TABLE I

PYROLYSIS OF n-C_5F_{12}

Temp. Pt filament, °C.	Approx. half time of reaction, min.	Initial pressure C_5F_{12} vapor	Volatile products Moles per mole of C_5F_{12} used					Solid polymer, g./mole of C_5F_{12} used
			CF_4	C_2F_6	C_3F_6	C_3F_6, $+ C_3F_8$	C_4F_8 + higher FC's	
840	∞	150						
900	300	155	0.0	0.0	..	0.4	0.8[a]	12
940	60	262	.0	.2	0.33	.8	.4	5.5
960	12	153	.0	> .14	..	.7	.2	10
1150	3	155	.02	.9	0.38	.6	.2	9
1325	<2	219	.005	1.1	..	.14	.0	37

[a] Most of this material was unreacted C_5F_{12}.

measure the temperature of the filament and it is probable that the temperatures so observed were correct to within about 20°. After the reaction appeared to be complete, the products were identified by making an analytical fractional distillation using a very small fractionating column. Vapor densities and boiling ranges of the different cuts were measured, and in two runs the C_3 cut was chlorinated to permit determination of perfluoropropene. Under these conditions pyrolysis of the fluorocarbon was not detected at 840° and it was slow when the filament was held at 900°. As the temperature was increased above this value the rate became much greater.

The clearly identified reaction products were CF_4, C_2F_6, C_3F_8 and C_3F_6 (perfluoropropene). Evidence was also obtained for the presence of one or more forms of C_4F_8. A high polymer having properties of polytetrafluoroethylene collected on the walls of the flask. A trace of a black material, thought to be free carbon, because it disappeared when heated in air, formed on the hot filament.

Results of the different runs are summarized in Table I. Data regarding rates are too few in number to justify their consideration as a means of determining the order of the reaction. The proportions of the different products as given are not to be regarded as very accurate; however, they do indicate in general the influence of temperature upon the composition of the product.

While the observations do not permit one to draw definite conclusions about the mechanism of the reaction, they do furnish some basis for speculation. The data are in accord with a mechanism in which a molecule of C_5F_{12} may dissociate in either of two ways

$$C_5F_{12} = C_2F_4 + C_3F_8 \qquad (1)$$

$$C_5F_{12} = C_2F_6 + C_3F_6 \qquad (2)$$

If C_2F_4 is formed, it disappears due to rapid polymerization to yield one or more forms of C_4F_8, and $(CF_2)_n$. A part of the perfluoropropene, C_3F_6, may also polymerize. Carbon tetrafluoride may be formed at the higher temperatures due to the decomposition of fluorocarbons resulting from the first steps of the pyrolysis of C_5F_{12}. If reactions 1 and 2 are the primary reactions, it follows that reaction 1 predominates at about 900° and that reaction 2 is the more prevalent at the higher temperatures.

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The Reaction of Benzyl Chloride with n-Heptylmagnesium Bromide[1]

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The effect of a number of aliphatic Grignard reagents on benzyl chloride and substituted benzyl chlorides at 100° has been studied by Späth.[3] Fair yields of the normal reaction products were obtained. From the reaction of methyl or ethyl Grignard reagents with benzyl chloride, a product later shown[7] to be 1-benzyl-4-(phenylethyl)-benzene was isolated. Miller and Bachman[4] examined the action of phenyl-, n-butyl, n-amyl- and cyclohexylmagnesium bromide and ethylmagnesium iodide on 9-chlorofluorene (a "benzyl" type halide). They found that in ether solution only ethylmagnesium iodide gave an appreciable yield of alkylfluorene. The other Grignard reagents produced 70 to 95% yields of bifluorenyl, in either benzene or ether solution.

Earlier in this Laboratory[5] it was found that the action of n-heptylmagnesium bromide on benzyl chloride produced a high yield of bibenzyl instead of the coupling product, phenyloctane. The present investigation was undertaken to determine other products of the reaction and to gain some understanding of this result, since with allyl bromide and a normal alkyl Grignard reagent the yield of coupling product is usually about 90%.

Benzyl chloride was added to a filtered[6] ether solution of n-heptylmagnesium halide. Aliquots were removed at regular intervals to follow the disappearance rates of the Grignard reagent and halide. Concentrations of the two reactants were determined by an hydrolysis procedure, plots of log concentration of Grignard reagent and benzyl chloride $vs.$ time appear in Fig. 1.

[1] American Petroleum Institute Project 42. Presented before the Organic Division American Chemical Society, Atlantic City, N. J., 1949.

[2] American Petroleum Institute Research Fellow. Abstracted from an M.S. thesis by Rhoads M. Speck, 1949.

[3] Späth, *Monatsh.*, **34**, 1965 (1913).

[4] Miller and Bachman, THIS JOURNAL, **57**, 766 (1935).

[5] F. B. Fischl and R. W. Schiessler, unpublished data.

[6] See Experimental.

For the first 40% of the reaction (after all the benzyl chloride had been added) straight line relationships were obtained and the slopes of the curves are roughly equivalent. Approximately 25% of the Grignard reagent and benzyl chloride disappeared during the addition of the benzyl chloride, which required one hour. After 5.25 hours, when about 75% of the *n*-heptylmagnesium bromide and benzyl chloride had been consumed, the temperature control was lost.

The reaction products were separated by fractional distillation and identified by the physical properties of the fractions. The products and yields are shown in Table I.

TABLE I

Products	Yields		
	Moles[a]	Mole %[b]	Wt. %[c]
n-Heptane	1.68	46.5	24.5
1-Heptene	1.11	30.8	15.9
Benzyl chloride	0.34	9.4	6.2
Bibenzyl	1.14	63.2	30.3
1-Phenyloctane	Trace	..	..
n-Tetradecane	Trace	..	..
1-Benzyl-4-phenylethylbenzene[7]	0.04	2.2	1.5
Unidentified	..	..	21.6

[a] Although 4.38 moles of Grignard reagent and the same amount of benzyl chloride were charged, 17.6% of the original volume was lost by the removal of aliquots and spurting of the reaction mixture when aliquots were taken. Thus 3.61 moles of each reactant would yield 687 g. of products. [b] The mole % is based on 3.61 moles of each reagent and assuming the reaction: $2C_6H_5CH_2Cl + 2C_7MgBr = C_6H_5CH_2CH_2C_6H_5 + C_{7(+H)} + C_{7(-H)} + 2Mg(Br)Cl$. [c] The weight % is based on the 687 g. of products as noted in (*a*).

There appears to be a relation between the amounts of *n*-heptane, 1-heptene and bibenzyl that are formed. If the heptane formed from decomposition of the unreacted Grignard reagent (0.37 mole) is deducted, the amounts of *n*-heptane and 1-heptene found are 1.31 and 1.11 moles, respectively. Therefore, it appears from the bibenzyl equivalents isolated (1.18 moles) that for every mole of bibenzyl approximately one mole each of *n*-heptane and 1-heptene is formed. The proportion probably is even more exact since some bibenzyl undoubtedly was lost during purification.

Although the amount of metallic impurities present was extremely small (maximum 3×10^{-2} mole %), their concentration may be sufficient to initiate a free radical reaction of the type suggested by Kharasch, *et al.*[8,9] This postulation assumes the formation of an intermediate organo-metallic compound, $C_7H_{15}MBr$, which may dissociate into two free radicals, $C_7H_{15}\cdot$ and $\cdot MBr$. Disproportionation of the heptyl radical would account for the formation of equivalent amounts of *n*-heptane and 1-heptene. The benzyl halide is presumed necessary to regenerate MBrX so that the chain can be continued. In the case of ethyl, *n*-propyl and *n*-butyl halides, Kharasch[10] found that the corresponding radicals do not dimerize to any appreciable extent, if at all, but disproportionate to alkanes and alkenes. This was found to be the case with *n*-heptyl bromide in the present study, for a negligible amount of tetradecane was found. Furthermore, the mechanism accounts for the formation of nearly equivalent amounts of bibenzyl, *n*-heptane and 1-heptene. If any benzylmagnesium bromide was formed during the reaction, it probably reacted with benzyl chloride to give bibenzyl since no toluene was isolated. In the reaction only a small amount of phenyloctane was formed, and thus the "allylic" coupling reaction seems to be much slower than some of the others.

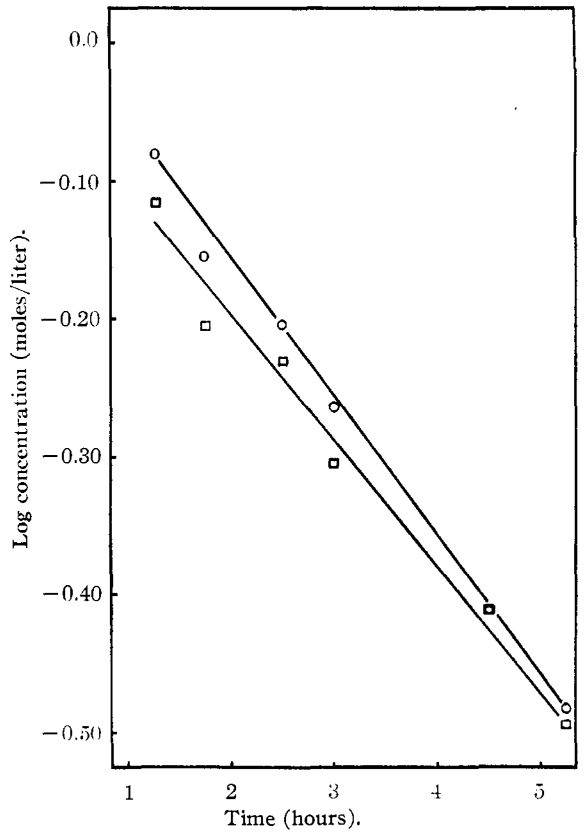

Fig. 1.—Log concentration *vs.* time: O, benzyl chloride; □, *n*-C_7MgBr.

If "free and uncombined" alkyl radicals were formed during the reaction, it is probable that they would attack the solvent, producing a preponderance of heptane over heptene. The data, however, do not agree with this idea. Perhaps the radicals are not "free," but combined in some sort of complex from which they can disproportionate.[11]

Experimental

Magnesium.—The Dow Chemical Co. furnished the following analysis: aluminum, 0.003%; copper, 0.003; iron, 0.03; manganese, 0.08; nickel, 0.001; silicon, 0.005; magnesium (by difference), 99.878.

***n*-Heptyl Bromide.**—*n*-Heptanol (Columbia Organic Chemical Co.) was purified by fractional distillation,[12a] b.p. 177° (738 mm.), n^{20}_D 1.4238. The alcohol was saturated with

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(7) Fuson, THIS JOURNAL, **48**, 2937 (1926), has shown that this product is probably formed from bibenzyl and benzyl chloride during distillation of the reaction mixture rather than during the actual process of the Grignard reaction.

(8) Kharasch and Fuchs, *J. Org. Chem.*, **10**, 292 (1945).

(9) Kharasch, Lambert and Urry, *ibid.*, **10**, 298 (1945).

(10) Kharasch, Lewis and Reynolds, THIS JOURNAL, **65**, 493 (1943).

(11) Kharasch and Urry, *J. Org. Chem.*, **13**, 10 (1948).

(12) (a) The columns are of the total condensation–partial takeoff type, packed with carefully sorted 3/32" single turn glass helices. The columns had packed sections of 2.5 × 90 cm. and 35–40 theoretical plates. (b) Same as (12a) except that packed section was 1.5 × 46 cm.

anhydrous hydrogen bromide (Dow Chemical Co.) at 110–115° to constant weight. After separation of the aqueous layer the organic material was chilled to 2°, washed with two ice-cold portions of concentrated sulfuric acid, 3% ammonia water, twice with water, and dried over anhydrous calcium chloride followed by anhydrous potassium carbonate. Fractional distillation[12a] gave the purified bromide, b.p. 111° (96 mm.), n^{20}D 1.4500, in 85% yield.

Benzyl Chloride.—Fractional distillation[12a] of Eastman Kodak Co. White Label benzyl chloride yielded pure material: b.p. 124° (150 mm.), n^{20}D 1.5386.

The Grignard reagent prepared in 2500 ml. of anhydrous ether from 121.5 g. (5 g. atoms) of magnesium and 860 g. (4.8 moles) of *n*-heptyl bromide was filtered from the excess magnesium. After standing 84 hours the Grignard reagent was pumped away from the sludge. It was heated to reflux (42°), and 554 g. (4.38 moles) of benzyl chloride added over a period of one hour. The reaction was continued for 44 hours, removing aliquots intermittently for analysis. The analytical data are shown in Table II. The product was hydrolyzed on ice and the organic material separated by ether extraction. After removal of the ether, fractionation[12b] of the organic material led to the isolation of an unidentified low boiling material: 35.7 g., b.p. 51–52.5°, n^{20}D 1.3604–1.3929; 280.3 g. of heptane and heptene; 42.6 g. of unreacted benzyl chloride; 41.4 g. of a complex high boiling material and a 286.5 g. of residue. Refractionation[13] of the heptane–heptene mixture yielded 109 g. (1.11 moles) of 1-heptene, b.p. 92.0–92.7°, n^{20}D 1.3989–1.3998 and 168 g. (1.68 moles) of *n*-heptane, b.p. 97.0–97.3°, n^{20}D 1.3877–3882. The hydrocarbons were identified by comparing their properties with those of the pure materials. The benzyl chloride fractions (50.9 g.) contained 42.6 g. (0.34 mole) of the halide as determined by the hydrolysis procedure.[14] An anilide prepared from the benzyl chloride had a m.p. 115–116°, mixed m.p. 114–115°. The residue was chilled to −5° to give 186 g. (1.02 moles) of bibenzyl, which after recrystallization from ether melted at 51–52°, mixed m.p. 51–52°. The liquid residue plus the high boiling fractions above were distilled through a high vacuum column,[15] at 1 mm. The following products were identified: an additional 21.8 g. (0.12 mole) bibenzyl; 2.0 g. of tetradecane, m.p. 5.5–6.5°, mixed m.p. 6.0–6.5°; 10 g. (0.04 mole) benzylphenylethylbenzene, mol. wt. calcd. 273, found 265, mol. ref. calcd. 88.5, found 86.7, n^{20}D 1.5929,[7] found 1.5941. A few fractions (5.2 g.), which were suspected to contain 1-phenyloctane, were selectively adsorbed on silica gel. Two-tenths gram of material was obtained which is believed to be 1-phenyloctane; n^{20}D 1.4847,[16] found 1.4846–1.4850, m.p.[16] −37.0°, found −43 to −36°. The bulk of the fractions could not be identified but from their properties appeared to be mixtures of polyaromatics.

TABLE II

Sample	Time, hr.	Temp., °C.	Moles of Grignard	Moles of C$_6$H$_5$CH$_2$Cl
1	0	20	4.38	0.0
2	1.25	42	3.42	3.13
3	1.75	41	2.86	2.54
4	2.5	41	2.43	2.29
5	3	42	2.11	1.95
6	4.5	41.5	1.39	1.39
7	5.25	41.5	1.18	1.15
8	7.5	38	0.76	0.70
9	9	36	.69	..
10	13.75	33	.55	.53
11	20	32	.45	.45
12	44	28	.37	.33

Analysis of the C$_6$H$_5$CH$_2$Cl–RMgX Mixtures.—*n*-Heptylmagnesium bromide was determined using a procedure similar to Gilman's[17] except that the heating operation was avoided. After the addition of the sample to 50 ml. of cold distilled water, a measured excess of standard acid was added. The mixture was allowed to stand for one-half hour at 25° and then the acid neutralized with standard base. This titration yielded the amount of RMgX present. The method of estimating benzyl chloride in the presence of *n*-heptylmagnesium bromide depends on the difference in the rate of hydrolysis of the two compounds.

After the Grignard titration, the benzyl chloride was determined by adding 50 ml. of 0.2 *N* NaOH and making the solution up to a volume of about 150 ml. To the alkaline solution was added 60 ml. of 95% ethanol; thus the solution was approximately 0.045 *N* NaOH in 27% ethanol. Hydrolyses were carried out at the reflux temperature of the mixture for one-half hour. After cooling, excess alkali was titrated with standard acid. A blank determination was run. Analyses of synthetic mixtures indicated an accuracy of ±2% and infrared analyses of two mixtures for benzyl chloride agreed within ±2% of the titration values.

Acknowledgment.—The authors express their appreciation to the American Petroleum Institute for the grant which made this research possible.

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(13) The column was of the total condensation, partial take-off type packed with $^3/_{64}''$ stainless steel helices. The column, with a packed section 1.1 × 75 cm., had 80 theoretical plates.

(14) The fractions had amounts of benzyl chloride varying from 33–100%. Qualitative tests showed no halogen present but chlorine; however analysis for total halogen indicated that some additional chlorine-containing compound was present in these fractions. This could not be identified and amounted to approximately 4 g.

(15) Nine to ten theoretical plates. To be described in a separate publication to be submitted to *Analytical Chemistry*.

(16) Schiessler, *et al.*, *Proc. A.P.I.*, **26** (III), 254–302 (1946).

(17) Gilman and Meyers, THIS JOURNAL, **45**, 159 (1923).

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Dehalogenation of 2-Amino-4-methyl-6-chloropyrimidine

BY D. SHAPIRO

Hydrogen is evolved vigorously from an alcoholic or aqueous solution of ammonium chloride, when heated with zinc in presence of Raney nickel. It appears that Raney nickel catalyzes the otherwise sluggish[1,2] reaction

$$2NH_4Cl + Zn \longrightarrow ZnCl_2 + 2NH_3 + H_2$$

Part of the ammonia, liberated according to this equation, accompanies the hydrogen; part is bound by the zinc salt.

The above system was found to dehalogenate smoothly 2-amino-4-methyl-6-chloropyrimidine to the 2-amino-4-methyl compound which is an intermediate in the synthesis of sulfamerazine.[3]

A solution of 20 g. of 2-amino-4-methyl-6-chloropyrimidine[4] in a mixture of 16 cc. of concentrated hydrochloric acid and 250 cc. of water (40–50°) was neutralized with a solution of 7 g. of sodium hydroxide in 100 cc. of water, with vigorous stirring; the temperature was raised to 70–75°, and 20 g. of ammonium chloride and 1.5 g. of Raney nickel added. Over a period of 90 minutes, 40 g. of zinc dust was introduced, causing a lively effervescence of the mass. (Occasionally, it was found advisable to add another 2 g. of Raney nickel to the mixture.) Stirring and heating were continued for one more hour and, after addition of a solution of 26 g. of sodium hydroxide in 80 cc. of water, for 30 more minutes and at 90–95°. The solid was removed by filtration, washed with hot water, and the filtrate evaporated *in vacuo* to a volume of about 200 cc. At boiling temperature, 100 cc. of 30% sodium hydroxide solution was added. After 12 hours, the crystals of 2-amino-4-methyl-pyrimidine were filtered and dissolved in boiling acetone. The filtered solution, upon concentration, gave 12 g. (80%) of product of correct m.p. 159–161°. The method is quicker

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(1) Ritthausen, *J. prakt. Chem.*, **60**, 473 (1893).

(2) Drucker, *Z. Elektrochem.*, **29**, 412 (1923).

(3) Roblin, *et al.*, THIS JOURNAL, **62**, 2002 (1940).

(4) Gabriel and Coleman, *Ber.*, **32**, 2921 (1899).