

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF HOPE COLLEGE]

## Condensations of Aldehydes with 2-Thienyllithium, 2-Thienylsodium and 2-Thienylmagnesium Bromide

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A series of 1-(2-thienyl)-carbinols has been made by treating thienylmetallic reagents with aldehydes. The reaction of 2-thienylsodium with aldehydes has proven satisfactory in most instances, and thus an inexpensive method of preparing 2-thienylalkanols exists. The effectiveness of 2-thienyllithium, 2-thienylsodium and 2-thienylmagnesium bromide are compared in this series of reactions. The carbinols were dehydrated to form a series of 2-thienyl olefins.

Although there has been considerable interest in the uses of organometallic reagents as applied to thiophene chemistry, their reactions with aldehydes have not been thoroughly explored. Steinkopf and Boker<sup>1</sup> added monomeric anhydrous formaldehyde to 2-thienylmagnesium iodide to obtain good yields of 2-thienylcarbinol. Blicke and Burckhalter<sup>2</sup> repeated this work with equally good results. Bachman and Heisey<sup>3</sup> chose to utilize thienyllithium. They treated 5-chloro-2-thienyllithium with acetaldehyde to obtain an 81% of 1-5-chloro-(2-thienyl)-ethanol.

reagent was used. It is to be noted, however, that in these investigations, only the method using 2-chlorothiophene with sodiumamalgam and benzene was used to prepare the 2-thienylsodium.

Magnesium is known to form typical Grignard reagents with 2-iodothiophene and 2-bromothiophene.<sup>5</sup> 2-Chlorothiophene is relatively inactive with magnesium. Accordingly, 2-thienylmagnesium bromide was used for this study. Hydrolysis was accomplished by using a saturated solution of ammonium chloride, since thienylalkanols are unstable in the presence of strong acids.

TABLE I  
LIQUID THIENYLALKANOLS PREPARED USING 2-THIENYLMAGNESIUM BROMIDE

Ident.	Aldehyde used	Alcohol formed <sup>a</sup>	Yield, %	Fraction collected,		$n_D^{20}$
				°C.	Mm.	
I	Formaldehyde	C <sub>2</sub> H <sub>4</sub> OS	60.0	80-90	2.5	1.5647
II	Acetaldehyde	C <sub>2</sub> H <sub>4</sub> OS	86.5	90-92	6.0	1.5430
III	Propionaldehyde	C <sub>7</sub> H <sub>10</sub> OS	81.8	88-92	7.0	1.5318
IV	<i>n</i> -Butyraldehyde	C <sub>8</sub> H <sub>10</sub> OS	74.0	92-94	4.0	1.5232
V	<i>n</i> -Valerylaldehyde	C <sub>9</sub> H <sub>14</sub> OS	76.0	80-83	1.0	1.5220
VI	<i>n</i> -Hexaldehyde	C <sub>10</sub> H <sub>16</sub> OS	85.0	92-95	0.5	1.5120
VII	2-Ethylbutyraldehyde	C <sub>10</sub> H <sub>16</sub> OS	80.0	73-77	0.1	1.5195
VIII	2-Ethylhexaldehyde	C <sub>12</sub> H <sub>20</sub> OS	80.5	122-125	4.0	1.5150

<sup>a</sup> I, 2-thienylmethanol; II, 1-(2-thienyl)-1-ethanol; III, 1-(thienyl)-1-propanol; IV, 1-(2-thienyl)-butanol; V, 1-(2-thienyl)-1-pentanol; VI, 1-(2-thienyl)-1-hexanol; VII, 1-(2-thienyl)-2-ethyl-1-butanol; VIII, 1-(2-thienyl)-2-ethyl-1-hexanol.

TABLE II  
DEHYDRATION PRODUCTS OF THE THIENYLALKANOLS

Alcohol used	Boiling range °C.	Mm.	Products	$n_D^{20}$	Carbon, %		Hydrogen, %	
					Calcd.	Found	Calcd.	Found
II	50.5-51	28	C <sub>6</sub> H <sub>6</sub> S	1.5731	65.41	65.26	5.49	5.31
III	46-47	7.0	C <sub>7</sub> H <sub>8</sub> S	1.5705	67.68	67.45	6.51	6.60
IV	39-40	0.4	C <sub>8</sub> H <sub>10</sub> S	1.5558	69.51	70.07	7.29	7.60
V	77-77.5	8.0	C <sub>9</sub> H <sub>12</sub> S	1.5481	71.00	71.55	7.95	8.09
VI	109-110	7.0	C <sub>10</sub> H <sub>14</sub> S	1.5396	72.22	72.58	8.49	8.38
VII	90-91	8.0	C <sub>10</sub> H <sub>14</sub> S	1.5526	72.22	71.95	8.49	8.38
VIII	112-114	8.0	C <sub>12</sub> H <sub>18</sub> S	1.5380	74.16	74.49	9.34	9.29

<sup>a</sup> II, 2-thienylethylene; III, 1-(2-thienyl)-1-propene; IV, 1-(2-thienyl)-1-butene; V, 1-(2-thienyl)-1-pentene; VI, 1-(2-thienyl)-1-hexene; VII, 1-(2-thienyl)-2-ethyl-1-butene; VIII, 1-(2-thienyl)-2-ethyl-1-hexene.

This study was undertaken for the purpose of expanding the series of aldehydes reacting with thienyl-metallic reagents. It was also of interest in that it offered a new opportunity for the comparison of the relative effectiveness of the different thienyl-metallic reagents. In a previous study,<sup>4</sup> epoxides were treated with 2-thienylsodium and 2-thienylmagnesium bromide, and in every case the results were found to be more satisfactory when the latter

The alcohols prepared (Table I) were stable if kept cold and from strong light. Upon standing for 24 hours at 120°, much dehydration was observed, and upon attempted distillations of mixtures thus produced the olefin could be isolated. A high boiling residue also remained which gave no definite analysis, indicating that perhaps polymerization also had taken place. These alcohols, with the exception of I, were observed to dehydrate readily in the presence of small amounts of strong mineral acids.

The alcohols in Table I, with the exception of I,

(1) W. Steinkopf and G. Boker, *Ann.*, **540**, 23 (1939).  
 (2) F. F. Blicke and J. H. Burckhalter, *This Journal*, **64**, 477 (1942).  
 (3) G. B. Bachman and L. V. Heisey, *ibid.*, **70**, 2378 (1948).  
 (4) G. Van Zyl, J. F. Zack, Jr., E. S. Huyser and P. L. Cook, *ibid.*, **76**, 707 (1954).

(5) H. D. Hartough, "Thiophene and Its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1952, p. 442.

were dehydrated by distillation through a tube containing activated alumina and heated to a temperature of 250°. The distillate was collected and fractionated through a column of about 10 theoretical plates. The data obtained are shown in Table II.

These dehydration products were found to be stable over a period of eight months when kept cold and away from light. They were soluble in benzene, but only slightly miscible with methanol. Very little tendency to polymerize was evidenced, with the exception of II which polymerized readily.<sup>6</sup>

The urethans of all of the alcohols listed in Table I were prepared, and the results were observed as shown (Table III). The urethans prepared proved to be very stable, and were used as a final reference in both the sodium and lithium metalation reactions. It seems interesting to note that with increasing molecular weight, there is a corresponding decrease in the melting point.

TABLE III  
THE PROPERTIES OF THE URETHANS PREPARED

Alcohol	Product	M. p., °C.	Nitrogen, %		Sulfur, %	
			Calcd.	Found	Calcd.	Found
I	C <sub>12</sub> H <sub>11</sub> O <sub>2</sub> NS	75.0-75.4	6.00	..	13.75	..
II	C <sub>11</sub> H <sub>10</sub> O <sub>2</sub> NS	83.4-84.0	5.66	5.66	12.97	12.64
III	C <sub>14</sub> H <sub>13</sub> O <sub>2</sub> NS	82.8-83.2	5.36	5.25	12.27	12.22
IV	C <sub>16</sub> H <sub>17</sub> O <sub>2</sub> NS	58.6-59.4	5.09	5.16	11.65	11.60
V	C <sub>16</sub> H <sub>15</sub> O <sub>2</sub> NS	57.8-58.0	4.84	4.76	11.08	11.06
VI	C <sub>17</sub> H <sub>21</sub> O <sub>2</sub> NS	65.8-66.5	4.62	4.58	10.57	10.60
VII	C <sub>17</sub> H <sub>21</sub> O <sub>2</sub> NS	58.3-59.2	4.62	4.61	10.57	10.61
VIII	C <sub>19</sub> H <sub>23</sub> O <sub>2</sub> NS	48.4-49.5	4.23	4.25	9.68	9.53

The aromatic aldehydes used in this investigation produced alcohols which were low-melting solids. 1,2,3,6-Tetrahydrobenzaldehyde, an unsaturated aldehyde with usual aliphatic properties, also produced an alcohol which was a solid at room temperature. Despite repeated attempts, no pure derivative could be obtained. The pure alcohols were observed to decompose slowly at room temperature, especially in the presence of strong light, producing greenish-brown to black viscous, tarry residues. These tars were soluble in benzene, but all efforts to recrystallize them failed. The aldehydes used and the results obtained are as recorded (Table IV).

TABLE IV  
SOLID THIENYLALKANOLS PREPARED USING MAGNESIUM

Aldehyde used	Alcohol formed <sup>a</sup>	M. p., °C. (Cr. alc.)	Yield, %	M. p., °C. (pure alc.)	Sulfur, %	
					Calcd.	Found
Benzaldehyde	IX C <sub>11</sub> H <sub>10</sub> OS	54-57	54	57.5-59	16.86	16.97
Anisaldehyde	X C <sub>12</sub> H <sub>12</sub> O <sub>2</sub> S	50-52	68	52.7-53.6	14.56	14.68
Piperonal	XI C <sub>12</sub> H <sub>10</sub> O <sub>2</sub> S	68-70	75	70.0-70.5	13.69	13.69
Diethoxybenzaldehyde	XII C <sub>16</sub> H <sub>18</sub> O <sub>3</sub> S	80-84	66	85.2-86.0	11.50	11.51
Thiophene-2-carboxaldehyde	XIII C <sub>9</sub> H <sub>8</sub> O <sub>2</sub> S	57-58	72	57.5-58.3	16.33	16.48
1,2,3,6-Tetrahydrobenzaldehyde	XIV C <sub>11</sub> H <sub>14</sub> OS	65-70	58	74.8-75.2	16.70	17.01

<sup>a</sup> IX, 2-thienylphenylcarbinol; X, 2-thienyl-*p*-methoxyphenylcarbinol; XI, 2-thienylpiperonyl alcohol; XII, 2-thienyl-3,4-dihydroxyphenylcarbinol; XIII, di-2-thienylcarbinol; XIV, 2-thienyl-Δ<sup>3</sup>-cyclohexenylcarbinol.

2-Thienyllithium was prepared by a transmetallation in which lithium sand, *n*-butyl bromide and thiophene, in ethyl ether as a solvent, were used. The method of Gilman and Shirley,<sup>7</sup> was referred to in which 2-thienyllithium was carbonated to produce 2-thiophenecarboxylic acid. Useful information concerning the nature and preparation of lith-

ium compounds was obtained from the Lithium Corporation of America.<sup>8</sup> The yields of *n*-butyllithium and also of the 2-thiophenecarboxylic acid obtained from carbonation as reported,<sup>7,8</sup> were checked in this investigation to determine the amount of aldehyde to be added. In general, the reaction proceeded readily, and the reaction mixture remained light and free from tars.

The same aldehydes were used as shown in Table I, and Table IV. In the case of those shown in Table I, the refractive indexes were compared, the urethans prepared and melting points and mixed melting points observed. On this basis, thienylalkanols prepared using 2-thienyllithium proved to be identical to those produced using 2-thienylmagnesium bromide. The yields are shown and compared in Table V. The aldehydes shown in Table IV were used and melting points and mixed melting points taken on the pure thienylalkanols produced. Again the results were the same as those obtained with 2-thienylmagnesium bromide (Table V).

2-Thienylsodium was prepared by the method of Schick and Hartough<sup>9</sup> using 2-chlorothiophene in benzene as a solvent. Carbonation and subsequent acidification indicated an 82% yield of thienylsodium. When acetaldehyde, propionaldehyde and butyraldehyde were added to the 2-thienylsodium as prepared above, no yield was obtained. With *n*-hexaldehyde, the yield was 10.1%.

In an effort to eliminate the tendency for either an aldol condensation, or polymerization of the aldehyde, the quantities of reactants were changed to prevent, as much as possible, the presence of free sodium. A small excess of 2-chlorothiophene was added, and the aldehyde was added very slowly. No difference in yield was observed, however. It was noted that 2-thienylmagnesium bromide as well as 2-thienyllithium were soluble in the ethyl ether solvent used for the reaction, whereas the 2-thienylsodium was found to be insoluble in benzene, which was used as a solvent for the sodium reaction. This insolubility factor was at first thought to be somewhat responsible for the failure of the expected reaction to take place, al-

though the insoluble salt reacts readily with carbon dioxide and ethylene oxide in benzene.<sup>9,10,5</sup> Various solvents, including ethyl *n*-butyl ether, ethylene glycol-dimethyl ether, and tetrahydrofuran were then employed. Upon carbonation and acidi-

(8) Lithium Corporation of America, Inc., Rand Tower, Minneapolis 2, Minnesota (Bulletin CX-SE Form 20).

(9) J. C. Schick and H. D. Hartough, *THIS JOURNAL*, **70**, 286 (1948).

(10) J. C. Schick and H. D. Hartough, *ibid.*, **70**, 1645 (1948).

(6) Reference 5, p. 166.

(7) H. Gilman and D. A. Shirley, *THIS JOURNAL*, **71**, 1870 (1949).

TABLE V

Aldehyde used	R	M MgBr	Yield, % M Li	M Na
Formaldehyde	H	60.0	..	..
Acetaldehyde	CH <sub>3</sub>	86.5	73.0	25.5
Propionaldehyde	CH <sub>2</sub> CH <sub>3</sub>	81.8	68.3	49.0
<i>n</i> -Butyraldehyde	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	74.0	76.0	44.0
<i>n</i> -Valerylaldehyde	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	76.0	..	..
<i>n</i> -Hexaldehyde	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	85.0	63.0	..
2-Ethylbutyraldehyde	CH(C <sub>2</sub> H <sub>5</sub> )CH <sub>2</sub> CH <sub>3</sub>	80.0	72.0	76.0
2-Ethylhexaldehyde	CH(C <sub>2</sub> H <sub>5</sub> )CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	80.5	74.5	76.5
Benzaldehyde	C <sub>6</sub> H <sub>5</sub>	54.0	53.5	86.0
Anisaldehyde	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	68.0	..	73.0
Piperonal	CH <sub>2</sub> O <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	75.0	..	89.0
3,4-Diethoxybenzaldehyde	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	66.0	..	78.0
2-Thiophenecarboxaldehyde	C <sub>4</sub> H <sub>3</sub> S	72.0	..	89.0
1,2,3,6-Tetrahydrobenzaldehyde	C <sub>6</sub> H <sub>3</sub>	58.0	63.5	52.0

fication, however, the yield of 2-thienylsodium was found to be very poor, about 10% in the case of tetrahydrofuran. Final hydrolysis was attempted with dilute hydrochloric acid, anhydrous hydrogen chloride dissolved in ether, and with a saturated solution of ammonium chloride. Excessive tar formation resulted in every case, and the yields could not be improved.

Another method<sup>9</sup> was used with some modifications. This consisted of a transmetallation of thiophene with bromobenzene and sodium amalgam sand. A slight excess of bromobenzene and thiophene was added to prevent the presence of free sodium as much as possible. The reaction was hydrolyzed with a saturated solution of ammonium chloride, and the hydrolyzed mixture was surprisingly clear and free from tars.

Polymerization of the aldehydes was still observed, however, being greatest with the lower aliphatic aldehydes and not noticeable with the aromatic aldehydes. Various yields were obtained (Table V).

It was interesting to note that with the aromatic aldehydes the yields were very high. There was very little tar formation, and the hydrolyzed mixture was easily separated and the thienylalkanols isolated in a relatively pure condition from the reaction. The physical constants, melting points and mixed melting points again showed that the expected thienylalkanols were formed. No attempts were made to account for the failure of the sodium reaction to take place in benzene; however when considering the effect of benzene upon an ordinary type of Grignard reaction the results are not surprising. It was also observed that 2-ethylbutyraldehyde and 2-ethylhexaldehyde reacted with 2-thienylsodium in ether to produce a relatively high yield of the two thienylalkanols. Presumably the reduced acidity of the  $\alpha$ -hydrogen in the branched aldehydes is responsible for the improvement in yield.

Considering the relative yields using the various thienyl-metallic reagents, and also the relative cost of the reactants, it is seen that lithium and sodium both have distinct advantages over magnesium. With magnesium, 2-bromothiophene must be used, whereas with sodium or lithium, thiophene, now available commercially, is used. Although with the transmetallation procedure an intermedi-

ate alkyl or aryl halide must be used, it is still far more economical. On this basis the use of ethyl chloride was investigated and found to be satisfactory economically for both the lithium and sodium transmetallation reactions. However, the halides as used in this paper were found to be more satisfactory on a laboratory scale. The yields using ethyl chloride were considerably smaller.

Transmetallation with magnesium Grignards, though known, has not been studied to any extent, although this possibility is being investigated in this Laboratory at the present time.

### Experimental

The 2-chlorothiophene and 2-bromothiophene used in this investigation were obtained from the Michigan Chemical Co., Saint Louis, Michigan. These reactants were dried and distilled prior to use.

**Magnesium.** 1-(2-Thienyl)-ethanol.—To the Grignard reagent prepared from 10 g. (0.4 mole) of purified<sup>11</sup> magnesium and 67 g. (0.4 mole) of 2-bromothiophene was slowly added 16.5 g. ( $\frac{3}{8}$  mole) of acetaldehyde, keeping the reaction temperature below 25°. After addition of the aldehyde was completed the mixture was stirred at room temperature for about 2 hours, and hydrolyzed with a saturated solution of ammonium chloride. Complete hydrolysis was indicated when the mixture suddenly became clear and the salt formed became rather sticky, at which point the addition of the ammonium chloride was stopped, and the filter cake washed with dry ether. After removal of the ether from the filtered solution, a clear colorless liquid boiling at 90–92° (6.0 mm.) was collected,  $n_D^{25}$  1.5430.

**(2-Thienyl)-phenylcarbinol.**—2-Thienylmagnesium bromide prepared as previously stated, was treated slowly with 39.8 g. ( $\frac{3}{8}$  mole) of benzaldehyde. After hydrolysis with ammonium chloride solution, the ether was removed, and the residual oil poured into 600 ml. of cold petroleum ether (b.p. 30–60°) which was being vigorously agitated in a Waring Blendor. The solid residue was collected on a filter, washed with cold petroleum ether, and dried. The light tan solid melting at 54–57° amounted to 71.3 g. (54%). Three further recrystallizations from an ether/petroleum ether solution produced fine white needles, m.p. 57.5–59.0°. *Anal.* Calcd. for C<sub>11</sub>H<sub>10</sub>OS: S, 16.86. Found: S, 16.97.

**Lithium-1-(2-Thienyl)-hexanol.**—To 14 g. (2 moles) of lithium sand covered with 200 ml. of dry ether, was added slowly 137 g. (1 mole) of *n*-butyl bromide, maintaining a gentle reflux. After continued refluxing with stirring for 0.5 hour the reaction mixture was cooled to 15°, and 71.4 g. (0.85 mole) of thiophene added over a period of 15 minutes. After addition was complete, the mixture was heated carefully and a gentle reflux maintained for 0.5 hour. The reaction mixture was cooled to 5° and 70 g. (0.7 mole) of *n*-hexaldehyde added slowly, keeping the temperature below 25°. After addition was complete, the mixture was stirred for one hour, cooled to 5°, and hydrolyzed with an excess of satu-

(11) *Chemist Analyst*, **41**, No. 3, 62 (1952).

rated ammonium chloride solution. The remaining clear liquid was filtered, the ether layer removed and dried over anhydrous magnesium sulfate. After removal of the ether, there remained an oily residue boiling at 94–98.5° (1.0 mm.),  $n_D^{25}$  1.5122, yield 81 g., 63%.

**Sodium. Di-(2-thienyl)-carbinol.**—A sodium amalgam sand<sup>12</sup> containing 25 g. (1.09 g. atoms) of sodium and 10 g. (0.05 gram-atom) of mercury was covered with 200 ml. of ether to which 63 g. (0.75 mole) of thiophene was added. The mixture was cooled to 5°, and 78 g. (0.5 mole) of bromobenzene added over a 1-hour period.<sup>13</sup> Stirring of the cooled mixture was continued for one hour, after addition, and then refluxed for two hours, after which it was cooled, and 77.6 g. (0.4 mole) of 2-thiophenecarboxaldehyde added slowly with cooling. The mixture was hydrolyzed after one hour with a saturated solution of ammonium chloride, the reaction mixture becoming quite clear when an excess of  $\text{NH}_4\text{Cl}$  solution was added. The solution was filtered, dried over anhydrous magnesium sulfate, and the ether removed. The residue was poured into petroleum ether with vigorous agitation and a tan solid was collected and dried, m.p. 74–76°, yield 84.5 g. (76%). Further purification from an ether/petroleum ether mixture yielded long white needles, m.p. 57.5–58.3°. *Anal.* Calcd. for  $\text{C}_9\text{H}_8\text{OS}_2$ : S, 16.33. Found: S, 16.48.

(12) Reference 5, p. 506.

(13) J. C. Schick and H. D. Hartough, *THIS JOURNAL*, **70**, 1645 (1948).

**Dehydration Products. 2-Vinylthiophene.**—Forty grams of 1-(2-thienyl)-ethanol was distilled under reduced pressure (50 mm.) through a tube filled with activated alumina which was heated to 250°. The condensed water-olefin mixture was separated, the olefin taken up in 100 ml. of ether and the solution dried over anhydrous magnesium sulfate. After removal of the ether, there remained a clear colorless oil which was distilled through a 10-plate column; b.p. 50.5–51° (28 mm.),  $n_D^{25}$  1.5731. *Anal.* Calcd.: H, 6.51; C, 67.68. Found: H, 6.60; C, 67.45.

**Urethans.**—To 2 g. of the pure 2-thienylalkanol in a small glass stoppered vial, was added an equal volume of phenyl isocyanate. The reaction mixture was placed in a desiccator under refrigeration for about 2 weeks at which time a white, soft, solid was observed. This residue was stirred for 15 minutes in 100 ml. of boiling petroleum ether (b.p. 30–60°), the mixture filtered, cooled and let stand for several days. The white crystals formed were collected on a filter. After two more crystallizations in the same manner, the dried sample was sent in for analysis.

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[CONTRIBUTION FROM THE DIVISION OF NATURAL SCIENCES, GRINNELL COLLEGE]

## Studies in the Synthesis of Long-chain Compounds<sup>1,2</sup>

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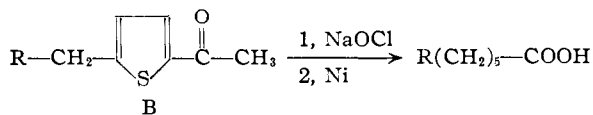
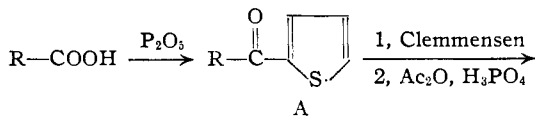
A synthetic scheme is described for the preparation of long-chain mono- and dicarboxylic acids, ketones, alcohols and hydrocarbons.

Although the reductive removal of sulfur from sulfur containing organic compounds has been known for over fifteen years,<sup>3</sup> it is only recently that this versatile reaction has been applied to synthetic problems. The conversion of a carbonyl group to a methylene group,<sup>4</sup> and the conversion of a thioester to an aldehyde<sup>5</sup> are typical examples. More specifically related to the present work are the studies pertaining to the reductive removal of sulfur from thiophene compounds<sup>6–8</sup> using either Raney nickel or nickel aluminum alloy.<sup>8</sup>

More recently three groups of investigators<sup>9a,b,c</sup> have started to investigate the desulfurization of substituted thiophenes for the preparation of a number of fatty acids.

The purpose of our investigation has been to establish a synthetic route to a variety of long-chain

compounds using thiophene and bithienyl as synthetic intermediates which are eventually transformed by reductive desulfurization into four and eight carbon chains, respectively. To date the type of compounds prepared include mono- and dicarboxylic saturated fatty acids, straight-chain and branched-chain hydrocarbons, straight and branched-chain secondary and tertiary alcohols and straight-chain ketones. The lengths of the chains have been varied from ten to thirty-six carbon atoms for representative examples.



The synthesis of fatty acids commences with the acylation of thiophene with a carboxylic acid,<sup>10</sup> the ketone A thus produced (see Table I) yielding another ketone B after reduction and reacylation. The latter (B) are converted smoothly by hypochlorite oxidation, followed by Raney nickel desulfurization to the desired fatty acid. It is evident from the above scheme that the readily available even-

(10) H. D. Hartough and A. I. Kosak, *THIS JOURNAL*, **69**, 3098 (1947).

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(2) Presented at the 128th Meeting of the American Chemical Society, September, 1955.

(3) J. Bougeault, E. Cattelain and P. Chahrier, *Bull. soc. chim. France*, **7**, 781 (1940).

(4) M. Wolfrom and J. Karahinos, *THIS JOURNAL*, **66**, 909 (1944).

(5) E. Mosettig, "Organic Reactions," Coll. Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 232.

(6) E. Modest and Szmuzkovicz, *THIS JOURNAL*, **72**, 577 (1950).

(7) F. Blicke and D. Sheets, *ibid.*, **70**, 3768 (1948).

(8) D. Papa, E. Schwenk and H. Ginsberg, *J. Org. Chem.*, **14**, 723 (1949).

(9) (a) G. M. Badger, H. J. Rodda and W. H. F. Sasse, *Chemistry & Industry*, 308 (1954); (b) J. F. McGhie, H. K. Pradhan and W. A. Ross, *ibid.*, 578 (1954); (c) M. M. Michel-Sy, N. P. Buu-Hoi and N. Dat. Xuong, *Compt. rend.*, **239**, 1224 (1954).