

SYNTHESIS AND REACTIONS OF SOME PENTABROMOPHENYL ORGANOMETALLICS

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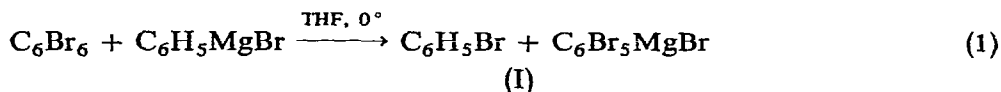
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SUMMARY

The reactions of pentabromophenylmagnesium bromide (I) with chlorosilanes, benzoyl chloride, sulfur, iodine, and iodotrifluoroethylene are described. The synthesis of a pentabromophenylcopper complex (IX) from the Grignard, and some of its reactions are also reported.

SYNTHESIS AND REACTIONS

In our earlier communication¹ we reported the synthesis of pentabromophenylmagnesium bromide, (I), through the exchange reaction between phenyl- (or ethyl-) magnesium bromide and hexabromobenzene (eqn. (1)). Of the two solvents studied, tetrahydrofuran (THF) and diethyl ether, THF was found to give a higher



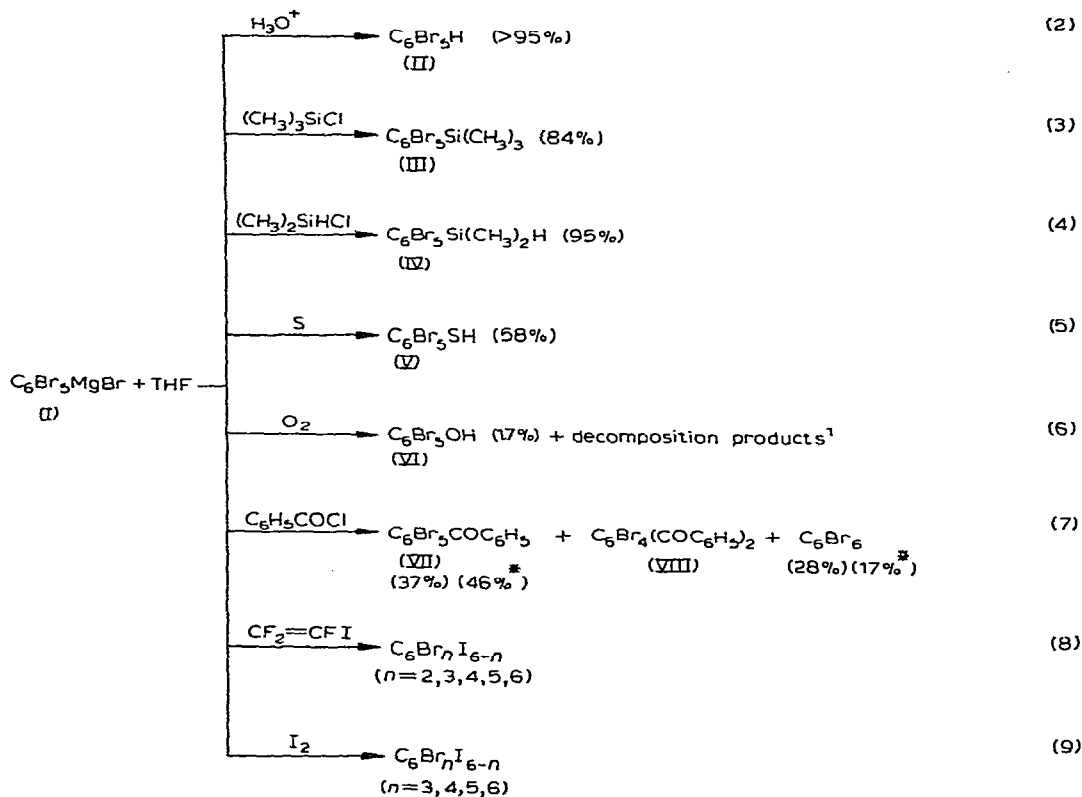
yield of Grignard reagent(I). Whereas the hexabromobenzene is quite insoluble in THF, the resultant Grignard reagent(I) formed is soluble in the concentration range studied (0.05–0.5 M). When prepared at 0°, (I) undergoes very little decomposition within the first 3–4 hours¹. In the case of the exchange reaction employing ethylmagnesium bromide, the decomposition is faster because of the Grignard reagent's subsequent reaction with ethyl bromide yielding ethylated polybromobenzene products.

The Grignard reagent (I) gives many reactions characteristic of its nonhalogenated analog², and some that can only be explained on the basis of multiple intermolecular metal-halogen exchange reactions. The Grignard reagent (I) can be readily hydrolyzed (eqn. (2)) to pentabromobenzene, (II), in almost quantitative yields, the yield being based on pentabromobenzene formed. Trimethylchlorosilane and dimethylchlorosilane react readily with (I) to give the expected silanes (III) and (IV) in excellent yields (eqns. (3) and (4)). Grignard reagent (I) reacted with sulfur to yield pentabromothiophenol (V) in 58% yield (eqn. (5)). However, oxidation of (I) yielded pentabromophenol (VI) (eqn. (6)) in only 1.7% yield. The oxidation of the Grignard reagent (performed by bubbling dry air through the THF solution for 18 h

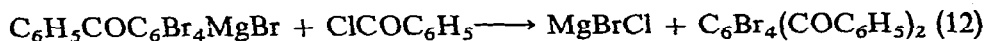
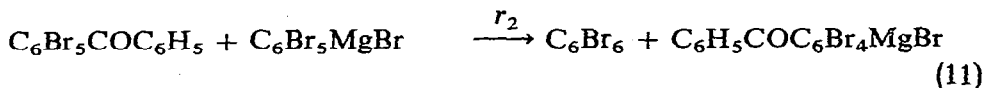
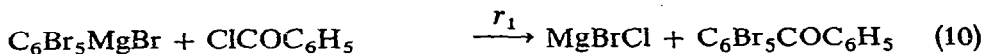
at 0°) yielded only the time-dependent decomposition products¹. No biphenyl coupling products were detected, although such products might be expected to arise through intermediate benzyne formation^{3,4}.

SCHEME 1

REACTIONS OF PENTABROMOPHENYLMAGNESIUM BROMIDE



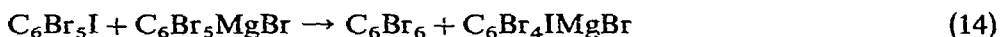
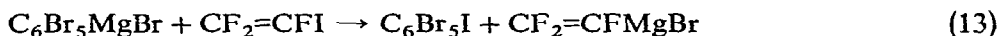
The reaction between Grignard reagent (I) and benzoyl chloride (eqn. (7)) is of considerable interest since it is an example of a multiple intermolecular metal-halogen exchange reaction. In this reaction, three major products were obtained, benzoylpentabromobenzene (VII), dibenzoyltetrabromobenzene (VIII), and hexabromobenzene. These results can be explained by considering the following equations (eqns. (10)–(12)).



* Percent yield obtained by reverse addition. See experimental results for details.

If the rate of the initial reaction (eqn. (10)) is sufficiently slow (r_1 less than r_2) then the product, benzoylpentabromobenzene, has an opportunity to further undergo metal-halogen exchange to give hexabromobenzene and benzoyltetrabromophenylmagnesium bromide (eqn. (11)). This intermediate organometallic compound subsequently reacts with benzoyl chloride to yield the dibenzoyltetrabromobenzene (eqn. (12)). In order to substantiate this argument, reverse addition of the reactants (Grignard reagent (I) added slowly to benzoyl chloride) was attempted. In this manner, excess (I) in the presence of the benzoylpentabromobenzene (VII) was minimized. Using this procedure a small increase (46% vs. 37%) of the monosubstituted product (VII) was obtained. Although this increase is minimal, it does indicate that r_2 is somewhat larger than r_1 and that limiting the concentration of Grignard (I) in the presence of benzoyl chloride improves the yield of the monoketone, (VII).

Two other examples of multiple intermolecular metal-halogen exchange reactions were evidenced by the reactions between the Grignard reagent (I)/iodotrifluoroethylene (eqn. (8)) and Grignard (I)/iodine (eqn. (9)). In the reaction with iodotrifluoroethylene, only polyiodinated bromobenzenes of the type $C_6Br_nI_{6-n}$ were found. No vinyl substituted products, *e.g.*, $C_6Br_5CF=CF_2$, were present. These results can be rationalized by considering a similar sequence of reactions used in explaining the reaction between Grignard (I) and benzoyl chloride:



Again only polyiodobromobenzenes were found in the reaction between Grignard (I) and I_2 . This phenomenon of a multiple intermolecular metal-halogen exchange reaction has not been observed thus far in the reactions of perchloro- or perfluorophenylmagnesium bromides*.

The Grignard reagent reacts with cuprous bromide to yield a new organometallic complex, (IX). No attempt was made to isolate this organocopper complex; however, reactions of this complex were studied and were shown to be similar to those of other perchloro-⁶ and perfluorophenylcopper⁷ complexes studied previously. This organocopper complex** exhibits a number of reactions different from its precursor, Grignard reagent (I). For example, oxidation of the copper complex, (IX), gives the pentabromophenol*** (VI), in 84% yield, whereas (I), as expected, yields the phenol in only 1.7% yield. Reaction between " C_6Br_5Cu " and benzoyl chloride gives only the monosubstituted benzoylpentabromobenzene (VII) in 90% yield, with no evidence of intermolecular copper-halogen exchange. " C_6Br_5Cu " reacts with iodotrifluoroethylene to give the perhalostyrene, $C_6Br_5CF=CF_2$ (X) in 50% yield. Unlike the Grig-

* We have previously observed⁵ multiple intermolecular metal-halogen exchange reactions in our studies on carbonation of 2-bromotetrafluorophenylmagnesium bromide. The reaction products were 1,2-dibromotetrafluorobenzene and tetrafluorophthalic acid.

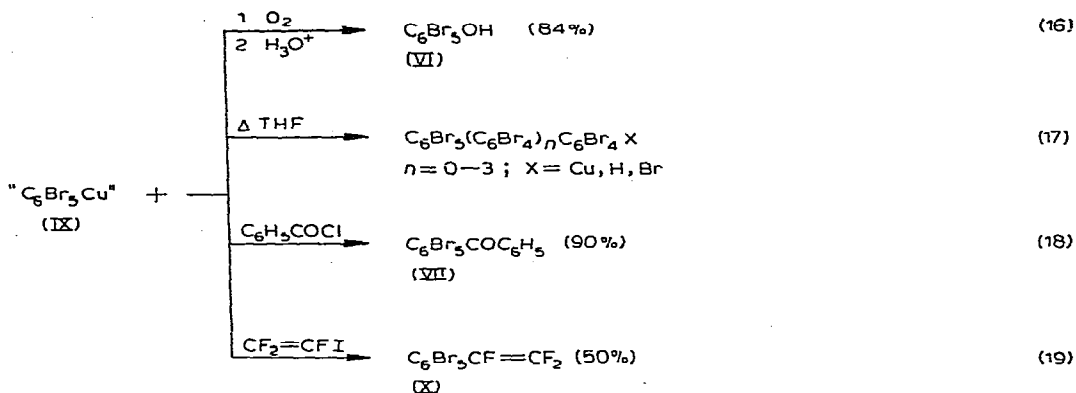
** Since the complex has not been isolated and characterized, for the sake of simplicity only, it will be referred to as " C_6Br_5Cu " (IX).

*** Oxidation of " C_6F_5Cu "^{7b} yields decafluorobiphenyl as the principle reaction product. However, " C_6Cl_5Cu "⁶ yields pentachlorophenol as the principal product. These differences could be accounted for by considering the ease of formation of the sterically hindered perhalobiphenyl compounds.

nard (I), which decomposes via reaction with the THF solvent¹, the copper complex (IX) decomposes on heating in THF to intractable materials believed to be poly-bromo-biphenyls, -terphenyls and quaterphenyls.

SCHEME 2

REACTIONS OF PENTABROMOPHENYL COPPER



This convenient synthesis of pentabromophenylmagnesium bromide and pentabromophenyl copper now makes it possible to utilize these organometallic intermediates for the synthesis of numerous pentabromophenyl derivatives.

EXPERIMENTAL

General comments

Reactions involving organometallic reagents were carried out under dry nitrogen with the usual precautions for the rigorous exclusion of moisture and air. The hexabromobenzene used in these experiments was obtained from Aldrich Chemical Co., m.p. 328–330°, and was used without further purification. Tetrahydrofuran was distilled from metallic sodium followed by calcium hydride prior to use. Anhydrous diethyl ether (Mallinckrodt) was used without further purification. All other solvents used were analytical grade. Melting points were determined with a "Mel-Temp" apparatus and are uncorrected. Infrared spectra were recorded using a Perkin-Elmer Model 521 grating infrared spectrophotometer. NMR spectra were recorded on a Varian A56/60 spectrometer. Chemical shifts are expressed in ppm units using tetramethylsilane (TMS) as internal standard for ¹H, and fluorotrichloromethane as internal standard for ¹⁹F. GLC analyses were performed on an F & M Model 700 instrument using a 6 ft., 10% SE-30 on Chromosorb W column. A helium flow rate of 110–120 ml/min was employed. Mass spectral analyses were performed on a CEC-21-110B mass spectrometer. All products were characterized by GLC retention time with calibrated known samples, and by mass spectral analysis. Yields of all products were determined by GLC analysis using appropriate hydrocarbon internal standards. Empirical response factors were determined separately using standard solutions.

Preparation of pentabromophenylmagnesium bromide

As reported previously¹, pentabromophenylmagnesium bromide was prepared by the dropwise addition of ethyl- (Method E) or phenylmagnesium bromide (Method P) to a cooled (0°) THF slurry of hexabromobenzene. The mixture was stirred for 1–3 h at this temperature. Excellent yields (95%) of the desired Grignard reagent (I) were obtained by this method.

Oxidative stability of pentabromophenylmagnesium bromide in THF

Pentabromophenylmagnesium bromide (25 mmoles) (Method P) was oxidized by bubbling dry air for 18 h through a previously cooled (0°) THF solution. The reaction mixture was hydrolyzed (6N HCl) and worked up in benzene. GLC analysis showed pentabromophenol (1.7%) to be the only product of oxidation. All other products could be attributed to normal time-dependent decomposition of the Grignard(I)¹. Pentabromophenol was collected by preparative GLC and characterized as follows: m.p. 229–230°, (lit.⁸ 229.5°). NMR ¹H (TMS): 6.4 ppm (s, –OH). Mass spectral analysis showed parent *m/e* 484; C₆H⁷⁹Br₅O calcd.: *m/e* 484. Mass spectral analysis of the benzene-soluble and insoluble material revealed no coupling products, i.e. C₁₂Br₁₀.

Reaction of pentabromophenylmagnesium bromide with dimethylchlorosilane

Dimethylchlorosilane (12.3 g, 130 mmoles) was added dropwise (15 min) to a THF (0°) solution of pentabromophenylmagnesium bromide (65 mmoles) (Method P). The reaction mixture was stirred for 1h, and then allowed to warm to room temperature. After it had been stirred at this temperature for 16 h, the mixture was hydrolyzed (6 N HCl) and worked up in benzene. GLC analysis showed dimethylpentabromophenylsilane (95%) as the major product. The benzene solution was concentrated yielding a gray solid, which after recrystallizing from anhydrous ethanol gave a white powder, (29 g, 90%), dimethylpentabromophenylsilane, m.p. 89–91°. Dimethylpentabromophenylsilane was characterized as follows: NMR ¹H (TMS): 0.51 ppm (d, –Si(CH₃)₂); 5.3 ppm (t, –Si(H)(R)₂). Mass spectral analysis gave parent *m/e* 526; C₈H₇⁷⁹Br₅Si calcd.: *m/e* 526. (Found: C, 18.61; H, 1.41; Br, 75.58. C₈H₇Br₅Si calcd.: C, 18.10; H, 1.33; Br, 75.28).

Reaction of pentabromophenylmagnesium bromide with trimethylchlorosilane

Trimethylchlorosilane (8.5 g, 78 mmoles) was added rapidly to a previously cooled (0°) THF solution of pentabromophenylmagnesium bromide (43.2 mmoles) (Method E). The mixture was allowed to warm to room temperature and stirred for 19 h, after which it was concentrated to a solid, hydrolyzed (6 N HCl) and worked up in benzene. The benzene solution was concentrated, yielding a tan solid, which was recrystallized from hexane, producing 19.6 g (83%) of a white solid, pentabromophenyltrimethylsilane, m.p. 107–108°, characterized as follows: NMR ¹H (TMS) 0.6 ppm (s, –Si(CH₃)₃). Mass spectral analysis gave parent *m/e* 540; C₉H₉⁷⁹Br₅Si calcd.: *m/e* 540. (Found: C, 19.85; H, 1.60; Br, 72.60. C₉H₉Br₅Si calcd.: C, 19.84; H, 1.66; Br, 73.34).

Reaction of pentabromophenylmagnesium bromide with sulfur

Sulfur (1.6 g, 60 g atoms) was added to a previously cooled (0°) THF solution of pentabromophenylmagnesium bromide (11.3 mmoles) (Method P). After stirring

1.5 h at this temperature, the reaction mixture was hydrolyzed (6 *N* HCl), and worked up in benzene. GLC analysis of the benzene solution showed only one peak, pentabromobenzene (3.8%). The benzene solution was stripped of solvent, giving a tan solid, which was extracted with hot dilute NaOH (5–10%). Acidification (6 *N* HCl) of the basic solution precipitated crude pentabromothiophenol (5.22 g, 91%), a light yellow solid. A solution of this material in benzene, gave a green color. Boiling with activated charcoal produced a clear light yellow solution after filtration. Upon cooling, a light yellow solid precipitated, pentabromothiophenol, (3.31 g, 58%), m.p. 229–300° (decomp). A small sample sublimed at 208° (0.04 mmHg) gave a light yellow solid, m.p. 306–308° (decomp.). NMR ¹H (TMS) 5.41 ppm (s, –SH). Mass spectral analysis gave parent *m/e* 500; C₆H⁷⁹Br₅S calcd.: *m/e* 500. (Found: C, 14.42; H, 0.22; Br, 78.93; S, 6.33. C₆HBr₅S calcd.: C, 14.26; H, 0.20; Br, 79.18; S, 6.35).

Reaction of pentabromophenylmagnesium bromide with benzoyl chloride

(a). *Normal addition.* To a cooled (0°) THF solution of pentabromophenylmagnesium bromide (11.6 mmoles) (Method P), was rapidly added an excess of benzoyl chloride (1.93 g, 13.8 mmoles). The mixture was stirred for 6 h at 0° and then warmed to room temperature. After stirring 24 h, the mixture was hydrolyzed (6 *N* HCl) and worked up in benzene. The benzene insoluble material was found to be hexabromobenzene (1.58 g, 25%), m.p. 328–330° (Aldrich Chemical Co., m.p. 328–330°). GLC mass spectral analysis of the benzene solution showed benzoylpentabromobenzene (37%) as the major product, the remaining material being pentabromobenzene (1%) and hexabromobenzene (3%). The solution was concentrated to a white solid, which was shown by mass spectral analysis to contain benzoylpentabromobenzene, and dibenzoyltetrabromobenzene, as well as pentabromobenzene and hexabromobenzene. Acetone washing (4 × 25 ml) of the solid gave 2.23 g of crude benzoylpentabromobenzene, m.p. 170–180°. Repeated recrystallization (3) from ethanol gave an analytical sample of benzoylpentabromobenzene, m.p. 193.5–195°.

NMR ¹H (TMS): 8.1 ppm (m, C₆H₅C=O). Mass spectral analysis gave parent *m/e* 572; C₁₃H₅⁷⁹Br₅O calcd.: *m/e* 572. (Found: C, 27.18; H, 0.93; Br, 70.18. C₁₃H₅Br₅O calcd.: C, 27.07; H, 0.87; Br, 69.30).

(b). *Reverse addition.* A THF solution of pentabromophenylmagnesium bromide (11.3 mmoles) (Method P) at 0° was added dropwise (70 min) to a cooled (0°) solution of benzoyl chloride (1.93 g, 13.75 mmoles) in THF (125 ml). After stirring 1 h at this temperature, the reaction mixture was gradually warmed to room temperature. After 20 h the reaction mixture was hydrolyzed (6 *N* HCl) and worked up in diethyl ether. The diethyl ether insoluble material was identified as crude hexabromobenzene (0.95 g, 15%), m.p. 325–328° (Aldrich Chemical Co. m.p. 328–330°). GLC analysis of the diethyl ether layer showed benzoylpentabromobenzene (46%) as the major product, with pentabromobenzene (12%) and hexabromobenzene (2%) as the only other significant materials present. Elution of the diethyl ether soluble material with heptane/chloroform on a silica gel column afforded a mixture of crude diketones (0.60 g). Recrystallization from benzene gave a mixture of dibenzoyltetrabromobenzenes (0.12 g), m.p. 309–314°. Mass spectral analysis gave parent *m/e* 598; C₁₈H₁₀⁷⁹Br₄O₂ calcd.: *m/e* 598. (Found: C, 40.07; H, 1.69; Br, 52.83. C₁₈H₁₀Br₄O₂ calcd.: C, 39.89; H, 1.66; Br, 53.13).

Reaction of pentabromophenylmagnesium bromide with iodotrifluoroethylene

Iodotrifluoroethylene (6.18 g, 32.2 mmoles) was added to a previously cooled (0°) THF solution of pentabromophenylmagnesium bromide (24.2 mmoles) (Method P). After 6 h stirring at this temperature, the white precipitate that formed was filtered (9.99 g), and the filtrate was hydrolyzed (6 N HCl) and worked up in benzene. GLC analysis of the benzene solution showed pentabromobenzene (2.4%) as the major material present. The benzene insoluble material was found by mass spectral analysis to be a mixture of the following products: iodopentabromobenzene, diiodotetrabromobenzene, tribromotriiodobenzene, dibromotetraiodobenzene, and hexabromobenzene. No styrene products (*i.e.*, $C_6Br_5CF=CF_2$) were detected in either the benzene soluble or insoluble fractions.

Reaction of pentabromophenylmagnesium bromide with iodine

Iodine (1.59 g, 12.5 g atoms) was added to a cooled (0°) THF solution of pentabromophenylmagnesium bromide (12.5 mmoles) (Method P). The reaction mixture was stirred at 0° for 1.5 h, and then slowly warmed to room temperature. After 16 h at this temperature, the precipitate that formed was filtered (3.8 g) and the filtrate hydrolyzed and worked up in benzene. GLC analysis of the benzene solution showed one major material present, pentabromobenzene (22%). The benzene solution was concentrated to a solid, which was shown to contain the following materials by mass spectral analysis: hexabromobenzene, pentabromobenzene, iodopentabromobenzene, iodotetrabromobenzene, and diiodotetrabromobenzene.

Preparation and oxidation of pentabromophenylcopper

Anhydrous cuprous bromide (4.53 g, 31.6 mmoles) was added rapidly to a previously cooled (0°) THF solution of pentabromophenylmagnesium bromide (25 mmoles) (Method P). The brown mixture was stirred at this temperature for 2 h, resulting in the formation of a white precipitate. The mixture was then oxidized with dry oxygen for 2 h causing a change in color from brown to green. It was then hydrolyzed (6 N HCl), and worked up in benzene. GLC analysis showed pentabromophenol (84%) as the major product, with only a small amount of pentabromobenzene (4%). The solution was concentrated, and the solid extracted with hot dilute (10%) NaOH solution. Acidification of the basic solution yielded 10.10 g (85%) of a white solid, crude pentabromophenol. Recrystallization from benzene gave pentabromophenol (7.12 g, 60%) as long white needles, m.p. 228.5–229.5° (lit⁸, 229.5°). NMR ¹H (TMS): 6.4 ppm (s, –OH). Mass spectral analysis gave parent *m/e* 484, $C_6H^{79}Br_5O$ calcd.: 484. (Found: C, 14.71; H, 0.26; Br, 81.80; O, 3.35. C_6HBr_5O calcd.: C, 14.74; H, 0.20; Br, 81.78; O, 3.28.)

Thermal stability of pentabromophenylcopper in THF

A THF solution of pentabromophenylcopper (12.5 mmoles) prepared according to the above procedure (Method E) was refluxed for 1 h, after which it was oxidized with dry air for 1 h, hydrolyzed (6 N HCl), and worked up in benzene. The benzene insoluble material (0.63 g) was filtered and GLC analysis of the filtrate showed pentabromobenzene (1.7%) to be the only significant product. The benzene layer was concentrated under vacuum leaving a yellow solid, (3.97 g). The benzene soluble/insoluble solids were combined and put under vacuum (0.04 mmHg) at 220°. Mass spectral

analysis of the sublimate showed only penta-, ethylpenta- and hexabromobenzene present. Mass spectral analysis of the residue suggested polymers of the type $C_6Br_5-(C_6Br_4)_nX$, where $n=2,3$ and $X=H, Br, OH$. No attempt was made to isolate individual products. Another sample treated as above, but not oxidized, gave polymers of the same type $C_6Br_5(C_6Br_4)_nX$ where $X=H, Br$.

Reaction of pentabromophenylcopper with benzoyl chloride

Benzoyl chloride (1.97 g, 14 mmoles) was added rapidly to a THF solution (0°) of pentabromophenylcopper (10.2 mmoles). After it had been stirred for 1 h at this temperature, the mixture was warmed gradually to room temperature. After 22 h the reaction mixture was hydrolyzed (6 N HCl), and worked up in benzene. GLC analysis of the solution showed benzoylpentabromobenzene (90%) as the major product with a small amount of pentabromobenzene (8%) present. The solution was concentrated to a solid, washed with acetone (4×50 ml), and the acetone washings concentrated to a thick gum. Distillation of the gum under vacuum (0.2 mmHg) at 104° gave bromobenzene (exchange product) and n-dodecane (internal standard). The residue was placed under vacuum (0.01 mmHg) at 160° yielding pentabromobenzene. The remaining residue (4.94 g, 84%), m.p. $192-193.5^\circ$, was taken up in benzene and heated 1 h with activated charcoal, filtered, concentrated and recrystallized from heptane, giving white crystals (3.25 g, 55%), m.p. $195-96^\circ$. NMR 1H (TMS) 8.1 ppm (m, $C_6H_5C=O$). Mass spectral analysis gave parent m/e 572, $C_{13}H_5^{79}Br_5O$ calcd.: m/e 572. (Found: C, 27.21; H, 0.87; Br, 70.18; O, 2.33. $C_{13}H_5Br_5O$ calcd.: C, 27.07; H, 0.87; Br, 69.28; O, 2.79.)

Reaction of pentabromophenylcopper with iodotrifluoroethylene

Iodotrifluoroethylene (2.67 g, 13.9 mmoles) was added dropwise (5 min) to a stirred slurry of pentabromophenylcopper (12.5 mmoles) in THF at 0° . The formation of 1,1,2 trifluoro-2-pentabromophenylethylene was followed by injecting samples directly onto the GLC column. The reaction mixture was allowed to stir for 0.5 h at 0° , and then warmed to room temperature. After 13 h at this temperature, GLC analysis showed 25% of the desired styrene present. The mixture was then heated to reflux for 2 h, hydrolyzed (6 N HCl) and worked up in benzene. GLC analysis showed 1,1,2-trifluoro-2-pentabromophenylethylene (50%) as the major product. The benzene solution was concentrated and washed with pentane (3×25 ml). The pentane washings were concentrated to a thick gum containing bromobenzene (exchange product), n-dodecane (internal standard) and the desired styrene. This material was put under vacuum (0.3 mmHg) at 110° , leaving crude 1,1,2-trifluoro-2-pentabromophenylethylene (3.16 g, 46%). Sublimation of the residue at $121-143^\circ$ (0.1-0.03 mmHg) gave a white solid (2.12 g 31%), m.p. $83-86^\circ$. Recrystallization of a small sample from petroleum ether ($35-56^\circ$) gave 1,1,2-trifluoro-2-pentabromophenylethylene as a white solid, m.p. $89-90^\circ$. NMR ^{19}F ($CFCl_3$) shows 3 doublets of doublets: F_1 , 101 ppm; F_2 , 113 ppm; F_3 , 167 ppm. Coupling constants are: J_{13} , 32 Hz; J_{23} , 118 Hz;

J_{12} , 65 Hz. $R-\overset{F_3}{\underset{|}{C}}=\overset{F_1}{\underset{F_2}{C}}$ Mass spectral analysis gave parent m/e 548; $C_8^{79}Br_5F_3$ 548. (Found: C, 17.52; Br, 72.53; F, 10.27. $C_8Br_5F_3$ calcd.: C, 17.38; Br, 72.31; F,

10.32). Mass spectral analysis of the pentane insoluble material was shown to contain normal thermal decomposition products of pentabromophenylcopper.

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