with 0.25 mole of powdered sodium under 250 cc. of dry ether. The sodium had all dissolved after three hours of refluxing, and the soluble sodium derivative was alkylated with diethyl sulfate approximately as in the similar alkylation of ethyl isopropylidenemalonate.[1a] A 58% yield of methyl (1-propyl-1-butenyl)-ethylcyanoacetate was obtained, b. p. 117–119° (4 mm.); n^{25}D 1.4489, d^{25}_{25} 0.9482. This ester gave satisfactory nitrogen analyses (calcd. for $C_{13}H_{21}O_2N$: N, 6.28; found: N, 6.38), but the low index of refraction, compared with that of the pure ester prepared in methyl alcohol and described in Table I, indicates the presence of the corresponding reduced ester as an impurity.

Ozonizations.—The esters indicated by footnote l in Table I were ozonized by the procedure described previously.[1b] The aldehydes formed on decomposition of the ozonides were converted to the 2,4-dinitrophenylhydrazones as before, and color tests for formaldehyde were made. In each case, a trace of formaldehyde was present, as indicated by positive ring tests with both gallic acid and resorcinol, but in no case was there enough to give the moderately sensitive resorcinol test with sodium hydroxide. As in the previous work, the most volatile portion of each of the distillates was treated with 2,4-dinitrophenylhydrazine and hydrochloric acid in alcohol solution. The derivatives formed were nearly pure as precipitated, and one recrystallization brought them to constant melting point in each case. The respective 1-alkyl-alkenyl esters gave the following aldehydes, as shown by the melting points of their 2,4-dinitrophenylhydrazones and mixed melting points with known samples. The 1-methylpropenyl ester gave acetaldehyde, m. p. and mixed m. p. of the derivative 163–165°. The 1-methyl-1-butenyl esters gave

propionaldehyde, m. p. and mixed m. p. of the derivative 153–154°. The 1-methyl-1-pentenyl esters gave butyraldehyde, m. p. and mixed m. p. of the derivative 121–122°. The 1,3-dimethyl-1-butenyl ester gave isobutyraldehyde, m. p. and mixed m. p. of the derivative 181–182°. The 1-methyl-1-hexenyl ester gave valeraldehyde, m. p. and mixed m. p. of the derivative 108–109°.[7] (These melting points are uncorrected.)

Summary

Alkylidenecyanoacetic esters derived from both symmetrical and unsymmetrical ketones give sodium derivatives when treated with sodium alkoxides in alcohol solution. Alkylation of these sodium derivatives with alkyl halides and dialkyl sulfates produces (dialkylvinyl)-alkylcyanoacetic esters, $RCH=C(R')C(R'')(CN)COOR'''$. In the formation of a sodium derivative from five alkylidenecyanoacetic esters derived from a series of methyl ketones, hydrogen is lost from the methylene of an alkyl group higher than methyl, rather than from the methyl group. Yields in the alkylation reactions are highest when sodium isopropoxide and isopropyl alcohol are employed, presumably because of the relatively slow alcoholysis of the products in this solvent.

(7) The valeraldehyde derivatives had a higher melting point than the one previously recorded. All others are in agreement with those reported by Campbell, *Analyst*, **61**, 391 (1936).

The Action of Bromine on Nitrothiophene

BY V. S. BABASINIAN

The literature has very little to reveal regarding the behavior of nitrothiophene toward bromine. Casual references to the changes involved merely imply that the halogen attacks the nitro group with avidity, converting the compound to tetrabromothiophene.[1] The reaction was studied more closely in this Laboratory. It was found that in direct contact with the theoretical amount of bromine, nitrothiophene yields mainly tetrabromothiophene, but the product invariably is contaminated with the unattacked nitro compound. On the other hand, when the amount of bromine is reduced to the required minimum for the replacement of a single hydrogen in the thiophene nucleus, brominated intermediates appear

in the product along with tetrabromothiophene. The reaction is likewise modified if brominations are effected in neutral or alkaline aqueous suspensions, or in ordinary organic solvents. Small-scale experiments performed under these conditions[2] give every indication that in the direct bromination of nitrothiophene the nitro group offers a degree of resistance to replacement by bromine, permitting the formation of a number of substituted derivatives, and under proper control the reaction pursues a course that can be followed with reasonable certainty.

The author proposes to show that with bromine vapor at room temperature, nitrothiophene

(1) (a) Meyer, "Die Thiophengruppe," Braunschweig, 1888, p. 102; (b) Steinkopf and co-workers, *Ann.*, **512**, 137 (1934).

(2) The author desires to record his gratitude to Messrs. John B. Fishel and Horace F. Ether who performed the preliminary experiments. The analytical data for tetrabromothiophene, given later, were secured by Mr. Ether.

yields four compounds in quantities ample for conclusive identification, and the presence of a fifth derivative of thiophene may be demonstrated by qualitative tests. In the following list the approximate yield of each crude product from 50 g. of nitrothiophene is indicated. The melting points are those of the purified compounds.

—Thiophene	2-Bromo-5-nitro-	2,3-Dibromo-5-nitro-	2,5-Dibromo-3-nitro-	Tetrabromo-
Formula	NO_2⟨S⟩Br	Br / NO_2⟨S⟩Br	NO_2 / Br⟨S⟩Br	Br—Br / Br⟨S⟩Br
Yield, g.	8.5	6.0	0.8[3]	10.0
M. p., °C.	47–48	75.5–76	61	116–117

In the reaction product a fifth derivative of thiophene was isolated in extremely small quantities. Its composition as 2,3,5-tribromothiophene, Br⟨S⟩Br' with Br, is provisionally inferred from a superficial examination of physical properties.

Discussion of Results

The results attained in this bromination justify the assumption that in bromonitrothiophene the substituents occupy positions 2 and 5. They also elucidate the course of the reaction, and offer criteria for the evaluation of the relative stability of intermediates.

The Structure of Bromonitrothiophene.—There are two factors that are likely to control the course of the reaction between bromine and nitrothiophene: namely, (a) the alpha orienting effect of sulfur, and (b) the meta orienting effect of the nitro group. Under the predominating influence of (a) or (b) one would expect the formation of either 2-bromo-5-nitrothiophene or 3-bromo-5-nitrothiophene. If both factors were effective the two isomers might appear as a mixture. It is quite significant that in this reaction approximately 9 g. of an homogeneous bromonitrothiophene was isolated. More important is the fact that the compound produced was in every detail identical with the bromonitrothiophene prepared from 2-bromothiophene by nitration.[4] The

(3) This product could originate only from β-nitrothiophene. Steinkopf and Höpner were able to prove that ordinary nitrothiophene contains about 97.5% of the alpha compound and 2.5% of the beta isomer [*Ann.*, **501**, 176, 182–183 (1933)]. In the course of the present study a partial separation of the two isomers was made by the repeated crystallization of ordinary nitrothiophene from petroleum ether. In one of the bromination experiments a sample of ordinary nitrothiophene was used which had not been separated into the two isomers. Omission of this procedure resulted in a marked increase in the yield of 2,5-dibromo-3-nitrothiophene.

(4) Babasinian, THIS JOURNAL, **57**, 1763 (1935). Compare also ref. 1b, p. 161. The compound produced in this way was provisionally described as 2-bromo-5-nitrothiophene, but no evidence was offered in support of this structure.

formation of the same bromonitrothiophene, whether one brominates *2-nitrothiophene* or nitrates *2-bromothiophene*, points to the conclusion that the product is 2-bromo-5-nitrothiophene.[5] There is no valid reason to doubt the meta orienting capacity of the nitro group. And if under the influence of this factor 3-bromo-5-nitrothiophene was also produced in any quantity, it quickly changed to 2,3-dibromo-5-nitrothiophene because of the available alpha position which an additional bromine could readily occupy.

The Course of the Reaction and Relative Stability.—In the brominated product 2,3-*dibromo-5-nitrothiophene* is also present in moderate quantities. It is natural to assume that this compound was formed by the further bromination of 2-bromo-5-nitrothiophene. Had the reaction followed a normal course, a large percentage of the latter would have produced the former. When the yields of the two products are compared, it will be seen that the amount of 2-bromo-5-nitrothiophene is much larger than that of 2,3-dibromo-5-nitrothiophene. This means that the 2-bromo compound is more resistant to the action of the halogen than the 2,3-dibromo derivative. As the latter accumulates in the reaction product, it is attacked by bromine and ultimately changed to tetrabromothiophene.[6]

From the results it is also possible to determine with reasonable assurance the relative stability of the nitro group toward bromine in these two compounds. That in 2-bromo-5-nitrothiophene this group is not vulnerable may be inferred from the complete absence of 2,5-dibromothiophene in the reaction product. 2,3-Dibromo-5-nitrothiophene shows an altogether different behavior. Had the nitro group been firmly held by the nucleus, further bromination would have resulted in the formation of 2,3,4-tribromo-5-nitrothiophene; but not a trace of this product could be isolated in these experiments. Moreover, if any importance could be attached to evidence gleaned from tests of purely qualitative

(5) *Cf.* von Schweinitz, *Ber.*, **19**, 640, 648 (1886).

(6) 2,5-Dibromo-3-nitrothiophene is not expected to manifest this behavior. Steinkopf and co-workers[1b] (pp. 137 and 161) had pointed out that, unlike 2,3-dibromo-5-nitrothiophene, this compound remains quite stable in an excess of bromine.

nature, 2,3,5-tribromothiophene was formed, at
any rate, in detectable quantities. The appear-
ance of this compound and the complete absence
of 2,3,4-tribromo-5-nitrothiophene led to the
inference that in 2,3-dibromo-5-nitrothiophene
the nitro group is too weakly held by the nucleus
to resist replacement by the halogen. In conse-
quence, the loosely held group leaves the nucleus
to favor the formation of tetrabromothiophene.

Experimental

Fifty grams of nitrothiophene, prepared in the usual
way,[7] was spread in a crystallizing dish and supported over
27 cc. of bromine in a covered desiccator. The reaction
was allowed to proceed at room temperature for thirty
days. In twelve hours over one-half of the bromine had
been absorbed and the solid had completely liquefied into
a dark red oil. In the following twenty-four hours the oil
had in part changed to fine crystals. The final product
was a mixture consisting of light red crystals and a yellow
oil. Bromine was more rapidly absorbed during the last
few days of the allotted period than at the beginning.

Tetrabromothiophene in the Oily Mixture.—The re-
action product was chilled and filtered under suction. The
precipitate was washed with water, dried, and refluxed with
several portions of petroleum ether. The solvent ex-
tracted a small quantity of nitrothiophene. The un-
dissolved white residue weighed about 9 g. It was crystal-
lized from hot alcohol and melted at 116–117°.

Anal. Calcd. for C_4Br_4S: S, 8.00; Br, 79.97. Found:
S, 7.86; Br, 80.23.

The oily filtrate was neutralized with dilute sodium
carbonate, washed with water, and steam-distilled.[8] The
distillate was collected in four fractions: Fraction I con-
tained a white solid and an almost colorless oil; II was
uniformly oily; III was also uniformly oily; IV distilled
slowly as a pure white solid.

Each of the first three fractions was dissolved in ether
and dried with calcium chloride. Fraction IV was filtered
and dried. Ether was removed from the first three frac-
tions and the oily residues were examined.

2-Bromo-5-nitrothiophene in Fractions I and II.—
Fraction I was cooled in ice for a long time and filtered
under suction. The crystalline precipitate was brownish-
white, yield 7.5 g. It was dissolved in boiling petroleum
ether and decolorized with darco. Upon cooling the fil-
trate yielded snow-white needles which acquired a faint
yellow color in air. The recrystallized product melted at
47–48°. The mixed melting point with a pure sample of 2-
bromo-5-nitrothiophene was 46–47°.

Anal. Calcd. for $C_4H_2S(NO_2)Br$: S, 15.41; Br, 38.42.
Found: S, 15.36; Br, 38.26.

Fraction II was cooled in a freezing mixture and filtered.
The solid proved to be 2-bromo-5-nitrothiophene.

(7) Babasinian, This Journal, **50**, 2749 (1928).

(8) A dark brown semi-solid remained in the distillation flask.
Weight, after drying, about 10 g. Insoluble in most ordinary sol-
vents. Boiling acetone removed from it a dark red heavy oil
leaving an insoluble brown powder which burned very slowly over a
direct flame. The oil and the brown powder were not examined
further.

2,3-Dibromo-5-nitrothiophene in Fraction III.—Frac-
tion III was cooled and filtered. The precipitate yielded
3.5 g. of bright yellow crystals which melted at 74–75°.
A petroleum ether solution, after treatment with darco,
yielded white crystals which acquired a faint yellow coating
when exposed to air. The compound is moderately vola-
tile with steam. The distilled solid is pure white, while
the clear aqueous residue in the distillation flask retains
the faint yellow color. After recrystallization from
petroleum ether the steam-distilled solid remained almost
white in a brown desiccator for several weeks. It melted
at 75.5–76°.[9]

Anal. Calcd. for $C_4HS(NO_2)Br_2$: S, 11.17; Br, 55.70.
Found: S, 11.04; Br, 55.80.

**Fraction IV Yields Tetrabromothiophene, 2,3-Dibromo-
5-nitrothiophene, and a Trace of Lower-melting Crys-
tals.**—The solid obtained as Fraction IV weighed 9.5 g.
It was crystallized from a large volume of methanol. The
nitrogen-free crystals melting at 113–114° proved to be
tetrabromothiophene. After concentration the alcoholic
filtrate yielded 2.5 g. of 2,3-dibromo-5-nitrothiophene.
Upon further concentration the mother liquor was found
to contain a trace of a white solid which melted at 62–67°.

The isolation of compounds in the oily filtrates was ac-
complished by distillation *in vacuo* at constant pressure.
Serious decomposition could be reduced to a negligible
minimum if the process was carried out slowly, below 130°.

Oily filtrates from Fractions I, II and III were distilled
under a pressure of 5 mm. and collected at the following
temperature ranges: A, at or below 105° (trace of solid or
oil); B, at 109–110° (mainly solid); C, at 112–115° (oil);
D, at 118–123° (mainly solid); E, at 123–128° (solid and
oil). Distillates containing mixtures of oil and solid were
cooled and filtered. The precipitate was freed from im-
purities by the usual methods. Oils, or oily filtrates, were
dissolved in solvents and cooled; when the solution failed
to form crystals, the solvent was evaporated and the oil
was refractionated. Purified products could be obtained
only in small quantities. When melting points and
qualitative tests furnished fair indications of identity with
previously analyzed compounds, results were checked by
determinations of mixed melting points.

Distillate A was composed mainly of unattacked *nitro-
thiophene.*

Distillate B yielded *2-bromo-5-nitrothiophene.*

Distillate C produced a compound melting at 28–32° in
quantities too small for complete purification. This is
probably *2,3,5-tribromothiophene*[1a] (p. 79).

Distillate D contained almost exclusively *2,3-dibromo-5-
nitrothiophene.*

Distillate E was found to be a mixture of *tetrabromo-
thiophene, 2,3-dibromo-5-nitrothiophene,* and *2,5-dibromo-3-
nitrothiophene.* For the isolation of these compounds the
distillate was cooled and filtered. The solid was dissolved
in methanol and purified with darco. From the clear
solution bright yellow crystals of 2,3-dibromo-5-nitrothio-
phene were obtained.

The oily filtrate was dissolved in boiling alcohol. Upon

(9) There can be no doubt that the white product, showing this
melting point, is 2,3-dibromo-5-nitrothiophene. Steinkopf and co-
workers describe it as a bright yellow solid and give its melting point
as 75° (ref 1b, p. 156).

cooling crystals were obtained which had the characteristics of tetrabromothiophene. The mother liquor was carefully concentrated. When cooled in a freezing mixture, white, shiny crystals were formed which melted at 55–65°; weight less than 1 g. It was recrystallized from petroleum ether, then distilled with steam and the solid distillate was again crystallized from the same solvent. The final product melted at 61°. Analysis showed that the compound was 2,5-dibromo-3-nitrothiophene.[10]

Anal. Calcd. for $C_4HS(NO_2)Br_2$: S, 11.17; Br, 55.70. Found: S, 10.90; Br, 56.16.

Summary

In the vapor phase and at room temperature a limited quantity of bromine converts ordinary nitrothiophene into 2-bromo-5-nitrothiophene, 2,3-dibromo-5-nitrothiophene, 2,5-dibromo-3-nitrothiophene and tetrabromothiophene.

Qualitative tests also indicate the formation in traces of one other brominated derivative of thiophene.

The reaction confirms the heretofore assumed structural formula of bromonitrothiophene.

The reaction leads to the inference that in 2-nitrothiophene the nitro group resists replacement by bromine during the entry of the first atom of halogen into the thiophene nucleus; but this group is considerably loosened after the entry of the second bromine atom.

(10) The same compound had been produced by the direct bromination of 3-nitrothiophene,[1b] p. 161.

BETHLEHEM, PENNA.　　　RECEIVED SEPTEMBER 12, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF TRINITY COLLEGE]

Ternary Systems. V. Phthalic Acid, Magnesium Phthalate and Water. VI. Magnesium Phthalate, Lithium Phthalate and Water

BY STERLING B. SMITH AND EDWARD C. ELY[1]

Introduction

A number of phase rule studies of ternary systems involving phthalates and acid phthalates, particularly of the alkalies, have been made in this Laboratory. It is for the purpose of gaining further information regarding the solubilities of these salts that this investigation has been undertaken.

Experimental Part

Materials and Methods.—The phthalic acid used was prepared by crystallizing from aqueous solution sublimed phthalic anhydride obtained from the Eastman Kodak Company.

Magnesium phthalate was prepared by adding to an aqueous solution of phthalic acid an excess of magnesium carbonate, A. R. The solution was boiled to drive off carbon dioxide and filtered hot to remove the insoluble magnesium carbonate. The filtrate was evaporated to a small volume and allowed to stand several days while the magnesium phthalate crystallized out. The salt was filtered on a Büchner funnel and allowed to dry in the air. The composition of this salt was found by analysis to be $2MgC_8H_4O_4 \cdot 11H_2O$. Air dried samples heated to constant weight in an electric oven at 120° lost weight corresponding to 34.72, 34.60, 34.58, 34.45, 34.27 and 34.23% of water. The theoretical value for the per cent. of water in $2MgC_8H_4O_4 \cdot 11H_2O$ is 34.47%.

Lithium phthalate, $2Li_2C_8H_4O_4 \cdot 3H_2O$, was prepared as described in a previous publication.[2]

Magnesium acid phthalate, while not a component of either of these systems, appears as one of the solid phases and is used in the preparation of mixtures for analysis. It was prepared by adding slightly more than one-half the equivalent weight of magnesium carbonate to an aqueous solution containing the equivalent weight of phthalic acid, boiling off the carbon dioxide and evaporating to crystallization.

Solubilities were determined by analyzing solutions obtained by rotating mixtures of the three components in an electrically controlled thermostat for a minimum of twenty-four hours. In making up the mixtures, as far as possible the salts were used which exist as solid phases after equilibrium has been reached. At 0° the temperature was maintained constant by the use of ice and a small amount of salt. Temperature variations were within ±0.1°. When equilibrium was attained, the mixtures were allowed to settle and samples for analysis removed from the clear supernatant liquid by means of a pipet. When necessary to ensure a clear solution, a small plug of cotton or glass wool was inserted in a short piece of rubber tubing and slipped over the end of the pipet. Due to the viscosity of many of these solutions, density determinations were not attempted.

The composition of the solid phases was determined by the analysis of wet residues according to Schreinemakers.[3]

In the system phthalic acid, magnesium phthalate and water, phthalic acid was determined by titration with standard alkali. Magnesium phthalate was determined by precipitation of the magnesium as magnesium am-

(2) Smith, Sturm and Ely, THIS JOURNAL, **57**, 2406 (1935).
(3) Schreinemakers, *Z. physik. Chem.*, **11**, 76 (1893).