tween 30 and 150°K. Working thermocouples, used in various pieces of apparatus in the Laboratory, are from the same lot of wire as TC 80, and have been directly intercompared with TC 80 in the manner described by Giauque, Buffington and Schulze.[4] Calibration graphs of the small deviations from TC 80 are used to correct the readings of these couples to the Standard Table.

The smooth calibration curve of RT 4 is probably 0.005 to 0.01° more accurate than the Thermocouple Table. By comparing this thermometer with one recently calibrated at the National Bureau of Standards, we hope soon to have a comparison between our basic temperature scale and the one currently in use at the National Bureau of Standards.

An independent, although somewhat insensitive, check of our Standard Thermocouple Scale was recently provided by data of state carried out in this Laboratory for hydrogen and for nitrogen. Extrapolation of PV products to zero pressure and division by the figure 82.0567 cc.–atm./deg., the molal gas constant, yielded values for T that agreed in all cases with values computed from its thermocouple to within the accuracy of the PV extrapolations, namely, 0.05°.

COLUMBUS, OHIO RECEIVED DECEMBER 21, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Effects of Substituents on the Rate of Hydrolysis of Triarylsilanes in Wet Piperidine

BY HENRY GILMAN AND G. E. DUNN

This investigation was initiated in order to compare the effects of a series of substituents on the rates of reactions occurring at analogous silicon and carbon atoms. Six new monosubstituted triphenylchlorosilanes were prepared and reduced to the corresponding triphenylsilanes. The rates of hydrolysis of these triphenylsilanes in wet piperidine were found to be in agreement with those predicted on the basis of Hammett's σ-constants, with the exception of that for diphenyl-*p*-dimethylaminophenylsilane. It was shown that the value of σ reported previously for the *p*-dimethylamino group is in error, and that two σ-constants are required for this group—one to be used with conjugated and one with non-conjugated side chains.

A little over twenty years ago Kipping, in reporting the failure of all his attempts to prepare organosilicon compounds containing silicon-to-silicon or silicon-to-carbon double bonds, noted that such compounds had never been isolated, and recorded his conclusion that "an ethylenic binding between carbon and silicon is either impossible or can only be produced under exceptional circumstances."[1] Since that time, the complete absence from the literature of reference to any such compound has shown his belief to be well founded. Furthermore, several authors have pointed out the probability that resonance structures having such double bonds make relatively small contributions to the ground states of organosilanes.[2] Thus, while triarylmethyl cations, anions and free radicals are rendered relatively stable by the ability of such resonating systems to spread out electron surpluses or deficiencies, the corresponding triarylsilyl fragments are comparatively unknown.[3] These considerations indicated that electrical interactions between the silicon atom and other atoms or groups in a silane molecule might be different from those between the same atoms or groups and the corresponding carbon atom of an analogous carbon compound. It was the purpose of this investigation to study these differences by observing the changes in the rate of a reaction occurring on the silicon atom of an organosilane as a series of substituents were introduced into the molecule, and comparing these changes with the changes produced when the same series of substituents were introduced into a similar carbon compound.

Hammett has shown[4] that the effect of a meta or para substituent on the rate of a reaction occurring on the side chain of a benzene derivative can be represented by the equation

$$\log k - \log k^0 = \rho\sigma$$

where k^0 is the specific rate constant for the unsubstituted derivative and k is that for the substituted one. Rho is constant for any given type of reaction and σ is constant for any particular substituent. This generalization simplifies the comparison of organosilicon compounds with their carbon analogs. It is only necessary to measure the rates of reaction of a series of substituted aryl silanes and plot the logarithms of the specific rate constants against the σ-constants reported by Hammett. A linear relationship would indicate that the silicon and carbon atoms interact in the same way with other substituents in the type of molecule investigated. A non-linear relationship would indicate the reverse.

The reaction chosen for study was the basic hydrolysis of monosubstituted triarylsilanes. These compounds are easily prepared, are sufficiently

---

[1] F. S. Kipping, *J. Chem. Soc.*, 104 (1927); F. S. Kipping, A. G. Murray, and J. G. Maltby, *ibid.*, 1180 (1929).

[2] (a) H. Gilman and G. E. Dunn, THIS JOURNAL, **72**, 2178 (1950); C. G. Swain, R. M. Esteve and R. H. Jones, *ibid.*, **71**, 965 (1949); (b) J. D. Roberts, E. A. McElhill and R. Armstrong, *ibid.*, **71**, 2923 (1949).

[3] Siliconium ions have been proposed as intermediates in certain reactions of organosilanes by F. C. Whitmore, *Chem. Eng. News*, **26**, 672 (1948) and F. C. Whitmore, L. H. Sommer, J. Gold and R. E. Van Strien, THIS JOURNAL, **69**, 1551 (1947), but doubt has been cast upon the correctness of this interpretation by subsequent work. See Footnote 2a. Triphenyl- and triethyl-silyllithium were prepared by C. A. Kraus and H. Eatough, *ibid.*, **55**, 5008 (1933) and C. A. Kraus and W. K. Nelson, *ibid.*, **56**, 195 (1934), respectively. However, it was found necessary to use a procedure much more involved than those commonly employed for the preparation of the corresponding carbanions, and the products were of a greater order of reactivity than their carbon analogs. Kraus and Eatough, *loc. cit.*, also reported the preparation of a solvated triphenylsilyl radical, but gave no evidence that their product actually contained an unpaired electron.

[4] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, Chapter VII.

stable to be worked with conveniently, and react with most reagents considerably more slowly than do the halo- or ethoxy-silanes.[5] Furthermore, Price has examined the hydrolysis of trialkylsilanes and found it to agree satisfactorily with a pseudo first order kinetic expression during the first three-fourths of the reaction.[6]

The hydrolysis of triarylsilanes in Price's medium (aqueous alcoholic potassium hydroxide) proceeded much too rapidly for measurement, so advantage was taken of Kipping's observation that certain polysilanes slowly evolve hydrogen when dissolved in piperidine.[7] Triarylsilanes were found to hydrolyze at convenient rates in piperidine containing a twenty-fold excess of water, and the reaction was found to be pseudo first order until about 80% complete.

$$R_3SiH + H_2O \longrightarrow R_3SiOH + H_2$$

Table I illustrates the constancy of the pseudo rate constant with varying concentrations of silane and a constant concentration of water. Table II gives the pseudo rate constants for a series of substituted silanes, and in Fig. 1 these constants are plotted against the σ-constants for the corresponding substituents as reported by Hammett.[4] It is seen that, with the exception of the point representing the *p*-dimethylamino group, a satisfactory linear relationship exists between the two series of constants. The slope of the line gives ρ for the hydrolysis of triarylsilanes in wet piperidine as $+3.09 \pm 0.12$.

TABLE I

HYDROLYSIS OF TRIARYLSILANES IN PIPERIDINE CONTAINING 0.96 MOLE OF WATER PER LITER AT 38.8°

Silane	Concn., mole/liter	$k \times 10^4$, sec.$^{-1}$
Diphenyl-*p*-tolyl-	0.0267	1.08 ± 0.08
Diphenyl-*p*-tolyl-	.0497	1.13 ± .09
Diphenyl-*p*-tolyl-	.0848	1.03 ± .07
Diphenyl-*p*-dimethylaminophenyl-	.0267	.215 ± .075
Diphenyl-*p*-dimethylaminophenyl-	.0519	.208 ± .050
Diphenyl-*p*-dimethylaminophenyl-	.0584	.210 ± .008

TABLE II

HYDROLYSIS OF MONOSUBSTITUTED TRIARYLSILANES IN PIPERIDINE CONTAINING 0.96 MOLE OF WATER PER LITER AT 38.8°

Substituent	$k \times 10^4$, sec.$^{-1}$	Probable error $\times 10^4$
p-Cl	16.9	1.2
H	3.22	0.27
m-CH_3	2.75	.20
p-CH_3	1.08	.09
m-$N(CH_3)_2$	0.75	.05
p-OCH_3	.89	.08
p-$N(CH_3)_2$	.21	.05

Branch and Calvin have pointed out the anomalous fact that the σ-constant for the dimethylamino group is more negative in the meta than in the para position (−0.211 and −0.205, respectively), while for all other electron releasing groups the reverse is true. They suggest that the value of σ reported for the *m*-dimethylaminophenyl group is erroneous.[8] There is now evidence that the error is in the constant for the para position rather than that for the meta. Figure 1 shows that the value of σ reported by Hammett for the *m*-dimethylamino group fits the data of this experiment reasonably well, and is probably correct. Hammett's value of the *p*-dimethylamino σ-constant was obtained from data in the literature on the reaction of tetramethyl-*p*-phenylenediamine with trinitroanisole,[9] and a statistical factor of two was introduced into the calculation. If the factor of two is omitted from the calculation, the result is represented by the point A, Fig. 1, which is in considerably better agreement with the data of this experiment. Since Hammett's tables were published, two studies of the rate of hydrolysis of substituted ethyl benzoates, including ethyl *p*-dimethylaminobenzoate, have been made. The *p*-dimethylamino σ-constant obtained from this work is shown as point B, Fig. 1. The data leading to the various values of σ for the *p*-dimethylamino group are presented in Table III. It is seen that the value of σ obtained from the hydrolysis of benzoic acid esters (−0.574) is considerably more negative than that obtained from silanes (−0.411).

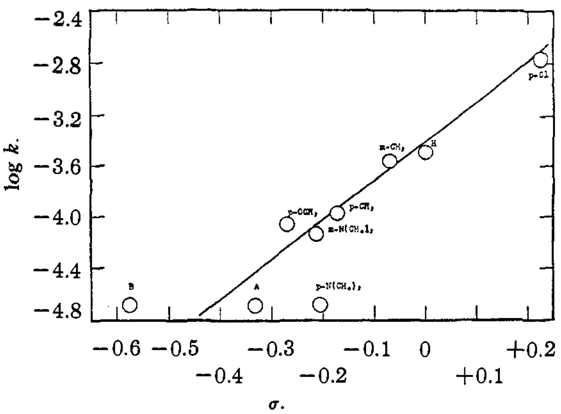
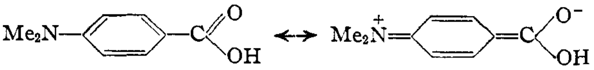


Fig. 1.—Hydrolysis of triarylsilanes in wet piperidine.

A related phenomenon has been reported by Westheimer.[10] The acid-weakening effect of most para substituents on aromatic acids can be predicted with satisfactory accuracy by means of calculations which depend only on the electrostatic effects of the substituent. The *p*-amino and *p*-dimethylamino groups, however, have a greater weakening effect than can be accounted for as the result of electrostatic effects alone. Westheimer interpreted the enhanced weakening effect of these groups as being due to resonance of the type



which both increases the negative charge on the oxygen atoms, thus increasing their attraction for protons, and at the same time interferes with the internal resonance tending to stabilize the carboxyl anion. Such resonance is of importance only when substituents having a strong tendency to use their

---

[5] H. Gilman and G. N. R. Smart, *J. Org. Chem.*, **15**, 720 (1950).

[6] F. P. Price, THIS JOURNAL, **69**, 2600 (1947).

[7] F. S. Kipping, *J. Chem. Soc.*, **119**, 848 (1921).

[8] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 418.

[9] E. Hertel and J. Dressel, *Z. physik. Chem.*, **B29**, 178 (1935).

[10] F. H. Westheimer, THIS JOURNAL, **62**, 1892 (1940); F. H. Westheimer and R. P. Metcalf, *ibid.*, **63**, 1339 (1941).

TABLE III

σ-CONSTANT FOR THE p-DIMETHYLAMINO GROUP

Reaction	ρ	log k^0	log k	σ
Alkaline hydrolysis of ethyl benzoates, 88% alcohol, 30°[a]	+2.498	−3.072	−4.597	−0.610
Alkaline hydrolysis of ethyl benzoates, 56% acetone, 25°[b]	+2.842	−2.670	−4.198	− .538
Dimethylanilines with trinitroanisole, acetone, 25°[c]	−2.382	−4.500	−3.712	− .331
Hydrolysis of triarylsilanes, wet piperidine, 38.8°	+3.086	−3.407	−4.678	− .411

[a] F. H. Westheimer and R. P. Metcalf, THIS JOURNAL, **63**, 1339 (1941). [b] E. Tommila, *Ann. Acad. Sci. Fennicae, Ser. A57*, **13**, 3 (1941) [*C. A.*, **38**, 6171 (1944)]. [c] E. Hertel and J. Dressel, *Z. physik. Chem.*, **B29**, 178 (1935).

TABLE IV

PREPARATION OF MONOSUBSTITUTED TRIARYLCHLOROSILANES FROM DIPHENYLDICHLOROSILANE

Organometallic compound	Time of reflux, hr.	B.p. of product t, °C.	p, mm.	Yield, %	Silicon, % Calcd.	Found	Chlorine, % Calcd.	Found
p-ClC_6H_4MgBr	72	149–150	0.3	36	8.51	8.40	10.8	10.7
m-$CH_3C_6H_4Li$	0.5	150–151	.05	79	9.07	9.04	11.5	11.2
p-$CH_3C_6H_4Li$	0.5	147–148	.2	79	9.07	9.10	11.5	11.2
m-$(CH_3)_2NC_6H_4Li$	4	184–185	.2	78	8.30	8.30	10.5	10.7
p-$CH_3OC_6H_4MgBr$	120	189–192	1.0	78	8.62	8.46	10.9	10.6
p-$(CH_3)_2NC_6H_4Li$	24	227–228	2.5	70	8.30	8.17	10.5	9.87

unshared electron pairs in the formation of coördinate bonds are located in the para position with respect to a side chain which can become doubly bonded by accepting a pair of electrons from the benzene nucleus.

Our results are in agreement with Westheimer's, and can be explained in the same way. The σ-constant for the p-dimethylamino group obtained from the reactions of benzoic acid derivatives will be valid only for reactions occurring on side chains which can enter into resonance interaction with the substituent through the conjugated system supplied by the benzene ring. For silane and amine side chains such interaction is not of importance. The amine side chain cannot accept electrons from the ring without exceeding its coördination number of four; and, while the silicon atom of an arylsilane could presumably increase its coördination number, it will not readily form double bonds with carbon. For such a side chain the electron releasing effect of the p-dimethylamino group will be less than for a carboxyl side chain, and the σ-constant will be correspondingly less negative.[11] This is analogous to the interaction of electron attracting groups with amino and hydroxyl side chains. Just as the p-NO_2,[4] p-CN[12] and p-CF_3[13] groups have two σ-constants to take account of this phenomenon, the evidence presented here suggests that the p-dimethylamino group may also need two σ-constants, one for conjugated, and one for non-conjugated side chains. The average values from the data at present available would be: for conjugated side chains −0.57 ± 0.04, and for non-conjugated side chains −0.41 ± 0.04.

Experimental

Preparation of Silanes.—The triarylsilanes used in this investigation were prepared by the series of reactions

$$(C_6H_5)_2SiCl_2 \xrightarrow[\text{or } AC_6H_4Li]{AC_6H_4MgBr} AC_6H_4(C_6H_5)_2SiCl$$

$$AC_6H_4(C_6H_5)_2SiCl \xrightarrow{LiAlH_4} AC_6H_4(C_6H_5)_2SiH$$

A substituted aryllithium compound was used whenever it could be made by direct reaction of aryl bromide with lithium metal. In all other cases a Grignard reagent was used. The procedure for the preparation of diphenyl-p-dimethylaminophenylchlorosilane and diphenyl-p-dimethylaminophenylsilane are described in detail below, and data for the others are summarized in Tables IV and V.

Diphenyl-p-dimethylaminophenylchlorosilane.—Twenty-one and four-tenths grams (0.085 mole) of diphenyldichlorosilane was dissolved in 70 ml. of dry ether in a three-necked flask equipped with reflux condenser, mechanical stirrer and nitrogen inlet. With the stirrer operating at moderate speed, 0.085 mole of p-dimethylaminophenyllithium[14] was added dropwise over a period of 30 minutes. When the addition was complete, the mixture was stirred and heated to reflux until Color Test I[15] became negative (24 hours). Dry benzene was then added dropwise to the reaction flask, and simultaneously ether was distilled off until the distillation temperature reached 78°. The mixture was allowed to settle, then the benzene was siphoned off under nitrogen pressure, and the insoluble residue (inorganic salts) was washed twice with dry benzene by a similar siphoning procedure. The solvent was distilled from the combined benzene solutions, and the residue was distilled at reduced pressure to give 21.0 g. (70%) of diphenyl-p-dimethylaminophenylchlorosilane, b.p. 227–228° at 2.5 mm. Analysis is reported in Table IV.

Diphenyl-p-dimethylaminophenylsilane.—To 19.5 g. (0.055 mole) of diphenyl-p-dimethylaminophenylchlorosilane dissolved in 125 ml. of dry ether was added 1.0 g. (0.026 mole) of lithium aluminum hydride. The mixture was protected from atmospheric moisture by a calcium chloride tube and refluxed for 3 hours. Excess lithium aluminum hydride was hydrolyzed by adding ether saturated with water, followed by dilute aqueous acetic acid. The ether layer was separated and washed with dilute acetic acid, then dried over sodium sulfate and distilled at reduced pressure. Diphenyl-p-dimethylaminophenylsilane, boiling

TABLE V

PREPARATION OF MONOSUBSTITUTED TRIARYLSILANES

Substituent	B.p. of product t, °C.	p, mm.	Yield, %	Silicon, % Calcd.	Found	Hydrogen a Si–H, % Calcd.	Found
p-Cl	161–162	1.0	56	9.51	9.48	0.340	0.336
m-CH_3	155–156	1.2	62	10.2	10.2	.364	.355
p-CH_3	147–148	0.2	79	10.2	10.2	.364	.360
m-$N(CH_3)_2$	176–177	0.1	83	9.24	9.19	.334	.344
p-OCH_3	183–184	1.5	76	9.67	9.60	.345	.343
p-$N(CH_3)_2$	186–187	0.15	55	9.24	9.20	.334	.334

---

(11) The same should be true of the amino group, but, unfortunately, amino substituted arylsilanes are not readily available for study.

(12) J. D. Roberts and E. A. McElhill, THIS JOURNAL, **72**, 628 (1950).

(13) J. D. Roberts, R. L. Webb and E. A. McElhill, *ibid.*, **72**, 411 (1950).

(14) H. Gilman, E. A. Zoellner and W. M. Selby, *ibid.*, **55**, 1252 (1933).

(15) H. Gilman and F. Schulze, *ibid.*, **47**, 2002 (1925).

at 186–187° at 0.15 mm., was obtained in 55% yield. Analysis is reported in Table V.

Rate Measurements.—The piperidine used as solvent and catalyst for hydrolysis of the triarylsilanes was an Eastman Kodak Co. white label product which had been redistilled through a twelve-inch column packed with $^1/_8$ inch glass helices. Distilled water was added to this material until the water concentration was 0.96 molar, as determined by titration with the Karl Fischer reagent. The silanes were redistilled at reduced pressure from a flask having a five-inch Vigreux neck until a sample was obtained which, when hydrolyzed, would give a total volume of hydrogen equal to 100.0 ± 0.3% of the theoretical volume. In most cases not more than two distillations were required.

The kinetic runs were made as follows. Depending upon the size of the sample to be used, either 10 or 20 ml. of the piperidine reagent described above was pipetted into a 50-ml. erlenmeyer flask, which was placed in the clamp of a shaking machine arranged in such a way that about half the height of the flask was immersed in an oil-bath maintained at 38.80 ± 0.05°. The flask was loosely stoppered, the shaker started, and the contents allowed 15 minutes to come to bath temperature. The sample (0.1–0.4 g.) was weighed into a small glass cup made by cutting the bottom from a 12 cm. test-tube just above its hemispherical base. The shaker was stopped, cup and sample were dropped into the erlenmeyer flask, and the flask was connected to a 10-ml. gas buret by means of capillary glass tubing and a short length of Tygon tubing. Shaker and timer were then started, and the volume of hydrogen was read at intervals. No advantage was found in the use of a flask with side bulb to hold the piperidine so that the system could be closed before silane and base were mixed, since there was no evolution of hydrogen during the few moments between mixing the reagents and starting the shaker. A constant positive blank of 0.10 ml. of hydrogen was observed for all runs.

Analysis of the silanes for hydrogen as Si–H was carried out in the same way, except that a few pellets of potassium hydroxide were added to the piperidine in order to hasten the reaction.

Acknowledgment.—The authors wish to thank Dr. G. S. Hammond for suggestions.

AMES, IOWA RECEIVED AUGUST 18, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CARSON–NEWMAN COLLEGE]

Quaternary Salts of Styryl Pyridines and Quinolines

BY CARL T. BAHNER, EDWIN S. PACE AND ROBERT PREVOST

New quaternary salts of substituted styryl pyridines and quinolines have been prepared for cancer chemotherapy screening and their physical properties have been described.

Continuing the search for additional compounds which are capable of damaging malignant cells *in vivo*,[1] quaternary salts of styryl substituted pyridines and quinolines have been prepared. These series were selected for study because a number of the compounds known to have anti-tumor action are quaternary salts which contain two rings joined by a two carbon chain,[2] 4-dimethylaminostilbene

TABLE I

QUATERNARY SALTS OF STYRYL PYRIDINES AND QUINOLINES

Methiodide salt of	Empirical formula	M.p., °C.	Analyses, % Calcd.	Found[a]
2-(*p*-Dimethylaminostyryl)-quinoline	$C_{20}H_{21}IN_2$	276	I, 30.49	30.46
2-(*p*-Diethylaminostyryl)-quinoline	$C_{22}H_{25}IN_2$	224–226	I, 28.56	28.42
2-(2,4-Dichlorostyryl)-quinoline	$C_{18}H_{14}Cl_2IN$	226–227	I, 28.71	28.40
2-(2,6-Dichlorostyryl)-quinoline	$C_{18}H_{14}Cl_2IN$	247–248	I, 28.71	28.82
4-(*o*-Hydroxystyryl)-quinoline	$C_{18}H_{16}INO$	272–273	C, 55.55	55.56
			H, 4.14	4.22
2-(3,4-Dichlorostyryl)-quinoline	$C_{18}H_{14}Cl_2IN$	255–256	I, 28.71	28.62
2-(*p*-Methoxystyryl)-quinoline	$C_{19}H_{18}INO$	236–237	I, 31.47	31.43
2-(*o*-Ethoxystyryl)-quinoline	$C_{20}H_{20}INO$	224–226	I, 30.42	30.47
2-(2,3-Dimethoxystyryl)-quinoline	$C_{20}H_{20}INO_2$	224–225	I, 29.29	29.27
2-(3,4-Dimethoxystyryl)-quinoline	$C_{20}H_{20}INO_2$	259–260	C, 55.44	55.56[b]
			H, 4.65	4.46
2-(3,4-Diethoxystyryl)-quinoline	$C_{22}H_{24}INO_2$	239–240	C, 57.28	57.22[c]
			H, 5.24	5.33
2-(3,4-Methylenedioxystyryl)-quinoline	$C_{19}H_{16}INO_2$	259–260	I, 30.42	30.41
6-Ethoxy-2-(*p*-dimethylaminostyryl)-quinoline[d]	$C_{22}H_{25}IN_2O$	274–276	C, 57.39	57.07[b]
			H, 5.47	5.55
4-(*p*-Dimethylaminostyryl)-quinoline	$C_{20}H_{21}IN_2$	302	I, 30.49	30.35
4-(*p*-Diethylaminostyryl)-quinoline	$C_{22}H_{25}IN_2$	273–275	I, 28.56	28.40
2-(*o*-Ethoxystyryl)-pyridine	$C_{16}H_{18}INO$	252–253	I, 34.56	34.49
2-(3,4-Diethoxystyryl)-pyridine	$C_{18}H_{22}INO_2$	231–232	I, 30.88	30.73
2-(*p*-Nitrostyryl)-pyridine	$C_{14}H_{13}IN_2O_2$	262–263	I, 34.47	34.51
Allyl bromide salt of				
2-Styrylquinoline	$C_{20}H_{18}NBr$	234–235	Br, 22.69	22.68

[a] Average of two Volhard analyses for ionic halogen unless otherwise indicated. [b] Carbon and hydrogen analyses by Galbraith Microanalytical Laboratories. [c] Carbon and hydrogen analyses by Analytical Laboratory of National Cancer Institute. [d] *Cf.* Browning, *et al.*, ref. 4.

---

[1] *Cf.* W. K. Easley and C. T. Bahner, THIS JOURNAL, **72**, 3803 (1950).

[2] Virginia B. Peters, in "Approaches to Cancer Chemotherapy," American Association for the Advancement of Science, F. R. Moulton, Editor, Washington, D. C., 1947, p. 244; *cf.* J. L. Hartwell and S. R. L. Kornberg, THIS JOURNAL, **68**, 1131 (1946).