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PERFLUOROPHENYL DERIVATIVES OF THE ELEMENTS

VIII*. UNSTABLE ORGANOMETALLIC INTERMEDIATES IN THE SYNTHESIS OF POLYHALOAROMATIC COMPOUNDS

S. C. COHEN, D. E. FENTON, A. J. TOMLINSON AND A. G. MASSEY
Chemistry Department, Queen Mary College, University of London, London, E1 (Great Britain)
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It has been shown previously[2] that decomposing pentafluorophenyl organometallic reagents can sometimes be used to generate tetrafluorobenzyne and this has been exploited, for example, in the synthesis of 2-substituted nonafluorobiphenyls[3]. We now wish to report the findings of our search for a reagent which would generate C_6F_5 since this also would be of obvious use in synthesis.

The first system tried was that containing mercurous pentafluorophenyl (I); if formed (I) would be expected to decompose readily by transfer of a C_6F_5 group from one mercury atom to the other [to give $(C_6F_5)_2Hg$ and mercury] and it might prove possible to trap the pentafluorophenyl group during this shift. However, attempts to make (I) at temperatures between −80° and −100° always led to very rapid darkening of the solution as mercury was precipitated:

$$LiC_6F_5 + Hg_2Cl_2 \xrightarrow[-80^\circ \text{ to } -100^\circ]{\text{ether/hexane}} LiCl + Hg + Hg(C_6F_5)_2$$

Similar experiments employing the reaction of sodium amalgam and pentafluorophenylmercuric bromide (prepared by reacting equimolar amounts of mercuric chloride and pentafluorophenylmagnesium bromide) gave only mercury and bis(pentafluorophenyl)-mercury.

However, the reaction between pentafluorophenyllithium and an excess of titanium tetrachloride in an ether/hexane solvent gave good yields (*ca.* 70%) of decafluorobiphenyl on being allowed to warm up to room temperature from −78°. This is thought to be due to the thermal decomposition in the solution of an unstable pentafluorophenyltitanium species, probably $C_6F_5TiCl_3$:

$$[TiC_6F_5] \rightarrow C_6F_5 \rightarrow C_6F_5C_6F_5$$

but so far we have not isolated any pentafluorobenzene which might be expected to arise from attack of the solvent by pentafluorophenyl radicals.

By the exploitation of this coupling reaction we have prepared many substituted biphenyls in good yield. If a polyhalobenzene derivative is chosen which contains a

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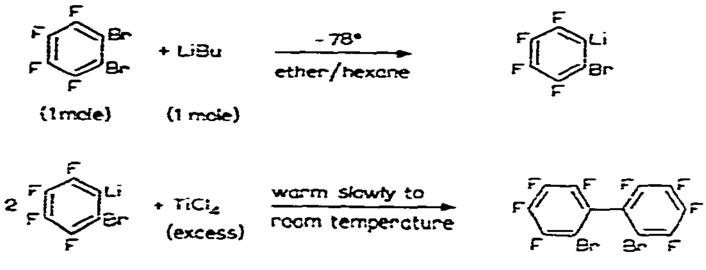
* For Part VII see ref. 1.

group capable of exchange with butyllithium, then the coupling can be carried out very simply by a reaction sequence such as:



Since hydrogen atoms on polyhalobenzene rings can often be lithiated readily by exchange with butyllithium, this method of biphenyl formation is capable of more extensive use than the Ullman reaction; also only a single coupling product is formed from a multi-substituted benzene whereas the Ullman reaction can lead to several products including polymers in such cases.

Both bromine atoms in 2,2'-dibromooctafluorobiphenyl and 4,4'-dibromooctafluorobiphenyl are capable of lithium exchange with butyllithium at low temperatures. For example, after treatment of 2,2'-dibromooctafluorobiphenyl with 2.5 moles of butyllithium, hydrolysis with distilled water gave 2,2'-dihydrooctafluorobiphenyl which proved identical to the product obtained from 3,4,5,6-tetrafluorobenzene using the LiBu/$TiCl_4$ coupling reaction. The addition of one mole of butyllithium to 4,4'-dibromooctafluorobiphenyl at —78° results in the formation of 4-lithio-4'-bromooctafluorobiphenyl as shown by the isolation of a good yield of 4,4'-bis(*p*-bromotetrafluorophenyl)octafluorobiphenyl on treatment of the solution with an excess of titanium tetrachloride.

Benzene (or other aromatic solvents) cannot be used as the solvent for these reactions since we have shown that pentafluorophenyllithium readily decomposes to tetrafluorobenzyne in this medium, the benzyne then giving an adduct $C_6F_4C_6H_6$ with the benzene. This adduct does not undergo Diels–Alder addition with maleic anhydride but forms a complex $Fe(CO)_3C_6F_4C_6H_6$[4] with iron pentacarbonyl in agreement with the structure proposed by Heaney[5] for the identical compound produced by decomposing pentafluorophenylmagnesium bromide in the presence of benzene.

EXPERIMENTAL

Reactions were carried out under an atmosphere of dry oxygen-free nitrogen; analyses were performed by A. Bernhardt, Mülheim, Ruhr, and Beller, Göttingen. Gifts of fluorobenzenes from the Imperial Smelting Corporation are gratefully acknowledged.

Preparation of 2,2'-dibromooctafluorobiphenyl

Butyllithium (16 ml of a 15% hexane solution; 0.025 mole) was added to 1,2-dibromotetrafluorobenzene (7.7 g, 0.025 mole) in ether (100 ml) in a three-necked flask, cooled to —78°. Titanium tetrachloride (~ 3 ml, 5.2 g) was added and the mixture stirred as follows: —78°, 2 h; —43°, 1½ h; —7°, ¾ h; room temperature, 17 h. The yellow-brown suspension at —78° initially lightened and then darkened as the temperature was allowed to rise, giving, at room temperature, a mauve-brown solution. Removal of the ether/hexane solvent under vacuum yielded a mauve-brown resinous residue which, on addition of ethanol, gave a mauve solution, heat being evolved. Evaporation of the ethanol solution followed by vacuum sublimation at 80–95° (*ca.* 10^{-2} mm) gave fine white crystals of 2,2′-dibromooctafluorobiphenyl; physical data as per Table 1.

TABLE 1

BIPHENYL DERIVATIVES PREPARED BY THE $TiCl_4$ COUPLING REACTION

Starting material	*Biphenyl formed*	*M.p.* (°*C*)	*Yield* (%)	*Analysis found (calcd.)* *C*	*H*	*F*	*Hal*
C_6F_5H C_6F_5Br C_6F_5I	$C_{12}H_{10}$	67.5–69	68	43.2 (43.1)	0.2 (0)	57.1 (56.9)	
1,2-$Br_2C_6F_4$	2,2′-$Br_2C_{12}F_8$	97.5–98.5	48	31.8 (31.6)	0.1 (0)	33.1 (33.3)	35.3 (35.1)
1,2-$H_2C_6F_4$	2,2′-$H_2C_{12}F_8$	79–80	35	48.3 (48.4)	0.5 (0.7)	50.8 (51.0)	
1,4-$Br_2C_6F_4$	4,4′-$Br_2C_{12}F_8$	112–114	40	31.8 (31.6)	0.2 (0)	33.3 (33.3)	35.3 (35.1)
2-$BrC_6F_4C_6F_5$	2,2′-$(C_6F_5)_2C_{12}F_8$	167.5–169.5	50	45.9 (45.8)	0.1 (0)	54.4 (54.3)	
4,4′-$Br_2C_{12}F_8$	4,4′-(*p*-$BrC_6F_4)_2C_{12}F_8$	272–274	56	38.6 (38.3)	0.1 (0)	40.0 (40.4)	21.4 (21.2)
C_6Cl_6	$C_6Cl_5C_6Cl_5$	308–310[a]	low				

[a] Literature[6] value 310°.

Experimental details for the other biphenyls and tetraphenyls listed in the Table are similar to the above but with the following differences.

For the reaction of 1,2-dihydrotetrafluorobenzene in ether/hexane, the solid obtained was devoid of aromatic peaks in the infrared spectrum and showed a colour change (mauve to yellow-brown) on air exposure. This suggests that the butyllithium had not reacted with the benzene derivative but had attacked the titanium tetrachloride. Replacement of the ether with tetrahydrofuran gave the expected product in agreement with the work of Tamborski[7].

For reactions of 2-bromononafluorobiphenyl and 4,4′-dibromooctafluorobiphenyl, ethanol addition to the residue obtained after ether evaporation gave the quaterphenyl directly, an indication of its insolubility in that solvent, and a red-brown solution. In the experiment using hexachlorobenzene, the decachlorobiphenyl product was precipitated out of solution during the reaction.

Reaction of 2,2'-dibromooctafluorobiphenyl with butyllithium

Butyllithium (3 ml, ~ 0.004 mole) was added to 2,2'-dibromooctafluorobiphenyl (0.54 g, 0.0012 mole) in ether (50 ml) at −78° and stirred for 2¼ h. Distilled water (50 ml) was added and the mixture allowed to reach room temperature over 3 h. The ether layer was separated, dried over $MgSO_4$ for 16 h and filtered. Removal of ether under vacuum yielded a light yellow-brown solid. Vacuum sublimation at 40–60° gave a white solid (0.18 g, 51 % yield) which gave identical IR and ^1H NMR spectra and VPC retention times as the biphenyl formed by coupling 1,2-dihydrotetrafluorobiphenyl.

4,4'-Dibromooctafluorobiphenyl could be lithiated in the same way using excess of butyllithium; hydrolysis produced 4,4'-dihydrooctafluorobiphenyl in 75 % yield; m.p. 81–83°. (Found: C, 48.2; H, 0.55; F, 50.65. $C_{12}H_2F_8$ calcd.: C, 48.4; H, 0.7; F, 51.0 %.)

Infrared spectra

These were recorded on a Grubb-Parsons double beam grating spectrophotometer by Mr. P. Cook. Peaks are reported in cm^{-1} for mulls in nujol and hexachlorobutadiene.

$C_6F_5C_6F_5$: 1869 v wk, 1786 v wk, 1706 v wk, 1664 w sh, 1650 m, 1629 w, 1587 w, 1560 w, 1522 s, 1508 s, 1488 s, 1429 v wk, 1401 v wk, 1368 w, 1337 v wk, 1284 w, 1267 v wk, 1166 v wk, 1152 v wk, 1144 v wk, 1129 v wk, 1105 w, 1089 w sh, 1075 s, 1063 w, 1036 m, 1008 s, 997 s, 980 s br, 805 v wk, 794 v wk, 778 v wk, 725 s br.

2,2'-$Br_2C_{12}F_8$: 1653 v wk, 1629 m, 1616 m, 1600 w, 1534 m sh, 1504 s sh, 1493 s, 1475 s, 1458 s, 1416 s, 1408 m sh, 1351 m, 1333 m, 1326 m, 1267 m, 1256 w, 1136 w, 1124 m sh, 1111 s, 1083 m sh, 1073 s, 1064 m sh, 1031 s, 1022 s, 1008 m sh, 945 s, 837 s, 828 s, 775 w, 769 w, 736 w br, 715 s, 709 s.

2,2'-$H_2C_{12}F_8$: 1754 v wk, 1730 v wk, 1724 v wk, 1618 m, 1597 w, 1538 s, 1513 s, 1490 s, 1404 s, 1364 m sh, 1321 s, 1314 m sh, 1294 w, 1277 w sh, 1266 m, 1203 s, 1136 v wk, 1094 s sh, 1086 s, 1048 s, 1031 w sh, 1002 s sh, 995 s, 971 w, 939 w, 923 s, 876 m, 862 s, 828 v wk, 813 v wk, 789 v wk, 749 s, 740 m, 713 s, 681 s, 667 w.

4,4'-$Br_2C_{12}F_8$: 1634 w, 1618 w sh, 1592 w, 1493 s, 1471 s, 1447 s sh, 1420 m sh, 1370 m, 1333 v wk, 1295 v wk, 1269 v wk, 1255 v wk, 1236 m, 1232 m sh, 1147 v wk, 1138 v wk, 1045 w, 1020 w, 992 s, 983 m, 958 s, 874 m, 865 m, 823 v wk, 775 v wk, 753 v wk, 719 s, 714 s sh.

2,2'-$(C_6F_5)_2C_{12}F_8$: see ref. 8.

4,4'-$(p\text{-}BrC_6F_4)_2C_{12}F_8$: 1637 w, 1590 v wk, 1508 m sh, 1495 s sh, 1488 s sh, 1471 s, 1441 s sh, 1418 w sh, 1379 m sh, 1372 s, 1364 m sh, 1302 v wk, 1250 v wk, 1230 s, 1136 w, 1111 v wk, 1053 v wk, 1037 w, 1006 w sh, 990 s, 985 m sh, 973 s, 961 s, 935 w, 851 m, 845 m sh, 815 v wk, 744 m, 720 w sh, 711 s.

Attempted preparation of $Hg_2(C_6F_5)_2$

Pentafluorophenyllithium (prepared from 6.8 ml of a 15 % solution of butyllithium in hexane and 3.2 g of bromopentafluorobenzene) in 25 ml of ether at −78° was slowly added (over 3 h) to a suspension of mercurous chloride (3 g) in 80 ml of ether held at −95°. Immediately mercury was precipitated and bis(pentafluorophenyl)mercury (m.p. 140–141°) was the only product isolated on working up the reaction mixture.

Preparation of tetrafluorobenzobicycloocta[2,2,2]triene

Butyllithium (20 ml of 15 % solution in hexane) was added to bromopentafluorobenzene (8 g) in 120 ml of benzene at 0°. After being stirred for 2 h the solvent was removed to leave an off-white solid which on vacuum sublimation gave tetrafluorobenzobicycloocta[2,2,2]triene (m.p. 70–71°) in 55 % yield. (Found: C, 63.6; H, 2.6; F, 33.8; mol. wt. 239. $C_{12}H_6F_4$ calcd.: C, 63.7; H, 2.7; F, 33.6 %; mol. wt., 226.) The infrared and proton NMR spectra were identical to those of an authentic sample[5].

No Diels–Alder product was formed on refluxing the adduct (0.5 g) with maleic anhydride (0.22 g) in 50 ml of xylene for 30 minutes.

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SUMMARY

The formation of substituted halobiphenyls from polyhalobenzene derivatives using butyllithium and excess titanium tetrachloride is described.

REFERENCES

1 A. G. Massey and A. J. Park, *J. Organometal. Chem.*, 5 (1966) 218.
2 P. L. Coe, R. Stephens and J. C. Tatlow, *J. Chem. Soc.*, (1962) 3227.
3 D. E. Fenton and A. G. Massey, *Tetrahedron*, 21 (1965) 3009.
4 A. J. Tomlinson and A. G. Massey, unpublished work.
5 J. P. N. Brewer and H. Heaney, *Tetrahedron Letters*, (1965) 4709.
6 F. L. W. van Roosmalen, *Rec. Trav. Chim.*, 53 (1934) 359.
7 R. J. Harper, E. J. Soloski and C. Tamborski, *J. Org. Chem.*, 29 (1964) 2385.
8 D. E. Fenton, A. J. Park, D. Shaw and A. G. Massey, *J. Organometal. Chem.*, 2 (1964) 437.