Tetrahedron Letters No.16, pp. 949-950, 1964. Pergamon Press Ltd.
Printed in Great Britain.

2 - SUBSTITUTED NONAFLUORODIPHENYLS

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(Received 27 February 1964)

Addition of a molar quantity of bromopentafluorobenzene to pentafluorophenyllithium in ether at room temperature gave 2-bromononafluorodiphenyl (m.p. 69-71°) in 30% yield.

This reaction is of interest on two main counts. First, the pentafluorophenyllithium apparently does not act as a nucleophilic reagent towards bromopentafluorobenzene since it would then have been expected to produce 4-bromononafluorodiphenyl (1); possibly, the reaction proceeds via a perfluorobenzyne intermediate which then could react further with the bromopentafluorobenzene. Second, although several 4, 4'-disubstituted fluorodiphenyls are known 2-bromononafluorodiphenyl (I) is the first polyfluorodiphenyl to be prepared which contains a functional bromine group capable of lithium exchange with butyllithium at -78° and able to give a Grignard reagent in tetrahydrofuran. From these two metallic derivatives it is possible to prepare other 2-substituted nonafluorodiphenyls. A classical Ullman reaction gives the corresponding perfluoroquaterphenyl, 2, 2'-bis (pentafluorophenyl) octafluorodiphenyl. Some typical compounds we have prepared are:

$C_6F_5C_6F_4Br$	Found	C, 36.5	F, 43.3	Br, 20.1	M, 407
	Calc.	C, 36.5	F, 43.3	Br, 20.2	M, 395
$C_6F_5C_6F_4H$	Found	C, 45.5	F, 54.0	H, 0.32	M, 308
m.p. 42-43°	Calc.	C, 45.6	F, 54.1	H, 0.32	M, 316
$(C_6F_5C_6F_4)_2Hg$	Found	C, 34.8	F, 41.1	H, 0.11	M, 811
	Calc.	C, 34.7	F, 41.2	H, 0.00	M, 831

$(C_6F_5C_6F_4)_2$ Found C, 45.8 F, 54.1 M, 624

Calc. C, 45.7 F, 54.25 M, 630

The position of substitution in these nonafluorodiphenyls was deduced mainly from ^{19}F nuclear magnetic resonance chemical shifts and, in the case of $C_6F_5C_6F_4H$, the magnitude of the H-F coupling constants in the 'H nuclear magnetic resonancespectrum using 2-bromo -3, 4, 5, 6 - tetrafluorobenzene as a confirmatory model (2). Further chemical evidence for the configuration of I is the fact that it also arises from the reaction of pentafluorophenyl-lithium and 1,2 - dibromo-tetrafluorobenzene (3).

REFERENCES

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2) A.G. Massey, E.W. Randall and D. Shaw, Chem. and Ind. 1244 (1963)

3) We are indebted to the U.S. Department of the Army for support of this research through its European Research Office.