PREPARATION OF ALPHA, BETA UNSATURATED NITROALKENES
AND THEIR REACTIONS

by

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INTRODUCTION

Previous to the year 1930, the nitro paraffins could be prepared only on a laboratory scale (13). No practical industrial method of preparation was known. The work of Hass (13) at Purdue University first employed the technique of vapor phase nitration of lower alkanes for the preparation of nitro paraffins. This process was developed industrially and the first large scale production of nitro paraffins, using readily available paraffins, was achieved by the Commercial Solvents Corporation in 1940. Since that time the production of nitro paraffins has steadily increased and new uses are being found for them, primarily as solvents and as organic intermediates.

This investigation was undertaken for the purpose of (a) studying and evaluating the synthesis of 2-nitro-1-butene, (b) investigating its reactions with chloroform and acetyl chloride, and (c) attempting to prepare new types of products which might have industrial value.

It is intended to show that the reactivity of 2-nitro-1-butene, brought about by the strong katio-enoid activation therein, is sufficient to cause addition of an acid chloride to the nitrobutene. This objective is met by reporting the results of experimental work on acetyl chloride as an addition agent for 2-nitro-1-butene.

Attempts also were made to show that the katio-enoid activation in 2-nitro-1-butene is strong enough to cause addition of

chloroform as H^+ and $^{(-)}CCl_3$ to the alpha, beta unsaturation in the nitrobutene. This would be analogous to the addition of chloroform in such manner to the fundamentally similar katio-enoid structure in 2-cyano-1-propene (i.e., acrylonitrile) as reported by Bruson, Niederhauser, Riener, and Hester (7).

LITERATURE REVIEW

In the evaluation of a 1,2-unsaturated nitroolefin as to the practicability of its synthesis, the methods necessary for its manipulation, and its applicability in new reaction studies, it was necessary to review the literature.

At the present time, nitroolefins are not on the market and must therefore, be prepared in the laboratory as needed. Several interesting preparative methods are given in the literature. The Schmidt and Rutz reaction (13) gave nitroolefins by the inter-action of nitro alcohol esters and sodium bicarbonate. The nitra-tion of tertiary alcohols gave nitroolefins (13). Blomquist, Tapp, and Johnson (6) prepared 2-nitro-1-propene in good yield by the pyrolysis of 2-nitro-1-propanol benzoate. Gold (11, 12) pre-pared 2-nitro-1-butene by the passage of β-nitrobutyl acetate vapors over calcium sulfate at 300° C. Blomquist and Shelly (5) prepared 2-nitro-1-butene by: (a) reaction of nitropropane, diethylamine, and formaldehyde to form N-(2-nitrobutyl)-diethylamine, (b) conversion of the latter to its hydrochloride salt, followed by pyrolysis of this nitroamine salt to yield 2-nitro-1-butene. This appeared to be the best method available

in the literature since it made use of readily available starting
materials. It was therefore, employed in the preparation of the
2-nitro-1-butene used in this investigation.

Nitroolefins were found to polymerize readily in the presence
of alkalies. Thus, Blomquist, Tapp, and Johnson (6) found that
2-nitro-1-propene passed rapidly into a polymer when heated with
aqueous potassium bicarbonate. Buckley and Scaife (10) observed
that nitroethylene, a pale yellow oil, darkened slowly on stand-
ing. A polymer was readily formed in the presence of water and
a trace of alkali caused violent polymerization. Similar be-
havior with alkali was found with 1-nitro-1-propene even though
it was unaffected by water (10).

Nitroolefins were found to react with compounds containing
active hydrogen atoms. Bahner (3) prepared 2-nitrobutyl diethyl
malonate in good yield from the reaction of 2-nitro-1-butene and
diethyl malonate. Sodium in dioxane was used as catalyst.
Acetoacetic ester and 2-nitro-1-butene also reacted in the pres-
ence of sodium to give (2-nitrobutyl)-acetoacetic ester (1).
Bahner (2) also reacted sodium acetyl acetone and 2-nitro-1-
butene to give 2-nitrobutyl acetyl acetone.

Heath and Rose (14) reacted alpha-nitroolefins with an-
hydrous hydrogen chloride in ether and obtained 1,2-dichloro-
nitroso compounds. If an alpha hydrogen atom was present, these
rearranged into 1,2-dichloro-oximes. The same investigators (15)
reacted alpha-nitroolefins with ammonia and primary and secondary
amines to give 2-nitroalkyl amines. They also found that primary

or secondary aliphatic nitro compounds reacted with alpha nitro-
olefins to give 1,3-dinitro paraffins; these on reduction af-
forded 1,3-diamines.

Buckley (8) added nitro ethylene to 3 mols of ethyl mag-
nesium bromide, then treated this with water. Nitrobutane and
hexan-3-one oxime were formed. Addition of the Grignard reagent
to an ethereal solution of the nitroolefin resulted in immediate
polymerization. Buckley and Ellery (9), found that nitroparaf-
fins are prepared by 1:4 addition of alkyl or aryl magnesium
halides or alkyl zinc halides to alpha-nitroolefins. By reacting
below 10° and avoiding excess of organo metallic halide, the
yield of nitroparaffin could be raised to 65 percent. Higher
yields could not be attained, due to some 1:2 addition. Lambert,
Rose, and Weedon (16) performed a Friedel-Crafts synthesis with
2-methyl-3-nitro-1-propene in benzene and aluminum chloride to
give high yields of 1-nitro-2-phenyl-2-methylpropane.

No reactions of acid chlorides or of haloforms with 2-nitro-
1-alkenes were reported in the literature.

DISCUSSION OF RESULTS

Preparation of 2-Nitro-1-butene

The method developed by Blomquist and Shelley (5) was em-
ployed with good results for the preparation of 2-nitro-1-butene.
The method consisted essentially of first preparing N-(2-nitro-
butyl)-diethylamine by the reaction of 1-nitropropane, diethyl-
amine, and formaldehyde. This nitro amine was then purified, con-

verted to its hydrochloride salt, and the latter pyrolyzed to give crude 2-nitro-1-butene. Distillation of the crude 2-nitro-1-butene by fractionation under reduced pressure then gave pure 2-nitro-1-butene, a pale blue liquid.

The writer was unable to obtain the 77 percent yield of 2-nitro-1-butene claimed by Blomquist and Shelley (5); however, yields of 46 to 53 percent were obtained. The writer's results were confirmed by two students in an organic preparations course, Mr. Blair and Mr. Pumpelly, in that they obtained 35 and 50 percent yields, respectively, of the pure 2-nitro-1-butene. So far as is known from a search of Chemical Abstracts, this is the first time that the methods of Blomquist and Shelley (5) have been checked.

Regarding the intermediate or precursor; viz., N-(2-nitrobutyl)-diethylamine, the 79 percent yield thereof reported by Blomquist and Shelley (5) was exceeded by the writer, since yields of 81, 95, and 90 percent of this nitroamine were obtained in the present work. Decomposition of the nitroamine during its distillation was a serious difficulty in certain cases, and then lower yields of 44, 55, and 57 percent of the N-(2-nitrobutyl)-diethylamine were obtained. Such decomposition was mentioned by Blomquist and Shelley as occurring at only 14 mm of mercury pressure, but in the present work, decomposition of the nitro amine occurred in some cases at 2-3 mm pressure. No satisfactory explanation was found for this seemingly inconsistent behavior.

The pure N-(2-nitrobutyl)-diethylamine decomposed slowly

during storage, accompanied by pronounced darkening of the pale
yellow material and formation of a strong amine-like odor. No
mention of such decomposition was made in the literature. The
observed composition occurred in the dark under an atmosphere of
nitrogen. It is believed that the reaction shown in Fig. 1
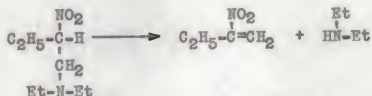slowly took place.

$$C_2H_5-\overset{\overset{\textstyle NO_2}{|}}{\underset{\underset{\textstyle Et-N-Et}{|}}{\underset{\textstyle CH_2}{\overset{|}{C}}}}-H \longrightarrow C_2H_5-\overset{\overset{\textstyle NO_2}{|}}{C}=CH_2 \quad + \quad \overset{\overset{\textstyle Et}{|}}{HN}-Et$$

Fig. 1. Possible decomposition reaction for N-(2-Nitro-
butyl)-diethylamine.

The 2-nitro-1-butene so-produced was thought to polymerize
under the influence of the diethylamine as in Fig. 2. A similar
reaction was postulated by Blomquist, Tapp, and Johnson for 2-
nitropropene (6).

$$C_2H_5-\overset{\overset{\textstyle NO_2}{|}}{C}=CH_2 \longrightarrow \left(\overset{\overset{\textstyle NO_2}{|}}{\underset{\underset{\textstyle C_2H_5}{|}}{C}} - \overset{\overset{\textstyle H}{|}}{\underset{\underset{\textstyle H}{|}}{C}} - \right)_X \quad \text{(gives dark solution)}$$
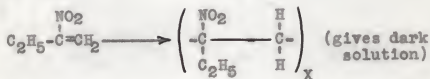
Fig. 2. Possible polymerization reaction for 2-Nitro-
1-butene.

The above two reactions would explain the strong amine-like
odor and darkening in color observed upon decomposition of the
N-(2-nitrobutyl)-diethylamine. The polymerization as shown in
Fig. 2 is promoted by alkaline materials (6, 10, 15).

No difficulty with decomposition was experienced during the
preparation of 2-nitro-1-butene. Storage at room temperature re-
sulted in some polymerization and darkening in color to a deep
brown but this change was prevented by storing the 2-nitro-1-
butene in a deep freeze cold room at -20° C. Buckley and Scaife
(10) reported a similar behavior for nitroethylene and 2-nitro-
propene upon storage. The above polymerization of 2-nitro-1-
butene was believed to be catalyzed by alkali in the glass storage
bottles, and was probably a polymerization reaction of the type
shown in Fig. 2.

Reactions of 2-Nitro-1-butene and Chloroform

Reactions were carried out to determine if a compound could
be formed by addition of chloroform across the olefinic double
bond of 2-nitro-1-butene. The postulated reaction is given in
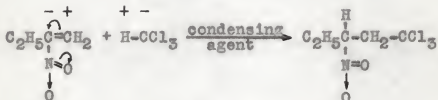Fig. 3. In theory 1,1,1-trichloro-3-nitro pentane might be
formed.

Fig. 3. Postulated addition of chloroform to 2-Nitro-
         1-butene.

A reaction similar to the one postulated in Fig. 3 was found
by Bruson, Niederhauser, Riener, and Hester (7). They reported
that chloroform and acrylonitrile gave a 12 percent yield of

alpha-trichlorobutyronitrile. Potassium hydroxide was used as condensing agent. The course of reaction was considered to be as in Fig. 4.

$$CH_2\text{=}CH\text{-}C\text{≡}N \ + \ HCCl_3 \ \xrightarrow[\text{0-5° C.}]{\text{potassium hydroxide}} \ Cl_3C\text{-}C_2H_4\text{-}C\text{≡}N$$
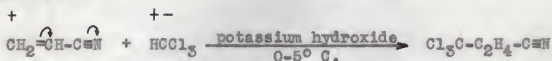
Fig. 4. Addition of chloroform to acrylonitrile.

From consideration of this reaction, it was felt that the nitro group in 2-nitro-1-butene should have as strong an activating effect on the alpha, beta carbon-to-carbon double bond as the nitrile group did in acrylonitrile, and a similar reaction could be expected to take place between chloroform and 2-nitro-1-butene. Remick (19) lists a table of relative electronegativities in which the nitro group is slightly more electro negative than the nitrile group; from this it is reasonable to expect that the activity of 2-nitro-1-butene with chloroform should be of the same order as that of acrylonitrile, if not stronger. In general, in the present work, it was found that addition products of chloroform and 2-nitro-1-butene were not obtained, even under a variety of conditions.

Since Blomquist et al. (6), and Buckley and Scaife (10) had reported rapid polymerization of nitroolefins under basic conditions in the presence of moisture, it was felt best to investigate the reaction of 2-nitro-1-butene and chloroform at a low temperature (0° C.) and use a ten-fold excess of chloroform to dilute the 2-nitro-1-butene molecules away from each other. This procedure was followed, using powdered potassium hydroxide

under anhydrous conditions as the condensing agent. It was
thought that with these conditions, the polymerization reaction
might be inhibited and the desired reaction proceed, at least to
an appreciable extent. From the results of all experiments, how-
ever, polymerization was evidently the predominant reaction.
Only dark, gummy, plastic materials were formed as reaction
products. They were considered to be polymers of 2-nitro-1-
butene with itself as was substantiated by tests and later evi-
dence found. No addition product with chloroform was obtainable.
Investigation of the water washes of one of the reaction mixtures
showed that no water-soluble product was present in any of the
water extracts.

The solids obtained from experiments were dark brown plastic
gums. They could not be crystallized after extractive digestions
with chloroform or with ether. The chloroform-soluble and the
ether-soluble portions of the plastic gums also could not be
crystallized. The ether insoluble portion of the plastic (called
"Plastic A" in Experimental section) did give a melting range of
96 -120° C. indicating a fair degree of homogenity. The plastics
obtained always contained nitrogen, but no halogen, and hence
were polymers of 2-nitro-1-butene with itself. With the exception
of the brown gums, no new products could be isolated. No un-
changed 2-nitro-1-butene was recovered.

From the above findings, it was believed, therefore, that the
brown gums were polymerization products of 2-nitro-1-butene form-
ed under the influence of anhydrous potassium hydroxide at 0° C.

The polymerization involved was probably similar to that postulated for 2-nitropropene by Blomquist and Tapp (6).

$$C_2H_5\underset{NO_2}{\overset{|}{C}}{=}CH_2 \xrightarrow[\text{anhydrous}]{\text{potassium hydroxide}} \left(-\underset{C_2H_5}{\overset{NO_2}{\underset{|}{\overset{|}{C}}}}-\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}- \right)_x$$
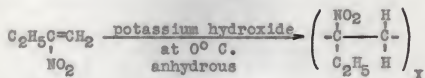
Fig. 5. Postulated polymerization reaction of 2-Nitro-1-butene.

The above type of results was not changed when 2-nitro-1-butene was added dropwise to a rapidly stirred mixture of 0.5 mol chloroform and 0.02 mol potassium hydroxide. The competing reaction of polymerization was much faster than any tendency for chloroform to add across the olefinic linkage of 2-nitro-1-butene, even though the frequency of contact of chloroform with 2-nitro-1-butene was much greater than the frequency of contact of the 2-nitro-1-butene with itself.

From the latter type of mechanical addition, a brittle,solid plastic was isolated that compared well in its properties with the Plastic A previously obtained. Thus, the ether-insoluble plastic from the modified procedure ("Plastic B") had a melting range of about 100°-150° C.

The plastic polymer of 2-nitro-1-butene so produced was found to dissolve in acetic acid and to reprecipitate on addition of water. The reprecipitated plastic softened at 89-90° C. and melted completely at 150° C. This good agreement of melting range before and after solution indicated a plastic material of reasonable purity.

Since the basic conditions with anhydrous potassium hydroxide caused 2-nitro-1-butene to polymerize exclusively, the reaction of 2-nitro-1-butene with chloroform under weakly acid conditions was attempted. It was hoped that 2-nitro-1-butene would be active, without a basic condensing agent, at 61.2° C., the boiling point of chloroform. When such a reaction was attempted at this temperature, only a small amount of plastic was formed; the bulk of the starting materials were recovered unchanged.

In view of the above findings, irradiation with ultraviolet light was used in an attempt to force reaction of 2-nitro-1-butene with chloroform at 61.2° C. in the presence of a trace of acetic acid. It was ascertained that the Pyrex equipment used would permit transmission of the ultraviolet light down to a wave length of about 3000 Angstrom Units. However, even with intense irradiation, the results were similar to those obtained in the absence of ultraviolet light. The conclusion was made that the ultraviolet radiation had no activating effect in promoting the desired addition of chloroform to 2-nitro-1-butene.

Reactions of 2-Nitro-1-butene and Acetyl Chloride

Experiments were carried out to determine if a compound could be formed by addition of acetyl chloride across the olefinic double bond of 2-nitro-1-butene. No catalyst was used in these experiments. The postulated reaction is given in Fig. 6. In theory, 1-chloro-2-acetyl-2-nitrobutane should be formed.

$$C_2H_5\overset{-}{C}\overset{+}{=}CH_2 \quad + \quad Cl-\overset{+}{C}\overset{-}{=}O \quad \longrightarrow \quad C_2H_5\overset{\overset{O}{\parallel}}{\underset{\underset{O}{\parallel}}{\underset{N}{C}}}-CH_2Cl$$

$$\underset{\underset{O}{\downarrow}}{\overset{}{N}}\overset{}{=}O \qquad\qquad \underset{CH_3}{} \qquad\qquad \underset{\underset{O}{\downarrow}}{N}\overset{}{=}O$$
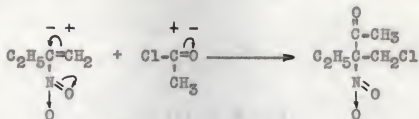
Fig. 6. Postulated addition of acetyl chloride to 2-Nitro-1-butene.

It was found that reaction did take place between the two starting materials. The results of characterization tests and quantitative analyses on the product formed indicated that the reaction postulated in Fig. 6 occurred under certain conditions.

No reaction occurred between 2-nitro-1-butene and acetyl chloride at a temperature of 0° C. When the temperature was slowly increased to the boiling point of the mixture, 75° C., then an exothermic reaction occurred and the temperature rose to 98° C. accompanied by black tar formation. It was concluded then that the reaction temperature should not be allowed to go above 75° C.

In the next trial, a mixture of 2-nitro-1-butene and acetyl chloride was heated and the temperature controlled at 70° C. to 75° C. No decomposition was noted in this case even after twenty-one hours. A deep blue crude liquid product ("Liquid A") was isolated from the reaction mixture by distillation at reduced pressure. Liquid A had a strong somewhat sweetish odor and was somewhat lachrymatory. The amount of gas given off during reaction indicated that only about 1 percent of the total 2-nitro-1-butene decomposed. This decomposition occurred only during the

heating-up-period to 70° C.

Characterization tests on the "Liquid A" product showed the presence of nitrogen and halogen. It also reacted with alcoholic silver nitrate. A test for unsaturation with bromine in carbon tetrachloride was negative. The test was positive with a neutral solution of potassium permanganate. "Liquid A" was insoluble in and unreactive to water. The boiling point of this liquid was 105° C. (uncorrected) at atmospheric pressure by the micro method of McElvain (17).

The above characterization tests indicated that "Liquid A" might contain 1-chloro-2-acetyl-2-nitro-butane and that an addition reaction might have taken place as postulated in Fig. 6. The formula for the product, 1-chloro-2-acetyl-2-nitro-butane, is reproduced as Fig. 7.

$$
\begin{array}{c}
\overset{O}{\overset{\|}{C}}-CH_3 \\
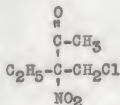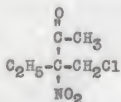C_2H_5-\overset{|}{\underset{|}{C}}-CH_2Cl \\
NO_2
\end{array}
$$

Fig. 7. Postulated addition compound from acetyl chloride and 2-Nitro-1-butene.

According to Beilstein (4) compounds of the above type which are beta activated acetyl compounds, react with potassium permanganate and are oxidized. In some cases cleavage occurs and acetic acid is produced. This in turn reacts with the potassium hydroxide produced during a permanganate oxidation. In view of these facts, it is possible that a similar oxidation of the

1-chloro-2-acetyl-2-nitrobutane present in "Liquid A" took place when it was treated with dilute aqueous potassium permanganate.

The reaction of 2-nitro-1-butene and acetyl chloride at 45° C. instead of 70-75° C. was studied next. No signs of decomposition were noted during the reaction. Distillation of the reaction mixture under reduced pressure gave a deep blue liquid (termed "Liquid C") as the main part of this distillate; this boiled at 30-35° C. (10 mm). Redistillation of "Liquid C" gave a deep blue liquid, (termed "Liquid E"). A number of characterization tests and two quantitative analyses were carried out on "Liquid E." From the results of these, it appears that this liquid was 1-chloro-2-acetyl-2-nitrobutane:

$$
\begin{array}{c}
\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-CH}_3 \\
|\\
\text{C}_2\text{H}_5\text{-}\overset{}{\underset{|}{\text{C}}}\text{-CH}_2\text{Cl} \\
\text{NO}_2
\end{array}
$$

The characterization tests that should be true theoretically for 1-chloro-2-acetyl-2-nitrobutane are:

(a) A positive 2,4-dinitrophenylhydrazine test showing presence of a ketone carbonyl group,

(b) A positive test with sodium amalgam showing the presence of a nitro group,

(c) Positive tests for nitrogen and halogen,

(d) A negative reaction toward water showing absence of admixed acetyl chloride,

(e) A negative test for unsaturation by bromine in carbon tetrachloride showing the absence of admixed 2-nitro-1-butene,

(f) A positive test with alcoholic silver nitrate with precipitation of silver chloride showing the presence of halogen,

(g) A positive test with potassium permanganate showing the presence of an activated methyl ketone group such as is characteristic of 1,3 diketones and beta-keto nitro compounds.

The above characterization tests were obtained on the deep blue distillate ("Liquid E") having a boiling point of 98° C. (micro method).

Quantitative analyses for chlorine in the deep blue distillate showed 19.12 percent chlorine compared to 19.75 percent chlorine calculated for pure 1-chloro-2-acetyl-2-nitrobutane.

Quantitative analysis for the carbonyl group in the deep blue distillate by Siggia's method (18) showed 96.9 percent of the theoretical content of carbonyl group of 1-chloro-2-acetyl-2-nitrobutane.

In view of the above analytical results, it seems reasonable to postulate 1-chloro-2-acetyl-2-nitrobutane as the isolated reaction product of acetyl chloride and 2-nitro-1-butene. The yield of this product (1-chloro-2-acetyl-2-nitrobutane) was 29.8 percent, based on theoretical yield calculated from 2-nitro-1-butene.

It is interesting to note that during distillation of "Liquid C" to give "liquid E"; even at reduced pressure, considerable decomposition appeared to have taken place with the formation of uncondensable by-products. These appear to account for about 50 percent of the starting material, "Liquid C". From

this behavior, "Liquid C" appeared to be a mixture of the postulated 1-chloro-2-acetyl-2-nitrobutane and some as yet unknown product.

It was considered possible that low temperature crystallization might bring about a separation by freezing out one of the components in "Liquid C". However, when this method was tried, no separation could be made. At about -55° C., the mixture solidified as a sort of jelly. No crystallization was observed and filtration of this frozen material could not be accomplished.

In addition to the main product, 1-chloro-2-acetyl-2-nitrobutane contained in "Liquid C", as shown above, a higher-boiling product, "Liquid D" was isolated.

Characterization tests on "Liquid D" showed the presence of nitrogen and halogen. Test for unsaturation with bromine in carbon tetrachloride was negative. A positive test for unsaturation was given with neutral potassium permanganate solution. Treatment with alcoholic silver nitrate solution gave a precipitate of silver chloride in a few seconds at room temperature. These tests and the observed decomposition of "Liquid D" at its boiling point of 160° C. to 165° C., indicated the presence of a high boiling but somewhat unstable addition compound of 2-nitro-1-butene and acetyl chloride. No further work was done on this liquid.

From consideration of the above results, the reaction of 2-nitro-1-butene with acetyl chloride at 60-65° C. was investi-

gated. On account of an accident in the heating control, the temperature of reaction rose as high as 85° C. but only during one hour.

Distillation of the reaction mixture at reduced pressure gave 7.70 gm of a clear, colorless liquid. Test of a portion of this liquid with ethyl alcohol caused formation of ethyl acetate, indicating the distillate was mainly acetyl chloride. Assuming this recovered distillate was practically all acetyl chloride, it indicates a 50 percent recovery of that substance.

Considerable amounts of black, tarry products were separated as a residue from the above distillation. These products were the most interesting features of this experiment. By means of solvent extraction with ether and chloroform, the original tarry residue was separated into a small amount (1.42 gm) of ether soluble tar ("Plastic C") and a larger amount (6.28 gm) of chloroform soluble tar ("Plastic D"). A somewhat stiffer tar (8.48 gm) remained as insoluble residue ("Residue A"). These tars were sticky and difficult to handle. No softening or melting points of these tars could be obtained.

Characterization tests showed that all three of the tars contained nitrogen and halogen. Alcoholic silver nitrate solution gave a quick reaction with all three at room temperature. Positive tests were also obtained with potassium permanganate solution. On account of the dark brown color of the tar solutions, unsaturation tests with bromine in carbon tetrachloride could not be run.

In addition to the above tests, the tars were analyzed for

chlorine. "Plastic C" was found to contain 35.08 percent chlorine, "Plastic D", 32.55 percent; and "Residue A", 33.85 percent. In view of the above results, it is believed that these tars are mixtures of polymerized addition products of acetyl chloride and 2-nitro-1-butene. At the present time, however, the writer has been unable to postulate a structure for these products which would harmonize with their relatively high chlorine content.

The amount of gas given off during reaction of 2-nitro-1-butene with acetyl chloride was so small as to be relatively insignificant.

The reaction of 2-nitro-1-butene with acetyl chloride at a temperature of 50° C. to 55° C. was carried out and a new unknown product, "Liquid F" was isolated. During distillation of the reaction mixture at reduced pressure, water accidently entered the apparatus. The water was removed and distillation completed on the dried water-insoluble organic layer. A dark blue liquid was obtained as the main fraction.

Redistillation of this dark blue liquid (main fraction) at an elevated temperature 50 degrees higher than in the first distillation resulted in isolation of the new unknown product, "Liquid F" accompanied by a weight loss of about 50 percent of the original liquid. This weight loss was of gases and decomposition by-products non-condensable at the temperature of the dry ice cooled trap (-78° C.) used in the distilling system.

Characterization tests on "Liquid F" showed the presence of both nitrogen and active halogen, and absence of a double bond.

The product gave a negative test with potassium permanganate in the cold. A positive test for the ketone carbonyl group was given by standard 2,4-dinitrophenyl-hydrazine reagent. Carius analysis gave 31.5 percent chlorine in "Liquid F". It is of interest to observe that this chlorine content approximates fairly closely that found in the polymeric plastics isolated from reaction of acetyl chloride and 2-nitro-1-butene. However, it has not been possible to postulate a formula which fits these particular analytical chlorine contents and the qualitative analyses.

After several weeks' storage in the cold room at -20° C., a small quantity of needle-like crystals was observed to separate from "Liquid F". Time did not permit their purification and analysis. The formation of these crystals indicated several possibilities; the "Liquid F" may have slowly crystallized on standing, or was a mixture of two compounds, or a slow decomposition produced the crystals. Inasmuch as "Liquid F" had been stored at a temperature of -20° C. since it was produced, and had been kept in a tightly stoppered container in the dark, a decomposition reaction seemed unlikely. The insolubility in sodium hydroxide solution and the negative potassium permanganate test both suggest that a change had occurred in the postulated methyl ketone group to render this resistant to alkaline cleavage. At present, it is felt that a logical structure cannot be postulated for "Liquid F".

Prolonged reaction of 2-nitro-1-butene with acetyl chloride at room temperature for 65 hours followed by redistillation of

the first deep blue distillate at much higher temperature and
pressure, (at 71° C. to 73° C. at 190 mm of Hg instead of at 30
mm of Hg pressure) gave a new fraction, termed "Liquid I". This
new product gave the same qualitative organic characterization
tests as did the 1-chloro-2-acetyl-2-nitrobutane isolated in an
earlier experiment, and as noted above. However, the deep blue
"Liquid I" product had a boiling point 14 degrees higher than the
1-chloro-2-acetyl-2-nitrobutane, and unlike the latter, darkened
to a brown color at the boiling point. These facts indicated
that "Liquid I" was not the same as 1-chloro-2-acetyl-2-nitro-
butane. The 1-chloro-2-acetyl-2-nitrobutane that was formed in
the original reaction mixture appeared to have been changed by
the much higher temperature used during distillation.

In connection with the thermal instability of the initial
reaction products of 2-nitro-1-butene and acetyl chloride, it was
observed that the initial deep blue distillate behaved as follows.
Heated in a test tube at atmospheric pressure, it began to boil
at a relatively low temperature, and rapidly turned black with
deposition of black tar. Only a slight amount of blue distillate
came off under these conditions.

All of the above facts indicated that products obtained from
reaction of 2-nitro-1-butene with acetyl chloride are extremely
sensitive to heat, and must be handled at low temperatures of
30° C. to 45° C. in order to isolate the primary product,
1-chloro-2-acetyl-2-nitrobutane.

Experimental evidence obtained so far indicates that one of

the compounds prepared in the reaction of 2-nitro-1-butene and acetyl chloride is 1-chloro-2-acetyl-2-nitrobutane; there is no final proof of this as yet. To establish the structure of the compound, quantitative analyses for carbon and hydrogen, and particularly of absolute nitrogen will be required in some future investigation.

EXPERIMENTAL

For the final work of this investigation, 11 reactions with 2-nitro-1-butene were run. Five of these were with 2-nitro-1-butene and chloroform; the other six were with 2-nitro-1-butene and acetyl chloride.

Starting Materials

Chloroform. The Baker and Adamson product, U.S.P. grade, was distilled. The fraction distilling at 60.0° C. to 61° C. was used.

Acetyl Chloride. The Matheson practical grade, code number P5104 was purified by mixing it with one-tenth its volume of dimethylaniline, refluxing for one hour, and then fractionating through a column packed with glass helices. The fraction distilling at 50.0° C. to 51.0° C. was used.

1-Nitropropane. The Eastman practical product, code number 4675, was distilled. The fraction distilling at 131.0° C. to 132.0° C. was used.

Diethylamine. The Eastman product, code number 92, was dis-

tilled. The fraction distilling at 55.0° C. to 56.0° C. was used.

Formaldehyde. The Baker and Adamson product, reagent grade, 36 percent assay, code number 1778, was used without further purification.

2-Nitro-1-butene. This compound was prepared by the method reported by Blomquist and Shelley (5). 1-Nitropropane, diethyl- amine, and formaldehyde were reacted to produce N-(2-nitrobutyl)- diethylamine. The nitro amine was purified by distillation under reduced pressure and treated with dry hydrogen chloride in toluene to produce the amine hydrochloride. This salt was de- composed by pyrolysis under a controlled reduced pressure to yield the crude 2-nitro-1-butene. The latter was then distilled under reduced pressure to give the pure nitroolefin. This was obtained in yields of 46 to 53 percent, and was a pale blue liquid of pungent irritating odor and strong lachyramatory properties. The 2-nitro-1-butene obtained distilled at 59.0° C. to 60° C. at 45 mm of Hg pressure, and had a boiling point of 118° C. by the micro method (17), uncorrected.

Storage of the 2-nitro-1-butene at room temperature resulted in its color fading to a pale yellow, and precipitation of a trace of solid polymer in the course of two weeks. This polymeri- zation was greatly retarded by storage of the nitroolefin at a temperature of -20° C. All later samples of the nitroolefin and most of its reaction products with chloroform and acetyl chlo- ride were stored at -20° C.

N-(2-Nitrobutyl)-diethylamine (intermediate for preparation

of 2-Nitro-l-butene). When 250 gm of freshly prepared, pure
N-(2-nitrobutyl)-diethylamine intermediate, a pale yellow,mobile
liquid of pleasant odor, was stored in a scrupulously clean
glass-stoppered bottle at room temperature in the desk, the com-
pound became dark brown in color, developed a strong, sharp odor,
and became somewhat viscous. This change took place in about a
month's time, even though the amine was kept in the dark and
stored under an atmosphere of nitrogen. Distillation of this ma-
terial at reduced pressure under an atmosphere of nitrogen did
not yield any N-(2-nitrobutyl)-diethylamine.

In the course of six distillations of N-(2-nitrobutyl)-
diethylamine, three distillations went smoothly, and yields of
81.3, 95.0, and 90.3 percent, respectively, were obtained. How-
ever, the other three distillations proceeded with difficulty,
had to be stopped, and gave yields of 44, 54.6, and 57 percent.
In the latter three cases, the boiling liquid turned from a de-
sired characteristic light orange to an undesirable dark red.
In one case where distillation was not stopped promptly, vigorous
decomposition occurred. Copious amounts of gas were evolved ac-
companied by excessive carbonization. In the successful distil-
lations, condensation took place in a narrow band inside the con-
denser tube and the flow of condensate was comparatively rapid
(3-4 drops per second). Condensation was dropwise in the unsuc-
cessful distillations and the condensation flow was correspond-
ingly slow (about 1 drop per second).

Reactions of 2-Nitro-1-butene and Chloroform

All experiments were carried out in a three-necked Pyrex flask, fitted with a motor-driven, mercury-sealed stirrer, thermometer, and water cooled reflux condenser. All flask connections were with ground glass taper joints. From the top of the water condenser, a tube led through a calcium chloride tube and trap to a graduate immersed in water. In this graduate, any water insoluble gases evolved during reaction were collected.

All distillations of reaction mixtures were made with a fractionating column 10 mm in diameter and about 200 mm long. The column was jacketed and contained a spiral glass insert to increase fractionating efficiency. In all cases, a dry ice trap was used to condense low boiling vapors which would pass through the water-cooled condenser.

In Experiment 1, 10.1 gm (0.1 mol) 2-nitro-1-butene and 119.5 gm (1.0 mol) chloroform were cooled in the reaction flask to -3° C. To the agitated mixture, 1.1 gm (0.02 mols) of powdered anhydrous potassium hydroxide were slowly added. The mixture turned light yellow in color and after four hours stirring, was allowed to come to room temperature and stand over night. The next day some yellow plastic material had settled out. The reaction solution was filtered to remove the solids, and the filtrate was washed with two 100-ml portions of water to which 10 ml of hydrochloric acid was added to break the emulsion and neutralize the alkali. The water insoluble chloroform layer was then

dried over anhydrous magnesium sulfate and the chloroform distilled off at room temperature under a reduced pressure of 150 mm Hg. Next, a water bath, raised finally to boiling, was used as a source of heat during the latter part of the distillation while the pressure was reduced to 50 mm Hg in order to remove unchanged 2-nitro-1-butene and other volatile material. This procedure gave an additional amount of a gummy, brown, plastic residue which was soluble in chloroform and insoluble in both petroleum ether (b. p. about 70° C.), and ethanol.

Extraction of 2 gms of this plastic with ether gave 1.15 gm of brown, brittle residue which could be powdered when dried. This dried material softened at 96° C. and melted with some gas formation at approximately 120° C. This purified plastic is here termed "Plastic A". Evaporation of the ether extract from this plastic left about 0.7 gm of a dark brown, gummy, plastic material, apparently the gummy constituent of the original plastic.

Tests on "Plastic A". A small piece of this plastic ignited readily with a bunsen burner and burned with a brilliant flame with some smoke.

A sodium fusion was run on "Plastic A" and the fusion product tested for nitrogen and halogen. A positive test was found for nitrogen, and a negative test for halogen.

The water insoluble fraction that was distilled from the reaction mixture at reduced pressure was redistilled at atmospheric pressure (736 mm). From this, 76.9 gm of chloroform (b. p. 59.5-60° C.) were recovered.

In Experiment 2, 10.1 gm (0.1 mol) 2-nitro-1-butene was added slowly to a stirred mixture of 61 gm (0.5 mol) chloroform and 1.1 gm (0.02 mol) powdered anhydrous potassium hydroxide held at 0° C. This mixture was stirred for four hours at this temperature and then processed in a manner similar to Experiment 1. From this mixture, 2.9 gm of light yellow plastic separated during the reaction period. Upon distillation of the reaction mixture at 100 mm Hg, 3.9 gm of dark brown, gummy, plastic material remained as residue while 31.0 gm of water insoluble liquid were distilled off. The brown plastic material showed the same solubility behavior as that in Experiment 1. Ether extraction of a 2 gm portion of this material left 1 gm of a brittle, yellow solid which had a softening point of about 105° C. and a complete melt at about 150° C. This purified plastic is here termed "Plastic B". Solution in and re-precipitation from acetic acid did not change these values significantly. Evaporation of the ether extract from the above plastic left about 0.5 gm of a light yellow, gummy liquid which polymerized after a few days storage.

Tests on "Plastic B". A sodium fusion was run on "Plastic B" and the fusion product tested for nitrogen and halogen. A positive test was found for nitrogen and a negative test for halogen.

The water insoluble fraction that was distilled from the reaction mixture under reduced pressure was redistilled at atmospheric pressure (742 mm). There were obtained 23.84 gm of chloro-

form distillate (b. p. 60.0-60.5° C).

In Experiment 3, 10.1 gm (0.1 mol) 2-nitro-1-butene were slowly added with stirring to a mixture of 61 gm (0.5 mol) chloroform and 0.3 gm (0.05 mol) of acetic acid. After addition was completed, the mixture was heated to the boiling point of chloroform and refluxed for 23 hours. The mixture was then cooled and the components separated by distillation. About 0.9 gm of brown plastic material was obtained, but 80 percent of the 2-nitro-1-butene and 83 percent of the chloroform were isolated unchanged, indicating that very little, if any reaction occurred with the chloroform. No evidence was obtained of interreaction between the two starting materials.

Experiment 4 was run with the same amounts of starting materials and under the same temperature conditions as Experiment 3. In addition, the mixture was subjected for 12 hours to ultraviolet light from a 100 watt General Electric lamp, type H-4. The mixture was then cooled and distilled. As in Experiment 3, plastic material was obtained, but again the greater part of the starting materials were recovered unchanged. Indeed 58 percent of the 2-nitro-1-butene and 64 percent of the chloroform were recovered. No evidence was obtained of interreaction between the two starting materials.

Experiment 11 was run with the same amounts of starting materials and under the same conditions of reaction time and temperature as for Experiment 2. In Experiment 2, however, the reaction mixture had been washed twice with water before distilla-

tion and it appeared that possibly an unknown water-soluble
product had been lost in the water wash liquid. In Experiment 11,
seven water extractions were made and tested for water soluble
compounds. The water-insoluble layer was then distilled as in
Experiment 2, and it was found that substantially the same re-
sults were obtained, thus reproducing the earlier experiment.
No unknown water-soluble product was obtainable.

Reactions of 2-Nitro-1-butene and Acetyl Chloride

These experiments were carried out in the same type of ap-
paratus as used for the reactions of 2-nitro-1-butene and chloro-
form. All experiments were run using 10.1 gm (0.1 mol) 2-nitro-
1-butene and 15.7 gm (0.2 mol) acetyl chloride. All distillations
of reaction mixtures were made with the same type of apparatus as
described under the reactions of 2-nitro-1-butene and chloroform.

Experiment 5 was started at 0° C. No reaction appeared to
take place, so the mixture was slowly heated. The mixture began
to boil at a temperature of 70° C. The internal liquid tempera-
ture continued to rise and the mixture grew darker in color;
at 75.0° C. the heating jacket was shut off. The temperature
rose to 98° C., even though the heating jacket had been removed.
At this temperature, there was excessive carbonization and de-
composition.

Experiment 6 was run in the same manner as Experiment 5,
except for holding the temperature to a maximum of 75° C. The
experiment ran for 18 hours during which time 157 ml of gas were

evolved and collected over water. Orsat analysis of this gas showed 3.9 percent carbon dioxide, 14.4 percent oxygen, 32.3 percent expressed as carbon monoxide and hydrogen, and 49.4 percent nitrogen by difference. Most of the gas was evolved during the heating period from room temperature to 75° C. At the end of the reaction period, the mixture was dark brown in color. This mixture was then distilled at a reduced pressure of 50 mm Hg. Small amounts of a deep blue liquid began to distill over almost at once, part of the condensate collecting in the receiver, part in the dry ice trap. The distillation flask was heated with an oil bath which was slowly raised from 65° C. to 96° C. as distillation progressed. When the latter temperature was reached, however, condensate stopped coming over and the absolute pressure in the system began to rise. At this point, a vacuum pump was connected to the system in an attempt to lower the absolute pressure and remove more distillate without additional heating for the distillation flask. While this change was being made, however, the material in the distilling flask, already very dark in color, began to bubble strongly and give off white vapors. The distilling flask was cooled with ice water, but the apparent decomposition could not be stopped. Decomposition was not violent and no explosion or splattering of material resulted. The residue left in the flask appeared to be mainly carbon.

A clear, deep blue liquid was found in the distillation receiver. This liquid was mobile, had a strong, pungent odor, and a weight of 7.80 gm. This liquid is here termed "Liquid A".

Tests on "Liquid A". A sodium fusion was run on "Liquid A" and the fusion product tested for nitrogen and halogen. Positive tests were found for nitrogen and halogen. The liquid gave a positive test with alcoholic silver nitrate solution. Test for unsaturation with bromine in carbon tetrachloride was negative. A test with neutral potassium permanganate solution was positive.

"Liquid A" had a b. p. of 105° C. (micro method of McElvain) (17) at 740 mm. Analysis showed the presence of 11.95 percent chlorine.

From the dry ice trap, 4.5 gm of a light green liquid of irritating odor was recovered. It appeared that this liquid was unreacted acetyl chloride mixed with the blue green color of unreacted 2-nitro-1-butene. The decomposition residue remaining in the distilling flask amounted to 11.2 gm. This was not analyzed since it appeared to be mainly carbon.

Experiment 7, Synthesis of Postulated 1-Chloro-2-acetyl-2-nitrobutane. Experiment 7 was run in the same manner as Experiment 6, except that the temperature was held to a maximum of 45° C. During the reaction time of twenty-four hours, 40 ml of gas was evolved. The reaction mixture became a dark green color. It was distilled at 50 mm and gave 1.8 gm of a light blue mobile liquid which collected in the dry ice cooled trap. This liquid is here termed "Liquid B".

At this point, the distilling pressure was reduced to 10 mm of Hg and gave 17.5 gm of deep blue liquid which distilled over a temperature range of 30° C. to 35° C. It had a somewhat sweetish

pungent odor. This liquid is here termed "Liquid C". When the distillation was continued, 0.9 gm of a cloudy green liquid distilled over a temperature range of 95° C. to 100° C. This liquid was somewhat viscous and slowly turned brown on standing. This liquid is here termed "Liquid D". The residue in the distilling flask amounted to 1.2 gm of black carbonaceous material. This residue was not analyzed.

Tests on "Liquid B". A sodium fusion was run on "Liquid B" and the fusion product tested for nitrogen and halogen. Nitrogen test was negative, halogen test positive. The liquid gave a positive test with alcoholic silver nitrate solution. Test for unsaturation with bromine in carbon tetrachloride was negative, a similar test with neutral potassium permanganate solution was also negative.

Tests on "Liquid C". A sodium fusion was run on this liquid and gave positive tests for both nitrogen and halogen. Bromine unsaturation test was negative. Test with potassium permanganate was positive. Test with alcoholic silver nitrate was positive. The sodium amalgam test for nitro groups was positive.

"Liquid C" had a b. p. of 97° C. (uncorrected) at 740 mm. The liquid turned dark and decomposed at the boiling point.

Tests on "Liquid D". A sodium fusion was run on this liquid and gave positive test for nitrogen, and positive test for halogen. The unsaturation test with bromine was negative and the potassium permanganate test was positive. Test with alcoholic silver nitrate was positive.

"Liquid D" had a b. p. of 160° C. to 165° C. at 740 mm. This liquid decomposed at the boiling point.

Redistillation of 8 gm of "Liquid C" at 30 mm gave 2.5 gm of deep blue liquid with a boiling point range of 32° C. to 35° C. No other products were recovered from this distillation; only a gram of black tar remained in the distilling flask. Nothing was condensed in the dry ice trap. The remaining weight of material was evolved as gases uncondensable at -78° C. The dark blue condensate obtained had a pungent, rather sweetish odor and some lachrymatory effect. This liquid is here termed "Liquid E".

Tests on "Liquid E", Postulated Product 1-Chloro-2-acetyl-2-nitrobutane. A sodium fusion was run on this liquid and gave positive tests for both nitrogen and halogen. Unsaturated test with bromine was negative. The liquid also gave positive tests with potassium permanganate solution and with alcoholic silver nitrate. The sodium amalgam test for nitro groups and the 2,4-dinitrophenylhydrazine test for a ketone carbonyl group were both positive. The liquid was insoluble in water, but partly soluble in 5 percent sodium hydroxide solution with evolution of heat. Shaking of the compound with water gave off no heat nor was any evidence of reaction observed. Boiling point of this liquid, by micro method, was found to be 98° C.

Chlorine analysis of "Liquid E" by the Carius method gave 19.12 percent chlorine present; the theoretical chlorine calculated for 1-chloro-2-acetyl-2-nitrobutane is 19.75 percent.

Analysis for carbonyl group content by hydroxyl amine titration, using the method described by Siggia (18) gave 96.9 percent of the theoretical value of the carbonyl group content that should be present for 1-chloro-2-acetyl-2-nitrobutane.

Experiment 8 was run in the same manner as Experiment 7, except for allowing a higher temperature of 60 °C. to 65° C. for reaction. The experiment was run for 43 hours during which time 160 ml of gas were evolved and collected over water. Orsat analysis of this gas showed 0.2 percent carbon dioxide, 14.8 percent oxygen, 71.6 percent expressed as carbon monoxide and hydrogen, and 13.3 percent nitrogen by difference. Part of this gas was evolved during the heating period from room temperature to 60° C. There was no difficulty in holding the temperature within the proper range except during an hour period when the writer was called away. During this time the temperature rose to 85° C. but was lowered to 60° C. at once upon the writer's return to the laboratory. At the end of the 43 hour period, the mixture was black and some black deposit had come out on the flask walls. This mixture was then distilled at a reduced pressure of 30 mm. Boiling began at room temperature and colorless mobile liquid began to distill. During the distillation, the mixture was slowly heated with an oil bath. At a bath temperature of 77° C., however, the pressure began to rise slowly. A vacuum pump was connected to the system and the pressure lowered to 15 mm. When the flask was now heated with the oil bath, the pressure began to rise again and white vapors appeared in the distilling flask.

At this stage the heating was discontinued. Meanwhile, 7.70 gm of the colorless distillate (vapor temperature 28° C. to 36° C. at 30 mm Hg) had collected. A test on a portion of the liquid with ethyl alcohol caused the formation of ethyl acetate, indicating that the distillate was mainly acetyl chloride.

The black tar remaining in the distillation flask was extracted with ether. It gave a dark brown solution, leaving a dark brown, gummy residue. Evaporation of the ether solution gave 1.42 gm of a dark, sticky, tar-like material. This is here termed "Plastic C".

The gummy ether insoluble residue was extracted with chloroform, the solution refluxed for fifteen minutes, and filtered. The dark brown filtrate was evaporated and gave 6.28 gm of a dark brown, sticky, tar-like material. This is here termed "Plastic D".

The residue, remaining after the chloroform filtration, was dried; 8.48 gm of a black, somewhat plastic material was obtained. This residue is here termed "Residue A".

Tests on Plastics "C" and "D" and "Residue A". Sodium fusions were run on all three of these materials and the fusion products tested for nitrogen and halogen. Nitrogen and halogen were found in all three of these products. Due to the dark brown color of these materials, satisfactory bromine unsaturation tests could not be run. Tests with potassium permanganate solution on all three products were positive. Satisfactory sodium amalgam tests for the nitro group could not be used because of the dark color

of their solutions. Alcoholic silver nitrate gave positive tests
with all three materials.

Chlorine analyses by means of the Parr Bomb method gave
35.08 percent for "Plastic C", 32.55 percent for "Plastic D", and
33.85 percent for "Residue A".

Experiment 9, Isolation of New Unknown Product, "Liquid F".

Experiment 9 was run in the same manner as Experiment 8, ex-
cept the temperature was held in the range of 50° C. to 55° C.
The experiment was run for 42 hours. No gas was evolved and at
the end of the reaction period, this reaction mixture was deep
blue, and some carbon formation appeared to be starting. The
mixture was distilled at a reduced pressure of 30 mm, a few drops
of blue condensate came over at room temperature as soon as the
pressure was lowered. The distilling flask was slowly warmed with
an oil bath and the blue liquid began to distill. At this point
the writer was called away for a few minutes; when he returned,
it was found that some water had sucked back through the safety
trap attached in line to the water suction pump, thus flooding
the distillation apparatus. Rather than abandon the experiment,
it was decided to clean out the water and finish the distillation.
The dark blue distillate was insoluble in water and most of it
was recovered by drawing off the water and extracting the blue
distillate with ether. The blue ether solution was then distilled
at 100 mm and yielded 3.90 gm of dark blue liquid with a boiling
point range of 80° C. to 83° C. This liquid is here termed
"Liquid F". A weight loss of about 50 percent of the starting

material was observed as a result of this distillation.

After the blue condensate from the distillation of the re-
action mixture at 30 mm had stopped, the pressure was lowered to
5 mm and heating with the oil bath continued. At a boiling
point range of 54° C. to 58° C., 0.8 gm of a light green distil-
late came over. This distillate, upon standing over night, de-
posited some short needle-like crystals. These were filtered
off and washed with acetone, yield 0.05 gm. These crystals are
here termed "Crystals A".

The distilling flask residue was black and somewhat tarry
and weighed 3.5 gm. This residue was extracted with alcohol in
an attempt to recover more of the crystalline product. The re-
sulting dark brown solution was concentrated on the steam bath
and allowed to stand over night. No crystallization took place,
however, and only a brown tar remained when the solvent was
evaporated.

Tests on "Liquid F". A sodium fusion was run on this liquid
and the fusion products gave positive tests for both nitrogen and
halogen. Both bromine and potassium permanganate tests for un-
saturation were negative. Alcoholic silver nitrate gave a
positive test. Sodium amalgam test for nitro group was positive.
A positive test for carbonyl group was found with 2-4-dinitro-
phenylhydrazine. "Liquid F" was insoluble in and unreactive
toward water, thus showing absence of acetyl chloride.

Analysis of "Liquid F" by means of the Carius method gave
31.58 percent chlorine.

The boiling point of "Liquid F" was 108° C. to 110° C. at 740 mm. Decomposition occurred at the boiling point.

Tests on "Crystals A". These crystals were light brown in color and were found to be insoluble in warm acetone, ether, and chloroform. They were soluble in ethyl alcohol and in water. The water solution was acid to litmus. These crystals had a softening point at 147° C. and a melting point at 148° C. with decomposition. There was no noticeable color change on decomposition but gas appeared to be evolved. The amount of crystals on hand (0.05 gm) was insufficient to permit any further tests.

Experiment 10 was run for 65 hours at room temperature; i.e., about 31° C. No gas was evolved. The mixture was dark green in color; no carbon formation was observed. It was distilled at room temperature under a reduced pressure of 30 mm. A few drops of pale blue liquid appeared in the water condenser, but no blue condensate was observed in the fractionating column until the distilling flask was gently heated with an oil bath. Distillation was stopped at this point and 3.0 gm of light blue mobile liquid of irritating odor were recovered from the dry ice trap. No tests were run on this liquid (here termed "Liquid G").

A dark green liquid (19.25 gm) remained in the distilling flask after the removal of "Liquid G". This green liquid (here termed "Liquid H") was slowly cooled in a dry ice bath to -50° C. by 10-degree increments in an attempt to crystallize out a solid compound. Although the liquid became stiff at a temperature somewhat below -50° C., there was no crystal formation.

Nine grams of the above "Liquid H" were distilled at a re-
duced pressure of 190 mm Hg. The distilling flask was slowly
heated with an oil bath in a range of about 100 to 150° C., and
the first fraction, 0.86 gm of a blue liquid, taken off in a
boiling range of 65° C. to 72° C. The second fraction, 1.48 gm
of a deep blue liquid, was taken off in a boiling range of 71-
73° C. at 190 mm Hg. This liquid is here termed "Liquid I".
There appeared to be more blue condensate in the fractionating
column that would not come over unless the oil bath temperature
was increased. In order to prevent possible decomposition of the
distilling flask residue at a higher temperature, the oil bath
temperature was held constant (145° C.) and the pressure lowered
to 45 mm. A small amount of a third fraction, 0.5 gm of blue
liquid came over quickly ("Liquid K").

The material remaining in the distilling flask was very dark,
but still appeared to contain some yellow liquid. This could not
be distilled over, even with pressure lowered to 11 mm Hg and
oil bath temperature raised to 200° C. Upon cooling, 2.2 gm of
dark, sticky residue remained in the distilling flask.

Tests on "Liquid I". The boiling point of this liquid,
using the micro method of McElvain, was found to be 112° C. (un-
corrected). The sample changed to a brown color at this tempera-
ture.

Test with alcoholic silver nitrate was positive within a
few seconds at room temperature. A 2,4-dinitrophenylhydrazine
test for a ketone group was definitely positive.

SUMMARY

The synthesis of 2-nitro-1-butene by the technique of Blom-
quist and Shelley was confirmed. A 53 percent yield of the com-
pound was obtained instead of the 73 percent yield which they re-
ported.

N-(2-Nitrobutyl)-diethylamine, one of the intermediates in
the 2-nitro-1-butene preparation, was observed in certain cases
to partially decompose during purification. This step was found
to be the most critical in the preparation of the 2-nitro-1-
butene. In certain cases, yields of 90 percent of N-(2-nitro-
butyl)-diethylamine were obtained as compared to the 79 percent
yields reported previously. The purified amine was observed to
slowly decompose upon storage at room temperature.

The reaction of 2-nitro-1-butene and chloroform did not,
under any of the conditions employed, give an addition product.
In three cases where reaction occurred, polymers of 2-nitro-1-
butene were formed (Plastics "A" and "B"). In two cases in which
the polymerization reaction was suppressed, the starting materials
were recovered unchanged.

The reaction of 2-nitro-1-butene and acetyl chloride at a
temperature of 45° C. gave a new compound postulated as 1-chloro-
2-acetyl-2-nitrobutane. The structure of this compound was sup-
ported by characterization tests and by the results of quanti-
tative analyses for chlorine and titration of the ketone carbonyl
group in the compound. The product was obtained in 29.8 percent

yield.

The reaction of 2-nitro-1-butene with acetyl chloride, when
allowed to occur for only a short time at 85° C., resulted in a
mixture of viscous tars. Characterization tests and the results
of quantitative analyses for chlorine indicated that these tars
were also addition products of 2-nitro-1-butene and acetyl chlo-
ride. From the unexpected high chlorine content obtained (32.6
percent to 35.1 percent) in the tarry products, it was not pos-
sible to postulate a plausible polymeric structure for them. Ex-
tractive digestions on the tars did not make particularly marked
changes on the chlorine contents of the respective fractions so
obtained.

The reaction of 2-nitro-1-butene with acetyl chloride at a
temperature of 55° C. over a prolonged period of time gave a deep
blue liquid product, "Liquid F". Characterization tests and
quantitative chlorine analysis showed that this product differed
from the 1-chloro-2-acetyl-2-nitrobutane product. "Liquid F"
may have been changed by a very brief accidental contact with
water but considering all the facts, did not appear to be. There
is possible significance in the observation that the chlorine
content of "Liquid F" was about the same as the high chlorine con-
tent found in the tar-products from higher reaction temperature.
It did not appear that a plausible structure could be postulated
for "Liquid F" at this time, although it had the characteristics
of a distinct entity.

ACKNOWLEDGMENTS

LITERATURE CITED

(1) Bahner, C. T.
    Aliphatic nitro derivatives of halo esters and method for
    preparing them. U.S. Patent 2,425,276. August 5, 1947.

(2) Bahner, C. T.
    Beta diketones and process for preparing them. U.S.
    Patent 2,447,626. August 24, 1947. Original not seen.
    Abstract in Chem. Abstr. 42:8819. 1948.

(3) Bahner, C. T.
    Nitroolefin derivatives of malonic esters and process
    for preparing same. U.S. Patent 2,431,451. November 25,
    1947. Original not seen. Abstract in Chem. Abstr. 42:
    2615. 1948.

(4) Beilstein, F. K.
    Handbuch der Organischen Chemie, Berlin; Julius Springer,
    1918. Band 1, p. 778.

(5) Blomquist, A. T., and T. H. Shelley, Jr.
    Preparation of 2-nitro-1-alkenes from nitro amines. Amer.
    Chem. Soc. Jour. 70: 147-149. 1948.

(6) Blomquist, A. T., W. J. Tapp, and J. R. Johnson.
    The preparation of 2-nitropropene polymer and of derived
    vinylamine polymers. Amer. Chem. Soc. Jour. 67: 1519-
    1522. 1945.

(7) Bruson, H. A., W. Niederhauser, T. Riener, and W. F. Hester.
    The chemistry of acrylonitrile. VI. Cyanoethylation of
    the haloforms. Amer. Chem. Soc. Jour. 67: 601-602.
    1945.

(8) Buckley, G. D.
    Aliphatic nitro-compounds. Part X. Action of Grignard
    reagents on the alpha nitroolefines. Jour. Chem. Soc.
    (London) pt. 2. 1494-1497. 1947.

(9) Buckley, G. D., and E. Ellery.
    Aliphatic nitro-compounds. Part XI. Preparation of nitro-
    paraffins by 1:4 addition of organometallic halides to
    alpha nitroolefins. Jour. Chem. Soc. (London) pt. 2,
    1497-1500. 1947.

(10) Buckley, G. D., and C. W. Scaife.
    Aliphatic nitro-compounds. Part I. Preparation of nitro-
    olefins by dehydration of 2-nitroalcohols. Jour. Chem.
    Soc. (London) pt. 2. 1471-1472. 1947.

(11) Gold, M. H.
Method of preparing unsaturated nitro compounds. U.S.
Patent 2,414,594. January 21, 1947.

(12) Gold, M. H.
Nitroolefins by catalytic cleavage of nitroalcohol
esters. Amer. Chem. Soc. Jour. 68: 2544-2546. 1946.

(13) Hass, H. B., and E. F. Riley.
The nitroparaffins. Chem. Reviews 32: 373-430. 1943.

(14) Heath, R. L., and J. D. Rose.
Aliphatic nitro compounds. Part VI. Reaction of alpha
nitroolefins with hydrochloric acid. Jour. Chem. Soc.
(London) pt. 2. 1485-1486. 1947.

(15) Heath, R. L., and J. D. Rose.
Aliphatic nitro compounds. Part VII. Preparation of
2-nitroalkylamines. Jour. Chem. Soc. (London) pt. 2.
1486-1489. 1947.

(16) Lambert, A., J. D. Rose, and B. C. L. Weedon.
Aliphatic nitro compounds. XIX. Friedel-Crafts reactions
with alpha and beta nitroolefins. Jour. Chem. Soc.
(London) pt. 1. 42-46. Original not seen. Abstract in
Chem. Abstr. 43: 6993.

(17) McElvain, S. W.
The characterization of organic compounds. New York:
The Macmillan Company. 282 p. 1949.

(18) Siggia, S.
Quantitative organic analysis via functional groups.
New York: John Wiley & Sons. 152 p. 1949.

(19) Remick, A. E.
Electronic interpretations of organic chemistry. New
York: John Wiley & Sons. 600 p. 1949.