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REDUCTIVE COUPLING OF POLYFLUOROVINYL HALIDES IN THE PRESENCE OF COPPER-BRONZE

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Abstract—1-Chloro-1,2-difluoroiodoethylene, 1-bromononafluorocyclohexene and 1-bromoheptafluorocyclopentene undergo reductive coupling reactions when heated with copper bronze to give 1,4-dichlorotetrafluorobuta-1,3-diene and perfluorobicyclo-hex-1,1′-enyl and -pent-1,1′-enyl, respectively. The same olefins undergo crossed coupling reactions with phenyl and pentafluorophenyl halides and, in the first case, with 1-iodoheptafluoropropane.

INTERMOLECULAR dehalogenation of polyfluoro alkyl and alkenyl halides has been achieved using zinc in a range of solvents,[1–3] the reactions being of the type $2R{\cdot}X + Zn \rightarrow R{\cdot}R + ZnX_2$. In all cases reported the halogen eliminated was either bromine or iodine attached to a $—CF_2—$ or $—CFCl—$ group. However, there appears to be no report of a dehalogenative coupling reaction with vinyl bromides or iodides. By analogy with the facile Ullmann reactions of electron-deficient aryl bromides and iodides[4] it was expected that polyfluorovinyl bromides and iodides might be coupled to give fluoro dienes and also be cross-coupled with aryl iodides and bromides. This has now been established with a range of components.

1-Chloro-1,2-difluoroiodoethylene was obtained, in improved yield, from a reaction sequence based on the manganic fluoride fluorination of trichloroethylene.[5] The penultimate stage involves the addition of iodine monochloride to 1-chloro-1,2-difluoroethylene and in the present work this was proved to be not entirely uni-directional. The major product, 1,1-dichloro-1,2-difluoro-2-iodoethane, was accompanied by 4% of 1,2-dichloro-1,2-difluoro-1-iodoethane as shown by the final dehydrohalogenation which gave some 1,2-dichlorodifluoroethylene, as well as the anticipated 1-chloro-1,2-difluoro-iodoethylene.

When 1-chloro-1,2-difluoroiodoethylene (I) and copper bronze were kept at 145° for 24 hr, the three geometrical isomers of 1,4-dichlorotetrafluorobuta-1,3-diene were formed, *viz. cis,cis-* (II; 19%), *cis,trans-* (III; 51%) and *trans,trans-* (IV; 30%); this was clearly established by mass spectrometry which gave the same top mass peak

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[1] A. L. Henne, *J. Amer. Chem. Soc.* **75**, 5750 (1953).
[2] A. L. Henne and W. Postelnek, *J. Amer. Chem. Soc.* **77**, 2334 (1955).
[3] A. H. Fainberg and W. T. Miller, *J. Amer. Chem. Soc.* **79**, 4170 (1957).
[4] P. E. Fanta, *Chem. Revs.* **38**, 139 (1948); **64**, 613 (1964).
[5] G. Fuller, M. Stacey. J. C. Tatlow and C. R. Thomas, *Tetrahedron* **18**, 123 (1962).

($C_4Cl_2F_4$) and nearly identical fragmentation patterns.[6] The IR spectra of the three isomers were closely similar, each double bond "stretching" frequency was displayed at 1690 cm^{-1}. The UV absorption spectra revealed conjugated systems, and the extinction coefficients increased markedly in passing from the lowest to the highest boiling isomer and this was used to allocate the geometry of each. Courtauld molecular models showed that each isomer had a degree of steric compression in the coplanar state which was greatest with the *cis,cis*- and least with the *trans,trans*-isomer. Assuming that conjugation and hence UV absorption is greatest for coplanar (or nearly coplanar) double bonds, then the highest boiling isomer is the *trans,trans*-form and the lowest boiling isomer has the *cis,cis*-structure, with the component of intermediate volatility possessing the *cis,trans*-geometry. These structural allocations were unambiguously confirmed by ^{19}F NMR spectroscopy.[7] The spectra of the highest and lowest boiling isomers each consisted of two identical signals, showing that both molecules had only two "types" of ^{19}F nuclei. The spectrum of the highest boiling isomer was analysed as an A_2B_2 system and gave a coupling constant of 132 c/s, which must be attributed to an $(F—F)_{trans}$ "olefinic" coupling, so that this component must be 1,4-dichloro-*trans, trans*-tetrafluorobuta-1,3-diene (IV). Consequently, the lowest boiling isomer must be 1,4-dichloro-*cis,cis*-tetrafluorobuta-1,3-diene (II). The spectrum of the third component consisted of four signals, and, therefore, could be assigned to 1,4-dichloro-*cis,trans*-tetrafluorobuta-1,3-diene (III) in which all the ^{19}F nuclei have different environments.

Previous syntheses of 1,4-dichlorotetrafluorobuta-1,3-diene involved zinc dust dechlorination of either 1,1,2,3,4,4-hexachlorotetrafluorobutane[8] or 1,3,4,4-tetrachlorotetrafluorobut-1-ene[9] (V and/or VI). In no case, however, was the exact composition of the product considered. Therefore, 1,2-dichlorodifluoroethylene was dimerized in the established way[9] and the product separated by gas chromatography to give 1,3,4,4-tetrachlorotetrafluorobut-1-ene[9] (51%; V and/or VI) which on treatment with zinc dust in methanol gave 1,4-dichlorotetrafluorobutadiene[9] (80%) and this was separated into its three geometrical isomers by gas chromatography. It was of interest to find a significantly different ratio of the isomers, *viz*, 4% *cis,cis*- (II), 42·5% *cis,trans*- (III) and 53% *trans,trans*- (IV). This indicates that the above dimerization product consists largely of *trans*-1,3,4,4-tetrachlorotetrafluorobut-1-ene (V).

The thermal isomerization of 1,4-dichlorotetrafluorobuta-1,3-diene to 3,4-dichlorotetrafluorocyclobutene (VII) has been described.[9] In the present work the mixed dienes gave a 3,4-dichlorotetrafluorocyclobutene (VII; 46%), of unknown stereochemistry, at 230° in a sealed glass tube. Similarly, when thermal isomerization was carried out in an empty nickel tube at 330° consistent results were obtained in the first few experiments. However, the pattern of reaction products slowly became more complicated. The major component after six experiments was found to be an unresolved mixture of three components in approximately equal amounts as shown by IR spectroscopy. The latter revealed three equally intense bands at 1800, 1720 and 1630 cm^{-1} and these were attributed to the double bond stretching frequencies of 3,4- (VII),

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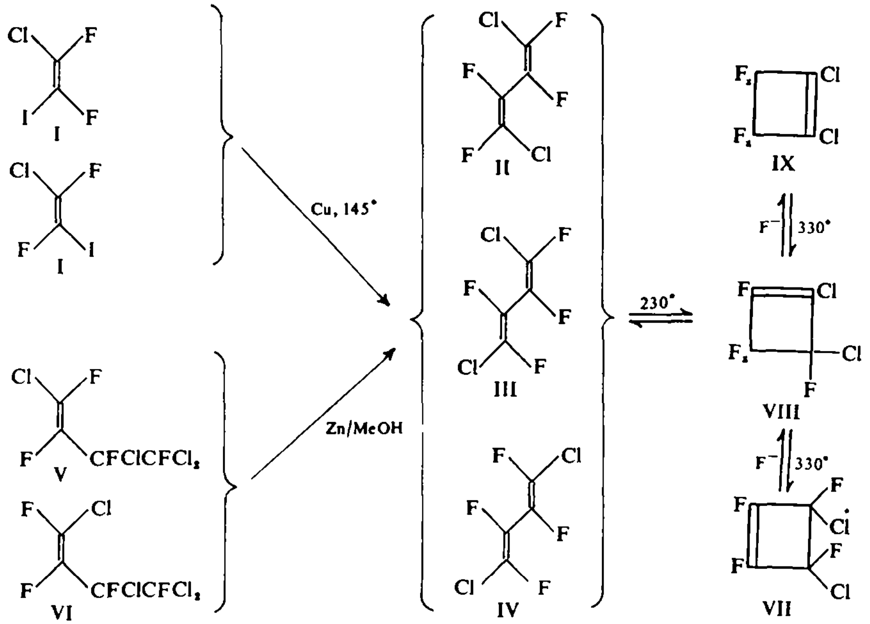
[6] J. R. Majer, unpublished work.

[7] L. F. Thomas, unpublished work.

[8] W. T. Miller, *Preparation, Properties and Technology of Fluorine and Organic Fluoro-compounds* (Edited by C. Slesser and S. R. Schram) p. 670 McGraw-Hill (1951).

[9] R. N. Haszeldine and J. E. Osborne, *J. Chem. Soc.* 3880 (1955).



1,4- (VIII), and 1,2- (IX) dichlorotetrafluorocyclobutene, respectively. The latter two compounds arising from double bond migrations catalysed by fluoride ion.[10] During the first few runs slight decomposition of the dienes produced a layer of nickel fluoride; this was proved at the end of the pyrolysis study by passing hydrogen through the nickel tube at 500°, when hydrogen fluoride was formed. It was also shown that 3,4-dichlorotetrafluorocyclobutene can be isomerized to the known[11] 1,2-dichloro-isomer (IX) by passage over sodium fluoride pellets at 360°.

Pentafluoroiodobenzene, 1-chloro-1,2-difluoroethylene and copper bronze at 165° gave a mixture of 1-chloro-1,2-difluoropentafluorophenylethylene, the three isomeric 1,4-dichlorotetrafluorobuta-1,3-dienes and decafluorobiphenyl. The first named, presumably a mixture of the *cis* and *trans* forms, was characterized by mass spectrometry,[6] UV and IR spectroscopy and by its oxidation to pentafluorobenzoic acid; it was identical with the product obtained from pentafluorophenyl-lithium and chlorotrifluoroethylene.[12]

Iodobenzene, 1-chloro-1,2-difluoroiodoethylene and copper bronze at 210° gave a mixture of *cis*- and *trans*-1-chloro-1,2-difluoro-2-phenylethylene, the isomeric 1,4-dichlorotetrafluorobutadienes, 3,4-dichlorotetrafluorocyclobutene and biphenyl. The first named was identical with the product obtained from chlorotrifluoroethylene and phenyl-lithium;[13] the presence of both *cis*- and *trans*-forms was established by ^{19}F NMR spectroscopy.[7]

1-Iodoheptafluoropropane, 1-chloro-1,2-difluoroiodoethylene and copper bronze at 155° gave an unidentified viscous liquid and a volatile complex mixture containing

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[10] W. J. Feast and R. Stephens, *J. Chem. Soc.* 3502 (1965); W. T. Miller, J. H. Fried and H. Goldwhite, *J. Amer. Chem. Soc.* **82**, 3091 (1960).

[11] A. J. Henne and W. J. Zimmerschied, *J. Amer. Chem. Soc.* **69**, 281 (1947).

[12] D. D. Callender, P. L. Coe and J. C. Tatlow, *J. Chem. Soc.* under consideration.

[13] S. Dixon, *J. Org. Chem.* **21**, 400 (1956).

one major component which was shown by elemental analysis, IR spectroscopy, mass spectrometry,[6] and oxidation to perfluorobutyric acid, to be 1-chlorononafluoropent-1-ene. The viscous liquid was probably a mixture of telomers produced from the reaction of 1-iodoheptafluoropropane with the olefin. Thus, its IR spectrum displayed only very weak absorptions ascribable to double bond stretching modes.

Two perfluorocyclic vinyl bromides, 1-bromononafluorocyclohexene[14] and 1-bromoheptafluorocyclopentene, also underwent reductive coupling with copper bronze.

1-Bromononafluorocyclohexene and copper bronze at 230° gave 1H-nonafluorocyclohexene and perfluorobicyclohex-1,1′-enyl; there was no reaction under these conditions in the absence of copper bronze. The latter was characterized by IR, UV and ^{19}F NMR spectroscopy[7] and mass spectrometry.[6] With potassium permanganate in acetone it readily gave octafluoroadipic acid. With chlorine it gave two dichlorides with properties indicative of a 2,2′-dichloroperfluoro-1,1′-bi(cyclohexylidene) system, i.e. two of the four possible products of 1,4-addition of chlorine to the diene.

1-Bromononafluorocyclohexene, bromobenzene and copper bronze at 230° gave a mixture of starting materials, 1H-nonafluorocyclohexene, benzene, biphenyl and 1-phenylnonafluorocyclohexene which was characterized in the usual way and was identical with a compound obtained from phenyl-lithium and decafluorocyclohexene.

The analogous reaction with pentafluorobromobenzene at 225° gave 1H-nonafluorocyclohexene, pentafluorobenzene, perfluorobicyclohex-1,1′-enyl, decafluorobiphenyl and 1-(pentafluorophenyl)nonafluorocyclohexene which was characterized in the usual way and was identical with a compound obtained from pentafluorophenyllithium and decafluorocyclohexene.[12]

1-Bromoheptafluorocyclopentene was prepared by the addition of bromine to 1H-nonafluorocyclopentene[15] under UV irradiation, followed by dehydrobromination of the crude dibromide with aqueous alkali. Pure 1H,1,2-dibromoheptafluorocyclopentane was not obtained since pyrolytic dehydrobromination was so facile. Thus, attempted purification by gas chromatography at 100° resulted in dehydrobromination. The main product of dehydrobromination by aqueous alkali was 1-bromoheptafluorocyclopentene in agreement with the presence of facile coplanar *cis*- and *trans*-dehydrobrominations in the *trans*- and *cis*-dibromides respectively. Some dehydrofluorination occurred, also, to give 1,5- and 1,2-dibromohexafluorocyclopentene as minor products.

1-Bromoheptafluorocyclopentene was characterized by mass spectrometry,[6] IR spectroscopy, and by its oxidation to hexafluoroglutaric acid with potassium permanganate in acetone. 1,5- and 1,2-Dibromohexafluorocyclopentene were also characterized by mass spectrometry[6] and IR spectroscopy; the 1,2-dibromide was oxidized to hexafluoroglutaric acid by potassium permanganate in acetone.

1-Bromoheptafluorocyclopentene and copper bronze at 230° gave 1H-heptafluorocyclopentene and perfluorobicyclopent-1,1′-enyl. The structure of the latter diene was clearly established by its IR, UV and ^{19}F NMR spectra[7] and by its ready oxidation to hexafluoroglutaric acid with potassium permanganate in acetone.

1-Bromoheptafluorocyclopentene, bromobenzene and copper bronze at 245° gave a mixture of 1H-heptafluorocyclopentene, perfluorobicyclopent-1,1′-enyl, benzene, biphenyl and 1-phenylheptafluorocyclopentene. The last named was obtained also

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[14] S. F. Campbell and R. Stephens, *J. Chem. Soc.*, 7367 (1965).

[15] R. J. Heitzman, C. R. Patrick, R. Stephens and J. C. Tatlow, *J. Chem. Soc.* 281 (1963); D. J. Burton and R. L. Johnson, *J. Amer. Chem. Soc.* 5361 (1964).

from octafluorocyclopentene and phenyl-lithium in ether; a reaction which gave both this compound and 1,2-diphenyl-hexafluorocyclopentene, presumably from two consecutive addition-elimination processes.[16]

1-Phenylheptafluorocyclopentene was characterized by elemental analysis, IR and UV spectroscopy and by its ready oxidation to 5-phenyl-5-keto-2,2,3,3,4,4-hexafluoro-n-valeric acid with potassium permanganate in acetone. The crystalline 1,2-diphenyl-hexafluorocyclopentene was characterized using the same technique. In accord with the presence of a deactivated double bond it was not oxidized by potassium permanganate in acetone.[17] Indeed, it was substantially (50%) unaffected by aqueous potassium permanganate in an autoclave at 140°; and hexafluoroglutaric acid (36%) was obtained.

These examples of copper-promoted reductive couplings of vinyl bromides and iodides with themselves and with aryl bromides and iodides may well follow the same mechanistic pathway as the Ullmann reaction, which produces biaryls from aryl halides and copper bronze;[4] that is, a two-step process, the reaction starting with an attack by copper at the carbon bearing the bromine or iodine to form an activated complex at the metal surface. The occurrence of this step should be influenced by the susceptibility of the system to nucleophilic attack and is thus favoured by electron-withdrawing substituents. In the second step the activated complex would react with a second molecule of the bromide or iodide at the copper surface to give the diene or phenyl ethylene and cupric halide. The electron movements being such as to make the process either essentially ionic or free-radical in character.[18] With respect to this point it is perhaps significant that there is an almost quantitative loss of bromine from pentafluorobromobenzene (or of I from C_6F_5I), in reactions with copper bronze, compared with similar loss of fluorine from the same compounds with nucleophilic reagents. This would suggest that the reactions involving copper bronze are essentially homolytic. However, the precise nature of these reactions remains a subject for speculation.

The formation of small amounts of 1H-nonafluorocyclohexene and 1H-heptafluorocyclopentene in the coupling reactions of the corresponding bromides parallels the occurrence of substitutive reduction of aryl halides as a side reaction in the Ullmann coupling reaction.[19] Indeed, it may well be that a similar process is occurring here and that a trace of water is the effective hydrogen donor.

EXPERIMENTAL

Gas chromatography. Analytical work was carried out using glass columns 2 m long × 4 mm diam packed with dinonyl phthalate–kieselguhr (1:2; unit A), a column 1 m × 4 mm packed with silicon gum–kieselguhr (1:2; unit B) and a column 1 m × 4 mm packed with Kel F oil–kieselguhr (1:4; unit C). For preparative work 3 Cu-columns 488 cm × 35 mm were used. Column A contained the same packing as unit A, column B contained the same packing as unit B and column C the same packing as unit C.

Mass spectra. These were measured on a Metropolitan-Vickers M.S.2 instrument.[6]

1-*Chloro*-1,2-*difluoroiodoethylene*(*I*). Iodine monochloride (44 ml) was added dropwise, with vigorous stirring, to 1-chloro-1,2-difluoroethylene[5] (61 g) over a period of 1 hr, then the mixture was kept at 50° for 1 hr and poured into water. The iodine free (KI) organic layer was washed with water,

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[16] D. R. Sayers, R. Stephens and J. C. Tatlow, *J. Chem. Soc.* 3035 (1964).

[17] J. Burdon and J. C. Tatlow, *J. Appl. Chem.* **8**, 293 (1958).

[18] R. G. R. Bacon and H. A. O. Hill, *Quart. Revs.* **19**, 95 (1965).

[19] R. G. R. Bacon and H. A. O. Hill, *J. Chem. Soc.* 1112 (1964).

dried (P_2O_5), filtered and distilled at a red. press. (ca. 78–80°/100 mm) to give 1,1-dichloro-1,2-difluoroiodoethane (128 g) b.p. 125° (lit.[5] 124–126°). The latter (128 g) was shaken with 2N NaOHaq. (350 ml) for 3 days. The organic layer was separated, washed with water until neutral, dried (P_2O_5), filtered and distilled to give: (i) 1,2-dichlorodifluoroethylene (2·0 g), b.p. 21–22° with a correct IR spectrum; (ii) a mixture of i (14%) and iii (86%) (9·4 g), b.p. 22·5–81°; (iii) compound I (78·0 g), b.p. 81·5–84° with a correct IR spectrum; (iv) a mixture of iii and starting material (10·0 g).

1,4-*Dichlorotetrafluorobuta*-1,3-*diene*

(a) *From* 1-*chloro*-1,2-*difluoroiodoethylene.* The olefin (8·0 g) and Cu-bronze (8 g) were kept together in a sealed "Pyrex" glass tube (2·5 × 30 cm) at 145° for 24 hr. After cooling, the tube was opened, the reaction mixture crushed and the organic material distilled *in vacuo* (0·1 mm) from P_2O_5 to give a liquid (1·8 g) which could be stored under N_2 or at −25° but not in contact with the atmosphere at room temp. Gas chromatographic analysis (unit A; 82°; N_2, 0·9 l./hr) revealed 3 main components (with peak hts in the ratio 1:2·6:1·5) and two minor components of longer retention time (the shorter of which was identical with that of starting material). The main components were separated by preparative scale gas chromatography (column A; 70°; N_2, 16 l./hr); in a typical case, the mixture (3·0 g) gave: (i) 1,4-*dichloro*-cis,cis-*tetrafluorobuta*-1,3-*diene* (II; 0·2 g), b.p. 79–80°. (Found: C, 24·6. $C_4Cl_2F_4$ requires: C, 24·6%), mass spectrometry gave a top mass peak of 194 ($C_4Cl_2F_4$) and a consistent fragmentation pattern,[6] ν_{max} 1690 cm^{-1} (—CF═CFCl), λ_{max} 2250 Å (ε = 7480 in n-hexane); (ii) a mixture (0·4 g) of components i and iii; (iii) 1,4-*dichloro*-cis,trans,-*tetrafluorobuta*-1,3-*diene* (III; 0·8 g), b.p. 82–83°, (Found: C, 24·8%), mass spectrometry gave a top mass peak of 194 ($C_4Cl_2F_4$) and a consistent fragmentation pattern,[6] ν_{max} 1690 cm^{-1} (—CF═CFCl), λ_{max} 2290 Å (ε = 11330 in n-hexane); (iv) 1,4-*dichloro*-trans,trans-*tetrafluorobuta*-1,3-*diene* (II; 0·6 g), b.p. 88° (Found: C, 24·3%), mass spectrometry gave a top mass peak of 194 ($C_4Cl_2F_4$) and a consistent fragmentation pattern,[6] ν_{max} 1690 cm^{-1} (—CF═CFCl), λ_{max} 2310 Å (ε = 15860 in n-hexane). The minor components were not detected on this scale.

The mixture of dienes (3·96 g) was kept in a sealed "Pyrex" tube at 230° for 24 hr. After cooling, the tube was opened and the liquid (3·72 g) separated by gas chromatography (column A; 100°; N_2, 16 l./hr) to give: (i) compound VII (1·80 g) with a correct IR spectrum, and (ii) the unchanged dienes (1·65 g).

(b) *From* 1,3,4,4-*tetrachlorobut*-1-*ene.* To a vigorously boiling mixture of Zn dust (2·1 g), $ZnCl_2$ (0·2 g) and MeOH (8 ml) 1,3,4,4-tetrachlorobut-1-ene (5·4 g) (prepared from 1,2-dichlorodifluoroethylene at 260° [9]) was added dropwise and the product distilled from P_2O_5 to give a mixture of II, III and IV (3·2 g) which were separated by gas chromatography to give: *cis,cis* II (0·1 g), *cis,trans* III (1·0 g), and *trans,trans* IV (1·2 g) all with correct IR spectra.

1-*Chloro*-1,2-*difluoropentafluorophenylethylene.*

Pentafluoroiodobenzene (7·6 g), 1-chloro-1,2-difluoroiodoethylene (5·8 g) and Cu-bronze (13·2 g) were kept together in a sealed "Pyrex" tube (2·5 × 46 cm) at 165° for 24 hr. The total liquid product (11·0 g) from two such experiments were distilled at a red. press. (10 mm) to give: (i) b.p. <47° (1·5 g); (ii) b.r. 47–51° (3·3 g); (iii) >51° (3·0 g). Fraction (i) was shown by analytical gas chromatography (unit A; 90°; N_2, 1·0 l./hr) and IR spectroscopy to be largely mixed II, III and IV. Fraction ii was redistilled to give cis- and trans-1-*chloro*-1,2-*difluoropentafluorophenylethylene* (3·1 g) b.p. 47–48°/10 mm, 151°/758 mm, (Found: C, 36·4. C_8ClF_7 requires: C, 36·3%), mass spectrometry[6] gave a top mass peak of 264 (C_8ClF_7), ν_{max} 1720 (—CF═CFCl), 1650, 1510 and 1500 cm^{-1} (fluorinated aromatic ring), λ_{max} 2430 Å (ε = 8615 in n-hexane). A portion (0·16 g) was oxidised with fuming HNO_3 (5 ml) to give pentafluorobenzoic acid (0·09 g) with a correct IR spectrum. Fraction iii was redistilled *in vacuo* to give a crystalline solid which was recrystallized from benzene to give decafluorobiphenyl (1·3 g) m.p. 68–69°, alone and in admixture with an authentic specimen; it displayed a correct IR spectrum.

1-*Chloro*-1,2-*difluorophenylethylene.* Iodobenzene (4·5 g), I (5·0 g) and Cu-bronze (10 g) were kept together in a sealed "Pyrex" tube at 210° for 24 hr. The liquid product (12·7 g) from 4 such reactions, was distilled to give: (i) b.r. 65–90° (2·1 g); (ii) b.r. 90–170° (1·4 g); (iii) b.r. 173–175° (5·3 g); (iv) a residue (3·4 g). The analytical gas chromatographs and IR spectra of fractions (i) and (ii) revealed the presence of VII and II, III and IV in addition to the components present in fraction (iii). The analytical gas chromatograph (unit B; 117°; N_2, 5 l./hr) of fraction (iii) consisted of 3 overlapping peaks, the shortest retained appearing as a very slight inflexion of identical retention time to that of iodobenzene (by enrichment). The IR spectrum of (iii) was correct for *cis*- and *trans*-1-chloro-1,2-difluoro-2-phenylethylene (prepared from chlorotrifluoroethylene and phenyl-lithium[13]) containing a trace of iodobenzene. The ^{19}F NMR spectrum indicated 43% of the *cis* and 57% of the *trans* isomer,[7] in agreement with the gas chromatographic peak areas (45 and 55%). The residue (iv) crystallized on cooling and after 2 recrystallizations from benzene gave diphenyl (2·5 g), m.p. 70–71°, alone and in admixture with an authentic specimen.

1-*Chlorononafluoropent*-1-*ene*

1-Iodoheptafluoropropane (4·8 g), I (3·6 g), and Cu-bronze (9 g) were kept together at 155° in a sealed "Pyrex" tube (2·5 × 30 cm) for 24 hr. The crude liquid product (3·3 g) was distilled (40°/0·1 mm) to give a colourless liquid (1·2 g) and a viscous red residue (2·1 g). The former was shown by gas chromatography (unit C; 68°; N_2, 2·4 l./hr) to contain one major and twelve minor components. When the latter mixture was separated (column C; 66°; N_2, 19 l./hr) only the major peak was collected and distilled from P_2O_5 to give a 1-*chlorononafluoropent*-1-*ene* (0·5 g), b.p. 60°. (Found: C, 22·9. C_5ClF_9 requires: C, 22·5%), mass spectrometry[8] gave a top mass peak of 266 (C_5ClF_9), ν_{max} 1710 cm^{-1} (—CF═CFCl).

This olefin (0·4 g), $KMnO_4$ (0·25 g) and acetone (25 ml) gave perfluoro-n-butyric acid in an exothermic reaction; it was characterized as its S-benzylthiuronium salt (0·4 g), m.p. 186°, alone and in admixture with an authentic specimen, it displayed a correct IR spectrum.

Perfluorobicyclohex-1,1′-*enyl.*

1-Bromononafluorocyclohexene[14] (5·0 g) and Cu-bronze (5·0 g) were kept together in a sealed "Pyrex" tube at 230° for 48 hr. A portion (2·0 g) of the liquid product (4·0 g) was separated by gas chromatography (column C; 70°; N_2, 15 l./hr) to give 1H-nonafluorocyclohexene (0·3 g) with a correct IR spectrum and *perfluorobicyclohex*-1,1′-*enyl* (1·2 g) b.p. 152°. (Found: C, 29·6; F, 69·0. $C_{12}F_{18}$ requires: C, 29·6; F, 70·4%), ν_{max} 1715 and 1695 cm^{-1} (—CF═C—C═CF—), λ_{max} 2800 Å (ε = 11600, in EtOH), mass spectrometry gave a top mass peak 486 at ($C_{12}F_{18}$) and a consistent fragmentation pattern,[8] its ^{19}F NMR spectrum consisted of four bands in the relative intensity ratio of 2:1:2:4.[7]

The diene (0·4 g) $KMnO_4$ and acetone, in the usual way, gave octafluoroadipic acid, which was characterized as its dianilinium salt (0·3 g), m.p. 211–212° (lit.[17] 214°).

The diene (3·0 g) and Cl_2 (0·5 g) were kept together in a sealed "Pyrex" tube under UV irradiation for 110 hr at ca. 15°. The liquid product (1·6 g) was shown by gas chromatography (unit B; 108°; N_2, 3 l./hr) to contain 2 components which were separated on a preparative scale (column B; 95°; N_2, 18 l./hr) to give: (i) one of the stereo isomers of 2,2′-dichloro-perfluoro-1,1′-bi(cyclohexylidene) (0·6 g). (Found: C, 25·9; Cl, 12·6. $C_{12}Cl_2F_{18}$ requires: C, 25·9; Cl, 12·8%), ν_{max} 1650 cm^{-1}; (ii) another of the stereo isomers of 2,2′-dichloroperfluoro-1,1′-bi(cyclohexylidene) (0·1 g). (Found: C. 26·0; H, 0·0; Cl, 12·8%), ν_{max} 1650 cm^{-1}.

1-*Phenylnonafluorocyclohexene.* 1-Bromononafluorocyclohexene (3·0 g), bromobenzene (4·0 g) and Cu-bronze (8·0 g) were kept together in a sealed "Pyrex" tube at 230° for 48 hr. The liquid product (4·0 g) was distilled *in vacuo* to give a liquid (3·7 g) and a residue (0·3 g). The latter was combined with the material (0·4 g) obtained by ether extraction of the Cu-bronze residue, and recrystallized from MeOH to give biphenyl (0·7 g), m.p. 65°. The liquid (3·7 g) was separated by gas chromatography (column B; 135°; N_2, 10 l./hr) to give (i) suspected 1H-nonafluorocyclohexene (trace amount); (ii) 1-bromononafluorocyclohexene (0·1 g); (iii) benzene (0·3 g); (iv) bromobenzene (0·5 g); all displaced correct IR spectra; (v) 1-phenylnonafluorocyclohexene (1·8 g), b.p. 183–184° (Found: C, 45·0; H, 1·6. $C_{12}H_5F_9$ requires: C, 45·0; H, 1·6%), ν_{max} 1693 (—CF═CPh—), 1505 and 1455 cm^{-1}. (aromatic nucleus), λ_{max} 2450 Å (ε = 6820, in EtOH), the ^{19}F NMR spectrum consisted of 4 bands in the relative intensity ratio of 2:2:1:4.[7] This olefin (0·2 g) and $KMnO_4$ in acetone gave octafluoroadipic acid, isolated as its bis(anilinium) salt (0·1 g), m.p. 209°.

1-(*Pentafluorophenyl*)*nonafluorocyclohexene.* 1-Bromononafluorocyclohexene (4·0 g) bromopentafluorobenzene (4·0 g) and Cu-bronze (8·0 g) were kept together in a sealed "Pyrex" tube at 225° for 51 hr. As before a liquid (5·0 g) and a residue (1·1 g) were obtained. The former was separated by gas chromatography (column B; 135°; N_2, 10 l./hr) to give (i) 1H-nonafluorocyclohexene (0·2 g), with a correct IR spectrum; (ii) a mixture (1·5 g) which was separated by further gas chromatography (column A; 95°; N_2, 15 l./hr) to give perfluorobicyclohex-1,1′-enyl (1·0 g) and pentafluorobenzene (0·2 g) both with correct IR spectra; (iii) 1-*(pentafluorophenyl)nonafluorocyclohexene* (1·0 g), m.p. 27–28°, b.p. 174° (Found: C, 34·9, F, 64·5. $C_{12}F_{14}$ requires: C, 35·1; F, 64·9%), ν_{max} 1715 [—CF═C(C_6F_5)—], 1660, 1535 and 1515 cm^{-1}. (fluorinated aromatic nucleus), λ_{max} 2640 Å and 2270 Å (ε = 1320 and 3020, respectively in EtOH); the ^{19}F NMR spectrum consisted of 4 bands, attributable to the nonafluorocyclohexene ring, in the intensity ratio 2:1:2:4 and 3 bands, attributable to the pentafluorophenyl system, in the intensity ratio of 2:1:2;[7] (iv) a solid (0·5 g) which was combined with the residue (1·1 g) mentioned earlier to give decafluorobiphenyl (1·6 g; from benzene), m.p. 68–69°, with a correct IR spectrum.

1-(Pentafluorophenyl)nonafluorocyclohexene (0·4 g) and $KMnO_4$ in acetone gave, in the usual way, octafluoroadipic acid which was characterized as its dianilinium salt (0·15 g), m.p. 206°, with the expected IR spectrum.

Bromination of 1H-*heptafluorocyclopentene*

This olefin[15] (12·0 g) and Br_2 (20·5 g) were kept together in a sealed "Pyrex" tube under UV irradiation for 96 hr at ca. 15°. Fumes of HBr were evolved when the tube was opened; excess Br_2 was destroyed by washing with sodium metabisulphite solution and finally with water. The liquid product (13·3 g) was shown by gas chromatography (unit A; 100°; N_2, 1·0 l./hr) to contain 3 components with retention times consistent with 1H-nonafluorocyclopentene, 1-bromoheptafluorocyclopentene and 1H-1,2-dibromoheptafluorocyclopentane. Separation of this mixture by preparative scale gas chromatography (column A; 100°; N_2, 15 l./hr) was prevented by extensive dehydrobromination.

Dehydrobromination of the crude 1H-,1,2-*dibromoheptafluorocyclopentane*

The impure 1H,1,2-dibromoheptafluorocyclopentane (40·0 g), obtained previously, and KOH (40 g) in water (40 ml) were mixed at room temp., when an exothermic reaction occurred. The mixture was refluxed for 1 hr and the liquid product (31·6 g) was separated in portions by gas chromatography (column A; 92°; N_2, 17 l./hr) to give: (i) 1H-heptafluorocyclopentene (17·2 g); (ii) 1-bromoheptafluorocyclopentene (10·2 g) (Found: C, 22·1. C_5BrF_7 requires: C, 22·0%), ν_{max} 1712 cm^{-1} (medium intensity: —CF═CBr—), mass spectrometry[6] gave a top mass peak of 273 (C_5BrF_7), $KMnO_4$ in acetone gave hexafluoroglutaric acid (65%) which was characterized as its bis(S-benzylthiuronium) salt, m.p. 188–190° (Found: C, 44·0; H, 3·9. Calc. for $C_{21}H_{22}F_6N_4O_4S_2$: C, 44·0 H, 3·9%); (iii) minor products (0·7 g) which were separated by gas chromatography (column A; 98°; N_2, 15·3 l./hr) to give; (i) an unidentified component (0·1 g); (ii) 1,5-*dibromohexafluorocyclopentene* (0·3 g), ν_{max} 1700 cm^{-1} (medium intensity; —CF═CBr—), mass spectrometry[6] gave a top mass peak of 332 ($C_5Br_2F_6$) and a consistent fragmentation pattern; (iii) 1,2-*dibromohexafluorocyclopentene* (0·2 g), ν_{max} 1700 and 1620 cm^{-1} (very weak intensity; —CBr═CBr—), mass spectrometry[6] gave a top mass peak of 332 ($C_5Br_2F_6$) and a consistent fragmentation pattern; $KMnO_4$ (0·15 g) in acetone (15 ml) oxidized this olefin (0·1 g) to hexafluoroglutaric acid which was characterized as its bis(S-benzylthiuronium) salt (0·1 g), m.p. 187–188° (Found: C, 43·7; H, 3·9%).

Perfluorobicyclopent-1,1′-*enyl*

1-Bromoheptafluorocyclopentene (1·6 g) and Cu-bronze (1·8 g) were kept in a sealed "Pyrex" tube at 230° for 48 hr. The organic product (0·9 g) was separated by gas chromatography (column A; 82°; N_2, 15·5 l./hr) to give: (i) 1H-heptafluorocyclopentene (0·06 g); (ii) *perfluorobicyclopent*-1,1′-*enyl* (0·5 g), m.p. 22–23°, b.p. 131° (Found: C, 31·4; H, 0·3. $C_{10}F_{14}$ requires: C, 31·1%), ν_{max} 1710, 1700 (i) and 1670 cm^{-1} (—CF═C—C═CF—), λ_{max} 2600 Å (ε = 18300, in EtOH), mass spectrometry gave a top mass peak of 386 ($C_{10}F_{14}$) and a fragmentation pattern consistent with the presence of two linked cyclopentene rings,[6] the ^{19}F NMR spectrum was consistent with a monosubstituted heptafluorocyclo pentene.[7] The diene (0·1 g) was oxidized with $KMnO_4$ (0·2 g) in acetone (20 ml) to give hexafluoroglutaric acid which was characterized as its bis(S-benzylthiuronium) salt (0·1 g), m.p. 188–189° (Found: C, 44·1; H, 4·0%).

1-*Phenylheptafluorocyclopentene*

(a) *From octafluorocyclopentene and phenyl-lithium.* A solution of phenyl-lithium in ether (60 ml; 0·078 g of phenyl-lithium/ml) was slowly added to octafluorocyclopentene (16·1 g) at −65° in an atmosphere of dry N_2 and the mixture allowed to warm to ca. 15°; it was then stirred for 16 hr, N H_2SO_4 added, the ether solution and the ether extract of the aqueous phase were combined, dried ($MgSO_4$), filtered and distilled to give: (i) octafluorocyclopentene (4·9 g) b.p. 25°; (ii) ether; (iii) higher boiling liquids (4·0 g); (iv) a solid which was recrystallized from petrol (b.p. 60–80°) to give 1,2-*diphenylhexafluorocyclopentene* (0·6 g), m.p. 76–77° (Found: C, 62·4; H, 3·1. $C_{17}H_{10}F_6$ requires: C, 62·2; H, 3·1%), ν_{max} 3050 (>CH), 1442, 779 and 694 cm^{-1} (substituted benzene ring), λ_{max} 2710 Å ($\varepsilon = 9600$, in EtOH); $KMnO_4$ (7·0 g), water (30 ml) and the olefin (3·1 g) were kept in an autoclave for 17 hr at 140° to give unchanged olefin (1·9 g) and hexafluoroglutaric acid (0·8 g) which was characterized as its bis(S-benzylthiuronium) salt, m.p. 190° (Found: C, 44·5; H, 3·9%).

Fraction (iii) was separated by gas chromatography (column B; 150°; N_2, 19 l./hr) to give (i) ether and octafluorocyclopentene (0·5 g); (ii) bromobenzene (0·4 g); both with correct IR spectra; (iii) 1-*phenylheptafluorocyclopentene* (2·5 g) b.p. 176–177° (Found: C, 48·9; H, 1·9. $C_{11}H_5F_7$ requires: C, 48·9; H, 1·9%), ν_{max} 3035 (>CH), 1684 (—CF=CPh—), 1504, 771 and 700 cm^{-1} (monosubstituted benzene ring), λ_{max} 2513 Å ($\varepsilon = 16900$, in EtOH). This olefin (2·9 g) and $KMnO_4$ (2·3 g) in acetone (24 ml) gave the crystalline 5-*phenyl*-5-*keto*-2,2,3,3,4,4-*hexafluoro*-n-*valeric acid* (1·5 g), ν_{max} 3200–3050 and 1710 cm^{-1} (—COOH) and 1790 cm^{-1} (>CO) which was characterized as its S-*benzylthiuronium* salt, m.p. 129–130° (Found: C, 49·1; H, 3·7. $C_{19}H_{16}F_6N_2O_3S$ requires: C, 48·9; H, 3·4%).

(b) *Using* 1-*bromoheptafluorocyclopentene.* This olefin (2·20 g) bromobenzene (2·20 g) and Cu-bronze (4·00 g) were kept together in a sealed "Pyrex" tube at 245° for 63 hr. The volatile products (2·60 g) were separated by gas chromatography (column B; 150°; N_2, 19 l./hr) to give: (i) 1H-heptafluorocyclopentene (0·05 g); (ii) perfluorobicyclopent-1,1′-enyl (0·20 g); (iii) benzene (0·10 g); (iv) an unidentified material (trace amount); (v) bromobenzene (0·05 g); (vi) 1-phenylheptafluorocyclopentene (1·33 g); (vii) diphenyl (0·13 g); all displayed correct IR spectra.

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