fluorochloroacetimidoyl)perfluorobutyramidine: bp 72° (4.6 mm), d^{26} 1.6259, n^{26}_{D} 1.3763.

Triazine was prepared by adding 38.87 g of N'-(difluorochloroacetimidoyl)perfluorobutyramidine (0.12 mole) to 133.2 g of perfluorobutyric anhydride (0.325 mole). The reaction mixture was heated with stirring at 40–50° for 77 hr, then washed with water, distilled twice, and finally fractionated to give 41.7 g (70%) of 2,4-bis(perfluoropropyl)-6-difluorochloromethyl-1,3,5-triazine as a colorless liquid: bp 158–159°, d^{26} 1.6788, n^{26}_{D} 1.3303.

Anal. Calcd for $C_{10}ClF_{16}N_3$: C, 23.93; Cl, 7.08; F, 60.62; N, 8.37. Found: C, 24.23; Cl, 7.32; F, 60.49; N, 8.68.

2,4-Bis(perfluoropropyl-6-methyl-1,3,5-triazine.—Freshly distilled acetic anhydride (25 ml) was placed in a flask protected from atmospheric moisture and N'-(perfluorobutyrimidoyl)perfluorobutyramidine (22.23 g, 0.0546 mole) was added slowly over a 45-min period. The reaction mixture was stirred and refluxed for 21 hr, then washed with water to separate the crude triazine. Fractionation gave pure 2,4-bis(perfluoropropyl)-6-methyl-1,3,5-triazine: bp 162–163°, d^{26} 1.6079, n^{27}_{D} 1.3339.

Anal. Calcd for $C_{10}H_3F_{14}N_3$: C, 27.84; H, 0.69; F, 61.72; N, 9.74. Found: C, 28.03; H, 0.80; F, 61.57; N, 9.84.

2,4-Bis(perfluoroethyl)-6-methyl-1,3,5-triazine.—The preparation of 2,4-bis(perfluoroethyl)-6-methyl-1,3,5-triazine was carried out in the manner described for the previous preparation by treating 10.0 g of N'-(perfluoropropionimidoyl)perfluoropropionamidine with 20 g of acetic anhydride at reflux temperature for 5 hr. This reaction mixture was washed with water to yield 8.8 g of crude triazine. Fractionation through an 18-in. spinning-band column yielded pure 2,4-bis(perfluoroethyl)-6-methyl-1,3,5-triazine: bp 137–138°, d^{22} 1.5337, n^{23}_{D} 1.3427.

Anal. Calcd for $C_8H_3F_{10}N_3$: C, 29.00; H, 0.91; F, 57.40; N, 12.69. Found: C, 29.29; H, 0.87; F, 57.60; N, 13.01.

Fluorinated Acylthiophenes. Preparation of 5,5'-Diheptafluorobutyryl-2,2'-bithiophene *via* a Grignard Coupling Reaction

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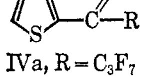
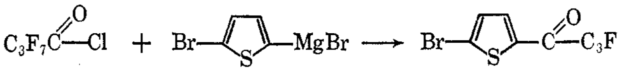
In general, 2,2'-bithiophenes (dithienyls) are prepared by the coupling of halothiophenes with metals[1-3] or less often by the coupling of Grignard reagents in the presence of a cohalide catalyzed by means of cobaltous chloride,[4,5] cupric chloride,[6] or oxygen.[7,8] (The uncatalyzed Grignard coupling reaction has been sparsely reported in the literature except in the case of benzyl halides.[9-11]) Few examples of the preparation of bithiophenes by the Grignard method have been effected without either a metal halide or treatment with oxygen.[12] Minnis isolated 5,5'-di(triphenylmethyl)-2,2'-bithiophene in an attempt to prepare triphenylthienylmethane from triphenylchloromethane and thienylmagnesium iodide.[13] Others[14] have reported the isolation of 5,5'-dichloro-2,2'-bithiophene in 5% yield during the preparation of 5-chloro-2-vinylthiophene from 5-chloro-2-thienylmagnesium bromide and acetaldehyde. Attempts in this laboratory to prepare 2,5-diheptafluorobutyrylthiophene (I) from the Grignard compound of 2,5-dibromothiophene also gave, in the presence of ethyl bromide alone, a coupled product, 5,5'-diheptafluorobutyryl-2,2'-bithiophene (III, discussed below).

We have previously shown that many synthetic approaches used for the acylation of thiophene and substituted thiophenes cannot be utilized for the preparation of a fluorinated acylthiophene.[15] The desired product (IVa) was prepared, however, by the addition of 2-thienylmagnesium bromide to the acid chloride. This work has now been extended to the preparation of other fluorinated acylthiophenes by the same Grignard technique. The use of the intermediates pentafluoropropionyl chloride and pentadecafluorocaprylyl chloride gave the expected compounds IVb and IVc.

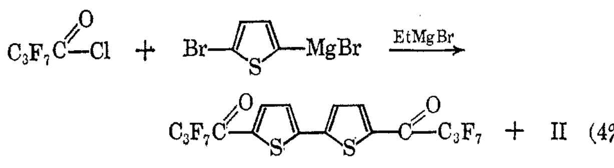


IVa, R = C_3F_7
b, R = C_2F_5
c, R = C_7F_{15}

An attempt to prepare I, under reaction conditions similar to the preparations of IVa–c, gave, instead, 2-heptafluorobutyryl-5-bromothiophene (II). To facilitate the formation of Grignard in the 5 position of 2,5-dibromothiophene, the entrainment method for inactive halides was attempted using ethyl bromide as the cohalide.[16,17] As in the previous case, the expected product (I) could not be isolated. The main product obtained was the bithiophene (III) in 26% yield. The reaction also gave a 4% yield of II.



II



III

In the reactions for the preparations of II and III, the metal impurities contained in the commercial magnesium turnings[18] apparently do not significantly promote the Wurtz reaction. This is indicated by the failure to isolate the coupled products III or 5,5'-dibromo-2,2'-bithiophene from the reaction for the

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[1] O. Eberhard, *Ber.*, **27**, 2919 (1894).

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[3] J. H. Uhlenbroek and J. D. Bijloo, *Rec. Trav. Chim.*, **79**, 1181 (1960).

[4] J. P. Morizur and R. Pallaud, *Compt. Rend.*, **254**, 1093 (1962).

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[6] W. Steinkopf and W. Köhler, *Ann.*, **522**, 17 (1936).

[7] C. D. Hurd and K. L. Kreuz, *J. Am. Chem. Soc.*, **72**, 5543 (1950).

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[9] R. C. Fuson, *ibid.*, **48**, 830, 2681 (1926).

[10] R. C. Fuson, J. J. Denton, and J. W. Kneisley, *ibid.*, **63**, 2652 (1941).

[11] M. S. Kharasch and W. H. Urry, *J. Org. Chem.*, **13**, 101 (1948).

[12] It has been reported that small amounts of metal impurities in ordinary commercial magnesium turnings promote the Wurtz reaction and give coupled products. See (a) G. O. Johnson and H. Adkins, *J. Am. Chem. Soc.*, **53**, 1520 (1931); (b) *ibid.*, **54**, 1943 (1932); (c) M. S. Kharasch, S. C. Kleiger, J. A. Martin, and F. R. Mayo, *ibid.*, **63**, 2305 (1941); (d) ref 5.

[13] W. Minnis, *J. Am. Chem. Soc.*, **51**, 2143 (1929).

[14] G. B. Bachman and L. V. Heisey, *ibid.*, **70**, 2378 (1948).

[15] S. Portnoy and H. Gisser, *J. Org. Chem.*, **22**, 1752 (1957).

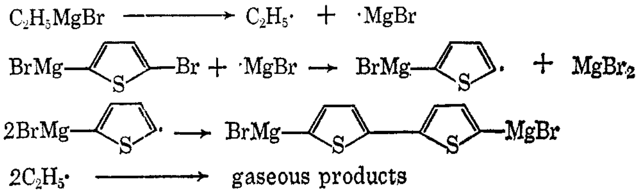
[16] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall Co., Inc., New York, N. Y., 1954, pp 38–45.

[17] D. E. Pearson, D. Cowan, and J. D. Beckler, *J. Org. Chem.*, **24**, 504 (1959).

[18] Per cent metal impurities: Al, 0.001; Cu, 0.004; Mn, 0.1; Ni, 0.02; Fe, 0.02.

preparation of II. Coupling occurred only on use of ethyl bromide.

A suggested mechanism for the formation of III is *via* the formation of the Grignard of 5,5′-dibromo-2,2′-bithiophene by a thermal, free-radical reaction involving ethylmagnesium bromide,[11] followed by its subsequent reaction with heptafluorobutyryl chloride.



Experimental Section[19]

2-Pentafluoropropionylthiophene (IVb).—An ether solution of 1.0 mole of 2-thienylmagnesium bromide was added over a period of 2 hr to an ether solution of 1.2 moles of pentafluoropropionyl chloride maintained at a temperature of −30°. The mixture was stirred for 2 hr during which time the temperature was allowed to rise to 25°. The mixture was then refluxed for 6 hr and worked up in a manner previously described.[15] Distillation through a 12-in. Vigreux column gave a 17% yield, bp 66.5–67.2° (21 mm), $n^{20}\text{D}$ 1.4515.

Anal. Calcd for $C_7H_3F_5OS$: C, 36.53; H, 1.31; F, 41.27. Found: C, 36.98; H, 1.40; F, 40.96.

The 2,4-dinitrophenylhydrazone, recrystallized from an alcohol–water mixture, melted at 107–108°.

2-Pentadecafluorocaprylylthiophene (IVc).—The reaction was performed in the same manner as above, employing 2-pentadecafluorocaprylyl chloride as the fluorinated intermediate. After addition of the Grignard to the ether solution of the acid chloride (room temperature), the mixture was refluxed for 6 hr. Distillation through a 12-in. Vigreux column gave a 19% yield, bp 64.4–65.8° (0.32 mm), $n^{20}\text{D}$ 1.3914.

Anal. Calcd for $C_{12}H_3F_{15}OS$: C, 30.01; H, 0.63; F, 59.35. Found: C, 30.34; H, 0.91; F, 56.75.

Several recrystallizations of the 2,4-dinitrophenylhydrazone from an alcohol–water mixture afforded pure product, mp 92.0–93.6°.

5-Bromo-2-heptafluorobutyrylthiophene (II).—In an attempt to synthesize I, a two-to-one ratio of magnesium turnings to halide was used in order to prepare the di-Grignard of 2,5-dibromothiophene. Iodine crystals and heat were found necessary to initiate the reaction. The Grignard was refluxed for 10 hr, filtered under nitrogen through glass wool,[20] and added over a period of 4 hr to an ether solution of the acid chloride. The mixture was then refluxed for 18 hr and worked up by the usual procedure. The crude, orange product was separated from tars by distillation at 5 mm,[21] collecting the fraction from 75–85°. Distillation through a 3-in. Vigreux column gave a purple forecut and a light yellow middle cut, bp 91–92 (7.5 mm). Fractionation of the middle cut through a 3-in. column containing $^1/_8$ in. helices gave a 17% yield, bp 145.0–145.3 (93 mm), $n^{20}\text{D}$ 1.4733. Infrared bands (neat) appeared at 3100 (vw–b),[22] 1678 (vs), 1663 (sh), 1512 (w), 1403 (vs), 1351 (s), 1326 (s), 1116 (vs),[23] 1066 (m), 987 (s), 962 (s), 930 (m), 865 (vw–b), 841 (sh), 823 (s–b), 802 (s–b), 748 (s), 728 (m–b), 715 (m–b), and 687 (m) cm^{-1}.

Anal. Calcd for $C_8H_2BrF_7OS$: C, 26.76; H, 0.56; Br, 22.26; F, 37.04; S, 8.93. Found: C, 27.03; H, 0.62; Br, 22.03; F, 36.89; S, 9.04.

5,5′-Diheptafluorobutyryl-2,2′-bithiophene (III).—The reaction was performed initially in the same manner as that for II, employing 0.7 g-atom of magnesium turnings and 0.1 mole of 2,5-dibromothiophene. The mixture was refluxed for 3 hr and cooled to room temperature; 0.5 mole of ethyl bromide in ether was added in 1 hr. The ether solution of the Grignard compounds was refluxed for 17 hr, filtered under nitrogen through glass wool (1.7 g of magnesium recovered), and added over a 45-min period to 0.7 mole of heptafluorobutyryl chloride in ether. The mixture was refluxed for 10 hr and worked up in the usual manner. Distillation removed the liquid portion boiling from 28 to 113° (22 mm)[24] and left a tarry residue. Extraction of the residue with hot petroleum ether (bp 30–60°) gave the orange, crude product. Crystallization from petroleum ether and recrystallization from heptane gave yellow platelets, mp 152.6–153.8°, 26% yield. Infrared bands (Nujol mull) appeared at 3100 (w), 1670 (vs), 1510 (w), 1440 (s), 1360 (m), 1317 (m), 1290 (m), 1262 (m), 1230 (s), 1212 (s), 1190 (m), 1176 (m), 1149 (m), 1122 (vs), 1088 (m), 970 (w), 940 (m), 917 (vw), 893 (w), 828 (m), 811 (m), 754 (m), and 733 (vw–b) cm^{-1}.

Anal. Calcd for $C_{16}H_4F_{14}O_2S_2$: C, 34.42; H, 0.72; F, 47.64; S, 11.49. Found: C, 34.29; H, 0.97; F, 47.32; S, 11.06.

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(19) All melting and boiling points are uncorrected; analyses were by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Infrared spectra were obtained on a Perkin-Elmer Model 21 spectrophotometer.

(20) Almost one-half the magnesium charge was recovered.

(21) Distillation was stopped upon appearance of decomposition vapors.

(22) b = broad, vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder.

(23) A strong, broad band appears in the C–F absorption regon, 1290–1130 cm^{-1}.

(24) At 80°, a small quantity of orange product crystallized on the condenser wall.

Radical Anions Derived from Indigo and 2,2′-Bibenzimidazole[1]

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We have previously discussed radical anions and cations derived from 2,2′-biindan-1,1′,3,3′-tetraone (**3**) and particularly the very stable diprotonated form of **4**.[2] We now report an investigation of various aza derivatives of 2,2′-biindan including dehydroindigo (**6**), indigo (**8**), leucoindigo (**10**), $\Delta^{2,2'}$-biisobenzimidazolylidene (**11**), and 2,2′-bibenzimidazole (**13**). We find that whereas both **7** and **9** can be prepared, apparently only **12** is readily prepared in the bibenzimidazole series. There appears to be a trend in stability from the more highly reduced structure in series A (**4** is stable) to the more highly oxidized structure in series C (**12** is stable). Series B is intermediate, (**7** and **9** both stable). We have been unable to detect the oxidized radical anion in series A (**2**) or the reduced radical anion in series C (**14**) (see Chart I).

Two radical anions were detected in series B which we attribute to the dehydroindigo radical anion (**7**) and the indigo radical ion (**9**). Reduction of **6** yielded a poorly resolved esr spectrum which is consistent with hyperfine splitting by two equivalent nitrogen atoms, $a^N \sim 2$ gauss. Reduction of **8** or oxidation of **10** gave a more highly resolved spectrum previously observed by Bruin, Heineken, and Bruin.[3] The previous workers assigned this radical structure **7** but the method of synthesis in the present work strongly suggests structures **9**. The concentration of **9** formed from equimolar mixtures of **8** and **10** in dimethyl sulfoxide (80%)–*t*-butyl alcohol (20%) solution containing potassium *t*-

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(1) Part IV. Electron Transfer Processes. For part III, see O. W. Maender and G. A. Russell, *J. Org. Chem.*, **31**, 442 (1966). This work was supported by a grant from the National Science Foundation.

(2) G. A Russell and M. C. Young, *J. Am. Chem. Soc.*, **88**, 2007 (1966).

(3) F. Bruin, F. W. Heineken, and M. Bruin, *J. Org. Chem.*, **28**, 562 (1963). These workers report a somewhat better spectrum (below room temperature) than we have observed at 25°. Both spectra have 19 sets of lines.