

*Anal.* Calcd. for  $C_{22}H_{20}O_2$ : C, 83.51; H, 6.37. Found: C, 8.360; H, 6.54.

**9-(*p*-Hydroxyphenyl)-10-methylphenanthrene.**—The above ketone (2.3 g.) was refluxed for 18 hours with a mixture of hydrobromic and acetic acids and the reaction mixture was worked up as in the synthesis of the homolog (IX). The product crystallized from benzene-ligroin as clusters of white needles, m.p. 149–150.5°; yield 1.7 g. (82%). The analytical sample melted at 150.5–151°.

*Anal.* Calcd. for  $C_{21}H_{18}O$ : C, 88.70; H, 5.67. Found: C, 89.00; H, 5.89.

**The methyl ether**, prepared by the action of methyl sulfate, crystallized as colorless, parallelogram-shaped plates, m.p. 137–138°.

*Anal.* Calcd. for  $C_{22}H_{18}O$ : C, 88.56; H, 6.08. Found: C, 88.67; H, 6.22.

**The acetate**, prepared as in the case of the homolog, crystallized as colorless irregular plates, m.p. 158–158.5°.

*Anal.* Calcd. for  $C_{23}H_{18}O_2$ : C, 84.62; H, 5.56. Found: C, 84.58; H, 5.68.

DURHAM, N. C.

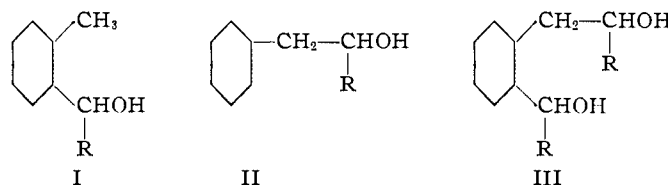
RECEIVED JANUARY 25, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

## The Reaction of Benzylmagnesium Chloride with Aliphatic Aldehydes<sup>1</sup>

BY SAMUEL SIEGEL, WILLIAM M. BOYER AND RAYMOND R. JAY

The reaction of benzylmagnesium chloride with seven 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<sup>2</sup> but contradicts the recent report of Mousseron and Du.<sup>3</sup> The latter claim that gaseous formaldehyde, or formaldehyde dissolved in ether, reacts to form II (R = H) but agree that polyoxymethylene yields I (R = H).



Acetaldehyde, propionaldehyde, *n*-butyraldehyde, *i*-butyraldehyde, 2-ethylhexaldehyde and *n*-heptaldehyde yield mixtures of compounds of types II and III but none of type I. The mole per cent. of "abnormal" product (III) formed is in the order of the aldehydes listed: 47, 64, 45, 15, 20 and 8. These results are consistent with the mechanism proposed previously for the reaction of citronellal with benzylmagnesium chloride.<sup>4</sup> The relation of structure of the aldehyde to the ratio of "abnormal" (III) to normal (I) products is explained in terms of the contributions of hyperconjugation and steric factors.

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).<sup>2</sup> Other reactants such as acetyl chloride and chloromethyl ether give rise to *o*-tolyl derivatives as well as products which would normally be expected.<sup>5,6</sup> Benzaldehyde<sup>7,8</sup> and citronellal<sup>4</sup> appear to be unique in that compounds (III) 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<sup>9</sup> with benzylmagnesium chloride is reported to yield only the normal product but this investigation was incomplete.<sup>10</sup> 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.<sup>4,7,8</sup>

TABLE I

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

Aldehyde	Theoretical yield, %	Mole per cent. abnormal product
Formaldehyde	40 <sup>a</sup>	100
Acetaldehyde	61	47
Propionaldehyde	97	64
<i>n</i> -Butyraldehyde	73	45
<i>i</i> -Butyraldehyde	88	15
<i>n</i> -Heptaldehyde	69	20
2-Ethylhexaldehyde	72	8

<sup>a</sup> This yield is a minimum value based upon the quantity of polyoxymethylene used in preparing the monomeric formaldehyde.

Proceeding along the homologous series of straight chained aliphatic aldehydes beyond formaldehyde the yield of "abnormal" product (III) reaches a maximum with propionaldehyde. The yield decreases with increasing chain length and par-

(1) Presented before the Organic Division at the Chicago Meeting of the American Chemical Society, September 3–10, 1950.

(2) M. Tiffeneau and Delange, *Compt. rend.*, **137**, 573 (1903).

(3) M. Mousseron and N. P. Du, *Bull. soc. chim.*, [5] **15**, 91 (1948).

(4) W. G. Young and S. Siegel, *THIS JOURNAL*, **66**, 354 (1944).

(5) H. Gilman and J. E. Kirby, *ibid.*, **54**, 345 (1932).

(6) P. R. Austin and J. R. Johnson, *ibid.*, **54**, 647 (1932).

(7) J. Schmidlin and A. Garcia-Banús, *Ber.*, **45**, 3193 (1912).

(8) S. Siegel, S. K. Coburn and D. R. Levering, *THIS JOURNAL*, **73**, 3164 (1951).

(9) F. C. Whitmore and T. K. Sloat, *ibid.*, **64**, 2968 (1942).

(10) J. R. Johnson, *ibid.*, **55**, 3029 (1933) in a footnote referred to . . . "unpublished work of Mr. L. G. Davy shows that acetaldehyde and *n*-butyraldehyde induce the *o*-tolyl rearrangement to an appreciable extent." To our knowledge nothing more has appeared on this matter.

TABLE II  
 PROPERTIES OF NORMAL PRODUCTS

Aldehyde	°C. B.p.	Mm.	$n_D^{20}$	Formula	Carbon, % <sup>a</sup>		Hydrogen, %	
					Calcd.	Found	Calcd.	Found
Acetaldehyde	64-65	0.7	1.5205	C <sub>2</sub> H <sub>4</sub> O	79.36	79.32	8.88	9.00
Propionaldehyde	76-78	3.0	1.5167	C <sub>3</sub> H <sub>6</sub> O	79.96	80.06	9.39	9.71
<i>n</i> -Butyraldehyde	73-74	0.5	1.5082	C <sub>4</sub> H <sub>8</sub> O	80.44	79.28	9.82	9.87
<i>i</i> -Butyraldehyde	72-73	.5	1.5091	C <sub>4</sub> H <sub>8</sub> O	80.44	80.54	9.82	10.00
<i>n</i> -Heptaldehyde	101-102	.7	1.4982	C <sub>7</sub> H <sub>14</sub> O	81.50	81.27	10.75	10.71
2-Ethylhexaldehyde	106-107	.6	1.4986	C <sub>8</sub> H <sub>16</sub> O	81.76	82.02	10.98	10.90

<sup>a</sup> Micro-analyses by Charles Beazley, Micro-Tech Laboratories, Skokie, Illinois.

 TABLE III  
 PROPERTIES OF THE "ABNORMAL" PRODUCTS

Aldehyde used	°C. B.p.	Mm.	M.p., °C.	Yield of oxidn. prod., % <sup>b</sup>	Formula	Carbon, %		Hydrogen, %	
						Calcd.	Found	Calcd.	Found
Formaldehyde	72-74	0.7	31.5-32.5	50	.....	...	...	...	...
Acetaldehyde <sup>c,d</sup>	128-129	1.0	83-84	82	C <sub>11</sub> H <sub>16</sub> O <sub>2</sub>	73.30	73.47	8.95	8.96
Propionaldehyde <sup>c,d</sup>	152-153	3.0	65.5-66.5	79	C <sub>13</sub> H <sub>20</sub> O <sub>2</sub>	74.96	75.00	9.68	9.82
<i>n</i> -Butyraldehyde <sup>c</sup>	160-167	2.0	79.5-79.8	43	C <sub>15</sub> H <sub>24</sub> O <sub>2</sub>	76.22	76.10	10.24	10.18
<i>i</i> -Butyraldehyde	128-131	0.5	86.5-87.0	..	C <sub>15</sub> H <sub>24</sub> O <sub>2</sub>	76.22	76.73	10.24	10.48
<i>n</i> -Heptaldehyde	180-186	.5	53.5-54.0	..	C <sub>21</sub> H <sub>36</sub> O <sub>2</sub>	78.69	78.44	11.32	11.35
2-Ethylhexaldehyde	177-179	.5	.....	..	.....	...	...	...	...

<sup>a</sup> 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. <sup>b</sup> The oxidation product was *o*-phthalic acid except for the product from the reaction with formaldehyde which gave *o*-toluic acid. <sup>c</sup> These products showed 1.9 active hydrogens per mole by the Zerewitinoff method. <sup>d</sup> The molecular weights of the products from acetaldehyde and propionaldehyde were 180 (calcd. 180) and 208 (calcd. 207), respectively. These were obtained by the Rast method.

ticularly with the substitution of alkyl groups in the  $\alpha$ -position to the carbonyl group.

A recent report<sup>3</sup> claims that gaseous formaldehyde in contrast to the polymer reacts with benzylmagnesium chloride to produce  $\beta$ -phenylethyl alcohol. Our results are contrary to this claim since we found only *o*-tolylcarbinol. A small fraction of higher boiling material was not identified but may contain a substance of type (III). The formaldehyde introduced into the Grignard reagent in our experiments was unquestionably the monomer since it was obtained directly from liquid formaldehyde. The monomer can be retained so long as moisture is rigorously excluded.<sup>11</sup>

### Experimental

**Reaction of Benzylmagnesium Chloride with Aliphatic Aldehydes.**—Benzylmagnesium chloride was prepared as described previously.<sup>4</sup> Approximately 0.3 mole of the appropriate 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 acetic acid. The ether-soluble portion was washed repeatedly with 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.

**Identification of Normal Products.**<sup>4,8</sup>—The normal products were identified by elementary analysis, oxidation by permanganate in pyridine which yields benzoic acid and analysis for active hydrogen by the Zerewitinoff method. No more than a trace of phthalic acid was isolated from the oxidation experiments showing the complete absence of "abnormal" products in the lower boiling fraction. The results are presented in Table II.

**Identification of "Abnormal" Products.**—The "abnormal" products were distillable at reduced pressure in each case, providing precautions were taken to exclude acids.

(All glassware was rinsed with dilute ammonia, then water and dried. A few tenths of a gram of potassium carbonate was added to the boiler of the still before the distillation was begun.) The "abnormal" products were viscous liquids which partly crystallized after standing several weeks at room temperature. The product from the reaction with acetaldehyde was recrystallized most satisfactorily from ethyl acetate. Petroleum ether (60-80°) was a more suitable solvent for the higher molecular weight compounds. They were identified by elementary analysis, oxidation with potassium permanganate in pyridine which yielded *o*-phthalic acid, Zerewitinoff analysis for active hydrogen and/or analogy to previously examined examples<sup>4,8</sup> (see Table III). An example of the typical procedure is the following:

**The "Abnormal" Product from the Reaction of Propionaldehyde with Benzylmagnesium Chloride.**—From 0.50 mole of propionaldehyde and 0.57 mole of benzylmagnesium chloride was obtained 40 g. (0.19 mole) of the "abnormal" product, b.p. 155-156° (4 mm.),  $n_D^{20}$  1.5272.

A portion of this product (2.90 g.) was oxidized with potassium permanganate (29 g.) in pyridine for eight hours, the potassium permanganate being added as needed. The products were isolated as described previously<sup>4</sup> and consisted of phthalic acid (1.83 g., 79% yield) and some incompletely oxidized material. The phthalic acid was sublimed to yield the anhydride (m.p. 129.5-130°). No benzoic acid was isolated.

The molecular weight (Rast method<sup>4</sup>) was 207 (calculated 208), and the Zerewitinoff analysis<sup>4</sup> showed 1.89 active hydrogens per mole.

On standing for several weeks at room temperature the "abnormal" product partially crystallized. The crystals were separated by filtration and recrystallized from petroleum ether which contained a small amount of ethyl acetate (m.p. 65.5-66.5°). This material showed 1.89 active hydrogen atoms per 208 and is, therefore, one of the possible isomers constituting the "abnormal" product.

**The Reaction of Monomolecular Formaldehyde with Benzylmagnesium Chloride.**—Liquid formaldehyde was prepared from  $\alpha$ -polyoxymethylene (20 g., 0.66 mole of formaldehyde) according to the method of Walker.<sup>11</sup> It was distilled in a stream of nitrogen into the reaction vessel containing benzylmagnesium chloride (0.85 mole in one liter of solution). The inlet tube was above the surface of the solution.

The reaction mixture was stirred for one-half hour after the addition of the aldehyde was complete. It was decom-

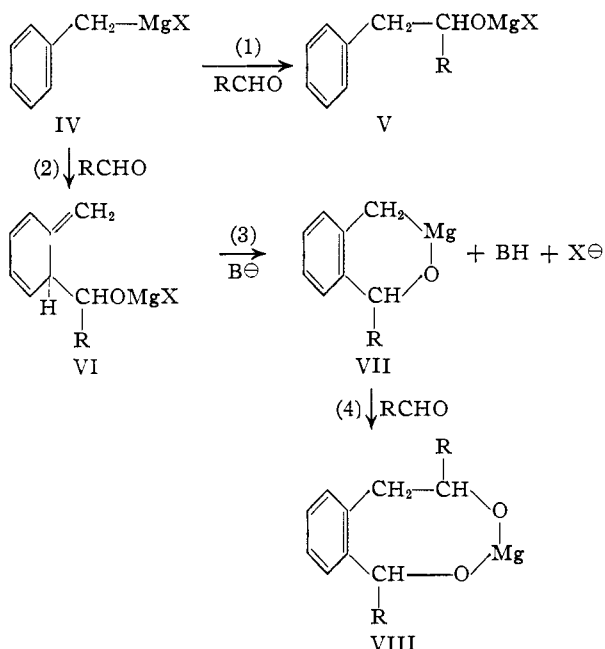
(11) J. F. Walker, THIS JOURNAL, 55, 2825 (1935).

posed by a saturated solution of ammonium chloride which was added dropwise until a heavy precipitate separated from the clear ether solution.<sup>12</sup> 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° (10 mm.), m.p. 30–32°; and a higher boiling fraction (6.8 g.), b.p. 124–180° (10 mm.), from which bibenzyl was isolated, m.p. 48–50°, and mixed m.p. with an authentic sample 47–50°. Refractionation of the *o*-tolylcarbinol yielded a center cut which had the properties: b.p. 72–74° (0.7 mm.), m.p. 31.5–32.5°, and  $n_D^{20}$  1.5403.

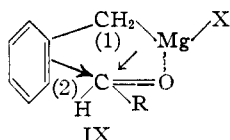
The *o*-tolylcarbinol (0.5 g.) was oxidized with an excess of 5% potassium permanganate solution until the aldehyde odor disappeared. The mixture was not heated. The excess oxidant was destroyed with a small amount of sodium bisulfite. The solution was filtered free of manganese dioxide, which was washed 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 0.30 g., m.p. 102.5–103.5°. A mixed melting point with authentic *o*-toluic acid was 103–104°.

### 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<sup>5</sup> and Johnson.<sup>10</sup> The sequence of reactions which led to the "normal" and "abnormal" products may be formulated as

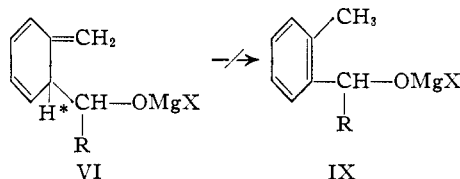


An interpretation of reactions (1) and (2) as two possible transformations within a reaction complex (IX) was first proposed by Johnson.<sup>10</sup>



(12) L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., New York, N. Y., 1941, p. 410.

His detailed mechanism was later modified by Young and Siegel<sup>4</sup> 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).<sup>13</sup> The formation of the "abnormal" product of type III ( $\text{R} \neq \text{H}$ ) demands that the transformation VI  $\rightarrow$  VII require a base ( $\text{B}^-$ ) which is probably the Grignard reagent. An intramolecular transfer of the hydrogen (\*) VI  $\rightarrow$  IX is improbable because no *o*-tolylcarbinols (ex-

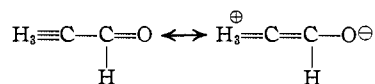


cept the one formed in the reaction with formaldehyde) are isolated.

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 alkylating agents than structurally related "normal" reactants, *e.g.*, acyl halides give some "abnormal" products, esters give the "normal."<sup>6</sup> 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 acetaldehyde should be less electrophilic than formaldehyde because the hyperconjugation between



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

The hyperconjugation effect appears clearly in the assignment by Pauling<sup>14</sup> 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).

(13) See C. G. Swain and L. Kent, THIS JOURNAL, **72**, 518 (1950), for a kinetic study and interpretation of a Grignard reaction.

(14) L. Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, New York, 1945, p. 131.

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.<sup>15</sup> 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

(15) For a discussion of the dipole moments of carbonyl compounds in terms of hyperconjugation see E. C. Hurdis and C. P. Smyth, *This Journal*, **65**, 89 (1943).

groups has been placed in the order Me > Et > Pr<sup>β</sup> > Bu<sup>γ</sup> (which correlates small differences in reaction rates),<sup>16</sup> the effect is too small to make a significant variation in thermochemical data.<sup>17</sup> 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. And  $\alpha$ -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.

(16) E. D. Hughes, C. K. Ingold and N. A. Taber, *J. Chem. Soc.*, 949 (1940).

(17) G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 54.

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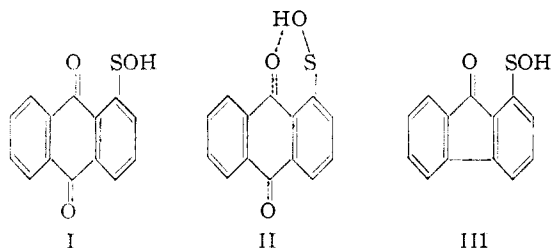
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

## Derivatives of Sulfenic Acids. V. 1-Fluorenone Sulfur Compounds<sup>1</sup>

BY NORMAN KHARASCH AND THOMAS C. BRUCE

In an earlier paper, it was suggested that hydrogen bonding might be responsible for the unique stabilization of 1-antraquinonesulfenic acid. As one approach to testing this hypothesis, the synthesis of the structural analog, 1-fluorenesulfenic acid, was attempted. This objective was, however, not attained; and the conclusion is made that the isolation of 1-fluorenesulfenic acid and its salts is precluded by the predominant tendency of these substances to disproportionate to 1-fluorenyl disulfide and 1-fluorenesulfonic 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-antraquinone analogs are noted. Some improvements in the synthesis of 1-aminofluorenone and the 1-halofluorenes are described.

In 1912, Fries<sup>2</sup> reported the successful isolation of 1-antraquinonesulfenic acid (I) and certain of



its salts. Since then, however, all attempts to find other sulfenic acids—in the anthraquinone series,<sup>3,4</sup> as well as in the benzene series<sup>5-9</sup>—have not been successful. In contrast, in the less extensively investigated selenium analogs, three selenenic acids (ArSeOH) have been reported.<sup>10</sup> 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.<sup>11</sup>

In a recent review,<sup>11</sup> it was suggested that the stabilization of 1-antraquinonesulfenic 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-fluorenesulfenic acid (III). The work in the fluorenone series was therefore patterned closely on that in the anthraquinone series.

Fries accomplished the isolation of 1-antraquinonesulfenic acid by converting methyl 1-antraquinonesulfenate to potassium 1-antraquinonesulfenate (by treatment with potassium hydroxide), then liberating the free sulfenic acid from the salt by the action of acetic acid.<sup>12</sup> When methyl 1-fluorenesulfenate was treated similarly, however, we obtained only 1-fluorenyl disulfide

(11) N. Kharasch, S. J. Potempa and H. L. Wehrmeister, *Chem. Rev.*, **39**, 269 (1946).

(12) The original work of Fries on 1-antraquinonesulfenic acid was confirmed in this Laboratory by Mr. Albert T. Fowler.

(1) This paper is based on an undergraduate research thesis submitted by Thomas C. Bruce.

(2) K. Fries, *Ber.*, **45**, 2965 (1912).

(3) K. Fries and G. Schürmann, *ibid.*, **52**, 2170 (1919).

(4) K. Fries and G. Schürmann, *ibid.*, **52**, 2182 (1919).

(5) T. Zincke and J. Baeumer, *Ann.*, **416**, 86 (1918).

(6) T. Zincke and K. Eismayer, *Ber.*, **51**, 751 (1918).

(7) T. Zincke and F. Farr, *Ann.*, **391**, 55 (1912).

(8) T. Zincke and S. Lenhardt, *ibid.*, **400**, 1 (1913).

(9) T. Zincke and H. Röse, *ibid.*, **406**, 103 (1914).

(10) O. Behaghel and co-workers, *Ber.*, **65**, 812 (1932); **66**, 708 (1933); **68**, 1540 (1935); **72**, 582, 697 (1939). For a brief review of this work see reference 11, pp. 277-278.