NEW METHOD FOR THE SYNTHESIS OF MACROCYCLIC COMPOUNDS

XVI.* EFFECT OF SILICA GEL ON THE INTRAMOLECULAR ACYLATION OF ACID CHLORIDES OF ω-(METHYLTHIENYL)ALKANOIC ACIDS

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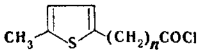
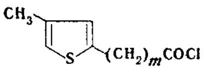
The intramolecular acylation of acid chlorides of ω-thienylalkanoic acids of various structures in the presence and absence of silica gel was investigated. The reaction of aluminum chloride etherate and the indicated acid chlorides with the surface groups of silica gel was studied by IR spectroscopy, and the role of the compounds formed on the surface in the reaction under consideration was discussed. A sequence of processes and a mechanism involving participation of the solid phase in the intramolecular acylation of acid chlorides of ω-thienylalkanoic acids are formulated.

It has been found that aluminum hydroxychlorides [1, 2], aluminum oxide [3], and silica gel [3], which are inactive as condensing agents in intramolecular acylation of acid chlorides of ω-(2-thienyl)alkanoic acids, raise the yield of cyclization product considerably as compared with the yield observed in the reaction in a homogeneous medium in the absence of a sorbent. Assumptions have been expressed that the solid phase, by fixing the cyclized molecule on its surface, promotes separation of the molecules and thereby hinders the intermolecular condensation. In addition, one can imagine that free rotation is, within certain limits, inhibited on the surface of the solid phase (because of the formation of the so-called "rigid groups" [4]); this may promote the development of molecular conformations that are favorable for the occurrence of the intramolecular reaction. It seemed of interest to investigate intramolecular acylation in the case of alkyl-substituted (in the thiophene ring) acid chlorides of ω-thienylalkanoic acids both in the presence and absence of silica gel. The objects of this study were the acid chlorides of ω-(5-methyl-2-thienyl)alkanoic acids (I), ω-(4-methyl-2-thienyl)alkanoic acids (II), and ω-(3-methyl-2-thienyl)alkanoic acids (III).



I



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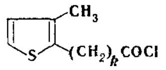

III

$n = 9\text{-}11$; $m = 9\text{-}10$; $k = 9\text{-}10$

All of the experiments were carried out under identical conditions that did not differ from the conditions used previously in the cyclization of acid chlorides of unsubstituted ω-thienylalkanoic acids [3]. As seen from the data presented in Table 1, the previously found regularities [3] are also confirmed in the case of alkyl-substituted thienylalkanoic acids. Thus the yield of cyclization product increases as the chain length increases in the presence of (experiments Nos. 5 and 10) and in the absence of (Nos. 2, 6, and 8) silica gel. An increase in the aluminum chloride etherate (ACE) concentration (experiments Nos. 2, 3, 6, 7, 8, and 9) also leads to an increase in the yield of cyclization product. We have previously noted [5, 6] that in the cy-

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*See [15] for communication XV.

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TABLE 1. Intramolecular Acylation of Acid Chlorides of ω-Thienylalkanoic Acids

Expt. No.	Compound	Amount of acid, g	Volume of chloroform for dissolving of the acid chloride, ml	Reaction time, h	$AlCl_3$ etherate,[a] g	MSK silica gel gel, g	Yield, %
1	I, $n=9$	5	40	13	30	100	8,4
2	I, $n=9$	5	40	13	30	—	15
3	I, $n=9$	5	40	13	90	—	34
4	I, $n=9$	15	60	17,5	92	300[b]	15
5	I, $n=10$	5	40	13	30	100	18
6	I, $n=10$	5	40	13	30	—	37
7	I, $n=10$	5	40	13	90	—	51
8	I, $n=11$	5	40	13	30	—	42,5
9	I, $n=11$	5	40	15	90	—	55
10	I, $n=11$	5	40	13	47	100	39,3
11	I, $n=11$	5	60	15	30,6	300	0[c]
12	II, $m=9$	2,5	20	6,5	15	—	26
13	II, $m=9$	2,5	20	6,5	15	50	57
14	II, $m=10$	1	8[d]	2,6	6	—	14
15	II, $m=10$	3,8	30[d]	9	22,8	76	56
16	III, $k=9$	2,5	20[d]	6,5	15	—	27
17	III, $k=9$	2,5	20[d]	6,5	15	50	55
18	III, $k=10$	2,5	20[d]	6,5	15	—	55
19	III, $k=10$	2,5	20[d]	6,5	15	50	72

[a] All of the experiments were carried out in 520 ml of chloroform per 5 g of starting acid. [b] The volume of chloroform was 1.5 liter. [c] The starting acid (60%) was isolated from the reaction mass. [d] Heptane was used as the solvent for the acid chloride in these experiments.

clization of acid chlorides I the addition of silica gel to the reaction mixture does not have a positive effect on the process. On the contrary, it is seen from the results of experiments Nos. 1-10 that the presence of silica gel in the case of these acid chlorides not only does not lead to an increase in the yield of cyclization product but even lowers it substantially. For this reason, cyclization in a homogeneous medium at high ACE concentrations [3] was used in the papers [5, 6] cited above. In contrast to this, in the cyclization of ω-[3(4)-methyl-2-thienyl]alkanoic acids [7] the addition of silica gel leads to a substantial increase in the yield by approximately the same amount as in the case of cyclization of acid chlorides of ω-thienylalkanoic acids. In order to find the explanation for the differences that we observed in the behavior of acid chlorides I, II, and III, we investigated: a) the reaction of ACE with silica gel; b) the reaction of acid chlorides I and III with silica gel; c) the reaction of acid chlorides I and III with silica gel treated with ACE.

First of all, it should be noted that we observed hydrogen chloride evolution during the addition of ACE to a suspension of silica gel in chloroform. This fact compelled us to make a closer investigation of the interaction of ACE with silica gel. As in the previous studies, we used MSK silica gel with a surface area of 300 m^2/g and a pore size of 100 Å, calcined at 450-500°. Samples of this silica gel were treated with a solution of ACE in chloroform both at room temperature and with heating, during which the evolved hydrogen chloride was collected. In addition, using the previously demonstrated possibility of the quantitative determination of ACE in solution by means of IR spectroscopy [8] [from the optical density of the absorption band at 1000 cm^{-1} in the IR spectrum; this band is related to the C–O–C vibrations in the complex (also see [9])], the amount of it remaining in solution was established. As shown by these measurements and the parallel data from the titration of the ACE remaining in solution (by the Volhard method after removal with argon of the hydrogen chloride gas, which, as is well known, is not tied up by $AlCl_3$ [10]), the ACE is initially absorbed and its concentration then increases in proportion to the starting concentration of the solution used (Fig. 1); this attests to saturation of the silica gel surface with ACE. It is seen from Fig. 1 that the data obtained by titration and the spectral method coincide quite satisfactorily. It should be noted that the sensitivity of the spectral method is lower in this case than the accuracy of the Volhard determination, but the points of saturation of the silica gel, which were determined both by titration (Table 2) and by the spectral method, practically coincide. The capacity of silica gel, calculated from these data, with respect to ACE is $5.6 \cdot 10^{-4}$ mole/g or 0.116 g of ACE per gram of silica gel. A comparison of the amount of ACE absorbed by silica gel, which was found by the methods presented above, with the amount of evolved hydrogen chloride shows that ~ 1 mole of evolved hydrogen chloride corresponds to each mole of ACE tied up. The hydrogen chloride formed was determined under conditions of isolation of the reaction mixture from the action of air

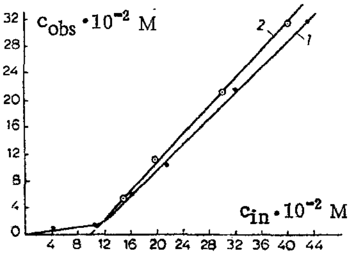

Fig. 1

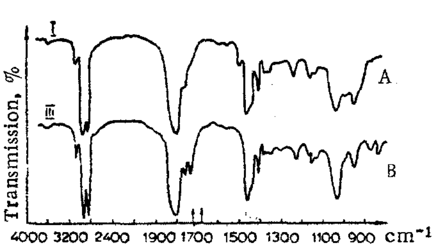

Fig. 2

Fig. 1. Dependence of the observed $AlCl_3$ etherate concentration (c_{obs}) determined by titration (1) and spectrally (2) on the initial concentration (c_{in}) as silica gel is added to the solution in $CHCl_3$.

Fig. 2. IR spectra of acid chlorides I (A) and III (B). The arrows indicate the positions of the C = O bands of the corresponding acids and ketones.

moisture and with allowance for a correction for Cl^-, determined in an experiment without added ACE. The amount of ACE absorbed by silica gel and the amount calculated from the amount of hydrogen chloride evolved differ only slightly from the amounts found by the methods indicated above and is $5.5\cdot 10^{-4}$ mole/g, or 0.114 g of ACE per gram of silica gel. It should be noted that the quantitative data presented pertain to the interaction of aluminum chloride etherate and silica gel at room temperature. The amount of aluminum chloride absorbed from solution at the boiling point of chloroform increases from 0.114 to 0.151 g per gram of silica gel. The data obtained can be compared with the data available in the literature. At present it has been established that the surface of silica gel has primarily two types of groups – silanol and siloxane [11] – the quantitative interrelationship between which depends on the temperature of the preliminary treatment of the silica gel. For example, according to the data in [11], the amount of silanol groups for Aerosil that has been calcined at 500° is 25 meq per 100 g ($2.5\cdot 10^{-4}$ equivalent/g), which in order of magnitude approximately corresponds to the absorbed amount of ACE. Starting from these data, it can be assumed that in the case under consideration the reaction proceeds via the scheme

$$\rangle Si{-}OH + AlCl_3\cdot Et_2O \rightarrow \rangle Si{-}OAlCl_2\cdot Et_2O.$$

The silanol groups are quite far removed from one another on the surface, so that the evolution of only one molecule of hydrogen chloride is fully explicable from the point of view of the so-called "equimolecular" neutralization of the surface silanol groups [11]. In itself, the $AlCl_2\cdot OEt_2$ grouping has a considerable volume and may shield approach to other silanol groups. It is possible that the increase in the amount of ACE that is absorbed on heating is explained by the fact that these silanol groups become more accessible under more severe temperature conditions.

It is interesting to note that the optical method of monitoring the reaction of silica gel with ACE provides a possibility for determining the presence or absence of ether, which is possibly evolved from the ACE in this process. It followed from previously published data [8] that even when only small amounts of silica gel were present an absorption band at 1108 cm^{-1}, which corresponds to the ether, appeared in the spectrum. Belen'kii and Lopatin [8] ascribed the appearance of this band to either dissociation of ACE under the influence of silica gel or to its hydrolysis. In the present research we also observed a weak absorption band at 1108 cm^{-1}, but the quantitative evaluation of this band shows that its intensity is practically independent of the amount of silica gel and amounts to 0.003 mole/liter at ACE concentrations from 0.1 to 0.65 mole/liter. Thus the appearance of an absorption band at 1108 cm^{-1} in [8] and in this case can be ascribed to hydrolysis of ACE as a result of its interaction with traces of water in the solvent but not with silica gel. On the basis of these observations, it can be concluded that ACE is absorbed by silica gel without splitting out of a molecule of ether but rather with splitting out of HCl. In this connection, it is interesting to note that the hydrolysis of ACE with water dissolved in chloroform proceeds with the absorption of ~ 2.5 moles of water per mole of ACE and with splitting out of a molecule of ether [3].

The spectra of acid chlorides I and III are presented in Fig. 2. As seen from these figures, the absorption band corresponding to the vibrations of the CO group in the acid chloride lies at 1796 cm^{-1}. The bands corresponding to the vibrations of the CO group in acids and ketones are shifted to the low-frequency region and lie, respectively, at 1710 and 1671 cm^{-1}. It should be noted that the absorption in these regions for the starting samples of acid chlorides I and III is weak. In the case of acid chlorides III it may be some-

TABLE 2. Determination of Aluminum Chloride Etherate (ACE) Absorbed by Silica Gel

Amount of ACE in solution, mole $\cdot 10^{-3}$	Amount of Cl^- (A) in solution, g-equiv $\cdot 10^{-3}$	n*	Amount of ACE remaining in solution, g-equiv Cl^{-1} (B) $\cdot 10^{-3}$	A–B, g-equiv $\cdot 10^{-3}$	$\frac{B}{3}$, mole $\cdot 10^{-3}$	$\frac{A-B}{3}$, mole $\cdot 10^{-3}$	Amount of ACE absorbed by the silica gel, (mole/g) $\cdot 10^{-4}$
8,46	25,38	9,15	9,52	15,86	3,17	5,29	5,29
11,3	33,9	16,01	16,65	17,25	5,55	5,73	5,73
16,9	50,7	32,31	33,6	16,1	11,2	5,37	5,37
22,36	67,08	47,31	49,2	17,88	16,4	5,96	5,96

*The symbol n is the amount of 0.1 N $AgNO_3$ per milliliter that is consumed in the titration of 5 ml (out of 52 ml) of the solution after interaction with the silica gel.

what more clearly expressed because of the previously indicated [7] instability of these acid chlorides and the possible development of polycondensation products under the catalytic action of traces of hydrogen chloride. Judging from the spectral data, acid chlorides I and III react with silica gel in a different manner. As seen from Fig. 3, in the case of acid chloride I the intensity of the COCl band decreases sharply on reaction of solutions of these acid chlorides with silica gel, and the intensity of the COOH band simultaneously increases considerably. However, in the case of acid chloride III, the decrease in the intensity of the COCl band is not accompanied by a corresponding increase in the intensity of the COOH absorption band. This can be evaluated such that in both cases the acid chloride reacts with surface silanol groups of silica gel in a manner similar to the interaction of thionyl chloride with them [12], but the subsequent fate of the acid formed is completely different. In the case of acid chloride I, the acid formed goes into solution, while in the case of acid chloride III the acid that arises apparently remains on the surface of the silica gel. The assumption that it is converted to the corresponding ketone is unlikely, since no absorption band at 1671 cm^{-1} is observed in the spectrum. This sort of behavior of these acids may be explained by the different sorption properties of the various substituted thiophenes. It is known that substitution of the thiophene ring in the 2 and 5 positions by alkyl residues has a pronounced effect on the adsorption capacity of thiophene compounds on sorbents of a similar type. For example, on alumogel [13] 2,5-disubstituted thiophenes have the shortest retention times during adsorption displacement chromatography, i.e., they are sorbed to the least extent on its surface. In our case, the silica gel surface is modified by ACE, and absorption can be realized through the field of positive potential formed by the Al atom, apparently just as on alumogel. The above-indicated peculiarities of the behavior of our acids are therefore in good agreement with the data in [13], and the reasons why acid III remains on the surface while acid I goes into solution are understandable. In addition, it becomes understandable why aluminum oxide and silica gel, as well as aluminum hydroxychlorides, have the same effect on intramolecular acylation. The absorption of acid chlorides of carboxylic acids by silica gel proceeds like the adsorption of ACE, i.e., the acid chloride is initially absorbed by silica gel, after which saturation of the adsorbent surface commences, and the concentration of unchanged substance in solution increases in proportion to the starting concentration of the solution used.

In the case of the interaction of acid chlorides I and III with silica gel that has first been treated with aluminum chloride etherate, the behavior of both acid chlorides is identical (Fig. 3). In both cases, the addition of silica gel that has been treated with aluminum chloride etherate causes a sharp change in the intensity of the absorption band at 1796 cm^{-1}, which corresponds to the vibrations of the COCl group, and does not entail the appearance of the band at 1710 cm^{-1}, which corresponds to the vibrations of the COOH group. In both cases, an intense absorption band at 1108 cm^{-1}, which corresponds to the ether, appears in the spectrum during interaction of the acid chlorides with silica gel. Calculations* made with data from these spectra show that in the case of acid chloride III, ether is evolved approximately equimolecularly with respect to the added acid chloride (Fig. 4), while in the case of I the amount of ether passing into solution is somewhat lower, and an appreciable amount of unchanged acid chloride I is detected in the solution. These data can be interpreted in such a way that, in the reaction of the acid chlorides with ACE applied to silica gel, a molecule of the acid chloride displaces the ether from the complex, occupying its position, and compounds of the $R\overset{+}{C}O[AlCl_3{-}O{-}Si\langle\,]^-$ type are formed.

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*In connection with the strong background (its origin is presently unclear) observed in the region of the analytical band, the accuracy in the determination of the percentage of ether is somewhat reduced.

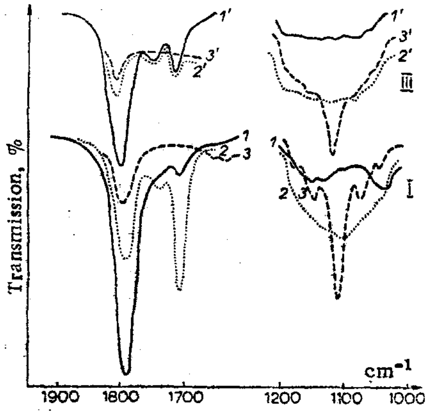

Fig. 3

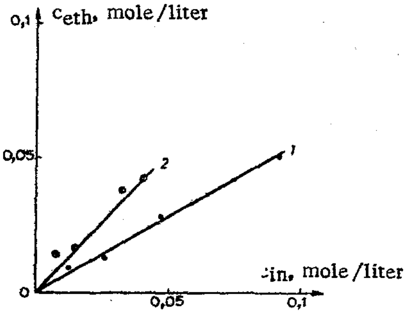

Fig. 4

Fig. 3. Changes in the spectra of solutions of acid chlorides I (1) and III (1') in $CHCl_3$ when silica gel (2, 2') and silica gel saturated with $AlCl_3$ etherate (3, 3') are added to the solutions.

Fig. 4. Change in the observed ether concentration (c_{eth}) as a function of the initial acid chloride concentration (c_{in}) when silica gel saturated with $AlCl_3$ etherate is added to the solutions: 1) acid chloride I; 2) acid chloride III.

On the basis of the phenomena found, it seems possible to formulate a sequence of processes and a mechanism for the interaction of the surface of the solid phase in intramolecular acylation reactions. First of all, it should be pointed out that the reaction does not proceed when free ACE is not present in solution [3]. If the applied amount of aluminum chloride etherate is insufficient for all of the silanol groups to undergo reaction, the reaction does not proceed, and unchanged acid is isolated (see experiment No. 11, Table 1). Finally, when the silica gel surface is completely modified by the etherate and there is excess ACE in solution, the acid chloride introduced into the solution reacts with ACE to give a complex of the $R\overset{+}{C}O[AlCl_4]^-$ type (which is capable of acylation), which can coordinate with the Al atom of the $\rangle Si{-}O{-}AlCl_2 \cdot Et_2O$ group through the π-electron system of the thiophene ring. In this case, the mobility of the particle is lost, and this decreases the probability of its collision with another similar particle or, in other words, the probability of the occurrence of an intramolecular process increases. If the capacity for sorption is reduced, as in the case of acid chlorides I, which are substituted in the 2 and 5 positions of the thiophene ring, the effect of a decrease in the probability of collision with another particle is not manifested, and the reaction proceeds just as it would in a homogeneous medium in the absence of a sorbent, i.e., its rate increases as the ACE concentration increases (see experiments Nos. 6 and 7 and 8 and 9, Table 1). The decrease in the yield in the presence of silica gel for acid chlorides I becomes understandable, since the addition of silica gel lowers the ACE concentration in solution. In fact, as seen from experiments Nos. 8 and 10, the addition of silica gel to the reaction mass with a simultaneous increase in the amount of ACE (in conformity with the relationships found in the present research) brings about practically no change in the yield of reaction product.

EXPERIMENTAL

The IR spectra were measured with a DS-301 spectrophotometer with a NaCl prism. The spectra were obtained for solutions of the substances in chloroform. The accuracy in the measurement of the frequencies was ± 2 cm^{-1}, while the accuracy in the measurement of the intensities was ± 5%.

The chromatograms of the intramolecular acylation products were recorded at 200-220° with an LKhM-7A chromatograph with a stainless steel column (l 50 cm, d 4 mm) filled with polyethylene glycol adipate on Chromosorb W (15%). The carrier gas was helium, and the substances were detected from their thermal conductivities.

The starting 12-(5-methyl-2-thienyl)lauric acid was obtained by the method described in [5]. The starting 10-(5-methyl-2-thienyl)capric and 11-(5-methyl-2-thienyl)undecanoic acids were synthesized by the method presented in [6]. 10-(3-Methyl-2-thienyl)- and 10-(4-methyl-2-thienyl)capric acids, as well as 11-(3-methyl-2-thienyl)- and 11-(4-methyl-2-thienyl)undecanoic acids were obtained by the method indicated in [7]. Cyclization in a homogeneous medium was carried out under the conditions described in [5, 6]. The method of cyclization in a heterogeneous medium is reported in [7].

Absorption of Aluminum Chloride Etherate by Silica Gel with Collection of the Evolving Hydrogen Chloride. A chloroform solution of 2.61 mmole of ACE was added to 10 g of silica gel in chloroform in such a way that the overall volume of the chloroform and ACE solution was 52 ml. Dry argon was then bubbled into the reaction mixture with stirring in the course of 5 h, and the resulting hydrogen chloride was collected in a titrated 0.1 N solution of hydrochloric acid.* An experiment without $AlCl_3$ etherate was carried out similarly. The amount of absorbed HCl was determined by titration with 0.1 N NaOH with correction for the blank experiment. The amount of evolved HCl corresponded to 29.25 ml of 0.1 N NaOH or 2.93 mmole of hydrogen chloride. Thus on the average, one atom of chlorine in each molecule of the etherate reacts with the silica gel. By titration of the contents of the receivers after each 60-min interval it was found that the evolution of HCl is terminated after 3 h at 20°.

Cyclization of 12-(5-Methyl-2-thienyl)lauryl Chloride. A. The standard method of cyclization [7] gave the product in 42% yield.

B. Intramolecular acylation of acid chloride I with replacement of the aluminum chloride etherate that had reacted with the silica gel was used in this case. A solution of 5 g (0.017 mole) of 12-(5-methyl-2-thienyl)lauric acid in 25 ml of absolute ether was treated with 5 ml of thionyl chloride, after which the mixture was stirred at room temperature for 1 h and refluxed for 1 h. The solvent and excess thionyl chloride were then removed by distillation without access to the air moisture. The residue was dissolved in 40 ml of anhydrous chloroform, and the solution was added, with stirring, by means of a syringe doser at a rate of 3.5 ml/h through an adapter for high dilution [1] to a vigorously refluxing mixture of 47 g† of aluminum chloride etherate and 100 g of silica gel in 520 ml of anhydrous chloroform. The addition was completed in 13 h, after which it was refluxed for another 2 h and cooled to below 15°. It was then treated gradually with 300 ml of dilute (1:10) hydrochloric acid. The chloroform solution was washed with water and evaporated, and the residue was refluxed with hexane to separate the high-molecular-weight products. The hexane solution was treated with a saturated $Ba(OH)_2$ solution (25 ml) to separate acidic substances, and the hexane was evaporated. The residue was treated with alcohol (three 25-ml portions), and the alcohol-insoluble compounds were separated; the solution was evaporated, and the reaction product was sublimed under high vacuum (10^{-3}–10^{-5} mm) at a bath temperature of 60-80° to give a mixture of cyclic ketones in 39% yield.

Comparative Investigation of the Absorption of $AlCl_3$ Etherate by Silica Gel at 20° with Refluxing of the Solvent. The reaction of 1.8 g (8.67 mmole) of $AlCl_3$ etherate with 10 g of silica gel in 52 ml of chloroform solution was studied under conditions similar to those indicated above at 20° and at the boiling point of chloroform. The amount of evolved HCl corresponded to 5.52 mmole (20°) and 7.32 mmole (at the boiling point of chloroform). Thus at 20°, 1.1 molecules of $AlCl_3$ etherate were absorbed for each 100 Å^2 of surface area (i.e., $5.52 \cdot 10^{-4}$ mole of $AlCl_3 \cdot Et_2O$ per gram of silica gel).

Determination of Aluminum Chloride Etherate Remaining in Solution after Reaction with Silica Gel. The concentration of the starting $AlCl_3$ etherate solution in chloroform was determined by Volhard titration with corrections for the hydrolysis of the chloroform (a correction for an experiment without $AlCl_3$ etherate was introduced). It was found that 1 liter of solution contains 0.667 mole of $AlCl_3$. Two series of solutions [52 ml of solution in each sample, which contained definite (see Table 2) numbers of moles of $AlCl_3$ expressed in the number of gram atoms of Cl^-] were then prepared by dilution. After this, one of the series was shaken for 3 h under hermetic conditions with weighed (10 g each) samples of silica gel, and the number of gram equivalents of Cl^- in solution was again determined after filtration without access to air moisture.

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*The HCl solution was used for absorption to avoid the loss of hydrogen chloride as an aerosol of hydrochloric acid, the formation of which was observed when water was used. Alkali was not used for the absorption because of the fact that the vapors of the chloroform solvent would markedly distort the results because of hydrolysis.

† Under standard conditions, 30 g of $AlCl_3$ etherate was used. Since it was found that 1 g of silica gel absorbs 0.151 g of $AlCl_3$ etherate when the $CHCl_3$ is boiled, while 100 g of silica gel was used in this experiment, the amount of etherate was increased by 17 g.

The HCl formed evaporated during the filtration because of its very low solubility in $CHCl_3$ [14]. Samples of both series were analyzed in parallel by means of IR spectroscopy and were determined volumetrically by the Volhard method.

Reaction of Acid Chlorides with Silica Gel. Acid chlorides I and III were obtained by a known method; for their identification and determination of their purity, they were converted to the anilides [5, 7]. Sample solutions in chloroform, from which the calibration curves in IR spectroscopy were constructed, were prepared from each acid chloride. Another two series of solutions of known concentration were then prepared, and the reaction of these solutions with silica gel and silica gel saturated with ACE were investigated. Acid chloride I was used in concentrations of 0.092, 0.048, 0.0256, and 0.0128 mole/liter, while acid chloride III was used in concentrations of 0.06, 0.0325, 0.0162, and 0.0081 mole/liter. The solutions were treated with silica gel for 3 h.

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