chrysanthemum monocarboxylic acid chloride gave a tetrahydropyrethrin I which yielded a semicarbazone having a melting point slightly lower than the products obtained on hydrogenation of purified pyrethrin I semicarbazone.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE CITY COLLEGE, COLLEGE OF THE CITY OF NEW YORK]

Alkanolamines. II. Reaction of the Chloronitrobenzenes with Monoethanolamine

BY CHESTER B. KREMER

In a previous communication[1] there was reported the condensation of triethanolamine with aniline to form phenylpiperazine-ethanol. This condensation involved the hydroxyl groups of the alkanolamine and subsequent splitting out of water molecules. In the present research, it is the amine hydrogen of the alkanolamine which is made to combine with a chlorine atom on the benzene nucleus, giving rise to anilino-ethanols. Compounds of this type are usually synthesized by treating aromatic amines with the appropriate chlorohydrin.

All attempts to condense chlorobenzene directly with an alkanolamine failed. The introduction of a nitro group into the ring, ortho or para to the chlorine atom, enables this reaction to proceed. The reaction proceeds more readily as the number of substituted groups on the benzene ring increases. Thus, 2,4-dinitrochlorobenzene reacts easily with monoethanolamine to form the substituted anilino-ethanol.[2] If the benzene ring be heavily loaded, it is even possible to effect the replacement of a nitro group, as seen in the condensation of 3,4,6-trinitrotoluene with monoethanolamine to give 2-(4,6-dinitro-*m*-toluino)-ethanol.[3]

This paper presents the results obtained in condensing the chloronitrobenzenes with monoethanolamine in the presence of anhydrous sodium carbonate. In all of these reactions, there was an accompanying reduction of the chloronitrobenzenes to the azo and/or aniline state. The reduction of organic compounds by mono-, di- and triethanolamines was first reported by Meltsner, *et al.*[4] In the present research, *m*-chloronitrobenzene was found not to condense, only reduction occurring. The other two isomeric chloronitrobenzenes yielded solid condensation products in addition to the reduction products. Of these condensation compounds, 2-(*o*-nitroanilino)-ethanol has been reported previously.[5]

Experimental

Reaction with *o*-Chloronitrobenzene.—One mole of the chloronitrobenzene was placed in a 3-necked round-bottomed flask with two moles of anhydrous sodium carbonate. The mixture was heated with a small flame until the chloronitrobenzene was melted completely. Then one mole of monoethanolamine was added slowly by means of a dropping funnel, mechanical stirring being employed and heating with a small flame continued. After addition of the ethanolamine had been completed, the mixture was refluxed for eight hours with continued stirring.

The mixture was then steam distilled, the steam distillate extracted with ether (ethyl), and the extract dried over sodium hydroxide. Upon removal of the ether and fractionation of the resulting residue, a light yellow oil boiling at 208° was obtained. By conversion to its hydrochloride, the liquid was further identified as *o*-chloroaniline; yield 5–8%.

The residue in the steam distillation flask consisted of two layers; a reddish water layer and a heavy black oil. The latter was run off by means of a separatory funnel and was found to solidify on cooling. Several recrystallizations of the black crystalline solid from chlorobenzene gave an orange-red product melting at 76°: calculated % N for 2-(*o*-nitroanilino)-ethanol, 15.38; N found, 15.46; yield, 60–70%.

Reaction with *m*-Chloronitrobenzene.—The relative amounts and procedure were the same as those given above for the ortho compound, and the ether extract of the steam distillate yielded, after removal of ether and fractionation of residue, a light orange liquid boiling at 229–231°. Conversion of this product into its hydrochloride completed its identification as *m*-chloroaniline; yield 50–60%.

A solid residue in the steam distillation flask was filtered off and recrystallized several times from ethyl alcohol. A light orange product melting at 101° was obtained. This corresponds to the azo compound. A mixed melting point with an authentic sample of 3,3′-dichloroazobenzene showed no depression; yield 30–40%.

Reaction with *p*-Chloronitrobenzene.—The relative amounts and procedure were the same as above, except

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(1) C. B. Kremer, THIS JOURNAL, **58**, 379 (1936).

(2) LeRoy V. Clark, *J. Ind. Eng. Chem.*, **25**, 1385 (1933).

(3) Giovanni Racciu, *Atti. accad. sci. Torino Classe sci. fis. mat. nat.*, **69**, 364 (1934).

(4) M. Meltsner, C. Wohlberg and M. J. Kleiner, THIS JOURNAL, **57**, 2554 (1935).

(5) P. Karrer, E. Schlittler, K. Pfaehler and F. Benz, *Helv. Chim. Acta*, **17**, 1516–1523 (1934).

that heating was continued for ten hours. Examination of the steam distillate revealed the presence of some unreacted *p*-chloronitrobenzene and a yellow solid which, after recrystallizations from water, gave a pure white substance melting at 70°. By checking its hydrochloride, this was shown to be *p*-chloroaniline; yield 5-8%.

A solid residue in the steam distillation flask was filtered off from the hot mother liquor. By fractional crystallization from benzene, this residue was separated into two fractions. The first, after recrystallization from ethyl alcohol, gave light orange crystals melting at 186-187°. This was shown to be 4,4'-dichloroazobenzene; a mixed melting point with an authentic sample of that compound causing no depression; yield 15-20%. The second fraction upon recrystallization from chlorobenzene gave yellow plates melting at 111-111.5°. Calculated % N for 2-(*p*-nitroanilino)-ethanol, 15.38; % N found, 15.64.

The filtrate from the steam distillation flask, upon cooling and standing overnight, deposited shiny, golden crystals. These upon recrystallization from chlorobenzene also melted at 111° and proved to be a further yield of the anilino-ethanol: total yield, 15-20%.

Reduction of the Nitro Condensation Products.—Mossy tin and concentrated hydrochloric acid were used and the mixture refluxed for one hour, made strongly alkaline with sodium hydroxide and extracted with ether. Upon evaporation of the ether, the ortho condensation compound yielded pearly white plates melting, after recrystallization from benzene, at 107°. Calculated % N for 2-(*o*-aminoanilino)-ethanol, 18.42; % N found, 18.28. The para compound gave only an unstable product on reduction which rapidly oxidized to a purple resin.

Summary

1. Monoethanolamine condenses directly with *o*- and *p*-chloronitrobenzenes, in the presence of anhydrous sodium carbonate, to form substituted anilino-ethanols.

2. Under similar conditions, *m*-chloronitrobenzene does not condense.

3. Reduction of the chloronitrobenzenes by the alkanolamine is also effected in these reactions.

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[CONTRIBUTION FROM GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 554]

The Isomeric 2-Pentenes[1]

BY HOWARD J. LUCAS AND ARTHUR N. PRATER

The work herein described was undertaken for the purpose of accounting for the properties of the bromopentanes and dibromopentanes which Kharasch and Darkis[2] and Sherrill and coworkers[3] prepared from various samples of 2-pentene by the respective addition of hydrogen bromide and bromine, for it was these properties which Kharasch and Darkis used as a basis for their hypothesis of electronic isomerism of ethylene compounds. For this purpose it was necessary to synthesize *cis*- and *trans*-2-pentene, and to study the behavior of each hydrocarbon with these reagents. Lauer and Stodola[4] have synthesized the *trans*, by a somewhat different procedure, but did not obtain the *cis* isomer. The *trans* isomer herein described is quite pure, for its properties agree well with those observed by Lauer and Stodola, but it is probable that the *cis* is contaminated by some of the *trans* hydrocarbon.

The configurations herein assigned to the isomeric 2-pentenes are based upon those of the 2-butenes, since the former have been synthesized by a series of operations strictly parallel to those previously employed in the case of the latter.[5] Brockway and Cross, by electron diffraction studies, have established the configurations of the 2-butenes.[6] The previously assumed configurations[5] are in agreement. In this synthesis, 2-pentanone,[7] I, was the starting material; the operations involved are

$$\underset{\text{I}}{\mathrm{CH_3CH_2CH_2COCH_3}} \xrightarrow{\mathrm{HCN}}$$

$$\underset{\text{II}}{\mathrm{CH_3CH_2CH_2C(OH)(CH_3)CN}} \longrightarrow$$

$$\underset{\text{III}}{\mathrm{C_2H_5CH_2C(OH)(CH_3)COOH}} \xrightarrow{\text{heat}}$$

$$\underset{\text{IV}}{\mathrm{C_2H_5CH{=}C(CH_3)COOH}} \xrightarrow{\mathrm{HI}}$$

$$\underset{\text{V}}{\mathrm{C_2H_5CHICH(CH_3)COOH}} \xrightarrow{\mathrm{Na_2CO_3}} \underset{\text{VI}}{\mathrm{C_2H_5CH{=}CHCH_3}}$$

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[1] Presented before the San Francisco Meeting of the American Chemical Society, August 21, 1935. Original manuscript received on July 15, 1936.

[2] Kharasch and Darkis, *Chem. Rev.*, **5**, 571 (1928).

[3] Sherrill, Otto and Pickett, THIS JOURNAL, **51**, 3023 (1929); Sherrill, Baldwin and Haas, *ibid.*, **51**, 3034 (1929).

[4] Lauer and Stodola, *ibid.*, **56**, 1215 (1934).

[5] Young, Dillon and Lucas, *ibid.*, **51**, 2528 (1929).

[6] Brockway and Cross, *ibid.*, **58**, 2407 (1936).

[7] Kindly supplied by the Standard Oil Development Company through the courtesy of H. E. Buc.