

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY, LAFAYETTE, IND.]

## The Effect of Coplanarity on the Rates of Solvolysis of Several *t*-Cumyl Chloride Derivatives. Electrophilic Substituent Constants for Polycyclic Aromatics<sup>1,2</sup>

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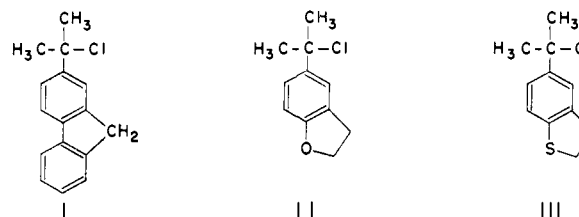
The influence of coplanarity on the rates of solvolysis has been investigated by the synthesis of and rate studies on a number of derivatives of *t*-cumyl chloride: 2-fluorenyl-, 5-coumaranyl- and 5-thiocoumaranyldimethylcarbinyl chlorides, and *o*-methyl-*p*-phenyl and *o*-methyl-*p*-methoxy-*t*-cumyl chlorides. 2-Fluorenyldimethylcarbinyl chloride undergoes solvolysis in 90% acetone at 25° at a rate 173 that of *t*-cumyl chloride, whereas the related *p*-phenyl-*t*-cumyl chloride undergoes solvolysis at a rate which is only 6.5 greater than that of the parent compound. The enhanced rate of the 2-fluorenyl derivative is attributed predominantly to the effect of the coplanar arrangement of the biphenyl system in facilitating resonance stabilization of the electron deficient center in the transition state. In 98% aqueous acetone, 5-coumaranyldimethylcarbinyl chloride undergoes solvolysis at a rate 5.6-fold greater than *p*-methoxy-*t*-cumyl chloride, and 5-thiocoumaranyldimethylcarbinyl chloride undergoes solvolysis at a rate 4.7 times greater than the related *p*-methylthio-*t*-cumyl chloride. These modest increases in rates accompanying the incorporation of the oxygen and the sulfur atoms within a 5-membered ring indicate that there is no significant inhibition of resonance either in the *p*-methoxy or the *p*-methylthiophenyl structures. Finally, an *o*-methyl substituent decreases the activating effect of *p*-phenyl by a small factor, 25%, and that of *p*-methoxy by a larger factor, 67%. However, the small factors involved indicate that the incipient carbonium ion in the transition state must be able to accommodate deviations from coplanarity of the dimethylcarbinyl system with only minor costs in energy.

The systematic study of the effect of substituents upon the rates of solvolysis of phenyldimethylcarbinyl chloride<sup>5</sup> was undertaken to provide a fuller understanding of the nature and importance of the electronic contributions of various substituents in electron deficient systems.<sup>6,7</sup>

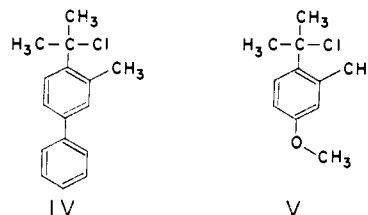
In the course of these studies we observed that the activating effect of the *p*-phenyl substituent is quite low ( $k_{p-Ph}/k_H$  6.5)<sup>6f</sup> relative to *p*-methyl ( $k_{p-Me}/k_H$  26).<sup>6a</sup> It was also considered surprising that the activating effect of *p*-methylthio ( $k_{p-MeS}/k_H$  6860)<sup>6f</sup> was not more different from that of *p*-methoxy ( $k_{p-MeO}/k_H$  41700).<sup>6d</sup>

An interpretation of these phenomena was suggested,<sup>6f</sup> based upon the assumption that the phenyl<sup>8,9</sup> and methoxy<sup>10</sup> substituents encounter difficulty in assuming the coplanar arrangement most favorable for resonance interactions with the electron-deficient center. Both to test this explanation and to obtain quantitative data as to the magnitude of these effects in the *t*-cumyl system, we undertook to examine the solvolysis of derivatives of *t*-cumyl chloride in which the *p*-phenyl (I),

the *p*-methoxy (II) and *p*-methylthio (III) substituents must assume a coplanar configuration as a result of the geometrical requirements of the structures.



An *o*-methyl substituent ( $k_{o-Me}/k_H$  3.63) is much less effective than a *p*-methyl substituent ( $k_{p-Me}/k_H$  26) in facilitating the ionization of the *t*-cumyl chloride.<sup>6a</sup> This was attributed to the effect of the *o*-methyl substituent in reducing the stabilizing conjugation between the methyl group and the incipient *t*-cumyl cation by hindering the coplanar configuration most conducive to such interactions.<sup>11</sup> However, it was not possible to exclude the possibility that hindered solvation of the incipient carbonium ion was a contributing factor. In order to examine the importance of such steric inhibition of resonance upon the transmission of the electronic contributions of electron-supplying groups, we also synthesized and examined the solvolysis of *o*-methyl-*p*-phenyl-*t*-cumyl chloride (IV) and *o*-methyl-*p*-methoxy-*t*-cumyl chloride (V).



### Results

**2-Fluorenyldimethylcarbinyl Chloride.**—Fluorene was acetylated to form 2-acetylfluorene and the latter was converted into 2-fluorenyldimethyl-

(11) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955.

(1) Directive Effects in Aromatic Substitution. XLIV.

(2) This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society.

(3) Research associate, 1956–1958, on a grant (G 95) from the Petroleum Research Fund.

(4) Research associate, 1958–1959, on a grant (G 6271) from the National Science Foundation.

(5) For convenience the parent molecule will be referred to as *t*-cumyl chloride and the derivatives named as substitution products of *t*-cumyl chloride.

(6) (a) H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, *J. Am. Chem. Soc.*, **79**, 1897 (1957); (b) Y. Okamoto and H. C. Brown, *ibid.*, **79**, 1903 (1957); (c) H. C. Brown, Y. Okamoto and G. Ham, *ibid.*, **79**, 1906 (1957); (d) Y. Okamoto and H. C. Brown, *ibid.*, **79**, 1909 (1957); (e) H. C. Brown and Y. Okamoto, *ibid.*, **79**, 1913 (1957); (f) H. C. Brown, Y. Okamoto and T. Inukai, *ibid.*, **80**, 4964 (1958); (g) Y. Okamoto, T. Inukai and H. C. Brown, *ibid.*, **80**, 4969 (1958); (h) **80**, 4972 (1958); (i) Y. Okamoto and H. C. Brown, *ibid.*, **80**, 4976 (1958); (j) H. C. Brown and Y. Okamoto, *ibid.*, **80**, 4979 (1958).

(7) For a summary of these studies, see H. C. Brown, Chapter IX in "Steric Effects in Conjugated Systems," C. W. Gray, editor, Butterworths Scientific Publications, London, 1958.

(8) E. Berliner and N. Shieh, *J. Am. Chem. Soc.*, **79**, 3849 (1957).

(9) P. B. D. de la Mare, D. M. Hall, M. M. Harris and M. Hassan, *Chemistry & Industry*, 1088 (1958).

(10) G. Baddeley, N. H. P. Smith and M. A. Vickars, *J. Chem. Soc.*, 2455 (1956).

TABLE I  
RATE CONSTANTS AND DERIVED DATA FOR THE SOLVOLYSIS OF *p*-PHENYL-*t*-CUMYL CHLORIDE AND RELATED DERIVATIVES IN 90 VOL. % AQUEOUS ACETONE

Aryldimethylcarbinyl chloride ArC(CH <sub>3</sub> ) <sub>2</sub> CCl	Rate constant, $k_1$ , sec. <sup>-1</sup> × 10 <sup>5</sup>			Rate ratio at 25° $k/k_H^d$	$E_{act}$	log $A$	$\Delta H^\ddagger$	$\Delta S^\ddagger$
	-19.2°	0.0°	25.0°					
2-Fluorenyl	12.0	138	2080 <sup>a</sup>	173 <sup>e</sup>	17.5	11.2	17.0	-9.2
4-Biphenyl <sup>b</sup>		4.56	80.8	6.52 <sup>f</sup>	18.6	10.6	18.0	-12.2
3-Methyl-4-biphenyl		11.6	213	17.7 <sup>e</sup>	18.8	11.1	18.3	-9.5
2-Methylphenyl <sup>c</sup>		2.21	45.0	3.63 <sup>f</sup>	19.6	11.0	19.0	-10.4

<sup>a</sup> Calculated from the rate constants at lower temperatures. <sup>b</sup> Data from ref. 6f. <sup>c</sup> Data from ref. 6a. <sup>d</sup>  $k_H$  is the observed rate constant at 25.0° for *t*-cumyl chloride in the particular batch of solvent used in the solvolysis study. <sup>e</sup>  $k_H$  12.0 × 10<sup>-5</sup> sec.<sup>-1</sup>. <sup>f</sup>  $k_H$  12.4 × 10<sup>-5</sup> sec.<sup>-1</sup>.

carbinol *via* the Grignard reaction. The carbinol was treated with hydrogen chloride to form the chloride.

The rate of solvolysis was determined in 90 vol. % acetone.<sup>6</sup> Because the rate proved to be so fast, it was determined at -19.2° and 0.0° and the value extrapolated to 25.0°. The results are summarized in Table I.

**5-Coumaranyl- and 5-Thiocoumaranyldimethylcarbinyl Chlorides.**—Coumaran and thiocoumaran (2,3-dihydrothionaphthene) were synthesized by standard procedures. These compounds were acetylated by the Friedel-Crafts procedure and the 5-acetyl derivatives treated with methylmagnesium iodide to form the desired tertiary carbinols. The latter were converted into the chlorides with hydrogen chloride.

The rates of solvolysis of these compounds in 90% acetone are far too fast to be measured by the usual procedures. In the case of *p*-methoxy-*t*-cumyl chloride, we had obtained its rate of hydrolysis at 25° in 90% acetone, required for the calculation of the  $\sigma^+$ -value, by means of a double extrapolation, first calculating the rate constant at 25° for 94.8 wt. % aqueous acetone from the observed values at lower temperatures (-45.8, -36.8 and -23.7°) and then calculating the rate constant for a medium with the dielectric constant of 90 vol. % aqueous acetone.<sup>6a</sup>

In the present study we were interested primarily in examining the relative effects of incorporating the *p*-methoxy and *p*-methylthio substituents into the five-membered rings of the coumaranyl (IV) and thiocoumaranyl (V) derivatives. Accordingly, we decided to avoid this tedious extrapolation with its accompanying uncertainties. Consequently, the rates of solvolysis were determined in 98 wt. % aqueous acetone at 0.0°, even though this procedure made necessary the measurement of the rates of solvolysis of *p*-methoxy- and *p*-methylthio-*t*-cumyl chlorides in this particular medium for comparison of the relative rates. The data are summarized in Table II.

***o*-Methyl-*p*-phenyl-*t*-cumyl and *o*-Methyl-*p*-methoxy-*t*-cumyl Chlorides.**—*m*-Toluidine was converted into 4-bromo-*m*-toluidine and the diazonium salt of this base treated with benzene (Gomberg-Bachmann reaction) to form 3-methyl-4-bromobiphenyl. The latter was converted into the acid *via* the Grignard reaction, transformed into the methyl ester, and then into the tertiary carbinol by treatment with methylmagnesium iodide. The observed rates of solvolysis of the tertiary chloride in 90% aqueous acetone are reported in Table I.

TABLE II

RATE CONSTANTS AND RELATIVE RATES OF SOLVOLYSIS OF *p*-METHOXY- AND *p*-METHYLTHIO-*t*-CUMYL CHLORIDES AND RELATED DERIVATIVES IN 98 WT. % AQUEOUS ACETONE AT 0.0°

Aryldimethylcarbinyl chloride ArC(CH <sub>3</sub> ) <sub>2</sub> Cl	Rate, constant, $k_1$ , sec. <sup>-1</sup> × 10 <sup>5</sup>	Rel. rate
<i>p</i> -Methoxyphenyl	93.7	1.00
5-Coumaranyl	523 <sup>a</sup>	5.58
<i>o</i> -Methyl- <i>p</i> -methoxyphenyl	113	1.21
<i>p</i> -Methylthiophenyl	4.41	0.047 1.00
5-Thiocoumaranyl	21.0	0.224 4.76

<sup>a</sup> Calculated from the observed rate constants: 22.5 × 10<sup>-5</sup> sec.<sup>-1</sup> at -31.2° and 82.6 × 10<sup>-5</sup> sec.<sup>-1</sup> at -19.2°,  $\Delta H^\ddagger$  12.8 kcal./mole,  $\Delta S^\ddagger$  -22.1 e.u.

The synthesis of *o*-methyl-*p*-methoxy-*t*-cumyl chloride was carried out *via* the rearrangement of *m*-tolyl acetate to 4-acetyl-*m*-cresol under the influence of aluminum chloride, methylation to form 2-methyl-4-methoxyacetophenone, followed by treatment with methylmagnesium iodide to form the carbinol. Solvolysis of the chloride was examined at 0° in 98% acetone. The result is included in Table II.

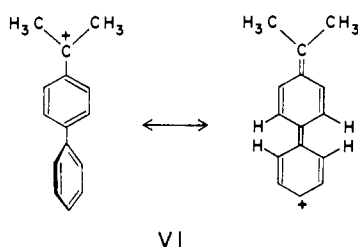
### Discussion

**The Effect of Coplanarity on the Phenyl Substituent.**—In the course of our earlier studies on the influence of substituents on the rates of solvolysis of *t*-cumyl chlorides,<sup>6</sup> it was observed that a *p*-phenyl substituent increases the rate of solvolysis of *t*-cumyl chloride in 90% acetone at 25° by a factor of 6.5,<sup>6i</sup> whereas a *p*-methyl group increases the rate by a factor of 26.<sup>6a</sup> It was considered anomalous that the electron-rich phenyl group should be less activating than the methyl substituent.

Biphenyl has been reported to exist in the gas phase in a non-planar configuration with an angle of approximately 45° between the planes of the two aromatic rings.<sup>12</sup> The non-planar configuration is presumably the result of the steric interactions between the four *ortho* hydrogen atoms of the biphenyl system. On this basis it appears reasonable to ascribe the low activating effect of the electron-rich phenyl substituent to the non-planar arrangement which markedly reduces the resonance contributions of the phenyl substituent to the incipient carbonium ions (VI).

The fluorene molecule contains the biphenyl system with the two phenyl rings forced into coplanarity by the methylene bridge.<sup>3,9</sup> In support of the proposed explanation is the fast rate of

(12) O. Bastiansen, *Acta Chem. Scand.*, **3**, 408 (1949); **4**, 926 (1950).



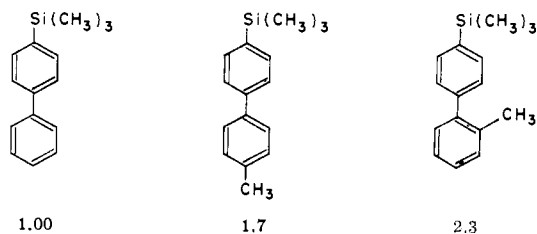
solvolysis of 2-fluorenylmethylcarbonyl chloride<sup>8</sup> and the fast rate of chlorination of fluorene in the 2-position.<sup>9</sup>

In the present study, it was observed that 2-fluorenyldimethylcarbonyl chloride undergoes solvolysis in 90% acetone at 25° at a rate some 173-fold greater than that of *t*-cumyl chloride, as compared to the relative rate of 6.5 exhibited by *p*-phenyl-*t*-cumyl chloride. Before concluding that the enhanced rate actually supports the proposed interpretation, it is necessary to assess the inductive and hyperconjugative contributions of the methylene bridge.

The *m*-methyl (or *m*-ethyl) substituent in the *t*-cumyl system increases the rate by a factor of 2. Presumably, then, a factor of 2 should be allowed for the effect of the methylene substituent in the 3-position of the biphenyl system.

The methylene substituent also occupies the 2'-position in the second phenyl ring. Unfortunately, it is far more difficult to arrive at a precise estimate of its effect. The inductive effect of an alkyl substituent in the more remote second ring doubtless will be much smaller than that of the 3-methyl group. However, the methyl substituent in the 2'- and 4'-position should be capable of hyperconjugative interaction with the electron deficient carbon in the 4-position.

There is considerable evidence that resonance contributions in the second ring are poorly transmitted to the first ring.<sup>13</sup> Moreover, Benkeser and his students observed that a methyl group, either in the 4'- or 2'-positions of the biphenyl system, had approximately the same effect on the rate of protonolysis of the trimethylsilyl group in the 4-position as a *m*-methyl substituent in phenyltrimethylsilane ( $k_{m-Me}/k_H$  2.1).<sup>14</sup> On this basis we



may estimate the reactivity of the fluorene derivative to be  $6.5 \times 2 \times 2 = 26$ . The observed relative rate, 173, is considerably larger, presumably the result of the greater resonance contributions of the coplanar *p*-phenyl substituent.

(13) E. Berliner and E. A. Blommers, *J. Am. Chem. Soc.*, **73**, 2479 (1951).

(14) R. A. Benkeser, W. Schroeder and O. H. Thomas, *ibid.*, **80**, 2283 (1958); R. A. Benkeser, R. A. Hickner and D. I. Hoke, *ibid.*, **80**, 2279 (1958).

From the observed rate constant and the reaction constant,  $\rho = -4.54$ , we obtain  $-0.490$  as the value of the electrophilic substituent constant,  $\sigma^+$ , for 2-fluorenyl.

**The Effect of Coplanarity on the Methoxy and Methylthio Substituents.**—In 90% acetone at 25°, a *p*-methoxy substituent increases the rate of solvolysis of *t*-cumyl chloride by a factor of 41700, whereas the corresponding value for the methylthio substituent is 6860. The latter is smaller, in accordance with the reduced resonance contributions of second row elements. However, it appeared that the ratio,  $k_{p-MeO}/k_{p-MeS} = 6.1$  (10 at 0°), was smaller than would have been anticipated for this factor.

Baddeley and his co-workers have noted the influence of the configuration of the alkoxy substituent on its resonance contributions in a number of systems.<sup>10</sup> Consequently, it appeared reasonable that steric interference between the *ortho* hydrogen atoms of the aromatic ring and the hydrogen atoms of the methoxy and thiomethoxy groups might force these groups out of the plane of the aromatic ring and reduce their resonance contributions. As a consequence of the larger steric requirements of the sulfur atom, the effect should be somewhat smaller in the methylthio derivative. This would result in a reduced value of the ratio,  $k_{p-MeO}/k_{p-MeS}$ .

The incorporation of the oxygen and sulfur atoms in the 5-membered ring system provides a test of this interpretation.

5-Coumaranyldimethylcarbonyl chloride undergoes solvolysis in 98% aqueous acetone at 0° at a rate 5.58 that of the parent compound, *p*-methoxy-*t*-cumyl chloride. Moreover 5-thiocoumaranyldimethylcarbonyl chloride undergoes solvolysis under these conditions at a rate 4.76 that of *p*-methylthio-*t*-cumyl chloride. Since a *m*-methyl (or *m*-ethyl) substituent increases the rate by a factor of 2, it is evident that the ring closure accomplishes only minor increases in the rate of solvolysis, with only an insignificant difference between the oxygen and sulfur derivatives.

These results do not support the earlier suggestion of a significant inhibition of resonance in the solvolysis of *p*-methoxy- and *p*-methylthio-*t*-cumyl chlorides, with a larger effect in the oxygen derivative. It appears that both the methoxy and the methylthio substituents in the *t*-cumyl structure are in position to provide full resonance stabilization to the electron-deficient center without significant restrictions arising from steric causes.

In the present case, the observed value of  $k_{p-MeO}/k_{p-MeS}$  is 21, considerably larger than the earlier value of 10 (0°). The discrepancy presumably arises from both the experimental difficulties in measuring these fast reactions at low temperatures and the combined uncertainties in both the reaction medium and temperature extrapolations. However, even the value of 21 indicates that the methylthio group possesses an ability to provide resonance stabilization to an electron-deficient center comparable with the highly activating group, methoxy.

**The Effect of an *o*-Methyl Substituent.**—In the *t*-cumyl carbonium ion, the two methyl groups

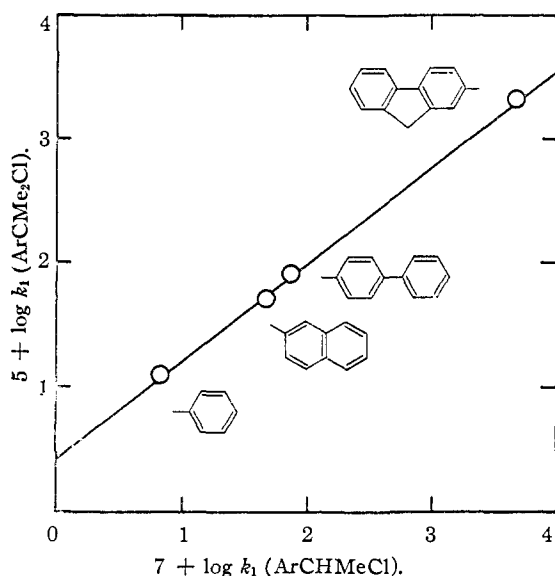
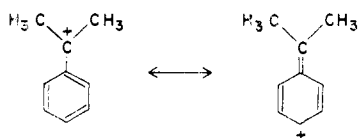


Fig. 1.—Linear free energy relationship between the rate constants for the solvolysis of the aryldimethylcarbinyl chlorides in 90% acetone at 25° and the related arylmethylcarbinyl chlorides in 80% acetone at 25°.

are presumably coplanar with the aromatic ring to permit maximum resonance stabilization of the electron-deficient center (VII).



VII

An *o*-methyl substituent would be expected to resist the attainment of the coplanar arrangement and to reduce the resonance interaction between the carbonium carbon and the aromatic ring. Although the transition state for the solvolysis of a *t*-cumyl chloride is not the fully formed carbonium ion, the available evidence is that it closely approaches such an ion in character. Consequently, an *o*-methyl substituent might be expected to reduce somewhat the resonance contributions of substituents in the *p*-position.

An *o*-methyl group increases the rate of hydrolysis of *t*-cumyl chloride at 25° by a factor of 3.63.<sup>6a</sup> Assuming strict additivity, the rate of solvolysis of *o*-methyl-*p*-phenyl-*t*-cumyl chloride will be given by the product,  $3.52 \times 3.63 = 23.7$ . The observed relative rate (Table I) is 17.7. The observed decrease of 25% is presumably due to the inhibition of resonance achieved by the *o*-methyl substituent.

The factor for *o*-methyl-*t*-cumyl chloride is not available in 98% acetone. However, these values of  $k/k_H$  do not change significantly in aqueous acetone of varying composition.<sup>6d</sup> Accordingly, we shall adopt the value 3.68 observed for 90% aqueous acetone at 0°.<sup>6a</sup> Assuming additivity, *o*-methyl-*p*-methoxy-*t*-cumyl chloride should undergo solvolysis at a rate approximately 3.68 greater than *p*-methoxy-*t*-cumyl chloride. However, the observed value of 1.21 (Table II) is only one-third of

the predicted value. Here also the *o*-methyl group definitely reduces the resonance contributions of the *para* substituent.

The effect is considerably greater in the case of the *p*-methoxy substituent than in the case of the phenyl substituent. It may be that the large resonance contributions of the *p*-methoxy substituent causes the transition state to approach somewhat closer to the carbonium ion and increases thereby the inhibiting effect of the *o*-methyl substituent.

In any case, the results point to the conclusion that the effect of an *o*-methyl substituent in reducing resonance contributions from a substituent in the *para* position is relatively small.

A *p*-methyl group increases the rate of solvolysis of *t*-cumyl chloride by a factor of 26, whereas an *o*-methyl group increases the rate by a much smaller factor, 3.63.<sup>6a</sup> In view of the observation here reported that an *o*-methyl group has a relatively small effect in reducing the resonance contributions of groups in the *para* position, it no longer appears possible to ascribe the large decrease, from 26 to 3.63, solely to the effect of steric inhibition of resonance.<sup>6a</sup> It is probable that the influence of the *o*-alkyl substituent in hindering solvation of the incipient carbonium ion is also a factor in the observed rate decreases accompanying the introduction of such groups.

**Electrophilic Substituent Constants for Polycyclic Aromatics.**—Omitting compounds with *peri* hydrogen interactions, there results an excellent linear free energy relationship between the rate data for the solvolysis of the *t*-cumyl chlorides and the rate data for the related secondary chlorides, ArCHClCH<sub>3</sub>, of Berliner and Shieh<sup>8</sup> (Fig. 1). Least squares treatment of the data leads to a calculated reaction constant for the solvolysis of the secondary chlorides of -5.78. From this reaction constant and the rate data of Berliner and Shieh, it is possible to calculate  $\sigma^+$ -constants for a number of polycyclic aromatic groups.

The data are summarized in Table III.

TABLE III  
ELECTROPHILIC SUBSTITUENT CONSTANTS FOR POLYCYCLIC AROMATIC GROUPS

Aromatic group	Rate constants, sec. <sup>-1</sup> × 10 <sup>6</sup> ArCHMeCl <sup>a</sup>	Rate constants, sec. <sup>-1</sup> × 10 <sup>6</sup> ArCMe <sub>2</sub> Cl <sup>b</sup>	Substituent constant, $\sigma^+$
Phenyl	0.0679	12.4	0
2-Phenanthryl	.330	(41.2) <sup>d</sup>	-0.119 <sup>c</sup>
2-Naphthyl	.476	50.6	-.135
4-Biphenyl	.746	80.8	-.179
3-Phenanthryl	.916	(92.1) <sup>d</sup>	-.196 <sup>c</sup>
2-Anthryl	3.45	(261) <sup>d</sup>	-.295 <sup>c</sup>
2-Fluorenyl	47.7	2080	-.490

<sup>a</sup> Solvolysis in 80% aqueous acetone at 25°,  $\rho = -5.78$ .

<sup>b</sup> Solvolysis in 90% aqueous acetone at 25°,  $\rho = -4.54$ .

<sup>c</sup> Calculated from the observed rates and the reaction constant,  $\rho = -5.78$ . <sup>d</sup> Calculated from the expression:  $\log k_1$  (sec.<sup>-1</sup>) ArCHMeCl = 1.272  $\log k$  (sec.<sup>-1</sup>) ArCMe<sub>2</sub>Cl - 1.177.

The utility of the  $\sigma^+$  constant for 2-fluorenyl in correlating the available electrophilic substitution data for fluorene will be examined in detail shortly.<sup>15</sup>

(15) L. M. Stock and H. C. Brown, paper in preparation.

### Experimental Part

**2-Fluorenyldimethylcarbinol.**—2-Acetylfluorene, m.p. 130–131°, from acetylation of fluorene,<sup>16</sup> was converted by methylmagnesium iodide into the carbinol in 64% yield, m.p. 125.5–126.5° from benzene.

*Anal.* Calcd. for C<sub>16</sub>H<sub>14</sub>O: C, 85.68; H, 7.19. Found: C, 85.92; H, 7.47.

**5-Coumaranyldimethylcarbinol.**—2-(*o*-Methoxyphenyl)-ethanol, b.p. 128–134° at 10 mm., *n*<sub>D</sub><sup>20</sup> 1.5398 (lit. b.p. 136° at 12 mm.,<sup>17</sup> *n*<sub>D</sub><sup>20</sup> 1.5388<sup>18</sup>) was prepared by the action of *o*-methoxyphenylmagnesium bromide on ethylene oxide<sup>17</sup> in 81% yield. The alcohol was converted, following the procedure of Chatelus,<sup>18</sup> into coumaran, b.p. 77–78° at 14 mm., *n*<sub>D</sub><sup>20</sup> 1.5497 (lit.<sup>18</sup> b.p. 75–77° at 12 mm., *n*<sub>D</sub><sup>20</sup> 1.5495) in 60% yield. Acetylation of coumaran was carried out following the directions given for the acetylation of homocoumaran.<sup>19</sup> The product, 5-acetylcoumaran, b.p. 170–171° at 21 mm., was recrystallized from hexane; m.p. 61.5–62.5° (lit.<sup>20</sup> b.p. 168° at 22 mm., m.p. 62°). 5-Coumaranyldimethylcarbinol, m.p. 42–43° from hexane, was prepared by the usual Grignard procedure.

*Anal.* Calcd. for C<sub>11</sub>H<sub>10</sub>O<sub>2</sub>: C, 74.13; H, 7.92. Found: C, 74.30; H, 8.28.

**5-Thiocoumaranyldimethylcarbinol.**—Thionaphthene-1-dioxide, m.p. 142–3°,<sup>21</sup> prepared from thionaphthene (Columbia Organic Chemicals) was reduced to 2,3-dihydrothionaphthene by a modification of the directions of Bordwell and co-workers.<sup>22</sup> A solution of the sulfone (24.8 g., 0.15 mole) in 200 ml. of anhydrous tetrahydrofuran was added dropwise with stirring to 400 ml. of a 1.0 *M* solution of lithium aluminum hydride in ether over a period of 4 hours under gentle reflux. The mixture was heated under reflux for a further 20 hours. The product, isolated by the usual procedure, distilled at 105–106° at 13.5 mm., 6.4 g., 32% yield, m.p. of mercuric chloride addition compound 127–128° (lit.<sup>23</sup> b.p. 105–107° at 13.5 mm., m.p. mercuric chloride addition compound 127–128°). Acetylation of dihydrothionaphthene with acetyl chloride and aluminum chloride in *sym*-tetrachloroethane at 5° gave 5-acetyldihydrothionaphthene, m.p. 44–45° from hexane, 54% yield.

*Anal.* Calcd. for C<sub>10</sub>H<sub>10</sub>OS: C, 67.38; H, 5.65. Found: C, 67.19; H, 5.72.

The carbinol was prepared from the above ketone in the usual manner and recrystallized from a mixture of hexane and benzene; m.p. 76.5–77.5°.

*Anal.* Calcd. for C<sub>11</sub>H<sub>14</sub>OS: C, 68.00; H, 7.26. Found: C, 67.89; H, 7.17.

**2-Methyl-4-methoxyphenyldimethylcarbinol.**—*m*-Tolyl acetate, b.p. 210–211° at 746 mm., prepared from *m*-cresol, was rearranged to 4-acetyl-*m*-cresol by the action of aluminum chloride in nitrobenzene at room temperature.<sup>24</sup>

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The product, m.p. 126–128° from benzene (lit.<sup>25</sup> 128°), was obtained in 22% yield. Methylation by dimethyl sulfate and sodium hydroxide gave 2-methyl-4-methoxyacetophenone, b.p. 108–109° at 2.5 mm., *n*<sub>D</sub><sup>20</sup> 1.5536 (lit.<sup>26</sup> b.p. 116.5° at 3 mm., *n*<sub>D</sub><sup>20</sup> 1.5510), in 84% yield. 2-Methyl-4-methoxyphenyldimethylcarbinol, m.p. 67.5–68.5° from heptane, was obtained from this ketone by the usual Grignard procedure in 85% yield.

*Anal.* Calcd. for C<sub>11</sub>H<sub>14</sub>O<sub>2</sub>: C, 73.30; H, 8.95. Found: C, 73.26; H, 9.09.

**4-(3-Methyl)-biphenyldimethylcarbinol.**—*m*-Toluidine was acetylated and brominated in glacial acetic acid. Hydrolysis of the product by concentrated hydrochloric acid gave 4-bromo-*m*-toluidine, m.p. 80–81° from 70% aqueous ethanol (lit.<sup>27</sup> m.p. 80–81.5°, 79.5–80°). This was converted by the Gomberg-Bachmann reaction into 3-methyl-4-bromobiphenyl, b.p. 150–151° at 3 mm., m.p. 39–39.5° from pentane, *n*<sub>D</sub><sup>20</sup> 1.6390 for supercooled liquid (lit.<sup>28</sup> b.p. 165–170° at 3 mm., *n*<sub>D</sub><sup>20</sup> 1.6358), in 32% yield. The bromide was converted into the Grignard reagent and carbonated to form 2-methyl-4-phenylbenzoic acid, m.p. 168–169° from heptane (lit.<sup>29</sup> m.p. 169–170°). The acid was converted into the methyl ester, m.p. 62.5–63.5° from methanol (lit.<sup>29</sup> m.p. 61–63°), and the latter transformed into the carbinol, b.p. 148–150° at 0.3 mm., *n*<sub>D</sub><sup>20</sup> 1.6050, by the usual Grignard procedure.

*Anal.* Calcd. for C<sub>16</sub>H<sub>18</sub>O: C, 84.91; H, 8.02. Found: C, 84.79; H, 8.04.

The preparation of the *p*-methoxy-, *p*-methylthio- and *p*-phenylphenyldimethylcarbinols has been described earlier.<sup>6d,f</sup>

**Preparation of the Tertiary Chlorides.**—For the highly unstable oxygen and sulfur compounds, the procedure previously utilized for the anisyl derivative<sup>6d</sup> was followed. For the remaining compounds, the general procedure<sup>6f</sup> was utilized. As in earlier cases, no attempt was made to isolate analytically pure samples of the tertiary chlorides, since the kinetic procedure did not require such pure products.

**Solvents.**—The 90 vol. % acetone was essentially the same as that utilized in the earlier study.<sup>6f</sup> The rate of solvolysis of *t*-cumyl chloride in this solvent was found to be  $12.0 \times 10^{-5}$  sec.<sup>-1</sup> at 25.0°. The 98 wt. % acetone was prepared by adding the calculated quantity of distilled water to anhydrous acetone.

**Kinetic Measurements.**—The procedures for kinetic measurements in 90% acetone were similar to those previously described. In the kinetic studies involving highly reactive compounds in 98 wt. % acetone, the aliquots were removed with a fast-delivery pipet in a cold room (–3°) and added to 100-ml. portions of dry acetone, precooled in a –80° bath, and titrated with ethanolic sodium ethoxide. The aliquots utilized for determination of the value of the infinity titer were hydrolyzed completely by adding water, prior to dissolving them in the dry acetone. This procedure was necessary because the solvolysis of the chloride does not proceed to completion in the 98% acetone medium.

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