that of the product formed from the hydrogen transfer reaction (Fig. 3).

Summary

The reaction of 4-methylcyclohexene with *p*-isobutyltoluene or with *p*-*s*-butyltoluene in the presence of hydrogen fluoride or of sulfuric acid yielded main products resulting from a hydrogen transfer in which the aromatic hydrocarbon acted as donor and 4-methylcyclohexene as acceptor.

The products obtained from the respective aromatic hydrocarbons through a hydrogen transfer were 1-*p*-tolyl-1-(2-methyl-5-isobutylphenyl)-2-methylpropane and 1,2,3,6-tetramethyl-3-ethyl-1-*p*-tolylindan.

The following new compounds and some of their derivatives were prepared: 2-methyl-5-isobutyl-1-bromobenzene, 1-*p*-tolyl-1-(2-methyl-5-isobutylphenyl)-2-methyl-1-propene, 1-*p*-tolyl-1-(2-methyl-5-isobutylphenyl)-2-methylpropane, 1-(4-methylcyclohexyl)-1-(2-methyl-5-isobutylcyclohexyl)-2-methylpropane, 2-acetyl-4-isobutyltoluene, 3,4-dimethyl-4-*p*-tolylhexanone, 3,4-dimethyl-2,4-di-*p*-tolylhexanol-2, 1,2,3,6-tetramethyl-3-ethyl-1-*p*-tolylindan and 1,2,3-trimethyl-3-ethyl-1-(4-carboxyphenyl)-6-carboxyindan.

EVANSTON, ILLINOIS RECEIVED AUGUST 29, 1949

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES, UNIVERSAL OIL PRODUCTS COMPANY]

Reaction of Thiophene with Olefinic Compounds[1]

BY HERMAN PINES, BRUNO KVETINSKAS AND J. A. VESELY

The present paper describes the alkylation of thiophene and 2-bromothiophene with olefins in the presence of various catalysts.

Boron Fluoride.—Contrary to the statement made by Kutz and Corson[1a] and in agreement with the recent paper by Caesar,[2] it was found that either boron fluoride–ethyl ether complex or boron fluoride is an efficient catalyst for the interaction of thiophene with propene, 2-butene, 1-octene, 2,2,4-trimethylpentenes, cyclohexene, bicycloheptene, cyclopropane, α-methylstyrene, and methallyl chloride. The reaction proceeded at temperatures varying from 30 to 90° in an autoclave or at atmospheric pressure. The product consisted of mono- and disubstituted thiophene (Table I). The position of the substituents on the thiophene ring was shown in a few cases to be predominantly on the two carbon atom. In the case of disubstituted thiophene it was assumed that the two and five carbon atoms were substituted inasmuch as the products gave a negative test with ceric nitrate–alcohol reagent.[3]

In the experiments in which the structure of the compound was not proved it was assumed that the substitution was also in the 2 and 5 positions of the thiophene ring.

The monosubstituted product obtained by treating cyclopropane with thiophene was a mixture consisting of 47% of 2-*n*-propyl- and 52% of isopropylthiophene, as determined by comparing the infrared spectra of the pure 2-*n*-propylthiophene (Fig. 1) and isopropylthiophenes; the latter were obtained from the interaction of propylene with thiophene. The 2-*n*-propylthiophene was obtained by the Clemmensen reduction of 2-propionylthiophene. The wave lengths used for the calculation of 2-*n*-propylthiophene were 8.6 and 11.2 microns and for isopropylthiophene 7.7 and 10.7 microns. The strong bands beyond 11.5 microns could not be used for calculation since the spectra of isomers were similar in this region.

In the presence of boron fluoride–ethyl ether complex methallyl chloride reacted with thiophene forming predominantly 2- and some 3-(chloro-*t*-butyl)-thiophene. The structure of this compound was determined by converting it to *t*-butylthiophenes, which was accomplished by reaction of the (chloro-*t*-butyl)-thiophene with magnesium and decomposing the resulting organomagnesium compound with water. The *t*-butyl-thiophenes produced were characterized by means of infrared analysis; they consisted of about 70% of 2- and 30% of 3-*t*-butylthiophene. This was determined by comparing the infrared absorption spectra with those of the pure *t*-butylthiophenes described by Appleby and co-workers.[4a,b] The organomagnesium compound was also treated with air and hydrolyzed. This resulted in the production of a primary alcohol, (hydroxy-*t*-butyl)-thiophene.

Stannic Chloride.—It was observed that olefinic hydrocarbons, in which the double bond was attached to a completely substituted carbon atom, reacted with thiophene in the presence of stannic chloride at 38 to 50° at atmospheric pressure. Isobutylene yielded *t*-butyl- and 2,5-di-*t*-butylthiophene, and trimethylethylene formed *t*-amyl- and 2,5-di-*t*-amylthiophene. The *t*-butylthiophene was found, according to infrared spectra, to consist of about 70% of 2- and 30% of 3-*t*-butylthiophene. Olefinic hydrocarbons such as propene, 2-butene, isopropylethylene, cyclohexene, or 4-methylcyclohexene did not react

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(1) Presented before the Sulfur Symposium, Division of Petroleum Chemistry, San Francisco meeting of the American Chemical Society, April, 1949.

(1a) W. Kutz and B. B. Corson, THIS JOURNAL, **68**, 1477 (1946).

(2) P. D. Caesar, *ibid.*, **70**, 3623 (1948).

(3) H. D. Hartough, *Anal. Chem.*, **20**, 860 (1948).

(4) (a) W. G. Appleby, A. F. Sartor, S. H. Lee, Jr., and S. W. Kapranos, THIS JOURNAL, **70**, 1552 (1948); (b) W. M. Kutz and B. B. Corson, *ibid.*, **71**, 1503 (1949).

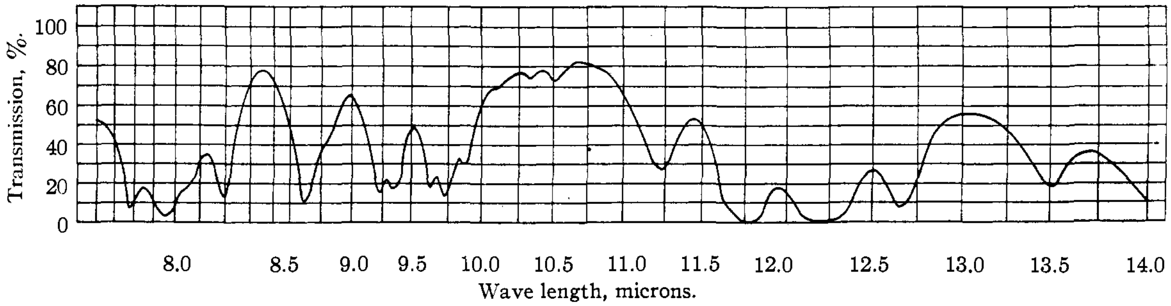


Fig. 1.—Spectrum of 2-*n*-propylthiophene.

with thiophene in the presence of stannic chloride under the above-indicated conditions; at higher temperature decomposition of the thiophene occurred. It was found, however, that the above-indicated olefins reacted with thiophene in the presence of stannic chloride when nitromethane was present. Propene, 2-butene and cyclohexene yielded, respectively, mono- and di-isopropyl, *s*-butyl- and cyclohexylthiophene. Isopropylethylene on reaction with thiophene in the presence of the above-indicated catalysts formed *t*-amylthiophene, which indicated a shifting of the double bond prior to alkylation. The structure of this compound was proved by comparing the infrared spectrum of this compound and the melting point of its solid derivatives with that of a known sample of *t*-amylthiophene. In the case of the reaction of 4-methylcyclohexene with thiophene it was assumed that a shifting of the double bond had also occurred and that the product was probably (1-methylcyclohexyl)-thiophene.

Nitroethane also promoted the condensation of thiophene with cyclohexene in the presence of stannic chloride; the yield of mono- and dicyclohexylthiophene was lower than in the case of nitromethane. A large amount of high boiling product was formed. The experimental results are summarized in Table I.

TABLE I

REACTION OF THIOPHENE AND 2-BROMOTHIOPHENE WITH OLEFINIC COMPOUNDS

Olefins	Catalyst[a]	Temp., °C.	Yield of substituted thiophene,[b] % Mono	Di
Propene	A	85	48[c]	36
2-Butene	A	80	48[d]	27
1-Octene	A	80	56[e]	9
2,2,4-Trimethylpentenes	[f]	33	39	49
Cyclohexene	A	80	45	18
Cyclopropane	A	90	39[g]	16
Bicycloheptene	A	40	31	30
α-Methylstyrene	A	33	11	32
Methallyl chloride	A	80	47	9
Propene	B	78	14	6
2-Butene	B	65	11	2
Isobutylene	C	50	28	33
Isobutylene	B	50	31	17
Isopropylethylene	B	45	14	24
Cyclohexene	B	51	30	14
4-Methylcyclohexene	B	35	31	40
Trimethylethylene	D	70	49	12
Trimethylethylene	E	25	78	7
Cyclohexene	E	23	5	0
4-Methylcyclohexene	D	76	1	1
4-Methylcyclohexene	E	21	20	3
α-Methylstyrene	D	80	54[h]	13
Trimethylethylene	F	32	33	17
Methallyl chloride	F	73	50[i]	
2-Bromothiophene				
Isobutylene	A	43	38[j]	
Trimethylethylene	C	69	58[j]	
Methallyl chloride	A	66	60[j,k]	

[a] A, Boron fluoride–ethyl ether complex; B, stannic chloride–nitromethane composed of 1 part by weight of $SnCl_4$ and 1.5 parts of CH_3NO (30–40% by weight of $SnCl_4$ based on thiophene used was employed in each experiment); C, stannic chloride; D, 85% phosphoric acid; E, equal volumes of 85% phosphoric acid and 96% sulfuric acid; F, ethanesulfonic acid. [b] The yield was based on olefins reacted. [c] A yield of 11.2% of triisopropylthiophene was obtained; b. p. 72° (1.8 mm.) or 236° (760 mm.); $n^{20}D$ 1.4970. *Anal.* Calcd. for $C_{18}H_{22}S$: C, 74.30; H, 10.48; S, 15.24. Found: C, 74.20; H, 10.86; S, 15.10. [d] 17.5% of butenes was recovered. [e] 25.4% of octenes was recovered. [f] Boron fluoride gas was bubbled through the bottom of the glass reaction flask. [g] 16% of C_3H_6 hydrocarbons was recovered consisting of 30% of propene and 70% of cyclopropane. [h] 38% of α-methylstyrene was recovered. [i] About 60% of methallyl chloride was recovered. [j] Expressed as monosubstituted 2-bromothiophene. [k] About 80% of methallyl chloride was recovered.

Acid Catalysts.—It was found that 85% phosphoric acid catalyzed the reaction between thiophene and olefinic hydrocarbons containing a double bond on a completely substituted carbon atom, such as trimethylethylene or α-methylstyrene, at 70 to 80°. Under similar conditions propene, cyclohexene, styrene, bicycloheptene, and methallyl chloride reacted with thiophene to an extent of only a few per cent. When 96% sulfuric acid was used as a catalyst the thiophene underwent decomposition. It was found, however, that an equal volume of 85% phosphoric acid and 96% sulfuric acid catalyzed the alkylation of thiophene at room temperature. A substantial amount of thiophene seemed to undergo sulfonation as shown by the increase in the acid layer.

Ethanesulfonic acid was also found to catalyze the condensation of thiophene with olefinic compounds. In the presence of this catalyst trimeth-

TABLE II

ANALYSIS OF MONO- AND DISUBSTITUTED THIOPHENES

Substituent on thiophene ring	Boiling point °C.	Boiling point Mm.	$n^{20}D$	d^{20}_4	Dispersion[e] at 20°	MR_D[d] Calcd.	MR_D[d] Obs.	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Sulfur Calcd.	Sulfur Found
$CH_3CHC_2H_5$	76	24	1.5013	0.9773	135.3	43.1	43.1	68.57	68.35	8.57	8.43	22.85	23.07
2,5-Di-($CH_3CHC_2H_5$)	108	12.5	1.4946	0.9238	124.1	61.5	68.8	73.5	73.23	10.2	9.99	16.3	16.53
2,5-Di-(C_6H_{11}[a])	147	2	1.5433	1.0294	131.6	75.7	75.9	77.42	77.43	9.68	9.56	12.90	13.04
C_7H_{13}[b,c]	84	1	1.5352					73.35	73.31	8.88	8.70	17.77	18.12
2,5-Di-(C_7H_{13}[b])	160	1	1.5393					78.26	77.97	10.15	9.88	11.59	11.97
C_7H_{11}[c]	90	2	1.5564					74.16	74.24	7.87	7.99	17.98	17.83
2,5-Di-(C_7H_{11}[c])	178–181	2	1.5670									11.76	11.64
$C_6H_5C(CH_3)_2$	115	2.5	1.5775	1.0698	161.8	62.8	62.6	77.23	77.38	6.93	7.14	15.84	15.46
2,5-Di-[$C_6H_5C(CH_3)_2$]	181[f]	1.5	1.5934	1.0733		101.5	100.5	82.50	82.72	7.50	7.50	10.00	9.90
$ClCH_2C(CH_3)_2$	57	1.5	1.5315	1.1318	142.1	47.6	47.6	55.00	55.01	6.38	6.30	18.30	18.34[g]
2,5-*Di*-[$ClCH_2C(CH_3)_2$]	133	1.3	1.5364	1.1567	136.7	71.4	71.5	54.34	54.88	6.79	6.98	12.07	12.52
2-Br-5-$(CH_3)_3C$–	102–103	16	1.5291									14.61	14.20
2-Br-5-$C_2H_5C(CH_3)_2$	56	1	1.5315									13.73	12.80
2-Br-5-$ClH_2C(CH_3)_2$	79–81	1.3	1.5649									12.64	12.36

[a] Cyclohexyl. [b] Presumably 1-methylcyclohexyl. [c] Bicycloheptyl. [d] For sulfur the value of 7.00 was used. This value was obtained from the index of refraction and density of pure 2- and 3-methylthiophene, described by F. S. Fawcett, THIS JOURNAL, 68, 1420 (1946). [e] Specific dispersion, ($\delta H_\beta - H_\alpha$). [f] Melting point, 37°. [g] Cl calcd., 20.88; found, 20.34.

ylethylene reacted with thiophene at room temperature forming 33% mono- and 17% di-*t*-amylthiophene. Methallyl chloride required more drastic conditions; at 73° only about 40% of the methallyl chloride reacted. The yield of chloro-*t*-butylthiophene, based on the methallyl chloride reacted, amounted to 50%. The experimental results are given in Table I.

2-Bromothiophene reacted with isobutylene, trimethylethylene and methallyl chloride under experimental conditions similar to those used for thiophene. 2-Bromothiophene is less reactive than thiophene (Table I). All of the methallyl chloride charged reacted with thiophene but under similar conditions only 20% of the chloroölefin reacted with 2-bromothiophene. The product of the reaction between trimethylethylene and 2-bromothiophene was investigated. The alkyl bromothiophene gave a negative test with ceric nitrate–alcohol reagent, which indicated that the 2 and 5 carbon atoms on the thiophene ring were substituted. The structure of the *t*-amylbromothiophene was determined by converting it to *t*-amylthiophene; this was done by treating the alkylbromothiophene with magnesium and decomposing the resulting organomagnesium compound with water. The alkylthiophene obtained was identical, according to infrared analysis, to the *t*-amylthiophene obtained from the interaction of thiophene with trimethylethylene.

On the basis of the above-given proof of structure it is assumed that the products obtained from the reaction of 2-bromothiophene with isobutylene and with methallyl chloride were 5-*t*-butyl- and 5-(chloro-*t*-butyl)-2-bromothiophenes.

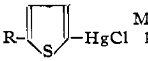
The physical constants and analyses of previously unreported substituted thiophenes are summarized in Table II. The physical constants of the known compounds agree with those described in the literature.

Solid Derivatives.—A satisfactory method for the characterization of the alkyl- and cycloalkylthiophenes produced was to acetylate to the corresponding acetothiophenes; the latter were then converted to solid semicarbazones and 2,4-dinitrophenylhydrazones. The yield of the ketones amounted to about 75 to 85%. This procedure for characterization of the thiophenes was not satisfactory for (chloro-*t*-butyl)-thiophene. The melting points of some of the derivatives are given in Table IV.

Solid mercuric chloride derivatives of some of the monosubstituted thiophenes were also prepared. The reaction was usually accompanied by the formation of a small amount of dichloromercuryalkylthiophenes, which could easily be separated from the desired material through its insolubility in hot alcohol (Table III).

TABLE III

MERCURYCHLORIDE OF MONOSUBSTITUTED THIOPHENES

 R =	Melting point, °C.	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Isopropyl-	158.5	C_7H_9SHgCl	23.27	22.68	2.49	2.51
s-Butyl-	134	$C_8H_{11}SHgCl$	25.48	24.61	3.16	2.92
t-Butyl-	195.5	$C_8H_{11}SHgCl$	25.48	25.60	3.16	2.94
t-Amyl-	130.5	$C_9H_{13}SHgCl$	27.76	26.82	3.34	3.42
Cyclohexyl-	146	$C_{10}H_{13}SHgCl$	29.92	29.80	3.22	3.40
t-Octyl-	153	$C_{12}H_{19}SHgCl$	33.40	33.14	4.41	4.32

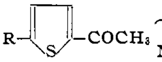
Experimental Part

The following are some of the standard procedures used in the reaction of thiophene with olefinic compounds.

Atmospheric Pressure Reactions.—The apparatus consisted of a 250 or 1000 ml. three-neck flask provided with a mechanical stirrer, a dropping funnel, a water or Dry Ice-cooled condenser, an inlet at the bottom of the flask for passing in gaseous hydrocarbons, and an opening for immersing a thermometer in the reaction liquid. The usual procedure was to place one-half of the thiophene and the catalyst, amounting to about 10–20% by weight of the reactants used, in the reaction flask, mix the liquid olefinic compound with the remaining thiophene and add the mixture slowly to the reaction flask from the dropping funnel. The temperature of the reaction was controlled by the rate of addition or by means of a bath. The product of the reaction was separated from the catalyst whenever

TABLE IV

DERIVATIVES OF ACETYLATED ALKYLTHIOPHENES

	Semicarbazone				2,4-Dinitrophenylhydrazone			
			Nitrogen, %				Nitrogen, %	
	M. p., °C.	Formula	Calcd.	Found	M. p., °C.	Formula	Calcd.	Found
n-Propyl-	...	....	...	...	175	$C_{15}H_{16}N_4SO_4$	16.10	15.97
Isopropyl-	202	$C_{10}H_{15}N_3SO$	18.67	18.42	181	$C_{15}H_{16}N_4SO_4$	16.10	15.87
s-Butyl-	182	$C_{11}H_{17}N_3SO$	17.57	17.02	145	$C_{16}H_{18}N_4SO_4$	15.47	15.44
t-Butyl-	219	$C_{11}H_{17}N_3SO$	17.57	17.12	221	$C_{16}H_{18}N_4SO_4$	15.47	15.42
t-Amyl-	214	$C_{12}H_{19}N_3SO$	16.60	16.26	189	$C_{17}H_{20}N_4SO_4$	14.89	14.86

possible and was washed free of catalyst by successive washes with water, dilute caustic, and water. In order to facilitate washing, enough ether was usually added to the product so that the ether solution of the product would float on water.

Superatmospheric Pressure Reaction.—(a) Rotating autoclaves of 450 and 850 ml. capacity were employed in many of the experiments in which gaseous hydrocarbons or higher temperatures were used. The reagents were sealed in the stainless steel autoclave and the latter was placed in a furnace provided with a rotating device.

(b) A stirring autoclave (Turbo-mixer) was used in some of the experiments. It consisted of a sealed-in induction stirring motor and a gasket-sealed reaction vessel which was fitted with inlet and outlet tubes and a thermocouple well. The thiophene and the catalyst were sealed in the reaction vessel, and it was heated to the desired temperature; then the olefinic compound was introduced at the desired rate from a pressured charger equipped with a calibrated sight gage. The products were worked up in the same manner as described for atmospheric pressure experiments.

Reactions of 2-(Chloro-*t*-butyl)-thiophene: (a) **_t_-Butylthiophene.**—(Chloro-*t*-butyl)-thiophene, 8.7 g., reacted with 1.2 g. of magnesium in 25 ml. of ether. The Grignard reagent was hydrolyzed with ice. Four grams of *t*-butylthiophene was obtained, boiling at 56.5 to 57° at 16 mm., n^{20}D 1.4985. The chloromercury derivative of this compound melted at 194°; it showed no depression when mixed with a sample prepared from *t*-butylthiophene. By comparing however the infrared absorption spectra with those reported in the literature[2] it was found that the product obtained consisted of 70% of 2- and 30% of 3-*t*-butylthiophene.

(b) **(Hydroxy-*t*-butyl)-thiophene.**—The Grignard reagent of (chloro-*t*-butyl)-thiophene prepared as indicated above from the same amount of the chloride, was treated with dry air for six hours. The oxidized product was then hydrolyzed with water, dried and distilled. Three and a half grams of the alcohol was obtained boiling at 113 to 115° at 14 mm., n^{20}D 1.5330. *Anal.* Calcd. for $C_8H_{12}SO$: C, 61.54; H, 7.69; S, 20.51. Found: C, 61.02; H, 7.76; S, 20.44. The α-naphthylurethan of the alcohol melted at 87 to 88°.

2-Bromo-5-*t*-amylthiophene.—The alkylated 2-bromothiophene obtained by treating 2-bromothiophene with trimethylethlyene in the presence of stannic chloride was converted to the Grignard reagent which in turn was hydrolyzed with water. The product, after drying, boiled at 107 to 108° at 69 mm., n^{20}D 1.5009; the yield was 70%. The infrared spectra were identical to that of *t*-amylthiophene.

Acetylation of Thiophenes.—The acetylation was made by a procedure described in the literature.[5] In each case about 2.5 g. of the alkylthiophenes was used for reaction. The ketones were distilled at reduced pressure. The semicarbazone and the 2,4-dinitrophenylhydrazone were prepared by the standard procedures.

Chloromercuration of Thiophenes.—The procedure was: Eighty-five ml. of saturated aqueous solution of mercuric chloride, 18 ml. of 33% sodium acetate, 10 ml. of ethanol, and 0.85 ml. of the substituted thiophene were shaken for six hours. The white precipitate formed was filtered, washed with water, and extracted with hot ethanol. When the alcohol cooled, white crystals separated from the solution; they were recrystallized twice from ethanol.

Summary

Propene, 2-butene, 1-octene, cyclohexene, bicycloheptene, cyclopropane, α-methylstyrene, and methallyl chloride reacted with thiophene in the presence of boron fluoride–ethyl ether complex.

Stannic chloride catalyzed the alkylation of thiophene with olefinic hydrocarbons only when the double bond was attached to a completely substituted carbon atom. In the case of olefinic hydrocarbons such as propene, 2-butene, isopropylethylene, cyclohexene or 4-methylcyclohexene, the alkylation did not take place unless nitromethane was added.

Phosphoric acid, a mixture of phosphoric and sulfuric acids and ethanesulfonic acid were investigated as catalysts for the alkylation of thiophene.

2-Bromothiophene was alkylated.

RIVERSIDE, ILLINOIS RECEIVED APRIL 14, 1949

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[5] H. Scheibler and F. Rettig, *Ber.*, **59**, 1194 (1926).