Summary

Various compounds, formally derived from di-, tri- and tetraphenylmethane compounds by replacement of one phenyl group with a thienyl group, have been prepared by synthetic methods analogous to those used in preparing the corresponding phenyl compounds. The thienyl compounds were in general less stable than their phenyl analogs. The free radical, diphenylthienylmethyl, was found to possess the same instability as phenylthioxanthyl.

BUFFALO, NEW YORK

[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

MONONITRO- AND DINITROTHIOPHENES. II. A STUDY OF VAPOR PRESSURES

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RECEIVED JANUARY 9, 1929 PUBLISHED JULY 5, 1929

Introductory

It is a noteworthy fact that, while the physical properties of thiophene have been made the subject of extensive study, its derivatives have received scanty attention only. Aside from sparse references to crystallographic, microscopic, optical, spectrochemical or physico-chemical studies, the literature makes no mention of the critical constants of the numerous derivatives of thiophene. This scarcity of information is probably explained by the fact that difficulty has often been experienced in the synthesis of thiophene compounds. Throughout the literature one is impressed by the glaring omission of references to percentage yields. In their extensive researches on the thiophene series, Steinkopf and co-workers[1] have recently described improved methods of preparation, but if percentage yield be taken as a measure of efficiency, the results of these workers will in numerous instances be found to leave a great deal to be desired.

During the past three years methods have been developed in this Laboratory for the quantity production of mononitro- and dinitrothiophene. The notable absence in the literature of critical data for the thiophene series has suggested a study of the vapor pressures of these nitro compounds.

Preparation and Purification of Materials.—The compounds employed in this study were synthesized by the methods outlined by one of the authors.[2] Mononitrothiophene was readily purified by steam distillation and by subsequent crystallization

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[1] (a) Steinkopf and co-workers, *Ann.*, **403**, 1–72 (1914); (b) **407**, 94–108 (1915); (c) **413**, 310–349 (1917); (d) **424**, 1–71 (1921); (e) **428**, 123–163 (1922); (f) **430**, 41–161 (1923); (g) **437**, 14–36 (1924); (h) **448**, 205–222 (1926).

[2] Babasinian, THIS JOURNAL, **50**, 2749, 2751 (1928).

from petroleum ether. Repeated crystallization from this solvent produced snow-white needles which melted at 45.5°.[3]

Dinitrothiophene obtained by ordinary methods of crystallization always contains a weighable fraction of an isomer. Prolonged distillation with steam was found to remove the more volatile isomer to a great extent.[4] The residue was then freed from traces of tarry impurities by repeated crystallization from alcohol. The product was almost white and melted at 52°.[5,3a]

Method.—The apparatus employed for the vapor pressure determination was that of Smith and Menzies,[6] as shown in Fig. 1, with modifications as outlined below. Accurate temperature control was obtained by very rapid stirring of a glycerin bath A (shielded by G) by the rotary stirrer B. Temperature readings were made by means of the certified thermometer C. In order to secure greater compactness in the glass system, to eliminate leakage into the reservoirs H and I and to insure increased facility in manipulation, the apparatus of Smith and Menzies was modified as shown in Fig. 1a. In the modified form, V, L and N remained unchanged except that L was placed on the vacuum side of Cock N, but the reservoirs H and I were replaced by the special Cock P.[7]

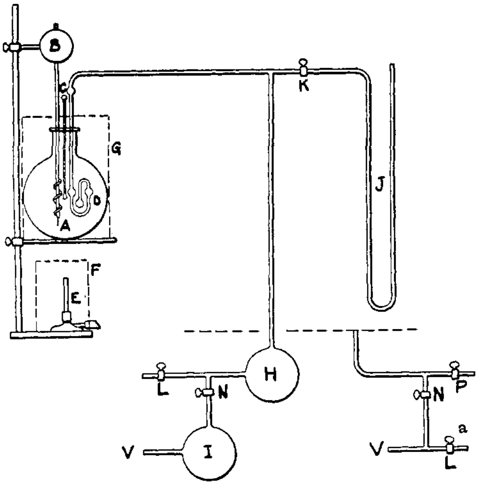

Fig. 1.—Diagram of apparatus.

Each determination required about twenty-four hours. Several readings were made at each temperature in order to insure accuracy. No decomposition was noticed in the case of mononitrothiophene at the maximum temperature of 170° employed with the compound. The liquid dinitrothiophene darkened and bore evidence of carbonization at 250°. At 256° decomposition became so rapid that it was impossible to obtain vapor pressure readings in the manometer J with any hope of accuracy. The vapor slowly attacked the mercury in the manometer at 195°. At 250° the action was more rapid, and at 260° a noticeable quantity of golden yellow flakes condensed on the surface of the mercury.

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[3] Meyer and Stadler reported 44° as the melting point of mononitrothiophene (a) *Ber.*, **17**, 2649 (1884). Steinkopf obtained a small quantity which melted at 46.5°; (b) ref. 1a, p. 18.

[4] The isomer occurs in such small quantities and is so difficult to purify that no attempt was made to produce it in quantity for vapor pressure studies.

[5] Meyer and Stadler's dinitrothiophene also melted at 52°.

[6] (a) Smith and Menzies, THIS JOURNAL, **32,** 1414, 1434, 1448 (1910). This method has been employed by (b) Monroe, *Ind. Eng. Chem.*, **12,** 969 (1920), on phthalic anhydride; (c) Nelson and Senseman, *ibid.*, **14,** 58 (1922), on naphthalene, anthracene, phenanthrene and anthraquinone; (d) Berliner and May, THIS JOURNAL, **47,** 2350 (1925); (e) *ibid.*, **48,** 2630 (1926), on nitranilines and mononitrotoluenes.

[7] Cock P was specially constructed by filling the opening in the movable member of an ordinary stopcock with de Khotinsky cement, except for a small pocket at one end, in order that a minute quantity of air could be admitted when desired.

Discussion of Results

According to the Clausius–Clapeyron Equation[8]

$$L = \frac{RT^2}{p}\frac{\mathrm{d}p}{\mathrm{d}t} \tag{1}$$

where p is the corrected vapor pressure in millimeters of mercury, T the absolute temperature, L the molar latent heat of vaporization and R the gas constant. Thus the curve obtained by plotting $\log_{10} p$ against $1/T$ will be a straight line. This was done on a very large scale in the case of each substance. The result is shown in Fig. 2. The deviation of the curves from a straight line below a seems to indicate that the observations are not dependable in this region. In Tables I and II the vapor pressures of the substances are given at various temperatures, as ascertained from Fig. 2.

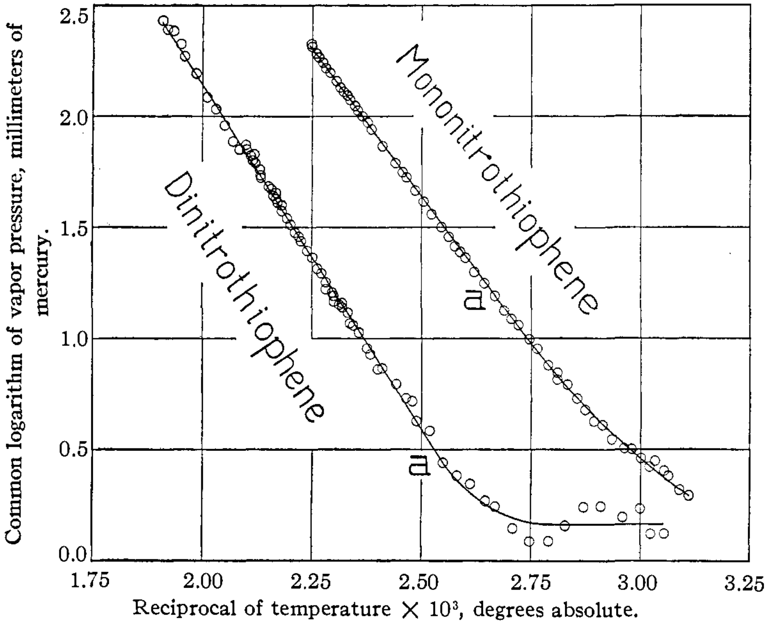

Fig. 2.

TABLE I

VAPOR PRESSURE OF MONONITROTHIOPHENE IN MM. OF MERCURY

$\log_{10} p = 8.334 - 2679.6/T$

t, °C.	105	110	115	120	125	130	135	
V.p., mm.	17.7	21.9	26.9	33.0	40.1	48.7	58.5	
t, °C.		140	145	150	155	160	165	170
V.p., mm.		70.3	83.9	99.8	118.6	139.6	164.8	193.6

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[8] Hugh S. Taylor, "A Treatise on Physical Chemistry," D. Van Nostrand Co., New York, **1924**, Vol. I, p. 118.

TABLE II

VAPOR PRESSURE OF DINITROTHIOPHENE IN MM. OF MERCURY

$\log_{10} p = 8.385 - 3116.1/T$

t, °C.	115	120	125	130	135	140	145	150	155	160
V.p., mm.	2.5	2.9	3.6	4.5	5.6	7.0	8.6	10.5	12.8	15.2
t, °C.	165	170	175	180	185	190	195	200	205	
V.p., mm.	18.8	22.6	27.1	32.3	38.3	45.4	53.5	62.9	73.8	
t, °C.	210	215	220	225	230	235	240	245	250	
V.p., mm.	85.9	100.0	115.6	134.3	154.2	178.2	204.2	233.9	267.3	

By extending the curve for mononitrothiophene in Fig. 2, the theoretical boiling point of that substance was found to be 218.2°, as compared with previously published results of about 224–225°.[3a] The theoretical boiling point of dinitrothiophene was found to be 293.3°, while the value given by Meyer and Stadler[3a] is 290°.

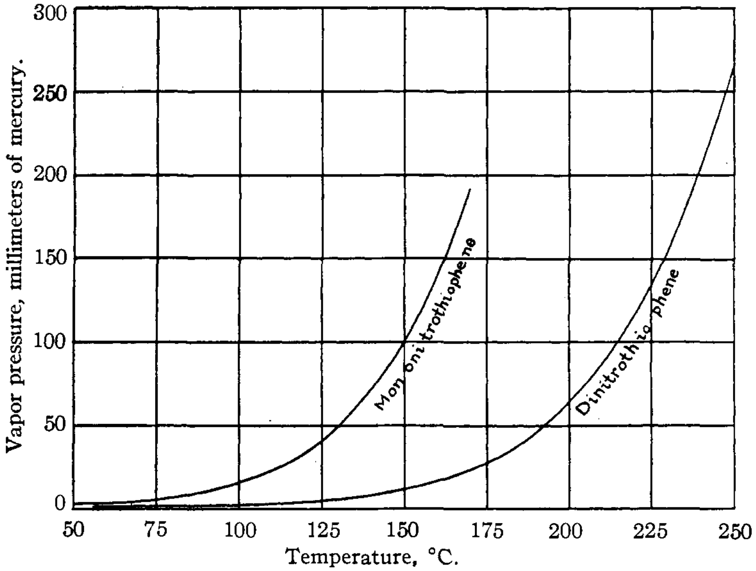

Fig. 3.

From Equation 1 the average value of L, the molar latent heat of vaporization, was found to be 12,300 cal. for mononitrothiophene above 100°, and 14,300 cal. for dinitrothiophene above 110°. From these it may be determined by the method of Hildebrand[9] whether the substances are normal liquids, since

$$S = \frac{L}{RT'} \tag{2}$$

where S is the entropy of vaporization, L the molar latent heat of vaporization and T' the temperature at which the concentration of the vapor is

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[9] Hildebrand, THIS JOURNAL, **37**, 970, 974 (1915).

0.00507 mole per liter. According to the data of Hildebrand,[10] the value of S should be between 13.1 and 13.9 for a normal liquid. The values obtained for S were 14.7 for mononitrothiophene and 14.8 for dinitrothiophene, thus indicating that neither is a normal liquid within the range of temperature considered.

Acknowledgment

The authors desire to express their sincere acknowledgment to Professor Warren W. Ewing for numerous helpful suggestions and assistance during the progress of this study.

Summary

A study of the literature showed a marked absence of critical data for the thiophene series.

The vapor pressures of mononitro- and dinitrothiophene were measured, and their theoretical boiling points, molar latent heats of vaporization and entropies of vaporization calculated.

Mononitrothiophene showed no decomposition at the maximum temperature to which it was subjected. Dinitrothiophene was found to decompose above 250° and to attack mercury at much lower temperatures.

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[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

ADDITION REACTIONS OF VINYL PHENYL KETONE. I. PHENYLNITROMETHANE

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RECEIVED JANUARY 17, 1929 PUBLISHED JULY 5, 1929

Vinyl phenyl ketone (I) is the lowest member of the series of unsaturated phenyl ketones having a conjugated system. It should be of interest to compare the properties and reactions of the products derived from it by the addition of certain substances having active hydrogen with those obtained by the addition of the same compounds to a substituted vinyl phenyl ketone, such as benzalacetophenone (II)

$$\underset{\text{I}}{CH_2{=}CHCOC_6H_5} \qquad \underset{\text{II}}{C_6H_5CH{=}CHCOC_6H_5} \qquad \underset{\text{III}}{CH_2ClCH_2COC_6H_5}$$

Since it combines very readily with substances[1] that have an active hydrogen atom, it can be used for making saturated ketonic compounds which are unsubstituted in the beta position and which it is difficult to secure in any other manner. It seemed probable that these addition products could be converted into other substances which would be useful in connection with the study of reactions of which the mechanism is at

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[10] Ref. 9, p. 975.

[1] Kohler, *Am. Chem. J.*, **42**, 375 (1909).