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AROMATIC POLYFLUORO-COMPOUNDS—XLV[1]

THE REACTIONS OF OCTAFLUOROSTYRENE

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Abstract—Octafluorostyrene with bromine and hydrogen bromide in the presence of UV light yielded α,β-dibromooctafluoroethylbenzene and β-bromo-α,β,β,2,3,4,5,6-octafluoroethylbenzene respectively. With dimethylamine, N,N-dimethylpentafluorophenylfluoroacetamide was obtained arising via N,N-dimethyl-α,β,β,2,3,4,5,6-octafluorophenylethylamine. The structure of the acetamide was established by NMR spectroscopy, analysis and hydrolysis to pentafluorobenzoic acid and pentafluorophenylfluoro acetic acid. With methanol, octafluorostyrene gave β-methoxy-α,β,β,2,3,4,5,6-octafluoroethylbenzene, and 4-methoxyheptafluorostyrene (established by oxidation of the reaction mixture to yield *p*-methoxytetrafluorobenzoic acid) Reduction of octafluorostyrene with LAH gave a four component mixture of the *cis* and *trans* isomers of α,β,2,3,4,5,6-heptafluorostyrene and α,β,2,3,5,6-hexafluorostyrene.

THIS paper describes some reactions of octafluorostyrene the preparation of which has been reported by defluorination[2] and from pentafluorophenyl magnesium bromide.[3] The octafluorostyrene used in this work was prepared by the former method. Due to the difficulty in separating octafluorostyrene from decafluoroethylbenzene by preparative scale GLC or distillation an alternative procedure was adopted. The products from the defluorination of decafluoroethylbenzene were brominated under free radical conditions, resulting in the saturation of the olefinic double bond to yield α,β-dibromooctafluoroethylbenzene, which was readily separated by distillation from starting material and some pyrolysis products. The dibromo compound was then debrominated using zinc dust in methanol to yield octafluorostyrene in high yield. The presence of pentafluorobenzene and decafluorobiphenyl in the pyrolysis products may be ascribed to the further reactions of phenyl groups produced during the pyrolysis with one another or with traces of hydrogen containing materials in the defluorination reactor.

The reactions of octafluorostyrene are those to be expected of a perfluoroaromatic olefin. Addition of bromine to the olefinic double bond proceeded smoothly and in good yield with UV illumination at room temperature to yield α,β-dibromooctafluoroethylbenzene. The structure of the dibromo addition product was established by chemical analysis and NMR spectroscopy, and confirmed by debromination to octafluorostyrene. Addition of hydrogen bromide took place under the same conditions with the formation of β-bromo-α,β,β,2,3,4,5,6-octafluoroethylbenzene. The direction of addition was determined by NMR spectroscopy, the H^1 resonance spectrum consisting of a single band consisting of a doublet of triplets with coupling constants typical of $—CFH—CF_2$ grouping. It should be noted that the spectrum of the alternative product would have been a triplet of doublets. The observed direction of addition is the same as that found for other fluoro olefins[4] and could be ascribed to the stabilization of the intermediate secondary radical by the C_6F_5— group, supplemented by the steric effect of that group.

In methanol/potassium hydroxide solution octafluorostyrene reacted to give two products, one from addition of methanol across the double bond, and the other from nucleophilic displacement of the *para* fluorine, in an approximate ratio 1:1. The mixture could not be separated, but after oxidation with acetone-permanganate, the adduct, β-methoxy-α,β,β,2,3,4,5,6-octafluoroethylbenzne was obtained pure. Attempts to convert it to β-methoxyheptafluorostyrene using potassium hydroxide solution or heated sodium fluoride were unsuccessful. The oxidation of the mixed methanol reaction products gave the known β-methoxytetrafluorobenzoic acid. The observed *para* substitution parallels that found for the reaction of nucleophiles with octafluorotoluene[5] and decafluoroethylbenzene.[6] There was no evidence for the formation of 4,β-dimethoxy-α,β,β,2,3,5,6-heptafluoroethylbenzene.

The reaction of octafluorostyrene with dimethylamine gave N,N-dimethylpentafluorophenylfluoroacetamide, presumably *via* the initial formation of.N,N-dimethyl-α,β,β,2,3,4,5,6-octafluorophenylethylamine, with subsequent loss of HF and hydrolysis in the presence of water to yield the acetamide. Under anhydrous conditions the product of the reaction with dimethylamine was an unstable liquid which fumed in moist air. The structure of the acetamide was confirmed by hydrolysis using sulphuric acid to the known pentafluorobenzoic acid. Mild acid hydrolysis gave pentafluorophenylfluoroacetic acid, which formed an S-benzyl thiouronum salt.

Reduction of octafluorostyrene with LAH formed a mixture of products resulting from substitution in the side chain and nucleus. In contrast with methoxide ion, mono and disubstituted compounds were found; monosubstitution occurred in the olefinic double bond at the β carbon atom to form *cis*- and *trans*-α,β,2,3,4,5,6-heptafluorostyrene. A second substitution also took place in the nucleus in the *para* position with the formation of *cis*- and *trans*-α,β,2,3,5,6-hexafluorostyrene. The orientation of the second substitution was confirmed by oxidation of the mixed reaction products to penta- and 2,3,5,6-tetrafluorobenzoic acid, with subsequent decarboxylation to penta- and 1,2,4,5-tetrafluorobenzene. In addition the *cis*-α,β,2,3,5,6-hexafluorostyrene and *trans*-α,β,2,3,4,5,6-heptafluorostyrene which were obtained pure, were oxidized to the known 2,3,5,6-tetrafluoro- and pentafluorobenzoic acids respectively.

EXPERIMENTAL

Gas chromatography. Preparative scale GLC was carried out using two columns each 4·88 m long × 35 mm diam. Unit A was packed with dinonyl phthalate–kieselguhr (1:2) and unit B with silicone gum 301–kieselguhr (1:5). The column temp and N_2 flow rate used are quoted where reference to the unit is made. Fractions were collected in traps cooled in liquid N_2 and distilled from the traps *in vacuo*.

Preparation of materials. Octafluorostyrene was prepared by the pyrolytic defluorination of decafluoroethylbenzene as described.[3] The products (85·1 g) obtained from decafluoroethylbenzene (171 g) were sealed with Br_2 (18 g) in glass tubes and irradiated with UV light for 48 hr. The contents of the tubes was washed with 10% sodium metabisulphite soln, 10% KOHaq, and water to give a product (80·7 g), which was distilled at atmospheric press to give a distillate (60·5 g) and a residue (12·6 g). A sample (7 g) of the distillate was separated by preparative GLC (Unit A, 85°, 15 l/hr N_2) to give decafluoroethylbenzene (4·1 g), and pentafluorobenzene (0·5 g) identified by a comparison of IR spectra. A sample (4 g) of the residue was separated by preparative GLC (Unit B, 150°, 17 l/hr N_2) to give decafluorobiphenyl (0·5 g) (identified by m.p., mixed m.p. and IR spectrum), and a liquid (1·4 g), subsequently identified as α,β-dibromooctafluoroethylbenzene. In a representative experiment for the preparation of octafluorostyrene, decafluoroethylbenzene (222 g) gave a pyrolysis product (95 g) which after bromination and distillation gave a distillate (70 g), consisting largely of unchanged decafluoroethylbenzene and a residue (24 g). The residue was debrominated as described below to give octafluorostyrene (12·5 g).

Debromination of α,β-dibromooctafluoroethylbenzene. The dibromo compound (3·7 g) in MeOH (10 ml) was added dropwise to a stirred suspension of Zn dust (1·8 g) in MeOH (40 ml) at a rate sufficient to maintain reflux. After completion of the addition, the mixture was refluxed for 30 min. The product was then distilled through a short fractionating column and the mixture of fluorocarbon and MeOH obtained added to water (100 ml), when *octafluorostyrene* (2·0 g) was separated.

Reactions of octafluorostyrene

(a) *Hydrogen bromide.* To octafluorostyrene (3 g) was added anhyd HBr (2 g) and the mixture sealed in a glass tube, which was irradiated with UV light for 24 hr. The product was washed with water, the organic layer separated and distilled from P_2O_5 to give *β-bromo-α,β,β,2,3,4,5,6-octafluoroethylbenzene* (3 g). (Found: C, 29·5; H, 0·4. C_8HBrF_8 requires: C, 29·2; H, 0·3%). The H^1 NMR spectrum consisted of one band (5·6 ppm) which was a doublet (*J* 42·5 c/s) of triplets (*J* 9·5 c/s) corresponding to the —CFH—CF_2— proton.

(b) *Bromine.* Octafluorostyrene (2·7 g) and Br_2 (2·2 ml) were sealed in a glass tube and irradiated with UV light for 18 hr. The product was washed with 10% sodium metabisulphite soln, water, and distilled from P_2O_5 to give *α,β-dibromooctafluoroethylbenzene* (3.4 g, b.p. 210°). (Found: C, 24·0; F, 37·3. $C_8Br_2F_8$ requires: C, 23·6; F, 37·3%). The F^{19} NMR spectrum consisted of five bands at −19·1 ppm, +37·9 ppm, +54·0 ppm, +69·7 ppm, and +101·7 ppm corresponding in splitting to the —$BrCF_2$—, —CFBr—, *ortho, meta* and *para* F atoms respectively.

(c) *Methanol.* MeOH (1 ml) was added dropwise to a stirred mixture of octafluorostyrene (3 g) and KOH (1 g) at 0°. After 45 min the product was poured into water and the organic layer (2·4 g) separated and distilled from P_2O_5. Separation of the product by preparative GLC (Unit B, 115°, 18 l/hr N_2) gave octafluorostyrene (0·6 g) and a mixture (1·6 g) of two closely retained compounds. The mixture (1·6 g), acetone (75 ml) and $KMnO_4$ (1·3 g) were shaken at room temp for 30 min, water (10 ml) was added and the acetone removed under reduced press. The aqueous layer was decolourized with SO_2, and the organic layer separated to give *β-methoxy-α,β,β,2,3,4,5,6-octafluoroethylbenzene* (0·6 g). (Found: C, 38·8; H, 1·6. $C_9H_4F_8O$ requires: C, 38·6; H, 1·4%). The H^1 NMR spectrum consisted of two bands at 1·6 ppm and 2·7 ppm in the ratio 1:3. The lower intensity band was a doublet (*J* 43 c/s) of triplets (*J* 6·5 c/s) and was assigned to the —CFH—CF_2— proton. The higher intensity band was a singlet assigned to the H atoms of the OMe group.

Attempts were made to convert β-methoxy-α,β,β,2,3,4,5,6-octafluoroethylbenzene to β-methoxyheptafluorostyrene by dehydrofluorination with 50% KOH aq and by passage of the vapour over NaF at 200–300°. There was no evidence (GLC) that dehydrofluorination had occurred.

The aqueous layer from the oxidation was continuously extracted with ether for 24 hr. The ether layer was dried ($MgSO_4$) and evaporated. The residue was recrystallized from water and identified by m.p.,[7] mixed m.p. and IR spectrum as *p*-methoxytetrafluorobenzoic acid (0·4 g, m.p. and mixed m.p. 121°).

(d) *Dimethylamine.* To dimethylamine (1·0 g) in dry ether (10 ml) was added dropwise octafluorostyrene (1 g) in ether (15 ml), and the mixture stirred at 0° for 60 min. Water was added and the ether layer separated and dried ($MgSO_4$). The ether was then evaporated by distillation through a short fractionating column to give a residue which was shown by GLC to contain single component. Sublimation of the residue and recrystallization from water gave *N,N-dimethylpentafluorophenylfluoroacetamide* (0·9 g, m.p. 42·5°, b.p. 250°). (Found: C, 44·2; H, 2·5. M.W. by osmometry 272 ± 3. $C_{10}H_7F_6NO$ requires: C, 44·3; H, 2·6% m.w. 271). The H^1 NMR spectrum showed two bands of intensity ratio 1:5; the lower intensity band (6·4 ppm) was a doublet (*J* 45·5 c/s) due to the —CFH— proton, and the high intensity band (3·1 ppm) was a broad doublet corresponding to the —N —Me_2 proton resonance. The F^{19} NMR spectrum consisted of four bands at 38 ppm, 45 ppm, 52 ppm and 62 ppm corresponding in intensity and splitting to the aromatic F atoms and the expected doublet (*J* 50 c/s) of the F atom attached to the C atom bearing a single proton.

(e) *Dimethylamine under anhydrous conditions.* Dimethylamine in dry ether (8·1 ml, M/2) was added dropwise to octafluorostyrene (1 g) in dry ether (20 ml) and the mixture stirred at 0° for 90 min. The soln was filtered and the ether evaporated as previously. The residue (0·9 g) fumed in moist air: GLC analysis gave a nonreproducible series of peaks. On shaking with water a vigorous reaction occurred, the product being mixture of N,N-dimethylpentafluorophenylfluoroacetamide and unreacted octafluorostyrene.

(f) *Lithium aluminium hydride.* Octafluorostyrene (6·3 g) in dry ether (15 ml) was added dropwise over a period of 20 min to a stirred suspension of LAH (1·2 g) in dry ether (50 ml) at 0°, and the mixture stirred for a further 70 min. Water (25 ml) and dil H_2SO_4 (25 ml) was added to destroy excess LAH, and the ether layer separated, dried ($MgSO_4$) and fractionally distilled. The residue (3·5 g) was separated by preparative GLC (Unit B, 115°, 18 l/hr N_2) into (i) *trans-α,β,2,3,4,5,6-heptafluorostyrene* (0·4 g). (Found: C, 41·9; H, 0·8. C_8HF_7 requires: C, 41·8; H, 0·4%). The H^1 NMR spectrum was a single band at 7 ppm which was a doublet (*J* 73 c/s) of doublets (*J* 3·5 c/s) assigned to a vinylic proton coupling with a F atom on the same C atom and another *cis* across the double bond. (ii) *cis-α,β,2,3,5,6-Hexafluorostyrene* (0·5 g). (Found: C, 45·5; H, 1·2. $C_8H_2F_6$ requires: C, 45·3; H, 1·0%). The H^1 NMR spectrum consisted of two bands of intensity ratio 1 : 1. The band at 6·5 ppm was a doublet (*J* 72 c/s) of doublets (*J* 16 c/s) assigned to a vinylic proton resonance coupled with a F atom on the same C atom and another in a position *trans* across the double bond. The other band at 6·8 ppm was a triplet (*J* 7 c/s) of triplets (*J* 7 c/s) and was assigned to a proton in the aromatic ring at the *para* position. (iii) A mixture (0·7 g) of two components (which could not be separated chromatographically) in the approximate ratio 3 : 1 which were identified by H^1 NMR spectra as *cis-α,β,2,3,4,5,6-heptafluorostyrene* and *trans-α,β,2,3,5,6-hexafluorostyrene.* The H^1 NMR spectrum of the larger component was single band at 6·4 ppm consisting of a doublet (*J* 73 c/s) of doublets (*J* 16 c/s) assigned to the proton of the —CF=CFH— group. The spectrum of the smaller component was two bands in the intensity ratio 1 : 1 at 7·0 ppm and 7·1 ppm. The former was a triplet (*J* 7 c/s) of triplets (*J* 7 c/s) assigned to a proton in the aromatic ring at the *para* position, and the latter a doublet (*J* 74·0 c/s) of doublets (*J* 4·0 c/s) assigned to the proton of the —CF=CFH— group. (iv) A mixture (1·6 g) of components (i) and (ii).

Hydrolysis of N,N-*dimethylpentafluorophenylfluoroacetamide.* (a) *Concentrated sulphuric acid.* The amide (0·3 g) was warmed (100–120°) with conc H_2SO_4 (10 ml) for 30 min. The soln was diluted with water (50 ml) and extracted continuously for 24 hr with ether. The residue (0·12 g) remaining after evaporation of the dried ($MgSO_4$) ether layer and recrystallization from water was shown by a comparison of IR spectra to be pentafluorobenzoic acid.

(b) *Dilute hydrochloric acid.* The amide (0·5 g) was dissolved in dil HCl (20 ml, 4N) and heated under reflux for 20 hr. On cooling a solid precipitated which after recrystallization from water gave *pentafluorophenylfluoroacetic acid* (0·3 g, m.p. 138–139°). (Found: C, 36·9; H, 1·7. $C_8H_2F_6O_2H_2O$ requires: C, 36·7; H, 1·5%). A sample of the acid was dissolved in water and a saturated soln of S-benzyl thiouronium chloride added. The ppt was recrystallized from water to yield the S-benzyl thiouronium salt (m.p. 175–176°). (Found: C, 46·6; H, 2·9. $C_{16}H_{12}F_6N_2O_2S$ requires: C, 46·8; H, 3·0%).

Oxidation of cis-α,β,2,3,5,6-hexafluorostyrene. cis-α,β,2,3,5,6-Hexafluorostyrene (0·4 g) was shaken for 15 min at room temp with acetone (15 ml) and $KMnO_4$ (1·2 g). Water (20 ml) was added and the acetone removed under reduced press. The aqueous layer was acidified (H_2SO_4) decolourized (SO_2) and continuously extracted with ether. The ether layer was dried ($MgSO_4$) and evaporated to leave a residue (0·3 g) which, after recrystallization from water was identified by IR spectrum, m.p. and mixed m.p.[8] as 2,3,5,6-*tetrafluorobenzoic acid* (m.p. 148·5–149·5°, mixed m.p. 150°).

Oxidation of trans-α,β,2,3,4,5,6-heptafluorostyrene. The compound (0·3 g) was oxidized with $KMnO_4$ (1·0 g) in acetone (15 ml) and the product (0·15 g) obtained as above. This was identified by IR spectrum as pentafluorobenzoic acid.

Oxidation and subsequent decarboxylation of the mixed products from the lithium aluminium hydride reaction. A sample (1·3 g) of products from the reaction of octafluorostyrene with LAH was shaken with $KMnO_4$ (2·8 g) in acetone (50 ml) at room temp for 30 min. The product (0·7 g) was extracted as above, and a sample (0·6 g) was sealed with ammonia soln (10 ml, $d = 0{\cdot}88°$) in a glass tube and heated at 120° for 18 hr. The organic layer (0·1 g) was separated, and identified by GLC and IR spectra as a mixture (3 : 2 *w/w*) of pentafluorobenzene and 1,2,4,5-tetrafluorobenzene. The aqueous layer from the decarboxylation reaction was acidified and extracted with ether to yield unreacted starting material (0·3 g).

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