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Metalation Studies in the Thiophene Series. III. Condensation of Thienyl- and Substituted Thienyl-sodium Compounds with Ethylene Oxide

BY JOHN W. SCHICK AND HOWARD D. HARTOUGH

The preparation of the carboxylic acids of thiophene,[1] halothiophenes[1] and the alkylthiophenes[2] has been previously described. Although organometallic compounds are reported to react similarly to Grignard reagents, the only literature references that can be found deal with their reactions with carbon dioxide and formaldehyde or its polymers. Amylsodium, phenylsodium and benzylsodium have been condensed only with trioxymethylene[3] to yield hexyl alcohol (28%), benzyl alcohol (17%) and phenylethyl alcohol (17%), respectively.

The study of the reaction of ethylene oxide with thienyl-, halothienyl- and alkylthienylsodium compounds was undertaken in order to obtain the corresponding ethanols and vinyl compounds. Previously, the simple alcohols such as 2-thienylcarbinol[4] and 2-(2-thienyl)-ethanol[5] were prepared from 2-thienylmagnesium bromide or iodide and monomeric formaldehyde and ethylene oxide, respectively.

2-Thienylsodium and substituted 2-thienylsodiums, namely, 4-methyl-, 5-methyl-, 5-*t*-butyl- and 5-chlorothienylsodium, were condensed with ethylene oxide to yield the corresponding thienylethanols. Dehydration of the thienylethanols by conventional means yielded vinyl and substituted vinyl-thiophenes which may be useful in the plastics and rubber industries. Table I records several vinylthiophenes thus obtained with their observed properties. The vinylthiophenes polymerized at room temperature, and more rapidly at elevated temperatures in the presence of a catalyst, benzoyl peroxide, to yield very pale yellow to orange colored, clear polymers.

TABLE I

VINYLTHIOPHENES

	B. p., °C.	Mm. Hg pressure	n^{20}_D	Yield, %	Formula	Sulfur, % Calcd.	Sulfur, % Found
2-Vinylthiophene	65.5–66.5	48	1.5720	80	C_6H_6S	29.1	28.9
4-Methyl-2-vinylthiophene	86.5–87.5	45	1.5590[a]	95	C_7H_8S	25.8	25.7
5-*t*-Butyl-2-vinylthiophene	104–105	24	1.5357	94	$C_{10}H_{14}S$	19.3	19.9

[a] Refractive index at 25°.

Experimental

2-(2-Thienyl)-ethanol.—A mixture of 118 g. (1.0 mole) of 2-chlorothiophene in 500 ml. of benzene was added to a freshly prepared sodium amalgam sand[1] containing 50 g. (2.17 gram atoms) of sodium and 20 g. (0.10 gram atom) of mercury and the reaction mixture was stirred and refluxed for three hours in a nitrogen atmosphere. The mixture was cooled to 0–10° in an ice-bath and 44 g. (1.0 mole) of ethylene oxide in 100 ml. of benzene was added over a twenty-minute period. The temperature rose rapidly to about 50° and then slowly fell. The ice-bath was removed and the stirring was continued until the temperature dropped to 25°. A solution containing 125 ml. of concentrated hydrochloric acid in 325 ml. of distilled water was cautiously added with stirring and the whole solution was filtered to remove salt and sludge. The benzene layer was separated, dried over anhydrous sodium sulfate and the benzene removed by distillation. The residue was distilled under reduced pressure. Sixty grams (47%) of 2-(2-thienyl)-ethanol, a white oily fluid having the odor of roses, was obtained; b. p. 99–100° (7 mm.); n^{20}_D 1.5478.

The phenylurethan was recrystallized from petroleum ether, m. p. 52–53°.

Anal. Calcd. for $C_{13}H_{13}O_2NS$: S, 12.96; N, 5.67. Found: S, 12.95; N, 5.79.

2-(5-Chloro-2-thienyl)-ethanol.—One mole (118 g.) of 2-chlorothiophene was converted to the corresponding 5-chloro-2-thienylsodium by a method described earlier.[1] To the ice-cooled reaction mixture was added 66 g. (1.5 moles) of ethylene oxide in 200 ml. of ether over a period of one hour. The mixture was then stirred at room temperature for thirty minutes and then warmed to reflux for two hours. Unreacted sodium was decomposed with 150 ml. of alcohol and a solution of 170 ml. of concd. hydrochloric acid in 500 ml. of water added cautiously over a period of thirty minutes. The resultant emulsion was broken with sodium chloride. The ether layer was separated, dried and the ether distilled. Thirty-five grams (22%) of 2-(5-chloro-2-thienyl)-ethanol, a white, oily fluid having the odor of roses was obtained; b. p. 98.5–100° (1–2 mm.); n^{20}_D 1.5576. The phenylurethan derivative was recrystallized from petroleum ether, m. p. 57–58°.

Anal. Calcd. for $C_{13}H_{12}ClNO_2S$: N, 4.97. Found: N, 4.81.

2-(4-Methyl-2-thienyl)-ethanol.—A cold mixture of 64 g. (1.0 mole) of ethyl chloride in 300 ml. of diethyl ether was added dropwise over one hour (in a nitrogen atmosphere) to a stirred mixture of sodium amalgam sand containing 46 g. (2.0 gram atoms) of sodium and 12 g. (0.06 gram atom) of mercury and 147 g. (1.5 mole) of 3-methylthiophene in 200 ml. of diethyl ether which was cooled to 0–5°. After the addition was completed, the ice-bath was removed and the temperature kept below the reflux temperature of ether for one hour, after which it was warmed to the reflux temperature for fifteen minutes. The reaction was cooled below 10° and a cold solution of 44 g. (1.0 mole) of ethylene oxide in 100 ml. of ether was added with stirring over a period of one hour. The temperature was permitted to rise to room temperature. The reaction mixture was worked up as described in the preparation of 2-(5-chloro-2-thienyl)-ethanol. Seventy-one grams (51%) of 2-(4-methyl-2-thienyl)-ethanol was obtained; b. p. 87–89° (2 mm.); n^{20}_D 1.5397. The phenylurethan derivative was recrystallized from petroleum ether, m. p. 68–69°.

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[1] Schick and Hartough, THIS JOURNAL, **70**, 286 (1948).

[2] Schick and Hartough, *ibid.*, **70**, 1645 (1948).

[3] Morton and Fallwell, *ibid.*, **60**, 1429 (1938).

[4] Steinkopf, *Ann.*, **540**, 23 (1939).

[5] Blicke and Burckhalter, THIS JOURNAL, **64**, 477 (1942).

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.; $n^{20}D$ 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.

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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%.

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Acylation of Benzene Compounds with Iodine as a Catalyst

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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 × 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°.

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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°.