The reaction of benzylmagnesium chloride with aliphatic aldehydes was studied. Monomeric formaldehyde yields o-tolylcarbinol (I, R = H) but no 2-phenylethanol, which is in accord with the classical example of Tiffeneau and Delange, but contradicts the recent report of Mousseron and Du. The latter claim that gaseous formaldehyde, or formaldehyde dissolved in ether, reacts to form II (R = H) but agree that polyoxymethylene yields I (R = I).

Other reactants such as acetyl chloride and chloro-methyl ether give rise to o-tolyl derivatives as well as products which would normally be expected. Benzaldehyde and citronellal appear to be unique in that compounds (II) resulting from the combination of two molecules of the aldehyde and one of the Grignard reagent are formed along with the normal product (II). In contrast to the behavior of these aldehydes, the reaction of acetaldehyde with benzylmagnesium chloride is reported to yield only the normal product but this investigation was incomplete. In an attempt to clarify this problem, the reaction of benzylmagnesium chloride with seven aliphatic aldehydes was studied including a reinvestigation of the reaction with monomolecular formaldehyde.

The classical example of the abnormal reaction of benzylmagnesium chloride is that with formaldehyde in which o-tolylcarbinol (I, R = H) is formed instead of the expected benzylcarbinol (II, R = H). Other reactants such as acetyl chloride and chloromethyl ether give rise to o-tolyl derivatives as well as products which would normally be expected. Benzaldehyde and citronellal appear to be unique in that compounds (II) resulting from the combination of two molecules of the aldehyde and one of the Grignard reagent are formed along with the normal product (II). In contrast to the behavior of these aldehydes, the reaction of acetaldehyde with benzylmagnesium chloride is reported to yield only the normal product but this investigation was incomplete. In an attempt to clarify this problem, the reaction of benzylmagnesium chloride with seven aliphatic aldehydes was studied including a reinvestigation of the reaction with monomolecular formaldehyde.

With the exception of the latter, each aldehyde formed both normal products (II), and "abnormal" products of type (III), but no o-tolyl derivatives. Formaldehyde yielded o-tolylcarbinol. There was no evidence that a compound of type (II) was present.

Table I presents the yields of the products obtained under standardized conditions in which the aldehyde was added to the Grignard reagent. Addition of the Grignard reagent to the aldehyde has been shown to increase the per cent. of "abnormal" products.

Table I

YIELDS OF PRODUCTS FROM THE REACTION OF BENZYL MAGNESIUM CHLORIDE WITH ALDEHYDES

<table>
<thead>
<tr>
<th>Aldehyde</th>
<th>Theoretical %</th>
<th>Mole per cent. of abnormal product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formaldehyde</td>
<td>40</td>
<td>100</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>61</td>
<td>47</td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>97</td>
<td>64</td>
</tr>
<tr>
<td>n-Butyraldehyde</td>
<td>73</td>
<td>45</td>
</tr>
<tr>
<td>3-Butyraldehyde</td>
<td>88</td>
<td>15</td>
</tr>
<tr>
<td>n-Heptaldehyde</td>
<td>69</td>
<td>20</td>
</tr>
<tr>
<td>2-Ethylhexaldehyde</td>
<td>72</td>
<td>8</td>
</tr>
</tbody>
</table>

*This yield is a minimum value based upon the quantity of polyoxymethylene used in preparing the monomeric formaldehyde.

The methyl ether, prepared by the action of methyl sulfate, crystallized as colorless, paralellogram-shaped plates, m.p. 157-158º. Benzaldehyde, prepared as in the case of the homolog, crystallized as colorless irregular plates, m.p. 158-158.5º.
results are presented in Table 11.

...oxidation experiments showing the complete absence of "abnormal" products in the lower boiling fraction. The "abnormal" product. ...the crystalline isomers which separated from the fraction containing the "abnormal" product.

**Experimental**

**Reaction of Benzylmagnesium Chloride with Aliphatic Aldehydes.** Benzylmagnesium chloride was prepared as described previously. Approximately 0.3 mole of the appropriately freshly distilled aldehyde in three volumes of ether was added slowly to the stirred Grignard reagent (approximately 0.40 mole in 500 ml. of ether). The reaction mixture was stirred for one hour after all the aldehyde had been added. It was then decomposed with ice and aqueous sodium carbonate solution, dried over potassium carbonate and distilled. After removal of the solvent and toluene, the product was readily separated by distillation at reduced pressure into two fractions, the lower boiling constituting the normal product and the higher boiling the "abnormal" product.

**Properties of Normal Products.** The normal products were distillable at reduced pressure in each case, providing precautions were taken to exclude acids.

**Properties of the "Abnormal" Products.** The "abnormal" products showed 1.9 active hydrogens per mole by the Zerewitinoff method.

**Identification of Normal Products.** The normal products isolated were identified by elementary analysis, oxidation by potassium permanganate in pyridine which yields benzoic acid and/or analogy to previously examined examples. An example of the typical procedure is the following:

**Identification of Abnormal Products.** The abnormal products were identified by elementary analysis, oxidation by potassium permanganate in pyridine which yields o-tolylcarbinol. A small fraction of the "normal" product was obtained directly from liquid formaldehyde which gave o-tolylcarbinol. These were obtained by the Rast method.

**Aldehyde**

<table>
<thead>
<tr>
<th>Aldehyde</th>
<th>B.p.</th>
<th>M.p.</th>
<th>M.p., °C</th>
<th>Yield of ox. prod., %</th>
<th>Carbon, %</th>
<th>Hydrogen, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formaldehyde</td>
<td>72-74</td>
<td>0.7</td>
<td>31.5-32.5</td>
<td>50</td>
<td>C2H4O2</td>
<td>73.80</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>118-129</td>
<td>1.0</td>
<td>83-84</td>
<td>82</td>
<td>C2H4O2</td>
<td>73.30</td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>152-153</td>
<td>3.0</td>
<td>65.5-66.5</td>
<td>79</td>
<td>C3H6O2</td>
<td>74.96</td>
</tr>
<tr>
<td>n-Butyraldehyde</td>
<td>160-167</td>
<td>2.0</td>
<td>79.5-79.8</td>
<td>63</td>
<td>C4H8O2</td>
<td>76.22</td>
</tr>
<tr>
<td>α-Butyraldehyde</td>
<td>125-131</td>
<td>0.5</td>
<td>86.5-87.0</td>
<td>71</td>
<td>C4H8O2</td>
<td>76.72</td>
</tr>
<tr>
<td>α-Heptaldehyde</td>
<td>180-186</td>
<td>0.5</td>
<td>53.5-54.0</td>
<td>60</td>
<td>C7H14O2</td>
<td>76.89</td>
</tr>
<tr>
<td>2-Ethylheptaldehyde</td>
<td>177-179</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* ppm: Melting points of the crystalline isomers which separated from the fraction containing the "abnormal" product. Usually this was less than 30% of the fraction except for the reaction product from formaldehyde which consisted of a single isomer. The oxidation product was o-phthalic acid except for the product from the reaction with formaldehyde which gave α-toluic acid. * These products showed 1.9 active hydrogens per mole by the Zerewitinoff method.

The molecular weights of the products from acetaldehyde and propionaldehyde were 180 (calcd. 180) and 208 (calcd. 207), respectively. The reaction mixture was stirred for one-half hour while the addition of the aldehyde was complete. It was decom-
posed by a saturated solution of ammonium chloride which was added dropwise until a heavy precipitate separated from the clear ether solution. The precipitate was washed with three 100-ml. portions of ether, the washings being combined with the ether solution. From this ether extract toluene (35 g.), o-tolylcarbinol (35 g.), b.p. 100-105°C (10 mm.), m.p. 30-32°C; and a higher boiling fraction (6.8 g.), b.p. 124-130°C (10 mm.), from which bibenzyl was isolated, m.p. 48-50°C, and mixed m.p. with an authentic sample 47-50°C. Refractionation of the o-tolylcarbinol yielded a center cut which had the properties: b.p. 72-74°C (0.7 mm.), m.p. 31.5-32.5°C, and v 15 1.5403. The o-tolylcarbinol (0.5 g.) was oxidized with an excess of 5% potassium permanganate solution until the aldehyde odor disappeared. The mixture was not heated. The excess oxidant was destroyed with a small amount of sodium bisulfite. The solution was filtered free of manganese dioxide, which was washed with a little dilute NaOH solution. The washings were combined with the filtrate, and acidified with concentrated hydrochloric acid. The solution was cooled. The precipitate was collected, washed with distilled water and dried in vacuo. The product weighed 0.20 g., m.p. 102.5-103.5°C. A mixed melting point with authentic o-tolylcarbinol was 105-104°C.

**Discussion of Results**

We shall restrict our discussion to the effect of structural variations in the aldehyde upon the course of the reaction with benzylmagnesium chloride. Other important considerations pertaining to the abnormal reactions of this Grignard reagent have been discussed by Gilman and Johnson.

The sequence of reactions which led to the "normal" and "abnormal" products may be formulated as

$$\text{RCHO} + \text{CH}_2\text{MgX} \rightarrow \text{CH}_2\text{CHOMgX}$$

An interpretation of reactions (1) and (2) as two possible transformations within a reaction complex (IX) was first proposed by Johnson.

$$\text{CH}_2\text{CHOMgX} \rightarrow \text{CH}_2\text{CHO} + \text{H}_2\text{MgX}$$

His detailed mechanism was later modified by Young and Siegel to account for the marked increase in yield of abnormal product which accompanies an increase in the concentration of aldehyde. Their suggestion is equivalent to the statement that the molecularity of reaction (1) is less than that of reaction (2), a larger number of molecules of aldehyde being required in the transition state for the "abnormal" reaction (2). The formation of the "abnormal" product of type III (R ≠ H) demands that the transformation VI → VII require a base (B-) which is probably the Grignard reagent. An intramolecular transfer of the hydrogen (*) VI → IX is improbable because no o-tolylcarbinols (except the one formed in the reaction with formaldehyde) are isolated.

The structural distinction between the "abnormal" products obtained in the reaction with formaldehyde from the "abnormal" products obtained with other aldehydes suggests that with formaldehyde, reaction (2) is much faster than reactions (1), (3) or (4). For the other aldehydes studied reactions (3) and (4) must be faster than (2). However, the ratio of normal to "abnormal" product is a measure of the relative rates of reactions (1) and (2).

The ratio of "normal" to "abnormal" products is apparently a function of the electrophilic character of the reactant. The reactants which have been classed as "abnormal" are usually the better acylating or alkylation agents than structurally related "normal" reactants, e.g., acyl halides give some "abnormal" products, esters give the "normal." Although increasing the electrophilic power of the reactant should increase the rate of both reactions (1) and (2), the second reaction seemingly is favored.

The relation of structure to electrophilic character of an aldehyde can be drawn from a consideration of the hyperconjugation effects of the group attached to the carbonyl carbon atom. Thus acetaldheyde should be less electrophilic than formaldehyde because the hyperconjugation between

$$\text{H}_3\text{C}=\text{C}=\text{O} \leftrightarrow \Theta$$

the methyl and carboxyl groups of the former disperses the positive charge ordinarlly concentrated on the carbonyl carbon atom.

The hyperconjugation effect appears distinctly in the assignment by Pauling of three different values for the bond energies of the carbon–oxygen double bond in formaldehyde, other aldehydes and ketones (142, 149 and 152 kcal./mole, respectively).

The bond energies reflect the enhanced stability of the carbonyl group as the hydrogens in formaldehyde are replaced by alkyl groups.

If the energy differences are taken as a measure of the hyperconjugation effect then these carbonyl compounds should be placed in the following order for decreasing electrophilic power: formaldehyde > other aldehydes > ketones. This is the observed decreasing order for the per cent. of "abnormal" products. formaldehyde yielding only abnormal products, other aldehydes both "normal" and "abnormal" products and ketones only "normal" products.

The variation of the electrophilic property of the carbonyl group in going from acetaldehyde to its higher homologs should be much less pronounced than for the change formaldehyde to acetaldehyde. Although the hyperconjugative power of alkyl groups has been placed in the order Me > Et > Pr > Bu (which correlates small differences in reaction rates), the effect is too small to make a significant variation in thermochemical data. The theory of hyperconjugation would predict the following order for decreasing electrophilic powers: i-butyraldehyde > propionaldehyde > acetaldehyde but the differences might easily be masked by some other effect. Evidently, although propionaldehyde gives a higher per cent. of "abnormal" product than does acetaldehyde, the higher homologs give a lower proportion of "abnormal" product. Alkyl substituted aldehydes give particularly low yields of the "abnormal" product. The trend suggests that a steric effect is superposed on the electrical effect and causes the variation.

In an earlier paper, it was suggested that hydrogen bonding might be responsible for the unique stabilization of 1-anthraquinonensulfenic acid. As one approach to testing this hypothesis, the synthesis of the structural analog. 1-fluorenensulfenic acid, was attempted. This objective was, however, not attained; and the conclusion is made that the isolation of 1-fluorenensulfenic acid and its salts is precluded by the predominant tendency of these substances to disproportionate to 1-fluorenonyl disulfide and 1-fluorenoensulfonic acid. An entire series of 1-fluorenone sulfur compounds has, however, been synthesized, and several interesting similarities and differences between these compounds and their 1-anthraquinone analogs are noted. Some improvements in the synthesis of 1-aminofluorenone and the 1-halofluorones are described.

In 1912, Fies1 reported the successful isolation of 1-anthraquinonensulfenic acid (I) and certain of its salts. Since then, however, all attempts to find other sulfenic acids—in the anthraquinone series, as well as in the benzene series—have not been successful. In contrast, in the less extensively investigated selenium analogs, three selenenic acids (ArSeOH) have been reported. Interest in the sulfenic acids, as such, is thus enhanced by the unique isolation of the single member of this class (I), by the contrasting existence of corresponding selenenic acids, and by the circumstance that—in spite of their non-isolation—free sulfenic acids have very frequently been invoked as intermediates in studies concerned with the chemistry and biochemistry of various classes of organic sulfur compounds.

In a recent review, it was suggested that the stabilization of 1-anthraquinonensulfenic acid may be caused by hydrogen bonding as shown in structure II. As a first step in testing this hypothesis, it was desired to establish whether a similar stabilization would be observed in 1-fluorenoensulfenic acid. The work in the fluorenone series was therefore patterned closely on that in the anthraquinone series.

Fries accomplished the isolation of 1-anthraquinonensulfenic acid by converting methyl 1-anthraquinonesulfenolate to potassium 1-anthraquinonesulfenate (by treatment with potassium hydroxide), then liberating the free sulfenic acid from the salt by the action of acetic acid. When methyl 1-fluorenoensulfenate was treated similarly, however, we obtained only 1-fluorenoen disulfide

(1) This paper is based on an undergraduate research thesis submitted by Thomas C. Bruice.
(2) K. Fries, Ber., 45, 2965 (1912).
(3) K. Fries and G. Schürmann, ibid., 83, 2170 (1950).
(4) K. Fries and G. Schürmann, ibid., 85, 2182 (1951).
(6) T. Zincke and K. Elsmayer, Ber., 51, 751 (1918).
(8) T. Zincke and S. Lehnardt, ibid., 400, 1 (1913).
(9) T. Zincke and H. Röse, ibid., 406, 105 (1914).
(10) O. Behaghel and co-workers, Ber., 66, 812 (1932); 66, 708 (1933); 59, 1540 (1935); 73, 582, 697 (1950). For a brief review of this work see reference 11, pp. 277-279.
(12) The original work of Fries on 1-anthraquinonesulfenic acid was confirmed in this laboratory by Mr. Albert T. Powell.