cipitate of copper enolate salt was observed. 3,5-Diethylisoxazole gave no precipitate with cupric acetate solution in methanol, but 3,5-heptanedione formed an insoluble copper salt, mp 209-212°.[60] A second aliquot of the heptane-3,5-bisnitronate solution was treated with solid potassium dihydrogen phosphate to change the pH to *ca.* 7. The solution then became cloudy and, after standing overnight, was extracted with ether. The ether was evaporated and the residue steam distilled to yield 3,5-diethylisoxazole and nitropropane as the only products (identified by comparison of nmr spectra with those of authentic samples). Acidification of a third aliquot of this solution with acetic acid gave 3,5-diethylisoxazole which was separated from the reaction mixture by extraction with ether followed by distillation: bp 78° (28 mm) [lit.[14] bp 65° (11 mm)]. The compound was identified by comparison of its nmr spectrum with that of an authentic sample.

Registry No.—**3**, 19018-61-2; **11**, 19018-97-4; **12**, 19018-98-5; **13**, 19018-99-6; **14**, 12321-52-7; **15**, 19019-00-2; **16**, 19019-01-3; **20**, 19018-62-3; **24**, 19019-16-0; **27**, 19019-17-1; 1-nitro-1,2,3-triphenylpropane, 19019-18-2; 1-bromo-1-nitro-1,2,3-triphenylpropane, 19019-19-3; $C_6H_5CH{=}NO_2^-Na^+$, 12321-46-9; $C_6H_5CH{=}NO_2H$, 19019-20-6.

Acknowledgments.—The authors are indebted to G. C. Whitnack for the polarographic analyses and to Dr. Wayne R. Carpenter for aid in securing the mass spectral data.

---

[60] J. T. Adams and C. R. Hauser, *J. Amer. Chem. Soc.*, **66**, 1220 (1944).

The Alkyl Nitrate Nitration of Active Methylene Compounds. VI. The Nitration of Esters in Liquid Ammonia

HENRY FEUER AND ROBERT P. MONTER

Department of Chemistry, Purdue University, Lafayette, Indiana 47907

Received July 9, 1968

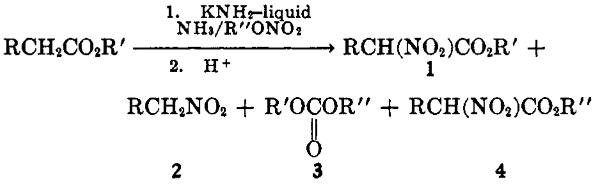
The nitration of aliphatic and phenyl acetate esters with alkyl nitrates in the presence of potassium amide in liquid ammonia gives not only α-nitro esters **1** but also nitroalkanes **2** and dialkyl carbonates **3**. In addition to these compounds, another α-nitro ester **4** forms when the alkoxy portion of the ester and alkyl nitrate are not the same. Compounds **2** and **3** arise from a fragmentation reaction and compound **4** from a transesterification reaction, both of which occur during the nitration step, and not during subsequent acidification. These reactions are not caused by direct base attack on the resulting α-nitro ester, however, except when the latter is tertiary.

In continuation of our studies of the alkyl nitrate nitration,[1] we are now reporting on its application to the preparation of α-nitro esters.

General methods which have been employed for the preparation of α-nitro esters are the Victor Meyer reaction as modified by Kornblum and coworkers,[2] and the carboxylation of nitroalkanes in the presence of magnesium alkoxide.[3-5] The latter method does not seem to be applicable to the preparation of tertiary α-nitro esters.

Attempts by Wislicenus and coworkers[6,7] to prepare ethyl α-nitrophenylacetate by treating ethyl phenylacetate with ethyl nitrate in the presence of potassium ethoxide led only to phenylnitromethane and diethyl carbonate. Emmons and Freeman, using acetone cyanohydrin nitrate in the presence of a 100% excess of sodium hydride to nitrate monosubstituted malonic or acetoacetic esters, developed a general synthesis of α-nitro esters.[8]

In the present study, the alkyl nitrate nitration of esters was investigated in such systems as potassium *t*-butoxide–THF,[2a] potassium *t*-butoxide–DMF,[2d] and potassium amide–liquid ammonia.[2e] Of these only the latter was found to be useful in regard to work-up and yield. The reaction afforded not only α-nitro esters **1** but also cleavage products, namely nitroalkanes **2** and dialkyl carbonates **3**. Moreover, in cases where the carboxylic and nitrate esters differed in their alkoxy portions, another α-nitro ester **4** was obtained, resulting apparently from a transesterification reaction (eq 1).



$$\mathrm{RCH_2CO_2R'} \xrightarrow[\text{2. H}^+]{\text{1. KNH}_2\text{-liquid NH}_3/\text{R''ONO}_2} \underset{\mathbf{1}}{\mathrm{RCH(NO_2)CO_2R'}} + \underset{\mathbf{2}}{\mathrm{RCH_2NO_2}} + \underset{\mathbf{3}}{\mathrm{R'O\underset{\overset{\|}{O}}{C}OR''}} + \underset{\mathbf{4}}{\mathrm{RCH(NO_2)CO_2R''}} \qquad (1)$$

In order to determine optimum reaction conditions, various reaction parameters were studied with ethyl and *t*-butyl caproates. The latter was chosen because amide formation was found to be negligible.[9] Because of amide formation, only a 10% excess of potassium amide could be employed in the conversion of ethyl esters into their anions. In the case of *t*-butyl esters, a 100% excess of potassium amide could be used; this

---

[1] For previous publications, see (a) H. Feuer, J. W. Shepherd, and C. Savides, *J. Amer. Chem. Soc.*, **78**, 4364 (1956); (b) H. Feuer and C. Savides, *ibid.*, **81**, 5826 (1959); (c) H. Feuer and B. F. Vincent, Jr., *J. Org. Chem.*, **29**, 939 (1964); (d) H. Feuer and P. M. Pivawer, *ibid.*, **31**, 3152 (1966); (e) H. Feuer, A. M. Hall, S. Golden, and R. L. Reitz, *ibid.*, **33**, 3622 (1968).

[2] N. Kornblum, "Organic Reactions," Vol. XII, John Wiley & Sons, Inc., New York, N. Y., 1962, Chapter 3.

[3] H. L. Finkbeiner and M. Stiles, *J. Amer. Chem. Soc.*, **81**, 505 (1959).

[4] H. L. Finkbeiner and M. Stiles, *ibid.*, **85**, 616 (1963).

[5] H. L. Finkbeiner and G. W. Wagner, *J. Org. Chem.*, **28**, 215 (1963).

[6] W. Wislicenus and A. Endres, *Chem. Ber.*, **35**, 1755 (1902).

[7] W. Wislicenus and R. Grützner, *ibid.*, **42**, 1939 (1909)

[8] W. Emmons and J. Freeman, *J. Amer. Chem. Soc.*, **77**, 4391 (1955).

[9] C. R. Hauser, R. Levine, and R. F. Kibler, *J. Amer. Chem. Soc.*, **68**, 26 (1946).

TABLE I

ALKYL NITRATE NITRATION OF ETHYL ESTERS[a]

$RCH_2CO_2C_2H_5$ R	Yield of *o*-nitro ester,[b] %	Yield of nitro-paraffin,[b,c] %	Yield of acid amide,[b,d] %	Total nitration[e] yield, %
n-C_4H_9	42.0	13.5	1.0	55.5[f]
C_2H_5	41.0	14.0	7.0	55.0[f]
CH_3	24.0	18.9	7.5	42.9[f]
p-$CH_3OC_6H_4$	72.0[g]	21.7[g]	0	93.7
C_6H_5	22.8	48.5	0	71.3

[a] Nitrations were carried out in potassium amide liquid ammonia at −33° with ethyl nitrate. [b] These compounds were identified by their physical data which were in agreement with those reported in the literature. [c] This is the expected cleavage product resulting from decarboxylation of the α-nitro ester. In most cases the other product of decarboxylation, dialkyl carbonate, was not isolated. [d] The acid amide resulted from ammonolysis of the starting ester. [e] Total nitration is the sum of α-nitro ester and nitroparaffin. [f] About 20–30% of starting ester was recovered. [g] Isolated as the potassium salt (see Experimental Section).

TABLE II

ALKYL NITRATE NITRATION OF *t*-BUTYL ESTERS[a]

$RCH_2CO_2C(CH_3)_3$ R	Yield of *t*-butyl α-nitro ester,[b,c] %	Yield of ethyl α-nitro ester,[c] %	Yield of nitro-paraffin, %	Total nitration[d,e] yield, %
n-C_4H_9	21.7	33.1	32.5	87.3
C_2H_5	22.1	30.8	24.5	77.3
CH_3	25.5	22.0	14.0	61.5
H	18.0	22.0	33.0	63.0
i-C_3H_7	33.2	17.5	26.0	76.7
$CH_3CH_2CHCH_3$	0	0	72.0	72.0
C_6H_5	35.6	3.2	49.0	87.8

[a] Nitrations were carried out in potassium amide liquid ammonia at −33° with ethyl nitrate. [b] See Table III for physical properties. [c] Ethyl and *t*-butyl α-nitro esters were obtained as a mixture and were separated by glpc. [d] Total nitration represents the sum of *t*-butyl and ethyl α-nitro ester, and nitroparaffin. [e] Approximately 1–8% of the starting ester was recovered as a mixture of ethyl and *t*-butyl esters.

resulted in more anion formation and over-all nitration (compare data in Tables I and II).

With regard to the nitrating agent, it was established that yields were highly improved when (1) a 50% excess of alkyl nitrate over the ester was employed,[10] (2) the addition of the alkyl nitrate was very fast, and (3) the reaction temperature during the addition was kept below −33°.

Acidification was found to be best with glacial acetic acid after the ammonia was replaced by dry ether.

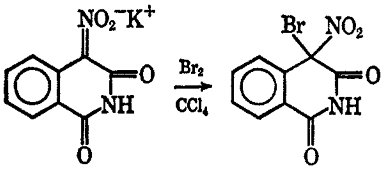
In order to determine the scope of the reaction, a number of ethyl and *t*-butyl esters were nitrated; the results are summarized in Tables I and II.

Aliphatic and Aryl Aliphatic Ethyl Esters.—As shown in Table I, nitration of ethyl esters led to the corresponding α-nitro esters, nitroalkanes, and amides. In the case of alkylphenyl acetates, no amides were formed; apparently the abstraction of the α hydrogen by base was faster than nucleophilic attack on the carboxyl group.

Ethyl propionate gave lower yields than other aliphatic ethyl esters because of a competing reaction, the self-condensation to ethyl α-propionylpropionate.

The importance of the acidity of the ester on the success of the alkyl nitrate nitration can be seen by comparing the results on the alkyl phenylacetates. The highest yield of over-all nitration occurred with the least acidic ethyl *p*-methoxyphenylacetate, and no nitration with ethyl *p*-nitrophenylacetate, 75% being recovered. Diethyl malonate and diethyl methylmalonate also failed to undergo nitration. These results seem to indicate that in the potassium amide–liquid ammonia system only compounds with pK_a greater than 16[11] would undergo nitration.[12]

Nitration of diethyl homophthalate gave instead of the expected α-nitro ester, potassium homophthalimidonitronate (**5**). On treatment with bromine, **5** was converted into 1-bromo-1-nitrohomophthalimide (**6**) (eq 2), whose infrared and nmr spectra were in agreement with the assigned structure. Compound **6** was unstable and slowly gave off oxides of nitrogen. Ethyl α-nitro esters which were known compounds were identified by comparison of physical data. Ethyl α-nitro-*p*-methoxyphenylacetate (**7**) was identified as its potassium salt, because attempts to convert the latter into **7** by the usual methods led to decomposition, as did bromination of the salt.



5 **6** (2)

Aliphatic and Aryl Alkyl *t*-Butyl Esters.—In general with the *t*-butyl esters over-all nitration was higher than with the ethyl esters (Table II). Also no amide formation occurred.

The importance of salt formation is readily seen in the nitration of *t*-butyl α-methylbutyrate, which can only lead to a nitro ester with a *t*-nitro group. Cleavage was the predominant reaction and gave 2-nitrobutane in 72% yield (eq 3). It has been previously observed

$$H_3CCH_2CH(CH_3)CO_2C(CH_3)_3 \xrightarrow[2.\ H^+]{1.\ KNH_2,\ EtONO_2} H_3CCH_2CH(NO_2)CH_3 \quad (3)$$

that cleavage also predominated in the alkyl nitrate nitration of cyclanones containing α-alkyl substituents.[1d]

The *t*-butyl α-nitro esters were identified by correct elemental analyses which are detailed in Table III. The infrared spectra showed the characteristic carbonyl stretching vibration at 1745–1761 cm^{-1} and the asymmetric nitro stretching vibration[13] at 1555–1575 cm^{-1}. These absorption maxima constitute only very small shifts to higher frequencies from their normal

---

[10] An excess of nitrating agent is needed because in a blank test it was found that potassium amide in liquid ammonia reacted with ethyl nitrate at −33° to give ethoxide.[1e]

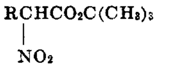
[11] According to R. G. Pearson and R. L. Dillon [*J. Amer. Chem. Soc.*, **75**, 2441 (1953)], the acidity of diethyl malonate and diethyl ethylmalonate lies in the range of 15–16 pK_a units.

[12] Most likely the reaction between ester anion and alkyl nitrate is reversible, and with carbanions of acidic esters the position of the equilibrium lies far to the left.

[13] The symmetric nitro stretching vibration at 1370–1390 cm^{-1} was masked by CH bending vibration.

TABLE III

PHYSICAL PROPERTIES OF *t*-BUTYL α-NITRO ESTERS



$\underset{\mathrm{NO_2}}{\mathrm{RCHCO_2C(CH_3)_3}}$

R^a	Bp (mm), °C	$n^{20}\mathrm{D}$	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
n-C_4H_9	65–68 (0.3)	1.4288	$C_{10}H_{19}NO_4$	55.30	8.75	6.45	55.57	8.82	6.51
C_2H_5	58–61 (1.6)	1.4229	$C_8H_{15}NO_4$	50.78	7.99	7.40	50.99	7.98	7.60
CH_3	45–47 (0.8)	1.4202	$C_7H_{13}NO_4$	48.00	7.43	8.00	48.11	7.68	8.03
H	53–56 (1.4)	1.4245	$C_6H_{11}NO_4$	44.72	6.83	8.69	44.86	6.84	8.57
i-C_3H_7	55–58 (0.5)	1.4262	$C_9H_{17}NO_4$	53.20	8.37	6.89	53.47	8.57	6.99
C_6H_5	101–102 (0.25)	1.4955	$C_{12}H_{15}NO_4$	60.76	6.33	5.91	60.76	6.62	5.96

[a] The respective registry numbers are 18598-90-8, 18598-91-9, 18598-92-0, 18598-93-1, 18598-94-2, and 18598-95-3.

positions.[14] In the nmr spectra of aliphatic α-nitro esters, the α hydrogen absorption occurred at 4.8–5.2 ppm. In the more acidic α-nitrophenylacetates, this absorption was shifted downfield to 6.1–6.2 ppm.

Study of the Cleavage and Transesterification Reactions.—It was recently reported that mononitration of ketones with alkyl nitrates led not only to α-nitro ketones but also to fragmentation products,[1d,e] which formed during the nitration step.

Since very little information was available about the cleavage and transesterification reactions, which were observed to occur during the alkyl nitrate nitration of esters, a study was undertaken to determine their course.

In the typical alkyl nitrate nitration, the alkyl nitrate was added to a mixture of the ester and potassium amide in ammonia at −33°, followed by acidification glacial acetic acid at −50° after the ammonia was replaced by ether.

That the acidification step was not the cause of the fragmentation and(or) transesterification was established by the following experiments.

(1) Treating the potassium salt of ethyl α-nitrocaproate (**8**) with an excess of glacial acetic acid in ethanol and ether led to a 91% recovery of **8**.

(2) When a mixture consisting of 72% **8** and 28% *t*-butyl α-nitrocaproate (**9**) was refluxed in an ethanolic acetic acid solution, the change in the ratio of **8** (70.5%) and **9** (29.5%) was negligible.

(3) Distilling the reaction mixture from the nitration of ethyl caproate (**10**) with ethyl nitrate *in vacuo* at 0° prior to acidification afforded one of the cleavage products, diethyl carbonate. Acidifying the residue gave the other cleavage product, 1-nitropentane, and nitro ester **8** (eq 4).

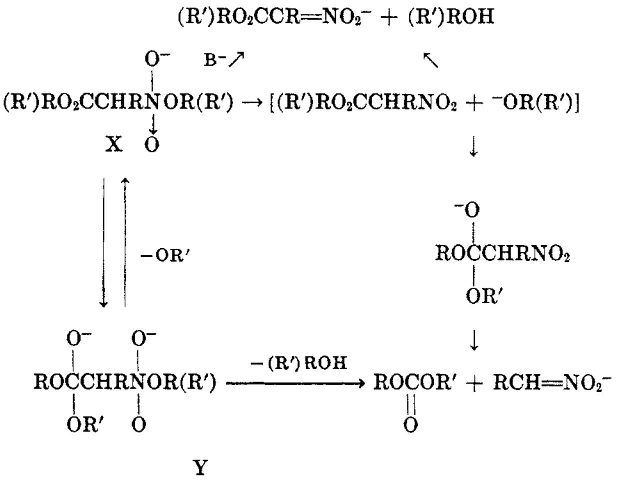
$$\underset{\mathbf{10}}{\mathrm{H_3C(CH_2)_4CO_2C_2H_5}} \xrightarrow[\mathrm{EtONO_2}]{\mathrm{KNH_2\text{–}liquid\ NH_3}}$$

$$\mathrm{(C_2H_5O)_2CO} + \text{“nitro salts”} \xrightarrow{\mathrm{HOAc}}$$

$$\underset{\mathbf{8}}{\mathrm{H_3C(CH_2)_3CH(NO_2)CO_2C_2H_5}} + \mathrm{H_3C(CH_2)_4NO_2} \quad (4)$$

It has been suggested[1b] that the alkyl nitrate nitration of an active methylene compound proceeds *via* an intermediate X which is formed by nucleophilic attack of a carbanion on the alkyl nitrate. In the case of an ester, collapse of intermediate X would lead to a nitro ester and an alkoxide ion. Direct alkoxide attack on the carboxyl group could then lead to cleavage and/or transesterification (Scheme I). This mode of attack has been reported to occur during the alkyl nitrate nitration of α-alkylcyclanones.[1d]

SCHEME I



It appeared that support for this reaction pathway was obtained when the addition of potassium ethoxide in ether prior to n-butyl nitrate during the nitration of *t*-butyl caproate (**11**) afforded a mixture of esters composed of 26.8% n-butyl α-nitrocaproate (**12**), 21.8% **8** and 2.4% **9**. However, in a control test, it was ascertained that transesterification occurred at −33° in the potassium amide–liquid ammonia system between ethoxide ion and n-butyl nitrate to give n-butoxide ion and ethyl nitrate.[15] Therefore, the formation of esters **8** and **12** in addition to **9** in the nitration of **11** could be accounted for by the presence of both ethyl and n-butyl nitrates in the reaction mixture.[16]

$$n\text{-BuO}^- + \mathrm{EtONO_2} \xrightleftharpoons{\mathrm{KNH_2\text{–}NH_3}} n\text{-BuONO}_2 + \mathrm{EtO^-}$$

Since it was established[10] that ethoxide was formed by the interaction of potassium amide and ethyl nitrate, ester **8** could also have formed by transesterification of *t*-butyl ester **11** to ethyl caproate (**10**) by reaction with ethoxide *prior* to nitration. In a control test, it

---

(14) J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall Inc., Englewood Cliffs, N. J., 1965, pp 34–38.

(15) It was previously found that no reaction took place in the potassium *t*-butoxide–THF system between ethoxide ion and amyl nitrate at a temperature as high as 0°.[1d]

(16) Surprisingly, only a trace amount of ester **12** was obtained when potassium n-butoxide was added prior to ethyl nitrate during the nitration of **11**. This might well be due to the low solubility of potassium ethoxide in the potassium amide–liquid ammonia system. In fact, a control experiment with potassium n-butoxide and ethyl nitrate gave only a small amount of transesterification. Thus the equilibrium between n-butoxide and ethyl nitrate lies far to the left.

was established that **10** was formed in ~23% yield when **11** was treated with ethoxide ion under the conditions of the nitration reaction. Therefore, it is quite possible that some of nitro ester **8** originated from the nitration of ester **10**. In any event, the formation of **8** was not due to direct ethoxide attack on nitro ester **9**.

With regard to the fragmentation reaction which gives rise to nitroalkane and dialkyl carbonate during the nitration, the following experimental observations seem to exclude direct alkoxide attack on the nitro ester under the conditions of the alkyl nitrate nitration.

(1) About 94% of ethyl α-nitrocaproate (**8**) was recovered after treatment at $-33°$ in liquid ammonia with potassium ethoxide followed by acidification with glacial acetic acid at $-50°$.

(2) When a mixture consisting of 53% **8** and 47% **9** was treated with potassium amide in liquid ammonia at $-33°$ and then acidified with glacial acetic acid at $-50°$, the change in the ratio of **8** (51%) and **9** (49%) was negligible.

A mechanism (Scheme I) consistent with our experimental observations involves nucleophilic attack[17] at the carboxyl group of intermediate X to give intermediate Y which on fragmentation is converted into the cleavage products. Also, abstraction of the α hydrogen in intermediate X by base could lead to the nitro ester salt. The collapse of intermediate Y, containing different alkoxy groups, to nitro ester *via* intermediate X could also explain the formation of a mixture of nitro esters **8**, **9**, and **12** on nitrating *t*-butyl ester **11** with *n*-butyl nitrate in the presence of potassium ethoxide (*vide supra*).

Experimental Section

Equipment.—All infrared spectra were taken with a Perkin-Elmer recording spectrophotometer, Models 21 and 421. Nuclear magnetic resonance spectra were determined on a Varian Model A-60 analytical nmr spectrometer using tetramethylsilane as an internal standard. Gas chromatographic analyses were performed on an Aerograph A-903 using a 4-ft SF-96 on Chromosorb P or Chromosorb W column. Solvents were evaporated on a Buchler flash evaporator. Nonaqueous titrations were performed by the method of Feuer and Vincent.[18]

Materials.—Ethyl nitrate of Eastman White Label grade was used as received. All aliphatic ethyl esters and malonic esters were from commercial sources. The ethyl phenylacetates were prepared from the corresponding acids and the *t*-butyl esters from the corresponding acid chlorides by methods described in the literature.

Nitration of Ethyl Esters.—The following experiment is typical of the procedure employed. An oven-dried, nitrogen-flushed, 500-ml round-bottom four-necked flask was fitted with a Dry Ice condenser, thermometer, mechanical stirrer, and dropping funnel which was provided with a side arm below the stopcock in order to allow the venting of ammonia. Potassium (4.10 g, 0.105 g-atom) and a catalytic amount of ferric nitrate were placed in 300 ml of anhydrous ammonia at $-33°$, and, after the potassium amide[19] had formed, ethyl *n*-butyrate (**13**) (11.05 g, 0.0995 mol) in 10 ml of dry ether was added all at once. After stirring for 3–5 min, ethyl nitrate (14.30 g, 0.152 mol) in 5 ml of dry ether was added as rapidly as possible (3–5 min),[20] and the mixture was stirred an additional 55 min at $-33°$. After the ammonia was replaced by ether, the reaction mixture was acidified at $-50°$ with glacial acetic acid (20.0 g, 0.33 mol), and stirring was continued for 12 hr. Filtering the potassium acetate, evaporating the filtrate, and distilling the residue *in vacuo* gave 6.55 g (41.0%) of ethyl *n*-α-nitrobutyrate: bp 58–61° (1.5 mm); $n^{20}\text{D}$ 1.4238.

Extracting the residue, which remained after distillation, with petroleum ether (bp 60–70°), and cooling the filtrate gave a white precipitate. Recrystallizing from a 50:50 mixture of petroleum ether (bp 60–70°) and chloroform gave 1.6 g (7.0%) of *n*-butyramide, mp 115–116°. The material which had remained in the Dry Ice trap was redistilled at 70 mm to give 1.95 g (18%) of unreacted **13**, 1.24 g (14%) of 1-nitropropane, and 0.12 g (10%) of diethyl carbonate, as determined by glpc analysis.

Nitration of Ethyl Caproate (10) without Subsequent Acidification.—The experimental procedure was the same as that described for the nitration of **13** up to the acidification step, except that potassium (4.16 g, 0.107 g-atom), ester **10** (14.00 g, 0.097 mol), and ethyl nitrate (13.30 g, 0.146 mol) were employed.

After the ammonia had been replaced by ether, the reaction mixture was distilled at 0° (1 mm). Glpc analysis of the distillate showed the presence of diethyl carbonate (5.5%) and unreacted **10** (5.3%).

Acidification of the residue at $-50°$ with glacial acetic acid (20.0 g, 0.33 mol) followed by distillation *in vacuo* gave two fractions. One fraction, bp 31–37° (0.5 mm), consisted of 1-nitropentane (2.0 g, 17.0%) and unreacted **10** (3.0 g, 21.4%) as determined by glpc analysis. The other fraction contained 7.7 g (41.0%) of nitro ester **8**, bp 62–65° (0.5 mm).

Nitration of Ethyl *p*-Methoxyphenylacetate (14).—The experimental procedure was the same as described for the nitration of **13** except that potassium (3.60 g, 0.092 g-atom), compound **14** (16.30 g, 0.084 mol), and ethyl nitrate (11.45 g, 0.126 mol) were employed.

Boiling off the ammonia and filtering gave 21.6 g of crude nitronate salts. Dissolving the solid material in hot isopropyl alcohol, filtering, and cooling to room temperature gave a precipitate. One recrystallization from isopropyl alcohol gave 16.80 g (72.0%) of potassium α-carbethoxy-*p*-methoxyphenylmethanenitronate: mp 220–222° dec; ir (Nujol) 1692 ($C{=}O$), 1524 ($C{=}NO_2$), 1250 (CH_3O-), and 1175 cm^{-1} ($-C-O-C$); nmr (D_2O) δ 7.55–6.95 (m, 4, C_6H_4), 4.25 (q, 2, $CO_2CH_2CH_3$), 3.86 (s, 3, CH_3O), and 1.19 (t, 3, $CH_3CH_2CO_2$).

Anal. Calcd for $C_{11}H_{12}NO_5K$: C, 47.65; H, 4.34; N, 5.05; K, 14.08; neut equiv, 277. Found: C, 47.79; H, 4.27; N, 5.06; K, 13.91; neut equiv, 280.

Placing the isopropyl alcohol filtrate in an ice chest gave a precipitate which after recrystallization from isopropyl alcohol gave potassium *p*-methoxyphenylmethanenitronate (3.73 g, 21.7%): mp 198–201° dec; ir (Nujol) 1550 ($C{=}NO_2$), 1250 (CH_3O), and 835 cm^{-1} (C_6H_4); nmr (D_2O) δ 8.05–6.85 (m, C_6H_4 and $CHNO_2$, and 3.88 (s, 3, CH_3O).

Anal. Calcd for $C_8H_8NO_3K$: C, 46.83; H, 3.90; N, 6.83; K, 19.07; neut equiv, 205. Found: C, 46.38; H, 4.17; N, 6.39; K, 18.78; neut equiv, 209.

Nitration of Diethyl Homophthalate.—The experimental procedure was the same as described for the nitration of **13** except that potassium (3.95 g, 0.101 g-atom), diethyl homophthalate (21.48 g, 0.091 mol), and ethyl nitrate (12.42 g, 0.136 mol) were employed. After acidifying at $-50°$ with glacial acetic acid (20.0 g, 0.33 mol) and filtering, the precipitate consisted of potassium acetate and yellow solid A.

After removing the ether from the filtrate, the residue was dissolved at 0° in an ethanol–potassium ethoxide solution which had been prepared from potassium (0.11 g, 0.028 g-atom) in 50 ml of absolute ethanol. Stirring the solution for 3 hr at 0°, removing the ethanol *in vacuo*, extracting the residue with ether, and removing the ether *in vacuo* gave 7.18 g (35.4%) of unreacted ester, mp 20–22°; glpc retention time was the same as that of an authentic sample.

The residue was placed in 50 ml of dry ether, acidified at 0° with glacial acetic acid (1.24 g, 0.021 mol), and stirred for 12 hr. Filtering the potassium acetate and removing the ether *in vacuo* gave 5.82 g (30.6%) of *o*-carbethoxy-α-nitrotoluene which after recrystallization from isopropyl alcohol had mp 50–51°; ir (KBr) 1724 ($C{=}O$) and 1570 cm^{-1} (NO_2); nmr ($CDCl_3$) δ 8.7–7.2 (m, 4, C_6H_4), 5.80 (s, 2, CH_2NO_2), 4.30 (q, 2, $CO_2CH_2CH_3$), and 1.33 (t, 3, $CO_2CH_2CH_3$).

Anal. Calcd for $C_{10}H_{11}NO_4$: C, 57.43; H, 5.26; N, 6.70. Found: C, 57.43; H, 5.46; N, 6.64.

Washing solid A copiously with water to remove potassium

---

[17] Amide ion, alkoxide ion or perhaps the ester anion itself could function as nucleophiles.

[18] H. Feuer and F. Vincent, Jr., *Anal. Chem.*, **35**, 598 (1963).

[19] R Levine and C. R. Hauser *J. Amer. Chem. Soc.*, **66**, 1768 (1944).

[20] *Caution!* The first few drops of alkyl nitrate should be added slowly because a considerable exotherm develops.

acetate, dissolving the residue in a minimum amount of warm 10% potassium hydroxide, adding methanol to the cloud point, and cooling in an ice chest gave after filtering and drying *in vacuo* 4.2 g (18.9%) of potassium α-homophthalimidonitronate (**5**): mp 307° dec; ir (KBr) 3425 (HN), 1689 and 1661 (CONHCO), 1618 (C=NO$_2$), and 749, 700, and 681 cm^{-1} (C_6H_4).[15]

Anal. Calcd for $C_9H_5N_2O_4K$: C, 44.25; H, 2.06; N, 11.46; K, 16.00; neut equiv, 244. Found: C, 44.21; H, 2.16; N, 11.57; K, 15.85; neut equiv, 245.

Bromination of Compound 5.—Bromine was added at 3-5° to compound **5** (0.33 g, 1.4 mmol) in 20 ml of dry carbon tetrachloride until the color of bromine just persisted. Evaporating the solvent *in vacuo* and recrystallizing the residue from warm carbon tetrachloride (50°) gave 0.32 g (80.0%) of α-bromo-α-nitrohomophthalimide (**6**): mp 110-112°; ir (KBr) 3390-3330 (NH), 1709-1695 (CONHCO), and 1580 cm^{-1} (NO$_2$); nmr (CDCl$_3$) δ 9.3 (s, 1, NH), and 8.4-7.6 (m, 4, C_6H_4).

Anal. Calcd for $C_9H_5N_2O_4Br$: C, 37.93; H, 1.75; N, 9.82; Br, 28.03. Found: C, 38.90; H, 1.85; N, 8.94; Br, 26.72. The analysis did not check because the compound was unstable as evidenced by the evolution of oxides of nitrogen.

Treatment of Ethyl α-Nitrocaproate (8) with Potassium Ethoxide at Alkyl Nitrate Nitration Conditions.—To 0.012 mol of potassium amide in liquid ammonia was added at −33° absolute ethanol (0.58 g, 12.6 mmol). After stirring the mixture for 5 min, compound **8** (2.72 g, 14.4 mmol) was added. After the mixture was stirred for 1 hr at −33°, the ammonia was replaced by dry ether. Then the reaction mixture was acidified at −50° with glacial acetic acid (2.3 g, 38.0 mmol) and stirring was continued for 16 hr.

Filtering the potassium acetate, removing the ether from the filtrate, and subjecting the residual liquid to glpc analysis showed only the presence of **8**. Distillation *in vacuo* gave 2.56 g (94%) of **8**: bp 64-67° (0.6 mm); n^{20}_{D} 1.4298.

Potassium 1-Carbethoxy-1-pentanenitronate.—To 1.24 g (0.021 mol) of potassium hydroxide in 100 ml of absolute ethanol at 0° was added compound **8** (5.0 g, 0.0264 mol), and the reaction mixture stirred for 6 hr. Removing the ethanol *in vacuo*, slurrying the remaining solid with dry ether, filtering, and drying *in vacuo* gave 4.15 g (76%) of potassium salt of **8**: mp 137-141° dec; ir (KBr) 1689 (C=O) and 1567 cm^{-1} (C=NO$_2$); nmr (D$_2$O) δ 4.25 (q, 2, $CO_2CH_2CH_3$), 2.6 (t, 2, CH_2CH_2C=NO$_2$), and 1.4-0.9 [m, $CH_3(CH_2)_2CH_2$ and $CO_2CH_2CH_3$].

Anal. Calcd for $C_8H_{14}NO_4K$: C, 42.29; H, 6.17; N, 6.17; K, 17.18; neut equiv, 227. Found: C, 42.41; H, 6.31; N, 6.32; K, 16.95; neut equiv, 230.

Conversion of Potassium 1-Carbethoxy-1-pentanenitronate into Ethyl α-Nitrocaproate (8) at Alkyl Nitrate Nitration Conditions.—To a mixture consisting of potassium salt of **8** (1.5 g, 6.6 mmol) and absolute ethanol (0.3 g, 6.6 mmol) in 50 ml of dry ether was added at −50° glacial acetic acid (0.9 g, 15.2 mmol). Stirring the reaction mixture for 16 hr, filtering, removing the solvent *in vacuo* and distilling gave 1.14 g (91.2%) of **8**: bp 59-62° (0.5 mm); n^{20}_{D} 1.4295; glpc analysis indicated only the presence of **8**.

Nitration of *t*-Butyl Esters.—The experimental procedure was the same as described for the nitration of **13** except that 1.0 equiv of *t*-butyl ester and 2.0 equiv of potassium amide instead of 1.1 equiv were employed. Upon distillation of the acidified reaction mixture both ethyl and *t*-butyl α-nitro esters were obtained which were separated and purified by glpc.

Nitration of *t*-Butyl Caproate (11) with "Solid Potassium Ethoxide" Added Prior to *n*-Butyl Nitrate.—To 0.168 mol of potassium amide in 300 ml of anhydrous ammonia was added at −33° compound **11** (14.45 g, 0.084 mol) in 10 ml of dry ether all at once. After stirring for 5 min, "solid potassium ethoxide"[21] (10.58 g, 0.126 mol) was added at −33°. After stirring for 5 min, *n*-butyl nitrate (14.99 g, 0.126 mol) in 5 ml of dry ether was added as rapidly as possible (3-5 min), and the reaction mixture was stirred 55 min longer at −33°. After the ammonia was replaced by ether, the reaction mixture was acidified at −50° with glacial acetic acid (40.0 g, 0.67 mol), and stirring was continued for 14 hr. The potassium acetate was filtered and the ether removed *in vacuo*.

Distillation *in vacuo* gave three fractions. The first fraction, bp 31-35° (0.5 mm), was identified as 1-nitropentane (2.79 g, 28.4%). The second fraction, bp 61-67°, consisted of 0.43 g (2.4%) of *t*-butyl α-nitrocaproate (**9**) and 3.44 g (21.8%) of ethyl α-nitrocaproate (**8**) as determined by glpc analysis. The third fraction was *n*-butyl α-nitrocaproate (**12**) (4.88 g, 26.8%): bp 78-82° (0.5 mm); n^{20}_{D} 1.4342; ir (neat) 1754 (C=O) and 1570 cm^{-1} (NO$_2$); nmr (CDCl$_3$) δ 5.11 (t, 1, H_2CCHNO_2), 4.22 (t, 2, $CO_2CH_2CH_2$) and 2.5-0.8 [m, $CH_3(CH_2)_3CNO_2$ and $CO_2CH_2(CH_2)_2CH_3$].

Anal. Calcd for $C_{10}H_{19}NO_4$: C, 55.30; H, 8.76; N, 6.45. Found: C, 55.38; H, 8.80; N, 6.37.

The Dry Ice trap contained 0.12 g (3.3%) of ethyl caproate (**10**) as determined by glpc analysis.

Treatment of a Mixture of Ethyl α-Nitrocaproate (8) and *t*-Butyl α-Nitrocaproate (9) with Potassium Ethoxide at Alkyl Nitate Nitration Conditions.—To 9.3 mmol of potassium amide in 50 ml of anhydrous ammonia was added at −33° absolute ethanol (0.43 g, 9.35 mmol). After stirring for 5 min, 2.0 g of a mixture consisting of compound **8** (53%) and compound **9** (47%) was added, and after 1 hr at −33° the ammonia was replaced by dry ether. Then the reaction mixture was acidified at −50° with glacial acetic acid (1.5 g, 25.0 mmol) and stirred for 14 hr.

Filtering the potassium acetate, removing the ether from the filtrate, and subjecting the residual liquid to glpc analysis showed the presence of **8** (51%) and **9** (49%). Glpc retention times of all compounds were the same as those of authentic samples.

Treatment of a Mixture of Ethyl α-Nitrocaproate (8) and *t*-Butyl α-Nitrocaproate (9) with Ethanolic Acetic Acid.—To 200 ml of a mixture consisting of compound **8** (72%) and compound **9** (28%) was added to 50 ml of absolute ethanol and 2 drops of glacial acetic acid. After the mixture was heated in a refluxing acetone bath for 16 hr and analyzed by glpc, it was found to contain only **8** (70.5%) and **9** (29.5%). Glpc retention times of both compounds were the same as those of authentic samples.

Conversion of *t*-Butyl Caproate (11) into Ethyl Caproate (10) in Potassium Amide-Liquid Ammonia Solution.—To 0.058 mol of potassium amide in 100 ml of anhydrous ammonia at −33° was added compound **11** (5.0 g, 0.029 mol), and stirring was continued for 5 min. Then "solid potassium ethoxide"[21] (3.70 g, 0.044 mol) was added, stirring continued at −33° for 5 min, and, after solid anhydrous ammonium chloride (6.4 g, 0.12 mol) was added, the ammonia was replaced by dry ether.

Filtering the potassium chloride, removing the ether *in vacuo*, and subjecting the residual liquid to glpc analysis showed the presence of **11** (77%) and **10** (23%) the retention times of which were the same as those of authentic samples. In a control test at the temperature of the glpc analysis, a mixture of compound **11** and ethanol did not give any compound **10**.

Ester Exchange between *n*-Butyl Nitrate and "Solid Potassium Ethoxide" at Conditions of the Alkyl Nitrate Nitration.—To *n*-butyl nitrate (6.55 g, 0.055 mol) in 100 ml of anhydrous liquid ammonia was added all at once at −33° "solid potassium ethoxide"[21] (4.62 g, 0.055 mol). After 5 min the mixture was neutralized with anhydrous ammonium chloride (5.88 g, 0.11 mol), and after stirring 5 min at −33°, the ammonia was replaced by dry ether. Filtering the potassium chloride, concentrating the filtrate *in vacuo* and subjecting the remaining liquid to glpc analysis showed the presence of *n*-butyl nitrate (88.8%) and ethyl nitrate (11.2%). Glpc retention times of both compounds were the same as those of authentic samples.

Subjecting a mixture of *n*-butyl nitrate and ethanol to glpc analysis at the same conditions showed that no transesterification occurred at the temperature of the glpc injector block.

Registry No.—Potassium α-carbethoxy-*p*-methoxyphenylmethanenitronate, 12313-38-1; potassium *p*-methoxyphenylmethanenitronate, 12313-35-8; *o*-carbethoxy-α-nitrotoluene, 18598-87-3; **5**, 12313-37-0; **6**, 18598-88-4; potassium salt of **8**, 12313-36-9; **12**, 18598-89-5; ammonia, 7664-41-7.

Acknowledgment.—We are indebted to the Office of Naval Research for the financial support of this work.

---

[21] "Solid potassium ethoxide" was prepared by adding potassium to absolute ethanol, removing excess ethanol *in vacuo*, and washing the residue copiously with dry ether. Since potassium ethoxide decomposed on drying *in vacuo*, the material used contained ether.