the cold trap, and only 2.2 g. of *n*-naphthol was recovered by acidification of the aqueous mother liquor.

Anal. Calcd. for $C_{11}H_8F_2O$: C, 68.02; H, 4.17; F, 19.57. Found: C, 68.38; H, 4.21; F, 18.92.

Tris(2-naphthyl) orthoformate. Crystallization of the crude orthoformate (for separation from the corresponding difluoromethyl ether, see above) from a mixture of toluene and hexane gave 5.2 g. of fine, white needles melting at 137–150°. The melting-point range was not narrowed by repeated crystallization from other solvents such as ethyl alcohol and isopropyl alcohol–toluene. Analytical data, solubility and chemical behavior, and the infrared spectrum are consistent with the assigned orthoformate structure.

Anal. Calcd. for $C_{31}H_{22}O_3$ C, 84.14; H, 5.02. Found: C, 84.05; H, 5.22.

α,α-Difluoro-2,4-dimethylanisole. The 2,4-xylenol was purchased from the Eastern Chemical Corp. At the end of the reaction there was no recovered chlorodifluoromethane in the cold trap, and the aqueous mother liquor gave no phenolic precipitate on acidification. The ether, a fruity-smelling liquid, boiled at 70° (12 mm.). A sizeable distillation residue underwent rapid decomposition, preventing isolation of the ortho ester.

Anal. Calcd. for $C_9H_{10}F_2O$: C, 62.78; H, 5.87; F, 22.07. Found: C, 62.58; H, 6.06; F, 21.82.

α,α-Difluoro-4-nitroanisole. The sodium salt of *p*-nitrophenol has very limited solubility in strong sodium hydroxide solutions. Consequently, agitation in this experiment was very inefficient, and the low yield of difluoromethyl ether obtained doubtless reflects this condition as well as any inherent lower reactivity of the *p*-nitrophenoxide ion. Twenty-one per cent of the chlorodifluoromethane was recovered unchanged in the cold trap, and acidification of the water layer yielded 50% of unchanged *p*-nitrophenol. The product was not distilled but was crystallized from petroleum ether (b.p. 30–60°) as shining, off-white plates, m.p. 32–32.5°.

Anal. Calcd. for $C_7H_5F_2NO_3$: C, 44.45; H, 2.67; F, 20.09; N, 7.41. Found: C, 44.68; H, 2.91; F, 20.37; N, 7.75.

1-Difluoromethoxy-4-methoxybenzene. Reaction of chlorodifluoromethane was complete as evidenced by the lack of any condensed gas in the cold trap. The product, a fruity-smelling liquid, boiled at 108° (29 mm.). A 10–12-g. residue remained after the distillation (see next section).

Anal. Calcd. for $C_8H_8F_2O_2$: C, 55.17; H, 4.63; F, 21.82. Found: C, 55.30; H, 4.87; F, 21.18.

Tris(p-methoxyphenyl) orthoformate. From the still residue left after distillation of the difluoromethyl ether 2 g. of the orthoester was isolated by crystallization from cyclohexane. The shining, white plates, melted at 50–51°.

Anal. Calcd. for $C_{22}H_{22}O_6$: C, 69.09; H, 5.80. Found: C, 68.82; H, 6.05.

EASTON, PA.

[CONTRIBUTION FROM ORGANIC CHEMISTRY BRANCH, CHEMISTRY DIVISION, U. S. NAVAL ORDNANCE TEST STATION]

Action of the Lewis Acids, Stannic Chloride and Boron Trifluoride, upon Nitrate Esters[1]

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The action of the Lewis acids, stannic chloride and boron trifluoride, upon several representative nitrate esters, namely, *n*-butyl, isopropyl, benzyl, and triphenylmethyl nitrates, has been investigated. Products have been isolated and free-radical mechanisms have been postulated which fit the experimental observations.

In previous studies[2] involving the polymerization of glycidyl nitrate, it was found that denitration always occurred to some extent when this polymerization was catalyzed by stannic chloride. It seemed evident, therefore, that this observed denitration was due to some reaction involving the Lewis acid and the nitrate ester moiety of the glycidyl nitrate monomer or polymer. In an attempt to elucidate the nature of this Lewis acid nitrate ester interaction, a study of the action of stannic chloride and boron trifluoride upon model simple nitrate esters, namely, *n*-butyl, benzyl, isopropyl, and triphenylmethyl nitrate, was undertaken.

When equimolar amounts of *n*-butyl nitrate and stannic chloride were mixed at room temperature, a single phase resulted, and no immediate reaction was apparent. After about one hour, greenish-yellow crystals formed in the reaction mixture and gradually increased in amount. About four hours after mixing, a vigorous decomposition took place with evolution of much heat and gas. Infrared analysis of the gas fraction showed it to contain nitric oxide and possibly nitrous oxide. Since the gases were colorless, however, it was assumed that no nitrogen dioxide (or tetroxide) was present. Butyl butyrate was isolated in small amounts from the residue, which contained considerable amounts of tarry material. The greenish-yellow crystals which were deposited on the walls were identified as dinitrosyl hexachlorostannate, $(NO)_2SnCl_6$, by tin and chlorine analyses and by comparison of the x-ray powder patterns with that of an authentic sample prepared as described by Rheinboldt and Wasserfuhr[3] from nitrosyl chloride and stannic chloride.

Several attempts were made to determine the nature of any chemical change that might take place between the time of mixing of stannic chlo-

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(1) Reported at the Tenth Meeting of the Joint Army-Navy-Air Force Solid Propellant Group at Wright Air Development Center, Dayton, Ohio, June 2–4, 1954.

(2) J. G. Meitner, C. J. Thelen, W. J. Murbach, and R. W. Van Dolah, unpublished work.

(3) H. Reinboldt and R. Wasserfuhr, *Chem. Ber.*, 60, 732 (1927).

ride and butyl nitrate and the time of the violet reactions.

The infrared spectrum of an equimolar mixture of butyl nitrate and stannic chloride remained essentially the same during the "induction period" of the reaction except for an over-all decrease in transmittance (due to fogging of the salt windows by stannic chloride). The only observed change was an increase in the peak at 2.9 μ in the OH stretch region.

Similarly, when aliquots of the reaction mixture taken during the induction period were poured into water and the organic materials extracted into petroleum ether, no substituents other than *n*-butyl nitrate could be found.

Other conceivable products, such as butyraldehyde, butyl butyrate, and butyl alcohol, would have been extracted into the petroleum ether. However there was no sign of any of these materials, and the infrared curve of all of these petroleum ether extracts was nearly identical with that of *n*-butyl nitrate. After the reaction had proceeded to the vigorous stage, water was added to the sirupy residue and the mixture extracted with petroleum ether to yield a material whose infrared spectrum was essentially that of *n*-butyl *n*-butyrate. Indeed, the only noticeable change was the production of a small amount of dinitrosyl hexachlorostannate in the gas phase above the reaction mixture. The fact that this reaction did occur in the gas phase was confirmed by conducting a run in a divided vessel where the liquids were not in contact with each other, but where their vapor phases could freely intermix. In this experiment, the reaction proceeded just as though the reactants were mixed, including the final violent reaction.

There appeared to be very little difference in the induction period of the reaction when the molar ratio of stannic chloride to butyl nitrate varied from 1:5 to 2:1.

The reaction of stannic chloride with benzyl nitrate was similar to that with butyl nitrate, except that the time between mixing and violent reaction was only a few minutes and their was no observed formation of dinitrosyl hexachlorostannate. The reaction seemed to be somewhat cleaner, as evidenced by higher yields of isolable products. Thus, benzaldehyde was isolated as its 2,4-dinitrophenylhydrazone in *ca.* 45% yield from this reaction. Benzaldehyde was likewise obtained as a product of the reaction of dinitrosyl hexachlorostannate upon benzyl nitrate.

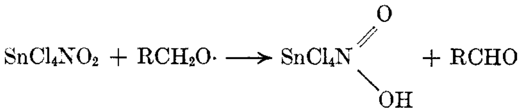
The action of stannic chloride upon triphenylmethyl nitrate appeared to be somewhat anomolous. There appeared to be no interaction between stannic chloride and triphenylmethyl nitrate when the two were mixed; however, since these compounds are not miscible, a solvent (diethyl ether) was used. The reaction appeared to be cleaner than the other degradations studied, crude triphenylmethane being isolated in nearly quantitative yield.

The substitution of another powerful Lewis acid, boron trifluoride, for the stannic chloride led to analogous reactions with the nitrate esters of butyl alcohol, isopropyl alcohol, benzyl alcohol, and triphenyl carbinol. Thus, butyl butyrate was isolated in low yield from the reaction between *n*-butyl nitrate and boron trifluoride, benzaldehyde and benzoic acid from benzyl nitrate, triphenylmethane and triphenylcarbinol from triphenylmethyl nitrate, and acetone from isopropyl nitrate.

Any mechanism derived from the experimental facts can be, at best, highly speculative, but it seemed desirable to demonstrate that one could be derived which would fit the experimental observations. The choice between a free-radical and an ionic mechanism is not an obvious one. The observed induction periods and the explosions which occurred in certain instances seemed typical for a free-radical reaction, while the catalysis by strong electrophiles such as stannic chloride and boron trifluoride pointed to the possibility of an ionic type of formulation. The free radical mechanism is discussed here.

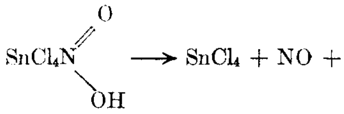
The reactions considered to be the important steps in the nitrate–ester–Lewis acid reaction are the following:

$$RCH_2ONO_2 + SnCl_4 \longrightarrow SnCl_4NO_2 + RCH_2O\cdot \quad (1)$$



$$SnCl_4NO_2 + RCH_2O\cdot \longrightarrow SnCl_4N(=O)OH + RCHO \quad (2)$$

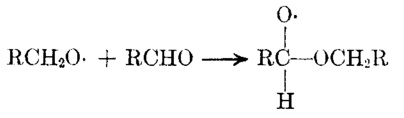
I



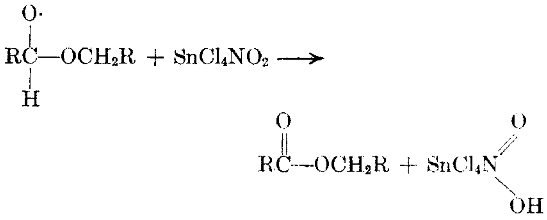
$$SnCl_4N(=O)OH \longrightarrow SnCl_4 + NO + HO\cdot \quad (3)$$

$$NO + SnCl_4 \longrightarrow NOCl + \cdot SnCl_3 \quad (4)$$

$$2NOCl + SnCl_4 \longrightarrow (NO)_2SnCl_6 \quad (5)$$



$$RCH_2O\cdot + RCHO \longrightarrow RCH(O\cdot)-OCH_2R \quad (6)$$



$$RCH(O\cdot)-OCH_2R + SnCl_4NO_2 \longrightarrow RC(=O)-OCH_2R + SnCl_4N(=O)OH \quad (7)$$

It seems difficult to envision initiation to be other than the coordination of the nitrate ester group with the electrophile (stannic chloride in this case) and cleavage of the O—N bond as in step (1). For the propagation steps, the unstable intermediate I (reaction 2) has been postulated which can propagate by chain-branching step (3).

Additional chain-branching steps may be written, but these will not be considered here.

Termination steps may be induced from the initiation and propagation steps. Reactions (4) and (5) have been introduced to explain the formation of dinitrosyl hexachlorostannate.

The available evidence seems to point to a strong autocatalysis *via* various chain-branching steps. Thus, the rate can become very fast after the reaction has proceeded only a very small extent.

The reaction of benzyl nitrate with stannic chloride to yield benzaldehyde may be formulated as in steps (1) and (2).

The products observed in the case of the boron trifluoride reactions can be explained by substitution of reactions similar to the initiation and propagation steps (1), (2) and (3).

The reaction between isopropyl nitrate and boron trifluoride was not very thoroughly investigated. The indications are that the reaction is fairly complex. However, acetone was identified as one of the products by its isolation in low yield as the 2,4-dinitrophenylhydrazone. The formation of acetone from isopropyl nitrate seems to be directly analogous to the formation of benzaldehyde from benzyl nitrate, and a similar sequence of reactions may be written.

The relatively high yields of triphenylmethane obtained from triphenylmethyl nitrate and either stannic chloride or boron trifluoride are attributed to the cleavage of the C—O bond of the triphenylmethyl nitrate in preference to the O—N bond, the resulting radical abstracting a hydrogen atom from the solvent:

$$(C_6H_5)_3CONO_2 + SnCl_4 \text{ (or } BF_3) \longrightarrow (C_6H_5)_3C\cdot + ONO_2SNCl_4 \text{ (or } ONO_2BF_3)$$

$$(C_6H_5)_3C\cdot + RH \longrightarrow (C_6H_5)_3CH + R\cdot$$

The triphenylcarbinol observed in the boron trifluoride-triphenylmethyl nitrate reaction very likely arose from the decomposition of the triphenylmethyl nitrate, as previously observed.[4,5]

Since this work was completed, an article has appeared in which the action of stannic chloride and of sulfuric acid upon ethyl nitrate was briefly studied.[6] The observations are very similar to those reported here, with the initial induction period and the final violent reaction yielding oxides of nitrogen.

EXPERIMENTAL

Reaction of n-butyl nitrate with stannic chloride. In order to have a sizable amount of the stannic chloride-butyl nitrate reaction product, twelve runs were made in the following manner: Stannic chloride, 13.02 g. (5.84 cc., 0.050 mole), and butyl nitrate, 5.97 g. (5.68 cc., 0.050 mole), were mixed and allowed to stand until the violent reaction took place (*ca.* 4 hr.). Each run was worked up as follows: The mixture was diluted with water and extracted with ether. To the mixture of ether, water, and reaction product was added solid sodium bicarbonate until carbon dioxide evolution ceased. The ether layer was removed, shaken once with saturated sodium bicarbonate solution, and dried over anhydrous magnesium sulfate. The ether extracts from all the runs were filtered and combined; and the ether was removed by distillation, the residue being transferred to a small distilling flask. In order to avoid polymerization observed in previous attempts to distill this product, the distillation was conducted at 1 mm. and the distillate, *ca.* 4.5 g., (10.4%) was collected in a Dry Ice trap, b.p. 30° (1 mm.), n_D^{20} 1.4047.[7] The infrared spectrum on this material was nearly identical with that of an authentic sample of *n*-butyl butyrate (prepared from *n*-butyl alcohol and *n*-butyryl chloride).

Saponification of stannic chloride-butyl nitrate reaction product. A sample of 1.00 g. of the product obtained above was added to a solution of 1.00 g. of sodium hydroxide and 20 cc. of water, and the mixture was refluxed 5 hr. The mixture was extracted with a total of 25 cc. of ether, and the extract was dried over anhydrous magnesium sulfate. The dried ether extract was filtered and the ether was removed by distillation. To the residue was added 1.00 g. of α-naphthyl isocyanate and this mixture was heated over the steam bath for 2 hr., after which time it was extracted with hot benzene. Evaporation of the benzene extract left an oil which gradually crystallized upon cooling. After one recrystallization from 10 cc. of ligroin (b.p. 60–80°) 0.48 g. of crystals, m.p. 65°, were collected, m.p. 70–71° after a second recrystallization, m.p. 70.5–71° when mixed with an authentic sample of *n*-butyl α-naphthyl urethan.

Isolation and characterization of the intermediate in the stannic chloride butyl nitrate reaction. The greenish-yellow solid from one of the butyl nitrate-stannic chloride runs was collected by filtering the reaction mixture through a sintered disk in a nitrogen atmosphere before the end of the induction period. This solid crystalline material vigorously evolved nitrogen dioxide upon addition of water. When aqueous silver nitrate was added to an acidified aqueous solution of this material, a precipitate of silver chloride appeared. Volhard titration of a sample showed it to contain 54.23% chlorine. A polarographic determination of tin showed the tin content to be 29.1 ± 0.9%.

Anal. Calcd. for $(NO)_2SnCl_6$: Cl, 54.34%; Sn, 30.32%.

Dinitrosyl hexachlorostannate. This compound was prepared by the procedure of Rheinboldt and Wasserfuhr.[3] To a solution of 0.05 mole (13.02 g., 5.84 cc.) of stannic chloride in 25 cc. of spectro grade carbon tetrachloride was added dropwise with agitation a solution of 0.20 mole (4.47 cc.) of purified nitrosyl chloride in 25 cc. of carbon tetrachloride. The nitrosyl chloride had been purified by two successive partial freezings and three distillations. A yellow-green precipitate appeared as the nitrosyl chloride was added. The product was filtered, taking precautions to exclude moisture, and was stored in a sealed ampoule. The x-ray powder pattern was identical with that of the product from the butyl nitrate-stannic chloride reaction.

Infrared study of the butyl nitrate-stannic chloride reaction. *n*-Butyl nitrate, 11.36 g. (0.10 mole), and stannic chloride, 11.68 g. (0.10 mole), were mixed and allowed to stand. Samples of 1.0 cc. of the mixture were removed at five different intervals throughout the induction period. To each sample was added 25 cc. of water and the mixture extracted with two 10-cc. portions of redistilled petroleum ether (b.p. 30–35°). The extracts were dried over anhydrous

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(4) R. T. Merrow and R. H. Boschan, *J. Am. Chem. Soc.*, **76**, 4622 (1954).

(5) S. J. Cristol and J. E. Leffler, *J. Am. Chem. Soc.*, **76**, 4468 (1954).

(6) R. A. Slavinskaya, *J. Gen. Chem. (U.S.S.R.)*, **27**, 844 (1957).

(7) *Handbook of Chemistry and Physics*, 37th ed. 1955–56, Cleveland, Ohio, Chemical Rubber Publishing Co., p. 822, reported n_D^{20} for *n*-butyl butyrate 1.4049.

magnesium sulfate, filtered, and evaporated. The infrared curves on each extract were essentially the same and virtually identical with the spectrum of *n*-butyl nitrate.

After the violent reaction took place, the residue was extracted with petroleum ether and the nearly colorless extract was dried and evaporated. The infrared spectrum of the residue from this extraction indicated that it consisted essentially of *n*-butyl *n*-butyrate.

Reaction of benzyl nitrate with stannic chloride. Benzyl nitrate, 3.06 g. (0.02 mole), was placed in a glass ampoule and cooled for *ca.* 10 min. in Dry Ice. Stannic chloride, 2.34 cc. (5.21 g., 0.020 mole), was added; the mixture again cooled; and the ampoule sealed off while still immersed in Dry Ice. The mixture was allowed to warm to room temperature behind an explosion shield. As the stannic chloride melted into the benzyl nitrate, a dark layer developed. In a very short time, copious brown fumes (probably nitrogen dioxide) effervesced from the reaction mixture. Just as the gases filled the ampoule, there was a brilliant flash of light, followed by a loud detonation which powdered the glass in the ampoule, completely shattering it.

Products from the reaction of benzyl nitrate with stannic chloride. To 3.0 g. (0.20 mole) of benzyl nitrate was added 2.34 cc. (5.21 g., 0.020 mole) of stannic chloride. The induction period followed by vigorous effervescence, as previously described, was observed in a few minutes after mixing. Water was added and the mixture extracted with ether. The ether extract was dried and filtered and the ether distilled, leaving a residue smelling strongly of benzaldehyde. Addition of 2,4-dinitrophenylhydrazine reagent to an alcoholic solution of this residue precipitated 2.45 g. (44% based on benzaldehyde) of derivative, m.p. 220–223°; m.p. 230° after two recrystallizations from absolute ethanol; m.p. 230–235° when mixed with an authentic sample of benzaldehyde-2,4-dinitrophenylhydrazone.

Reaction of benzyl nitrate with dinitrosyl hexachlorostannate. To 4.0 g. of dinitrosyl hexachlorostannate was added 5.0 cc. of benzyl nitrate, and the mixture was allowed to stand for a week in a stoppered flask; it was then poured into water to decompose the residual solid material. The water solution was extracted with three portions (total 150 cc.) of petroleum ether (b.p. 30–60°), and the extracts dried and evaporated. The residue was made up to 100 cc. in a volumetric flask with absolute ethanol. A 20-cc. portion was treated with dinitrophenylhydrazine reagent to yield 0.43 g. of benzaldehyde-2,4-dinitrophenylhydrazone, m.p. 236–237°. This corresponds to a total of 2.15 g. of derivative or to 0.80 g. of benzaldehyde.

A polarographic determination of the product showed the ratio of benzyl nitrate to benzaldehyde to be 5:15. Thus, 4.12 g. of benzyl nitrate remained.

Reaction of triphenylmethyl nitrate with stannic chloride. Triphenylmethyl nitrate, 3.0 g. (0.098 mole), was dissolved in *ca.* 25 cc. of ether and 4 cc. of stannic chloride was carefully added. A vigorous reaction ensued (probably coordination of stannic chloride and diethyl ether); and after the stannic chloride was added, the ether was boiled for a few minutes, then poured into water. An oil formed which crystallized after *ca.* 1 hr. The crystals were filtered to yield 2.34 g. (97.5% crude yield) of dark crystals, m.p. 91°. The crystals were dissolved in hot alcohol, and the solution boiled with Norit, filtered, and cooled to yield 1.32 g. (55%) of white crystals, m.p. 93–94°. The melting point was unchanged when this material was mixed with an authentic sample of triphenylmethane (from hydrogenation of triphenylmethyl chloride).

Reaction of n-butyl nitrate with boron trifluoride. Into 3.0 ml. of *n*-butyl nitrate was passed a slow stream of boron trifluoride for *ca.* 3 hr. Ten cubic centimeters of petroleum ether was added and the mixture was cooled. Some semisolid material appeared at the bottom of the flask. When the petroleum ether was evaporated from this mixture, an exothermic reaction occurred accompanied by loss of nitrogen oxide. An infrared spectrum of the residue, 1.49 g., which had an ester odor, identified it as being principally *n*-butyl *n*-butyrate.

Reaction of boron trifluoride with benzyl nitrate. Into a mixture of 4.9 g. of petroleum ether (b.p. 30–60°) and 6.9 g. (0.045 mole) of benzyl nitrate was passed a slow stream of boron trifluoride. Within a few seconds the reaction mixture turned yellow, and after *ca.* 1.5 min. an exothermic reaction took place which was sufficient to reflux the mixture. Boron trifluoride was passed through for a total of *ca.* 20 min. The mixture was then made basic with 40% sodium hydroxide and extracted successively with 20 cc. of petroleum ether, two 20-cc. portions of ethyl ether, 20 cc. of benzene, and two 20-cc. portions of ether, the extracts being combined and evaporated to *ca.* 25% of the volume. The residue was cooled and 50 cc. of saturated sodium bisulfite solution was added and the precipitate filtered, washed with ether, and dried. Liberation of the aldehyde and formation of the 2,4-dinitrophenylhydrazone yielded 3.83 g. (30%) of derivative. Acidification of the base solution precipitated 1.0 g. (18%) of benzoic acid to bring the total yield of products to 48%.

Reaction of boron trifluoride with triphenylmethyl nitrate. Into a solution of 1.5 g. (0.0051 mole) of triphenylmethyl nitrate was passed a slow stream of boron trifluoride for *ca.* 20 min. To the mixture was added *ca.* 25 cc. of ether. A reaction took place with apparently some evolution of nitrogen dioxide. The suspended solid was filtered to yield 0.26 g. of yellow powder, m.p. 145–155°. The melting point increased to 159–160° after washing with water, and the melting point of this latter material was unchanged when mixed with an authentic sample of triphenylcarbinol.

Evaporation of the ether solution left darkly colored crystals which were redissolved in ether and twice decolorized with Norit to yield 0.36 g. (29%) of material, m.p. 90–92°, mixed m.p., taken with an authentic sample of triphenylmethane, 91–92.5°.

Isopropyl nitrate. Isopropyl nitrate was prepared by the method of Silva[8] from isopropyl iodide and powdered silver nitrate in 69% yield, n_D^{20} 1.3897, b.p. 23–24° (27 mm.).

Reaction of isopropyl nitrate with boron trifluoride in petroleum ether. Isopropyl nitrate, 10.0 g. (0.0952 mole), was dissolved in 14 g. of petroleum ether (b.p. 40–60°). The mixture, in a round-bottomed flask fitted with an ice-water–cooled reflux condenser, was cooled in Dry Ice, and a slow stream of boron trifluoride was passed through for 20 min., at which time the solution was colored and appeared to contain some solid matter. The solution was allowed to warm to room temperature very slowly. Shortly after the mixture had reached room temperature, it effervesced and finally reacted very violently, with some volatile material escaping through the reflux condenser. After this violent reaction subsided, two phases were present, a nearly colorless upper phase and a dark brown lower phase. The layers were separated, and the lower phase washed with petroleum ether, the washings being added to the upper layer. Addition of a sample of 2,4-dinitrophenylhydrazine reagent to the petroleum ether extract precipitated 0.15 g. of acetone dinitrophenylhydrazone, m.p. 119–122°. Huntress and Mulliken[9] reported m.p. 126°.

The dark lower phase was connected to a vacuum pump through a Dry Ice trap, and the liquid distillate in the trap was treated with 2,4-dinitrophenylhydrazine to yield an additional 0.20 g. of derivative, m.p. 122–125° to give a total of 0.35 g. of acetone 2,4-dinitrophenylhydrazone.

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(8) R. V. Silva, *Ann.* **154**, 254 (1870).

(9) F. H. Huntress and S. P. Mulliken, *Identification of Pure Organic Compounds, Order 1.* New York, John Wiley and Sons, p. 374.