

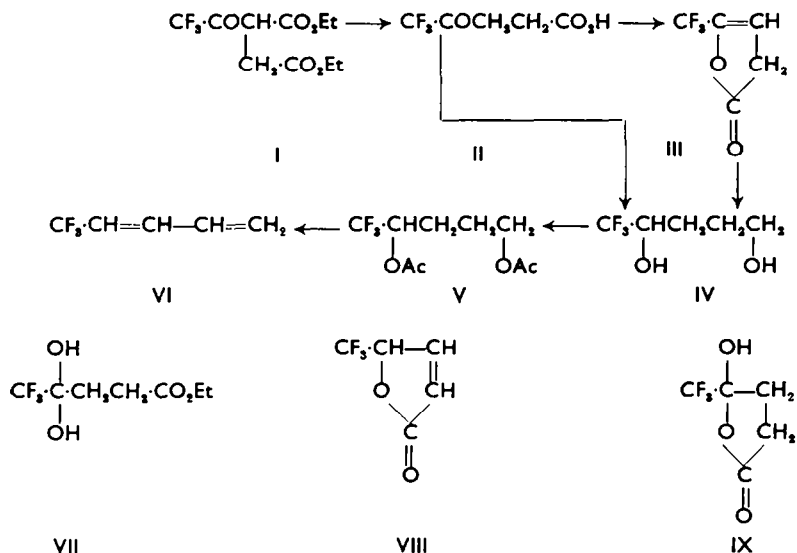
5,5,5-TRIFLUOROLAEVULIC ACID AND SOME DERIVED COMPOUNDS

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Abstract—5,5,5-Trifluorolaevulic acid (II) has been prepared by the acidic hydrolysis of the Claisen condensation product (I) of ethyl trifluoroacetate and diethyl succinate. Dehydration of the acid (II) with phosphoric oxide gave 4-hydroxy-5,5,5-trifluoropent-3-enoic acid lactone (III). Reduction of either this lactone or the acid (II) with lithium aluminium hydride gave 5,5,5-trifluoropentane-1,4-diol (IV), from which 5,5,5-trifluoropenta-1,3-diene (VI) has been obtained by acetylation followed by pyrolysis.

A RECENT publication by Groth,¹ which describes *inter alia* compounds derived from the Claisen condensation of ethyl trifluoroacetate and diethyl succinate, prompts us to publish our related, but more detailed, work on this topic. The main reactions which we have carried out are summarized below.



Groth¹ did not isolate diethyl trifluoroacetosuccinate (I) but instead, converted it, by acidic hydrolysis into an unsaturated lactone to which he assigned the structure VIII. He hydrogenated this material to give a saturated lactone which he condensed further with ethyl trifluoroacetate.

Three catalysts appear to have been employed to effect Claisen condensations of

¹ R. H. Groth, *J. Org. Chem.* **24**, 1709 (1959).

fluoro-esters. The usual one is sodium ethoxide; sodium hydride has also found application² and metallic sodium in one case.³ In other work in this Department⁴ we have found that sodium metal can be used generally for promotion of ester condensations with fluoro-esters. In the present study, all three reagents have been used to condense ethyl trifluoroacetate and diethyl succinate (Groth used sodium ethoxide only). All three catalysts gave the same product from the condensation, diethyl trifluoroacetosuccinate (I). Sodium was the best, it was easiest to use and gave the highest yield, 72 per cent of I. This boiled over a range (100–150°/0.5 mm); all the material appeared, however, to be diethyl trifluoroacetosuccinate, since the yields of the derived acid (II), which were obtained by hydrolysis of low- and high-boiling fractions, were almost identical with that obtained from material boiling over the complete range. This wide boiling-range may have been due to keto-enol tautomerism in I, presumably the lower-boiling material being mainly the enol-isomer, and the higher the keto. This was supported by infra-red spectroscopic analysis: the intensity of the —O—H stretching frequency at 3400 cm⁻¹ relative to that of the —C=O stretching frequency at 1850–1700 cm⁻¹ being greater in a low-boiling fraction than in a high.

Acidic hydrolysis of the Claisen ester (I) led to two products: the major one was the crystalline 5,5,5-trifluorolaevulic acid (II) and the minor its ethyl ester hydrate (VII). The structure of the acid (II) was confirmed by treatment with alkali when succinic acid was formed by a haloform reaction. The structure of the ester (VII) was demonstrated by hydrolysis to the parent acid (II), and by synthesis from this acid (II) by esterification with ethanol and sulphuric acid. Further confirmation was supplied by conversion of the ester (VII) into the diol (IV) and into the unsaturated lactone (III) (see later). That the ester was hydrated and the acid (II) was not is rather surprising. It is well-known⁵ that carbonyl groups flanked by perfluoroalkyl groups form addition compounds easily, so the formation of the ester hydrate (VII) is not unexpected. It is possible, however, that the acid actually has a cyclic structure (IX)—similar cyclic structures have been proposed⁶ for derivatives of laevulic acid itself. In the absence of some such addition at the carbonyl group it is difficult to explain the failure of the acid to form a hydrate. It is perhaps significant that the S-benzylthiuronium salt of the acid (II) is hydrated.

Prolonged heating of the acid (II) gave an unsaturated lactone which we consider to be 4-hydroxy-5,5,5-trifluoropent-3-enoic acid lactone (III), the trifluoro-analogue of α -angelicalactone. Other, non-fluorinated γ -keto-acids are known⁷ to dehydrate analogously. This unsaturated lactone (III) is, however, best prepared by distillation of the acid (II) from phosphoric oxide or from concentrated sulphuric acid. Groth¹ has suggested the alternative $\alpha\beta$ -unsaturated structure (VIII) for this product: he compared its behaviour towards catalytic hydrogenation, aniline, ethanolic hydrogen chloride and bromine water with the known⁸ behaviour of the unfluorinated analogues of III and VIII (α - and β -angelicalactone, respectively). In these tests the fluorinated

² E. T. McBee, O. R. Pierce, H. W. Kilbourne and E. R. Wilson, *J. Amer. Chem. Soc.* **75**, 3152 (1953); F. W. Swamer and C. R. Hauser, *Ibid.* **72**, 1352 (1950).

³ R. N. Haszeldine, W. K. R. Musgrave, F. Smith and L. M. Turton, *J. Chem. Soc.* **609** (1951).

⁴ J. Burdon, V. C. R. McLoughlin and J. C. Tatlow, to be published.

⁵ W. K. R. Musgrave, *Quart. Rev.* **8**, 331 (1954).

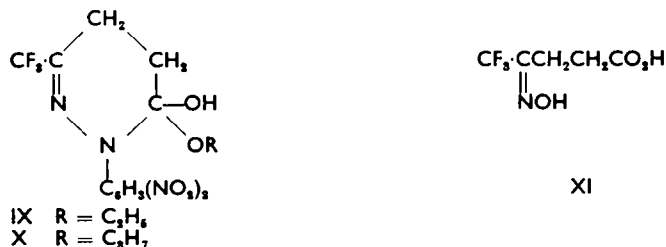
⁶ E. H. Rodd, *The Chemistry of Carbon Compounds* Vol. 1B, p. 879. Elsevier, Amsterdam (1952).

⁷ L. Wolff, *Liebigs Ann.* **229**, 249 (1885).

⁸ F. A. Kuehl, R. P. Linstead and B. A. Orkin, *J. Chem. Soc.* **2213** (1950); W. A. Jacobs and A. B. Scott, *J. Biol. Chem.* **87**, 601 (1930).

lactone showed a greater similarity towards β -angelicalactone than towards the α -isomer. Contrariwise, however, we have shown that the fluorinated lactone gives two tests which are given⁸ by α -angelicalactone but not by β : it affords a silver mirror with ammoniacal silver nitrate and a deep red colour with alkaline nitroprusside solution. It seems probable that the trifluoromethyl group so modifies the chemical properties of structures such as the angelicalactones that any deductions based on such analogies are invalid. Our fluorinated lactone (III) had almost no absorption in the ultra-violet whereas the $\alpha\beta$ -unsaturated structure (VIII) would show a large absorption (β -angelicalactone has⁹ ϵ , 10,000 at 214 $m\mu$). Again, the acidic hydrolysis of the fluorinated lactone (III) gave the laevulic acid (II) and lithium aluminium hydride reduction of it gave the diol (IV); neither reaction seems very likely on the basis of structure VIII. It is also difficult to see how the $\alpha\beta$ -compound (VIII) could form except by a prototropic rearrangement of the $\beta\gamma$ -compound (III), itself formed by simple dehydration of the enol of the acid (II): such rearrangements are usually very slow in acidic media.¹⁰ We therefore suggest that the fluorinated lactone is, in fact, the $\beta\gamma$ -unsaturated compound (III). Attempts at dehydration of the hydrated ester (VII) gave mixtures of the unsaturated lactone (III) and starting material. No anhydrous ester could be isolated.

Both the acid (II) and the lactone (III) reacted with aqueous ethanolic 2,4-dinitrophenylhydrazine to give the same product—probably the pyridazone derivative (IX). This could be produced by cyclization of the initially formed 2,4-dinitrophenylhydrazone, followed by addition of ethanol across the carbonyl group. Similar cyclizations¹¹ occur with non-fluorinated γ -keto-acids. In confirmation of this structure, when the reaction was conducted in aqueous propanol the acid (II) gave the analogous propanol adduct (X). Both the acid and the lactone gave the normal oxime (XI).



Reduction of either the acid (II), the ester (VII) or the lactone (III) with lithium aluminium hydride in ether gave an excellent yield of 5,5,5-trifluoropentane-1,4-diol (IV), although in the case of the lactone (III) a small amount of another, higher-boiling material, whose structure was not investigated, was also formed. The diol (IV) was characterized as its bis (3,5-dinitrobenzoate) and its diacetate (V). The latter compound underwent pyrolysis at 520° to give 5,5,5-trifluoropenta-1,3-diene (VI) in 75 per cent yield. The five-stage synthesis of 1-trifluoromethylbutadiene (VI) described here gives an overall yield of about 33 per cent from ethyl trifluoroacetate. Henne *et al.*^{12,13} have obtained about a 39 per cent yield from ethyl trifluoroacetate in

⁹ L. J. Haynes and E. R. H. Jones, *J. Chem. Soc.* 954 (1946).

¹⁰ C. K. Ingold, *Structure and Mechanism in Organic Chemistry* pp. 546–550. G. Bell, London (1953).

¹¹ Reference 6, p. 882.

¹² A. L. Henne, M. S. Newman, L. L. Quill and R. A. Staniforth, *J. Amer. Chem. Soc.* 69, 1819 (1947).

¹³ A. L. Henne and P. E. Hinkamp, *J. Amer. Chem. Soc.* 76, 5147 (1954).

a four-stage synthesis via 1,1,1-trifluoropentane-2,4-dione, which was reduced to the analogous diol, the acetate of which was pyrolysed.

Treatment of the diene (VI) with bromine in glacial acetic acid gave a dibromo-compound. This appeared to be a single substance since it showed only one (sharp) peak in gas-phase chromatography: its infra-red spectrum also was not suggestive of a mixture. The complete absence of any strong absorption in the region $900\text{--}950\text{ cm}^{-1}$ showed¹⁴ that the compound possessed no vinyl ($-\text{CH}=\text{CH}_2$) group, and was not, therefore, the 1,2-dibromo-compound. We have not, however, been able to distinguish between the other two possibilities, the 1,4- and 3,4-compounds. Oxidation led only to small yields (<10 per cent) of trifluoroacetic acid—too low to be of any significance.

EXPERIMENTAL

The condensation of ethyl trifluoroacetate with diethyl succinate

(a) *With sodium hydride as catalyst.* Ethyl trifluoroacetate (96.5 g, 0.68 mole) was added to powdered sodium hydride (17.0 g, 0.71 mole) over a period of about 10 min in an atmosphere of dry nitrogen. When reaction had subsided, the viscous solution was heated to 60° and diethyl succinate (48.5 g, 0.28 mole) was added, with stirring, over 5–6 hr; the resulting mixture was maintained at $65\text{--}70^\circ$ and was stirred vigorously for a further 15 hr. The reaction mixture was allowed to cool and crushed ice (ca. 100 g) was added to it, followed by water (100 ml) and sulphuric acid (50 ml, *d.* 1.84). The oily product was extracted with ether (3×100 ml), the extracts were dried (MgSO_4) and the ether was evaporated to leave crude *diethyl trifluoroacetosuccinate* (I, 55.5 g), b.p. $78\text{--}113^\circ/0.5$ mm, n_D^{20} 1.4070. This material contained diethyl succinate (ca. 3 g) since hydrolysis (see below) gave some succinic acid. When a smaller proportion of ethyl trifluoroacetate was used, greater amounts of diethyl succinate remained unreacted. Fractional distillation of this crude product under reduced pressure was unsatisfactory since only a very low boil-up rate could be achieved; this caused the reflux temperature to fluctuate widely. A pure product (Found: C, 44.6; H, 4.8. $\text{C}_{10}\text{H}_{14}\text{F}_6\text{O}_8$ requires: C, 44.5; H, 4.9%) was, however, obtained as a middle fraction.

(b) *With sodium ethoxide as catalyst.* A mixture of sodium ethoxide (63.5 g, 0.93 mole), ethyl trifluoroacetate (88.7 g, 0.62 mole) and diethyl succinate (48.5 g, 0.28 mole) was refluxed in dry ether for 16 hr. Isolation as in (a) gave crude *diethyl trifluoroacetosuccinate* (I, 11.9 g), n_D^{20} 1.4118. Groth¹ converted this crude product directly into the lactone (III or VIII) in 33–39% yield overall.

(c) *With sodium as catalyst.* Sodium wire (5.0 g, 0.22 mole), ethyl trifluoroacetate (31 g, 0.22 mole) and diethyl succinate (76 g, 0.44 mole) were mixed and then heated to 80° until reaction commenced, when the source of heat was removed. The reaction continued until all the sodium had dissolved. Dry ether (60 ml) was added and the solution was refluxed for 18 hr. The ether and excess of diethyl succinate were then distilled off, the latter *in vacuo*, to leave a black tarry residue of sodio-derivative. The free keto-ester was liberated by treatment with sulphuric acid (150 ml, 10 N) and was extracted with ether (6×50 ml). Distillation of the dried (MgSO_4) extracts gave crude *diethyl trifluoroacetosuccinate* (I, 42 g), b.p. $100\text{--}150^\circ/0.5$ mm, n_D^{20} 1.4104, shown by infra-red spectroscopy to be identical with the product prepared in (a). This crude material was used without further purification in the hydrolysis experiments.

Acidic hydrolysis of diethyl trifluoroacetosuccinate (I)

The ester [42 g, prepared as in (c), above] was refluxed with sulphuric acid (270 ml, 40% w/w) for 4 hr. After being cooled, the solution was extracted with ether (6×60 ml) and the extracts were dried (MgSO_4) and the ether evaporated. Distillation of the residue *in vacuo* gave (i) *ethyl 5,5,5-trifluorolaevalate hydrate* (VII, 3.5 g), b.p. $40\text{--}42^\circ/0.1$ mm, n_D^{20} 1.3725 (Found: C, 38.7; H, 4.9. $\text{C}_7\text{H}_8\text{F}_6\text{O}_8 \cdot \text{H}_2\text{O}$ requires: C, 38.9; H, 5.1%), and (ii) crude *5,5,5-trifluorolaevalic acid* (II, 20 g), b.p. $68\text{--}72^\circ/0.1$ mm, n_D^{20} 1.3900, which solidified, m.p. $54\text{--}56^\circ$, and after crystallization from benzene had m.p. $57\text{--}58^\circ$ (17.6 g) (Found: C, 35.2; H, 2.8; equiv., 171. $\text{C}_5\text{H}_5\text{F}_6\text{O}_8$ requires: C, 35.3; H, 3.0%; equiv., 170). Under the same conditions, hydrolysis of a fraction b.p. $77\text{--}85^\circ/0.15$ mm

¹⁴ L. J. Bellamy, *The Infra-red Spectra of Complex Molecules* p. 34. Methuen, London (1958).

(10 g) gave ester hydrate (0.68 g) and acid (4.7 g); a fraction b.p. 114–120°/0.15 mm (10 g) gave ester hydrate (0.57 g) and acid (4.9 g).

Treatment of an aqueous solution of the neutralized acid with a conc aqueous solution of *S*-benzylthiuronium chloride gave *S*-benzylthiuronium 5,5,5-trifluorolaevalate hydrate, m.p. 119° (from acetone-chloroform) (Found: C, 43.7; H, 5.1. $C_{13}H_{16}F_3N_2O_2S \cdot H_2O$ requires: C, 44.1; H, 4.8%).

Acidic hydrolysis of ethyl 5,5,5-trifluorolaevalate hydrate (VIII)

The ester hydrate (2.0 g) was refluxed with sulphuric acid (20 ml, 40% w/w) for 17 hr. Isolation by ether extraction (5 × 10 ml) gave 5,5,5-trifluorolaevalic acid (II, 1.1 g), b.p. 65–70°/0.2 mm, identified by infra-red spectroscopy.

Esterification of 5,5,5-trifluorolaevalic acid (II)

The acid (5.2 g), ethanol (10 ml) and sulphuric acid (3 ml, *d*, 1.84) were refluxed together for 6 hr. The reaction mixture was poured into water (50 ml) and, after the lower organic layer had been separated, the aqueous layer was extracted with ether (4 × 25 ml). The combined organic layers were dried ($MgSO_4$) and evaporated, and the residue was distilled *in vacuo* to give ethyl 5,5,5-trifluorolaevalate hydrate (VII, 3.0 g), b.p. 40–50°/0.2 mm, n_D^{25} 1.3689. Infra-red spectroscopy showed that this sample was identical with the sample from the hydrolysis of diethyl trifluoroacetosuccinate.

Treatment of 5,5,5-trifluorolaevalic acid (II) with alkali

The acid (0.5 g) was treated with an excess of 2 N sodium hydroxide. Effervescence occurred, the solution became warm and later turned purple. It was heated to 60°, allowed to cool, and kept at room temperature for 3 hr. Acidification with sulphuric acid followed by continuous ether extraction for 75 hr gave succinic acid (0.32 g), m.p. 185–187° (from water), unchanged on admixture with an authentic specimen (Found: equiv., 59. Calc. for $C_4H_4O_4$: equiv., 60).

Dehydration of 5,5,5-trifluorolaevalic acid (II)

(a) *With phosphoric oxide.* The acid (23 g) was refluxed with an excess of phosphoric oxide (6 g) for 2 min, and the crude product then distilled off: it was redistilled from fresh phosphoric oxide to give 4-hydroxy-5,5,5-trifluoropent-3-enoic acid lactone (III, 16.3 g), b.p. 180°, n_D^{25} 1.3831 (Found: C, 39.4; H, 2.3. $C_6H_5F_3O_3$ requires: C, 39.5; H, 2.0%) (Groth¹ quoted b.p. 170–172° and n_D^{20} 1.3853 for his product). Infra-red spectroscopy showed a carbonyl absorption at 1790 cm^{-1} , consistent¹⁵ with $\beta\gamma$ -unsaturation. Treatment of the lactone with alkali gave a deep purple colour: no tractable product could be obtained from this reaction. The compound had no maximum in the ultra-violet: the end absorption at 220 $m\mu$ had ϵ , approx 820 (in ethanol). The intensity fell steadily with increasing wavelength (ϵ , approx 60 at 260 $m\mu$).

(b) *With sulphuric acid.* The acid (4.0 g) was refluxed with sulphuric acid (10 ml, *d*, 1.84) for 3 min. The cooled solution was poured into water (50 ml) and the product isolated by ether extraction (5 × 10 ml). It was the lactone (III, 2.0 g), b.p. 179–182°, n_D^{25} 1.3860, shown by infra-red spectroscopic analysis to be identical with specimen obtained in (a).

An attempted dehydration of the acid by azeotropic distillation with benzene was unsuccessful.

Reaction of ethyl 5,5,5-trifluorolaevalate hydrate (VII) with phosphoric oxide

The ester hydrate (5.2 g) was treated with an excess of phosphoric oxide as described for the parent acid [(a), above]. Infra-red spectroscopic analysis of the product showed that it was a mixture of 4-hydroxy-5,5,5-trifluoropent-3-enoic acid lactone (III, 60%) and ethyl 5,5,5-trifluorolaevalate hydrate (VII, 40%).

Acidic hydrolysis of the lactone (III)

The lactone (1.13 g) and sulphuric acid (25 ml, 5 N) were refluxed together for 6 hr. Isolation by ether extraction (4 × 10 ml) gave 5,5,5-trifluorolaevalic acid (II, 0.71 g), b.p. 65–71°/0.1 mm, identified by infra-red spectroscopic analysis.

¹⁵ Reference 14, p. 179.

Reaction of the acid (II) and the lactone (III) with carbonyl reagents

(a) *2,4-Dinitrophenyl-hydrazine*. The acid (1.1 g) and 2,4-dinitrophenyl-hydrazine sulphate (1.1 g) were refluxed together for 1½ hr in ethanol containing 10% of water. Cooling gave a yellow precipitate of 1-(2',4'-dinitrophenyl)-6-ethoxy-6-hydroxy-3-trifluoromethyl-1,4,5,6-tetrahydropyrazine (IX, 0.5 g), m.p. 105.5–106° (from aqueous ethanol) (Found: C, 41.1; H, 3.5. $C_{11}H_{11}F_3N_4O_6$ requires: C, 41.3; H, 3.5%).

The same product (0.5 g), m.p. 105.5–106° (alone and on admixture with the specimen obtained from the acid) was obtained when the lactone (0.5 g) was treated in the same way.

The acid (0.5 g) reacted with 2,4-dinitrophenyl-hydrazine sulphate in 90% propanol to give 1-(2',4'-dinitrophenyl)-6-hydroxy-6-propoxy-3-trifluoromethyl-1,4,5,6-tetrahydropyrazine (X, 0.5 g), m.p. 62° (from aqueous propanol) (Found: C, 43.0; H, 3.9. $C_{14}H_{11}F_3N_4O_6$ requires: C, 42.9; H, 3.9%).

(b) *Hydroxylamine*. The acid (3.2 g), hydroxylamine hydrochloride (3.8 g), sodium acetate trihydrate (7.6 g) and water (30 ml) were refluxed together for 18 hr. Isolation by ether extraction (3 × 75 ml) gave a residue which was crystallized from benzene to give 5,5,5-trifluorolaevalic acid oxime (XI, 1.3 g), m.p. 130–131° (Found: C, 32.8; H, 3.6. $C_8H_8F_3NO_3$ requires: C, 32.4; H, 3.3%).

The lactone (3 g) was treated with hydroxylamine hydrochloride (3.8 g) and sodium acetate trihydrate (7.6 g) in water (30 ml) in the same way to give the oxime (1.2 g), m.p. 129–130°, alone and on admixture with the specimen obtained from the acid.

Preparation of 5,5,5-trifluoropentane-1,4-diol (IV)

(a) *From 5,5,5-trifluorolaevalic acid (II)*. The acid (25 g, 0.15 mole), dissolved in dry ether (100 ml), was added dropwise, with stirring, over a period of 1 hr to a solution of lithium aluminium hydride (10 g, 0.26 mole) in dry ether (250 ml). The mixture was refluxed, with stirring, for a further 3 hr, and then cautiously treated with water (100 ml), followed by sulphuric acid (300 ml, 20% v/v). The ether layer was separated and the aqueous layer extracted continuously with ether. Distillation of the dried ($MgSO_4$) extracts gave 5,5,5-trifluoropentane-1,4-diol (IV, 18.5 g), b.p. 113–115°/12 mm, n_D^{20} 1.3921 (Found: C, 38.3; H, 5.6. $C_5H_8F_3O_2$ requires: C, 38.0; H, 5.7%).

The diol (1.2 g), on treatment with 3,5-dinitrobenzoyl chloride (2.1 g) in pyridine (25 ml), gave 5,5,5-trifluoropentane-1,4-diol bis-3',5'-dinitrobenzoate (2.3 g), m.p. 133–134° [from acetone–light petroleum (b.p. 60–80°)] (Found: C, 41.9; H, 2.5. $C_{19}H_{18}F_3N_4O_{12}$ requires: C, 41.8; H, 2.4%).

(b) *From the lactone (III)*. The lactone (19.0 g, 0.125 mole) was reduced with lithium aluminium hydride (10 g, 0.26 mole) as described in (a) to give (i) the diol (IV, 10.7 g), b.p. 118–120°/14 mm, identified by infra-red spectroscopic analysis, and (ii) a higher-boiling fraction (2.6 g), b.p. 123–126°/0.3 mm, which has not been investigated further.

(c) *From ethyl 5,5,5-trifluorolaevalate hydrate*. The ester (3.0 g, 0.014 mole) was reduced with lithium aluminium hydride (1.34 g, 0.035 mole) as described in (a) to give the diol (IV, 1.65 g), b.p. 113–114°/12 mm, identified by infra-red spectroscopic analysis.

Acetylation of 5,5,5-trifluoropentane-1,4-diol (IV)

The diol (24.2 g), glacial acetic acid (100 ml) and acetic anhydride (100 ml) were refluxed together for 3 hr, then cooled and poured into water. After separation of the organic layer, the aqueous layer was extracted with ether (3 × 100 ml). The organic layers were combined and washed with a 10% aqueous solution of sodium bicarbonate. The washings were extracted with ether (2 × 50 ml) and the combined ethereal extracts were dried ($MgSO_4$) and concentrated to leave a residue which was distilled to give 5,5,5-trifluoropentane-1,4-diol diacetate (V, 32.7 g), b.p. 210–212°, n_D^{20} 1.3890 (Found: C, 44.9; H, 5.0. $C_9H_{13}F_3O_4$ requires: C, 44.6; H, 5.4%).

Pyrolysis of 5,5,5-trifluoropentane-1,4-diol diacetate (V)

The pyrolysis apparatus, which consisted of a silica tube (28 cm × 1 cm diameter) packed with hard glass chips, was mounted vertically and surrounded by an electrically heated furnace. The diacetate (67 g) was introduced slowly into the heated (520 ± 5°) tube in a stream of nitrogen over a period of 100 min. The pyrolysis products were collected in cooled traps (at 0° and –78°), combined, and fractionally distilled through a 6' long, vacuum-jacketed column packed with 1/16" stainless steel Dixon gauzes to give 5,5,5-trifluoropentane-1,3-diene (VI, 25.3 g), b.p. 45–46°, n_D^{25} 1.3569

(Found: C, 49.4; H, 4.2. Calc. for $C_6H_8F_3$: C, 49.2; H, 4.1%) (cited¹⁸ values: b.p. 45.2–45.9°, n_D^{20} 1.3571).

The diene (4.0 g) was treated overnight with an excess of bromine (4 ml) in glacial acetic acid (10 ml). The reaction mixture was poured into water (30 ml) and the lower layer was separated and distilled to give *dibromo-5,5,5-trifluoropentene* (8.0 g), b.p. 175°, n_D^{20} 1.4650 (Found: C, 21.5; H, 1.7. $C_6H_8Br_2F_3$ requires: C, 21.3; H, 1.8%). This product gave a single sharp peak in vapour phase chromatography (Didecyl phthalate/Kieselguhr, N_2 gas-stream) and its infra-red spectrum was also consistent with the presence of one isomer only. It had no strong absorption in the region 900–950 cm^{-1} .

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