of the other reactions made it unlikely that we could get as good results as are already available.[8] Qualitatively the extent of decomposition was in agreement with the published results. The study was not carried to higher temperatures because too much ester was lost to elimination.

The seasoning effect on k_α, shown by the downward drift, suggests a major heterogeneous component. Not shown in the table because it was only qualitatively ob-

---

[1] From a portion of the Ph.D. Thesis of E. R. Newman, Rice University, 1967.

[2] National Aeronautics and Space Administration Trainee, 1965–1967.

[3] See in this connection the "Quasiheterolytic" description of Maccoll (a recent summary is A. Maccoll, "Studies on Chemical Structure and Reactivity," J. Ridd, Ed., John Wiley & Sons, Inc., New York, N. Y., 1960, Chapter 4).

[4] E. S. Lewis, J. T. Hill, and E. R. Newman, *J. Am. Chem. Soc.*, **90**, 662 (1968).

[5] (a) A. Maccoll and E. S. Swinburn, *J. Chem. Soc.*, 149 (1964); (b) A. Maccoll and R. C. L. Bicknell, *Chem. Ind.* (London), 1912 (1961); (c) E. S. Lewis and W. C. Herndon, *J. Am. Chem. Soc.*, **83**, 1961 (1961); (d) M. Hanack, H.-J. Schneider, and H. Schneider-Bernlohr, *Tetrahedron*, **23**, 2195 (1967).

[6] E. S. Lewis and J. T. Hill, *J. Am. Chem. Soc.*, **91**, 7458 (1969).

[7] An ion pair which maintains the distinguishability of carboxylate oxygens is considered by H. L. Goering and M. M. Pombo [*J. Am. Chem. Soc.*, **82**, 2515 (1960)]; they do not consider complete shuffling to be a consequence of an intermediate ion pair.

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

Table I. Rate of Reaction of Optically Active *exo*-Norbornyl Trifluoroacetate

t, °C	$k_\alpha \times 10^4$, sec^{-1}	$k_{el}{}^{c} \times 10^4$, sec^{-1}	$k_\Delta{}^{d} \times 10^4$, sec^{-1}
262.3	25[a]		
262.3	14[a]		
262.3	10[a]		
262.3	10[a]		
262.3	8.5[a]		
262.3	6.9[a]		
262.3	5.0[a]		
261.2	3.4[b]	2.04	0.43
266.9	3.6[b]	3.06	0.50
273.2	5.2[b]	4.77	1.4
295.6	5.9[b]	21.7	1.7
319.5	12[b]	121	6.4

[a] In a vessel of volume V = 206 ml, calculated from the equation $k_\alpha = (U/V)(\alpha_0 - \alpha)/\alpha$, in which α is the rotation of recovered ester, α_0 is the original rotation, and U = flow rate. Results are listed in chronological order with the last taken after over 3 weeks of continuous flow. [b] Same as the others except V = 202 ml, each value given was taken after an extended period of seasoning and the rates are perhaps comparable with the last one marked a. [c] Calculated from $k_{el} = (X_B + X_C)U/X_AV$, where the X's are mole fractions and A, B, and C are ester, norbornene, and cyclopentadiene, respectively. [d] Calculated from $k_\Delta = k_{el}X_\Delta/(X_B + X_C)$, where X_Δ = mole fraction of nortricyclene.

served is the fact that nortricyclene was a more important product at early stages of seasoning. The temperature dependence leads to the same conclusion. The best Arrhenius equations, which are poor fits except for eq 2, are given by eq 1, 2, and 3.

$$k_\alpha = 10^{1.98} \exp(-13{,}300/RT) \qquad (1)$$

$$k_{el} = 10^{13.2 \pm 0.4} \exp[(-41{,}320 \pm 930)/RT] \qquad (2)$$

$$k_\Delta = 10^{7.6} \exp(-29{,}300/RT) \qquad (3)$$

Of these three only (2) is credible for a homogeneous reaction in terms of the preexponential term. Both products characteristic of a carbonium ion intermediate (racemic ester and nortricyclene) result from reactions with temperature behavior characteristic of a heterogeneous process and with serious seasoning effects. Thus eq 1 and 3 cannot be expected to be reproducible.

Cyclopropylcarbinyl trifluoroacetate was also passed through the flow reactor. Identified products included allylcarbinyl trifluoroacetate and butadiene. Another substance of retention time similar to the two esters was probably cyclobutyl trifluoroacetate, and another substance of retention time similar to that of butadiene was presumed to be methylenecyclopropane. The uncertain identification of some of these products turns out to be irrelevant to the conclusion we shall show. Seasoning effects were serious at all temperatures tried, and there was no evidence of any leveling off of the rates after weeks of flow. After 3 weeks at 350°, 10% of the exit material was rearranged ester, 20% was elimination products, and 70% was unaltered, yielding a "rate constant" for rearrangement, $k = 2.1 \times 10^{-4}$ sec^{-1}. At still higher temperatures some side reactions became more serious and we therefore did not attempt to determine the temperature dependence. This reaction therefore also has a serious, and possibly exclusive, heterogeneous component.

Discussion

The homogeneous part of either reaction is not identifiable, but we can reasonably put as an upper limit one-half of the slowest rate observed. Thus for the racemization of *exo*-norbornyl trifluoroacetate $k_{\text{homo}}{}^{319} \leq$ $\times\ 10^{-4}$ sec^{-1} and for the rearrangement of cyclopropylcarbinyl trifluoroacetate $k_{\text{homo}}{}^{350} \leq 1 \times 10^{-4}$ sec^{-1}. These numbers can be compared with the rates of isotopically labeled allyl trifluoroacetate, $k^{319} = 3.0 \times 10^{-3}$ and $k^{350} = 1.3 \times 10^{-2}$ sec^{-1} obtained by interpolation in the earlier data.[4]

If the "quasiheterolytic" description is equally applicable to all these reactions, then we should find a correlation between these gas phase rates and the ionization rates in solution. In ethanol *exo*-norbornyl *p*-bromobenzenesulfonate solvolyzes (polarimetrically) with $k = 7.8 \times 10^{-5}$ sec^{-1} at 25°.[9] Under about the same conditions allyl benzenesulfonate solvolyzes with $k = 8 \times 10^{-6}$ sec^{-1}.[10] If we allow about a factor of 2 for the difference between the two leaving groups, and ignore the probably serious nucleophilic component of the allyl compound, the norbornyl case is about five times more reactive than the allyl system. The factor for a pure ionization without nucleophilic participation by solvent will certainly be larger. The internal return present in the norbornyl system is clearly a good model for rearrangement *via* ion pair even in the gas. Thus in the gas phase the racemization of the norbornyl ester is five or more times slower than the allyl ester, in solvolysis the norbornyl compound is at least five times faster than the allyl compound. Thus the correlation associated with the quasiheterolytic mechanism fails by at least a factor of 25.

Cyclopropylcarbinyl benzenesulfonate solvolyzes about 14 times as fast as allyl benzenesulfonate in the same solvent.[11] The upper limit of the homogeneous gas-phase rearrangement is 1/80 times that of the allyl ester rearrangement. The discrepancy from the predictions based upon solvolysis rates is now a factor of 112 at the least and is even worse in this case than the norbornyl case. Again, the facile rearrangement of the system in solution accompanied by internal return makes the model seem entirely adequate.[12] The failure of both these attempts to correlate ionization rate with the rate of the gas phase rearrangements does not prove that the ionic path is impossible. Indeed it should be no cause for surprise that reactions with highly polar transition states should have a heterogeneous component, *i.e.*, that the transition states should be strongly adsorbed on glass surfaces. We can, however, conclude that the rearrangement of the allylic ester does not have this extreme dipolar transition state, hence it is reasonably well described as a Cope or Claisen rearrangement.

We can ask the further question whether there are in fact any well-established homogeneous rearrangements of the nature expected of carbonium ions, and we shall find that the answer is not entirely convincing either way. The rearrangements in chloroformate reactions[5c] can be readily dismissed; the rearrangement is found in the minor product (the olefin) only, no temperature dependence was measured, and heterogeneity has been a

---

(9) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, 74, 1154 (1952).

(10) C. G. Bergstrom and S. Siegel, *ibid.*, 74, 254 (1952).

(11) C. G. Bergstrom and S. Siegel, *ibid.*, 74, 145 (1952).

(12) J. D. Roberts and R. H. Mazur, *ibid.*, 73, 2509 (1951); M. C. Caserio, W. H. Graham, and J. D. Roberts, *Tetrahedron*, **11**, 171 (1960).

perpetual problem in these systems.[13] There is therefore in these chloroformates no convincing evidence for a homogeneous rearrangement. The rearrangements of some substituted cyclopropylcarbinyl acetates have been observed,[5d] but the conditions are very similar to ours in this paper, except that no search for heterogeneity was made. Here too there is no strong evidence for a homogeneous component. The observation that the fraction of rearranged product falls with increasing temperature is consistent with a heterogeneous process of low activation energy competing with the homogeneous elimination. The rearrangement of neopentyl chloride[5a] is of such mechanistic and kinetic complexity as to make a rigorous demonstration of anything difficult and the apparently cleaner conversion of bornyl chloride to tricyclene[5b] is not described in very much detail. A possible alternative route to rearranged compounds *via* the carbene produced by α-elimination was considered and rejected in one case[5c] but becomes more likely in the higher temperature reactions. An α-elimination was considered and rejected in one case[5c] but becomes more likely in the higher temperature reactions. An α-elimination mechanism has been convincingly postulated in an ester pyrolysis by Kwart.[14]

Thus the presence of carbonium ion rearrangements in the gas phase has not yet been convincingly demonstrated. This conclusion is supported by Kwart, who has rejected ion pairs as intermediates in ester pyrolysis even in rearranging systems because of the detailed nature of the products in some special cases.[14,15]

Experimental Section

Materials. Optically active *exo*-norborneol was prepared from inactive commercial material following published procedure[9,16] *via* the cinchonidine salt of the acid phthalate ester.

dl-exo-**Norbornyl trifluoroacetate** was prepared by adding *exo*-norboreol to about a threefold molar excess of trifluoroacetic anhydride held at 0° with which it reacted as fast as the addition. Ice was immediately added, and the mixture was extracted with petroleum ether (bp 20–40°). The organic layer was washed with water, dilute aqueous sodium bicarbonate, again with water, and then dried over anhydrous magnesium sulfate. The solution was fractionally distilled first at atmospheric pressure and then at reduced pressure, yielding 88% *exo*-norbornyl trifluoroacetate, bp 69–70° (18 mm), characterized by ir and nmr. *Anal.* Calcd for $C_9H_{11}O_2F_3$: C, 51.92; H, 5.32. Found: C, 51.52; H, 5.19.

Similarly the (+)-*exo*-norborneol gave 19% ester, $[\alpha]_{5461}$ −4.66° (chloroform, *c* 3.52), and (−)-*exo*-norborneol gave 96% trifluoroacetate, $[\alpha]_{5461}$ +4.68° (chloroform, *c* 3.70). The combination of two preparations of the ester was redistilled and gave a product showing only one peak on the gas chromatograph with $[\alpha]_{5461}$ +4.72° (chloroform, *c* 3.54). The inactive material was used for seasoning and for preliminary elimination.

Cyclopropylcarbinyl Trifluoroacetate. To a flask containing 29.4 g (0.408 mole) of cyclopropylcarbinol cooled to 0° was added with stirring 165 g (0.785 mole) of trifluoroacetic anhydride. After 5 min the mixture was shaken with ice and water and extracted several times with low boiling petroleum ether. The extracts were combined and washed successively with water, dilute sodium bicarbonate, and water again, then the petroleum ether solution was dried with magnesium sulfate and distilled, giving the ester, bp 108–109°. More ester was isolated by preparative scale gc from higher and lower boiling fractions giving a combined total of 60.3 g (87%).

The nmr (60 mc) showed a doublet at δ 4.22 (2 H), a multiplet 1.21 (1 H), and a multiplet at 0.53 (4 H), confirming the structure and excluding isomers.

Allylcarbinyl trifluoroacetate for gas chromatographic characterizations of reaction products was prepared from the alcohol by an analogous method and isolated by preparative gc. Other substances for gc reference were commercial.

Infrared and nmr characterizations of all these substances was carried out and is described in detail in the thesis of ref 1.

Rate Measurements. Rates were measured in the stirred flow system with nitrogen carrier gas described previously by Lewis and Witte[13] using an aluminum block thermostat. It is also the system described as II in the previous paper.[4]

Analyses were made by gc using a flame ionization detector; area measurements were made by the height *x* half-width method. For the racemization experiments, the products were trapped in cold methanol, which effectively prevents addition of trifluoroacetic acid to the olefin, and the ester was isolated by preparative scale gc. Rotations were measured in a 1-cm cell in a Bendix automatic recording polarimeter.[17] In the range of concentrations in chloroform used, the rotations were concentration independent.

Acknowledgment. Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

---

(13) A. R. Choppin and E. L. Compere, *J. Am. Chem. Soc.*, **70**, 3797 (1948); E. S. Lewis and K. Witte, *J. Chem. Soc., B*, 1198 (1968); J. N. Barlow, unpublished work.

(14) H. Kwart and H. G. Ling, *Chem. Commun.*, 302 (1969).

(15) H. Kwart and M. T. Waroblak, *J. Am. Chem. Soc.*, **89**, 7145 (1967); H. Kwart and D. P. Hoster, *Chem. Commun.*, 1155 (1967).

(16) J. A. Berson and S. Suzuki, *J. Am. Chem. Soc.*, **81**, 4088 (1959).

(17) This instrument was purchased with the aid of a research equipment grant from the National Science Foundation, which we gratefully acknowledge.