on pp. 259 and 269. The new constants do not alter any of our qualitative arguments.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TENNESSEE A. AND I. STATE COLLEGE]

The Synthesis, Properties and Dehydrohalogenation of Some α-Phenoxy and 2,4-Dichlorophenoxy Substituted Acid Chlorides

BY CARL M. HILL, HELEN I. SCHOFIELD, ALFRED S. SPRIGGS AND MARY E. HILL

This paper describes the synthesis and chemistry of several α-phenoxy and α-2,4-dichlorophenoxy substituted fatty acid chlorides; namely, propionyl, butyryl, valeryl, isovaleryl, caproyl and enanthyl. Although the acid chlorides of both series reacted smoothly with such reagents as ammonia, aniline, phenylhydrazine, ethanol and phenol, there was a noticeable difference in the reactivity of the chlorides of each series with a given reagent.

A previous paper[1] reported the dehydrohalogenating action of triethylamine on several phenoxy and chlorine-substituted phenoxyacetyl chlorides. In an effort to study the influence of different alkyl radicals upon the properties and character of alkylphenoxy disubstituted ketenic substances, these studies were extended to several α-phenoxy and α-2,4-dichlorophenoxy substituted fatty acid chlorides. It was observed that the nature of the alkyl and phenoxy group attached to the alpha carbon of an acid chloride apparently influences the extent and mode of polymerization of the disubstituted ketenes formed upon dehydrohalogenation with triethylamine.

TABLE I

PHYSICAL CONSTANTS AND ANALYTICAL DATA OF ACID CHLORIDES

α-Phenoxy	B.p.[a] °C.	Mm.	d^{20}_4	n^{20}_D	MR_D Found	MR_D Calcd.	Yield, %	Formula	Chlorine,[b] % Found	Chlorine,[b] % Calcd.
Propionyl[c]	105–106	5	1.1865	1.5184	47.15	47.16	73	$C_9H_9O_2Cl$	19.28	19.20
Butyryl[c]	104–105	6	1.1355	1.5138	52.60	51.78	74	$C_{10}H_{11}O_2Cl$	18.21	17.85
Valeryl	109–110	7	1.1127	1.5087	57.00	56.40	88	$C_{11}H_{13}O_2Cl$	16.64	16.67
Caproyl[d]	126–127	11	1.0885	1.5048	61.69	61.02	88	$C_{12}H_{15}O_2Cl$	15.99	15.64
Enanthyl	115–117	3	1.0643	1.5025	66.75	65.63	82	$C_{13}H_{17}O_2Cl$	14.20	14.77
α-2,4-Dichlorophenoxy										
Propionyl	137–139	9	1.3857	1.5475	58.05	56.90	84	$C_9H_7O_2Cl_3$	13.91	13.98
Butyryl	145–147	5	1.3516	1.5397	62.05	61.52	90	$C_{10}H_9O_2Cl_3$	12.85	13.25
Valeryl	160–162	10	1.3078	1.5350	67.01	66.14	54	$C_{11}H_{11}O_2Cl_3$	11.80	12.59
Isovaleryl	145–147	4	1.3028	1.5338	67.15	66.14	98	$C_{11}H_{11}O_2Cl_3$	12.45	12.59
Caproyl	150–153	3	1.2732	1.5301	71.70	70.76	96	$C_{12}H_{13}O_2Cl_3$	12.01	12.00
Enanthyl	175–176	7	1.2392	1.5268	76.76	75.38	98	$C_{13}H_{15}O_2Cl_3$	11.17	11.46

[a] Boiling and melting points are corrected. [b] Analyzed by potentiometric titration using silver, silver–silver chloride electrodes; %'s refer to ionizable chlorine. [c] Reported: R. Stoermer and P. Atenstadt, *Ber.*, **35**, 3565 (1902); b.p. 115–117° (10 mm.). [d] Reported: C. A. Bischoff, *ibid.*, **34**, 2127 (1901); b.p. 128–131° (38 mm.).

TABLE II

PHYSICAL CONSTANTS AND ANALYTICAL DATA FOR AMIDES AND ANILIDES OF ACID CHLORIDES

α-Phenoxy chloride	Amides[a] Yield, %	Amides[a] M.p., °C.	Amides[a] Formula	Amides[a] Nitrogen, % Found	Amides[a] Nitrogen, % Calcd.	Anilides Yield, %	Anilides M.p., °C.	Anilides Formula	Anilides Nitrogen, % Found	Anilides Nitrogen, % Calcd.
Propionyl[b]	90	128–129	$C_9H_{11}O_2N$	8.51	8.49	31	116–116.5	$C_{15}H_{15}O_2N$	6.13	5.80
Butyryl[c]	45	118–119	$C_{10}H_{13}O_2N$	8.30	7.82	30	79–81	$C_{16}H_{17}O_2N$	5.38	5.49
Valeryl	44	114–115	$C_{11}H_{15}O_2N$	7.65	7.25	28	98–99	$C_{17}H_{19}O_2N$	5.18	5.20
Caproyl	57	100–102	$C_{12}H_{17}O_2N$	6.98	6.76	24	93–93.5	$C_{18}H_{21}O_2N$	4.43	4.95
Enanthyl	87	106–108	$C_{13}H_{19}O_2N$	6.12	6.34	65	84–85	$C_{19}H_{23}O_2N$	4.65	4.71
α-2,4-Dichlorophenoxy										
Propionyl	97	81–82	$C_9H_9O_2Cl_2N$	5.96	5.98	98	138–139	$C_{15}H_{13}O_2Cl_2N$	4.50	4.52
Butyryl	94	108–109	$C_{10}H_{11}O_2Cl_2N$	5.76	5.65	66	126–127	$C_{16}H_{15}O_2Cl_2N$	4.48	4.32
Valeryl	94	86–87	$C_{11}H_{13}O_2Cl_2N$	5.54	5.34	99	149–150	$C_{17}H_{17}O_2Cl_2N$	4.11	4.14
Isovaleryl	93	94–96	$C_{11}H_{13}O_2Cl_2N$	5.38	5.34	83	123–124	$C_{17}H_{17}O_2Cl_2N$	4.11	4.14
Caproyl	98	101–102	$C_{12}H_{15}O_2Cl_2N$	5.10	5.07	59	136–137	$C_{18}H_{19}O_2Cl_2N$	4.03	3.98
Enanthyl	97	98–99	$C_{13}H_{17}O_2Cl_2N$	4.83	4.83	37	107–108	$C_{19}H_{21}O_2Cl_2N$	4.00	3.83

[a] Nitrogen analyses by semi-micro Dumas method. [b] Amide and anilide reported: C. A. Bischoff, *Ber.*, **34**, 1837 (1901); *ibid.*, **34**, 1839 (1901), m.p. 132–133° and 118.5–119°, respectively. [c] Amide and anilide reported: C. A. Bischoff, *ibid.*, **34**, 1837 (1901) and *ibid.*, **34**, 1840 (1901), m.p. 123° and 93–94°, respectively.

Dehydrohalogenation of propionyl and butyryl chlorides of the α-phenoxy series produced two iso-

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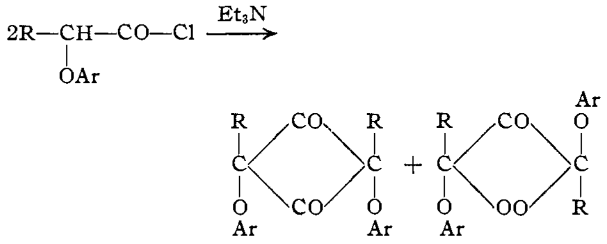
[1] C. M. Hill, G. W. Senter and M. E. Hill, THIS JOURNAL, **72**, 2286 (1950).

meric ketene dimers only. One monomer and one dimer were obtained from each of the other acid chlorides of this series. In the 2,4-dichlorophenoxy series, all acid chlorides except propionyl and enanthyl produced one monomer and two isomeric dimers. Formation of the isomeric dimers is indicated by the equation



While no attempt was made to determine the configuration of these isomeric ketene dimers, it is believed that, on the basis of the cyclobutanedione formulation, they represent the *cis* and *trans* geometric forms. Their solubility and boiling point differences indicated this to be the case. Of special interest was the marked tendency exhibited by the lower boiling and more soluble form to change into the higher boiling and less soluble form upon standing. This was strikingly noticeable with methylphenoxyketene dimer.

The monomeric ketenes gave a positive test with bromine and potassium permanganate; negative test for ionizable chlorine. Each monomer and the corresponding acid chloride reacted with dry ammonia to produce the identical amide.

The ketenes described in this paper have not been previously reported.

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Experimental

Fatty Acids.—The substituted fatty acids employed in this investigation were synthesized by reaction of the α-bromo esters with the sodium salt of phenol or its 2,4-dichloro derivative. The phenolic substituted fatty acids were purified by distillation under reduced pressure or recrystallization; their identity was established by determination of neutral equivalents and conversion to the acid chlorides.

Acid Chlorides.—The acid chlorides were prepared from the acids by use of thionyl chloride. Description of the chlorides is shown in Table I.

Amides.—A 0.5-g. sample of each chloride dissolved in 10 ml. of anhydrous ether was saturated with dry ammonia. The crude amide which separated was filtered and recrystallized from dilute ethanol. All amides were white solids. Physical properties and analytical data for the amides are given in Table II.

Anilides.—To a 1.0-g. sample of each chloride dissolved in 20 ml. of anhydrous benzene was added a slight excess of aniline. The solution was warmed on a water-bath. The precipitated anilide was filtered and recrystallized from dilute ethanol. Description of the anilides is given in Table II.

Phenylhydrazides.—To a 1.0-g. sample of each chloride dissolved in 25 ml. of benzene was added twice the equivalent amount of phenylhydrazine. The mixture was refluxed for two hours. The benzene was then removed by distillation over a water-bath, and replaced by 20 ml. of

TABLE III

PHYSICAL CONSTANTS AND ANALYTICAL DATA FOR PHENYLHYDRAZIDES, PHENYL AND ETHYL ESTERS OF ACID CHLORIDES

α-Phenoxy	Phenylhydrazides Yield, %	M.p., °C.	Formula	Nitrogen, % Found	Nitrogen, % Calcd.	Phenyl esters Yield, %	B.p., °C.	Mm.	Formula	Sapn. equiv.,[a] Found	Sapn. equiv.,[a] Calcd.	Ethyl Esters Yield, %	B.p., °C.	Mm.	Sapn. equiv. Found	Sapn. equiv. Calcd.
Propionyl[b]	54	142–143	$C_{15}H_{16}O_2N_2$	10.93	10.94	15	169–170	750	$C_{15}H_{14}O_3$	241	242	29	145–148	750	219	194
Butyryl[c]	44	123–124	$C_{16}H_{18}O_2N_2$	10.21	10.37	57	148–149	2	$C_{16}H_{16}O_3$	250	256	48	87–90	5	222	208
Valeryl	60	118–119	$C_{17}H_{20}O_2N_2$	10.04	9.86	55	190–192	750	$C_{17}H_{18}O_3$	269	270	85	125–126	750	228	222
Caproyl	95	132–134	$C_{18}H_{22}O_2N_2$	9.85	9.40	40	116–118	12	$C_{18}H_{20}O_3$	272	284	38	110–112	17	236	236
Enanthyl	77	134–135	$C_{19}H_{24}O_2N_2$	9.20	8.98	33	155–158	6	$C_{19}H_{22}O_3$	291	298	60	124–127	1	253	250
α-2,4-Dichlorophenoxy							M.p., °C.									
Propionyl	33	148–149	$C_{15}H_{14}O_2Cl_2N_2$	8.85	8.62	77	77–78		$C_{15}H_{12}O_3Cl_2$	314	311	97	130–132	4	260	263
Butyryl[d]	15	137–138	$C_{16}H_{16}O_2Cl_2N_2$	8.20	8.26	91	79–80		$C_{16}H_{14}O_3Cl_2$	330	325	29	116.5–118	3	269	277
Valeryl	33	114–115.5	$C_{17}H_{18}O_2Cl_2N_2$	7.85	7.93	25	63–64		$C_{17}H_{16}O_3Cl_2$	361	339	38	158–159	9	320	291
Isovaleryl	56	135–135.5	$C_{17}H_{18}O_2Cl_2N_2$	7.94	7.93	8	B. p., 175–177 (12 mm.)		$C_{17}H_{16}O_3Cl_2$	330	339	19	133–134	2	289	291
Caproyl	48	102–103	$C_{18}H_{20}O_2Cl_2N_2$	7.61	7.63	16	44–45		$C_{18}H_{18}O_3Cl_2$	334	353	38	148–149	3	333	305
Enanthyl[e]	25	110–111	$C_{19}H_{22}O_2Cl_2N_2$	7.33	7.35	27	45–46		$C_{19}H_{20}O_3Cl_2$	[f]	367	10	159–160	10	[f]	319

[a] Determined according to method reported by C. M. Hill, M. B. Towns and G. W. Senter, THIS JOURNAL, **71**, 258 (1949). [b] Phenyl and ethyl esters reported: C. A. Bischoff, *Ber.*, **39**, 3833 (1906); *ibid.*, **33**, 925 (1900), b.p. 190° (18 mm.) and 120–125° (6 mm.), respectively. [c] Phenyl and ethyl esters reported: C. A. Bischoff, *ibid.*, **39**, 3833 (1906); *ibid.*, **33**, 931 (1900); b.p. 202–203° (25 mm.) and 175–180° (41 mm.), respectively. [d] Ethyl ester reported: V. V. Foefilaktov and E. S. Tambovtseva, *J. Gen. Chem.* (*U. S. S. R.*), **17**, 253 (1947); b.p. 140–141° (5 mm.). [e] Ethyl ester reported: M. S. Newman, W. Fones and M. Renoll, THIS JOURNAL, **69**, 718 (1947); b.p. 126–127° (1 mm.). [f] Hydrolysis incomplete at end of 20 hours.

TABLE IV

PHYSICAL CONSTANTS AND ANALYTICAL DATA FOR PHENOXY-SUBSTITUTED KETENE MONOMERS AND DIMERS

Phenoxy, ketenes	B.p., °C.	Mm.	Yield, %	d^{20}_4	$n^{20}\text{D}$	MR_D Found	MR_D Calcd.	Formula	Analyses: Mol. wt. Found	Mol. wt. Calcd.	Carbon, % Found	Carbon, % Calcd.	Hydrogen, % Found	Hydrogen, % Calcd.
Methyl dimers	150–152	2	10		1.5309			$C_{18}H_{16}O_4$	291	296	72.35	72.97	5.80	5.41
	182–184	2	69	1.1818	1.5361	78.11	79.23		297	296	72.61	72.97	5.45	5.41
Ethyl dimers	135–137	2	33	1.1191	1.5165	87.52	88.47	$C_{20}H_{20}O_4$	326	324	73.67	74.04	6.35	6.17
	175–178	2	43	1.1541	1.5285	86.51	88.47		325	324	74.01	74.04	6.30	6.17
Propyl														
monomer	110–112	10	10		1.5303			$C_{11}H_{12}O_2$	172	176	75.11	75.00	6.87	6.82
dimer	226–229	6	74					$C_{22}H_{24}O_4$	354	352	75.15	75.00	6.97	6.82
	M.p. 108–109													
n-Butyl														
monomer	113–115	3	18	1.0044	1.4982	54.47	55.20	$C_{12}H_{14}O_2$	181	190	75.10	75.79	7.40	7.37
dimer	205–209	3	72					$C_{24}H_{28}O_4$	384	380	75.50	75.79	7.35	7.37
	M.p. 65–66													
n-Pentyl														
monomer	135–138	8	38	1.0186	1.4953	58.44	59.82	$C_{13}H_{16}O_2$	202	204	76.20	76.47	7.50	7.84
dimer	210–214	6	46		1.5055			$C_{26}H_{32}O_4$	351	408	76.35	76.47	7.67	7.84
2,4-Dichlorophenoxy ketenes														
Methyl														
monomer	68–70	2	9	1.2706	1.5489	54.32	49.83	$C_9H_6O_2Cl_2$	215	217	49.48	49.77	3.00	2.77
dimer	168–170	2	36					$C_{18}H_{12}O_4Cl_4$	427	434	49.60	49.77	2.90	2.77
	M.p. 110–111													
Ethyl														
monomer	130–133	4	16	1.3140	1.5380	54.99	54.45	$C_{10}H_8O_2Cl_2$	230	231	51.70	51.95	3.60	3.46
dimers	180–183	8	41					$C_{20}H_{16}O_4Cl_4$	427	462	51.81	51.95	3.35	3.46
	M.p. 92–93													
	M.p. 103–104		30						396	462	51.79	51.95	3.67	3.46
Propyl														
monomer	138–140	2	3		1.5074			$C_{11}H_{10}O_2Cl_2$	242	245	53.79	53.88	4.27	4.10
dimers	190–192	3	6		1.5381			$C_{22}H_{20}O_4Cl_4$	483	490	53.84	53.88	4.35	4.10
	M.p. 110–111		66						492	490	53.75	53.88	4.06	4.10
Isopropyl														
monomer	110–114	3	7		1.5153			$C_{11}H_{10}O_2Cl_2$	238	245	53.69	53.88	4.17	4.10
dimers	175–177	2	58		1.5446			$C_{22}H_{20}O_4Cl_4$	487	490	53.70	53.88	4.32	4.10
	M.p. 82.5–83.5		22						415	490	53.80	53.88	4.38	4.10
Butyl														
monomer	112–115	2	10		1.5230			$C_{12}H_{12}O_2Cl_2$	256	259	55.47	55.60	4.70	4.63
dimers	180–185	3	14		1.5169			$C_{24}H_{24}O_4Cl_4$	502	518	55.10	55.60	4.52	4.63
	M.p. 87–88		42						514	518	55.39	55.60	4.57	4.63
Pentyl														
monomer	174–176	3	6					$C_{13}H_{14}O_2Cl_2$	270	273	57.09	57.15	4.87	5.02
dimer	M.p. 93–94		25					$C_{26}H_{28}O_4Cl_4$	502	546	57.70	57.15	5.01	5.02

ethanol. Addition of the ethanol precipitated the hydrazide which was purified by recrystallization. Data describing the phenylhydrazides are given in Table III.

Phenyl Esters.—To a 1.0-g. sample of the chloride was added an equivalent amount of pure phenol. The mixture was refluxed for three hours over a hot-plate. The crude product was washed with water, dried over anhydrous calcium chloride and distilled under reduced pressure. The phenyl esters are described in Table III.

Ethyl Esters.—A 1.0-g. sample of each chloride was dissolved in 20 ml. of 95% ethanol and refluxed for one hour over a water-bath. The excess ethanol was removed by distillation; the crude ester washed with water, dried over anhydrous calcium chloride and distilled under reduced pressure. Physical constants and analytical data of the esters are shown in Table III.

Dehydrohalogenation.—A dilute diethyl ether solution of each acid chloride was dehydrohalogenated by treatment with an equimolar amount of triethylamine in a manner similar to that previously reported.[1]

In no case was unreacted acid chloride recovered.

When dehydrohalogenation of the chloride produced two forms of the dimeric ketene, it was found that a fairly satisfactory separation could be made by taking advantage of solubility differences. The procedure which proved most effective was as follows: The diethyl ether solution of the ketenic substances was concentrated, a small portion of dry petroleum ether added and the solution chilled. The mixture was filtered, thus separating one form of the dimeric ketene. This procedure was repeated several times. Finally, the residue was distilled under reduced pressure from a modified Claisen flask to isolate the second form of the dimeric ketene.

Physical constants and analytical data for the ketenic substances are shown in Table IV.

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