Oxidation of a Simple Alkene by Thallium(III) Trifluoroacetate

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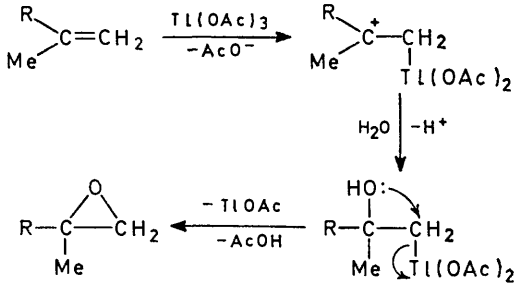
The oxidation of oct-1-ene by thallium(III) trifluoroacetate in a number of solvents has been studied. The initial organothallium adduct is stable under the reaction conditions used but on pouring into water it rapidly decomposes to give mainly octan-2-one, 1,2-epoxyoctane, and octane-1,2-diol. A feature of this decomposition is that a trifluoroacetoxy-substituent on C-2 is almost completely hydrolysed under conditions which leave octane-1,2-diol bistrifluoroacetate largely unchanged. It is suggested that the neighbouring thallium substituent aids hydrolysis, and a mechanism to account for this is proposed.

THALLIUM(III) is a versatile oxidant of organic compounds.[1] In its reactions with olefins it appears to offer advantages over the closely related mercury(II) and lead(IV) reagents.[2-5] For instance, whereas mercury(II) salts react readily with olefins in the presence of a wide variety of nucleophiles,[6-9] the resultant organomercury adducts are too stable to yield organic products directly, though it is possible to replace the mercury substituent by a hydrogen atom[7-9] or a halogen.[9,10] By contrast, lead tetra-acetate reacts sluggishly with most olefins;[2,11-13] the adducts are too labile to be isolated, and radical processes compete with the slow electrophilic addition.[13] The use of lead(IV) trifluoroacetate enables synthetically useful yields of products to be obtained, at least from aryl-substituted olefins,[14] but the problem of the considerable susceptibility of lead(IV) compounds to hydrolysis remains. Even thallium(III) is not an ideal oxidant for olefins. Earlier work with thallium(III) acetate showed that a variety of products are formed[2,3,11,15] and, though the use of the more electrophilic thallium(III) nitrate results in a predominant product in those cases where neighbouring-group displacement of the thallium is particularly easy, there is no evidence that the reactions of simple olefins are synthetically any more useful.[5]

Recently substantial yields of epoxides were obtained from propene and isobutene with thallium(III) in aqueous systems,[16] the mechanism shown in Scheme 1 being invoked to explain their formation. However,

[1] A. McKillop and E. C. Taylor, *Chem. in Britain*, 1973, **9**, 4.
[2] H.-J. Kabbe, *Annalen*, 1962, **656**, 204.
[3] S. Uemura, R. Kitoh, and K. Ichikawa, *Nippon Kagaku Zasshi*, 1966, **87**, 986.
[4] R. J. Ouellette, G. Kordosky, C. Levin, and S. Williams, *J. Org. Chem.*, 1969, **34**, 4104; J. R. Collier and A. S. Porter, *J.C.S. Chem. Comm.*, 1972, 618.
[5] A. McKillop, J. D. Hunt, E. C. Taylor, and F. Kienzle, *Tetrahedron Letters*, 1970, 5275.
[6] W. Kitching, *Organometallic Chem. Rev.* (*A*), 1968, **3**, 61; H. K. Hall, J. P. Schaefer, and R. J. Spanggord, *J. Org. Chem.*, 1972, **37**, 3069.
[7] F. G. Bordwell and M. L. Douglass, *J. Amer. Chem. Soc.*, 1966, **88**, 993; H. C. Brown and M.-H. Rei, *ibid.*, 1969, **91**, 5646; H. C. Brown and J. T. Kurek, *ibid.*, p. 5647.
[8] H. C. Brown and P. J. Geoghegan, *J. Org. Chem.*, 1970, **35**, 1844; J. J. Perie, J. P. Laval, J. Roussel, and A. Lattes, *Tetrahedron*, 1972, **28**, 675.
[9] D. H. Ballard and A. J. Bloodworth, *J. Chem. Soc.* (*C*), 1971, 945.
[10] R. Adams, F. L. Roman, and W. N. Sperry, *J. Amer. Chem. Soc.*, 1922, **44**, 1781; G. F. Wright, *ibid.*, 1935, **57**, 1993; G. Spengler and A. Weber, *Brennstoff-Chem.*, 1959, **40**, 22.
[11] C. B. Anderson and S. Winstein, *J. Org. Chem.*, 1963, **28**, 605.
[12] R. O. C. Norman and C. B. Thomas, *J. Chem. Soc.* (*B*), 1967, 604.
[13] R. O. C. Norman and C. B. Thomas, *J. Chem. Soc.* (*B*), 1967, 771; 1968, 994.
[14] A. Lethbridge, R. O. C. Norman, and C. B. Thomas, *J.C.S. Perkin I*, 1973, 35.
[15] J. B. Lee and M. J. Price, *Tetrahedron*, 1964, **20**, 1017.
[16] W. Kruse and T. M. Bednarski, *J. Org. Chem.*, 1971, **36**, 1154.

ethylene and the but-2-enes gave only traces of epoxides. In the course of a systematic investigation of the

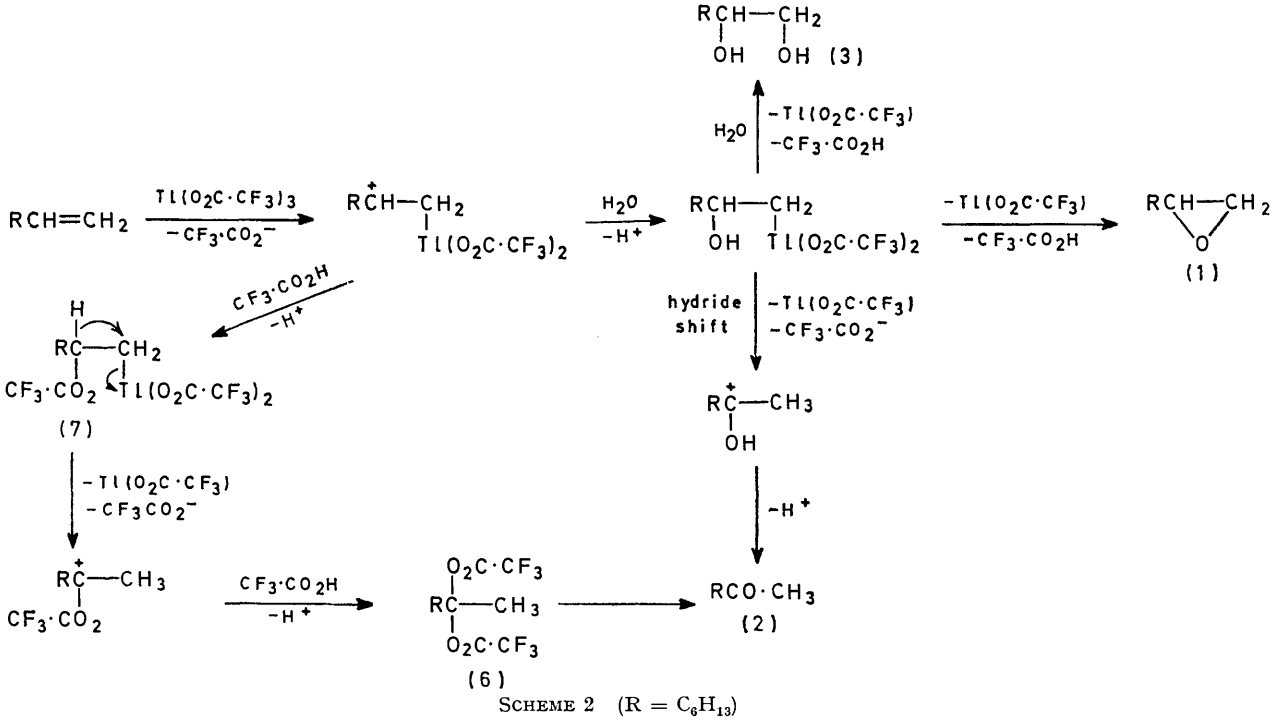


SCHEME 1

distribution of products from aliphatic olefins as a function of metal oxidant and solvent, we treated oct-1-ene with thallium(III) trifluoroacetate in trifluoroacetic acid and found some of the corresponding epoxide amongst the products, even when water was rigorously excluded from the oxidation system. We report here a study of the origin of the epoxide and of the other products.

RESULTS AND DISCUSSION

As a typical monosubstituted alkene for oxidation by metal ions we have employed oct-1-ene since this olefin is not so volatile as to make quantitative work difficult nor of such a high molecular weight that problems might be anticipated in analysing the reaction mixture by g.l.c. and mass spectrometry. On oxidation with thallium(III) trifluoroacetate in trifluoroacetic acid, oct-1-ene gave, after work-up, 1,2-epoxyoctane (1), octan-2-one (2), and octane-1,2-diol (3). Traces of the bistrifluoroacetate (4) and a small amount of the hydroxy-trifluoroacetate (5) * were also present. Of the three principal products the first and last, on the basis of accepted mechanisms,[16] require the presence of water to attack intermediate carbonium ions generated during oxidation (Scheme 2). An alternative possibility for diol formation, that (4) is hydrolysed during work-up, was ruled out when we found that, under these conditions, the diester could be recovered essentially unchanged and that the only other component was a small

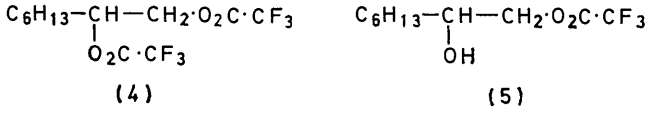


SCHEME 2 (R = C_6H_{13})

* No sample of hydroxy-trifluoroacetate was obtained pure. The material peak appeared homogeneous (g.l.c.) and is assigned the structure (5) on the basis of its mass spectrum. No molecular ion (*m/e* 242) was observed but two primary fragment ions, *m/e* 157 and 115, are attributable to cleavage on either side of the hydroxy-group. The latter ion then loses H_2O followed by C_3H_6. The presence of a peak at *m/e* 69 and the isotope ratio for the ion of *m/e* 157 confirm the presence of a trifluoroacetate group. However, we cannot be certain that none of the isomer $C_6H_{13}CH(O_2C{\cdot}CF_3){\cdot}CH_2{\cdot}OH$ is present. Though a small peak at *m/e* 31 might arise by another means, a very weak ion is observed at *m/e* 211 which could be attributable to $C_6H_{13}\overset{+}{C}H{\cdot}O_2C{\cdot}CF_3$. In analogous cases involving hydroxy-acetates both isomers are frequently found [13,17,18] and yet the material appears homogeneous by g.l.c. In such instances the two compounds are known to undergo fast equilibration in solution [17] and presumably the same is true of the gas phase. Interconversion of hydroxy-trifluoroacetates would be expected to be much slower but still occurs to a significant extent at room temperature.[19]

[17] T. Cohen, M. Dughi, V. A. Notaro, and G. Pinkus, *J. Org. Chem.*, 1962, **27**, 814.
[18] R. U. Lemieux, in 'Molecular Rearrangements,' ed. P. de Mayo, Interscience, New York, 1964, part 2, p. 763.
[19] J. Hine, D. Ricard, and R. Perz, *J. Org. Chem.*, 1973, **38**, 110.

amount of (5). As shown in Scheme 2 it is also possible to envisage the ketone arising from the common organothallium adduct, but a route not involving the participation of water is feasible in this case, for the 2,2-bistrifluoroacetate (6) might decompose to the ketone before or during work-up. The same is known to be true of *gem*-diacetates from ketones and the analogous bistrifluoroacetates would be expected to be even more labile.



(4) (5)

Now the trifluoroacetic acid employed was not rigorously dried but had been used as expeditiously as possible to minimise the uptake of water by this notoriously hygroscopic solvent. In order to eliminate adventitious water as a source of the hydroxy-groups we carried out oxidations in the presence of trifluoroacetic anhydride and in different solvents; the results are set out in the Table. Besides compounds (1)—(3) and residual olefin, five other products were detected in most experiments, but only two [(4) and (5)] were ever formed in more than 3% yield. The other three products have not been identified though we suspect from their mass spectra and their near constant ratio to each other that two of them are stereoisomers containing two olefin units and a trifluoroacetoxy-substituent. They are not formed in the absence of the oxidant and have been omitted from the Table.

Pretreatment of the trifluoroacetic acid with more than enough trifluoroacetic anhydride to remove any water (experiment 2) resulted in increased yields of the mono- and diesters. However, surprisingly, not only were the diol and ketone still present but also the yield of the epoxide actually increased, indicating that adventitious water is not the sole source of hydroxy-groups.

We then turned to non-nucleophilic solvents which could be obtained in an anhydrous condition. Reactions in methylene dichloride and ethylene dichloride gave broadly similar results: once again compounds (1)—(3) made up the bulk of the products. The addition of anhydride to the ethylene dichloride reaction mixture to make certain no water could be present again significantly altered the product distribution in favour of (4), (5), and residual olefin but did not substantially reduce the yield of diol and that of the epoxide was again slightly increased.

Products from the oxidation of oct-1-ene (0·005 mol) by thallium(III) trifluoroacetate (0·005 mol)

Expt.	Temp. (°C)	Solvent	Products (mol %) $C_6H_{13}CH{=}CH_2$	(1)	(2)	(3)	(4)	(5) [a]	Minimum accountability (%) [b]
1	25	$CF_3{\cdot}CO_2H$ (5 ml) [c]	<1	16	34	40	<1	2	93
2	25	$CF_3{\cdot}CO_2H$ (2·5 ml) + $(CF_3{\cdot}CO)_2O$ (2·5 ml) [c]	23	20	11	3	9	11	92
3	42	CH_2Cl_2 (10 ml) [c]	17	25	32	18	<1	3	98
4	60	$CH_2Cl{\cdot}CH_2Cl$ (10 ml) [c]	10	16	31	31	<1	1	92
5	60	$CH_2Cl{\cdot}CH_2Cl$ (10 ml) + $(CF_3{\cdot}CO)_2O$ (5 ml) [c]	24	18	2	20	8	22	97
6	60	$CH_2Cl{\cdot}CH_2Cl$ (10 ml) + $(CF_3{\cdot}CO)_2O$ (5 ml) [d]	26	<1	2	<1	45	<1	75
7	60	$CF_3{\cdot}CO_2H$ (2·5 ml) + $(CF_3{\cdot}CO)_2O$ (2·5 ml) [d]	26	<1			55	4	91

[a] No authentic sample of (5) available; g.l.c. calibration factor estimated. [b] Percentage of starting olefin accounted for including an allowance for the three unidentified minor products. [c] Products analysed after work-up. [d] Products analysed before work-up.

The key to the explanation of these results was provided when this same reaction mixture was injected into a gas chromatograph before work-up (experiment 6). The major product was now (4); (1), (3), and (5) were present in no more than trace amounts. This cannot be explained by partial conversion of the diester into the three other compounds during work-up for we have already shown that (4) is largely inert under these conditions. Further, n.m.r. spectrometry, after removal of the solvent, showed there to be no more than 8% of (4) present.

We believe that, under our conditions, all the thallium(III) trifluoroacetate had been consumed and the resultant organothallium adduct (7) is sufficiently stable to survive the reaction. On injection into the gas chromatograph very rapid decomposition occurs in the inlet heater leading principally to (4). This means that, in the ethylene dichloride–anhydride solvent system before work-up, the only species present in substantial quantities are (7) and unchanged olefin.* An exactly similar situation pertains to the mixed anhydride–acid solvent system; before work-up the only compound, other than olefin, detected in large amounts on g.l.c. was (4).†

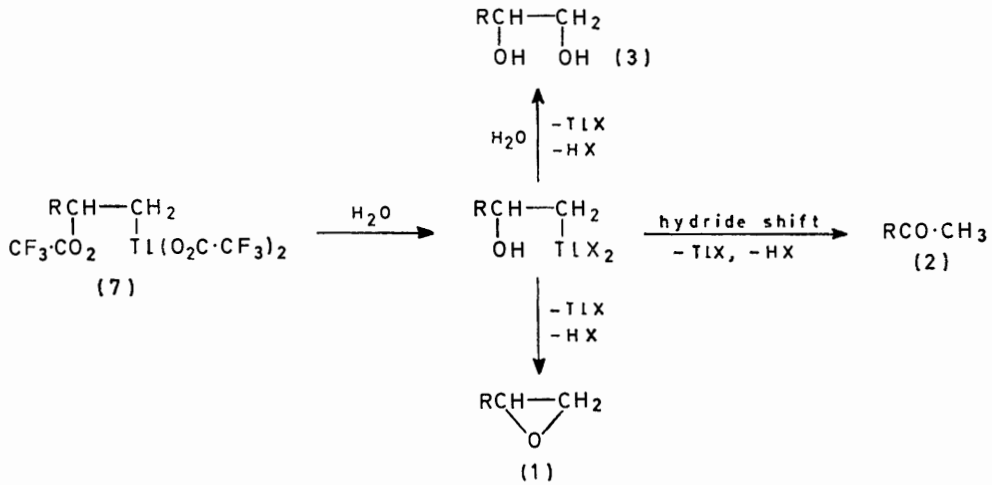
* However, we were unable to provide positive proof of the presence of (7) by n.m.r. spectrometry, for the following reasons. First, the adduct is very labile; the viscous oil obtained on removal of the solvent began to decompose even on such mild treatment as trituration with light petroleum. Secondly, it is not easy to predict the n.m.r. spectrum of (7). By analogy with the spectrum of (4) we should expect the β-proton signal to lie close to τ 5·0 but the position of that due to the α-protons is more speculative. Similar protons in oxymercurial adducts of oct-1-ene give signals around τ 7·7:[20] replacing the mercury by thallium and attaching a second strongly electron-withdrawing ligand to the metal should result in a downfield shift and we might therefore expect the signal due to the α-protons to occur at τ 6·5—7·0. Spin–spin coupling to the thallium should result in both proton resonances being split into doublets. Now the coupling constants in di- and tri-alkylthallium compounds vary greatly in size but $J_{Tl\text{-}CH_2}$ should lie between 200 and 350 Hz and $J_{Tl\text{-}CH}$ between 200 and 650 Hz.[21] The spectrum we obtained showed two broad resonances centred at τ 2·6 and 4·2 which we cannot assign to any other species likely to be present in the system; they may be the downfield components of the doublets (both coupling constants would then be *ca.* 300 Hz), but, if so, the upfield components would lie under the aliphatic envelope.

† The different accountabilities in experiments 6 and 7 are not unexpected for decompositions occurring in a gas chromatograph.

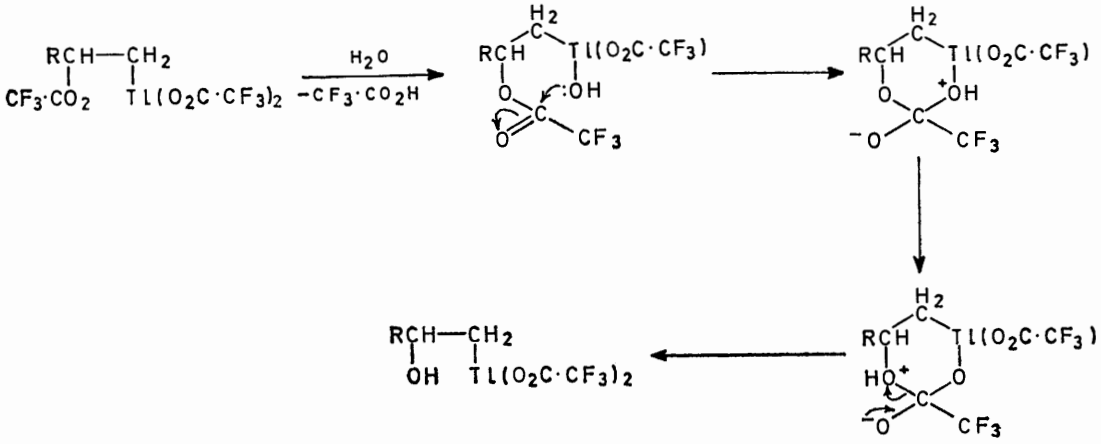
[20] A. Lethbridge, in preparation.
[21] J. V. Hatton, *J. Chem. Phys.*, 1964, **40**, 933; J. P. Maher and D. F. Evans, *J. Chem. Soc.*, 1965, 637.

Two other observations support the view that an organothallium compound must be a relatively stable intermediate. First, the epoxide cannot be present in the reaction mixture from experiment 1 before work-up. Thus, when this compound was treated with trifluoroacetic acid under the conditions used in that experiment, none was recovered and the hydroxy-trifluoroacetate (5) was formed. Secondly, treatment of the crude product from experiment 7 with sodium borohydride gave oct-1-ene in greater than 45% yield, together with small quantities of octan-2-ol and 1-methylheptyl trifluoroacetate. Attempted borohydride reduction of similar organothallium adducts is reported to give mainly the olefin,[22] in contrast to the behaviour of analogous organomercurials.[7,8] (This result is not as conclusive as we would have wished, but because of the lability of the adduct we dared not carry out the reduction in the normal aqueous medium; instead we used methylene dichloride as solvent but, since reduction was inordinately slow otherwise, we eventually had to add a few drops of water to the system after which deposition of *metallic* thallium occurred rapidly.)

Our conclusions are not incompatible with those of Kruse[16] and Henry[23] that the initial carbonium ion produced by reaction of electrophilic thallium with the olefin is attacked by water, since these workers employed aqueous solvents. Indeed, Kruse isolated an adduct to which he assigned the structure $Me_2C(OH)\cdot CH_2Tl(OAc)_2,H_2O$. Our results merely serve to show that hydroxy-substituents can be introduced into the molecule after reaction would normally be considered to be complete and that this can occur irrespective of the anhydrous nature of the solvent.



SCHEME 3 (R = C_6H_{13})



SCHEME 4 (R = C_6H_{13})

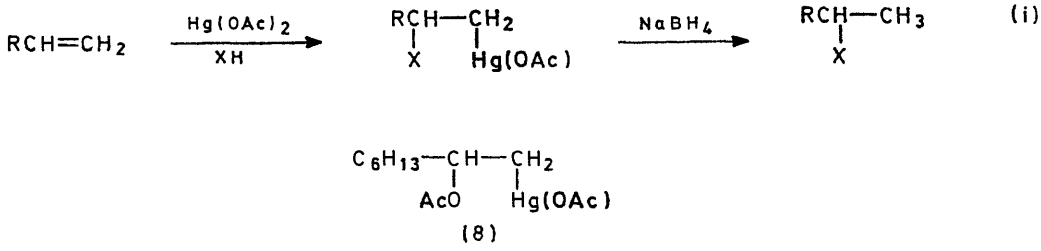
We are left with explaining how the organothallium adduct gives rise to the observed products when poured into water. The probable sequence would seem to be that shown in Scheme 3 (X = OH or $O_2C\cdot CF_3$, the stage at which exchange occurs being indeterminate). The initial conversion of the β-trifluoroacetoxy-group into a hydroxy-substituent is most likely to occur through

[22] S. Uemura, A. Tabata, and M. Okano, *J.C.S. Chem. Comm.*, 1972, 517.

[23] P. M. Henry, *J. Amer. Chem. Soc.*, 1965, **87**, 990, 4423; 1966, **88**, 1597.

nucleophilic attack on the carbonyl function. Now (4) is hydrolysed to only a small extent under the conditions of work-up, so that the neighbouring thallium substituent must provide considerable assistance to hydrolysis for the product distribution to be explained. How it does this is not clear but one possibility is shown in Scheme 4.

We have come across one other example of a metal substituent apparently facilitating nucleophilic attack on an adjacent ester function. When olefins are treated with mercuric acetate in nucleophilic solvents, an organomercurial results which, on reduction with sodium borohydride, gives a monosubstituted hydrocarbon [reaction (i)]. Oct-1-ene with mercuric acetate in acetic acid gave the expected adduct (8) in a crude state and this on reduction yielded not only the expected 1-methylheptyl acetate (40%) but also octan-2-ol (31%). Comparison of the n.m.r. and i.r. spectra of the product before reduction with those of the analogous adduct from reaction in aqueous tetrahydrofuran showed that no hydroxy-group arising from adventitious water was present on C-2. Since 1-methylheptyl acetate is inert under these conditions we conclude that partial reduction of the ester function occurs before replacement of the mercury substituent and is assisted by it; the key intermediate is possibly the organomercury hydride proposed by [24] Pasto and Gontarz.*



We are left to account for the effect of trifluoroacetic anhydride on the product composition. The Table shows that only in the presence of anhydride are significant yields of (4) and (5) obtained, at the primary expense of diol and ketone. In comparing experiment 2 with 1 we cannot be certain that this is not a result of the removal of water from the system by anhydride so that attack on the initial carbonium ion must be by acid or by a trifluoroacetate anion. As has been noted, this would be expected to result in diversion of (3) to (4) and, if a substantial percentage of adduct (7) survives till work-up, (5). It is also likely that the yield of ketone would be reduced, since hydride shift on displacement of the thallium should occur more readily if a hydroxy-group rather than a trifluoroacetoxy-substituent is present on C-2 to stabilise the positive charge.

However, two anomalies remain for which no satisfactory explanation can be offered. First, on the foregoing hypothesis, the yield of epoxide should also fall when the anhydride is included; in practice, in both experiments 2 and 5, it rises a little. Secondly, we might expect some correlation between the reduction in yield of the diol and that of the ketone; instead we find that in one case it is the diol yield which is cut and in the other the ketone yield. In the latter instance a further complication is that all the ketone appears to have been present before the reaction mixture was poured into water. A possible explanation of why, in reactions with anhydride present, (4) and (5) are favoured is that the anhydride in some way inhibits the thallium-assisted hydrolysis of the C-2 ester function.

* A superficially similar reaction to this reduction of an ester group with assistance from a neighbouring mercury substituent has recently been reported.[25] Borohydride reduction of the peroxymercury adduct RCH(O·OBu^t)·CH$_2$HgOAc gives, besides the expected peroxide RCH(O·OBu^t)Me, the epoxide RCH·CH$_2$·O. However, the authors consider that reaction proceeds by a free-radical route and not by nucleophilic attack on the β-substituent.

EXPERIMENTAL

^{1}H N.m.r. spectra were measured for solutions in deuteriochloroform on a Perkin-Elmer R10 60 MHz spectrometer. Mass spectra were determined on an A.E.I. MS12 spectrometer which was coupled *via* a heated capillary tube to a gas chromatograph. G.l.c. was performed on a Pye instrument (series 104, model 24) with 5 ft × 1/4 in columns packed with Carbowax 20M or Apiezon L, each as a 10% coating on Celite. Products were identified by comparison of retention times and mass spectra with those of authentic materials. For quantitative analysis naphthalene was added as a standard. A hydrogen-inject flame ionisation detector gave a linear response and the relationship between the quantity of a material injected and its peak area was established by analysis of synthetic mixtures.

Materials.—Oct-1-ene and octan-2-one (B.D.H.) were commercial reagents. Trifluoroacetic acid and trifluoroacetic anhydride (Fison Laboratory Reagents) were redistilled immediately before use. Methylene dichloride and ethylene dichloride were dried over phosphorus pentoxide for 24 h and then distilled onto sodium hydroxide pellets. Thallium(III) trifluoroacetate (Emanuel) was stored under anhydrous conditions.

1,2-Epoxyoctane was prepared by the method of Swern *et al.*[26] and had b.p. 56—59° at 15 mmHg (lit.,[26] 61° at 15 mmHg); τ 7·0—7·4 (2H, m, 2 × oxiran-H), 7·58 (1H, dd, *J* 4 and 6 Hz, oxiran-H), and 8·4—9·3 (13H, aliphatic envelope).

Octane-1,2-diol was made by a modification of Vogel's

[24] D. J. Pasto and J. A. Gontarz, *J. Amer. Chem. Soc.*, 1969, **91**, 719.
[25] A. J. Bloodworth and G. S. Bylina, *J.C.S. Perkin I*, 1972, 2433.
[26] D. Swern, G. N. Billen, and J. T. Scanlan, *J. Amer. Chem. Soc.*, 1946, **68**, 1504.

method.[27] Oct-1-ene (25 g) was added dropwise during 30 min at 40—45° to a well-stirred mixture of 90% formic acid (120 ml) and 30% hydrogen peroxide (12 ml). After 1 h at 40° and 16 h at room temperature the excess of formic acid and water was removed under reduced pressure and the residue was added to an ice-cold solution of sodium hydroxide (16 g) in water (30 ml). The mixture was stirred for 1 h, then poured into water and extracted with ether; the extract was dried ($MgSO_4$) and evaporated. Distillation of the residue gave octane-1,2-diol (28 g, 87%) as a low-melting solid, b.p. 104° at 2 mmHg (lit.,[26] 135—136° at 10 mmHg); τ 5·75br (2H, s, OH, removed by D_2O), 6·1—6·75 (3H, m, O·CH·CH_2·O), and 8·0—9·3 (13H, aliphatic envelope).

Octane-1,2-diol (2 g) was added dropwise with vigorous stirring to a solution of sodium carbonate (0·5 g) in trifluoroacetic anhydride (12 ml). The resultant pale yellow solution was refluxed for 1 h, excess of solvent was removed under reduced pressure, and the residue was distilled to give *octane*-1,2-*diyl bistrifluoroacetate* (3·8 g, 74%) as a liquid, b.p. 98° at 12 mmHg; τ 4·62 (1H, m, CH), 5·44 (2H, AB part of ABC system, J_{AB} *ca.* 12, J_{AC} *ca.* 7, J_{BC} *ca.* 3 Hz, CH_2·O), and 7·9—9·4 (13H, aliphatic envelope) (Found: C, 42·6; H, 4·7. $C_{12}H_{16}F_6O_4$ requires C, 42·6%; H, 4·8%).

Octan-2-ol was prepared by the method of Brown.[8] To a stirred suspension of mercury(II) acetate (31 g) in a mixture of water (100 ml) and tetrahydrofuran (100 ml) was added oct-1-ene (12 g). After 10 min 2M-sodium hydroxide (100 ml) was added, followed by a solution of sodium borohydride (0·2 g) in 2M-sodium hydroxide (100 ml). After 1 h the organic layer was decanted and evaporated. Distillation of the residue gave octan-2-ol (11·6 g, 85%) as a liquid, b.p. 76° at 14 mmHg (lit.,[28] 86° at 20 mmHg); τ 6·21br (1H, m, CH), 7·82br (1H, s, OH, removed by D_2O), 8·81 (d, *J* 6 Hz, Me), and 8·3—9·3 (16H total, aliphatic envelope).

Octan-2-ol (6 g) was added dropwise to a solution of sodium carbonate (0·1 g) in trifluoroacetic anhydride (10 ml). After refluxing for 1 h the solution was concentrated under reduced pressure and the residue distilled to give 1-*methylheptyl trifluoroacetate* (9·5 g, 79%) as a liquid, b.p. 70° at 18 mmHg; τ 4·87 (1H, sextet, *J* 6 Hz, CH), 8·65 (d, *J* 6 Hz, Me), and 8·0—9·3 (total 16H, aliphatic envelope); *m/e* 141 (9·8%, $M - C_6H_{13}$), 113 (16·8, $M - CF_3CO_2$), 112 (50, $M - CF_3CO_2H$), and 70 (100, $C_5H_{10}^{+\cdot}$) (Found: C, 53·1; H, 7·5. $C_{10}H_{17}F_3O_2$ requires C, 53·1; H, 7·6%).

Oxidations.—A typical oxidation was carried out as follows. Trifluoroacetic acid (2·5 ml) and trifluoroacetic anhydride (2·5 ml) were added to thallium(III) trifluoroacetate (0·005 mol) in a flask protected from atmospheric moisture. The solution was stored overnight to ensure removal of water and oct-1-ene (0·005 mol) was added dropwise with stirring at room temperature over 10 min. Reaction was near instantaneous, all the thallium(III) having been consumed by the time addition was complete as judged by the absence of a brown precipitate on adding a drop of the mixture to dilute sodium hydroxide solution. In some experiments (see Table) the reaction mixture was injected directly into a gas chromatograph at this stage. In most, however, the solution was poured into water (50 ml) and extracted with ether; the extract was washed with sodium hydrogen carbonate solution and dried ($MgSO_4$). The solvent was removed and the resultant yellow oil was analysed by g.l.c., mass spectrometry, and n.m.r. spectrometry.

In one instance (experiment 8) the solution was concentrated before work-up, care being taken to ensure that water did not enter the system. An n.m.r. spectrum of some of the crude product was obtained and the remainder was reduced as follows: to the crude product (1·6 g) in dry methylene dichloride (10 ml) sodium borohydride (0·3 g) was added with stirring. No apparent reaction took place over 2 h but on addition of one drop of water metallic thallium was immediately deposited. Further drops were added until effervescence no longer occurred. The organic layer was then separated, dried ($MgSO_4$), and evaporated before analysis by g.l.c. and mass spectrometry.

In another experiment an unsuccessful attempt was made to isolate octane-1,2-diol monotrifluoroacetate. This could not be obtained in a pure state but the mass spectrum of the major peak confirmed that this was the hydroxytrifluoroacetate: *m/e* 157 (5·7%, $M - C_6H_{13}$), 115 (24·5, $M - CF_3CO_2CH_2$), 110 (3·9, $M - CF_3CO_2H - H_2O$), 97 (58·0, $115 - H_2O$), 69 (41·3, CF_3^+ and $C_5H_9^+$), and 55 (100, $C_4H_7^+$).

Reaction of Oct-1-ene with Mercury(II) *Acetate.*—To a well-stirred suspension of mercury(II) acetate (3·2 g) in acetic acid (10 ml) containing acetic anhydride (2 ml) was added oct-1-ene (1·2 g). The mercury salt dissolved rapidly and after being stirred for ½ h the solution was poured into water (50 ml) and extracted with ether. The extract was washed with sodium hydrogen carbonate solution and dried ($MgSO_4$). Removal of the ether left crude 1-(acetoxymercuriomethyl)heptyl acetate which did not solidify; τ 4·95 (1H, m, CH), 7·95 (m, CH_2Hg), 7·99 and 8·01 (each s, OAc), and 8·25—9·4 (13H, aliphatic envelope). To this oil was added 2M-sodium hydroxide (5 ml), followed by sodium borohydride (0·2 g) in 2M-sodium hydroxide (5 ml). The mixture was stirred for 5 min and extracted with ether; the extract (20 ml) was shaken with sodium hydrogen carbonate solution, dried ($MgSO_4$), and evaporated to leave a mobile oil which was analysed by g.l.c. and n.m.r. spectroscopy. Omission of the borohydride resulted in no reaction other than conversion of the acetoxymercurio-substituent into a hydroxymercurio-system.

Solvolysis of 1,2-*Epoxyoctane.*—The epoxide (0·64 g) was added dropwise during 10 min to a stirred mixture of trifluoroacetic acid (2 ml) and trifluoroacetic anhydride (2 ml) in ethylene dichloride (10 ml). The mixture became warm during the addition and after 5 min at reflux was cooled. A sample of the crude product was injected directly into the gas chromatograph and the remainder was poured into water (50 ml). The organic layer was washed with sodium hydrogen carbonate solution, dried ($MgSO_4$), and evaporated, and the crude product was analysed by g.l.c.

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[27] A. I. Vogel, 'Practical Organic Chemistry,' 3rd edn., Longmans, London, 1956, p. 894.

[28] Heilbron's 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965.