

## Thienyl Methacrylates

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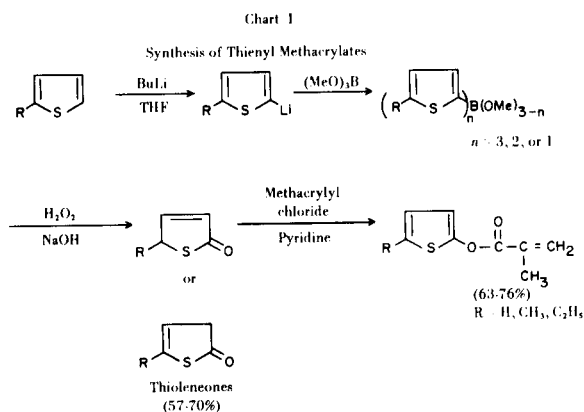
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Thienyl methacrylates have been synthesized and characterized. Thienyl methacrylate has been homo- and copolymerized.

Despite the importance of acrylates and methacrylates, esters derived from hydroxythiophenes and acrylic or methacrylic acids are conspicuous by their absence in the literature. Indeed, acyl esters of hydroxythiophenes in general are rare (1-3), probably because of the difficulty of access to hydroxythiophenes (4-10) and their known tendency to exist as somewhat unstable oils predominately in the keto form (11-17). Now a series of thienyl methacrylates has been prepared and characterized. In addition, the simplest member of the series has been polymerized under free radical conditions to a homopolymer and to copolymers with methyl methacrylate.

subjected to oxidation according to an established pattern (22-23) to yield the thioleoneones for which an extensive chemistry has been developed (13-16).

Since this scheme depends upon the attachment of boron to carbon on the thienyl residue for later oxidation, the ratios of methyl borate in the present work and the reaction conditions were chosen to favor formation of trisubstituted boron, or at least disubstituted, rather than monosubstituted boron, as in the preparation of boronic acids. Furthermore, it proved unnecessary and undesirable to isolate the thienylboron compounds. This resulted in a clean reaction sequence which proceeded readily in high yield. Table I compares the best yields obtained in the present work with those reported in the literature.



The synthesis scheme used in this work is represented in Chart 1. The first three stages of the reaction are run sequentially in a single flask with only the thioleoneones being isolated. Typical distilled yields for the thioleoneones and the final products are given in parentheses.

The metalation of thiophene and its derivatives in the 2 position by alkylolithiums has been known for some time (18) and thienyllithiums have been used by others (13-16, 19-21) in the preparation of thiopheneboronic acids by choice of appropriate alkyl borate reaction ratios. Moreover, the thiopheneboronic acids so isolated have been

TABLE I

Yields of Thioleoneones

Starting Thiophene	Present Work	Literature	Reference
Thiophene	70%	28%, 89.94%	14, 17
2-Methylthiophene	63%	47	14
2-Ethylthiophene	68%	59-71	15

In accordance with previous observations in the literature (4, 11-16), the tautomeric thiophenes prepared in this work were noted to exist almost exclusively in the liquid state as unsaturated thioleoneones (keto forms) rather than as hydroxythiophenes (enol forms). They proved to be somewhat unstable oils, but tractable if protected from oxygen and stored slightly below room temperature. It should be noted that the three forms represented are probably related by a common mesomeric anion, and that either of the keto forms should suffice for conversion to the methacrylate esters.

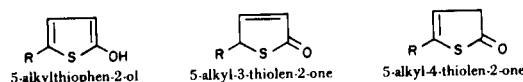


TABLE II  
Characterization of 2-Thienyl Methacrylates

Alkyl Substituent	$n_D^{23}$	Yield %	Boiling Point	Analyses			
				C	H	S	
None	1.5354	68	74-75/2.4 torr	Calcd.	57.12	4.79	19.06
				Found	57.24	4.52	18.99
5-Methyl	1.5312	63	99/4.0 torr to 99.5/4.2 torr	Calcd.	59.32	5.53	17.59
				Found	59.60	5.53	17.88
5-Ethyl	1.5253	76	103/3.1 torr to 106/3.2 torr	Calcd.	61.20	6.16	16.34
				Found	61.68	6.32	16.25

TABLE III (a)  
Chemical Shifts in Delta Units for 2-Thienyl Methacrylates

Structural Features	Unsubstituted (b)	5-Methyl (c)	5-Ethyl (c)
Alkyl substituent	None	CH <sub>3</sub> 2.28 singlet	CH <sub>3</sub> 1.20 triplet CH <sub>2</sub> 2.67 quartet
Thienyl protons	6.64-6.90	6.3-6.5	6.35-6.50
Methyl group	2.04	1.93	1.93
Terminal methylene protons			
Z to carbonyl	6.34	6.19	6.18
E to carbonyl	5.73	5.58	5.58

(a) The expected coupling constants, ratios, and splittings were observed. Shifts are given to the center of gravity of multiplets. (b) In carbon tetrachloride. (c) Neat.

TABLE IV  
Infrared Data for 2-Thienyl Methacrylates (a)

Structural Feature	(assignments in cm <sup>-1</sup> )		
	Unsubstituted	5-Methyl	5-Ethyl
Thienyl group	3100	3110	3100
	1538	1562	1560
2-substituted	685	---	---
2,5-disubstituted	---	786	795
Carbonyl group	1735	1745	1745
	1184	1190	1190
Ester group	1120	1124	1120
	1639	1641	1640
C=C linkage	1639	1641	1640
Terminal methylene	946	947	945

(a) Neat.

The acylation reaction of the thiolecones with methacrylyl chloride is poorly understood at present. Nevertheless, the yields are acceptable if the reaction is run in the presence of pyridine. Whether the pyridine serves to provide a more active acylating agent through reaction

with the acid chloride (24), or whether the pyridine promotes ionization of the thiolecones to the corresponding anions which are then more active nucleophiles is unclear. Without the pyridine, the acylations proceed sluggishly: 3-thiolen-2-one, for example, may be treated with neat acetic anhydride or methacrylyl chloride at elevated temperatures for long times with resultant low conversions to the corresponding thienyl esters; and it may even be treated with refluxing acetyl chloride for several hours with conversions below those noted in this work (14,15). Finally, it should be noted that, although the crude reaction mixtures from the acylations appear dark and formidable, the separation scheme is efficient and the products are easily purified.

Attempts to prepare the corresponding acrylates were not pursued further when preliminary probes showed that 3-thiolen-2-one reacted violently with acrylyl chloride, under the usual conditions, to yield intractable polymers. When the same reaction was conducted under more moderate conditions (e.g., ice-bath temperature, very slow addition of pyridine), a monomeric substance was isolated in low yield, which, from spectral data, appeared to be impure 2-thienyl acrylate.

TABLE V  
Properties of Polymers

	Homopolymer	Copolymers	
% MMA <i>via</i> NMR	0/100	97/3	75/25
Conversion, %	59	59	34
Inherent Viscosity at 27°, $\phi$ CH <sub>3</sub>	0.25	0.23	0.14
Glass Transition $\pm 5^\circ$	87	103	91
Sulfur, % Theory	19.06	---	---
% Found	19.67	---	---

Structure proofs for the thienyl methacrylates are based upon the following data:

The monomer 2-thienyl methacrylate was homopolymerized with 2,2'-azobis(2-methylpropionitrile) initiator in toluene solution at 70° and it was copolymerized with methyl methacrylate (MMA) at slightly higher temperatures. Some properties of the polymers obtained are listed in Table V.

Spectra (ir and nmr) of the polymers showed the expected characteristics compared to those of the monomers. For example, spectra showed retention of thienyl and ester groups, plus catenation with attendant loss of terminal methylene groups. Analysis of nmr spectra proved to be a convenient way to identify the relative proportions of thienyl methacrylate and methyl methacrylate in the copolymers (see Table V).

#### EXPERIMENTAL

The following two preparations are considered to be representative.

##### Preparation of 3-Thiolen-2-one.

A 500-ml. creased, 3-neck flask was equipped with an efficient stirrer, mantle, reflux condenser, thermometer, drying tube, and provision for blanketing with dry nitrogen. The apparatus was dried and purged thoroughly and maintained under positive nitrogen pressure. Additions of the air- or moisture-sensitive reagents were made by means of hypodermic syringes. A mixture of 160 ml. of dry tetrahydrofuran (THF, distilled from lithium aluminum hydride and stored over Linde Molecular Sieve Type 4A) and 15.9 ml. of thiophene (0.200 mole, dried over calcium chloride) was stirred in the flask while 130 ml. of 1.6 *M* *n*-butyllithium in hexane (from Foote Mineral Company) was injected over a 20-minute period. The resulting dark red solution was refluxed gently about 20 minutes and then cooled to 45°. In four portions, 15.1 ml. of methyl borate (0.133 mole, anhydrous, from Callery Chemical Company, dried and stored over lithium chloride) was injected as the temperature was allowed to rise. The mixture was heated to 55-63° for 50 minutes, after which it was cooled in ice and partially neutralized with 16.0 g. of 37% hydrochloric acid in 20 ml. of water, to yield a two-phase system. With efficient agitation, 48.0 ml. of 30% hydrogen peroxide was added dropwise over a 20-minute period. A red color soon developed which

deepened as the reaction proceeded. After the oxidant was added, the ice-bath was removed to allow the contents of the flask to warm to room temperature or slightly above. The total oxidation time was 2 hours. The reaction mixture was acidified and taken into water and ether. The layers were separated and the water layer was extracted thrice with ether. The combined ether layers were washed thoroughly with acidified ferrous ammonium sulfate solution and then twice with acidified water. The ether solution was dried over calcium sulfate and the ether was removed along with other low boiling material. The resulting dark oil was distilled under reduced pressure. The product boiling at 72-75° and 4.5 torr was collected (lit. (4), b.p. 75° at 5 torr) and shown to be high quality 3-thiolen-2-one by means of ir and nmr spectra (4,12). The yield was 14.0 g. or 70% of theoretical based upon thiophene taken.

##### Preparation of 5-Ethyl-2-thienyl Methacrylate.

From 2-ethylthiophene, 5-ethyl-3-thiolen-2-one, and 5-ethyl-4-thiolen-2-one were prepared by appropriate modifications of the procedure above. A solution was prepared by mixing 20 ml. of methacrylyl chloride with 17.2 g. of freshly distilled 5-ethyl-3-thiolen-2-one containing a little 5-ethyl-4-thiolen-2-one (the former predominates) with no detectable reaction. The addition of 50 ml. of dry pyridine caused progressive color change and rise in temperature. The mixture was heated to gentle reflux for an hour and then hydrolyzed in the cold. The reaction product was taken into water and ether; the two-phase system was very dark but it could be manipulated successfully. The layers were separated and the water phase was extracted with ether four times. The combined ether layers were washed thrice with 10% hydrochloric acid, once with water, thrice with 10% sodium hydroxide, and four times with water. The product was dried over calcium sulfate, concentrated, and distilled under reduced pressure with hydroquinone added. The product boiled at 101° and 3.6 torr to 102° and 2.4 torr; it consisted of 5-ethyl-2-thienyl methacrylate with a trace of 5-ethyl-3-thiolen-2-one. The yield was 17.8 g. or 76% of theoretical based upon the thiolenones taken. An analytical sample was prepared by washing the distilled material with dilute caustic and then refractionating.

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