Addition of potassium hydroxide gave an oil which was fractionally distilled. There was obtained 10.0 g. of aniline; 5.6 g., b. p. 95–98° at 5 mm.; 1.8 g., b. p. 126–130° at 3.5 mm.; and 7.5 g. of resinous residue.

The second fraction was *n*-amylaniline. It formed a *p*-toluenesulfonyl derivative, m. p. 72–74° (reported[6] 74°) (Found: C, 68.6; H, 7.1), and a **picrolonate**, yellow crystals from alcohol, m. p. 135–136°.

Anal. Calcd. for $C_{11}H_{17}N + C_{10}H_8N_4O_5$: C, 59.1; H, 5.9. Found: C, 59.6; H, 5.7.

The third fraction was **α,ϵ-dicyclohexylaminopentane**. It formed oily benzene and *p*-toluenesulfonyl derivatives, and a **picrate**, yellow crystals from alcohol, m. p. 218–218° dec.

Anal. Calcd. for $C_{17}H_{34}N_2 + 2C_6H_3N_3O_7$: C, 48.1; H, 5.6; N, 15.5. Found: C, 48.3; H, 5.3; N, 15.4.

Preparation of 1-Phenyl-3-hydroxypyridinium Chloride (II).—A solution of 372 g. of aniline and 166 ml. of concd. hydrochloric acid in one liter of 95% alcohol was cooled to 15° and treated with 192 g. of furfural in 200 ml. of alcohol. The mixture was kept in an ice-bath for three hours. The resulting solid mass was then subjected to steam distillation until two liters of distillate had been collected. The residue was cooled, and the aqueous part was decanted from resin and boiled for twenty minutes with 30 g. of charcoal. Evaporation then gave about 300 g. of crude crystalline material. This was boiled for thirty minutes with 400 ml. of absolute alcohol. The suspension was then cooled, and the solid was removed and washed with 50 ml. of cold alcohol. There was obtained 160–170 g. of nearly pure product, m. p. 204–210°; the alcohol washings contained an additional 30–35 g., a total yield of 49%. Crystallization from alcohol gave the pure substance, m. p. 212–214°, suitable for hydrogenation, with a recovery of 75%.

3-Hydroxy-1-phenylpyridinium bisulfate prepared by treating an alcoholic solution of II with sodium hydroxide and then with sulfuric acid, formed colorless crystals from alcohol, m. p. 153–154°.

Anal. Calcd. for $C_{11}H_9NO + H_2SO_4$: S, 11.9. Found: S, 11.6.

The corresponding **nitrate** formed colorless crystals from alcohol, m. p. 123–124°.

Anal. Calcd. for $C_{11}H_9NO + HNO_3$: C, 56.4; H, 4.3. Found: C, 56.1; H, 4.2.

Hydrogenation of II.—A solution of 20 g. of II in 210 ml. of 95% alcohol was boiled with charcoal, then treated with 0.15 g. of platinum oxide and hydrogen. The reaction required one to three hours. (Identical products and yields were obtained by hydrogenation in water, but the reaction required eight to ten hours.) The alcohol and catalyst were then removed, dilute sodium hydroxide was added, and the resulting oil was fractionated. There was obtained 5.3 g., b. p. 123° at 17 mm., and 5.5 g., b. p. 162° at 7 mm.

The first fraction was 1-phenylpiperidine (III); yield 34% (Found: C, 81.7; H, 10.0); the picrate (Found: C, 52.4; H, 4.6) melted at 148–149° (reported[7] 148°); the chloroplatinate melted at 185–188° dec. (reported[8] 190° dec.).

The second fraction was **3-hydroxy-1-phenylpiperidine** (IV) yield 31%.

Anal. Calcd. for $C_{11}H_{15}NO$: C, 74.5; H, 8.5. Found: C, 75.2; H, 8.5.

The **picrate** of IV was obtained in two allotropic forms, yellow crystals from acetone–benzene; α-, m. p. 126.5–127.5°, and β-, m. p. 135–138°. The α-form could be converted into the β- by seeding.

Anal. Calcd. for $C_{11}H_{15}NO + C_6H_3N_3O_7$: C, 50.3; H, 4.5. Found α-: C, 50.3; H, 4.4. β-: C, 50.4; H, 4.6.

Preparation of IV in quantity was best carried out by hydrogenating an alcoholic (one to three hours) or an aqueous (four to five hours) solution of II which had been mixed with nearly one equivalent of sodium bicarbonate and then boiled with charcoal. This gave less than 3% of III, and 71–72% of IV.

3-(*p*-Nitrobenzoyloxy)-1-phenylpiperidine, prepared in pyridine, crystallized from aqueous pyridine in the form of yellow plates, m. p. 98–99°.

Anal. Calcd. for $C_{18}H_{18}N_2O_4$: C, 66.2; H, 5.6. Found: C, 66.2; H, 5.6.

3-Hydroxy-1-(*p*-nitrosophenyl)-piperidine was obtained by treating a solution of 11 g. of IV in 40 ml. of 1:1 hydrochloric acid at 0° with a solution of 4.4 g. of sodium nitrite. After it had been kept cold for eight hours, the mixture was made alkaline with sodium hydroxide and extracted with benzene. Crystallization from benzene gave 6.5 g. (51%) of dark green needles, m. p. 119–120°.

Anal. Calcd. for $C_{11}H_{14}N_2O_2$: C, 64.1; H, 6.8. Found: C, 64.3; H, 7.0.

3-Hydroxypiperidine.—A solution of 7.1 g. of the nitroso compound in 100 ml. of 5% sodium hydroxide was boiled for one hour, then cooled, acidified with hydrochloric acid, and extracted with ether to remove quinone monoxime. The aqueous solution was evaporated, and the residue was taken up in 400 ml. of 40% potassium hydroxide. The product was removed by exhaustive extraction with ether, and distilled. It boiled at 113–116° at 26 mm., then solidified, m. p. 56–58°; yield 1.4 g. (40%).

Anal. Calcd. for $C_5H_{11}NO$: C, 59.3; H, 10.9. Found: C, 59.0; H, 10.5.

The ***p*-toluenesulfonyl derivative**, prepared in 5% aqueous sodium hydroxide, crystallized from dilute methyl alcohol in the form of stout needles, m. p. 97–99°, that were insoluble in dilute hydrochloric acid.

Anal. Calcd. for $C_{12}H_{17}NO_3S$: C, 56.5; H, 6.7. Found: C, 56.6; H, 6.5.

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RECEIVED OCTOBER 25, 1949

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[6] Hickenbottom, *J. Chem. Soc.*, 1119 (1937).

[7] v. Braun, *Ber.*, **40**, 3920 (1907).

[8] v. Braun, *ibid.*, **37**, 3213 (1904).

Preparation, Properties and Reactions of Six Chlorine-Substituted Phenoxyketene Monomers

BY CARL M. HILL, GILBERT W. SENTER AND MARY E. HILL

In a previous paper[1] it was shown that triethylamine dehydrohalogenates ω-cyclohexylalkyl acid chlorides with the formation of ketene dimers. This paper describes an extension of these dehydrohalogenation studies to a series of chlorine-substituted phenoxyacetyl chlorides; namely, phenoxy, 2-chloro, 4-chloro, 2,4-dichloro, 2,4,5-trichloro and 2,4,6-trichloro.

The monomeric ketenes were isolated in pure form, and their reactivity toward several reagents investigated. The monomers gave a negative test for ionizable chlorine; positive tests with bromine and potassium permanganate.

The ketene monomers studied in this investigation have not been previously reported.

Acknowledgment.—The authors wish to express appreciation to The Research Corporation for a Frederick Gardner Cottrell grant which assisted in support of this study. The authors are also indebted to Professor Alfred S. Spriggs for determination of molecular weights of monomers.

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[1] C. M. Hill and G. W. Senter, THIS JOURNAL, **71**, 364 (1949).

TABLE I

MONOMERIC KETENES

Phenoxyketene monomers	M. p., °C.	Yield,[a] %	Formula	Analyses: Mol. wt.[b] Calcd.	Mol. wt.[b] Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Phenoxy	92–93	31.5	$C_8H_6O_2$	134.1	140.5	71.66	70.76	4.51	4.05
2-Chloro	135–136 B. p. 110–115 (1 mm.)	55.2	$C_8H_5O_2Cl$	168.5	173.1	57.01	57.03	2.97	2.42
4-Chloro	141–142	77.5	$C_8H_5O_2Cl$	168.5	170.4	57.01	56.85	2.97	2.54
2,4-Dichloro	125–126	43.8	$C_8H_4O_2Cl_2$	203.0	224.0	47.33	48.05	1.97	1.54
2,4,5-Trichloro	146–147	41.7	$C_8H_3O_2Cl_3$	237.5	237.4	40.46	39.84	1.26	1.14
2,4,6-Trichloro	178–179	56.4	$C_8H_3O_2Cl_3$	237.5	245.0	40.46	40.08	1.26	1.39

[a] Based on the amount of unreacted acid chloride. [b] Molecular weights determined cryoscopically: Meldrum, Saxer and Jones, THIS JOURNAL, **65**, 2023 (1943).

TABLE II

PHENYLHYDRAZIDES OF MONOMERIC KETENES

Hydrazides, phenoxyketenes	Yield, %	M. p., °C.	Formula	Nitrogen, %[a] Calcd.	Nitrogen, %[a] Found
Phenoxy	20	97–98	$C_{14}H_{14}O_2N_2$	11.56	11.63
2-Chloro-	40	94–95	$C_{14}H_{13}O_2N_2Cl$	10.13	10.61
4-Chloro-	40	118–119 dec.	$C_{14}H_{13}O_2N_2Cl$	10.13	10.33
2,4-Dichloro-	38	112–113	$C_{14}H_{12}O_2N_2Cl_2$	9.00	[b]
2,4,5-Trichloro-	14	203–204	$C_{14}H_{11}O_2N_2Cl_3$	8.10	7.97
2,4,6-Trichloro-	55	135–135.5	$C_{14}H_{11}O_2N_2Cl_3$	8.10	8.24

[a] Determined by semi-micro Dumas method. [b] Compound decomposed upon prolonged drying.

Experimental

The dehydrohalogenation procedure used was similar to that reported by Sauer.[2] A small excess of triethylamine over acid chloride was employed in each experiment. Each monomer was purified by recrystallization from a suitable solvent. The ketene monomers were white crystalline solids which were highly hygroscopic. This fact made it exceedingly difficult to obtain dry samples for analysis.

A quantity of unreacted acid chloride was recovered from each preparation.

Analytical data and several physical constants of the six ketene monomers are shown in Table I.

All melting points in this paper are uncorrected.

Phenylhydrazides.—To a solution of the ketene (0.5 g.) in 25 ml. of anhydrous diethyl ether was added 2 ml. of phenylhydrazine. The hydrazide precipitated immediately as white crystals which were then filtered and recrystallized from dilute ethanol. Upon drying the hydrazides turned slightly brown.

Attempts were made to prepare the *p*-nitrophenyl and 3,5-dinitrophenylhydrazides. In each case the product formed as yellow crystals which decomposed rapidly upon isolation and drying.

Properties and analytical data of the phenylhydrazides are shown in Table II.

Amides.—A 0.5-g. sample of each ketene monomer was dissolved in diethyl ether, and dry ammonia gas passed into the solution until precipitation was complete. The crude amide was filtered and recrystallized from benzene. The pure amides were white crystalline solids.

Anilides.—A 0.5-g. sample of each ketene was dissolved in 25 ml. of anhydrous ether and 2 ml. of aniline was added. The mixture was then refluxed for five minutes. On cooling the anilide crystallized out and was filtered. Recrystallization was made from dilute ethanol.

Analytical data and physical constants for the amides and anilides are given in Table III.

TABLE III

AMIDES AND ANILIDES OF PHENOXYKETENES

Phenoxyketenes	Amides: Yield, %	M. p., °C.	Formula	Nitrogen, %[a] Calcd.	Nitrogen, %[a] Found	Anilides: Yield, %	M. p., °C.	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
Phenoxy	75	184–185	$C_8H_9O_2N$	9.27	9.35	40	103–104	$C_{22}H_{19}O_4N$	3.90[g]	4.15
2-Chloro-	73	179–180[b,3]	$C_8H_8O_2NCl$	7.55	7.52	65	121–122[e,3]	$C_{14}H_{12}O_2NCl$	5.35	5.69
4-Chloro-	73	197–198[c,3]	$C_8H_8O_2NCl$	7.55	7.50	52	120–121[f,3]	$C_{14}H_{12}O_2NCl$	5.35	5.40
2,4-Dichloro-	55	176–178	$C_8H_7O_2NCl_2$	6.40	6.48	60	116–117	$C_{14}H_{11}O_2NCl_2$	4.73	4.15
2,4,5-Trichloro-	56	174–175	$C_8H_6O_2NCl_3$	5.51	6.23	61	141–141.5	$C_{14}H_{10}O_2NCl_3$	4.24	4.46
2,4,6-Trichloro-	75	184–185	$C_{16}H_9O_4NCl_6$	2.90[d]	3.11	39	134–135	$C_{14}H_{10}O_2NCl_3$	4.24	4.00

[a] Analyzed by semi-micro Dumas method. [b,c,e,f] Minton and Stephens prepared these compounds from the acid chlorides and reported 149–155°; 133°; 121°; 125°, respectively. [d,g] Calculated on basis of dimeric ketene.

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RECEIVED DECEMBER 8, 1949

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[2] Sauer, THIS JOURNAL, **69**, 2444 (1949).

[3] Minton and Stephens, *J. Chem. Soc.*, **121**, 1598 (1922).

The Specific Rotation of Yeast Adenylic Acid in Anhydrous Formamide[1]

BY DAVID LIPKIN AND GEORGE C. MCELHENY

In connection with work in progress in this Laboratory on the chemistry of the nucleic acids, it became necessary to prepare considerable quantities of pure adenosine-3′-phosphoric acid. Several lots of commercial yeast adenylic acid were obtained[2] and purified by recrystallization of the brucine salt.[3] The yields of brucine

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[1] This research was supported in part by Contract No. AT-29-1-GEN-77 between the United States Atomic Energy Commission and Washington University.

[2] Schwarz Laboratories, Inc., Mount Vernon, N. Y.

[3] Jones and Kennedy, *J. Pharmacol. Exp. Therap.*, **13**, 45 (1919); Levene, *J. Biol. Chem.*, **40**, 415 (1919); Thannhauser, *Z. physiol. Chem.*, **107**, 157 (1919).