

189. *Mechanism of Substitution at a Saturated Carbon Atom. Part XXIV. Qualitative Survey of Nucleophilic Substitutions of Benzhydryl Halides in Sulphur Dioxide Solution.*

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In order to prepare the way to a closer kinetic study of the non-solvolytic unimolecular substitutions of alkyl halides (*e.g.*, halogen exchanges, combination with amines, etc.) a semi-quantitative survey of various substitutions of benzhydryl and *m*-chlorobenzhydryl chlorides has been made in sulphur dioxide, which was chosen as solvent for its ionising power towards alkyl halides and its non-participation in solvolytic decompositions. It is sought to discover, by means of experiments in which no attempt is made to elucidate the kinetics of any substitution process, whether reactions with such diverse substituting agents as fluoride ions, iodide ions, pyridine, triethylamine and water proceed at very different rates as they should in bimolecular substitution, or at substantially the same rate as they ought in unimolecular substitution. Comparing approximately determined initial specific rates, it is found that, for each alkyl halide, the rates of the various substitutions examined are of the same order of magnitude, differing from one another by less than can be explained by departures from conditions of ideal dilution, or, in the particular case of water as

* It is, however, possible to arrange for the production of a cationic centre in these cases by introducing a suitable substituent (*e.g.*, phenyl) at the carbon atom which bears the halogen.

reagent, by less than can be attributed to a special uncertainty that enters into the interpretation of the data for that reaction.

FOR the more detailed investigation of unimolecular (S_N1) substitutions of non-solvolytic type it is necessary to cut out simultaneous solvolytic processes; and for this purpose a solvent must be found which is sufficiently strongly ionising towards alkyl halides to promote the desired type of substitution, but is not sufficiently nucleophilic to be decomposed by the alkyl cation formed. Bateman and Hughes found such a solvent in anhydrous formic acid (J., 1937, 1187; this vol., pp. 935, 940 and 945), but the acidity of this material limits the range of its application: it could not, for instance, be employed as a solvent for the Menschutkin reaction (combination of an alkyl halide with an amine). In seeking a more widely applicable alternative solvent, we turned to sulphur dioxide, because of its known ionising power towards certain alkyl halides* (*e.g.*, triarylmethyl halides) and its generally high resistance to decomposition.

The alkyl halides which suggested themselves as likely to exhibit unimolecular nucleophilic substitution in sulphur dioxide were *tert.*-alkyl, α -phenylalkyl, and benzhydryl halides, all of which readily undergo unimolecular hydrolysis in aqueous solvents.† Bergmann and Polanyi had found that optically active α -phenylethyl chloride underwent a first-order racemisation in sulphur dioxide (*Naturwiss.*, 1933, 21, 378). It is certain that, as they stated, the rate of this racemisation is controlled by the ionisation of the halide, but it is not clear whether the racemisation is simply to be correlated with unimolecular substitution, or whether it involves a unimolecular elimination, with the reversible formation of hydrogen chloride and styrene (Hughes, Ingold, and Scott, J., 1937, 1271). It was in order to avoid possible complications of this kind that we decided to experiment with benzhydryl halides from which analogous elimination reactions are precluded by the structure. The substitutions of these halides have been followed by measurements of electrical conductivity.

This paper records a preliminary survey of a number of substitutions of benzhydryl halides, *viz.*, halogen exchanges, Menschutkin reactions and hydrolyses. The survey is confessedly qualitative. The test it seeks to apply is that of comparing the rates of substitution of the same alkyl halide by various reagents, such as fluoride ions, iodide ions, pyridine, triethylamine and water, which in bimolecular substitution should react at very different rates—rates ranging, indeed, over several powers of ten—but in unimolecular substitution should form their respective substitution products at one common rate, *viz.*, the rate of ionisation of the alkyl halide. We call this test qualitative, because, until we have carried through the lengthy task of working out the kinetics of all these reactions, we hardly know how to define "rate of substitution" from a quantitative standpoint, and we certainly do not know how to correct observed rates to correspond to the conditions of ideality‡ under which alone a strict comparison of the different reactions is possible. However, with reagents as diverse in chemical nature and general reactivity as those mentioned above, it would be a satisfactory *prima facie* indication that the unimolecular mechanism was at work if we were to find that the *initial specific* rates of substitution at the concentrations obtaining in the experiments were of the same order of magnitude. A more precise comparison cannot here be attempted, because it would require a more detailed experimental investigation than it was our purpose to carry out at this stage.§

The first series of tests were carried out with benzhydryl chloride. The reagents were

* Exaggerated ideas of this have arisen through insufficient attention to purity in some of the reported observations on conductivity in sulphur dioxide.

† Some caution is necessary in drawing such deductions, since sulphur dioxide does not appear to be as "rapid" a solvent as water for the ionisation of alkyl halides.

‡ In the kinetics of the unimolecular mechanism of non-solvolytic reactions, for example, the condition for ideality, *i.e.*, the condition that the observed rate of substitution will reduce to the rate of ionisation of the alkyl halide at vanishingly small concentrations, is not merely that the concentrations of the alkyl halide, the reagent, and all other solutes, shall be infinitesimals; it includes the further condition that, if the concentration of the reagent is a first-order infinitesimal, that of the halide ions liberated in substitution must be no larger than a second-order infinitesimal (following paper).

§ This was in 1937: a later detailed investigation of one reaction is described in the next paper.

tetraethylammonium fluoride, tetramethylammonium fluoride, pyridine, triethylamine and water. The observed changes of conductivity with time are in the experimental section: although we did not base any kinetic calculations on them, having in mind the production of more accurate data for this purpose, some approximate calculations probably could be made. What we have done is to express the initial slopes * given by the graphs of these data in reciprocal-time units defined in accordance with the following method of treatment. There are two cases. First, when the initial concentration, a , of benzhydryl chloride is smaller than the initial concentration, c , of the substituting agent, we take the slope as the initial conductivity change per second reckoned as a fraction of the total change of conductivity in the complete reaction: $k_1 = (d\kappa/dt)/(\kappa_\infty - \kappa_0)$ in sec.^{-1} . Considered as an initial specific rate of destruction of benzhydryl chloride, this value can only be approximate, perhaps not much better than an order of magnitude, first, because the method neglects departure from linearity in the relationship between conductivity and the concentration of the conducting substances, and secondly, because the method assumes that, when the reaction stops, all the benzhydryl chloride is destroyed, which it may not be unless the excess of substituting agent is very large. The second case arises when the initial concentration of the benzhydryl chloride is larger than that of the substituting agent. Now we take the slope as the former ratio multiplied by the ratio c/a , *i.e.*, we assume the relation $k_1 = [(d\kappa/dt)/(\kappa_\infty - \kappa_0)] (c/a)$ in sec.^{-1} . This is likewise only an approximate initial specific rate, because the method assumes, first, that the connexion between conductivity and concentration is a linear one, and secondly, that, when reaction stops, all the substituting agent is consumed, which it may not be unless the excess of benzhydryl chloride is very large. In spite of these shortcomings, it seems clear that initial specific rates obtained in this way should serve for an order of magnitude comparison, which is all that we are attempting. The values, which relate to the temperature -17.1° , are in Table I.

TABLE I.

Approximate Initial Specific Rates of Substitution of Benzhydryl Chloride in Sulphur Dioxide at -17.1° (k_1 in sec.^{-1}).

No.*	Reagent.	$[\text{CHPh}_2\text{Cl}]_{t=0}$.	$[\text{Reagent}]_{t=0}$.	$10^3 k_1$.
1	NEt ₃ F	0.120	~0.03	~1.2
2		"	~0.04	~1.3
3		"	0.10	1.2
4	NMe ₃ F	"	0.015	0.8
5		"	0.10	1.2
6		"	0.016	0.6
7	C ₅ H ₅ N	"	0.064	0.7
8		0.022	0.266	1.1
9		0.120	0.0083	0.8
10	H ₂ O	"	0.14	4.4
11		"	0.42	8.3

* Details under corresponding numbers are in Table III.

With fluoride ions, pyridine, and triethylamine as the reagents, we find all the rates of the order of magnitude of $1 \times 10^{-3} \text{ sec.}^{-1}$. The values obtained with water as reagent are 4—8 times higher. We believe that this apparent slight discrepancy is due to the uninteresting cause that, whilst in the halogen exchange and Menshutkin reactions, the electrolytes on which the measured conductivity depends are all fully ionised quaternary ammonium salts, in the case of hydrolysis the electrolyte is the largely covalent substance hydrogen chloride. Sulphur dioxide itself scarcely ionises hydrogen chloride, and therefore at the commencement of the reaction, when the concentration of hydrogen chloride is at a minimum whilst that of the water is at a maximum, the fraction ionised will be considerably greater than at the end of reaction, when the hydrogen chloride concentration is at a maximum and the water concentration at a minimum. This means that the factors

* In practice we find it more accurate not to read initial reaction rates directly from $x-t$ curves, but to deduce them from curves of x/t against x (in the present case, x is taken as proportional to the change of conductivity).

which would be required to translate (a) the initial rate of change of conductivity, $d\kappa/dt$, into a rate of change of concentration, and (b) the conductivity interval, $\kappa_{\infty} - \kappa_0$, into a concentration interval, may be very different, whereas our treatment has assumed them to be the same. It is easy to see that this disturbance must make the apparent initial specific rate of hydrolysis too high. We conclude that the results of Table I as a whole are a satisfactory indication of the prevalence of the unimolecular mechanism in these substitutions.

At -17° , the reactions of benzhydryl chloride in sulphur dioxide are really too rapid for precise measurement, and therefore, as this qualitative work was intended to lead to selected quantitative studies, we felt it necessary to find a less reactive benzhydryl halide. Accordingly, we prepared *m*-chlorobenzhydryl chloride, which gave rates of a more convenient order of magnitude. The same test which had been applied to benzhydryl chloride was now employed in order to obtain a preliminary assurance that the introduction of the electron-attracting substituent had not disturbed the supremacy of the unimolecular mechanism of substitution. The approximate specific rates of substitution of this substance were measured with three reagents, *viz.*, tetramethylammonium fluoride, ammonium iodide, and pyridine. The results are in Table II. At -10.75° , all the rates were of the order of magnitude of 4×10^{-5} sec. $^{-1}$; and, since the amount of variation shown by the individual values was obviously not necessarily attributable to the differences between the reagents, because the whole of it could be obtained with one and the same reagent, we accepted the results as a preliminary demonstration that the halogen exchanges and Menschutkin reactions of *m*-chlorobenzhydryl chloride take place by the unimolecular mechanism,* and proceeded with the study of the kinetics of these substitutions. The kinetics of unimolecular halogen exchange are discussed in the next paper, and we hope shortly to be in a position to report similarly on the unimolecular Menschutkin reaction.†

TABLE II.

Approximate Initial Specific Rates of Substitution of m-Chlorobenzhydryl Chloride in Sulphur Dioxide at -10.75° (k_1 in sec. $^{-1}$).

Reagent.	$[C_6H_4Cl-CHPhCl]_{t=0}$.	$[Reagent]_{t=0}$.	$10^5 k_1$.
NMe ₄ F	{ 0.0670	0.0028	2.38 *
	{ 0.0683	0.0502	7.70 *
NH ₄ I	{ 0.0647	0.0028	4.1
	{ 0.0662	0.0068	5.6
C ₅ H ₅ N	{ 0.0719	0.0127	2.8
	{ 0.0705	0.0485	4.0

* The original approximate values are here replaced by more accurate values obtained as described in the next paper, where the reason for their variation is considered.

EXPERIMENTAL.

Materials.—*m*-Chlorobenzoyl chloride, b. p. $100^{\circ}/19$ mm., prepared from *m*-chlorobenzoic acid and phosphorus pentachloride in 84% yield, was converted into *m*-chlorobenzophenone, m. p. 83° , in 54% yield, by interaction with benzene and aluminium chloride in carbon disulphide solution. The reduction of the ketone (94 g.) was effected by adding zinc dust (160 g.) to its boiling solution in ethyl alcohol (990 c.c.) containing water (110 c.c.) and sodium hydroxide (94 g.), and continuing the heating for 12 hours. The *m*-chlorobenzhydryl, m. p. 41° , was isolated (64 g.) by filtering the hot solution, pouring the filtrate into ice-water (4 l.) to which

* In contrast to these reactions in sulphur dioxide, we have found that the reactions of benzhydryl and *m*-chlorobenzhydryl chloride with iodide ions in acetone and acetonitrile as solvents have the bimolecular mechanism. Halogen exchange through the interaction of halide ions with alkyl halides was one of the substitutions for which Hughes and Ingold predicted (J., 1935, 253) that a change of mechanism could be caused by a change of solvent only, with the same alkyl compound and the same substituting agent.

† This has been delayed in part by the necessity of investigating the sulphur dioxide solvates formed by tertiary amines.

concentrated hydrochloric acid (400 c.c.) had been added, and crystallising the precipitate, obtained as a slowly solidifying oil, from light petroleum (b. p. 40—60°). For the preparation of the chloride, a solution of the alcohol (24 g.) in a mixture of light petroleum (175 c.c., b. p. 40—60°) and ether (50 c.c.), containing suspended calcium chloride, was saturated with hydrogen chloride. After 1 hour the solution was poured on fresh calcium chloride, again saturated with hydrogen chloride, and left for 2 days. The solution was then dried with sodium sulphate, evaporated to 50 c.c., diluted to 100 c.c. with a mixture of light petroleum and ether, and shaken with anhydrous potassium carbonate. The filtered solution was concentrated to 30 c.c., filtered into a distilling flask, and finally concentrated; and the residue was then distilled (oil-bath) at a low pressure. *m*-Chlorobenzhydryl chloride was thus obtained, in a middle fraction (12 c.c.), as a clear, colourless liquid, b. p. 160—162°/0.1—0.2 mm. (Found: C, 65.9; H, 4.3; *M*, by hydrolysis, 236. Calc.: C, 65.7; H, 4.2%; *M*, 237). The two special points about this chain of preparations are that the amount of water used in the reduction with zinc dust should be optimal, and that the *m*-chlorobenzhydryl chloride, before distillation, should be quite free from suspended particles of drying agent or other solid matter. Norris and Banta reported that this chloride could not be distilled (*J. Amer. Chem. Soc.*, 1928, 50, 1807), but we found that it could be, provided that one took care with the filtration, used well-cleaned apparatus, employed an oil-bath for heating, and used pressures below 0.5 mm.

Tetramethylammonium fluoride and chloride were prepared by converting the iodide by means of silver oxide and water into a solution of the hydroxide, and neutralising this with the appropriate halogen acid, traces of silver being then removed by treatment of the hot solution with hydrogen sulphide. The solution was concentrated, treated with norit, and evaporated on the steam-bath with additions of small amounts of water and acetone. The resulting thick paste, or hard cake, of salt was fully dried by heating at 150° for 6—7 hours under 0.5 mm. pressure.

Sulphur dioxide from a siphon was passed as gas through a U-tube containing phosphoric oxide, directly into the conductivity cell, which was cooled in a bath at —80°. At —10.75° its conductivity was below 5×10^{-6} ohm⁻¹ cm.⁻¹, the limit of the measuring apparatus.

Apparatus.—The low-temperature thermostat was that constructed by Dr. G. A. Benford (*J.*, 1938, 933). In building a conductivity apparatus, we benefited by advice from Dr. G. S. Hartley. Activated by a valve oscillator, the set-up contained the usual ratio-arm box and non-inductive resistance box, in earthed casings, and the cell, earthed on the side of the telephone indicator. A variable condenser, of capacity 0.0005μF., in an earthed casing was tapped across the cell; and a bank of fixed condensers, of capacities ranging from 0.0002μF. to 0.004μF., arranged in parallel, each with a key, was tapped across the resistance box.

The cell, which was graduated in the neck, was made of "Normal" Jena glass tubing, and had an electrode chamber, of about 15 c.c. capacity, containing smooth platinum electrodes. It was felt undesirable to use platinised electrodes in case of possible catalytic effects. With smooth electrodes considerable polarisation took place at the higher salt concentrations, but in these cases satisfactory readings were obtained by using a 10 : 1 ratio. The cell was cleaned before use with chromic acid, washed with distilled water, acetone, and distilled water successively, then treated with scrubbed steam, and finally dried at 120° for 1 hour in an electrically heated oven. The cell constant was determined by comparison with a standard cell at 25°, the same aqueous 0.01*N*-potassium chloride solution being used.

Methods.—The reagent was first introduced into the cell, and the sulphur dioxide was distilled on to it. When the solution had taken the temperature of the thermostat, the volume and conductivity were noted. The benzhydryl chloride or *m*-chlorobenzhydryl chloride was then added from a small, graduated pipette, and readings of conductivity were taken thereafter at suitable intervals. Solid reagents were introduced from weighing tubes, and liquids from special pipettes graduated by weight. The first two results of Table I are less accurate than the others, because in these first two experiments we had not become experienced in introducing known amounts of the extremely hygroscopic salt, tetraethylammonium fluoride.

Results.—These are given in detail for benzhydryl chloride, but not for *m*-chlorobenzhydryl chloride, because the work here reported on this substance is to be superseded by more exact studies of its substitution reactions; indeed this is in part already done in the work described in the next paper. In Table III conductivity values are recorded as reciprocal resistances (ohm⁻¹). They should be multiplied by the cell constant, 0.540 cm.⁻¹, for conversion to conductivities (ohm⁻¹ cm.⁻¹). The values corresponding to $t = 0$ represent reciprocal resistances as measured before the introduction of the benzhydryl chloride.

TABLE III.

Reactions of Benzhydryl Chloride with Substituting Agents, as followed by Conductivity Changes, in Sulphur Dioxide at -17.1°

(A) Tetraethylammonium Fluoride.

(1) Initially, $[\text{CHPh}_2\text{Cl}] = 0.120\text{M}$; $[\text{NEt}_4\text{F}] = \text{ca. } 0.03\text{M}$.								
t (mins.)	0.00	1.55	2.45	3.60	5.20	6.55	7.50	
$10^3 R^{-1}$	1.825	1.805	1.828	1.848	1.873	1.887	1.894	
t (mins.)	8.70	10.1	11.3	13.2	14.7	16.6	18.5	
$10^3 R^{-1}$	1.905	1.912	1.916	1.927	1.932	1.938	1.944	
t (mins.)	21.3	25.9	34.2	43.3	61.2	80.0	∞	
$10^3 R^{-1}$	1.946	1.955	1.963	1.967	1.969	1.971	1.980	
(2) Initially, $[\text{CHPh}_2\text{Cl}] = 0.120\text{M}$; $[\text{NEt}_4\text{F}] = \text{ca. } 0.04\text{M}$.								
t (mins.)	0.00	4.80	6.80	9.00	11.4	13.4		
$10^3 R^{-1}$	2.101	2.165	2.188	2.208	2.222	2.232		
t (mins.)	15.7	18.3	21.3	24.8	30.0	36.3		
$10^3 R^{-1}$	2.242	2.252	2.262	2.268	2.278	2.283		
t (mins.)	42.5	57.5	78.5	97.5	116.5	∞		
$10^3 R^{-1}$	2.288	2.294	2.299	2.303	2.306	2.315		
(3) Initially, $[\text{CHPh}_2\text{Cl}] = 0.120\text{M}$; $[\text{NEt}_4\text{F}] = 0.10\text{M}$.								
t (mins.)	0.00	2.40	4.60	6.80	9.10	11.7		
$10^3 R^{-1}$	6.135	6.042	6.117	6.193	6.232	6.270		
t (mins.)	14.8	18.9	22.9	26.5	32.4	38.5		
$10^3 R^{-1}$	6.329	6.369	6.410	6.431	6.473	6.494		
t (mins.)	47.7	57.3	76.9	102.5	120.0	∞		
$10^3 R^{-1}$	6.536	6.557	6.601	6.645	6.672	6.711		

(B) Tetramethylammonium Fluoride.

(4) Initially, $[\text{CHPh}_2\text{Cl}] = 0.120\text{M}$; $[\text{NMe}_4\text{F}] = 0.015\text{M}$.								
t (mins.)	0.00	1.25	2.20	3.00	4.50	6.05		
$10^3 R^{-1}$	0.9141	0.9009	0.9174	0.9259	0.9381	0.9461		
t (mins.)	7.75	10.5	14.7	20.75	32.8	49.5		
$10^3 R^{-1}$	0.9542	0.9597	0.9643	0.9681	0.9699	0.9718		
t (mins.)	69.0	92.0	120.0	143.0	170.0	∞		
$10^3 R^{-1}$	0.9723	0.9747	0.9761	0.9773	0.9784	0.9848		
(5) Initially, $[\text{CHPh}_2\text{Cl}] = 0.120\text{M}$; $[\text{NMe}_4\text{F}] = 0.10\text{M}$.								
t (mins.)	0.00	1.20	2.05	2.85	4.20	5.03		
$10^3 R^{-1}$	6.173	6.952	6.024	6.061	6.135	6.173		
t (mins.)	7.50	10.7	13.1	17.5	22.85	32.7		
$10^3 R^{-1}$	6.250	6.329	6.369	6.452	6.494	6.579		
t (mins.)	52.5	70.0	102.0	133.0	160.0	∞		
$10^3 R^{-1}$	6.711	6.757	6.849	6.921	6.949	7.092		

(C) Pyridine.

(6) Initially, $[\text{CHPh}_2\text{Cl}] = 0.120\text{M}$; $[\text{C}_5\text{H}_5\text{N}] = 0.016\text{M}$.								
t (mins.)	0.00	1.30	2.50	3.10	3.60	4.20	4.90	
$10^3 R^{-1}$	0.0455	0.1667	0.2083	0.2222	0.2381	0.2500	0.2632	
t (mins.)	6.00	7.60	8.90	10.7	12.3	15.8	21.9	
$10^3 R^{-1}$	0.2857	0.3125	0.3333	0.3572	0.3704	0.4167	0.4762	
t (mins.)	27.1	36.7	49.5	61.0	138.0	208.0	∞	
$10^3 R^{-1}$	0.5263	0.5848	0.6623	0.7143	0.9346	1.0417	1.1364	
(7) Initially, $[\text{CHPh}_2\text{Cl}] = 0.120\text{M}$; $[\text{C}_5\text{H}_5\text{N}] = 0.064\text{M}$.								
t (mins.)	0.00	1.20	1.70	2.40	3.20	4.30	5.60	
$10^3 R^{-1}$	0.0935	0.4049	0.4167	0.4546	0.5000	0.5556	0.6061	
t (mins.)	6.60	8.30	10.6	14.3	18.4	22.5	28.6	
$10^3 R^{-1}$	0.6452	0.6944	0.7692	0.8621	0.9615	1.0526	1.1696	
t (mins.)	36.2	45.8	60.3	76.8	316.0	∞		
$10^3 R^{-1}$	1.3158	1.4493	1.6667	1.8519	3.4483	4.7619		
(8) Initially, $[\text{CHPh}_2\text{Cl}] = 0.022\text{M}$; $[\text{C}_5\text{H}_5\text{N}] = 0.266\text{M}$.								
t (mins.)	0.00	1.20	2.10	2.50	3.70	5.10		
$10^3 R^{-1}$	0.074	0.286	0.400	0.435	0.524	0.614		
t (mins.)	5.90	7.80	9.20	11.2	13.5	16.1		
$10^3 R^{-1}$	0.662	0.752	0.820	0.901	0.990	1.075		
t (mins.)	19.5	22.7	27.6	33.2	48.9	∞		
$10^3 R^{-1}$	1.177	1.266	1.389	1.515	1.802	3.571		

TABLE III (continued).

(D) *Triethylamine.*(9) Initially, $[\text{CHPh}_2\text{Cl}] = 0.120\text{M}$; $[\text{NEt}_3] = 0.0083\text{M}$.

t (mins.)	0.00	2.05	3.00	3.80	5.10	6.00	7.25
$10^3 R^{-1}$	0.0855	0.1667	0.1786	0.1852	0.1942	0.2000	0.2083
t (mins.)	9.10	11.3	14.4	19.2	24.95	40.0	60.0
$10^3 R^{-1}$	0.2146	0.2222	0.2288	0.2353	0.2381	0.2392	0.2370
t (mins.)	90.0	107.0	129.0	153.0	180.0	240.0	∞
$10^3 R^{-1}$	0.2339	0.2329	0.2326	0.2320	0.2310	0.2307	0.2541

(E) *Water.*(10) Initially, $[\text{CHPh}_2\text{Cl}] = 0.120\text{M}$; $[\text{H}_2\text{O}] = 0.140\text{M}$.

t (mins.)	0.00	1.50	2.00	2.75	3.50	4.35	5.15
$10^3 R^{-1}$	~ 0.01	0.0333	0.0333	0.0400	0.0435	0.0476	0.0500
t (mins.)	6.20	7.60	10.1	12.2	14.5	18.1	23.3
$10^3 R^{-1}$	0.0526	0.0568	0.0621	0.0658	0.0690	0.0730	0.0769
t (mins.)	32.8	44.3	74.5	115.0	265.0	420.0	∞
$10^3 R^{-1}$	0.0813	0.0833	0.0862	0.0877	0.0909	0.0929	0.0943

(11) Initially, $[\text{CHPh}_2\text{Cl}] = 0.120\text{M}$; $[\text{H}_2\text{O}] = 0.420\text{M}$.

t (mins.)	0.00	1.50	2.40	3.40	4.30	5.70	7.65
$10^3 R^{-1}$	~ 0.01	0.0909	0.111	0.1266	0.1409	0.1587	0.1818
t (mins.)	9.20	11.0	13.0	16.85	22.0	29.0	61.0
$10^3 R^{-1}$	0.1976	0.2137	0.2299	0.2571	0.2732	0.2755	0.2882

Reaction Products.—With one of these reagents, *viz.*, pyridine, the product was isolated by evaporation of the sulphur dioxide at the end of a conductivity experiment. The benzhydrylpyridinium chloride, washed with ether, had *m. p. ca.* 203°, and gave a picrate, *m. p.* 173° (Found: C, 60.6; H, 3.5. Calc.: C, 60.8; H, 3.8%).

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