Perfluorocycloalkenyl-lithium Compounds

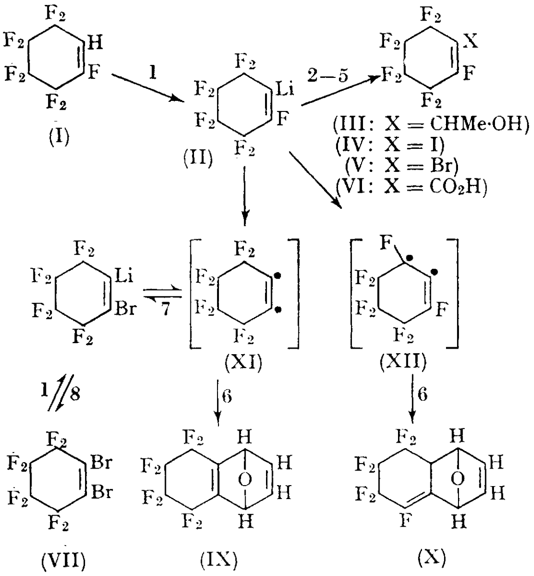
By S. F. CAMPBELL, R. STEPHENS, and J. C. TATLOW

(*Department of Chemistry, University of Birmingham, P.O. Box* 363, *Edgbaston, Birmingham,* 15)

POLYFLUOROCYCLOALKANES with strong bases undergo elimination to form olefins but 1*H*-undecafluorobicyclo[2,2,1]heptane[1] and pentafluorobenzene with methyl-lithium give the corresponding organolithium compound and methane (no easy elimination pathway from the carbanion exists). Another such stable fluorocarbanion system could arise from a 1*H*-fluorocycloalkene. However, fluoro-olefins, including perfluorocycloalkenes, react readily with nucleophiles, among them methyl-lithium,[2] to give substitution products. We have found that 1*H*-nonafluorocyclohexene (I), 1*H*-heptafluorocyclopentene, and 1*H*-pentafluorocyclobutene react with methyl-lithium in diethyl ether at −70° by loss of H and not of F (1 mol. of methane was evolved). Subsequent addition of acetaldehyde at −70° to the systems, followed by acid hydrolysis gave 1-(nonafluorocyclohexen-1-yl)ethanol (III) (63%), m.p. 44—45°, 1-(heptafluorocyclopenten-1-yl) ethanol (42%), b.p. 141°, and 1-(pentafluorocyclobuten-1-yl)ethanol (23%), b.p. 138°, respectively. Another class of relatively stable fluorocarbanions is therefore available by this route.

As with other halogeno-substituted vinyl-lithium compounds,[3,4] the above lithium compounds decomposed between −10° and 15° to give lithium fluoride and, largely, an intractable polymer.

The properties of nonafluorocyclohexenyl-lithium (II) were studied in some detail. Thus, it reacted readily with iodine, bromine, and carbon dioxide to give 1-iodononafluorocyclohexene (IV) (59%) b.p. 118°, 1-bromononafluorocyclohexene (V) (46%) b.p. 95—96°,[5] and nonafluorocyclohexene-1-carboxylic acid (VI) (77%) b.p. 174—177°, respectively. When a solution of the lithium compound (formed by methyl-lithium prepared from methyl bromide) in diethyl ether was allowed to attain room temperature and then refluxed for $\frac{1}{2}$ hr., 1,2-dibromo-octafluorocyclohexene[5] (VII) (13%) and a



Reagents: 1, MeLi; 2, MeCHO to give (III); 3, I_2 to give (IV); 4, Br_2 to give (V); 5, CO_2 to give (VI); 6, furan; 7,LiBr; 8, MeBr.

polymer (82%), suspected to be largely a poly-(octafluorocyclohex-1-ene) (VIII), but probably containing isomeric systems, m.p. 175—183° (sealed tube), were formed. Similarly, when a solution of the lithium compound was allowed to attain room temperature in the presence of furan, a polymer (80%), displaying the same i.r. spectrum, was obtained together with two adducts, one 5,8-epoxy-1,1,2,2,3,3,4,4-octafluoro-1,2,3,4,5,8-hexahydronaphthalene (IX) (14%) m.p. 38—40°, and the other probably the 5,8-epoxy-1,2,2,3,3,4,4,10-octafluoro-2,3,4,5,8,10-hexahydronaphthalenes (X) (4%), m.p. 50—68°. A minor component with the same v.p.c. retention time as 1,2-dibromo-octafluorocyclohexene was detected but could not be isolated on a preparative scale.

The above products of decomposition of nonafluorocyclohexenyl-lithium (II) are thought to arise from the two unstable species octafluorocyclohexyne (XI) and octafluorocyclohexa-1,2-diene (XII)* which would be formed in competing *syn*-periplanar eliminations of lithium fluoride.

All of the compounds isolated in this study had correct elemental analyses and consistent i.r., n.m.r. and mass spectra.

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* G. Wittig and P. Fritze (*Angew. Chem.*, 1966, **5**, 846) have detected cyclohexa-1,2-diene in the dehydrobromination of 1-bromocyclohexene but they obtained no evidence for a simultaneous formation of cyclohexyne.

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