calculated from the Hückel theory. Also, it should be possible to establish molecular electronegativities. These considerations are presently being investigated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS]

The Preparation of Organolithium Compounds by the Transmetalation Reaction. V. Perfluorovinyllithium[1-3]

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Perfluorovinyllithium has been prepared by the transmetalation reaction occurring between phenyltrisperfluorovinyltin and phenyllithium (1:3 molar ratio) in diethyl ether at *ca.* −40° and between *n*-butyltrisperfluorovinyltin and *n*-butyllithium (1:2 molar ratio) in pentane at *ca.* −40°. In both solvents the stability of perfluorovinyllithium decreases with increasing temperature; the reagent is completely decomposed at 0°. The decomposition of perfluorovinyllithium in ether in the presence of an excess of phenyllithium produced diphenylacetylene in *ca.* 40% yield, a result suggestive of the intermediacy of difluoroacetylene in perfluorovinyllithium decomposition. Reactions of perfluorovinyllithium in ether with organotin halides, trimethylbromosilane and carbon dioxide gave the expected perfluorovinyl derivatives.

The availability of the perfluorovinyl Grignard reagents[4,5] has made possible the synthesis of a large number of perfluorovinylmetal compounds.[6] Of particular interest to us have been perfluorovinyl derivatives of tin,[7] since these possibly could serve as precursors for the hitherto unknown reagent, perfluorovinyllithium.

Efforts to prepare perfluorovinyllithium in solution by the action of perfluorovinyl halides on metallic lithium were unsuccessful. Thus it was reported[8] that a noticeable reaction accompanied by tar formation resulted when iodotrifluoroethylene was added to metallic lithium, but no evidence could be obtained for the presence of perfluorovinyllithium. The use of the transmetalation reaction occurring between vinyltin compounds and organolithium reagents in the synthesis of vinyllithium[9] suggested that this procedure might also be applicable to the preparation of perfluorovinyllithium. Initial experiments showed that such exchange did indeed take place. Treatment of triphenylperfluorovinyltin[7] in diethyl ether with one equivalent of phenyllithium resulted in an immediate precipitate of tetraphenyltin (92% yield) and a dark brown solution. However, no evidence could be obtained for the existence of $CF_2{=}CFLi$ in this solution. The rather limited stability of perfluorovinyl Grignard reagents in ether and in tetrahydrofuran[5] provided an indication that the perfluorovinyllithium reagent might not be very stable. Furthermore, the relatively low stability of perfluoroalkyllithium reagents[10] suggested also that perfluorovinyllithium might be stable only at low temperatures.

Investigation of this factor—the effect of lower temperatures—led to the development of conditions under which the perfluorovinyllithium reagent is quite stable and useful in organic and organometallic syntheses.[3] The reaction of phenyllithium with phenyltrisperfluorovinyltin (3:1 molar ratio) in ether between −40 to −30° proceeded rapidly, giving a precipitate of tetraphenyltin and a brownish solution of perfluorovinyllithium

$$C_6H_5Sn(CF{=}CF_2)_3 + 3C_6H_5Li \xrightarrow{Et_2O} (C_6H_5)_4Sn + 3CF_2{=}CFLi$$

Such solutions were characterized by reaction with trimethyltin bromide, triethyltin chloride and trimethylbromosilane, as well as by carbonation. Trimethylperfluorovinyltin (64% maximum yield), triethylperfluorovinyltin (40%), trimethylperfluorovinylsilane (45%) and perfluoroacrylic acid (37%) were obtained in these reactions. In a separate experiment the perfluorovinyllithium-containing reaction mixture was filtered at −40° to remove tetraphenyltin, which was isolated, after recrystallization, in 92% yield. Optimum conditions for preparing perfluorovinyllithium by this procedure require very slow addition of phenyllithium to the phenyltrisperfluorovinyltin solution and the use of rather dilute solutions. The temperature range over

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(1) Part IV: D. Seyferth and M. A. Weiner, *J. Am. Chem. Soc.*, **84**, 361 (1962).

(2) Also Part XV in the series "Vinyl Derivatives of Metals"; Part XIV; D. Seyferth and H. M. Cohen, *Inorg. Chem.*, in press.

(3) Preliminary communication: D. Seyferth, T. Wada and G. Raab, *Tetrahedron Letters*, No. **22**, 20 (1960).

(4) J. D. Park, R. J. Seffl and J. R. Lacher, *J. Am. Chem. Soc.*, **78**, 59 (1956).

(5) 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).

(6) For a review see: D. Seyferth, in "Progress in Inorganic Chemistry," Vol. 3, F. A. Cotton, ed., Interscience Publishers, Inc., New York, N. Y., 1962.

(7) D. Seyferth, G. Raab and K. A. Brändle, *Angew. Chem.*, **72**, 77 (1960); *J. Org. Chem.*, **26**, 2934 (1961).

(8) J. D. Park and J. R. Lacher, WADC Technical Report 56-590, Part I, November 1957; ASTIA Document No. AD 142171.

(9) D. Seyferth and M. A. Weiner, *Chem. Ind.* (London), 402 (1959); *J. Am. Chem. Soc.*, **83**, 3583 (1961).

(10) O. R. Pierce, E. T. McBee and G. F. Judd, *ibid.*, **76**, 474 (1954).

which perfluorovinyllithium is stable in ether solution was investigated briefly. The reagent was prepared at −40° as above, then allowed to warm slowly to −15° and kept at that temperature for 30 minutes. In another experiment the solution was kept at 0° for 30 minutes. Both solutions were characterized by treatment with trimethyltin bromide. In the former case trimethylperfluorovinyltin was obtained in *ca.* 30% yield, but in the 0° run, none of this product was formed. The preparation of perfluorovinyllithium in ether at −78° is much less favorable. Conversion of phenyltrisperfluorovinyltin to tetraphenyltin was not complete, triphenylperfluorovinyltin also being isolated in 26% yield, and the yield of trimethylperfluorovinyltin isolated after treatment of the organolithium solution with trimethyltin bromide was only 28%.

A similar exchange reaction could be effected in pentane at *ca.* −30 to −40° between *n*-butyllithium and *n*-butyltrisperfluorovinyltin. However, in this solvent exchange was not complete, stopping at approximately the tri-*n*-butylperfluorovinyltin stage, and it was found most advantageous from the preparative point of view to use the *n*-butyllithium and the tin compound in 2:1 molar ratio in order to avoid the presence of unconverted *n*-butyllithium. Similar observations were made in the *n*-butyllithium/tetravinyltin in pentane system.[9]

$$n\text{-}C_4H_9Sn(CF{=}CF_2)_3 + 2n\text{-}C_4H_9Li \xrightarrow{C_5H_{12}} (n\text{-}C_4H_9)_3SnCF{=}CF_2 + 2CF_2{=}CFLi$$

Trimethyltin bromide or triethyltin chloride was used in the characterization of the perfluorovinyllithium reagent formed; perfluorovinyllithium yields of 45–50% were indicated. Since exchange was not complete, and since in fact a deficiency of *n*-butyllithium was used, the possibility existed that the trialkyltin halide could undergo direct exchange with any perfluorovinyltin compounds still present in the reaction mixture. To exclude this possibility the reaction mixture was shaken with aqueous-alcoholic potassium fluoride solution prior to removal of solvent and distillation of the products. This treatment removed unreacted trimethyltin bromide or triethyltin chloride as the insoluble fluorides. Other experiments showed that the exchange reaction between triethyltin chloride and di-*n*-butylbisperfluorovinyltin occurred only when this mixture was heated. Thus distillation at reduced pressure of a mixture of triethyltin chloride and di-*n*-butylbisperfluorovinyltin produced triethylperfluorovinyltin in *ca.* 9% yield. Perfluorovinyllithium appeared also to become less stable in pentane as the temperature was increased. At −15° a perfluorovinyllithium derivative yield was only 37%; after the perfluorovinyllithium reagent mixture in pentane had been kept at 0° for one hour or had been refluxed briefly, no active reagent remained.

The decomposition of perfluorovinyllithium in solution will be the subject of further studies. The $CF_2{=}CFLi$ structure suggests possible initial decomposition by loss of lithium fluoride by α- or by β-elimination. However, no conclusive evidence for difluoroacetylene as an intermediate in the decomposition is as yet in hand. The following preliminary observations, however, are suggestive. Small-scale attempts to prepare concentrated (~30%) solutions of perfluorovinyllithium in ether or in pentane for F^{19} n.m.r. studies invariably resulted in rapid decomposition and at times violent explosions, an observation in line with the known poor stability of haloacetylenes. The decomposition of dilute ethereal solutions of perfluorovinyllithium in the presence of an excess of phenyllithium (phenyllithium to phenyltrisperfluorovinyltin ratio was 9:1) produced diphenylacetylene in 38% yield. The formation of this product by the direct reaction of difluoroacetylene with phenyllithium seems a reasonable possibility in view of the recent demonstration that monofluoroacetylene reacts with organolithium reagents to give monosubstituted acetylenes.[11]

$$CF_2{=}CFLi \longrightarrow FC{\equiv}CF + LiF$$

$$FC{\equiv}CF + 2C_6H_5Li \longrightarrow C_6H_5C{\equiv}CC_6H_5 + 2LiF$$

The alternate C_2F_2 species, $CF_2{=}C$, is unknown, but the possibility of its formation from perfluorovinyllithium by α-elimination and its subsequent reaction with phenyllithium to give diphenylacetylene also must be considered.

Experimental[12]

Preparation of Perfluorovinyllithium in Diethyl Ether. (1) At −40°.—To 5.0 g. (11.4 mmole) of phenyltrisperfluorovinyltin[7] in 75 ml. of diethyl ether at −40° was added slowly with stirring 28.6 ml. of 1.19 *M* ethereal phenyllithium solution (43.2 mmoles). A white solid precipitated, and a dark brown solution resulted within a few minutes.[13] The mixture was stirred at −40° for 30 min., and 8.35 g. (43.2 mmoles) of trimethyltin bromide in 50 ml. of ether was added dropwise. After 10 min. the mixture was allowed to warm slowly to room temperature. Filtration gave 4.3 g. (88%) of crude tetraphenyltin (m.p. 228° after recrystallization from benzene). The filtrate was shaken with 2 ml. of 10% aqueous-alcoholic potassium fluoride solution (henceforth KF solution), and the precipitated trimethyltin fluoride (1.72 g., 27.5%), dec. 373° (lit.[14] dec. ~ 375°), was filtered. Distillation of the dried filtrate gave 5.3 g. (64%) of trimethylperfluorovinyltin, b.p. 112–115°, $n^{25}D$ 1.4150. The infrared spectrum (in carbon tetrachloride) showed the C=C stretching frequency at 1710 cm.$^{-1}$ (see ref. 7) and strong C–F absorption at 1282, 1265, 1105 and 1005 cm.$^{-1}$.

Anal. Calcd. for $C_5H_9F_3Sn$: C, 24.53; H, 3.71; F, 23.27. Found: C, 24.59, 24.62; H, 3.62, 3.66; F, 23.06.

In another experiment more concentrated solutions were used: 10 g. of phenyltrisperfluorovinyltin in 30 ml. of ether at −40° and 71 ml. of 0.96*M* phenyllithium solution. Triethyltin chloride was used to characterize the perfluorovinyllithium formed, and triethylperfluorovinyltin,[7] b.p. 56–59° at 9 mm., was isolated in 40% yield. Triethyltin fluoride was obtained in 54% crude yield from the KF treatment.

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(11) H. G. Viehe and E. Franchimont, *Chem. Ber.*, **95**, 319 (1962).

(12) All experiments involving organolithium reagents were carried out in an atmosphere of prepurified nitrogen or argon. Melting points are uncorrected. Analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. and Dr. Ing. A. Schoeller, Kronach.

(13) The rate of addition appeared to affect the appearance of the solutions but not the perfluorovinyllithium yields. Very slow addition of phenyllithium resulted in a light brown reaction mixture, which darkened on standing.

(14) E. Krause, *Ber.*, **51**, 1447 (1918).

(2) **At −78°.**—Phenyltrisperfluorovinyltin (11.4 mmoles) in 75 ml. of ether was stirred with 34.2 mmoles of ethereal phenyllithium (added very slowly) at −78° for 1 hr. Trimethyltin bromide (34.2 mmoles) was added, and the reaction mixture was worked up using the procedure described above. Tetraphenyltin was isolated in only 64% yield, while 2.3 g. (27.5%) of trimethylperfluorovinyltin, $n^{25}D$ 1.4150, was obtained. Unreacted trimethyltin bromide (62.5%) was isolated as the insoluble fluoride. At higher pot temperature during the distillation of trimethylperfluorovinyltin, 1.3 g. of white solid, m.p. 66–67°, sublimed into the condenser. This was identified as triphenylperfluorovinyltin by mixed m.p. with an authentic sample[7] and by its infrared spectrum. In another experiment the exchange reaction time was increased to 3 hr. No increase in the yield of perfluorovinyllithium resulted.

(3) **Stability of Perfluorovinyllithium in Diethyl Ether.** (a) **At −15°.**—A solution of perfluorovinyllithium was prepared as described above at −40° from 11.4 mmoles phenyltrisperfluorovinyltin was warmed slowly to −20 to −15° and maintained in this range for 30 min. Trimethyltin bromide (34.2 mmoles) was added to the dark brown mixture. Tetraphenyltin (93%), trimethyltin fluoride (equivalent to 63% unreacted trimethyltin bromide) and trimethylperfluorovinyltin (30% by gas chromatographic analysis of liquid remaining after most of the ether had been removed, 24% isolated yield, b.p. 110–112°, $n^{25}D$ 1.4148), were obtained by the usual work-up procedure.

(b) **At 0°.**—The experiment outlined above was repeated on the same scale, but the mixture was kept at 0° for 30 min. before trimethyltin bromide was added. Tetraphenyltin was isolated in 95% yield, and trimethyltin fluoride equivalent to 91% unreacted trimethyltin bromide. No trimethylperfluorovinyltin was obtained. If ether solutions of perfluorovinyllithium were warmed rapidly from −40°, a vigorous exothermic reaction resulting in a thick, dark reaction mixture commenced at *ca.* −20°.

(4) **Preparation of Trimethylperfluorovinylsilane via Perfluorovinyllithium in Ether.**—Five grams (11.4 mmoles) of phenyltrisperfluorovinyltin in 100 ml. of ether at −40° was treated with three molar equivalents of phenyllithium solution. The mixture was stirred at −40 to −30° for 1 hr., and then 5.24 g. (43.2 mmoles) of freshly distilled trimethylbromosilane in 75 ml. of ether was added during 1 hr. The reaction mixture was stirred at −30° for 2.5 hr., warmed slowly to room temperature and filtered under argon to give 4.4 g. (91%) of tetraphenyltin, m.p. 224–226°. The ether was very slowly distilled from the filtrate, and the residue (6.10 g.) was analyzed by gas chromatography (Dow Corning 710 Silicone Fluid on firebrick, jacket at 40°, preheated at 160°, helium carrier gas at 12.1 psi.) and was shown to contain *ca.* 39% trimethylperfluorovinylsilane, 40% trimethylbromosilane and 21% diethyl ether. Thus trimethylperfluorovinylsilane was obtained in *ca.* 45% yield. A sample of the perfluorovinylsilane was isolated by gas chromatography and had the same retention time, infrared spectrum and refractive index ($n^{25}D$ 1.3565) as an authentic sample of this compound (see below). Fractional distillation of the reaction product gave 2.0 g. (38%) of trimethylperfluorovinylsilane ($n^{25}D$ 1.3580), slightly contaminated with ether (by infrared spectrum).

(5) **Preparation of Perfluoroacrylic Acid via Perfluorovinyllithium in Diethyl Ether.**—A solution of 10.0 g. (22.8 mmoles) of phenyltrisperfluorovinyllithium in 90 ml. of ether was cooled to −40° under argon and treated with 70.5 ml. of 0.90 *M* (68.4 mmoles) of phenyllithium in ether (addition dropwise during 1 hr.). The resulting solution was stirred at −40° for 1 hr. and quickly poured onto *ca.* 300 g. of powdered Dry Ice. After 14 hr. the reaction mixture was filtered into a 1-liter separatory funnel. The residue, after recrystallization from benzene, yielded 8.8 g. (90.5%) of tetraphenyltin, m.p. 227–228°. The filtrate was hydrolyzed with 85 ml. of 2*N* sulfuric acid. The ether layer was separated and the aqueous phase extracted with fifteen 20 ml. portions of ether. The ether solutions were combined, dried and the ether removed slowly by distillation to a pot volume of *ca.* 50 ml. The residue was cooled under nitrogen to −78°, and the remainder of the ether was pumped off under high vacuum. The brown, low melting residue was sublimed at room temperature (0.1 mm., 0° cold finger) to give 3.2 g. (37%) of white solid, m.p. 35–36° (lit.[5] m.p. 36°), which showed principal absorption bands in the infrared region (carbon tetrachloride solution) at 3050, 1760, 1740, 1710, 1460, 1345, 1300, 1220 and 1100 cm.$^{-1}$; λ_{max} 210 mμ (ϵ 6460).

Anal. Calcd. for $C_3HO_2F_3$: C, 28.59; H, 0.79; F, 45.22; neutral equiv., 126.1. Found: C, 28.25; H, 1.00; F, 44.89; neutral equiv., 125.8, 126.4.

Preparation of Perfluorovinyllithium in Pentane. (1) **3 *n*-Butyllithium to 1 *n*-Butyltrisperfluorovinyltin.**—A solution of 5.0 g. (11.9 mmoles) of *n*-butyltrisperfluorovinyltin[7] in 70 ml. of pentane was cooled to −45° and 42.5 ml. of 0.84 *M* *n*-butyllithium in pentane (35.7 mmoles) was added very slowly during one hr. The mixture (a clear, pale yellow solution) was stirred at −45° for 1 hr. and then treated with 8.7 g. (35.7 mmoles) of trimethyltin bromide in 30 ml. of pentane. The reaction mixture was stirred at −40° for an additional 4.5 hr., warmed to room temperature and filtered. The filtrate was shaken with 10 ml. of KF solution. Filtration produced 1.97 g. (30%) of trimethyltin fluoride. The filtrate was dried and subsequently fractionally distilled to give 2.71 g. (31%) of trimethylperfluorovinyltin, b.p. 111–114°, $n^{25}D$ 1.4151, 2.32 g. (29%) of *n*-butyltrimethyltin, b.p. 150–155°, $n^{25}D$ 1.4553, (lit.[15] b.p. 149–150°, $n^{20}D$ 1.4560), and 3.84 g. (88%) of tri-*n*-butylperfluorovinyltin, b.p. 83–87° at 0.5 mm., $n^{25}D$ 1.4518.

(2) **2 *n*-Butyllithium to 1 *n*-Butyltrisperfluorovinyltin.**—A solution of 5.3 g. (12.7 mmoles) of *n*-butyltrisperfluorovinyltin in 80 ml. of pentane was cooled to −50° under argon, and 22.7 ml. of 1.12*M* *n*-butyllithium (25.4 mmoles) in pentane was added dropwise during 35 min. The resulting pale yellow solution was stirred at −50° for 1 hr., and then 6.2 g. (25.4 mmoles) of trimethyltin bromide in 100 ml. of pentane was added. The reaction mixture was stirred at −50° for 1 hr., warmed slowly to room temperature and filtered under argon. Treatment with KF solution and distillation gave 3.2 g. (51% based on *n*-butyllithium) of trimethylperfluorovinyltin and 4.0 g. (85%) of tri-*n*-butylperfluorovinyltin. Trimethyltin fluoride was obtained in 40% yield.

Experiments using this procedure were carried out at −40° and at −30° as well. The yields of trimethylperfluorovinyltin were 47.5 and 49%, respectively. In another experiment carried out at −30°, in which triethyltin chloride was used to characterize the lithium reagent present, triethylperfluorovinyltin was isolated in 46% yield.

(3) **Stability of Perfluorovinyllithium in Pentane.** (a) **At −15°.**—A solution of perfluorovinyllithium was prepared at −40° in pentane from 12.3 mmoles of *n*-butyltrisperfluorovinyltin and 24.7 mmoles of *n*-butyllithium in the usual manner. The mixture was stirred at −40° for 1 hr. and then warmed slowly to −15°. The originally pale yellow solution became darker in color. After it had been stirred at −15° for 30 min., 37 mmoles of trimethyltin bromide was added as a solution in 50 ml. of pentane. The reaction mixture was stirred at −15° for 1 hr., warmed to room temperature and trimethylperfluorovinyltin (31.5%) was isolated as described in the experiments above. Tri-*n*-butylperfluorovinyltin had been formed in 91% yield.

(b) **At 0°.**—A solution of perfluorovinyllithium was prepared at −40° in pentane from 12.3 mmoles of *n*-butyltrisperfluorovinyltin and 37 mmoles of *n*-butyllithium. After 40 min. at −40° the mixture was warmed slowly to 0° and kept at that temperature for 1 hr. During the warming of the mixture, the pale yellow solution became darker and between −15 and 0° turned dark brown to black. (If such solutions were warmed rapidly, sudden strong exotherm at temperatures above −15° caused the solvent to reflux for 2–3 min. and resulted in a brown-black mixture.) Addition of trimethyltin bromide to the mixture at 0°, followed by the usual procedure, gave only trimethyltin fluoride and no trimethylperfluorovinyltin. Tri-*n*-butylperfluorovinyltin (91%) and *n*-butyltrimethyltin (3.0 g.) also were isolated. Similar results were obtained when such a perfluorovinyllithium solution was heated to reflux. When solutions of *n*-butyltrisperfluorovinyltin (27.7 mmoles) and *n*-butyllithium (57 mmoles) in pentane were mixed at room temperature, an exothermic reaction accompanied by immediate turbidity and formation of a brown color was observed.

Reaction of *n*-Butyllithium with Tri-*n*-butylperfluorovinyltin in Pentane.—To a solution of 14.8 g. (40 mmoles) of tri-*n*-butylperfluorovinyltin[7] in 100 ml. of pentane at −30°

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[15] Z. M. Manulkin, *Zhur. Obshchei Khim.*, **13**, 42 (1943).

was added dropwise 43.5 mmoles of *n*-butyllithium in pentane. After the mixture had been stirred at −30° for 30 min., 9.6 g. (40 mmoles) of triethyltin chloride was added. The reaction mixture was filtered; the solvent was distilled from the organic phase, and the residue was diluted to 100 ml. with diethyl ether. This solution was treated with dry ammonia gas for 3 hr. in order to precipitate triethyltin chloride as its ammonia adduct. This solution was filtered and distilled to give 0.5 g. of crude triethylperfluorovinyltin (4.4%), b.p. 56–59° at 9 mm., $n^{25}\text{D}$ 1.4406 (lit.[7] $n^{25}\text{D}$ 1.4396), confirmed by infrared, 8.3 g. of crude *n*-butyltriethyltin, b.p. 71–77° at 4 mm., and 11.1 g. (75% recovery) of tri-*n*-butylperfluorovinyltin, b.p. 78–80° at 0.3 mm.

Reaction of Triethyltin Chloride with Di-*n*-butylbisperfluorovinyltin.—A mixture of 13 g. (33 mmoles) of di-*n*-butylbisperfluorovinyltin[7] and 5 g. (20 mmoles) of triethyltin chloride was distilled slowly between 80–100° at 12 mm. The distillate was treated with KF solution to remove triethyltin chloride, any di-*n*-butylperfluorovinyltin chloride which might have formed, and di-*n*-butylbisperfluorovinyltin (for the reaction of the latter two with KF solution, see ref. 7). Only 0.5 g. of crude triethylperfluorovinyltin could be isolated by distillation from the filtrate.

Decomposition of Perfluorovinyllithium in the Presence of Excess of Phenyllithium.—The reagent solution was prepared by adding 101 ml. of 1.02 *M* ethereal phenyllithium (103 mmoles) over 90 min. to 5 g. (11.4 mmoles) of phenyltrisperfluorovinyltin in 85 ml. of ether at −40°. The mixture was stirred at −40° for 30 min., warmed slowly to 0°, kept at this temperature for 30 min., and finally warmed to room temperature. After 3 hr. at room temperature, the mixture was filtered to give 4.6 g. (95%) of tetraphenyltin, m.p. 224–227°. The filtrate was shaken with 50 ml. of water, and the ether layer was dried. Removal of ether at reduced pressure left a deep red oil which crystallized on standing. The latter (2.75 g.) was dissolved in 8.17 g. of reagent grade xylene and analyzed by gas chromatography using Dow Corning 710 Silicon Oil on Chromosorb W (jacket at 240°, preheater at 210°, 14.3 psi. helium). Diphenylacetylene (43%) and minor amounts of biphenyl were present. The xylene solution was treated with Norite until colorless. Removal of xylene at reduced pressure gave 2.36 g. of diphenylacetylene (38%), m.p. and mixed m.p. 56°, whose infrared spectrum was identical with that of an authentic sample.

Preparation of Authentic Trimethylperfluorovinylsilane.—Freshly distilled trimethylchlorosilane (71 g., 0.65 mole) and 145 g. (0.9 mole) of bromotrifluoroethylene in 800 ml. of tetrahydrofuran were added dropwise over 5 hr. to 20.8 g. (0.85 g. atom) of magnesium turnings in 75 ml. of tetrahydrofuran at −15°. Upon completion of the reaction, all volatiles were distilled at reduced pressure into a receiver cooled to −78°. The colorless solution (at 0°) was treated with 62 g. (0.39 mole) of bromine during a 96 hr. period. The solvent and other low boiling compounds were removed at 27°(5 mm.), leaving 39.7 g. of pale yellow oil, $n^{25}\text{D}$ 1.4532, $(CH_3)_3SiCFBrCF_2Br$.

Anal. Calcd. for $C_5H_9Br_2F_3Si$: C, 19.10; H, 2.86; Br, 50.80. Found: C, 19.24; H, 2.90; Br, 51.03.

Thirty grams of this dibromide (0.0954 mole) in 50 ml. of diglyme was added dropwise to 7 g. (0.107 g. atom) of zinc dust in diglyme. The mixture was stirred for 1 hr., filtered, and the filtrate distilled to give 13.0 g. (89%) of trimethylperfluorovinylsilane, b.p. 65°, $n^{25}\text{D}$ 1.3569.

Anal. Calcd. for $C_5H_9F_3Si$: C, 38.94; H, 5.88; Si, 18.22. Found: C, 38.76; H, 5.73; Si, 18.31.

Its infrared spectrum (carbon tetrachloride solution) showed major absorption at 2950, 1715, 1285, 1260, 1130, 1040 and 850 cm.$^{-1}$.

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(16) D. Seyferth, W. Freyer and G. Raab, ASD Technical Report 61-1, Part I, July 1961; ASTIA Document No. AD-268334 (Div. 4).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY, ST. LOUIS 30, MO.]

Electron Transfer between Tris-*p*-nitrophenylmethyl Radical and Tris-*p*-nitrophenylmethide Ion Studied by Electron Spin Resonance Techniques[1]

BY M. THOMAS JONES[2] AND S. I. WEISSMAN

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The rate constants and the activation energies for the electron transfer between tris-*p*-nitrophenylmethyl radical and tris-*p*-nitrophenylmethide ion for all combinations of the sodium or potassium salts in 1,2-dimethoxyethane, tetrahydrofuran, pyridine, and acetonitrile have been measured by electron spin resonance (e.s.r.) methods. The rates lie in the range 10^7 to 10^9 liter mole^{-1} sec.$^{-1}$. The activation energies lie in the range 0.9 to 2.3 kcal. mole^{-1}. The analysis of the rate constants and the activation energies is straightforward except for the case of the sodium tris-*p*-nitrophenylmethide in THF, where the dependence of rate on total methide concentration is not linear. In a particular solvent the sodium salt yields a slower rate than the potassium salt except in acetonitrile.

In this paper we report measurements of the rates of electron transfer reactions between tris-*p*-nitrophenylmethyl and the sodium and potassium salts of the corresponding methide ion. Although the reaction rates lie close to the limit for diffusion controlled processes, heroic techniques are not required for their measurement. The e.s.r. spectrum of dilute solutions of tris-*p*-nitrophenylmethyl consists of about 100 lines in a span of 26 gauss.[3] Addition of the methide ion produces a broadening of the lines from which the mean time between electron transfer events may be determined. The principles of the method have been so thoroughly discussed[4] that we shall not take them up here.

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(2) E. I. du Pont de Nemours and Co., Central Research Department, Experimental Station, Wilmington 98, Delaware.

(3) M. T. Jones, *J. Chem. Phys.*, **35**, 1146 (1961).

(4) A recent review is given by S. I. Weissman, *Z. Elektrochem.*, **64**, 47 (1960).