zene, and 187 g. of 100% orthophosphoric acid under an initial nitrogen pressure of 10 kg./sq. cm. for six hours at 90, 150, 200, 250, and 300° were 0, 0, 2, 19, and 23%, respectively.

Perchloric Acid and Di-*t*-butylbenzene.—A mixture of 50 g. of 1,4-di-*t*-butylbenzene, 84 g. of 70–72% perchloric acid and 500 g. of benzene was stirred six hours at 85°. The acid became dark and viscous. Mono derivative was not obtained; 36 g. of di derivative was recovered.

Acknowledgment.—The authors express their thanks to Dr. Louis Schmerling for identifying the *t*-butyl and *t*-amylbenzenes and to Mr. Wilbur Shand for assistance in the experimental work.

Summary

Di-*t*-butyl- and di-*t*-amylbenzenes are dealkylated in the presence of ferric chloride and benzene to the corresponding mono derivatives. Di-*s*- and di-*prim*-alkylbenzenes are not dealkylated under the same conditions.

Hydrogen chloride is liberated during the reaction and ferric chloride is reduced to the ferrous state.

Di-*t*-butylbenzene reacts with benzene in the presence of sulfuric acid to give mono-*t*-butylbenzene and *p*-*t*-butylbenzenesulfonic acid. Di-*t*-butylbenzene is dealkylated in the presence of phosphoric acid and benzene, but mono derivative was not obtained in the presence of perchloric acid.

RIVERSIDE, ILLINOIS RECEIVED MAY 13, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Dielectric Properties of Acetylenic Compounds. VIII.[1] Propiolyl Chlorides and Some Other Acid Chlorides

BY S. MERCEDES KOEHL AND H. H. WENZKE

The acid chloride group contains two linkages quite polar in character. These are the C—Cl bond and that of the C═O group. Assuming the classical structure (see A below) for acetyl chloride and using the method of bond moments, the moment is calculated to be 2.28. In these calculations the values of the bond moments are assumed to be C—H, 0.4; C═O, 2.3; and C—Cl, 1.5. Interactions between the bond moments are neglected and the valence angles are those calculated for an undistorted tetrahedral structure. The valence angles in acetyl chloride have been determined by Dornte[2] using the method of electron diffraction. This author gives the compound a Y structure with the angle between the carbon–carbon bond and the carbon–halogen bond 110 ± 10° and the other two angles each 125 ± 10°.

Preparation of Compounds.—Butylpropiolyl chloride was synthesized from butyl bromide and a liquid ammonia solution of sodium acetylide. The butylacetylene thus obtained was refluxed with ethylmagnesium bromide. Carbon dioxide was bubbled through the acetylenic Grignard reagent to form the magnesium bromide complex of butylpropiolic acid. This complex was acidified with dilute hydrochloric acid. The butylpropiolic acid thus obtained was converted to the acid chloride by refluxing with thionyl chloride. The product was purified by fractional distillation.

The method of preparing amylpropiolyl chloride differed from that of the butyl homolog insofar as the respective acetylenic Grignard reagent was refluxed with ethyl chlorocarbonate. The ester was treated with alcoholic potassium hydroxide; the potassium amylpropiolate acidified with dilute hydrochloric acid. The amylpropiolic acid was chlorinated with thionyl chloride.

The best grades of acetyl, propionyl, butyryl and benzoyl chlorides, and the practical grade of cinnamoyl chloride were obtained from the Eastman Kodak Co. The first four chlorides were purified by distillation. The cinnamoyl chloride was recrystallized from petroleum ether solutions until a constant melting point was obtained.

The solvent used for dielectric constant determinations was Baker thiophene-free chemically pure analyzed benzene. It was dried over metallic sodium and then distilled within a 0.2° temperature range. A heterodyne beat method was employed for the determination of dielectric constants. The indices of refraction were read on an Abbé refractometer. The measurements were made at 25°.

TABLE I

PHYSICAL CONSTANTS OF ACID CHLORIDES

Compound	B. p., °C.	d	n_D
Acetyl	51.8	1.0983	1.3878
Propionyl	80	1.0469	1.4057
Butyryl	102	1.0154	1.4115
Benzoyl	197	1.2071	1.5520
Cinnamoyl	35 (m. p.)	1.1632[a]	1.6202[a]
Butylpropiolyl	65 (13 mm.)	1.0609	1.4695
Amylpropiolyl	88.5 (13 mm.)	1.0568	1.4797

[a] These data were obtained at 37.6°.

Table III shows that the moment of acetyl chloride when determined in the liquid state is

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[1] Article VII of this series, Curran and Wenzke, THIS JOURNAL, **59**, 943 (1937).

[2] Dornte, *ibid.*, **55**, 4126 (1933).

TABLE II

DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS OF ACID CHLORIDES

Solvent, benzene; temp. 25°

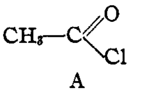
c_2	ϵ	d
	Acetyl chloride	
0.00000	2.2760	0.87388
.01889	2.4232	.87734
.02003	2.4380	.87754
.02061	2.4386	.87762
	Propionyl chloride	
0.00000	2.2760	0.87358
.01588	2.4104	.87629
.01614	2.4107	.87631
.02538	2.4893	.87789
	Butyryl chloride	
0.00000	2.2760	0.87338
.00998	2.3625	.87508
.01652	2.4196	.87607
.02391	2.4817	.87762
	Benzoyl chloride	
0.00000	2.2760	0.87358
.01356	2.4676	.87955
.02284	2.5970	.88394
.04102	2.8530	.89184
	Cinnamoyl chloride	
0.00000	2.2760	0.87320
.00822	2.4340	.87727
.00986	2.4630	.87775
.01578	2.5765	.88077
	Butylpropiolyl chloride	
0.00000	2.2760	0.87345
.00943	2.3986	.87568
.00988	2.4044	.87598
.01145	2.4220	.87622
	Amylpropiolyl chloride	
0.00000	2.2760	0.87350
.00615	2.3574	.87508
.01016	2.4102	.87614
.01606	2.4917	.87771

TABLE III

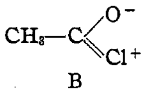
POLARIZATIONS AND MOMENTS OF ACID CHLORIDES

Acid chloride	P_∞	MR_D	P_{A+M}	$10^{18}\mu$	$10^{18}\mu$	$10^{18}\mu$
Acetyl	137.0	16.85	120.1	2.40	2.45[3]	2.68[5]
Propionyl	149.6	21.69	127.9	2.48	2.61[3]	
Butyryl	155.3	26.07	129.2	2.49	2.61[3]	
Benzoyl	241.6	37.19	204.4	3.13	3.33[3]	3.23[4]
Cinnamoyl	322.4	50.30	272.1	3.63		
Butyl-propiolyl	232.6	37.98	194.6	3.06		
Amyl-propiolyl	239.8	42.60	197.2	3.08		

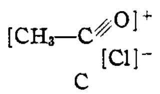
2.40, which is slightly higher than the value 2.28 calculated from bond moments. When one considers the uncertainty of the valence angles involved and the fact that dipole interaction has been neglected, it might be assumed that the classical formula is the only important contributing form. If forms A and B were the only electromeric forms, the moment of the molecule undoubtedly would be higher than the one actually found. The high reactivity found for acetyl chloride is hardly consistent with that expected from the simple classical structure, A. The authors are of the opinion that all three forms, A, B and C, enter into the resonance. Form C represents the chlorine atom in ionic form being held rigidly into position with the CH_3CO^+. Since form C is only one of the contributing forms, one would not expect to detect ionization in the compound. Form C might account for the high reactivity of the compound toward water or other hydroxylic compounds.



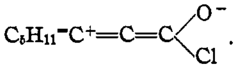
A

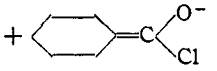


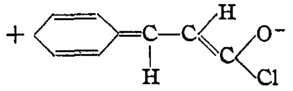
B



C

When the acid chloride group is attached to unsaturated hydrocarbon residues, we have an elevation of the over-all moment. With benzoyl chloride and cinnamoyl chloride the following forms in addition to those present above (A, B and C) contribute. As Table III shows, this increase is quite appreciable. In a similar manner the acetylenic acid chlorides have the additional contributing form,  $C_5H_{11}{-}C^{+}{=}C{=}C{<}^{O^-}_{Cl}$. The table shows that cinnamoyl chloride has a moment higher than that of any of the other unsaturated acid chlorides.





Summary

1. Electric moments have been determined for several acid chlorides: acetyl, propionyl, butyryl, benzoyl, cinnamoyl, butylpropiolyl and amylpropiolyl.

2. The data from dipole moments alone do not establish definitely the existence of resonance in the alkyl acid chlorides. The consideration of the data of dipole moments and chemical reactivity indicates quite strongly the existence of resonance in these compounds. Three forms have been assumed to contribute to the molecule.

3. The moments of the acid chlorides attached

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(3) Martin and Partington, *J. Chem. Soc.*, 158 (1936).

(4) Nespital, *Z. physik. Chem.*, **B16**, 178 (1932).

(5) Zahn, *Physik. Z.*, **33**, 686 (1932). Moment determined on gas.

to unsaturated hydrocarbon residues are higher than those of the alkyl acid chlorides. Resonance of the acid chloride group with the unsaturated hydrocarbon residue readily accounts for this increase in moment.

NOTRE DAME, INDIANA RECEIVED JUNE 1, 1937

[CONTRIBUTION FROM THE PHYSIOLOGICAL LABORATORY, PRINCETON UNIVERSITY]

The Attempted Use of Crystals as Calcium Electrodes. II

BY RUBERT S. ANDERSON

The concentration cell measurements previously attempted with calcite and fluorite crystals[1] have been repeated after increasing the conductivity of the crystals by the methods of Joffe, Gudden, Pohl and others.[2] Although after such treatments crystals frequently showed detectable photo-currents, only one method gave crystals with a conductivity great enough for easy measurements of e. m. f. with a Lindemann electrometer. So far, however, these e. m. f.'s have fluctuated too rapidly to be usable. This work is being continued and will be reported later.

During these experiments a new source of possible confusion has appeared. Data have been obtained which, although not due to the crystals, may erroneously be ascribed to them. Open Pyrex glass tubes of about 1-cm. diameter which had a crystal sealed over one end with paraffin (m. p. 48-50°), were used for the experiments. The solution inside of the tube, 0.01 *M* calcium nitrate plus 0.001 *M* sodium chloride, was connected directly to the electrometer through a silver-silver chloride electrode. The crystal end of the tube dipped into an outer solution from which contact was made either through a saturated potassium chloride bridge to a reference electrode or directly through a silver-silver chloride electrode. Because of the high resistance of the system many hours frequently were required before the electrical effects due to the preparation and handling of the tube had even approximately disappeared. Therefore *only* the outer solution was varied during a series of measurements.

Since the absolute readings were frequently not reproducible, owing to changing asymmetry potentials, only the changes in e. m. f. produced by changing the concentrations of the outer solutions are given. That is, the data are given either for cell 1

$$\mathrm{Ag}\;\Big|\;\mathrm{AgCl}\;\Big|\;\mathrm{KCl\ (satd.)}\;\Big|\;\begin{matrix}\mathrm{Ca(NO_3)_2}\ (C_1)\\ \mathrm{NaCl}\ (C)\end{matrix}\;\Big|\;\begin{matrix}\text{glass tube}\\ \text{with}\\ \text{crystal}\end{matrix}\;\Big|\;\begin{matrix}\mathrm{Ca(NO_3)_2}\ (C_2)\\ \mathrm{NaCl}\ (C)\end{matrix}\;\Big|\;\mathrm{KCl\ (satd.)}\;\Big|\;\mathrm{AgCl}\;\Big|\;\mathrm{Ag}$$

or for cell 2

$$\mathrm{Ag}\;\Big|\;\mathrm{AgCl}\;\Big|\;\mathrm{CaCl_2}\ (C_1)\;\Big|\;\begin{matrix}\text{glass tube}\\ \text{with}\\ \text{crystal}\end{matrix}\;\Big|\;\mathrm{CaCl_2}(C_2)\;\Big|\;\mathrm{AgCl}\;\Big|\;\mathrm{Ag}$$

The more concentrated solution was negative in the outer circuit.

Tubes 1, 2 and 3 in Table I carried crystalline fluorite plates, 0.1 to 0.2 mm. thick, which had been X-rayed for one-half hour. Each figure of voltage is the average of a number of readings. For purposes of comparison, figures calculated from data in the literature for concentration cells analogous to cells 1 and 2, but with calcium amalgam in the place of the tube and crystal, are given in Table I also. The data from tubes 1, 2 and 3

TABLE I

The changes in e. m. f. in volts given by several tubes when the concentrations of calcium nitrate or of calcium chloride in the outer solutions were alternately C_1 or C_2.

		Cell 1				
NaCl, *M*, *C*		0.001	0.001	0.01	0.01	0.1
$Ca(NO_3)_2$, *M*	C_1	.001	.01	.0003	.001	.001
	C_2	.01	.1	.003	.01	.01
Tubes, v.	1	.021	.024		.012	.001
	2	.021	.026		.016	.000
	3	.018	.029			.005
	P_1	.019			.023	.001
	P_2	.019	.023	.017[a]	.019[a]	.009[a]
	P_3	.019	.031		.024	.000
$CaCl_2$, *M*	C_1		.0012	.01	Contained no sodium chloride	
	C_2		.012	.1		
Ca amalgam, v.			.021[b]	.027[c]		
		Cell 2				
$CaCl_2$, *M*	C_1		0.01	0.03	0.01	0.001
	C_2		.03	.1	.1	.01
Ca amalgam,[d] v.			.036	.040	.076	
Tubes, v.	1		.034	.035		
	2		.034	.035	.070	.081

[a] These solutions also contained 0.001 *M* 1:1 phosphate buffer. [b] This figure is surprisingly small. From Fosbinder, THIS JOURNAL, **51**, 1345 (1929). [c] From Drucker and Luft, *Z. physik. Chem.*, **121**, 307 (1926). [d] From Lucasse, THIS JOURNAL, **47**, 743 (1925).

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(1) Anderson, *J. Biol. Chem.*, **115**, 323 (1936).

(2) See review by Hughes, *Rev. Modern Phys.*, **8**, 294 (1936).