

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° (reported⁶ 74°) (Found: C, 68.6; H, 7.1), and a picrolonate, yellow crystals from alcohol, m. p. 135–136°.

Anal. Calcd. for $C_{11}H_{17}N + C_{10}H_8N_4O_6$: 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 $C_{17}H_{34}N_2 + 2C_6H_5N_3O_7$: 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° (reported⁷ 148°); the chloroplatinate melted at 185–188° dec. (reported⁸ 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 $C_{11}H_{15}NO + C_6H_5N_3O_7$: 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 $C_8H_{11}NO$: 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

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

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In a previous paper¹ it was shown that triethylamine dehydrohalogenates ω -cyclohexyl-alkyl 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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