initial value of $[\alpha]^{25}\text{D}$ 94° (c, 1.86 in absolute methanol) and an equilibrium value of 34° was obtained.[7]

Anal. Calcd. for $C_5H_9O_5COOCH_3$: OCH_3 14.9, mol. wt., 208. Found: OCH_3 14.9; mol. wt. 202 (by reducing value), 210 (by saponification).

The ester was also isolated from a reaction mixture which had been allowed to proceed at 25° for seventeen hours in the presence of 0.01 N hydrochloric acid after which 93% esterification and 20% glycoside formation had occurred. The yield of pure ester was lower.

Esterification of Alginic and Pectic Acids.—Several 1-g. samples of finely ground alginic acid and orange pectinesterase-prepared citrus pectic acid were suspended in 31 ml. of anhydrous 0.025 N hydrogen chloride–methanol. After the desired time the solid was centrifuged off, washed with methanol, and dried for four hours at 100°. Solutions of 0.2-g. samples in water were titrated with 0.1 N alkali, and the per cent. esterification was calculated. This procedure appeared to give a good approximation, since a sample of alginic acid which had been 78% esterified according to this method of determination actually contained 11.7% methoxyl (72% of theoretical) after humidifying to remove retained alcohol[8] and redrying.

Summary

The esterification of galacturonic acid in methanol containing small concentrations of hydrogen chloride (0.005 to 0.1 N) proceeded at a rate at least 25 times more rapid at 25° and 55 times more rapid at 0° than did glycoside formation. Both reactions were first order to at least 50% conversion and the energies of activation for the esterification and glycoside formation reactions were 14,000 ± 700 and 21,000 ± 1,000 cal., respectively.

Methyl α-D-galacturonate was isolated in good yields from such reaction mixtures.

Alginic acid was partially esterified by a similar procedure. However, pectic acid under the same conditions was only very slowly esterified.

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[7] This value is lower than that of 38° reported by Morell and Link. However, we found that three days were necessary before equilibrium was reached either with this sample or with one prepared by the diazomethane method.

[8] Jansen, Waisbrot and Rietz, *Ind. Eng. Chem., Anal. Ed.*, **16**, 523 (1944).

[CONTRIBUTION FROM KOPPERS CO., INC., MULTIPLE FELLOWSHIP ON TAR SYNTHETICS, MELLON INSTITUTE]

Alkylation of Thiophene by Olefins and Alcohols

BY WALTER M. KUTZ AND B. B. CORSON

This paper describes for the first time the direct alkylation of thiophene by olefins and alcohols. The alumina–silica type of catalyst was found suitable for this reaction. Thiophene was alkylated by propylene, butylene-1, isobutylene, amylene, cyclohexene, isopropyl alcohol, and tertiary butyl alcohol. Suitable conditions were not found for the ethylation of thiophene.

In general, the catalysts and conditions employed for the alkylation of aromatics are not suitable for the alkylation of thiophene. For example, we were unable to find any set of conditions under which sulfuric acid or the chlorides of aluminum, iron, or tin catalyzed the isopropylation of thiophene. Strong sulfuric acid sulfonated the thiophene; dilute sulfuric acid allowed the thiophene to survive but did not catalyze the alkylation reaction. Sulfuric acid concentrations ranging from 96 to 50% were tested, the reaction temperature being 0–5°. Only very small yields of material boiling above thiophene were obtained. However, thiophene was alkylated at 60° by isobutylene with 100% phosphoric acid as catalyst. Aluminum chloride and ferric chlorides were tested at 0–5° and at 25°, respectively. Negligible yields of liquid product boiling above thiophene were obtained. When stannic chloride was employed according to the directions of Johnson and May[1] for the acetylation of thiophene, practically all the thiophene was recovered unchanged. Boron trifluoride–dimethyl ether complex and hydrogen fluoride yielded resinous products.

The structure of isopropylthiophene, obtained by the alkylation of thiophene by propylene and also by isopropyl alcohol, was established as the 2-isomer by specific color tests and by converting it into the known oxime and *p*-nitrophenylhydrazone of its 5-acetyl derivative.[2] Numerous unsuccessful attempts were initially made to oxidize isopropylthiophene to the corresponding thenoyl formic or thiophenic acid. The structures of the other alkyl thiophenes were not determined, but it is likely that they are also 2-isomers.

Experimental

Materials.—Thiophene, obtained from the Socony-Vacuum Oil Co., was used without further purification.[3] Ethylene and propylene were of 99.5 and 75% purity, respectively, the contaminant of the propylene being propane. Butylene-1 (99% pure) and isobutylene (95% pure) were products of the Phillips Petroleum Co. Amylene, obtained from the Sharples Solvents Co., consisted of a mixture of methylethylethylene and trimethylethylene. Filtrol catalyst (X-143) was supplied by the Filtrol Corp., anhydrous hydrogen fluoride by the Harshaw Chemical Co., and boron trifluoride–dimethyl ether complex by the General Chemical Co.

Apparatus and Procedure.—The superatmospheric pressure alkylation experiments with Filtrol, hydrogen fluoride, and boron trifluoride–dimethyl ether complex were made in a 3500-cc. stainless steel, rotating autoclave of the Ipatieff type, gaseous catalysts and olefins (except ethylene) being condensed in metal or glass traps which

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[1] Johnson and May, "Organic Syntheses," Coll. Vol. II, p. 8 (1944).

[2] Scheibler and Schmidt, *Ber.*, **54**, 139 (1921).

[3] Fawcett and Rasmussen, THIS JOURNAL, **67**, 1705 (1945).

TABLE I

ALKYLATION OF THIOPHENE OVER FILTROL

Alkylating agent	Agent, g.	Thiophene, g.	Mole ratio, T./alk.[a]	Catalyst, g.	Length of expt., hr.	T, °C.	Max. press., atm.	Product: Monoalkyl thiophene[c] g.	Product: Monoalkyl thiophene[c] Yield, %[d]	Product: High-boiling material, g.
Propylene	207	925	2.2	60	11	200	23	276	45	307
Isopropyl alcohol	180	1260	5.0	150	10	200	24	210	56	102
Isobutylene	100	540	3.6	100[b]	4	60	1	56	20	22
t-Butyl alcohol	222	1260	5.0	150	5	200	15	161	38	611
Butylene-1	234	953	2.7	60	5	200	24	306	52	209
Amylene	180	1260	5.8	50	5	200	17	260	65	365
Cyclohexene	164	336	2.0	35	5	200	12	88	27	173

[a] Mole ratio; thiophene/alkylating agent. [b] 100% phosphoric acid; catalyst in all other experiments, Filtrol X-143. [c] Crude product; see Table II for final distillation. [d] Based on alkylating agent.

TABLE II

CONSTANTS AND ANALYTICAL VALUES OF MONO ALKYL THIOPHENES

Alkylating agent	Substituents	B. p., °C. (760 mm.)	$n^{20}D$	d^{20}_4	% Sulfur Calcd.	% Sulfur Found	Mol. wt. Calcd.	Mol. wt. Found	Yield, % of crude fraction
Propylene	2-Isopropyl-	153.5-154	1.5043	0.9884	25.0	25.2	126	125	72
Isopropyl alcohol	2-Isopropyl-	153.5-154	1.5040	.9887	25.0	25.1	126	127	74
t-Butyl alcohol	2-*t*-butyl-	163-164	1.4987	.9527	22.9	23.5	140	139	70
Butylene-1	2-Butyl-	173.5-174.5	1.5001	.9551	22.9	22.8	140	139	86
Amylene	2-Amyl-	188-189.5	1.4995	.9484	20.8	21.2	154	151	66
	2-Amyl-	194-196	1.4992	.9480	20.8	21.1	154	151	14
Cyclohexene	2-Cyclohexyl-	100-130 (5 mm.)	1.5413	1.0390	19.4	19.2	166	170	100

were placed in the autoclave before closure. Ethylene was pressed into the autoclave at reaction temperature to a pressure of 68 atmospheres.

The atmospheric pressure alkylation experiments with sulfuric and phosphoric acids and with aluminum, ferric, and stannic chlorides were made in a 3-necked flask with mercury-sealed stirrer. The reaction products from the acids were washed with dilute alkali, dried, and distilled; those from the metal chlorides were first decomposed by pouring into a mixture of ice and hydrochloric acid.

The general distillation procedure was to remove thiophene and monoalkylated thiophene at atmospheric pressure through a 15-plate Fenske column and to distil the bottoms from a Claisen flask under reduced pressure. The monoalkylated fractions were redistilled through a Heligrid packed Podbielniak column with 50:1 reflux ratio between plateaus and with 10:1 reflux ratio on plateaus.

Discussion

Higher Boiling Products.—Tables I, II and III present the experimental data. Products boiling higher than the monoalkyl thiophenes usually showed analytical values and constants which indicated that they were mixtures of polyalkyl thiophenes, polythienyls, and thiophene condensation products from which some sulfur had been eliminated. Fractions, however, were obtained which showed the correct analytical values for diisopropylthiophene and dibutylthiophene. Usually the yield of higher boiling material was greater than that of the monoalkylated thiophene; in the case of alkylation by tertiary butyl alcohol, almost four times as great.

Unsuccessful Ethylation of Thiophene.—Using Filtrol as catalyst (at 250 and 275°), the same type of product was obtained in the presence and absence of ethylene. For example, at 275°, there was a 50% conversion to a product containing 30 g. of material boiling (5 mm.) at 80-100° ($n^{20}D$ 1.5656; mol. wt., 153; S, 27.0), 58 g. boiling at 100-150° ($n^{20}D$ 1.6082; mol. wt., 197; S, 27.3), 48 g. boiling at 150-200° ($n^{20}D$ 1.6388; mol. wt., 263; S, 31.1), and 304 g. of bottoms (mol. wt., 408; S, 32.5).

TABLE III

HIGHER BOILING PRODUCTS

Alkylating agent	Data on higher boiling products: B. p. °C.	Mm.	Yield, g.	$n^{20}D$	Mol. wt.	Sulfur, %
Propylene	178-198	760	77	1.5000	154[a]	19.8
	>198	760	230	....	...	26.8
t-Butyl alcohol	55-100	5	32	1.5134	166	19.1
	100-150	5	60	1.5568	180	25.6
	150-200	5	50	1.6050	227	..
	>200	5	469	....	...	..
Butylene-1	196-206	760	9	1.5022	...	..
	206-226	760	50	1.4986	185[b]	17.8
	>226	760	150	....	...	..
Amylene	60-160	3	65	1.5300	189	22.2
	160-225	3	90	1.6133	262	31.6
	>225	3	210	....	...	..
Cyclohexene	130-170	5[c]	25	1.5510	200	15.8
	170-190	5	37	1.5560	241	15.0
	190-210	5	25	1.5664	262	16.0
	>210	5	86	....	408	..

[a] Calcd. for diisopropylthiophene, $C_{10}H_{16}S$: mol. wt., 168; S, 19.0. [b] Calcd. for dibutylthiophene, $C_{12}H_{20}S$: mol. wt., 196; S, 16.4. [c] There was also a 35 g. fraction boiling at 90-100° (5 mm.): $n^{20}D$ 1.5365; mol. wt., 160; S, 20.6.

Constants and Analytical Values of Mono Alkyl Thiophenes.—The constants and analytical values of the mono alkyl thiophenes are listed in Table II. The mono butyl thiophene obtained from butylene-1 apparently contains the secondary group, as evidenced by the intermediate position of its boiling point between those of *t*-butylthiophene (163-164°, Table II) and *n*-butylthiophene (181-182° (740 mm.)).[4] The lower boiling of the two mono amyl thiophenes listed in Table II is probably *t*-amylthiophene (derived from trimethylethylene) and the higher boiling isomer is probably a secondary amylthiophene (derived from methylethylethylene).

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[4] Scheibler and Rettig, *Ber.*, **59**, 1194 (1926).

Proof of Structure of Isopropylthiophene.—The mono isopropyl thiophene obtained by the alkylation of thiophene by propylene and also by isopropyl alcohol showed constants in agreement with those given by Scheibler and Schmidt[5] for the 2-isomer. Two color tests, described by the same authors, indicated that our isopropylthiophene was the 2-isomer. More reliable evidence was obtained by converting it into its mono acetyl derivative, which was then converted into its known oxime (crystallized from Skellysolve B; m. p., 74–75° (cor.); lit., 74°) and *p*-nitrophenylhydrazone (crystallized from methyl alcohol; m. p., 193–194.5° (cor.); lit., 198°), both of which have been prepared by Scheibler and Schmidt from authentic 2-isopropylthiophene. The mixed melting point of the *p*-nitrophenylhydrazones showed that 2-isopropylthiophene was produced by both the propylene and the isopropyl alcohol alkylation of thiophene. This identity was confirmed by the color tests.

Anal. (oxime of 2-isopropyl-5-acetylthiophene). Calcd. for $C_9H_{13}NOS$: C, 59.0; H, 7.1; N, 7.6; S, 17.5. Found: C, 59.6; H, 7.5; N, 7.6; S, 17.7.

Anal. (*p*-nitrophenylhydrazone of 2-isopropyl-5-acetylthiophene). Calcd. for $C_{15}H_{17}N_3O_2S$: C, 59.4; H, 5.7; N, 13.9; S, 10.6. Found: C, 59.3; H, 5.5; N, 14.1; S, 10.4.

Acknowledgment.—The authors express their thanks to Patricia David and Elizabeth Depp for assistance in the experimental work.

Summary

Thiophene was alkylated by propylene, butylene-1, isobutylene, amylene, cyclohexene, isopropyl alcohol, and tertiary butyl alcohol. Several new mono and dialkyl thiophenes were prepared.

An alumina–silica type catalyst (Filtrol X-143) proved to be satisfactory for the alkylation of thiophene. Phosphoric acid can also be used, but other typical alkylation catalysts were found to be unsatisfactory, e. g., aluminum chloride, ferric chloride, stannic chloride, hydrogen fluoride, boron trifluoride–dimethyl ether complex, and sulfuric acid.

Suitable conditions were not found for the alkylation of thiophene by ethylene.

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(5) Scheibler and Schmidt, *Ber.*, **54**, 139 (1921).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Azidodithiocarbonic Acid. IX. Electrode Potential of the Azidocarbondisulfide-Azidodithiocarbonate Couple

BY ROBERT ULLMAN[1] AND G. B. L. SMITH

Previous studies on the azidodithiocarbonates described the preparation of azidocarbondisulfide by the addition of iodine to a solution of sodium azidodithiocarbonate.[2] This reaction indicated that the potential of the azidocarbondisulfide–azidodithiocarbonate couple was above that of the iodine–iodide couple in the electromotive series. The purpose of this research was to determine that potential.

Apparatus

The potential determinations were measured by a Leeds and Northrop hydrogen ion potentiometer, with a Leeds and Northrop no. 1230 box galvanometer as null-point indicator. Both normal and saturated calomel cells, used as standard electrodes, were prepared according to Clark.[3]

Preparation of Materials[1]

Six grams of sodium azide was dissolved in 25 ml. of distilled water, to which was added 7 ml. of carbon disulfide. The mixture was kept at 40° for forty-eight hours at which time the reaction was essentially complete.

$$NaN_3 + CS_2 \longrightarrow NaSCSN_3$$

Free azidocarbondisulfide was precipitated by concentrated hydrochloric acid at 0°. This was dried over phosphorus pentoxide and titrated with a standard solution of potassium hydroxide to form potassium azidodithiocarbonate.

Azidocarbondisulfide was precipitated by addition of a solution of iodine–potassium iodide to sodium azidodithiocarbonate.

$$2NaSCSN_3 + I_2 \longrightarrow 2NaI + (SCSN_3)_2$$

Experimental Procedure

The potential between a calomel half cell and a solution of potassium azidodithiocarbonate saturated with azidocarbondisulfide was measured at varying concentrations of potassium azidodithiocarbonate. The cell may be written

$$Hg \mid Hg_2Cl_2, KCl \parallel KSCSN_3, (SCSN_3)_2 \mid Pt$$

The potential is given by the Peters equation

$$E = E^0 - 0.059 \log c\gamma \qquad (1)$$

where E is the measured potential, E^0 the electrode potential, c the concentration of potassium azidodithiocarbonate, and γ its molar activity coefficient. Rewriting (1)

$$E^0 - 0.059 \log \gamma = E + 0.059 \log c$$

A plot of the right-hand side of (2) along the ordinate *vs.* the square root of c as abscissa was extrapolated to zero concentration. E^0, the intercept on the vertical axis, is equal to 0.275 volt (Fig. 1). All values were corrected to the normal hydrogen electrode.

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(1) An abstract of a thesis submitted in partial fulfillment for the degree of Master of Science in chemistry.

(2) Browne, Hoel, Smith and Swezey, THIS JOURNAL, **45**, 2541 (1923).

(3) W. M. Clark, "Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, 1920.