bon dioxide, which was generated in a vacuum system from 1.4000 g. of barium carbonate with sulfuric acid.

The same ionization chamber was used for all activity determinations. All samples were counted for 1.5 hours and a background correction was made. All three of the activity determinations for each set were made in close succession, in order to minimize variations in the instruments. The average counting error with samples run in close succession was approximately 0.5%. Many of the activity determinations were repeated one or more times.

Acknowledgment.—The authors would like to thank the Pan American Refining Corporation for fellowship aid for Mr. Carrick during 1953–1954.

FAYETTEVILLE, ARK.

[CONTRIBUTION FROM ROHM AND HAAS COMPANY, REDSTONE ARSENAL RESEARCH DIVISION]

Alkaline Nitration. I. The Nitration of Amines with Cyanohydrin Nitrates[1]

BY WILLIAM D. EMMONS AND JEREMIAH P. FREEMAN

RECEIVED MARCH 14, 1955

Acetone cyanohydrin nitrate (I) has been found to be a unique reagent for effecting nitration under alkaline conditions. By means of this reagent primary and secondary amines may be converted to the corresponding nitramines. Other cyanohydrin nitrates that were studied in this connection are discussed.

The introduction of a nitro group into an organic molecule almost always requires the use of a highly acidic reagent. This requirement limits the number and type of compounds that can be nitrated because of the sensitivity of some compounds to acids. A reagent which could effect nitration under neutral or alkaline conditions would be highly desirable. As a starting point in the search for such a reagent, the synthesis of nitramines[2] from amines has been examined.

Several attempts to convert amines to nitramines by the action of a nitrate ester in the presence of added base are recorded in the literature.[3] Thus, Bamberger isolated phenylnitramine in poor yield from the reaction of aniline, ethyl nitrate and sodium ethoxide.[4] This method has not been useful, however, as the predominant reaction is one of alkylation. For instance, pyridine is converted to a quaternary nitrate by the action of alkyl nitrates,[5] and piperidine is alkylated to form tertiary amines.[6] The predominance of this latter reaction suggests that nitrate esters behave more like alkyl halides or tosylates than like carboxylic esters. This view finds support in the work of Baker and Easty[7] who studied the solvolysis of nitrate esters. They interpreted their data on the basis that no reaction involving attack on nitrogen occurred. It has recently been shown,[8] however, that the hydrolysis of nitrate esters must occur by cleavage of the oxygen–nitrogen bond since a nitrate ester labeled with O^{18} yields an alcohol containing O^{18}. It has also been postulated that oxygen–nitrogen bond cleavage occurs during the reaction of hydrazine with certain nitrate esters.[9]

Efforts to effect the nitration of amines with simple alkyl nitrates appeared to be predestined to failure regardless of the strength of the added base because of the competition from side reactions. It was decided therefore to alter the structure of the nitrate ester with a view to weakening the oxygen–nitrogen bond so that nucleophilic attack on the molecule would occur on nitrogen. Efforts in this direction led to the synthesis of trichloroethyl nitrate whose reaction with secondary amines has been reported.[10] In this case the amine attacked the α-hydrogen atoms instead of the nitro group. Significantly, however, no alkylation was noted.

$$Cl_3CCH_2ONO_2 + R_2NH \longrightarrow R_2\overset{\oplus}{N}H_2\overset{\ominus}{N}O_2 + Cl_3CCHO$$

This preliminary study led to the imposition of certain restrictions on the structure of the nitrate ester to be used for alkaline nitrations.

First of all, the nitrate ester should possess no α-hydrogen atoms. Secondly, it should contain bulky groups around the α-carbon atom to hinder bimolecular displacement reactions. Lastly, it should contain an electronegative group to weaken the oxygen–nitrogen bond. The latter requirement is also desirable because it prevents the facile unimolecular solvolysis characteristic of most tertiary nitrate esters.[11] In the search for a molecule which possessed all these structural features, attention was focused on the heretofore unknown nitrate esters of ketone cyanohydrins. The nitration of the readily available acetone cyanohydrin was attempted first. The synthesis of acetone cyanohydrin nitrate (I) was accomplished smoothly by nitration of the cyanohydrin with fuming nitric acid in acetic anhydride. By this method the nitrate ester I was obtained consistently in yields of 65–70%. It proved to be a colorless liquid which could be

(1) This research was carried out under Army Ordnance Contract W-01-021-ORD-334.

(2) At present there are three good methods for the preparation of secondary nitramines, and all involve strongly acidic conditions. They are: (a) the oxidation of nitrosamines with peroxytrifluoroacetic acid [W. D. Emmons, THIS JOURNAL, **76**, 3468 (1954)]; (b) the chloride ion-catalyzed direct nitration of amines [W. J. Chute, K. G. Herring, L. E. Toombs and G. F Wright, *Can. J. Research*, **26B**, 89 (1948)]; and (c) the nitrolysis of dialkylamides with nitric acid [A. H. Lamberton, *Quart. Revs.*, **5**, 75 (1951)]. Only the second of these methods is applicable to the synthesis of primary nitramines.

(3) H. J. Backer, *Sammlung Chem. und Chem. Tech. Vorträge*, **18**, 365 (1912).

(4) E. Bamberger, *Ber.*, **53**, 2321 (1920).

(5) E. S. Lane, *J. Chem. Soc.*, 1172 (1953).

(6) D. T. Gibson and A. K. Macbeth, *ibid.*, 438 (1921).

(7) J. Baker and D. Easty, *ibid.*, 1193, 1207 (1952).

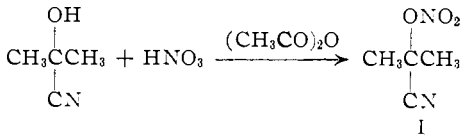
(8) M. Anbar, I. Dostrovsky, D. Samuel and A. D. Yoffe, *ibid.*, 3603 (1954).

(9) R. T. Merrow and R. W. VanDolah, THIS JOURNAL, **76**, 4522 (1954).

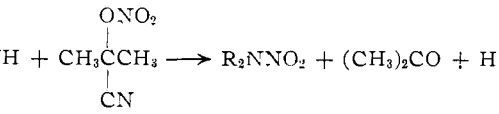
(10) W. D. Emmons, K. S. McCallum and J. P. Freeman, *J. Org. Chem.*, **19**, 1472 (1954).

(11) For instance, G. R. Lucas and L. P. Hammett [THIS JOURNAL, **64**, 1928 (1942)] have demonstrated that *t*-butyl nitrate undergoes unimolecular solvolysis in aqueous ethanol at a rate similar to that of *t*-butyl chloride.

distilled readily *in vacuo* and which was stable under all conditions of our use.



Acetone cyanohydrin nitrate (I) has been found to be a unique reagent for the conversion of amines to nitramines under alkaline conditions. Aliphatic and alicyclic secondary nitramines were obtained in yields varying from 55–80% and primary nitramines were produced in 50–60% yields. Our results are summarized in Table I. Under the conditions of the reaction it was also shown that the hydrogen cyanide and acetone produced in the nitration reaction in turn react with excess amine to form the corresponding α-aminonitrile.



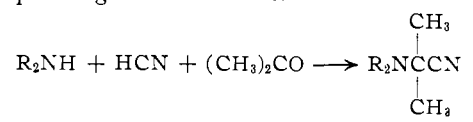


TABLE I

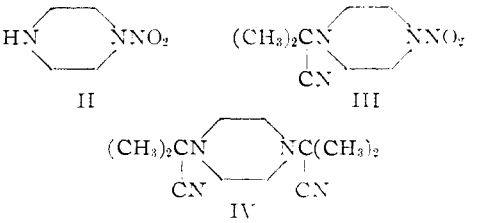
NITRATION OF AMINES TO NITRAMINES WITH ACETONE CYANOHYDRIN NITRATE

Nitramine	Yield, %	B.p., °C.	$n^{20}D$
Dimethyl[a]	76	M.p. 57–58	
Diethyl[b]	60	50–52 (0.2 mm.)	1.4525
Di-*n*-propyl[c]	42	90–92 (8 mm.)	1.4558
Di-*n*-butyl[d]	54	69–70 (0.1 mm.)	1.4562
Diisobutyl[e]	60	M.p. 79–80	
Diisoamyl[f]	64	112–114 (2 mm.)	1.4604
Mononitropiperazine	55	M.p. 127–128	
Nitropiperidine[g]	62	62–64 (0.2 mm.)	1.4968
Nitromorpholine[h]	81	M.p. 51–53	
Nitropyrrolidine[i]	60	M.p. 55–57	
n-Propyl[j]	50	52–56 (0.1 mm.)	1.4610
n-Butyl[k]	52	79–81 (0.5 mm.)	1.4596
Isobutyl[l]	54	58–60 (0.1 mm.)	1.4570
n-Amyl[m]	55	60–62 (0.2 mm.)	1.4611
Isoamyl[f,n]	54	62–64 (0.02 mm.)	1.4594

[a] Lit. m.p. 57° (ref. 2b). [b] Lit. b.p. 48° (0.5 mm.), $n^{20}D$ 1.4539 (ref. 2a). [c] W. R. Kingdon and G. F Wright [THIS JOURNAL, **72**, 1030 (1950)] report b.p. 103–104° (10 mm.), $n^{20}D$ 1.4559. [d] G. F Wright, *et al.* [*Can. J. Research*, **26B**, 114 (1948)] report b.p. 129–130° (11 mm.), $n^{25}D$ 1.4557. [e] This compound has previously been reported as an oil (see footnote *d*). [f] A. Berg [*Ann. chim.*, [7] **3**, 357 (1894)] has reported this compound as an unpurified oil. [g] Lit. b.p. 245° (765 mm.), $n^{26}D$ 1.4954 (I. Heilbron, "Dictionary of Organic Compounds," Vol. III, Oxford University Press, New York, N. Y., 1953, p. 775). [h] Lit. m.p. 53° (see footnote *d*). [i] Recrystallized from water. *Anal.* Calcd. for $C_4H_8N_2O_2$: C, 41.37; H, 6.94; N, 24.16. Found: C, 40.63; H, 6.58; N, 23.60. [j] Lit. b.p. 90–111° (13 mm.) (see footnote *c*). [k] G. N. R. Smart and G. F Wright [*Can. J. Research*, **26B**, 284 (1948)] report b.p. 123–125° (20 mm.), $n^{25}D$ 1.4603. [l] H. van Erp (*Rec. trav. chim.*, **14**, 1 (1895)] reported this compound as a solid, m.p. 32°, which very readily supercooled. [m] Calcd. for $C_5H_{12}N_2O_2$: C, 45.43; H, 9.16; N, 21.20. Found: C, 46.09; H, 9.44; N, 20.86. [n] Calcd. for $C_5H_{12}N_2O_2$: C, 45.43; H, 9.16; N, 21.20. Found: C, 45.72; H, 9.38; N, 21.02.

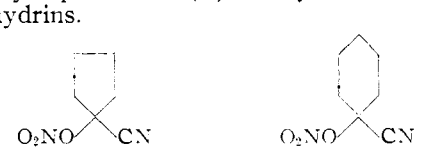
The effect of various solvents on this reaction was examined. It was found that the secondary amines function well as their own solvents although acetonitrile and tetrahydrofuran may be used if desired. The variation in yield between these three systems was less than 10%. In general, the amine was used in 5:1 excess and heated at 80° for four hours with the nitrate ester. On the other hand, the reactivity of the primary amines was profoundly affected by the choice of solvent. With solvents of low dielectric or in excess amine itself the reaction proceeded only to the extent of 20–25% and the product was difficult to purify. When a 3:1 excess of the amine was heated with the nitrate in acetonitrile or tetrahydrofuran at reflux for six hours, however, satisfactory yields of product were obtained.

The behavior of piperazine hydrate in this reaction was highly dependent upon the choice of reaction conditions. Mononitropiperazine (II) was obtained when the nitration was carried out in dimethylformamide using an excess of the amine. If an excess of the nitrate was used, N-nitro-N′-(α-cyanoisopropyl)-piperazine (III) was produced. In a methylene chloride–ethanol mixture and with an excess of the amine, N,N′-di-(α-cyanoisopropyl)-piperazine (IV) was the only product. The structures of compounds III and IV were proved by independent synthesis.



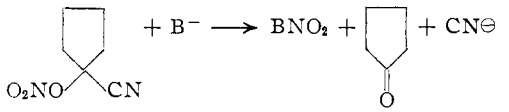
This reagent is not a completely general one as aromatic amines and aliphatic amines with branching on the α-carbon atom were unaffected by it. The failure with the latter compounds is probably due to steric interference of the alkyl groups of the two reactants at the locus of incipient bond formation (F-strain[12]). Support for this suggestion is found by a comparison of the reactivity of various amines. Reaction occurred most rapidly with the cyclic amines in which the methylene groups are pulled back from the face of the nitrogen atom, and with the relatively unhindered acyclic dimethylamine. As the chain length was increased to four carbon atoms, the reactivity gradually diminished and then leveled off. β-Substitution had no detrimental effect on reactivity. As a rule the primary amines reacted much more sluggishly than did the secondary amines.

Two other cyanohydrin nitrates have been examined in this reaction. They are the nitrate esters of cyclopentanone (V) and cyclohexanone (VI) cyanohydrins.



(12) H. C. Brown, H. Bartholomay and M. D. Taylor, THIS JOURNAL, **66**, 435 (1944).

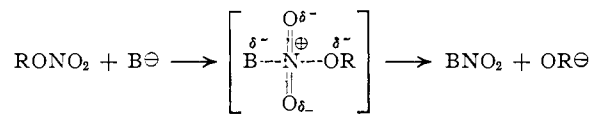
It was of interest to determine whether these two nitrates might possess some advantages over acetone cyanohydrin nitrate because of steric considerations. In both of these molecules the α-methylene groups are part of a ring and as a result are pulled back from the site of reaction. This decrease in steric interference might conceivably permit reactions to occur which were impossible with acetone cyanohydrin nitrate. On the basis of a recent correlation of reactivity with ring size,[13] cyclopentanone cyanohydrin nitrate might possess additional driving force for nitration as in the critical step of the reaction the coördination number of a ring atom changes from four to three. This change has been shown to be a thermodynamically probable one.[13]



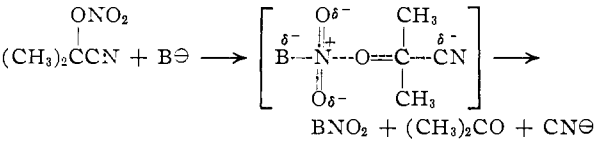
coörd. no. = 4 coörd. no. = 3

In practice, however, it was found that the reactivity of these cyclic cyanohydrin nitrates was grossly comparable to that of acetone cyanohydrin nitrate. The same steric limitations on their use were present, and the yields of the nitramines that were obtained were approximately the same. For instance, dibutylamine was nitrated in 63 and 54% yield and *n*-butylamine was nitrated in 51 and 48% yield by cyclopentanone and cyclohexanone cyanohydrin nitrates, respectively. Neither of these cyclic nitrates reacted with diisopropylamine or cyclohexylamine.

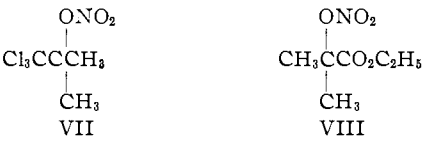
The unique reactivity of acetone cyanohydrin nitrate may be understood by an examination of the probable transition state for the reaction. Formally this reaction may be compared to the Claisen condensation and the transition state may be formulated as



When an ordinary nitrate ester is employed, the reaction amounts to a simple displacement on nitrogen and very little driving force for nitration is contributed by the leaving group. In the case of acetone cyanohydrin nitrate, the displacement reaction most likely occurs with concerted fragmentation of the leaving group. Thus the incipient formation of the carbon–oxygen double bond in the transition state gives the nitro group some nitro-



nium ion character and adds considerable driving force for nitration. The reactivity of this reagent appears to be due to three factors: (1) the tertiary nature of the nitrate ester which reduces the possibility of a simple alkylation reaction; (2) the presence of the electronegative nitrile group which weakens the oxygen–nitrogen bond, thereby favoring attack at the nitro group, and which prevents solvolysis of the tertiary nitrate ester; and (3) the facile decomposition of the cyanohydrin structure upon attack of a nucleophilic reagent which provides the driving force for nitration. The importance of this third factor is highlighted by the fact that neither trichloro-*t*-butyl nitrate (VII) nor ethyl α-nitratoisobutyrate (VIII) were found to be effective nitrating agents, yet both contain potent electronegative groups. Both were recovered unchanged from reactions with various amines.



The success attained in this investigation suggests the study of cyanohydrin derivatives in other displacement reactions.

Experimental[14]

Acetone Cyanohydrin Nitrate.—To a stirred solution of 462 g. of white fuming nitric acid (d. 1.48–1.50) in 1225 g. of acetic anhydride was added 255 g. (3.0 moles) of acetone cyanohydrin in one portion. The solution was stirred at room temperature for 30 minutes and then poured into 1500 ml. of ice-water. After one hour of intermittent stirring, the aqueous solution was extracted with three 300-ml. portions of methylene chloride. The combined methylene chloride solution was washed once with 200 ml. of 5% aqueous sodium bicarbonate solution and then dried over anhydrous magnesium sulfate. Fractional distillation at reduced pressure yielded 255–267 g. (65–68%) of acetone cyanohydrin nitrate, b.p. 65–66° (10 mm.), $n^{20}D$ 1.4172.

Anal. Calcd. for $C_4H_6N_2O_3$: C, 36.92; H, 4.65; N, 21.54. Found: C, 37.11; H, 3.90; N, 21.97.

Diisobutylnitramine.—The following method was found to be the most general one for the nitration of secondary amines. Individual cases in which this procedure was modified are noted.

To 64.5 g. (0.5 mole) of diisobutylamine in 100 ml. of acetonitrile was added slowly at room temperature 13.0 g. (0.1 mole) of acetone cyanohydrin nitrate in 50 ml. of acetonitrile. The mixture was heated at 80° for four hours, and then was poured into 200 ml. of 10% hydrochloric acid solution and extracted with methylene chloride. The organic extracts were washed with 5% sodium bicarbonate solution and water, and dried over magnesium sulfate. The solvent was removed by evaporation to yield 10.4 g. (60%) of a white solid. Recrystallization from ethanol and water yielded shiny white platelets, m.p. 79–80°.

Anal. Calcd. for $C_8H_{18}N_2O_2$: C, 55.14; H, 10.41. Found: C, 54.69; H, 9.90.

Nitromorpholine.—To 17.4 g. (0.2 mole) of morpholine was added 13.0 g. (0.1 mole) of acetone cyanohydrin nitrate at room temperature. A pale yellow color developed in the mixture which was heated at 80° for an hour. It was poured into dilute hydrochloric acid and extracted with methylene chloride. The extracts were dried, the solvent was evaporated and the residue was cooled until it solidified; yield 13.0 g. (95%). This material was recrystallized from ethanol and water to yield 10.9 g. (81%) of pure nitromorpholine, m.p. 51–53°.

***n*-Butylnitramine.**—The following procedure was typical of those used in the preparation of primary nitramines.

To a solution of 36.5 g. (0.5 mole) of *n*-butylamine in 50 ml. of acetonitrile was added 13.0 g. (0.1 mole) of acetone cyanohydrin nitrate. This mixture was heated under reflux for six hours and then poured into 100 ml. of 10% hydrochloric acid and extracted with ether. The organic extracts were dried over magnesium sulfate, the solvent was evaporated and the residue was distilled to yield 6.1 g.

(13) H. C. Brown, J. Brewster and H. Shechter, THIS JOURNAL, **76**, 467 (1954).

(14) We are indebted to Dr. Keith S. McCallum for infrared interpretations and to Miss Annie Smelley for microcombustion data.

(52%) of *n*-butylnitramine, b.p. 68–70° (0.05 mm.), $n^{20}D$ 1.4596.

The aqueous extracts were made alkaline with sodium carbonate and extracted with ether. After drying, these extracts were concentrated and distilled to yield **α-butylaminoisobutyronitrile**, b.p. 58–59° (8 mm.), $n^{20}D$ 1.4286; yield 5.6 g. (40%).

Anal. Calcd. for $C_8H_{16}N_2$: C, 68.52; H, 11.50. Found: C, 68.28; H, 10.95.

Reaction of Piperazine Hydrate with Acetone Cyanohydrin Nitrate (a).—To a solution of 38.4 g. (0.2 mole) of piperazine hexahydrate in 100 ml. of dimethylformamide was added 13.0 g. (0.1 mole) of acetone cyanohydrin nitrate. The mixture was heated at 80° for five hours and then the bulk of the solvent was removed by distillation *in vacuo*. The residue was cooled in a Dry Ice–acetone bath whereby crystallization was induced. The pale yellow solid was collected on a filter and recrystallized from ethanol to yield small white platelets of **mononitropiperazine**, m.p. 127–128°; yield 7.0 g. (55%).

Anal. Calcd. for $C_4H_9N_3O_2$: C, 36.64; H, 6.90; N, 32.04. Found: C, 35.94; H, 6.64; N, 32.14.

By treatment with phenyl isothiocyanate, mononitropiperazine was converted to its phenylthiourea, m.p. 204–205° (from ethanol).

Anal. Calcd. for $C_{11}H_{14}N_4O_2S$: C, 49.61; H, 5.30; N, 21.04. Found: C, 49.89; H, 5.38; N, 21.31.

(b).—To 38.4 g. (0.2 mole) of piperazine hydrate dissolved in a mixture of 100 ml. of ethanol and 50 ml. of methylene chloride was added 13.0 g. (0.1 mole) of acetone cyanohydrin nitrate. The mixture was heated under reflux for four hours and then allowed to stand at room temperature overnight. The solvents were evaporated to yield a solid residue of **N,N′-di-(α-cyanoisopropyl)-piperazine** which was recrystallized from ethanol, m.p. 178–180°; yield 6.7 g. (30%).

Anal. Calcd. for $C_{12}H_{20}N_4$: C, 65.42; H, 9.15. Found: C, 65.30; H, 8.66.

An authentic sample of this material was prepared from piperazine hydrate and acetone cyanohydrin by the method of Jacobson.[15] The infrared spectra of the two materials were identical and the melting point of their mixture was 180–181°.

(c).—To 19.4 g. (0.1 mole) of piperazine hydrate in 75 ml. of dimethylformamide was added 26.0 g. (0.2 mole) of acetone cyanohydrin nitrate. This mixture was heated at 75° for four hours. The solvent was then evaporated to yield a solid residue. Recrystallization from ethanol furnished **N-nitro-N′-(α-cyanoisopropyl)-piperazine**, m.p. 140–142°, yield 6.8 g. (37%).

Anal. Calcd. for $C_8H_{14}N_3O_2$: C, 48.47; H, 7.12; N, 28.27. Found: C, 48.88; H, 6.86; N, 28.27.

An authentic sample of this material was prepared by the condensation of nitropiperazine and acetone cyanohydrin. The melting point of this mixture was 141–142° and their infrared spectra were identical.

Cyclohexanone Cyanohydrin Nitrate.—Cyclohexanone cyanohydrin[16] was nitrated by the same method as described for acetone cyanohydrin. From 90 g. (0.72 mole) of the cyanohydrin, 111 g. of fuming nitric acid and 180 g. of acetic anhydride there was obtained 107.5 g. (88%) of cyclohexanone cyanohydrin nitrate, b.p. 62–64° (0.3 mm.), $n^{20}D$ 1.4660.

Anal. Calcd. for $C_7H_{10}N_2O_3$: C, 49.41; H, 5.88; N, 16.47. Found: C, 49.48; H, 5.58; N, 16.88.

Cyclopentanone Cyanohydrin.—The method described for the preparation of cyclohexanone cyanohydrin[16] was used in the synthesis of this compound after several attempts to duplicate other methods described in the literature[17] had failed. From 168 g. (2.0 moles) of cyclopentanone, 260 g. (4.0 moles) of potassium cyanide and 377 ml. (4.0 moles) of acetic anhydride in 500 ml. of water, there was obtained 183 g. (82%) of cyclopentanone cyanohydrin, b.p. 74–76° (0.3 mm.).

Cyclopentanone Cyanohydrin Nitrate.—By the method described, from 183 g. (1.65 moles) of cyclopentanone cyanohydrin, 310 g. of fuming nitric acid and 837 g. of acetic anhydride there was obtained 216 g. (84%) of cyclopentanone cyanohydrin nitrate, b.p. 50–51° (0.25 mm.), $n^{20}D$ 1.4592.

Anal. Calcd. for $C_6H_8N_2O_3$: C, 46.15; H, 5.13; N, 17.95. Found: C, 46.45; H, 4.97; N, 17.96.

Reaction of Dibutylamine with Cyclohexanone Cyanohydrin Nitrate.—A mixture of 8.5 g. (0.05 mole) of cyclohexanone cyanohydrin nitrate and 32.3 g. (0.25 mole) of dibutylamine was heated in 50 ml. of tetrahydrofuran for four hours. It was then poured into dilute hydrochloric acid and extracted with ether. The ether extracts were washed with 10% sodium bisulfite solution, dried and concentrated. The residue was distilled to obtain 5.0 g. (54%) of dibutylnitramine.

Reaction of Dibutylamine with Cyclopentanone Cyanohydrin Nitrate.—Following the same procedure, from 7.8 g. (0.5 mole) of cyclopentanone cyanohydrin nitrate and 32.3 g. (0.25 mole) of dibutylamine, there was obtained 5.5 g. (63%) of dibutylnitramine.

2,2,2-Trichloro-*t*-butyl Nitrate.—To a mixture of 102 g. of acetic anhydride and 18.9 g. of anhydrous nitric acid was added 21.3 g. (0.1 mole) of 2,2,2-trichloro-*t*-butanol dihydrate over a ten-minute period. The solution was stirred for 30 minutes at room temperature and quenched in 400 ml. of a water-ice mixture. The product was extracted with three 100-ml. portions of ether. The combined extracts were washed with 10% sodium carbonate solution and with water and dried over magnesium sulfate. The solvent was removed *in vacuo* and 20.0 g. (89%) of 2,2,2-trichloro-*t*-butyl nitrate, b.p. 46–50° (1.0 mm.), $n^{20}D$ 1.4810, was obtained by distillation.

Anal. Calcd. for $C_4H_6NO_3Cl_3$: C, 21.59; H, 2.72; N, 6.29. Found: C, 22.25; H, 2.98; N, 6.45.

No reaction was observed between this nitrate ester and piperidine.

Ethyl α-Nitratoisobutyrate.—To a mixture of 18.9 g. of absolute nitric acid, 51 g. of acetic anhydride and 30 g. of acetic acid was added 13.2 g. (0.1 mole) of ethyl α-hydroxyisobutyrate. The mixture was stirred at room temperature for two hours, then poured into ice-water and extracted with methylene chloride. These extracts were dried and concentrated and ethyl α-nitratoisobutyrate, b.p. 74–76° (12 mm.), $n^{20}D$ 1.4172, was obtained by distillation; yield 15.9 g. (90%).

Anal. Calcd. for $C_6H_{11}NO_5$: C, 40.67; H, 6.26. Found: C, 40.69; H, 5.96.

No reaction was observed between this nitrate ester and secondary amines.

Acknowledgment.—We are indebted to Dr. M. F. Hawthorne for helpful discussion concerning the mechanism of the alkaline nitration reaction, and to Dr. Robert M. Ross for several suggestions throughout the course of this investigation.

HUNTSVILLE, ALABAMA

(15) R. A. Jacobson, THIS JOURNAL, **67**, 1996 (1945).

(16) R. L. Frank, R. E. Berry and O. L. Shotwell, *ibid.*, **71**, 3889 (1949).

(17) A. H. Cook and R. P. Linstead, *J. Chem. Soc.*, 956 (1934).