such as di-isopropylphenol, carbon–carbon and carbon–oxygen coupling compete.

An example employing nitrobenzene as solvent and pyridine as the ligand will serve to illustrate the reaction. Thus, a solution of 0.04 g. (0.0004 mole) of copper (I) chloride in 30 ml. of nitrobenzene containing 9 ml. of pyridine was shaken with oxygen (one atmosphere) in a closed reaction vessel attached to an oxygen buret. After the copper (I) had been oxidized to the divalent state, 0.977 g. (0.008 mole) of 2,6-dimethylphenol was added, and shaking was continued. After 26 minutes the stoichiometric (equation 1) amount of oxygen was absorbed, and the reaction was allowed to continue for 18 minutes longer to give a total oxygen absorption of 101.5%. The product was isolated by precipitation in 1% (vol.) concentrated aqueous hydrochloric acid in methanol, resuspended in 5% (vol.) concentrated aqueous hydrochloric acid in methanol, and finally reprecipitated in methanol from chloroform solution. After drying in vacuum, there was obtained 0.81 g. (84%) of almost colorless polymer of intrinsic viscosity 0.95 decil./g. (chloroform, 25°) and osmotic molecular weight 28,000. *Anal.* Calcd. for $C_8H_8O$: C, 79.9; H, 6.7; found: C, 79.7; H, 6.8. The infrared spectrum of this polymer showed no evidence of hydroxyl.

The identical high molecular weight linear polymer is obtained by oxidation of 2,6-dimethyl-4-halophenol, where the halogen is either chlorine or bromine. However, the halide ion released deactivates the catalyst; thus it is necessary to use equimolar amounts of catalyst.

Further details of the reaction, its scope and a discussion of its mechanism will be published in the near future.

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## PERFLUOROVINYL METALLIC COMPOUNDS[1]

*Sir:*

Recently described[2] new perfluoroalkyl tin compounds, $R_3SnC_nF_{2n+1}$ (R = phenyl, alkyl), on treatment with electrophilic reagents ($H^+$ or $BCl_3$, etc.) release alkyl or phenyl groups in preference to perfluoroalkyl groups.[3] In terms of relative electronegativity of radicals based on preferential fission of groups from organometallic compounds[4] this result is surprising. However, although perfluoroalkyl groups are very electronegative, *e.g.*, trifluoroiodomethane on hydrolysis yields trifluoromethane not trifluoromethanol, it is conceivable that when such a group is bonded to a tin atom also carrying alkyl or phenyl groups it is the tin-bonded carbon atom of the perfluoroalkyl group which is the relatively electron deficient center and not the tin-bonded carbon atoms of alkyl or aryl groups. This could arise through the strong inductive effect of fluorine atoms acting on a carbon atom linked to tin. In these compounds it is reasonable to assume that the carbon atoms are $sp^3$-hybridized. For this reason, and also because of their intrinsic interest, it was pertinent to prepare the hitherto unknown perfluorovinyl metallics where $sp^2$-hybridized carbon atoms would be bonded simultaneously to fluorine and to metals. In such compounds the $\alpha$-carbon atom of a perfluorovinyl group might well be relatively electron rich because of its filled $p\pi$-orbital. A possible route to such compounds is by vinylation of metal halides with perfluorovinyl Grignard, a reagent known to us as $CF_2{=}CFMgI$,[5] but inaccessible because of rarity of the iodide from which it is derived. However, we have found that the commercially available halide $CF_2{=}CFBr$ readily forms a Grignard in tetrahydrofuran.[6]

With halides of metals and metalloids this perfluorovinyl Grignard affords a variety of new perfluorovinyl compounds. Dimethyltin dichloride yields bis-(perfluorovinyl)-dimethyltin, $Me_2Sn(CF{=}CF_2)_2$ (b.p. 58°(38 mm.)), 65% yield (calcd. for $C_6H_6F_6Sn$: C, 23.2; H, 2.0. Found: C, 22.9: H, 1.9). With trifluoroacetic acid the perfluorovinyltin compound gives trifluoroethylene quantitatively (identified by infrared spectrum). Methyl groups are not cleaved.

Similarly alkylperfluorovinyltin compounds with boron halides afford perfluorovinylhaloboranes, *e.g.*, $CF_2{=}CFBCl_2$ (analyzed as its $Me_3N$ adduct; calcd: C, 27.0; H, 4.0; N, 6.3. Found: C, 27.2; H, 4.3; N, 6.1; and by hydrolysis to yield $CF_2{=}CFH$ quantitatively), b.p. 38.5° (extrap.). This reaction is similar to that of $Bu_2Sn(CH{=}CH_2)_2$ with boron halides.[7]

Many properties of the perfluorovinyl compounds contrast strikingly those of their vinyl or perfluoroalkyl analogs: $Me_2Sn(CF{=}CF_2)_2$ is air sensitive, $Me_2Sn(CH{=}CH_2)_2$ is not; $CF_2{=}CFBCl_2$ slowly forms $BF_3$, $CH_2{=}CHBCl_2$ is stable: and $(CF_2{=}CF)_3As$ (b.p. 57.5° (83 mm.)) is stable to base, but $(CF_3)_3As$ is hydrolyzed readily.

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(1) This research was supported by the United States Air Force under Contract No. AF 49(638)-518, monitored by the Air Force Office of Scientific Research of the Air Research and Development Command.

(2) H. D. Kaesz, J. R. Phillips and F. G. A. Stone, *Chem. Ind.*, 1409 (1959).

(3) With base, in nucleophilic attack, perfluoroalkyl groups are cleaved preferentially.

(4) See H. O. Pritchard and H. A. Skinner, *Chem. Reviews*, **55**, 745 (1955), and references cited therein.

(5) J. D. Park, R. J. Seffl and J. R. Lacher, THIS JOURNAL, **78**, 59 (1956).

(6) During our work this Grignard was also formed by I. L. Knunyants, R. N. Sterlin, R. D. Yatsenko and L. N. Pinkina, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1345 (1958); *C.A.*, **53**, 6987g (1959), but only its hydrolysis with acid was studied.

(7) F. E. Brinckman and F. G. A. Stone, *Chem. Ind.*, 254 (1959); Abstracts of papers presented at 135th Meeting A.C.S. Boston, April, 1959, p. 26-M.

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## THE *n*-BUTYLTHIOMETHYLENE GROUPING: A SUPERIOR BLOCKING GROUP FOR THE ALKYLATION OF KETONES

*Sir:*

Recently, we had need of protecting the methylene adjacent to a ketone with a grouping that would not deactivate the carbonyl and could be removed easily after alkylation. The most promising such