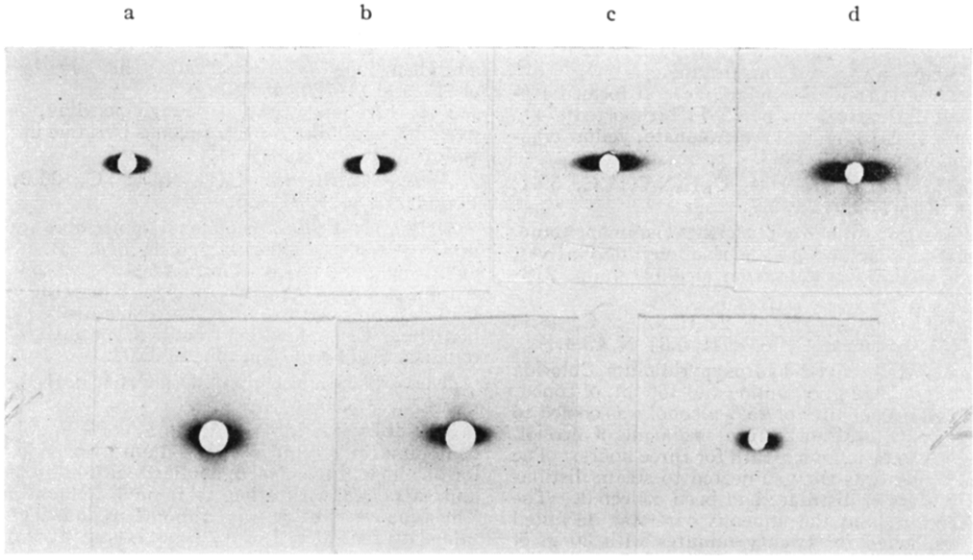

Fig. 2.—Small angle scattering by commercial rayons. Upper: (a) Avisco, Narco; (b) Supernarco; (c) Fortisan; (d) Fiber G. Lower: (e) Rayon after very low Godet stretch; (f) Rayon after 70% Godet stretch, and (g) cotton.

it was possible to study thoroughly the effects of different influences on the crystalline structure of cotton. For example, mercerization results in a widening of the scattering band along the equator indicating a smaller distance between the crystals which is probably due to the breaking down of crystals into smaller units by the action of the mercerizing solution. Another condition studied was that found in a sample of cotton treated with heptylamine (sample furnished by Dr. Segal of the Southern Regional Research Laboratory), which according to chemical determination had a lower degree of crystallinity.[3] The pattern of the treated sample showed a wider scattering band along the equator than did the untreated sample which may also indicate the breaking down of crystal size.

(3) L. Segal, M. L. Nelson, C. M. Conrad, Abstract, 116 Meeting Am. Chem. Soc., p. 12D (1949).

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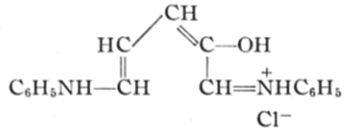
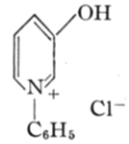
Hydrogenation of Hydroxyglutaconaldehyde Dianil and of 3-Hydroxy-1-phenylpyridinium Salts[1]

BY C. F. KOELSCH AND J. J. CARNEY

Aniline, aniline hydrochloride and furfural react in alcohol solution to form a red-violet dye[2] which has been shown[3] to have structure I.



I



II

Work in this Laboratory on the dye was apparently simultaneous with that cited[3] and covers much the same ground. Although our data are now not needed to establish I, it may be noted that the solution obtained by treating the dye with nitrous acid furnishes iodobenzene in 29% yield[4] with potassium iodide, chlorobenzene (36%) with cuprous chloride, *p*-hydroxyazobenzene (36%) with phenol, and *p*-dimethylaminoazobenzene (80%) with dimethylaniline. Further, it has been found that catalytic hydrogenation of the dye furnishes aniline, *n*-amylaniline and α,ϵ-dicyclohexylaminopentane.

When the dye is heated, it is converted into II.[5] A convenient procedure for obtaining II is described in the present paper. It has been found that the product II can be hydrogenated with platinum to III and IV, whereas hydrogenation of the base corresponding to II yields IV alone. From this compound (IV), by nitrosation and subsequent hydrolysis, there can be obtained 3-hydroxypiperidine.

III IV

Experimental

Hydrogenation of the Dye.—A suspension of 20 g. of the dye and 0.15 g. of platinum oxide in 150 ml. of absolute alcohol absorbed 4.7–4.8 moles of hydrogen during five to six hours shaking under a pressure of 4 atm. Alcohol and catalyst were then removed, and the residues, combined from two reductions, were taken up in dilute hydrochloric acid. No organic material could be extracted with ether.

(1) From the Ph.D. Thesis of James Joseph Carney, September, 1942.

(2) Stenhouse, *Ann.*, **156**, 199 (1870).

(3) Williams and Wilson, *J. Chem. Soc.*, 506 (1942).

(4) On the basis of two molecules of aniline per molecule of dye.

(5) Zincke and Mulhausen, *Ber.*, **38**, 3824 (1905).

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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(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.

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