622. *Aromatic Polyfluoro-compounds. Part XI.* Pentafluorophenyl-lithium and Derived Compounds.*

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Pentafluorophenyl-lithium has been prepared from bromopentafluorobenzene by halogen–metal interchange with n-butyl-lithium and by direct metallation with lithium amalgam; it has been characterised by reactions with water, ethyl formate, *N*-methylformanilide, bromine, chlorine, and mercury. The intermediate formation of tetrafluorobenzyne has been indicated in reactions with bromine, chlorine, and furan. The product of the last reaction, 5,8-epoxy-1,2,3,4-tetrafluoro-5,8-dihydronaphthalene, afforded 5,6,7,8-tetrafluoro-1-naphthol and 1,2,3,4-tetrafluoronaphthalene.

Halogenophenyl-lithium derivatives have been prepared[1-4] from halogenobenzenes by halogen–metal interchange with n-butyl-lithium, and by direct metallation with lithium amalgam.[5] A halogen atom other than fluorine is usually replaced, and subsequent reactions of the halogenophenyl-lithium depend on the orientation, with respect to that replaced, of the other halogen atoms, and on the reaction conditions. Thus, whilst *m*- and *p*-halogenophenyl-lithium compounds are relatively stable, *o*-halogeno-systems show a marked instability in the order: *o*-Br > *o*-Cl > *o*-F. The instability of such compounds has been attributed to ready elimination of lithium halide to form a benzyne system,[3,4] the transience of which has been established in various ways, *e.g.*, by coupling reactions of the Diels–Alder type with furan,[4] cyclopentadiene,[5] anthracene,[5] bicyclo[2,2,1]heptadiene,[6] and bicyclo[2,2,1]heptene.[6]

We have now prepared pentafluorophenyl-lithium by extensions of the above methods. Thus, a mixture of bromopentafluorobenzene (I)[7] and n-butyl-lithium in diethyl ether at $-78°$ reacted immediately with water and with ethyl formate to give pentafluorobenzene and pentafluorobenzaldehyde,[8] respectively, both in reasonable yield. Carbonation did not give pentafluorobenzoic acid, but carbonation of pentafluorophenylmagnesium bromide is known to be very difficult.[7] At temperatures above $-20°$, the halogen–metal interchange could not be controlled, fluoride ion being liberated and intractable organic material isolated. Such observations are parallel to those reported previously on *o*-halogenobenzenes.[3] In the present case there is the additional complication of possible nucleophilic substitution reactions by butyl ions.[8]

Direct metallation of bromopentafluorobenzene (I) was carried out with lithium amalgam in ether at 0° to give a good yield of pentafluorophenyl-lithium. This was characterised fully by reactions with *N*-methylformanilide and with benzaldehyde to give pentafluorobenzaldehyde and α-pentafluorophenylbenzyl alcohol,[8] respectively. At temperatures above 0°, fluoride ion was found in the system after the metallation. The stability of pentafluorophenyl-lithium was estimated by titration of the ethereal solution against aqueous acid at various times after the metallation. At 0°, an initial titre of the solution indicated a yield of pentafluorophenyl-lithium of 77% based on bromopentafluorobenzene. After 24 hours at $-10°$ about 58% of the original organolithium compound was still present. This enhanced stability, compared with that of halogenophenyl-lithium derivatives reported previously, is not unexpected and is presumably a consequence of the stabilisation of the carbanion by the electron withdrawal of five fluorine

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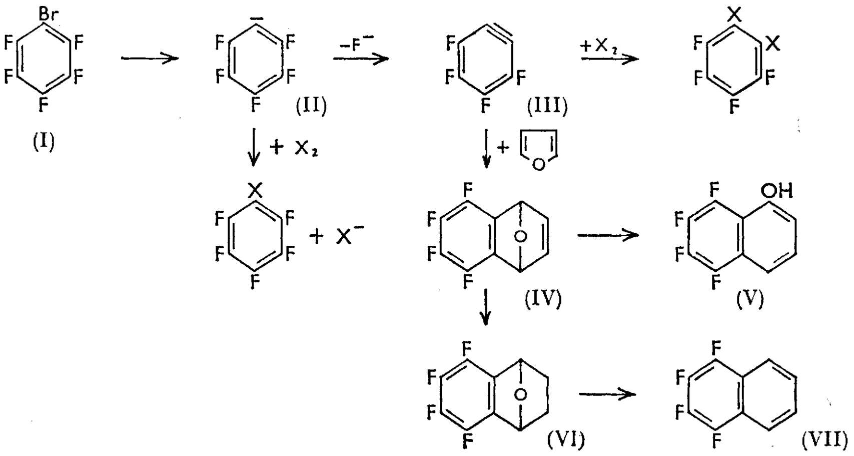
* Part X, Alsop, Burdon, and Tatlow, *J.*, 1962, 1801.

[1] Gilman, Longhorn, and Moore, *J. Amer. Chem. Soc.*, 1940, **62**, 2327.
[2] Gilman and Gorsich, *J. Amer. Chem. Soc.*, 1955, **77**, 3919.
[3] Gilman and Gorsich, *J. Amer. Chem. Soc.*, 1956, **78**, 2217.
[4] Gilman and Gorsich, *J. Amer. Chem. Soc.*, 1957, **79**, 2625.
[5] Wittig and Pöhmer, *Ber.*, 1956, **89**, 1334.
[6] Simmons, *J. Amer. Chem. Soc.*, 1961, **83**, 1657.
[7] Nield, Stephens, and Tatlow, *J.*, 1959, 166.
[8] Barbour, Buxton, Coe, Stephens, and Tatlow, *J.*, 1961, 808.

atoms. This is paralleled to a less noticeable degree by the comparatively high stability of pentafluorophenylmagnesium bromide[9] and 2-bromotetrafluorophenylmagnesium bromide.[9] These are apparently largely unaffected by refluxing diethyl ether, whereas *o*-fluoro-[10] and *o*-bromo-phenylmagnesium[11] halides are relatively unstable.

The relative stability of pentafluorophenyl-lithium was demonstrated also by the fairly slow reaction, at 15°, of the ethereal solution with the mercury from the lithium amalgam to give bispentafluorophenylmercury. This is a very stable compound and was characterised by cleavage with iodine at 150° to give pentafluoroiodobenzene and mercuric iodide. It was obviously desirable in some cases to remove the mercury after the metallation was complete, and this was done in reactions of pentafluorophenyl-lithium with benzaldehyde, *N*-methylformanilide, chlorine, and bromine. The first two gave α-pentafluorophenylbenzyl alcohol and pentafluorobenzaldehyde, respectively, as described before and with no significant improvement in yield.

The reaction of bromine with pentafluorophenyl-lithium gave a small amount of 1,2-dibromotetrafluorobenzene in addition to bromopentafluorobenzene. The reaction with chlorine was complicated, since the product was a mixture of bromo- and chloro-pentafluorobenzene, together with a small amount of 1,2-dibromotetrafluorobenzene. It was shown that the bromopentafluorobenzene used originally was free from the 1,2-dibromide, and also that none was left after the reaction with lithium (water was added to an aliquot portion, and the pentafluorobenzene produced contained none of the bromide). It appears that the chlorine must liberate some bromine, presumably from the lithium salt, and that both halogens can react with the organic species present. These reactions clearly demonstrate again the comparative stability of pentafluorophenyl-lithium in ether at 15°, but also, of course, strongly suggest its decomposition, by loss of fluoride ion, to tetrafluorobenzyne (III) which then adds halogen.



An additional indication of the formation of tetrafluorobenzyne (III) was obtained by using furan as solvent in the reaction of bromopentafluorobenzene with lithium amalgam; as expected from the work of Wittig and Pöhmer,[5] this gave an adduct of the benzyne, *viz.* 5,8-epoxy-1,2,3,4-tetrafluoro-5,8-dihydronaphthalene (IV). Hydrolysis of the latter gave 5,6,7,8-tetrafluoro-1-naphthol (V), and reduction followed by hydrolysis gave 1,2,3,4-tetrafluoronaphthalene (VII). The unexpected vigour of the reaction with

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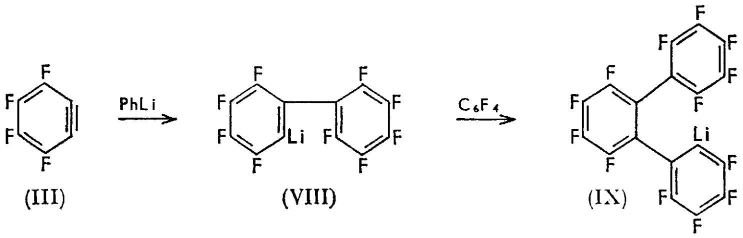
[9] Chaudhry, Nield, Stephens, and Tatlow, unpublished work.
[10] Wittig and Ludwig, *Angew. Chem.*, 1956, **68**, 40.
[11] Heaney, Mann, and Millar, *J.*, 1957, 3930.

furan may be associated with the observation[12] that hexafluorobenzene forms complexes with electron-rich systems, such as benzene and mesitylene. Thus, the furan may, by a process of this kind, facilitate the elimination of a fluoride ion from pentafluorophenyl-lithium to give tetrafluorobenzyne which would immediately condense with the furan. Attempted condensations with cyclopentadiene were unsuccessful owing to the rapid polymerisation of the diene.

As yet no tractable organic compound has been isolated from the decomposition of an ethereal solution of pentafluorophenyl-lithium. Neither octafluorobiphenylene nor dodecafluorotriphenylene has been detected in the amorphous product. The apparent absence of a biphenylene system parallels the observations by Gilman and Gorsich,[3] and that of a triphenylene probably reflects the high steric compression which would be introduced into such a system by complete fluorine substitution. Presumably an intermediate of type (VIII) would propagate by addition to another tetrafluorobenzyne rather than cyclise by elimination of fluorine. The situation is complicated further by the possibility of elimination of fluorine from intermediates such as (VIII) and (IX) to produce perfluoroaryltrifluorobenzyne types. A complex mixture of fluoropolyphenyls is obviously to be expected.



(III) (VIII) (IX)

In the preparation of pentafluorophenyl derivatives, the authors have found pentafluorophenylmagnesium halides easier to handle than pentafluorophenyl-lithium. However, some syntheses may necessitate the higher reactivity of the lithio-compound, and for 1,2,3,4-tetrafluorobenzyne-type additions it appears essential.

EXPERIMENTAL

Pentafluorophenyl-lithium from n-Butyl-lithium.—(*a*) *Pentafluorobenzene.* Bromopentafluorobenzene[7] (5 g.) in dry ether (10 c.c.) was added to a stirred ethereal solution of n-butyl-lithium (1·3N, 15·5 c.c.) maintained at −78°. After 5 min., water (25 c.c.) was added and the mixture allowed to warm to 15°. The ether layer was separated, dried ($MgSO_4$), and distilled through a 6-in. vacuum-jacketed column packed with glass helices. The residue was separated by preparative gas chromatography (column 16 ft. × 3 in. o.d.; packing silicone gum 301–kieselguhr, 1 : 3; temp. 102°, N_2 flow-rate 52 l./hr.) to give ether (2 g.), pentafluorobenzene (1·6 g.), and n-butyl bromide (1·2 g.); all had the correct infrared spectra.

(*b*) *Pentafluorobenzaldehyde.* Ethyl formate (0·6 g.) in dry ether (5 c.c.) was added to a cooled (−78°) solution of pentafluorophenyl-lithium prepared in the above manner from bromopentafluorobenzene (5 g.) and stirred. After 5 min. 5N-hydrochloric acid (100 c.c.) was added and the temperature allowed to rise to 15°. The ether layer was separated, combined with ether extracts (2 × 25 c.c.) of the aqueous phase, and treated with saturated sodium hydrogen sulphite solution. The crystalline pentafluorobenzaldehyde bisulphite compound (1·5 g.) was characterised as pentafluorobenzaldehyde 2,4-dinitrophenylhydrazone, m. p. 228—229° (lit.,[7] 229—230°).

Pentafluorophenyl-lithium from Lithium Amalgam.—(*a*) *Bispentafluorophenylmercury* Bromopentafluorobenzene (5 g.) in dry ether (10 c.c.) was added to a stirred suspension of lithium amalgam (lithium 0·3 g. and mercury 200 g.) in ether (30 c.c.) at 0°. A vigorous reaction occurred and the pasty amalgam became mobile. After 18 hr., water (50 c.c.) was

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[12] Patrick and Prosser, *Nature*, 1960, **187**, 1021.

added and the ether layer was separated and combined with the ether extracts (2 × 50 c.c.) of the aqueous phase, dried ($MgSO_4$), and distilled to leave a brown solid which, after steam distillation and sublimation, gave *bispentafluorophenylmercury* (2·75 g.), m. p. 117—118° * (Found: C, 27·2. $C_{12}F_{10}Hg$ requires C, 27·0%), $\nu_{max.}$ 1520 and 1645 cm.$^{-1}$ (highly fluorinated benzene ring). When heated with iodine (0·5 g.) for 15 hr. at 150—155° (sealed tube) the mercurial (0·15 g.) gave a small yield of pentafluoroiodobenzene (which had the correct infrared spectrum), and mercuric iodide.

(*b*) *Pentafluorobenzaldehyde.* To a stirred solution of pentafluorophenyl-lithium, prepared from bromopentafluorobenzene (5 g.) by the amalgam method, was added *N*-methylformanilide (8 g.) in dry ether (10 c.c.). After 2 hr. 5N-hydrochloric acid (100 c.c.) was added, and the ether layer was combined with the ether extracts (2 × 25 c.c.) of the aqueous phase. The dried ($MgSO_4$) ethereal solution was filtered and evaporated to leave a liquid which on distillation gave pentafluorobenzaldehyde (2·4 g.), b. p. 178—180°, possessing the correct infrared spectrum.[7]

(*c*) *α-Pentafluorophenylbenzyl alcohol.* Benzaldehyde (2·5 c.c.) in dry ether (10 c.c.) was added to a vigorously stirred solution at 0° of pentafluorophenyl-lithium prepared by the amalgam method from bromopentafluorobenzene (5 g.). After 1 hour's stirring, water (50 c.c.) was added and the ether layer was separated and combined with the ether extracts (2 × 25 c.c.) of the aqueous layer. The combined extracts were dried ($MgSO_4$), filtered, and evaporated to leave a liquid which gave α-pentafluorophenylbenzyl alcohol (4·4 g.), b. p. 160—162°/15 mm., m. p. 42—44°, possessing the correct infrared spectrum.[8]

(*d*) *Stability of pentafluorophenyl-lithium.* A solution of the compound was prepared at 0° as in (*a*) and when the amalgam had become completely fluid the mercury was poured off through a side arm fitted with a tap. The ethereal solution was then kept at −10° and portions (2 c.c.) were withdrawn and added to water (10 c.c.); the hydroxide released was titrated against standard acid. The first portion was removed 10 min. after the addition of bromopentafluorobenzene to the amalgam (temp. 0° throughout) and indicated a yield of organolithium of 77% (based on bromopentafluorobenzene). Yields (%) after storage at −10° were (at times after the initial addition): 74, 20 min.; 56, 40 min.; 54, 80 min.; 45, 24 hr.; 23, 72 hr.; 5, 144 hr.

1,2-*Dibromotetrafluorobenzene.*—Bromine (5 g.) in dry ether (10 c.c.) was added to a stirred solution of pentafluorophenyl-lithium prepared by the amalgam method from bromopentafluorobenzene (5 g.). When the vigorous reaction had subsided and most of the bromine had reacted, the ether layer was separated and combined with the ether extracts (2 × 25 c.c.) of the aqueous phase. The combined extracts were dried ($MgSO_4$) and distilled to give ether, bromopentafluorobenzene (3 g.), and 1,2-dibromotetrafluorobenzene (0·5 g.), possessing the correct infrared spectra.[13]

The experiment was also carried out after removal of mercury as in (*d*) before the addition of bromine (6 g.) to a refluxing ethereal solution of pentafluorophenyl-lithium, prepared from bromopentafluorobenzene (5 g.). When the vigorous reaction had subsided the solution was washed with dilute sodium dithionite solution, and the ether layer dried ($MgSO_4$), filtered, and evaporated to leave a liquid which gave bromopentafluorobenzene (2·95 g.), b. p. 134—136°, and 1,2-dibromotetrafluorobenzene (0·62 g.), b. p. 188—193°; both displayed correct infrared spectra.[13]

Pentafluorophenyl-lithium and Chlorine.—A solution of pentafluorophenyl-lithium in ether was prepared from lithium amalgam and bromopentafluorobenzene (10 g.). Hydrolysis of a portion of this solution with dilute sulphuric acid yielded an organic phase which was shown by gas chromatography to contain only ether and pentafluorobenzene.

Dry chlorine was bubbled through the remaining solution for 4 hr. at 15°. The solution was then washed with sodium dithionite solution and water, and, after being dried ($MgSO_4$), was concentrated to 20 c.c. A portion (1 c.c.) was separated by preparative gas chromatography (column 6 ft. × $\frac{1}{2}$ in.; packing dinonyl phthalate–kieselguhr, 1 : 4; temp. 100°;

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* After this work had been completed Professor W. K. R. Musgrave informed us that he had prepared this compound by a different route and that it had m. p. 140°. It appears that polymorphic forms may exist because our product, after being kept, had m. p. 136—137°, and if recrystallised from carbon tetrachloride immediately after preparation it had m. p. 138—139°. The infrared spectra of the two samples were identical.

[13] Nield, Stephens, and Tatlow, *J.*, 1960, 3800.

nitrogen flow rate 2 l./hr.) to yield chloropentafluorobenzene (0·12 g.), b. p. 115°, with an infra-red spectrum identical with that of an authentic specimen,[14] and bromopentafluorobenzene (0·18 g.), identical with an authentic specimen.

In a similar experiment the chloro- and bromo-pentafluorobenzenes were distilled off and yielded, on further distillation, a fraction of b. p. 180—190° (1·2 g.) which was shown by mass spectrometry and infrared spectroscopy to be mainly 1,2-dibromotetrafluorobenzene.

Exchange of bromine for chlorine has been noted also in attempts [15] to prepare chloropentafluorobenzene by the reaction of chlorine with pentafluorophenylmagnesium bromide.

5,8-*Epoxy*-1,2,3,4-*tetrafluoro*-5,8-*dihydronaphthalene*.—Bromopentafluorobenzene (5 g.) was added to a stirred suspension of lithium amalgam (lithium 0·3 g.; mercury 100 g.) in furan (10 c.c.). A vigorous reaction occurred and, after 18 hours' stirring at 15°, water (50 c.c.) and ether (50 c.c.) were added. The ether layer and combined ether extracts (2 × 50 c.c.) of the aqueous phase were dried ($MgSO_4$), filtered, and evaporated to leave an oil which solidified. Recrystallisation from methanol gave 5,8-*epoxy*-1,2,3,4-*tetrafluoro*-5,8-*dihydronaphthalene* (2·1 g.), m. p. 56—57° (Found: C, 55·2; H, 1·8. $C_{10}H_4F_4O$ requires C, 55·5; H, 1·8%). Absorption at 1510 cm.$^{-1}$ in the infrared region was ascribed to a fluorinated aromatic nucleus; $\lambda_{max.}$ (EtOH) 2375 (ε 825), inflexion 2700 mμ (ε 390).

1,2,3,4-*Tetrafluoronaphthalene*.—The epoxy-compound (2·0 g.) in ethanol (50 c.c.) and water (5 c.c.) was shaken in an atmosphere of hydrogen with Raney nickel (W6 grade). After 24 hr. the theoretical amount of hydrogen had been consumed and the nickel was filtered off and washed with ether; the filtrate was evaporated to leave unstable crystalline 5,8-epoxy-1,2,3,4-tetrafluoro-5,6,7,8-tetrahydronaphthalene, m. p. 74°. A portion (0·65 g.) was refluxed with glacial acetic acid (10 c.c.) and hydrogen bromide (48%, 2 c.c.) for 15 hr. When poured into water this produced a crystalline precipitate which sublimed to give 1,2,3,4-*tetrafluoronaphthalene* (0·54 g.), m. p. 110—111° (Found: C, 60·0; H, 2·3. $C_{10}H_4F_4$ requires C, 60·0; H, 2·0%). The presence of a fluorinated aromatic ring was indicated by peaks at 1515, 1610, and 1665 cm.$^{-1}$; $\lambda_{max.}$ (EtOH) 2670 (ε 2300), 2750 (ε 2400), 3020 (ε 2960), and 3170 mμ (ε 2580).

5,6,7,8-*Tetrafluoro*-1-*naphthol*.—5,8-Epoxy-1,2,3,4-tetrafluoro-5,8-dihydro-naphthalene (1 g.), concentrated hydrochloric acid (20 c.c.), and ethanol (20 c.c.) were refluxed for 15 hr.; addition of water then gave a white precipitate which was extracted with ether (2 × 50 c.c.). The ether extract was shaken with 10% aqueous sodium hydroxide, and the aqueous phase was separated, acidified, and extracted with ether (2 × 50 c.c.). The dried ($MgSO_4$) ether extract was filtered and evaporated to leave a solid which sublimed at 70°/8 mm. to give 5,6,7,8-*tetrafluoro*-1-*naphthol* (0·7 g.), m. p. 124—125° (Found: C, 55·3; H, 1·8. $C_{10}H_4F_4O$ requires C, 55·5; H, 1·8%), $\nu_{max.}$ 3300 and 1510 (OH), 1530, 1610, and 1625 cm.$^{-1}$ (fluoro-aromatic nucleus), $\lambda_{max.}$ 2975 (ε 5050), 3150 (ε 4500), and 3285 mμ (ε 4250).

The naphthol (0·2 g.), toluene-*p*-sulphonyl chloride (0·3 g.), and pyridine (5 c.c.) were kept at 100° for 1 hr. and then poured into dilute hydrochloric acid. The crystalline precipitate was recrystallised from methanol to give 5,6,7,8-*tetrafluoro*-1-*naphthyl toluene*-p-*sulphonate* (0·09 g.), m. p. 139—140° (Found: C, 55·0; H, 2·7. $C_{17}H_{10}F_4O_3S$ requires C, 55·2; H, 2·7%).

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[14] Brooke, Forbes, Richardson, and Tatlow, unpublished work.
[15] Aroskar, Stephens, and Tatlow, unpublished work.