of the photon-activated persulfate. Conductivity measurements gave no evidence for the formation of any weak electrolyte involving the persulfate and hydrogen ions in these solutions. The data obtained in the present research as well as the previous data can be represented by the following reactions

$$
\begin{array}{ll}
I & S_2O_8^{=} + h\nu = {}^*S_2O_8^{=} \\
k_1 & {}^*S_2O_8^{=} + H_2O = 2SO_4^{=} + {}^1/_2O_2 + 2H^+ \\
k_i & {}^*S_2O_8^{=} + M_i = S_2O_8^{=} + M_i + \text{heat}
\end{array}
$$

The equation for ϕ given by the above reactions is

$$1/\phi = 1 + a_2(\text{NaCl}) + a_3(\text{NaOH}) + a_4(\text{A}^{-2}) + a_5(\text{H}^+) + a_mM_m$$

The relationships between the rate constants, k, are $a_2 = k_2/k_1$, $a_3 = k_3/k_1$, etc. The numerical values of a_i are given by the corresponding coefficients of the concentrations in the equation for $1/\phi$ derived from the data. The value of $1 + a_mM_m$ is 1.776.

Hydrogen ions deactivate the photon activated persulfate anions 55.5 k_5/k_1 or four thousand times more efficiently than the measured reaction utilizes the absorbed light if the above mechanism is correct.

Sodium ions do not perceptibly deactivate photon activated persulfate because ϕ remained constant when the concentration of sodium persulfate (hence sodium ions) was increased about fivefold.[3] The value of 0.776 for a_mM_m therefore, equals k_w/k_1; so water is at most 0.776 as efficient in deactivating ${}^*S_2O_8^{=}$ as in bringing about the measured reaction.

Other mechanisms might be found which would also fit the data, but those that we have considered in which $S_2O_8^{=}$ is photo-dissociated into SO_4^- ions or the OH radical is produced would have ϕ depend upon the light intensity or produce hydrogen peroxide, or both, contrary to the experimental facts. The chief objection to our mechanism is the long half life required for the photon activated persulfate ion in order to account for the large deactivating effect of hydrogen ions.

In the second reaction oxygen atoms rather than molecules would be produced initially but the mechanism of the subsequent formation of oxygen molecules would not affect the quantum yield which is based on the observed change in the concentration of the persulfate.

Summary

1. The true value of the quantum yield for the photolysis of persulfate in water is found to be 0.567 ± 0.005 mole of $S_2O_8^{=}$ decomposed per einstein (6 × 10^{23} quanta) of light of λ 254 mμ absorbed by the persulfate in water at 25°.

2. Chloride and other ions deactivate photon activated persulfate anions. The efficiency of the deactivation decreases in the order H_3O^+, $A^{=}$, OH^- and Cl^-. $A^{=}$ is $SO_4^{=}$, $CO_3^{=}$ or $HPO_4^{=}$. The deactivation accounts quantitatively for the depressing effects of these ions upon the quantum yields.

CAMBRIDGE, MASSACHUSETTS RECEIVED APRIL 15, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Kinetics of the Thermal Chlorination of Benzal Chloride

BY HAROLD A. SCHERAGA[1] AND MARCUS E. HOBBS

The halogenation of hydrocarbons is of considerable interest from both the theoretical and practical points of view and has been the subject of many kinetic investigations. The thermal chlorination of methane[2a] and chloroform[2b] have been investigated kinetically and have given an insight into the nature of the mechanisms of these reactions. It was thought to be of interest to extend this work to aromatic substituted methanes by investigation of the chlorination of the alkyl side chain of toluene. In order to minimize the number of successive reactions that might take place in the chlorination process it seemed desirable to study the chlorination of benzal chloride, for, in this manner, it appeared that rather unambiguous information might be obtained about the ease of replacement of the last hydrogen atom of the side chain —$CHCl_2$ group.

Even in this relatively simple case there is the possibility of ring substitution, addition and/or side chain reaction. If one considers the factors determining whether a reaction will involve the side chain or the ring,[3] and the fact that the ring in benzal chloride is significantly less reactive than it is in toluene, it appears that chlorination at high temperatures, in the absence of catalysts, carriers and activating radiation, would result in a reaction that took place primarily, if not exclusively, in the side chain of an aromatic compound. That this expectation is in large measure fulfilled will be shown by the results obtained in this investigation. It might be pointed out that Mason and co-workers[4] have found that toluene may be con-

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[1] Part of a Thesis submitted by Harold A. Scheraga in partial fulfillment of the requirements for the Ph.D. degree in Chemistry at Duke University, October, 1946. Present address: Department of Chemistry, Cornell University, Ithaca, N. Y.

[2] (a) R. N. Pease and G. F. Walz, THIS JOURNAL, **63**, 3728 (1931); (b) H. A. Taylor and W. E. Hanson, *J. Chem. Phys.*, **7**, 418 (1939).

[3] P. H. Groggins, "Unit Processes in Organic Synthesis," 3rd ed., McGraw-Hill Book Co., Inc., New York, N. Y., (1947) Chap. IV.

[4] J. Mason, *et al.*, *J. Chem. Soc.*, 3150 (1931).

sidered as a substituted methane, the side chain reaction predominating if catalysts which promote ring chlorination are absent.

In this kinetic study, the chlorination of benzal chloride may be regarded as a double displacement reaction involving the formation of hydrogen chloride and benzotrichloride. The gas phase thermal chlorination was carried out in the absence of light to prevent photochemical reaction from taking place. The photochlorination of benzal chloride in solution at room temperature was studied at the same time by Manes and Hill[5] in this Laboratory.

Experimental

Purification of Benzal Chloride.—The procedure, crystallization apparatus and high vacuum system for outgassing which were used in the purification of benzal chloride were developed in conjunction with Manes and Hill.[5]

Since the benzal chloride was Eastman Kodak Co. best grade made from benzaldehyde it was assumed that benzaldehyde was the principal impurity. Such organic impurities and water were removed from freshly distilled benzal chloride by fractional crystallization in vacuum and dissolved gases were removed ($<10^{-6}$ mm.) by repeated distillation of the recrystallized material in an all-glass high vacuum system. The cooling curves of the final product indicated that there was less than 2.5×10^{-3} mole fraction of soluble impurity present. The value of the freezing point constant of benzal chloride necessary to make the above estimate was determined roughly as 6.7° C./mole/1000 g. of benzal chloride. Benzaldehyde was used as a solute in the determination of this constant.

The purified benzal chloride was distilled in the high vacuum system into volumed ampoules which were sealed off and stored in the dark. Each ampoule had a fragile portion which could later be broken by a magnetically controlled hammer to start the reaction in the reaction vessel. The density of benzal chloride was determined by distilling some of it into pycnometers on the high vacuum system. The following density data were obtained, each value being the average of three independent determinations in three different pycnometers.

t, °C.	*d*, g./ml.
20.00	1.25362 ± 0.00015
25.00	1.24727 ± 0.00024
30.00	1.24170 ± 0.00059

The known amount of benzal chloride in each ampoule was used to determine its initial concentration for each run.

Purification of Chlorine.—Chlorine from a partially used tank was introduced into a high vacuum system and purified by trap to trap distillation to remove traces of such impurities as water and gases not condensable in liquid air. When, after several stages of distillation, this residual gas pressure was of the order of 10^{-5} to 10^{-6} mm. the chlorine was fractionated twice into three fractions, the middle fraction being retained in each case. This purified material was distilled into ampoules of known volume at a determined temperature and pressure, the pressure having been determined as follows. A drawn out capillary attached to the ampoule train was immersed in an open beaker of concentrated sulfuric acid and the portion under the surface of the liquid broken. As a result chlorine escaped until the pressure inside the system was equal to the barometric pressure. The ampoules were then sealed off at capillary constrictions. No appreciable change of gas temperature or pressure occurred during the sealing operation.

The weight of chlorine in each ampoule was calculated from the equation of state of Ross and Maass[6] and was used to determine the initial chlorine concentration for the subsequent reactions carried out in the reaction vessel. Each chlorine ampoule had a breakseal sealed to it for subsequent transfer of the chlorine into the reactor. An analysis of the chlorine in one of the ampoules, performed in the system described below, showed that the chlorine concentration was accurate to 0.4%.

An indication of the efficiency of the outgassing of the starting materials may be obtained by reference to the data of Manes and Hill,[5] who used essentially the same procedures employed here. The equipment and procedures were worked out in conjunction with these investigators. They showed that the addition of 0.1 mg. of oxygen to their reactor caused a marked decrease in the initial reaction rate. No such effect was observed in their runs where oxygen was excluded. The effect of oxygen on the thermal reaction was not studied.

Method.—The gas phase reaction was carried out in a static system, the rate of chlorination being followed by observing the loss of chlorine after the reaction had proceeded for a given length of time. The amount of chlorine undergoing reaction was calculated from the initial and final concentrations. It was assumed that all of the chlorine reacted by substitution in the side chain of benzal chloride. The validity of this assumption will, within the required limits, be justified below. The initial concentrations of benzal chloride and chlorine were determined as indicated above and the final concentration of chlorine was determined by the iodide–iodine–thiosulfate method.

The reaction vessel was constructed from a one-liter round-bottom distilling flask. The benzal chloride and chlorine ampoules and also a new side-arm breakseal were sealed to the reactor before each run. The breakseal was of the bulb type so that when broken at the end of the reaction it afforded a wide opening (about 10 mm.) for escape of gases into the high vacuum analysis system. Each ampoule contained a "weak spot" and a glass-enclosed iron rod for breaking it at the appropriate time.

The runs which were made to determine the effect of surface on the reaction rate were carried out with the reactor packed with 7-mm. Pyrex tubing in 25-mm. lengths, the packing having been cleaned with nitric acid and fire-polished. The tubing served to increase the surface–volume ratio by a factor of 15.

The reactor was baked under high vacuum to outgas it in the usual manner. When the pressure was reduced to about 10^{-6} mm. the reactor was sealed off from the pump, the "weak spot" on the chlorine ampoule broken, the chlorine condensed in the reactor with liquid air and the empty ampoule sealed off from the reaction vessel. The reactor with the sealed in benzal chloride ampoule was then placed in a high temperature air thermostat with the side-arm breakseal tube sealed to the outside analysis system. When the thermostat was at the desired regulated temperature (±0.5°) the reaction was started by breaking the benzal chloride ampoule with a magnetically controlled hammer. The solenoids were wound on brass spools, the wiring being spaced with asbestos cord and asbestos paper since the wire insulation would not stand the high temperature of the thermostat. After a given length of time the reaction was stopped and the products analyzed as described below.

Analysis of Products.—The analysis of the reaction mixture was performed by stopping the reaction and separating the gases by a high vacuum distillation in an apparatus consisting of several traps (A → F) in series. This distillation was performed in the dark to prevent any photochemical reaction from taking place between the unreacted gases.

While the reaction was going on, the trap system connected to the high vacuum pump was outgassed and sealed off from the pump. To stop the reaction, the breakseal leading to the analysis system was broken and the gases trapped with Dry Ice–alcohol baths on traps A and B and

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(5) M. Manes and D. G. Hill, to be published at a later date.

(6) A. S. Ross and O. Maass, *Can. J. Research*, **18B**, 55 (1940).

TABLE I

CHLORINATION DATA

T, °C.	a, mole/liter	b, mole/liter	x, mole/liter	P, mm.	t, sec.	$k \times 10^4$, liters$^{1/2}$moles$^{-1/2}$sec.$^{-1}$
169 (unpacked reactor)	0.002761	0.002761	0.000157	153	14,145	0.799
	.002760	.002768	.000232	153	25,020	.684
	.002605	.002635	.000283	144	36,000	.638
	.002341	.0005483	.000075	80	25,200	.579
	.003002	.0005703	.000124	99	30,600	.616
	.002760	.0006134	.000187	93	36,000	.861
						Av. 0.70 ± 0.04[a]
195 (unpacked reactor)	0.002668	0.002651	0.000174	155	10,800	1.24
	.002830	.002854	.000402	165	25,200	1.18
	.002606	.0005776	.000059	93	7,200	1.35
	.002841	.0005359	.000116	99	14,400	1.33
	.002983	.0005612	.000202	103	21,600	1.51
						Av. 1.32 ± 0.05
195 (packed reactor)	0.003526	0.0007926	0.000075	125	7,200	1.08
	.003502	.0008394	.000150	126	14,400	1.11
						Av. 1.10
230[c] (unpacked reactor)	0.002725	0.002729	0.000226	170	2339	7.24
	.002657	.002581	.000435	163	3600	10.3
	.002891	.0005336	.000065	107	1500–1800	5.66–6.80[b]
	.002821	.0004194	.000119	101	2626	8.71
	.002904	.0005333	.000282	108	7236	7.27
						Av. 8.0 ± 0.5

[a] The deviation of the average value indicated in this column is the average deviation of the mean value. [b] Time measurement uncertain in this run; an average rate constant of 6.2 was chosen. [c] Two runs at 230° were discarded because they deviated so widely from the other values obtained for k. The values of a and b in these discarded runs were rather close to some of those shown in the table. One value deviated in a negative direction while the other showed a large positive deviation. The results were discarded on the basis of the application of Chauvenet's criterion.

a liquid air bath on trap C. The benzal chloride was almost completely stopped in trap A and most of the chlorine distilled to trap C. Traps A and C were then immersed in liquid air and the analysis system sealed off from the large volume reactor.

By subsequent manipulation of Dry Ice–alcohol and liquid air as coolants for the traps it was possible to make a quantitative separation of the chlorine from the organic matter. Trial runs showed that the chlorine loss was less than 0.4% in this operation. The chlorine was determined by the iodide–iodine–thiosulfate method and the organic matter was analyzed for ring chlorination by oxidation of the side chain with alkaline permanganate by the method of Shriner and Fuson[7] followed by ether extraction, washing free of chloride ion, and finally a Parr bomb fusion on the benzoic acid derivative obtained from the process. On the basis of our determined sensitivity of the ring chlorine test, about 1×10^{-5} mole of *o*-chlorobenzaldehyde in 3×10^{-3} mole of benzal chloride, the extent of ring chlorination was established as less than 5% of the total reacted benzal chloride. The organic matter was combined in sets of two runs each to increase the sensitivity of the test. It may be noted that addition products would probably[8] have led to ring substituted compounds because of the action of alkaline permanganate on the addition products.

Results

The data obtained are shown in Table I; the symbols used in the table and in the discussion are defined as

a = Initial concentration of benzal chloride.
b = Initial concentration of chlorine.
x = Concentration of hydrochloric acid produced in the reaction in the time t.
$a - x$ = Concentration of benzal chloride at the time t.
$b - x$ = Concentration of chlorine at the time t.
P = Total pressure in mm. of mercury.
t = Time in seconds.

The symbols BH and BCl are used to represent the chemical formulas of benzal chloride and benzotrichloride, respectively.

a and b were determined as described above; $(b - x)$ was determined by analysis of the chlorine remaining at the end of the reaction. x and $(a - x)$ were then calculated, assuming no ring chlorination. P was calculated using the ideal gas law. The value of P is probably in error by about 2 or 3%.

The analytical data are probably accurate to about 0.4%; however, the precision of the kinetic data is limited by other sources of error. While criteria of purity of the starting materials were established and the amounts of these impurities estimated, the data should be interpreted in light of the possible presence of small amounts of oxygen and benzaldehyde. Oxygen may act as an inhibitor and benzaldehyde may be chlorinated although the kinetics of the thermal chlorination of benzaldehyde have not been worked out. The surface activity was studied by packing the reaction vessel, but no attempt was made to change

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(7) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," J. Wiley and Sons, Inc., New York, N. Y., 1940, p. 164.

(8) (a) Van der Linden, *Ber.*, **45**, 236 (1912); (b) S. J. Cristol, THIS JOURNAL, **69**, 338 (1947).

the nature of the surface. It is commonly found very difficult to reproduce surface conditions. The fact that a fairly consistent set of rate constants are actually obtained from the data reported in this paper is some indication that such factors as variable surface activity, possible presence of impurities, possible ring chlorination and thermal stability of benzal chloride have not had too serious an effect on the reaction.

Discussion

Examination of the data leads one to the conclusion that the rate of formation of benzotrichloride depends on the one-half power of the chlorine concentration. Although the order in benzal chloride is not as directly determined by the data, it will be shown that the best set of rate constants are obtained from a rate law involving the first power.[9] It will thus be assumed that the reaction may proceed in this manner in its initial stages. It is worth noting that calculations based on a bimolecular reaction give a very poor set of rate constants. From a consideration of the data along the lines of the following discussion it appears that reaction is occurring by a chain mechanism in the temperature range studied.

The rate of the reaction is essentially independent of the surface–volume ratio. It may be recalled that in the runs with the packed reaction vessel the surface–volume ratio was increased by a factor of 15, but the change in the reaction rate caused by the surface–volume ratio change was not significant. Therefore, any attempt to include surface dependence in the rate law would result in a negligible order for the surface function.

In light of these remarks the empirical rate law which best fits the experimental data is

$$dx/dt = k(a - x)(b - x)^{1/2} \tag{1}$$

The integrated form of this rate law is

$$kt = \frac{2}{\sqrt{a - b}}\left[\text{arc tan}\sqrt{\frac{b}{a - b}} - \text{arc tan}\sqrt{\frac{b - x}{a - b}}\right] \text{ for a > b} \tag{2}$$

and

$$kt = \frac{2}{\sqrt{b - x}} - \frac{2}{\sqrt{b}} \text{ for } a = b \tag{3}$$

The values of k calculated from the integrated formulas are shown in the last column of Table I.

It will be noticed that equation (2) involves the term $(a - b)$. For the runs where a is approximately equal to b the precision of the data would be lost by such a difference term. Accordingly, the initial concentrations for the 1:1 runs were chosen to make a and b as close as practicable, and then their average value was taken for calculations, equation (3) being used rather than equation (2) . With the values of a and b as close as they are in these particular runs, this approximation is good to better than 1% in most cases, whereas if the approximation were not made, the errors would be 25% and greater because of the difference term mentioned above.

If the values of log k_{av} are plotted against $1/T$, the best straight line leads to a value of 17 kcal. for the over-all activation energy. The deviations of the points in this plot from a straight line are considerably larger than the experimental errors in the points and are larger than might be expected over such a small temperature interval from variation of the experimental activation energy with temperature. It appears that two different reactions may be involved or, at least, two different activation energies; however, it is felt that the experimental data are insufficient to justify a more detailed inquiry into this matter. This approximate value is sufficiently accurate to indicate that it is much lower than that which might be expected from the activation energies for the analogous reactions in the homogeneous chlorination of paraffin hydrocarbons. For a reaction whose rate is independent of surface one cannot ascribe the low activation energy to surface catalysis except as described below. For a mechanism derived on the basis of a homogeneous reaction the activation energy should be at least as great as one-half the dissociation energy of chlorine, or about 29 kcal. The low activation energy is indicative of a reaction that is not entirely dependent on the simple equilibrium dissociation of chlorine. However, it is pertinent to make a more detailed inquiry into the several reaction mechanisms which are consistent with the observed rate law.

In this reaction which is proceeding by a chain mechanism, the important features to be assigned to the reaction are the chain starters and chain breakers along with a reasonable chain carrier, the combination of which must be consistent with the observed rate law. The chain carrier is assumed to be (4)

$$\begin{aligned} Cl + BH &= B + HCl \\ B + Cl_2 &= BCl + Cl \end{aligned} \tag{4}$$

and the chain starters and breaker are either (5), (6) or (7)

$$\begin{aligned} Cl_2 + S &= 2Cl + S \\ Cl + Cl + S &= Cl_2 + S \end{aligned} \tag{5}$$

$$\begin{aligned} Cl_2 + M &= 2Cl + M \\ Cl + Cl + M &= Cl_2 + M \end{aligned} \tag{6}$$

$$\begin{aligned} Cl_2 + BH &= 2Cl + BH \\ B + Cl + Cl_2 &= BCl + Cl_2 \end{aligned} \tag{7}$$

In the heterogeneous case (5) S represents some function of the surface which must be the same for the starting and breaking steps to be consistent with the apparent independence of surface indicated by the data of Table I. In the first homo-

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(9) A run which was made with a five-fold excess of chlorine would have given the dependence on the benzal chloride concentration directly. Unfortunately, this run was lost and could not be repeated because of the shortage of the purified materials. However, as will be shown, the relation between the benzal chloride concentration and the total pressure enabled an indirect determination of the order in benzal chloride to be made.

geneous case (6) M represents any suitable third body present in the gas phase. In all cases, *viz.*, (4) and (5), (4) and (6), or (4) and (7), the rate is independent of the total pressure. This is consistent with our findings since the total pressure did vary by a factor of about 2 between several of the runs with no significant effect on the calculated rate constant. This independence of pressure supports the postulated first order in benzal chloride for if this order were not unity then the homogeneous mechanisms would involve a pressure dependence. Because of the two-fold variation in pressure and also because good rate constants were not found where the order of benzal chloride was assumed to be other than unity we may take that order as unity without a more direct determination.

The homogeneous chain starter (8)

$$Cl_2 = 2Cl \qquad (8)$$

has not been considered since the half-life of the excited chlorine molecule is smaller than the time between collisions at the pressures used in this investigation.

It is of some interest that if one uses the equilibrium concentration of chlorine atoms[10] and the observed rate constant and, by the method of Pease,[2a] calculates a chain length the value found is 10^8. The assumptions used make this value uncertain even as to order of magnitude. However, and more important, since any such chain length is highly improbable in the present reaction, the calculation argues in favor of the heterogeneously catalyzed reaction (5), *i.e.*, a higher rate for the chain starter than estimated in the calculation.

In the light of the above considerations one must conclude that either (or both) the heterogeneous, (5), or homogeneous, (6) and (7), mechanisms will account for the data obtained. There is some indication to favor the heterogeneous reaction in which chains are started and broken on the surface of the reactor it being implied that the surface in all of our reactions was such that it was not a limiting factor.

It might be of interest to point out that the surface reaction which we have suggested as one of the possible mechanisms is the same as the one found by Morris and Pease[11] for the thermal hydrogen–chlorine reaction.

Acknowledgment.—The authors wish to acknowledge the suggestion of this problem by Dr. Paul M. Gross.

Summary

1. The kinetics of the gas phase thermal chlorination of benzal chloride at 169, 195 and 230° have been studied with carefully purified materials.

2. The reaction is predominantly a side-chain substitution, a maximum of 5% ring chlorination having been observed.

3. No change in over-all rate with varying pressure or surface–volume ratio was observed.

4. Some discussion of the rate law and possible reaction mechanisms has been presented.

5. A rough calculation indicates that the reaction involves a long chain length.

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[10] W. F. Giauque and R. Overstreet, THIS JOURNAL, **54**, 1731 (1932).

[11] J. C. Morris and R. N. Pease, *ibid.*, **61**, 391, 396 (1939).

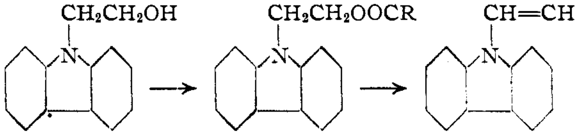
DURHAM, NORTH CAROLINA RECEIVED FEBRUARY 19, 1948

[CONTRIBUTION FROM THE PITTSFIELD LABORATORY, APPARATUS DEPARTMENT, GENERAL ELECTRIC COMPANY]

Some Reactions of N-(β-Hydroxyalkyl)-carbazoles

BY RALPH G. FLOWERS, HARRY F. MILLER AND LEOLA W. FLOWERS

In the preparation of N-vinylcarbazole (III) by decomposition of the N-acyloxyethyl derivatives, according to the scheme[1]



I II III

we have had the occasion to prepare N-(β-hydroxyethyl)-carbazole (I) and several of its esters (II). The esterification of (I) proceeded normally with good yields in all cases tried, except in the attempted preparation of a phthalate, where no reaction was observed. The use of small quantities of sulfuric acid to catalyze the reactions gave only tarry products.

The N-vinylcarbazole was best prepared by the decomposition of N-(β-acetoxyethyl)-carbazole, although many attempts were made to convert (I) directly into the vinyl derivative by various dehydration methods. These trials included treatment of (I) with phosphorus pentoxide and vapor phase treatment with alumina over a wide range of temperatures. Unreacted (I), carbazole and a small amount of polymer was obtained from these trials. Better conversion of N-(β-acetoxyethyl)-carbazole to (III) over that previously reported[1] is obtained when the reaction is carried out at reduced pressures in the presence of an inert vapor and a copper borate catalyst.

A similar program was carried out in an attempt to prepare N-propenylcarbazole (VI) from the de-

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[1] Miller and Flowers, U. S. Patent 2,426,465; *C. A.*, **42**, 224 (1948).