967. *Polyfluoroarenes. Part VI.*[1] *Propenylpolyfluoroarenes, Pentafluorobenzoic Acid, and Tetrafluoroterephthalic Acid.*

By J. M. Birchall, T. Clarke, and R. N. Haszeldine.

Propenyl-lithium (predominantly the *cis*-isomer) with hexafluorobenzene gives pentafluoropropenylbenzene, oxidation of which affords pentafluorobenzoic acid in *ca.* 70% overall yield. Use of 2 mol. of propenyl-lithium gives three stereoisomeric 1,2,4,5-tetrafluoro-3,6-dipropenylbenzenes, the di-*cis*-isomer predominating. Oxidation of the dipropenyl compounds provides an excellent route to tetrafluoroterephthalic acid. Stereospecific syntheses of pentafluoro-*cis*- and *trans*-propenylbenzene, and of tetrafluoro-di-(*cis*-propenyl)-, -di-(*trans*-propenyl)-, and 3-*cis*-propenyl-6-*trans*-propenyl-benzene are achieved by reaction of hexafluorobenzene with pure *cis*- and *trans*-propenyl-lithium, prepared from the corresponding chlorides.

Silver pentafluorobenzoate with iodine gives pentafluoroiodobenzene, and with nitrosyl chloride gives pentafluorobenzoyl nitrite. Pyrolysis of the latter yields pentafluoronitrosobenzene.

The ultraviolet spectra of polyfluoro-*cis*-propenylbenzenes suggest steric interference between the methyl group and the *ortho*-fluorine atom.

No convenient synthesis of pentafluorobenzoic acid or tetrafluoroterephthalic acid from hexafluorobenzene has yet been described. Hitherto pentafluorobenzoic acid has been most easily prepared by hydrolysis of octafluorotoluene with fuming sulphuric acid,[2] and tetrafluoroterephthalic acid similarly from decafluoro-*p*-xylene;[3] the perfluoroarenes required for these syntheses are not easily prepared. Pentafluorobenzoic acid may also be prepared by carbonation of pentafluorophenylmagnesium iodide,[4] by oxidation of pentafluorovinylbenzene,[4] by hydrolysis of pentafluorobenzonitrile[5] or pentafluorobenzotrichloride,[6] and by oxidation of 2,3,4,5,6-pentafluorotoluene.[7] Oxidation of 1,4-bisbromomethyltetrafluorobenzene gives tetrafluoroterephthalic acid.[6] None of these processes gives a good yield of acid from a readily available starting material.

Oxidation of alkenylpolyfluoroarenes, obtained in excellent yield by the reaction of hexafluorobenzene with alkenyl-lithium compounds, is now reported as the most convenient method for the conversion of hexafluorobenzene into pentafluorobenzoic or tetrafluoroterephthalic acid.

The reactions of alkyl-lithium compounds with hexafluorobenzene are known to give good yields of alkylpentafluorobenzenes.[6,7] Propenyl-lithium, one of the many alkenyl-lithium compounds studied by Braude and his co-workers,[8] was chosen as the most suitable reagent for the work described in the present communication. At first, the only preparative route to propenyl-lithium was the metallation of propenyl bromide ($CH_3{\cdot}CH{:}CHBr$),[9,10] which may be obtained either by the one-step dehydrobromination–decarboxylation of αβ-dibromobutyric acid[9] or by dehydrobromination of 1,2-dibromopropane.[10] The former route gives predominantly the *cis*-isomer, and the latter the *cis*- and the *trans*-isomer together with isopropenyl bromide. Separation of *cis*- and *trans*-propenyl bromide (b. p. 58—58·8° and 63·25°, respectively[11]) has been achieved by precise fractionation at

[1] Part V, Birchall, Haszeldine, and Parkinson, preceding paper.
[2] McBee and Rapkin, *J. Amer. Chem. Soc.*, 1951, **73**, 1366.
[3] Gething, Patrick, and Tatlow, *J.*, 1961, 1574.
[4] Nield, Stephens, and Tatlow, *J.*, 1959, 166.
[5] Pummer and Wall, *J. Res. Nat. Bur. Stand.*, 1959 **63 A**, 167.
[6] Barbour, Buxton, Coe, Stephens, and Tatlow, *J.*, 1961, 808.
[7] Birchall and Haszeldine, *J.*, 1961, 3719.
[8] Braude and Gofton, *J.*, 1957, 4720, and earlier papers in this series.
[9] Braude and Coles, *J.*, 1951, 2078.
[10] Curtin and Crump, *J. Amer. Chem. Soc.*, 1958, **80**, 1922.
[11] Harwell and Hatch, *J. Amer. Chem. Soc.*, 1955, **77**, 1682.

low pressures,[11] but this is possible only when extreme precautions are taken to avoid isomerisation.[10]

The rates of isomerisation of *cis*- and *trans*-propenyl bromide over a range of temperatures have been studied in some detail.[11] Although both compounds isomerise in the direction of an equilibrium *cis–trans*-mixture at room temperature, the formation of propenyl-lithiums from propenyl bromide, and subsequent reactions of the lithium compounds, appear to proceed with retention of configuration at the double bond. Thus, metallation of *cis*-propenyl bromide in ether and reaction of the resulting solution with benzaldehyde [9,10] gives 5 parts of *cis*-1-phenylbut-2-en-1-ol (CH_3·CH:CH·CHPh·OH) and 1 part of 1-phenylbut-2-yn-1-ol (CH_3·C:C·CHPh·OH). *trans*-Propenyl bromide gives the *trans*-alcohol under similar conditions, and the acetylenic compound is not formed.[10] The possibility that the formation and subsequent reactions of the propenyl-lithiums both proceed with inversion has been largely eliminated by the work of Nesmeyanov and his school.[12]

Syntheses with Propenyl-lithium from Propenyl Bromide.—A mixture of *cis*- and *trans*-propenyl-lithium in ether reacted with a small excess of hexafluorobenzene at −15° to give pentafluoro-*cis*- and *trans*-propenylbenzene * in 87% yield based on the hexafluorobenzene converted. No acetylenic compounds were isolated from this or any other of the experiments described in the present communication.

When a slight excess of a propenyl-lithium solution containing mainly the *cis*-isomer reacted with hexafluorobenzene at −20°, the product was mainly pentafluoro-*cis*-propenylbenzene (73% yield) and tetrafluoro-*p*-di-*cis*-propenylbenzene † (7%), characterised as its crystalline tetrabromide. No *p*-dipropenyl derivative containing a *trans*-propenyl group was detected, no position isomer was formed, and no hexafluorobenzene was recovered.

With 2 mol. of a propenyl-lithium solution in boiling ether hexafluorobenzene gave mainly the *p*-di-*cis*-compound (*ca.* 80% yield); traces of the di-*trans*- and *p*-*cis*–*trans*-compound were usually also formed. A similar mixture of products was obtained from the reaction of hexafluorobenzene with three mol. of propenyl-lithium, and in particular no trifluorotripropenylbenzene was formed. The resistance of the tetrafluorodi-(*cis*-propenyl)benzene to attack by propenyl-lithium was further demonstrated by almost quantitative recovery of this compound after prolonged refluxing with propenyl-lithium in ether.

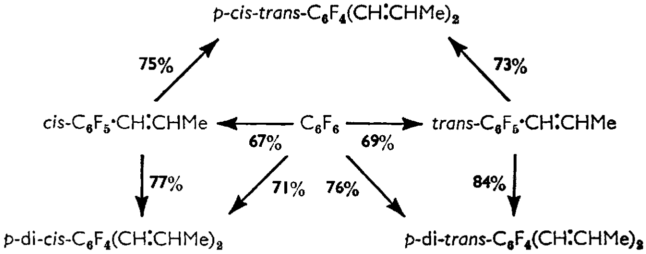
Propenyl-lithium from Propenyl Chloride.—*cis*- and *trans*-Propenyl chloride, prepared by dehydrochlorination of 1,2-dichloropropane, may be separated by careful fractionation at atmospheric pressure; each isomer is stable up to 135°. During the research described in this communication, these compounds were shown [13] to be convenient sources of pure *cis*- and *trans*-propenyl-lithium, respectively, and the use of stereochemically pure propenyl-lithiums so prepared as reagents for the preparation of propenylpolyfluorobenzenes has been investigated. The *cis*-, the *trans*-, the di-*cis*-, the di-*trans*-, and the *cis–trans*-compound shown in the annexed scheme were thus obtained pure and in good yields by use of the appropriate alkenyl-lithium.

Pentafluorobenzoic Acid and Tetrafluoroterephthalic Acid.—Oxidation of pentafluoropropenylbenzene with potassium permanganate in acetone is rapid and exothermic at room temperature and leads to extensive degradation of the ring. At 0°, however, pentafluorobenzoic acid is formed in up to 88% yield, and an excellent synthesis of this compound from hexafluorobenzene is thus provided. Although both geometrical isomers give

* The numerical prefixes to indicate that the fluorine is exclusively in the aryl nucleus are usually omitted in this paper.

† *p* is used to locate the propenyl substituents, the systematic name of this compound being 1,2,4,5-tetrafluoro-3,6-di-*cis*-propenylbenzene.

[12] Reviewed by Nesmeyanov and Borisov, *Tetrahedron*, 1957, **1**, 158.
[13] Allinger and Hermann, *J. Org. Chem.*, 1961, **26**, 1040.



(for use of *p*- see footnote †.)

pentafluorobenzoic acid, the acid is probably best prepared from the *cis–trans*-mixture obtained from propenyl bromide, since the bromide is easier to prepare free from its isopropenyl isomer than is the chloride.

The tetrafluoro-*p*-dipropenylbenzenes all give tetrafluoroterephthalic acid in good yield (>70%) when oxidised by the same procedure, and the orientation of the propenyl groups is thus established. The acid, which is characterised through its di-*S*-benzylthio-uronium salt, decomposes when strongly heated to give a nearly quantitative yield of

TABLE 1.

Infrared spectra of the polyfluoropropenylbenzenes (cm.$^{-1}$).

$C_6F_5\cdot CH{:}CHMe$		$C_6F_4(CH{:}CHMe)_2$			Assignments
cis	*trans*	di-*cis* *	3-*cis*-6-*trans*	di-*trans* *	
650w	654w				
661m		678m	667vw	660w	
697m		747m	697w		
767m	778w	771w	765m	762w	
797w		805w			
880vw †		879m †	888m	884m	
905m †		892m	899m	907w	
911s	913s		920m	917w	
966vs	967vs	952m	967vs		C–F stretching
986vs	980vs	972vs	977s †	975vs	C–F stretching
995vs	1001vs	1000m	1000w	1003m	C–F stretching
1036vw	1036m	1033w	1034vw	1031vw	
1083s		1089m	1076w		
1114s	1110m	1111w	1107w	1109w	
	1134s		1117w	1126vw	
	1149s	1235w			
		1258m	1253w	1247m	
	1263w	1267m	1269m	1266m	
	1299m	1282m	1290m	1292m	
1307m	1323w		1311m	1312m	
1351w	1333w		1330w	1333m	
1374m	1370w	1368m	1368m	1372m	
	1381w				
1403w		1399m	1399m		=C–H in-plane
1431w	1425w		1420w		
1453w	1451m		1445s	1443s	
1495vs, 1522vs	1502vs, 1524vs	1466vs	1479vs	1481vs	Ring vibration
1637w	1626m				C:C stretching
		1642w	1645m	1647m	
1656m	1658m				Ring vibration
1739vw	1715vw		1706vw		
2427vw	1783vw				
2653vw					
2899vw †	2882vw	2857vw	2882w	2857vw	$-CH_3$ stretching
		2924w			
2985w	2941w	2959w	2924w	2924w	$-CH_3$ stretching
3058w	3067vw	3030w	3030w	3049vw	=C–H stretching

* Mulls in Nujol or hexachlorobutadiene; remainder liquids. † Shoulder.

1,2,4,5-tetrafluorobenzene. Tetrafluoroterephthalic acid has been decarboxylated previously by use of soda lime.[3]

The action of heat on a mixture of silver pentafluorobenzoate and iodine gives pentafluoroiodobenzene (55%). Silver pentafluorobenzoate also reacts with nitrosyl chloride at $-10°$, giving an almost quantitative yield of pentafluorobenzoyl nitrite; this compound is sensitive to light and is rapidly hydrolysed by water to pentafluorobenzoic acid. Like the aliphatic perfluoroacyl nitrites,[14] pentafluorobenzoyl nitrite decomposes in the vapour phase at 300° to give the corresponding nitroso-compound, $C_6F_5{\cdot}NO$. The yield of pure pentafluoronitrosobenzene, obtained as a green solid, is low (18%), but is expected to be improved considerably by a study of the reaction variables. The preparation of pentafluoronitrosobenzene by oxidation of pentafluoroaniline with performic acid has been reported recently;[15] the physical properties and ultraviolet spectra of the products prepared by the two routes are in good agreement.

Infrared Spectra of the Propenyl Compounds.—The vibrations which are normally of value for the determination of the stereochemistry of compounds of the type CHR:CHR′ are the C:C stretching vibration, the C–H out-of-plane deformation, and the C–H in-plane deformation.[16] In compounds containing an unconjugated double bond, the C:C stretching vibration occurs in the range 1620—1680 cm.$^{-1}$, but aromatic conjugation usually results in its appearance near the low-frequency end of this range,[16] at about 1625 cm.$^{-1}$. In unconjugated alkenes,[17] the vibration in *trans*-CHR:CHR′ systems is near 1673 cm.$^{-1}$, and in *cis*-CHR:CHR′ systems near 1657 cm.$^{-1}$. Similar values have also been observed[18] for conjugated systems, *trans*-propenylbenzene giving a C:C stretching vibration at 1667 cm.$^{-1}$ and the *cis*-compound at 1653 cm.$^{-1}$.

In the polyfluoropropenylbenzenes (Table 1), assignments in the C:C region are complicated by the appearance of the 1650—1660 cm.$^{-1}$ band of the aromatic ring,[7] but a separate band at 1626 cm.$^{-1}$ for pentafluoro-*trans*-propenylbenzene and at 1637 cm.$^{-1}$ for the *cis*-propenyl compound may be assigned with reasonable confidence to the C:C stretching vibration. The unusual appearance of the vibration in the *trans*-compound at a lower frequency than that in the *cis*-isomer may be attributed to effective steric inhibition of resonance in the latter, discussed in more detail below. The tetrafluorodipropenylbenzenes show only a single broad band in the 1650 cm.$^{-1}$ region of the spectrum, and this probably includes contributions from both aromatic ring vibrations and C:C stretching of the side-chain.

The C–H out-of-plane deformation in compounds of the type CHR:CHR′ generally occurs at 965—990 cm.$^{-1}$ for *trans*-compounds and at 650—800 cm.$^{-1}$ for the *cis*-isomers, but a definite assignment for the latter is rarely possible.[16] The very strong C–F vibrations of the polyfluoroarene system (950—1000 cm.$^{-1}$) make it impossible to identify the C–H out-of-plane band in the polyfluoro-*trans*-propenylbenzenes, but the presence of only weak bands between 650 and 800 cm.$^{-1}$ in these compounds supports the *trans*-structures. On the other hand, all the compounds containing a *cis*-propenyl group give rise to much stronger bands in the 650—800 cm.$^{-1}$ region; which of these is due to the C–H out-of-plane deformation is uncertain.

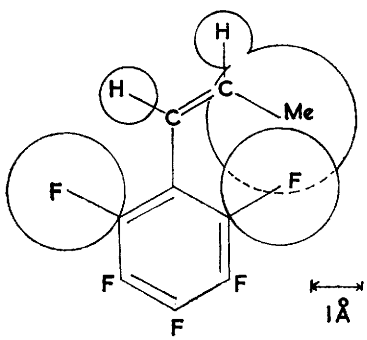
The large number of bands of weak to medium intensity in the vinylic C–H in-plane deformation region (1300—1400 cm.$^{-1}$) of the spectra of all the polyfluoropropenylbenzenes again makes assignment of particular bands to this mode of vibration difficult. However, only the compounds containing *cis*-propenyl groups give bands at about 1400 cm.$^{-1}$, and these are probably due to the C–H in-plane deformation in the *cis*-propenyl group. The band at 1412 cm.$^{-1}$ in the spectrum of *cis*-propenylbenzene has been assigned to this mode,[18]

[14] Banks, Haszeldine, and McCreath, *Proc. Chem. Soc.*, 1961, 64.
[15] Brooke, Burdon, and Tatlow, *Chem. and Ind.*, 1961, 832.
[16] Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Co., London, 1958 (2nd edn.), chapter 3.
[17] Sheppard and Simpson, *Quart. Rev.*, 1952, **6**, 17.
[18] Mixer, Heck, Winstein, and Young, *J. Amer. Chem. Soc.*, 1953, **75**, 4094.

and the corresponding band in the *trans*-compound is at 1309 cm.$^{-1}$. The medium-intensity band at 1307 cm.$^{-1}$ in the spectrum of *cis*-propenylpentafluorobenzene is not consistent with such an assignment in the present case.

Ultraviolet Spectra of the Propenyl Compounds.—The effects of steric inhibition of resonance on the ultraviolet spectra of conjugated systems are well established.[19] Theoretical considerations and molecular models have indicated that interference between the methyl group and the *o*-hydrogen atoms in *cis*-propenylbenzene should result in an angle of about 20° between the vinylic system and the plane of the benzene ring.[20] In *trans*-propenylbenzene, such interference cannot occur, and both the high-intensity ultraviolet band, characteristic of the completely conjugated system, and the low-intensity bands arising from the aromatic ring are at longer wavelengths and of greater intensity in the *trans*- than in the *cis*-compound [*cis*-CHPh:CHMe, $\lambda_{max.}$ 241 (ε 13,800), 279 (infl.), and 290 mμ (ε 120); *trans*-CHPh:CHMe, $\lambda_{max.}$ 250 (ε 17,300), 284 (ε 1100), and 293 mμ (ε 780) (in 95% ethanol) [18]]. Similar differences in the spectra of the cinnamic acids [*cis*-CHPh:CH·CO_2H, $\lambda_{max.}$ 261 mμ (ε 10,500); *trans*-CHPh:CH·CO_2H, $\lambda_{max.}$ 272 mμ (ε 19,500) (in methanol) [21]] have also been attributed to steric interference, resulting in non-planarity of the *cis*-compound,[22] and the different ionisation constants of the two acids have been explained on the same basis.[23]

In the polyfluoro-*cis*-propenylbenzenes, steric interference between the methyl group and an *o*-fluorine atom (shown with the appropriate distances and radii[19] in the Figure) would be expected to be more pronounced than the interaction between methyl and *o*-hydrogen in *cis*-propenylbenzene. Molecular models indicate that the angle between the *cis*-propenyl system and the aromatic ring in pentafluoro-*cis*-propenylbenzene is probably



appreciably larger than that in *cis*-propenylbenzene, and this is reflected in the ultraviolet spectra of the polyfluoropropenylarenes (Table 2). Pentafluoro-*trans*-propenylbenzene, which is expected to be flat and completely conjugated, shows a high-intensity band with some fine structure at 246 mμ, whilst the corresponding band in the *cis*-isomer is reduced in intensity and appears at 221 mμ. Similar, but less pronounced, changes occur in the position and intensity of the low-intensity benzenoid bands, and the wavelength shifts of all the bands are considerably greater than those in the propenylbenzenes themselves. The spectra of the tetrafluorodipropenylbenzenes show these effects to an even greater extent, the spectrum of tetrafluoro-*p*-*cis*-propenyl-*trans*-propenylbenzene fitting well between those of the di-*cis*- and the di-*trans*-compound. The ultraviolet spectra thus provide strong evidence for the structures assigned to the polyfluoropropenylbenzenes.

[19] See, for example, Braude and Sondheimer, *J.*, 1955, 3754, 3773; Braude and Timmons, *ibid.*, p. 3766.
[20] Guy, *J. Chim. phys.*, 1949, **46**, 469.
[21] Havinga and Nivard, *Rec. Trav. chim.*, 1948, **67**, 846.
[22] Gillam and Stern, " An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Arnold, London, 2nd edn., 1957, p. 268.
[23] Ingold, " Structure and Mechanism in Organic Chemistry," Bell and Sons, London, 1953, p. 743.

Spectra of the Acids.—The infrared spectrum of pentafluorobenzoic acid vapour shows aromatic ring absorptions at 1502, 1508, 1524 (very strong triplet), and 1647 (weak), and strong C–F absorption at 1002 cm.$^{-1}$. In the solid phase (mull) the aromatic bands are at 1499 and 1529 (strong) and at 1653 cm.$^{-1}$ (medium), and the strong C–F bands are at

TABLE 2.

Ultraviolet spectra (λ in mμ) of the polyfluoropropenylbenzenes.

	In hexane				In ethanol			
	$\lambda_{max.}$	ε	$\lambda_{min.}$	ε	$\lambda_{max.}$	ε	$\lambda_{min.}$	ε
cis-C_6F_5·CH:CHMe	221	10,600	205	6000	222	10,800	205	6000
	265 *	610			265 *	605		
trans-C_6F_5·CH:CHMe	237 *	14,100	211	5400	236 *	13,900	211	5300
	246	14,800			246	14,900		
	253 *	11,200			253 *	11,600		
	278 *	660			276 *	695		
di-*cis*-C_6F_4(CH:CHMe)$_2$	248	19,800	221	7300	249	19,200	222	7700
cis–trans-C_6F_4(CH:CHMe)$_2$	263	22,300	227	7700	262	22,900	227	8400
di-*trans*-C_6F_4(CH:CHMe)$_2$ ...	269	34,200	236	3400	269 *	36,500	235	4300
	279	42,800	271	34,000	279	43,400		
	290 *	29,200			290 *	27,200		

* Inflexion.

989 and 1005 cm.$^{-1}$. Bands in the carbonyl and O–H stretching regions in the spectra of pentafluorobenzoic acid in the vapour and the solid state and in solution are listed in Table 3; the variations in the spectra in these regions are attributed to changes in the degree of hydrogen bonding.

TABLE 3.

Infrared bands of pentafluorobenzoic acid (cm.$^{-1}$).

	O–H stretching		C:O stretching	
	Free	Bonded	Free	Bonded
Vapour	3559m	—	1776vs †	—
Solid *	—	3003m	—	1716, 1724vs, d
In CCl_4:				
0·0140M	—	3145m	1754vw	1721vs
0·0070M	—	3145m	1757w	1721s
0·0035M	3509w	3135m	1761m	1724s
0·0007M	3509m	3125m	1764s	1724s
0·0004M	3509m	3125w	1764s	1724m

* Mull. † This band contains a shoulder at 1799m cm.$^{-1}$.

The band at 1776 cm.$^{-1}$ in the solution spectra is attributed to the carbonyl vibration in the "free" monomeric acid since its intensity increases with increasing dilution. The band at 1716 and 1724 cm.$^{-1}$ (doublet) in the spectrum of solid pentafluorobenzoic acid, and at 1721—1724 cm.$^{-1}$ in the solution spectra, shows the reverse behaviour on dilution, and is attributed to carbonyl vibrations in the dimeric form.

Similarly, the "free" O–H stretching absorption is shown in the vapour spectrum at 3559 cm.$^{-1}$ and in 0·0004—0·0035M-solutions at 3509 cm.$^{-1}$, and does not appear in the spectra of the solid and more concentrated solutions. A broad diffuse band centred on 3003 cm.$^{-1}$ in the spectrum of the solid and near 3100 cm.$^{-1}$ in the solution spectra arises from O–H vibrations in the dimer.

The infrared spectrum of tetrafluoroterephthalic acid (mull) shows a very strong aromatic ring vibration at 1477 cm.$^{-1}$, carbonyl vibrations at 1701 and 1712 cm.$^{-1}$ (doublet), and a broad band, characteristic of hydrogen-bonded hydroxyl vibrations, at 2890 and 2950 cm.$^{-1}$ (doublet).

The ultraviolet spectrum of pentafluorobenzoic acid shows characteristics similar to those for benzoic acid; the presence of the five fluorine atoms causes small shifts to shorter wavelengths in the bands associated with the benzene ring (*ca.* 270 mμ) and the extended conjugated system (*ca.* 220 mμ). Ionisation of both acids causes further shifts of both these bands, but the shifts are less with the fluorinated acid than with benzoic acid itself ($\lambda_{max.}$: $C_6H_5{\cdot}CO_2H$, 228 and 272; $C_6H_5{\cdot}CO_2^-$, 224 and 262;[24] $C_6F_5{\cdot}CO_2H$, 219 and 268; $C_6F_5{\cdot}CO_2^-$, 217 and 263 mμ).

Experimental

Gas–liquid chromatography was carried out as described previously[1,7] with a Perkin-Elmer No. 116 instrument. Infrared spectra were recorded on a Perkin-Elmer No. 21 instrument, and ultraviolet spectra were measured over the range 210—800 mμ with a Unicam S.P. 700 instrument.

Propenyl-lithium was estimated in all cases by the total-alkali titration method;[25] operations involving lithium compounds were carried out under nitrogen.

Propenyl Bromide.[9]—αβ-Dibromobutyric acid (750 g.) and dry pyridine (1500 ml.) were heated under reflux for 6 hr. The fraction boiling below 112° was then distilled on to ice (400 g.) and concentrated hydrochloric acid (100 ml.). The organic layer of the distillate was steam-distilled, dried ($MgSO_4$), and distilled through a vacuum-jacketed column (50 × 0·7 cm.) packed with glass helices to give propenyl bromide (140 g., 33%), b. p. 56—59°, shown to be predominantly the *cis*-isomer (lit.,[11] b. p. 58—58·8°) by infrared spectroscopy. This material was rapidly redistilled, but not refractionated, immediately before use, a procedure which did not appreciably affect its isomer ratio.

Propenyl-lithium from Propenyl Bromide.—Propenyl bromide (27·0 g., 0·224 mole) was distilled rapidly from a small piece of sodium and added to a stirred suspension of finely cut lithium (5·0 g., 0·715 mole) in dry ether (300 ml.). About one-tenth of the bromide was added initially, and the remainder at a rate sufficient to maintain gentle refluxing. The mixture was refluxed for a further 45 min., allowed to cool, and filtered through glass-wool to give a solution of propenyl-lithium (5·84 g., 54%).

*Pentafluoro-*cis–trans*-propenylbenzene.*—Ethereal propenyl-lithium (6·0 g., 0·125 mole) [from propenyl bromide (25·0 g.), lithium (5·0 g.), and ether (300 ml.)] was added in 15 min. to a cold (−15°), stirred, solution of hexafluorobenzene (27·0 g., 0·145 mole) in ether (300 ml.). The mixture was stirred for a further 60 min. at −15°, then allowed to warm to room temperature and poured into water (200 ml.). The organic layer was separated, the aqueous phase was extracted with ether, and the combined ethereal solutions were dried ($MgSO_4$) and distilled. A fraction distilling at 35—90° was shown by gas–liquid chromatography (2 m. of Silicone " MS 550 ") to contain only ether and hexafluorobenzene (12·6 g., 47%), and a fraction distilling at 90—162° was similarly shown to be pentafluoro-*cis–trans*-propenylbenzene (14·0 g., 46%; 87% based on hexafluorobenzene converted). Pure *pentafluoro-*cis*-propenylbenzene* (5·5 g.) (Found: C, 52·0; H, 2·3. $C_9H_5F_5$ requires C, 51·9; H, 2·4%), b. p. 154°/751 mm., n_D^{21} 1·4440, d_4^{21} 1·361, was obtained by distillation of the *cis–trans*-mixture through a 30-cm. Podbielniak Heligrid column.

In a second experiment, ethereal propenyl-lithium (14·4 g., 0·37 mole) [from propenyl bromide (50·0 g.), lithium (7·0 g.), and ether (1000 ml.)] was added to hexafluorobenzene (50·0 g., 0·269 mole) and ether (200 ml.) at −20°. After a further 60 min. at −20° the mixture was poured into 2N-hydrochloric acid (200 ml.) and extracted with ether, and the extract dried, and distilled to give pentafluoro-*cis*-propenylbenzene (40·7 g., 73%), b. p. 53—60°/12 mm., containing only traces of the *trans*-isomer, and 1,2,4,5-tetrafluoro-3,6-di-(*cis*-propenyl)benzene (4·0 g., 7%), b. p. 90—104°/12 mm., m. p. 46—49°, identified by infrared spectroscopy.

Tetrafluorodipropenylbenzenes from Propenyl Bromide.—(*a*) *Hexafluorobenzene and two mol. of propenyl-lithium.* Ethereal propenyl-lithium (5·6 g., 0·12 mole) [from propenyl bromide (40·0 g.), lithium (8·0 g.), and ether (400 ml.)] was added, at a rate sufficient to maintain gentle reflux, to hexafluorobenzene (11·0 g., 0·06 mole) in ether (100 ml.). The mixture was heated under reflux for a further 60 min., 2N-hydrochloric acid (200 ml.) was added, and the mixture was extracted with ether. The combined extracts were dried ($MgSO_4$) and evaporated, and

[24] Ungnade and Lamb, *J. Amer. Chem. Soc.*, 1952, **74**, 3789.
[25] Gilman, Wilkinson, Fishel, and Meyers, *J. Amer. Chem. Soc.*, 1923, **45**, 150.

the brown residue (12·9 g.) was steam-distilled to give white crystalline 1,2,4,5-*tetrafluoro*-3,6-*di*-(cis-*propenyl*)*benzene* (11·1 g., 82%) (Found: C, 62·6; H, 4·1. $C_{12}H_{10}F_4$ requires C, 62·6; H, 4·3%), m. p. 51·5—52° (from methanol), shown to be pure by gas–liquid chromatography.

In a second experiment, ethereal propenyl-lithium (7·0 g., 0·146 mole) [from propenyl bromide (69 g.), lithium (12·0 g.), and ether (1250 ml.)] was added in the same way to hexafluorobenzene (13·5 g., 0·073 mole) in ether (100 ml.). Evaporation of the dry ethereal extract gave a semi-solid residue (15·5 g.), shown by gas–liquid chromatography (2 m. of Silicone "MS 550") and infrared spectroscopy to contain only pentafluoro-*cis*-propenylbenzene (2·48 g., 17%), tetrafluoro-*p*-di-(*cis*-propenyl)benzene (11·93 g., 71%), tetrafluoro-*p*-di-(*trans*-propenyl)benzene (0·16 g., 2%), and tetrafluoro-*p*-*cis*-propenyl-*trans*-propenylbenzene (0·93 g., 6%).

(*b*) *Hexafluorobenzene and three mol. of propenyl-lithium.* Ethereal propenyl-lithium (20·2 g., 0·42 mole) [from propenyl bromide (65·0 g.), lithium (10·0 g.), and ether (1000 ml.) at 0°] was added as before to hexafluorobenzene (24·0 g., 0·13 mole) in ether (100 ml.). The mixture was refluxed for 4 hr. and then poured into 2N-hydrochloric acid (200 ml.), and brown crystals (29·6 g.) were isolated by extraction with ether. Steam-distillation gave the *p*-di-(*cis*-propenyl) compound (19·61 g., 66%), m. p. 50—51°, which floated as a solid on the surface of the distillate and was identified by infrared spectroscopy, and a liquid (2·2 g.) which was heavier than water. The liquid was shown by gas–liquid chromatography to consist of pentafluoro-*cis*-propenylbenzene (*ca.* 0·3 g., 1%) and the *p*-*cis*–*trans*-compound (*ca.* 1·9 g., 6%).

Tetrafluoro-*p*-di-(*cis*-propenyl)benzene (2·00 g., 8·7 mmoles) was heated with propenyl-lithium (0·42 g., 8·8 mmoles) and ether (75 ml.) under reflux for 4 hr. and recovered (1·96 g., 98%; m. p. 45—47°); it was identified by infrared spectroscopy.

1,4-*Bis*-(1,2-*dibromopropyl*)*tetrafluorobenzene*.—Bromine (0·30 g., 1·88 mmoles) and tetrafluoro-*p*-di-(*cis*-propenyl)benzene (0·22 g., 0·96 mmole) in carbon tetrachloride (40 ml.) were shaken in a sealed tube for 12 hr. Evaporation of the solvent under a vacuum and recrystallisation of the residue (0·50 g.) from ethanol gave 1,4-*bis*-(1,2-*dibromopropyl*)*tetrafluorobenzene* (0·45 g., 86%) (Found: C, 26·4; H, 1·6. $C_{12}H_{10}Br_4F_4$ requires C, 26·2; H, 1·8%), m. p. 107°. The infrared spectrum of this compound (mull) shows a very strong aromatic ring vibration at 1497 cm.$^{-1}$ and very strong C–F vibrations at 965 and 974 cm.$^{-1}$ (doublet).

Pentafluorobenzoic Acid.—(*a*) *From pentafluoro*-cis-*propenylbenzene.* Pentafluoro-*cis*-propenylbenzene (1·00 g., 4·8 mmoles) was stirred with potassium permanganate (2·50 g., 15·8 mmoles) in dry acetone (100 ml.) at 0° for 4 hr. The mixture was poured into water (100 ml.) and decolorised with sulphur dioxide, the acetone was removed under a vacuum, and the colourless aqueous solution was acidified with 2N-hydrochloric acid (10 ml.) and extracted with ether. The extracts were dried ($MgSO_4$) and evaporated, and the residue (0·81 g.) was recrystallised twice from toluene–light petroleum and sublimed *in vacuo*, to give pentafluorobenzoic acid (0·52 g., 51%) (Found: C, 39·9; H, 0·6%; equiv., 214. Calc. for $C_7HF_5O_2$: C, 39·9; H, 0·5%; equiv., 212), m. p. 101·5—102° (lit., m. p. 103—104°,[4] 106—107° [2]), $\lambda_{max.}$ 268 (ε 1040) and 219 mμ (ε 5200), $\lambda_{min.}$ 246 mμ (ε 650) in ether, and $\lambda_{max.}$ 263 mμ (ε 640) and $\lambda_{infl.}$ 217 mμ (ε 4200) with $\lambda_{min.}$ 254 mμ (ε 570) in 0·01N-aqueous sodium hydroxide.

(*b*) *From the* cis–trans-*mixture.* Pentafluoro-*cis*–*trans*-propenylbenzene (10·0 g., 0·048 mole) was stirred in dry acetone (300 ml.) at 0° and potassium permanganate (25·0 g., 0·158 mole) was added in portions during 2 hr. The mixture was stirred at 0° for a further hour, then working up as above gave a crude product (9·5 g.) which recrystallised from benzene to yield pentafluorobenzoic acid (8·9 g., 88%), m. p. 98—99°, identified by infrared spectroscopy.

Pentafluorobenzoic acid gave its *S*-benzylthiouronium salt (Found: C, 47·2; H, 2·8; N, 7·5. Calc. for $C_{15}H_{11}F_5N_2O_2S$: C, 47·3; H, 2·9; N, 7·6%), m. p. 183—184° (lit.,[4] m. p. 178°), in 95% yield by the usual procedure.

Tetrafluoroterephthalic Acid.—Tetrafluoro-*p*-di-(*cis*-propenyl)benzene (3·00 g., 13·1 mmoles) was stirred in dry acetone (220 ml.) at 0°, and potassium permanganate (12·0 g., 76·0 mmoles) was added in portions during 2 hr. The mixture was stirred for a further hour, and worked up as described in (*a*) above, giving tetrafluoroterephthalic acid (recrystallised from water; 2·31 g., 74%) (Found: C, 40·4; H, 0·8%; equiv., 120. Calc. for $C_8H_2F_4O_4$: C, 40·3; H, 0·8%; equiv., 119), m. p. (sealed tube) 282—283° (lit.,[3] m. p. 283—284°), $\lambda_{max.}$ 220·5 (ε 8200) and 281·5 mμ (ε 1760), $\lambda_{min.}$ 264·5 mμ (ε 1400) in ether, and $\lambda_{max.}$ 225 mμ (ε 6200), $\lambda_{infl.}$ 268 mμ (ε 1500), $\lambda_{min.}$ 221 mμ (ε 6000) in 0·01N-aqueous sodium hydroxide.

Di-(*S*-benzylthiouronium) tetrafluoroterephthalate (Found: C, 50·4; H, 3·7; N, 10·0. Calc. for $C_{24}H_{22}F_4N_4O_4S_2$: C, 50·5; H, 3·9; N, 9·9%), m. p. 206° (from water) (lit.,[3] m. p.

211—212°), was prepared by addition of *S*-benzylthiouronium chloride to an aqueous solution of the acid, previously adjusted to pH 4.

Decarboxylation of Tetrafluoroterephthalic Acid.—Tetrafluoroterephthalic acid (0·70 g.) was heated in a 400-ml. sealed tube for 1 hr. at 340°. The contents of the tube were separated by fractional condensation *in vacuo* and gave carbon dioxide (0·26 g., 100%) (Found: *M*, 44·7. Calc. for CO_2: *M*, 44·0), condensing at −196°, and 1,2,4,5-tetrafluorobenzene (0·42 g., 96%) (Found: C, 48·0; H, 1·4%; *M*, 148. Calc. for $C_6H_2F_4$: C, 48·0; H, 1·3%; *M*, 150), condensing at −78°, identified, and easily distinguished from other tetrafluorobenzenes, by infrared spectroscopy.

Propenyl Chloride.—This was prepared by dehydrochlorination of 1,2-dichloropropane (500 g., 4·43 moles) with potassium hydroxide (300 g., 5·36 moles) in ethanol (3 l.).[13] Products boiling below 50° were removed continuously, and then distilled through a vacuum-jacketed column (50 × 0·4 cm.) packed with glass helices. The fraction distilling below 32° (175 g.) was mainly isopropenyl chloride (lit.,[26] b. p. 22·65°) containing some *cis*-propenyl chloride. The fraction distilling at 32—39° (178 g.) was redistilled through a Podbielniak Helipak column (60 × 0·3 cm.) to give chromatographically pure (2 m. of dinonyl phthalate) *cis*- (51 g.), b. p. 32·2—32·8° (lit., b. p. 30·8—31·3°,[13] 32·8° [27]), and *trans*-propenyl chloride (56 g.), b. p. 37·8—38·2° (lit., b. p. 37·9°,[13] 37·4° [27]), identified by infrared spectroscopy.

*Pentafluoro-*cis*-propenylbenzene.*—*cis*-Propenyl-lithium (1·6 g., 33 mmoles) in ether (150 ml.) (prepared from *cis*-propenyl chloride, lithium, and ether at 0° [13]) was added to a stirred solution of hexafluorobenzene (6·50 g., 35 mmoles) in ether (20 ml.) at −20°. The mixture was stirred at −20° for 2 hr., 2N-hydrochloric acid (100 ml.) was added, and the mixture was extracted with ether. The extracts were dried ($MgSO_4$) and distilled, to give pentafluoro-*cis*-propenylbenzene (4·50 g., 67%), b. p. 56°/12 mm., shown by infrared spectroscopy and gas–liquid chromatography (2 m. of Silicone "MS 550") to be identical with the compound prepared from propenyl bromide.

*Pentafluoro-*trans*-propenylbenzene.*—A procedure identical with that described above, with *trans*-propenyl-lithium (1·6 g., 33 mmoles) in ether (150 ml.) (from *trans*-propenyl chloride, lithium, and ether at 0° [13]) and hexafluorobenzene (6·50 g., 25 mmoles) in ether (20 ml.), gave chromatographically pure (2 m. of Silicone " MS 550 ") *pentafluoro-*trans*-propenylbenzene* (4·70 g., 69%) (Found: C, 52·1; H, 2·6. $C_9H_5F_5$ requires C, 51·9; H, 2·4%), b. p. 159—160°, n_D^{20} 1·4590, d_4^{20} 1·312.

Oxidation of the *trans*-isomer (0·80 g., 3·9 mmoles) with potassium permanganate (2·00 g., 12·7 mmoles) in acetone (50 ml.) at 0° gave pentafluorobenzoic acid (0·69 g., 84%), m. p. 100—101° (from benzene), mixed m. p. with the acid obtained from *cis*-propenylpentafluorobenzene 101—102°.

*Tetrafluoro-*p*-di-(*cis*-propenyl)benzene.*—(*a*) *From hexafluorobenzene.* *cis*-Propenyl-lithium (1·6 g., 33 mmoles) (from *cis*-propenyl chloride) in ether (150 ml.) was added to a stirred solution of hexafluorobenzene (3·00 g., 16 mmoles) in ether (20 ml.) at −20°. The mixture was stirred at −20° for 1 hr., allowed to warm to room temperature, and heated under reflux for 1 hr. Acidification and ether-extraction as before gave crystals (3·5 g.), which recrystallised from methanol to give tetrafluoro-*p*-di-(*cis*-propenyl)benzene (2·60 g., 71%), m. p. 50·5—51°, shown by infrared spectroscopy and mixed m. p. to be identical with the compound obtained from propenyl bromide.

(*b*) *From pentafluoro-*cis*-propenylbenzene.* Addition of *cis*-propenyl-lithium (0·48 g., 10 mmoles) in ether (50 ml.) to pentafluoro-*cis*-propenylbenzene (2·0 g., 9·6 mmoles) in ether (25 ml.) at −20° gave, after the usual purification, the *p*-di-(*cis*-propenyl) compound (1·70 g., 77%), m. p. 50—51°, mixed m. p. 51°.

*Tetrafluoro-*p*-di-(*trans*-propenyl)benzene.*—(*a*) *From hexafluorobenzene.* *trans*-Propenyl-lithium (1·5 g., 33 mmoles) in ether (150 ml.) was added to a stirred solution of hexafluorobenzene (3·00 g., 16 mmoles) in ether (20 ml.) at −20° and the mixture was stirred at −20° for 1 hr., allowed to warm to room temperature, and heated under reflux for 1 hr. Acidification and extraction with ether then gave chromatographically pure 1,2,4,5-*tetrafluoro*-3,6-*di*-(trans-*propenyl*)*benzene* (2·81 g., 76%) (Found: C, 62·1; H, 4·3. $C_{12}H_{10}F_4$ requires C, 62·6; H, 4·3%), m. p. 88—89°.

[26] " Handbook of Chemistry," ed. Lange, McGraw-Hill Book Co., New York, 10th edn. (1961), p. 662.

[27] Timmermans, *Bull. Soc. chim. belges*, 1927, **36**, 502.

(*b*) *From pentafluoro*-trans-*propenylbenzene*. *trans*-Propenyl-lithium (0·48 g., 10 mmoles) in ether (50 ml.) was added to pentafluoro-*trans*-propenylbenzene (2·00 g., 9·6 mmoles) in ether (25 ml.) at +20°, and the mixture was heated under reflux for 1 hr. Separation of the products as before gave tetrafluoro-*p*-di-(*trans*-propenyl)benzene (1·85 g., 84%), m. p. and mixed m. p. 88—89°.

Oxidation of the *p*-di-(*trans*-propenyl) compound (0·70 g., 3·0 mmoles) with potassium permanganate (3·0 g., 19 mmoles) in acetone (100 ml.) at 0° gave tetrafluoroterephthalic acid (0·50 g., 70%), m. p. (sealed tube) 265—268° (from water), identified by infrared spectroscopy and mixed m. p. (273°) with the pure sample obtained from the di-(*cis*-propenyl) isomer. Decarboxylation as described above gave only 1,2,4,5-tetrafluorobenzene and carbon dioxide.

Tetrafluoro-p-cis-*propenyl*-trans-*propenylbenzene*.—(*a*) *From pentafluoro*-trans-*propenylbenzene*. *cis*-Propenyl-lithium (0·72 g., 15 mmoles) in ether (100 ml.) was added to pentafluoro-*trans*-propenylbenzene (3·00 g., 14·4 mmoles) in ether (25 ml.) at +20°, and the mixture was heated under reflux for 2 hr. Acidification and extraction with ether gave chromatographically pure 1,2,4,5-*tetrafluoro*-3-cis-*propenyl*-6-trans-*propenylbenzene* (2·42 g., 73%) (Found: C, 62·5; H, 4·3. $C_{12}H_{10}F_4$ requires C, 62·6; H, 4·3%), b. p. 104—106°/12 mm., n_D^{20} 1·5153, d_4^{20} 1·223.

(*b*) *From pentafluoro*-cis-*propenylbenzene*. An identical procedure with *trans*-propenyl-lithium (0·72 g.) in ether (100 ml.) and pentafluoro-*cis*-propenylbenzene (3·00 g.) in ether (25 ml.) gave a product (2·50 g., 75%), b. p. 105—106°/12 mm., n_D^{20} 1·5151, shown by gas–liquid chromatography and infrared spectroscopy to be identical with the compound described above.

Oxidation of the *cis-trans*-compound (0·94 g., 4·1 mmoles) with potassium permanganate (3·5 g., 22 mmoles) in acetone (100 ml.) at 0° gave tetrafluoroterephthalic acid (0·70 g., 72%), m. p. (sealed tube) 268—270°, identified by infrared spectroscopy.

Silver Pentafluorobenzoate.—Pentafluorobenzoic acid (20 g.) in water (400 ml.) was added to an excess of silver carbonate, and the mixture was diluted with water (200 ml.) and kept for 2 hr. in darkness. The mixture was filtered, the filtrate was evaporated under suction, and the residue was dried *in vacuo* over phosphorus pentoxide, to give white *silver pentafluorobenzoate* (27·4 g., 91%) (Found: Ag, 33·4. $C_7AgF_5O_2$ requires Ag, 33·8%). The salt was stored in the dark, since it darkened rapidly in daylight.

Pentafluoroiodobenzene.—Silver pentafluorobenzoate (1·00 g., 3·14 mmoles) and iodine (1·5 g., 5·9 mmoles), in a sealed evacuated flask, were heated gently with a Bunsen burner for 5 min. The volatile products were shaken with mercury and fractionated *in vacuo*, to give carbon dioxide (0·117 g., 85%) (Found: *M*, 44·3. Calc. for CO_2: *M*, 44·0), pentafluorobenzene (0·025 g., 5%), and pentafluoroiodobenzene (0·395 g., 55%), identified by infrared spectroscopy.

Pentafluorobenzoyl Nitrite.—Silver pentafluorobenzoate (4·00 g., 12·5 mmoles) and nitrosyl chloride (5·00 g., 76·5 mmoles) were kept at −10° for 30 min. in the absence of air. The excess of nitrosyl chloride was distilled from the reaction vessel at room temperature, and the residue was distilled *in vacuo* to give yellow *pentafluorobenzoyl nitrite* (2·92 g., 97%) (Found: C, 34·9; N, 5·8. $C_7F_5NO_3$ requires C, 34·9; N, 5·8%), b. p. 46°/1 mm., m. p. 19·5°.

The nitrite was hydrolysed immediately by moist air. The nitrite (0·50 g.) and water (5 ml.) reacted instantaneously at room temperature to give pentafluorobenzoic acid (0·40 g., 91%), m. p. and mixed m. p. 100—101°.

Pentafluoronitrosobenzene.—Pentafluorobenzoyl nitrite (1·45 g., 6·0 mmoles) was pyrolysed continuously at 2 mm. pressure for 8·5 hr. in a platinum tube (56 × 1·0 cm.) at 300—305° (contact time, 5·6 sec.). The products were collected at −196° and were fractionated *in vacuo*, to give a green solid (0·33 g.) and a mixture of carbon dioxide and oxides of nitrogen (0·357 g.). The oxides of nitrogen were removed from the latter fraction by the admission of oxygen and shaking with mercury, to leave carbon dioxide (0·176 g., 67%) (Found: *M*, 44·9). The green solid was sublimed three times *in vacuo* at room temperature and gave pentafluoronitrosobenzene (0·21 g., 18%) (Found: C, 36·9; N, 7·2. Calc. for C_6F_5NO: C, 36·6; N, 7·1%), m. p. 44—45° (lit.,[15] m. p. 44·5°).

One of the authors (T. C.) is indebted to the D.S.I.R. for a Research Studentship.

FACULTY OF TECHNOLOGY, UNIVERSITY OF MANCHESTER. [*Received, June 4th*, 1962.]