Anal. Calcd. for $C_{14}H_{15}O_2NS$: S, 12.26; N, 5.35. Found: S, 12.15; N, 5.43.

2-(5-*t*-Butyl-2-thienyl)-ethanol.—To two moles of sodium amalgam sand was added 32 g. (0.5 mole) of ethyl chloride and 70 g. (0.5 mole) of 2-*t*-butylthiophene in 200 ml. of ether in a similar manner to that described directly above. After cooling below 10°, 22 g. (0.5 mole) of ethylene oxide in 100 ml. of ether was added during a one-hour period. The temperature rose rapidly but was controlled at about 30° by means of an ice-bath. After this addition the mixture was stirred for ninety minutes at ambient temperatures and then treated as described in the preparation of 2-(5-chloro-2-thienyl)-ethanol. Sixty-three grams (68%) of 2-(5-*t*-butyl-2-thienyl)-ethanol, a white, viscous fluid, was obtained; b. p. 115–116° at 3 mm.; $n^{20}\text{D}$ 1.5198. The phenylurethan derivative was recrystallized from petroleum ether, m. p. 73–74°.

Anal. Calcd. for $C_{17}H_{21}O_2NS$: S, 10.56; N, 4.62. Found: S, 10.71; N, 4.71.

General Procedure for Preparing the Vinylthiophenes.—The thienylethanol was dehydrated to the corresponding vinylthiophene by heating the ethanol with a large excess (1:4) of molten potassium hydroxide at a reduced pressure (45–50 mm.). The vinylthiophene distilled along with water and the distillate was extracted with ether. After drying the ether solution with anhydrous sodium sulfate, the ether was removed on a steam-bath and the residue was distilled under reduced pressure.

The 2-(5-chloro-2-thienyl)-ethanol did not dehydrate well by this method and the low yield of a vinyl compound did not contain the theoretical amount of chlorine.

Acknowledgment.—The authors wish to thank Dr. D. E. Badertscher for his advice and interest, and Mrs. Josephine Sindoni Piel, who carried out some of the experiments.

Summary

2-(2-Thienyl)-, 2-(5-*t*-butyl-2-thienyl)-, 2-(4-methyl-2-thienyl)- and 2-(5-chloro-2-thienyl)-ethanol have been prepared from the corresponding thienylsodium compound and ethylene oxide in yields of 47, 68, 51 and 22%, respectively.

Dehydration of several of the thienylethanols, namely, 2-(2-thienyl)-, 2-(4-methyl-2-thienyl)- and 2-(5-*t*-butyl-2-thienyl)-ethanol with molten potassium hydroxide at reduced pressure yielded the corresponding vinylthiophenes in yields of 80, 95 and 94%.

PAULSBORO, NEW JERSEY RECEIVED JULY 14, 1947

[CONTRIBUTION FROM THE FINE CHEMICALS DIVISION, NOPCO CHEMICAL CO.]

Acylation of Benzene Compounds with Iodine as a Catalyst

BY SAUL CHODROFF AND HOWARD C. KLEIN

Iodine has been used successfully as a catalyst in acylations of furan and thiophene.[1] It was of interest to extend this reaction to benzenoid compounds. Acylations were successful with the more active members of the benzene series, such as anisole[2] and acetanilide, whereas the alkylated benzenes, toluene and cumene, failed to react. As previously noted,[1] the aroyl halides gave higher yields than aliphatic anhydrides. Dibasic aliphatic anhydrides, such as succinic anhydride, failed to react with anisole. As might be expected from the reduced aromaticity of the benzenoid compounds compared to furan and thiophene, the reactions were not exothermic, required longer periods of time and higher temperatures, and generally required higher catalyst concentrations for optimum yields, the range of 2–7 $\times 10^{-2}$ mole of iodine per mole of reactant being quite effective.

The influence of catalyst concentration on yield in the reaction between naphthalene and benzoyl chloride was marked; the yield of ketone rose from 15 to 52% as the molar ratio of iodine to reactants was increased from 2.1×10^{-2} to 7.6×10^{-2}. The reaction favors the formation of the α-isomer predominantly, for, the ratio of the α to β isomers in the mixture of the crude benzoylnaphthalenes was 95 to 5, as determined by the precipitation of the picrate of the β isomer from a benzene solution,[3] after standing for two weeks at 5°.

Acknowledgment.—The authors are grateful to Dr. Roland Kapp of this Laboratory for encouragement and interest in the promotion of this work.

Experimental

***p*-Acetylanisole.**—Two hundred and fourteen grams (2.0 moles) of anisole and 102 g. (1.0 mole) of acetic anhydride were refluxed for two hours in the presence of 2 g. of iodine. After cooling, the dark brown solution was taken up in 300 ml. of ethylene dichloride and washed successively with dilute potassium carbonate, sodium bisulfite, and water. Drying over sodium sulfate, removal of the solvent, and distillation of the residue gave 98.6 g. (66%) of *p*-acetylanisole, b. p. 120–125° (5 mm.), as a colorless oil. Crystallization from aqueous methanol yielded crystals, m. p. 38°. The product formed a semicarbazone, m. p. 198–198.5°.[4]

***p*-Benzoylanisole.**—To a mixture of 37.8 g. (0.35 mole) of anisole and 22.4 g. (0.18 mole) of benzoyl chloride, was added 1 g. of iodine. The solution was refluxed gently for eight hours, until the evolution of hydrogen chloride had subsided. After cooling, the solution was diluted with 100 ml. of benzene, washed with potassium carbonate, sodium bisulfite, and water. The dried solvent was removed on the steam-bath and the residue distilled, yielding 33.8 g. (88.6%) of *p*-benzoylanisole, b. p. 175–179° (1 mm.), as a yellow liquid which solidified,

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(1) Hartough and Kosak, THIS JOURNAL, **68**, 2639 (1946).

(2) NOTE ADDED IN PROOF.—After this manuscript had been submitted, Kosak and Hartough, *ibid.*, **69**, 3144 (1947), reported the acetylation of ansole in 45% yield, using phosphoric acid as a catalyst. They also indicated that iodine and other acid catalysts may be employed in this reaction without reporting the yield.

(3) Rousset, *Bull. soc. chim. France*, [3] **15**, 71 (1896).

(4) Wahl and Silberzweig, *Bull. soc. chim.*, [4] **11**, 69 (1912), list m. p. of 197°.

m. p. 53-55°. Crystallization from 90% methanol raised the m. p. to 61-62.5°. A 2,4-dinitrophenylhydrazone was obtained, m. p. 180°.[5]

***p*-Acetylaniline.**—Fifty-four grams (0.4 mole) of acetanilide and 50 ml. of acetic anhydride were refluxed with 4 g. of iodine, distilling the acetic acid formed through a 38-cm. Vigreux column. In fifteen minutes, 30 ml. of distillate was collected, b. p. 110-120°. An additional 25 ml. of acetic anhydride was added to the reaction mixture and 25 ml. of distillate collected, the final vapor temperature rising to 132°. The reaction mass was poured into 250 ml. of water, the oil extracted twice with 75-ml. portions of ethylene dichloride and the excess iodine washed out with bisulfite. Removal of the solvent left a tarry residue which was hydrolyzed by refluxing for one hour with 50 ml. of concentrated hydrochloric acid. After being made strongly alkaline, the unreacted aniline was steam distilled and the residual black tar extracted twice with 75-ml. portions of ethylene dichloride, washed until neutral and dried over sodium sulfate. The solvent was removed and the residue distilled, yielding 10.5 g. (19.4%) of a golden yellow oil, b. p. 165-168° (6 mm.), which solidified, m. p. 67-68°. Crystallization from hot water gave white crystalline *p*-acetylaniline, m. p. 105-106°; acetyl derivative, m. p. 165-166°.[6]

Refluxing the reactants for two hours without removal of the acetic acid formed reduced the yield of *p*-acetylaniline to 7%.

α-Phenyl Naphthyl Ketone.—Twenty-five and six-tenths g. (0.2 mole) of naphthalene was refluxed gently with 28 g. (0.2 mole) of benzoyl chloride in the presence of 4 g. of iodine. A vigorous evolution of hydrogen chloride began immediately and ceased within two hours. The reaction mass was taken up in 150 ml. of ethylene dichloride, washed with dilute sodium hydroxide and bisulfite and the solvent and unreacted naphthalene removed by steam distillation. The black, tarry mass was extracted with benzene, washed with water and dried over sodium sulfate. The solvent was removed and the residue distilled, yielding 23.9 g. (51.7%) of a golden yellow, viscous liquid, b. p. 165-169° (1 mm.) which slowly solidified, m. p. 73-74°. The product was crystallized from ethanol, m. p. 74-75°, and gave an oxime, m. p. 161°.[7] One gram of the crude ketone dissolved in 20 ml. of benzene containing 1 g. of picric acid deposited, after fourteen days at 5°, 100 mg. of the picrate of the β-isomer, m. p. 112-113°, equivalent to 5% of β-benzoylnaphthalene.[3]

Summary

Acylations have been carried out successfully on the more active members of the benzene series, using iodine as a catalyst.

Harrison, New Jersey Received December 20, 1947

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[5] Ferrante and Bloom, *Am. J. Pharm.*, **105**, 383 (1933), report m. p. of 180°.

[6] Kunckell, *Ber.*, **33**, 2641 (1900), report m. p. of 166-167°.

[7] Betti and Poccianti, *Gazz. chim. ital.*, **45**, I, 374 (1915), list m. p. of 161°.

[Contribution from the University of Chicago Toxicity Laboratory]

The Volatility and Vapor Pressure of Ten Substituted 2-Chloroethylamines[1]

By C. Ernst Redemann,[2] Saul W. Chaikin and Ralph B. Fearing[3]

In a study of the toxicity and vesicancy of the so-called nitrogen mustards it soon became apparent that neither the necessary volatility nor vapor pressure data for assessing these agents were available. The first member of this group of 2-chloroethylamines to be prepared, and its potent vesicant action described, was tris-(2-chloroethyl)-amine.[4] However, no vapor pressure data were given nor were any subsequently reported. It was, therefore, necessary to measure the volatility before any quantitative evaluation of these compounds could be made. In the course of this study the volatility and vapor pressure were determined for ten substituted 2-chloroethylamines at temperatures between 0 and 60°. Their numerical values are reported here.

The method employed for measuring the volatility and the equations by which the vapor pressure was calculated from the volatility have been described in two earlier reports.[5] The equations derived for these compounds should not be used at temperatures much outside the specified range without recognizing that the values so computed may have errors considerably larger than the probable error over the 0 to 60° interval.

Experimental

The details of the measurements and the apparatus have been given in earlier reports.[5]

All the compounds employed in this study were prepared in laboratories other than that of the authors. The source of each compound is given in Table I. All but one of the 2-chloroethylamines were received as the hydrochlorides, well crystallized compounds of definite, reproducible melting point, which could be readily purified by crystallization from suitable solvents. These hydrochlorides were usually received in an analytically pure form and were stored in a cool, dry place until they were used. Each hydrochloride was converted into the free base by treatment with a cold 50% aqueous solution of potassium hydroxide. Where practical the base was separated from the aqueous solution without use of any solvent; when the amine phase would not separate cleanly from the aqueous phase the former was diluted with ethyl ether before separation. The amines were dried over anhydrous potassium carbonate before distillation. The dry amine was distilled under reduced pressure, the pressure being so chosen that the amine boiled below 100° in all but two cases (see Table I). For eight of the ten amines the boiling point was constant; for *t*-butyl-bis-(2-chloroethyl)-amine a one degree boiling range was tolerated, and for 4-(2-chloroethyl)-morpholine the sample submitted was too small to purify before use and was therefore run as received.

Since these amines slowly give self-condensation products, especially when not completely dry, they were placed in the vaporizer immediately after distillation and

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[1] This work was carried out under contract with the National Defense Research Committee of the Office of Scientific Research and Development.

[2] Present address: 770 S. Arroyo Parkway, Pasadena 2, Calif.

[3] Present address: 622 N. East Ave., Oak Park, Ill.

[4] Ward, This Journal, **57**, 914 (1935).

[5] (a) Bent and Francel, *ibid.*, **70**, 634 (1948); (b) Redemann, Chaikin and Fearing, *ibid.*, **70**, 631 (1948).