yield 69%, which was hydrolyzed and decarboxylated to 3-methylcyclopentylacetic acid, probably a mixture of *cis* and *trans* isomers, b.p. 93–95° (1.4 mm.), $n^{22}D$ 1.4499, m.p. of the amide 139–140.5°, mixed m.p. with degradation product 138–140.5°; m.p. of *p*-bromophenacyl ester 65°, mixed m.p. with degradation product 64–66°.

It was hoped that catalytic hydrogenation of 3-methylcyclopentylidene cyanoacetic ester might furnish the *cis* isomer due to interference of the methyl group with the catalyst surface (for a similar case see ref. 18). Hydrogenation in ethanol, 5% palladium-on-charcoal as catalyst, stopped after the absorption of 1.3 moles of hydrogen and distillation furnished 30 g. of a fraction, b.p. 103–106° (2 mm.), $n^{22}D$ 1.4520. Hydrolysis and decarboxylation gave an acid, virtually identical with the acid obtained by aluminum amalgam reduction, b.p. 89–91° (1.2 mm.), $n^{22}D$ 1.4494, m.p. of amide 138–139°, mixed m.p. with the other reduction product 137.5–139°, mixed m.p. with degradation product 138–140.5°, m.p. of *p*-bromophenacyl ester 66–67°, mixed m.p. with the other reduction product 64–66°, mixed m.p. with degradation product 66–67°. The infrared spectra of all fractions were identical. Apparently the relatively great distance of the methyl group from the reaction site operates to reduce the degree of steric control during reduction, but more work is needed to establish this point.

Cyclopentylacetone.—Ethyl cyclopentylacetoacetate was prepared by the method of Rydon[41] which gave better yields than the procedure described by Burschkies and Scholl.[42] A mixture of 110 g. of the ketoester, 60 g. of potassium hydroxide and 800 ml. of water was refluxed overnight and then steam distilled. The distillate was extracted with ether and the ether extracts were dried and distilled. The ketone was collected at 84–86° (31 mm.), yield 49.5 g. (71%). This method appears to be more convenient than the one described in the literature.[43] The 2,4-dinitrophenylhydrazone melted at 84° (lit.[43b] 78–79°).

Ethyl 2-Cyano-3-methyl-4-cyclopentylcrotonate.—A mixture of 49 g. of cyclopentylacetone, 45 g. of ethyl cyanoacetate, 16 g. of acetic acid, 5.9 g. of ammonium acetate and 200 ml. of benzene was refluxed in an apparatus fitted with a Stark–Dean trap until water was no longer evolved. The solution was washed with water, dried and distilled. The product distilled at 135–138° (2.5 mm.), $n^{22}D$ 1.4890, wt. 74.5 g. (87%).

Anal. Calcd. for $C_{13}H_{19}NO_2$: C, 70.65; H, 8.65. Found: C, 70.70; H, 8.73.

Ethyl 2-Cyano-3-methyl-4-cyclopentylbutyrate.—A solution of 74.5 g. of the unsaturated ester in 175 ml. of absolute alcohol was shaken with 5% palladium-on-charcoal in an atmosphere of hydrogen (3–4 atmospheres) until hydrogen uptake ceased. Distillation furnished 66 g. of product, b.p. 120–126° (2 mm.), $n^{22}D$ 1.4559.

Anal. Calcd. for $C_{13}H_{21}NO_2$: C, 69.92; H, 9.48. Found: C, 70.00; H, 9.57.

3-Methyl-4-cyclopentylbutyric Acid.—A mixture of 66 g. of the preceding ester, 100 g. of potassium hydroxide, 100 ml. of water and 350 ml. of water was refluxed for 16 hours. The alcohol was removed and the residue was diluted with water, extracted with ether and acidified. An oil separated which solidified on standing. It did not decarboxylate on distillation. A small amount was recrystallized several times from a benzene-petroleum ether mixture. Analysis of the colorless crystals, m.p. 99°, showed that the solid was 2-cyano-3-methyl-4-cyclopentylbutyric acid.

Anal. Calcd. for $C_{11}H_{17}NO_2$: N, 7.17. Found: N, 7.25.

In order to complete the hydrolysis, the remaining material was refluxed with 300 ml. of concd. hydrochloric acid. The mixture was cooled and extracted with ether. The dried ether extracts were distilled, furnishing 34 g. (67%) of the desired acid, b.p. 119–121° (2 mm.), $n^{22}D$ 1.4579. Its preparation has been reported previously[44] but no properties were given.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.82; H, 10.69.

The amide was recrystallized several times from ligroin and melted at 99.5–101°.

Anal. Calcd. for $C_{10}H_{19}NO$: C, 70.96; H, 11.32. Found: C, 71.16; H, 11.42.

The *p*-bromophenacyl ester was recrystallized three times from ethanol containing a little water and melted at 56–57°.

Anal. Calcd. for $C_{18}H_{23}O_3Br$: C, 58.86; H, 6.31. Found: C, 59.12; H, 6.48.

TALLAHASSEE, FLA.

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[41] H. N. Rydon, *J. Chem. Soc.*, 1544 (1939)

[42] K. Burschkies and J. Scholl, *Arch. Pharm.*, **281**, 328 (1943).

[43] (a) E. Rohrmann, U. S. 2,520,015; *C. A.*, **45**, 647 (1951); (b) Ming-Chien Chiang, *J. Chin. Chem. Soc.*, **18**, 65 (1951); *C. A.*, **46**, 4471 (1952).

[44] J. v. Braun, W. Rudolph, H. Kröper and W. Pinkernelle, *Ber.*, **67**, 269 (1934).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

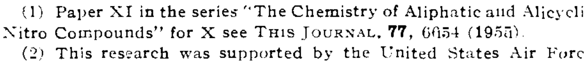
A New Reaction of α-Nitroesters[1,2]

BY NATHAN KORNBLUM AND JOHN H. EICHER

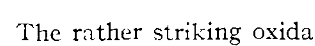
RECEIVED AUGUST 5, 1955

α-Nitroesters react with a solution of sodium nitrite in aqueous ethanol at room temperature giving α-oximinoesters in 70–78% yields. Ethyl nitroacetate reacts vigorously to give a mixture of nitrous oxide, nitrogen and carbon dioxide. If the α-nitroester does not have a hydrogen atom on the carbon holding the nitro group it is quantitatively recovered. The mechanism of this new reaction is discussed.

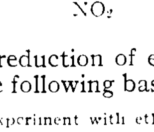
α-Nitroesters react with sodium nitrite according to eq. 1. This reaction, which takes place at room temperature, gives 70–78% yields of the α-oximinoesters.[3]


$$\underset{\displaystyle NO_2}{R-\underset{|}{C}HCOOC_2H_5} + NO_2^- \longrightarrow R-\underset{\displaystyle NOH}{\underset{\|}{C}}-COOC_2H_5 + NO_3^- \quad (1)$$

On the other hand, α-nitroesters I and II, which have no α-hydrogen atoms, are recovered in 94–96% yields after eleven days exposure to the action of aqueous ethanolic sodium nitrite.[4]


$$(C_2H_5OOC-CH_2CH_2)_2-\underset{\displaystyle NO_2}{\underset{|}{C}}-COOC_2H_5$$

I


$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle NO_2}{\underset{|}{C}}}}-COOC_2H_5$$

II

The rather striking oxidation–reduction of eq. 1 becomes readily intelligible on the following basis

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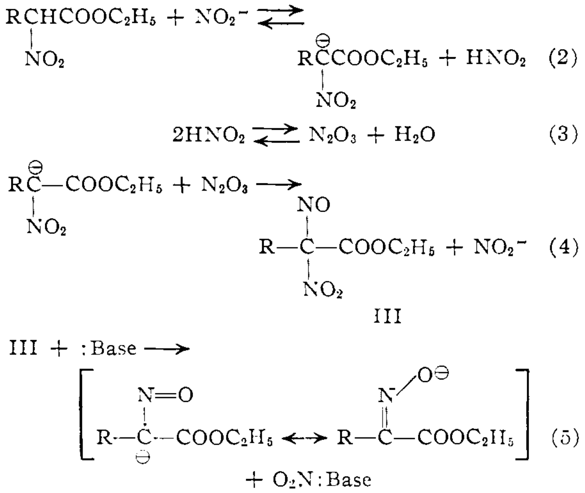
[1] Paper XI in the series "The Chemistry of Aliphatic and Alicyclic Nitro Compounds" for X see THIS JOURNAL, **77**, 6654 (1955).

[2] This research was supported by the United States Air Force under Contract No. AF18(600)-310 monitored by the Office of Scientific Research, Air Research and Development Command.

[3] The stereochemistry of these oximes is not known. The presence of nitrate ion in the reaction product has been established.

[4] We thank Dr. D. C. Iffland for the experiment with ethyl α-nitroisobutyrate.



$$\underset{\substack{|\\ \mathrm{NO_2}}}{\mathrm{RCHCOOC_2H_5}} + \mathrm{NO_2^-} \rightleftarrows \underset{\substack{|\\ \mathrm{NO_2}}}{\mathrm{R\overset{\ominus}{C}COOC_2H_5}} + \mathrm{HNO_2} \quad (2)$$

$$\mathrm{2HNO_2} \rightleftarrows \mathrm{N_2O_3} + \mathrm{H_2O} \quad (3)$$

$$\mathrm{R}\underset{\substack{|\\ \mathrm{NO_2}}}{\overset{\ominus}{\mathrm{C}}}\mathrm{{-}COOC_2H_5} + \mathrm{N_2O_3} \longrightarrow \mathrm{R{-}}\overset{\substack{\mathrm{NO}\\ |}}{\underset{\substack{|\\ \mathrm{NO_2}}}{\mathrm{C}}}\mathrm{{-}COOC_2H_5} + \mathrm{NO_2^-} \quad (4)$$

$$\text{III}$$

$$\text{III} + \text{:Base} \longrightarrow \left[\mathrm{R{-}}\underset{\ominus}{\overset{\substack{\mathrm{N{=}O}\\ |}}{\mathrm{C}}}\mathrm{{-}COOC_2H_5} \longleftrightarrow \mathrm{R{-}}\overset{\substack{\mathrm{N{-}O^{\ominus}}\\ \|}}{\mathrm{C}}\mathrm{{-}COOC_2H_5}\right] \quad (5)$$

$$+ \mathrm{O_2N{:}Base}$$

In the first step of this sequence the α-nitroester transfers a proton to nitrite ion thereby producing a significant amount of nitrous acid. That this should occur is really not surprising for α-nitroesters are distinctly more acidic than nitroparaffins.[5] Then, too, nitrite ion is a stronger base than water.

Nitrosation[6] (eq. 4) produces a carbethoxy substituted pseudonitrole (III). It is proposed that such compounds are intrinsically unstable because of the presence of three electron-withdrawing groups on a single carbon atom and that, in the presence of bases such as nitrite ion, water or ethanol, nucleophilic displacement on the nitrogen of the nitro group occurs readily (eq. 5). In this way the resonance-stabilized anion of an α-oximino ester is formed, the other product being N_2O_4, $[H_2O{-}NO_2]^+$ or $\left[\mathrm{C_2H_5{-}\overset{H}{O}{-}NO_2}\right]^+$.[7]

The notion of a nucleophilic displacement on the nitrogen of a nitro group seems not to have been explicitly employed heretofore although the literature contains examples of reactions which almost certainly involve such displacements, *e.g.*, the reactions of tetranitromethane[8] and 1,1,1-trinitroethane[9] with alkali

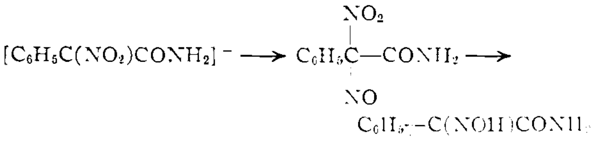
$$\mathrm{C(NO_2)_4 + 2OH^- \longrightarrow C(NO_2)_3^- + NO_3^- + H_2O}$$
$$\mathrm{CH_3C(NO_2)_3 + 2OH^- \longrightarrow CH_3C(NO_2)_2^- + NO_3^- + H_2O}$$

Actually this possibility is to be reckoned with whenever a nitro group is attached to a carbon atom which is also bonded to one or more atoms or groups (such as nitro, nitroso or carbonyl) capable of accommodating the charge on the anion as it separates from the NO_2 group undergoing nucleophilic displacement.[10]

The proposed mechanism (eq. 2 to 5) unambiguously predicts that the nitrogen atom of the α-oximinoester is not the nitrogen atom of the α-nitroester but that, instead, it comes from the sodium nitrite. Isotopic studies by Buchband and Johnston[11] confirm this prediction. From ethyl α-nitropropionate and sodium nitrite enriched with nitrogen-15 they obtained ethyl α-oximinopropionate with about 80% enrichment; likewise, from ethyl α-nitrobutyrate they obtained ethyl α-oximinobutyrate with about 100% enrichment. Although refinement of these isotope studies is desirable, for the light it may cast on the question of whether or not NO_2^- is the base of eq. 5, clearly the nitrogen atom in the α-oximinoester is not the nitrogen of the original α-nitroester.

Many years ago Lepercq found that α-bromoesters are converted to α-oximinoesters by sodium nitrite in aqueous ethanol.[12] The results of the present investigation, taken in conjunction with the recent finding that α-nitroesters can be prepared in excellent yields by the action of sodium nitrite on α-bromoesters,[13] strongly suggest that Lepercq's reaction proceeds *via* α-nitroesters, which then undergo the reaction described in this paper.

The present findings also afford a simple explanation for the observation of van Peski that phenyloximinoacetamide is obtained by the action of sodium nitrite in dilute sulfuric acid on the sodium salt of phenylnitroacetamide[14]: this, presumably, involves the sequence



$$\mathrm{[C_6H_5C(NO_2)CONH_2]^-} \longrightarrow \mathrm{C_6H_5}\overset{\substack{\mathrm{NO_2}\\ |}}{\underset{\substack{|\\ \mathrm{NO}}}{\mathrm{C}}}\mathrm{{-}CONH_2} \longrightarrow$$
$$\mathrm{C_6H_5{-}C(NOH)CONH_2}$$

When an aqueous solution of sodium nitrite is added to an ethanolic solution of ethyl nitroacetate an exothermic reaction occurs. The solution

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[5] Dr. R. K. Blackwood of this Laboratory has found that in 50% aqueous ethanol 2-nitrobutane has a pKa of 9.4 whereas ethyl α-nitropropionate and ethyl α-nitrobutyrate have pKa values of 7.5 and 7.6, respectively.

[6] The preference expressed for N_2O_3 as the nitrosating agent is reasonable but not crucial. Should $\mathrm{H{-}\overset{H}{\underset{+}{O}}{-}NO}$ or ethyl nitrite be shown to be the nitrosating agent the argument concerning the mechanism of the reaction of α-nitroesters with sodium nitrite would not be affected.

[7] None of these three would persist in aqueous ethanol. N_2O_4 and $[H_2O{-}NO_2]^+$ would give nitrate ion thereby preventing reversal of the reaction of eq. 5. $[C_2H_5OH{-}NO_2]^+$ would go over to $C_2H_5{-}ONO_2$ which could, in principle, nitrate the anion of the oxime (eq. 5). To our knowledge this has not been observed; but, even if it did occur, III in a subsequent reaction with NO_2^- or H_2O would be irreversibly destroyed for it is most improbable that only ethanol can serve as a base in the reaction of eq. 5. Consequently, eq. 5 is an irreversible process. In contrast, nucleophilic displacement on the nitrogen of the nitroso group would give the anion $\mathrm{R{-}\underset{\substack{|\\ NO_2}}{\overset{\ominus}{C}}{-}COOC_2H_5}$ along with N_2O_3, $[H_2O{-}NO]^+$ or $\left[\mathrm{C_2H_5\overset{H}{O}{-}NO}\right]^+$ and, since these latter would not be transformed by the solvent into substances incapable of nitrosating the anion $\mathrm{R\underset{\substack{|\\ NO_2}}{\overset{\ominus}{C}}{-}COOC_2H_5}$, such a displacement on the nitroso group is fully reversible.

[8] A. Hantzsch and A. Rickenberger, *Ber.*, **32**, 628 (1899).

[9] J. Meisenheimer, *ibid.*, **36**, 434 (1903).

[10] For example, E. Wolf (M. S. Thesis, Purdue University, 1952) has found that 1-nitro-1-nitrosocyclohexane (cyclohexane pseudonitrole) gives cyclohexanone oxime when treated with piperidine or thiourea. Related studies of this simple but fruitful idea are in progress.

[11] G. P. Buchband, M.S. Thesis, Purdue University, 1951. We are indebted to Professor W. H. Johnston of this Department for his kind coöperation.

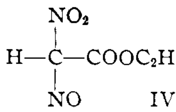
[12] G. Lepercq, *Bull. soc. chim.*, (3) **9**, 630 (1893); **11**, 295, 297, 883, 886 (1894). This reaction gives excellent yields (*cf.* Experimental).

[13] N. Kornblum, H. O. Larson, D. D. Mooberry, R. K. Blackwood, E. P. Oliveto and G. E. Graham, *Chemistry and Industry*, 443 1955; R. K. Blackwood, Ph.D. Thesis, Purdue University, June, 1955.

[14] A. J. van Peski, *Rec. trav. chim.*, **41**, 687 (1922).

becomes successively yellow, orange, red, dark red, orange and yellow over the course of six hours at room temperature and a colorless, odorless gas is evolved. Ether extraction of the reaction mixture gives mere traces of organic material other than ethanol. Orsat, as well as mass spectrometric analyses, show that the colorless gas consists of nitrous oxide, nitrogen and carbon dioxide (Table I).

This behavior of nitroacetic ester is readily intelligible when one considers that the nitrosation product IV is very unstable, being decomposed by water, by bases and by acids.[15] While it is not stated what the decomposition products are in water or in aqueous alkali, it is easy to envision the formation of nitrous oxide, nitrogen and carbon dioxide.[16]



$$\mathrm{H-\underset{NO}{\overset{NO_2}{C}}-COOC_2H_5}$$

IV

Acknowledgment.—We are indebted to Prof. Egil Ramstad, School of Pharmacy, Purdue University, for the mass spectrometric measurements.

Experimental[17]

Ethyl nitroacetate was prepared according to Rodionov, *et al.*,[18] except that a 100% excess of sodium dichromate was used and the crude product was washed with aqueous urea; yield 53%, b.p. 64-66° (3 mm.), n^{20}D 1.4244-1.4252.

Ethyl α-Nitropropionate.—Fuming nitric acid (186.8 ml., d. 1.5) was added dropwise at 35-45° to 174 g. of diethyl methylmalonate and 1.4 g. of 97% sodium nitrite over a period of 2 hours. The mixture was stirred an additional 2 hours and then poured onto 300 g. of ice. The aqueous layer was extracted with ether and the combined organic layers were washed with 10% aqueous urea solution until a negative starch-iodide test was obtained, after which the ethereal solution stood in contact with solid urea overnight. The ethereal solution was then dried and decarboxylated after the method of Ulpiani.[19] The crude product (mainly diethyl methylmalonate and ethyl α-nitropropionate) was washed with 400 ml. of 10% sodium carbonate solution to extract the nitroester. The ethyl α-nitropropionate was regenerated by acidification[20] and rectified; yield 22-32 g. (15-22%), b.p. 72-73° (6 mm.), n^{20}D 1.4205-1.4210. *Anal.* Calcd. for $C_5H_9O_4N$: C, 40.81; H, 6.17; N, 9.52. Found: C, 40.47, 40.51; H, 6.04, 6.06; N, 9.50, 9.42.

Ethyl α-nitrobutyrate was prepared by nitrating diethyl ethylmalonate and removing the carbethoxy group. Short path distillation at 0.08 mm. and a bath temp. of *ca.* 60° gave an 18% yield, n^{20}D 1.4238. Ulpiani[19] reports b.p. 123° (20 mm.). *Anal.* Calcd. for $C_6H_{11}O_4N$: C, 44.71; H, 6.88; N, 8.69. Found: C, 44.53, 44.62; H, 6.94, 6.84; N, 8.66, 8.61.

Diethyl α-nitroglutarate was obtained by adding 0.1 mole of ethyl nitroacetate to 0.1 mole of ethyl acrylate in the presence of 0.5 ml. of 40% aqueous benzyltrimethylammonium hydroxide.[21] Short path distillation at 0.01 mm. and a bath temp. of 70° gave a 66% yield of product, n^{20}D 1.4417-1.4420; lit. value n^{20}D 1.4417,[21] n^{20}D 1.4410.[22] *Anal.* Calcd. for $C_9H_{15}O_6N$: C, 46.35; H, 6.50. Found: C, 46.15; H, 6.52.

Diethyl γ-Carbethoxy-γ-nitropimelate.—When the above Michael condensation was carried out using 0.1 mole of ethyl nitroacetate, 0.2 mole of ethyl acrylate and 3 ml. of 40% aqueous benzyltrimethylammonium hydroxide, diethyl γ-carbethoxy-γ-nitropimelate was isolated in 89% yield by short path distillation at a bath temp. of 120° (0.08 mm.), n^{20}D 1.4530-1.4535. Leonard and Shoemaker[21] report b.p. 181-183° (2 mm.), n^{20}D 1.4525. *Anal.* Calcd. for $C_{14}H_{23}O_8N$: C, 50.44; H, 6.95; N, 4.20. Found: C, 50.52; H, 6.93; N, 4.30.

The Reaction of α-Nitroesters with Sodium Nitrite.[22a]—(a) Ethyl α-nitropropionate (7.36 g., 0.05 mole) was dissolved in 25.9 g. of ethanol and added to a solution of 8.90 g. (0.125 mole) of 97% sodium nitrite in 25.9 g. of water. The colorless solution became blue-green within 5 minutes and then turned bright yellow within 1 hour. After two days at room temperature, one-half of the solution was diluted with water and extracted with ether. The ethereal solution was dried over anhydrous sodium sulfate and, after removal of the solvent, the residue was recrystallized from petroleum ether (b.p. 30-60°); yield 2.59 g. (78%) of ethyl α-oximinopropionate, m.p. 95°. After a total of 5 days the second half of the reaction mixture was worked up, giving 2.49 g. of ethyl α-oximinopropionate, m.p. 95°, 76% yield; lit. m.p. 94°,[12] 95°.[23]

(b) Ethyl α-nitrobutyrate, 8.06 g. (0.05 mole) in 25.9 g. of ethanol, was treated with 8.90 g. (0.125 mole) of 97% sodium nitrite in 25.9 g. of water for 10 days at room temperature. There was obtained 5.11 g. of ethyl α-oximinobutyrate, m.p. 58-60°, 70% yield. This sublimed almost quantitatively to give oxime, m.p. 59-60°; lit. m.p. 58°.[24]

(c) Diethyl α-nitroglutarate, 7.0 g. (0.03 mole) in 16 g. of ethanol, was treated with 5.34 g. (0.075 mole) of 97% sodium nitrite in 16 g. of water. In order to obtain a homogeneous system an additional 16 g. of ethanol was added; the solution was set aside for 10 days at room temp. The crude oxime was recrystallized twice from pentane containing a few drops of benzene to give 4.89 g. of colorless crystals, m.p. 60-61° (75% yield), lit. m.p. 62-63°.[25]

In order to determine the nitrate present in the aqueous solution remaining from the reaction of diethyl α-nitroglutarate with sodium nitrite, the excess nitrite was first destroyed by adding urea (15 g.), diluting with water to about 100 ml., and then acidifying with 5 ml. of concd. sulfuric acid. The solution was warmed to 70° for one hour and then an aliquot representing 8.00% of the total solution was treated with 12 ml. of fresh nitron reagent. The solution was then refrigerated for 24 hours, filtered, washed with 10 ml. of ice-water, dried at 110° for 3 hours and weighed; a 66% yield of nitron nitrate was obtained. Determinations run in the same manner on equivalent quantities of 97% sodium nitrite gave from 2 to 4% nitron nitrate.

Treatment of Diethyl γ-Carbethoxy-γ-nitropimelate with Sodium Nitrite.—A solution of 6.67 g. (0.02 mole) of diethyl γ-carbethoxy-γ-nitropimelate, n^{20}D 1.4530, in 10.4 g. of ethanol was mixed with 3.56 g. (0.05 mole) of 97% sodium nitrite dissolved in 10.4 g. of water. In order to obtain one phase an additional 10.4 g. of ethanol was added. After 11 days at room temperature the organic material was isolated; 6.28 g. of diethyl γ-carbethoxy-γ-nitropimelate, n^{20}D 1.4529 was recovered, representing 94% of the starting material.

Treatment of Ethyl α-Nitroisobutyrate with Sodium Nitrite.[4]—A solution of 48.3 g. (0.30 mole) of ethyl α-nitroisobutyrate[13] (b.p. 50° at 1 mm., n^{20}D 1.4199) in 160 g. of absolute ethanol was added to a solution of 53.4 g. (0.75 mole) of 97% sodium nitrite in 160 ml. of water. An additional 160 g. of absolute ethanol was necessary to effect complete miscibility of the two solutions. The solution became yellow at once and was left at room temperature in the dark for 11 days. During this time there was no change in color of the solution. On working up the product there was obtained 46.1 g. of ethyl α-nitroisobutyrate, b.p. 51-52° at 1 mm., n^{20}D 1.4198, 96% recovery.

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(15) M. Z. Jovitschitsch, *Ber.*, **28**, 1213 (1895); **39**, 785 (1906).

(16) In this connection, the fact that nitroacetic acid on treatment with sodium nitrite gives nitrous oxide, nitrogen and carbon dioxide is of interest [A. T. Austin, *J. Chem. Soc.*, 149 (1950)].

(17) All m.p.'s and b.p.'s corrected. Analyses are by Galbraith Microanalytical Laboratories, Knoxville, Tenn., and by Dr. C. S. Yeh, Purdue University.

(18) V. M. Rodionov, E. V. Mashinskaya and V. M. Belikov, *Zhur. Obshchei Khim.*, **18**, 917 (1948).

(19) C. Ulpiani, *Gazz. chim. ital.*, **35**, I, 273 (1905); *Chem. Centr.*, **76**, I, 1590 (1905).

(20) N. Kornblum and G. E. Graham, THIS JOURNAL, **73**, 4041 (1951).

(21) N. J. Leonard and G. L. Shoemaker, *ibid.*, **71**, 1762 (1949).

(22) R. N. Boyd and R. Leshin, *ibid.*, **74**, 2675 (1952).

(22a) Absolute ethanol was employed in all these experiments.

(23) E. Sharratt and W. Wordlaw, *J. Chem. Soc.*, 563 (1936).

(24) L. Bouveault and R. Locquin, *Compt. rend.*, **135**, 179 (1902).

(25) W. Wislicenus and R. Grutzner, *Ber.*, **42**, 1930 (1909).

The Reaction of Ethyl Nitroacetate with Sodium Nitrite.—A 200-ml. flask was equipped with a stirrer, a dropping funnel, a thermometer and a condenser. The condenser exit was connected to two traps arranged in series and cooled to *ca.* −70°. The outlet of the second trap was attached to a 1500-ml. gas buret, filled with 20% aqueous sodium chloride. The system was swept with carbon dioxide for 2 hours then 13.3 g. (0.1 mole) of ethyl nitroacetate in 51.9 g. of ethanol was placed in the flask and, with stirring, a solution of 17.8 g. (0.25 mole) of 97% sodium nitrite in 51.9 g. of water was added dropwise. Addition was interrupted after 30 minutes when about 0.1 mole of the sodium nitrite had been added; the reaction became exothermic with the liberation of much gas and external cooling was needed to keep the temperature at 28 ± 5°. After 24 hours the evolution of gas had almost ceased; the remainder of the sodium nitrite was added but almost no additional gas was evolved. Gas evolution ceased altogether after a total of 31 hours when 2102 ml. (0.094 mole) had been collected (after correction to standard conditions). The gas evolved was colorless and odorless and no brown fumes were observed when a sample was mixed with air; the cold traps had only traces of moisture. Thus hydrogen cyanide, nitrogen dioxide and nitrogen trioxide were absent, or present only in traces.

Samples of the gas were analyzed in an Orsat apparatus using absolute ethanol for absorption of the nitrous oxide. Oxygen, carbon monoxide and nitric oxide were absent, or present only in small amount but carbon dioxide (a correction having been made for the volume of CO_2 initially present), nitrous oxide and nitrogen (by difference) were present in roughly equal volumes (Table I). In order to obtain a more direct identification of the nitrous oxide and nitrogen, samples were allowed to stand with 50% aqueous potassium hydroxide for 24 hours (samples so treated showed no carbon dioxide by Orsat analysis). The carbon dioxide-free samples were then dried with potassium hydroxide pellets and with Ascarite. Mass spectrometric measurements showed the significant masses to be 28 (nitrogen), 30 (nitrosyl ion) and 44 (nitrous oxide). Small masses were also detected at 29, 31, 32, 40, 45 and 46; these are thought to have been due to the natural occurrence of heavy nitrogen atoms and also to slight contamination by air. In order to establish that the mass 30 species was due to the presence of nitrous oxide, presumably because of the formation of nitrosyl ion (NO^+), a sample of nitrous oxide (Matheson) was treated with potassium hydroxide solution, dried and analyzed in the same manner as gas samples from the ethyl nitroacetate–sodium nitrite reaction. The ratio of masses 30 to 44 was found to be 0.303 for the nitroacetate reaction gases and 0.300 for the nitrous oxide sample.

TABLE I

GASEOUS PRODUCTS FORMED ON TREATMENT WITH $NaNO_2$

Compound	Method	Temp., °C.	% CO_2	% N_2O	% N_2
$O_2NCH_2CO_2Et$	Orsat	28 ± 5	38.3	33.0	28.7
$O_2NCH_2CO_2Et$	Mass spec.	29 ± 1[a]	..[b]	59.3	40.7
$O_2NCH_2CO_2Et$[c]	Orsat	28 ± 1	..[b]	64.0	36.0
$O_2NCH_2CO_2Et$[c]	Mass spec.	28 ± 1	.[b]	65.1	34.9
$BrCH_2CO_2Et$	Orsat	29 ± 1	28.2	40.5	30.7

[a] Except for 10 min. at 78°. [b] Contacted for 24 hours with 50% aqueous potassium hydroxide before analysis. [c] These two analyses are for the same sample of gas.

The Lepercq Reaction.[12]—In the early stages of this study ethyl α-oximinopropionate, butyrate, valerate and caproate were prepared from the corresponding α-bromoesters in 71 to 85% yields by allowing 0.1 mole of the bromoester to react with 0.25 mole of sodium nitrite in aqueous ethanol (50–55 weight per cent. ethanol) for 16 days.

Ethyl Nitritoacetate.—Ethyl glycolate (41.6 g., 0.4 mole, n^{20}_D 1.4170) was treated with 39.3 g. (0.6 mole) of nitrosyl chloride in the presence of 50 g. (0.85 mole) of anhydrous trimethylamine at 0° in a system protected from atmospheric moisture. Anhydrous ether was added from time to time to keep the solution from becoming too viscous due to the precipitation of trimethylammonium chloride. After the addition was completed, the mixture was stirred for another hour and then filtered rapidly using anhydrous ether to aid in the transfer. Most of the ether was removed by distillation at room temperature under reduced pressure; the residual solution was dried over Drierite at 0 to 5° in the dark and fractionated. There was obtained 13.4 g. (39% yield) of ethyl nitritoacetate, b.p. 32–33° at 7 mm. and 118° at 760 mm. (micro-Emich), n^{20}_D 1.4050, d^{20}_4 1.1148, d^{30}_4 1.0947. *Anal.* Calcd. for $C_4H_7O_4N$: C, 36.09; H, 5.30; N, 10.52. Found: C, 36.07; H, 5.17; N, 10.62.

Ethyl nitritoacetate proves to be a pale, yellow-green liquid which is water soluble and which hydrolyzes within a few seconds at room temperature to give ethyl glycolate and nitrous acid. It is soluble in ethanol, acetone, ether, benzene and petroleum ether.

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A New Method for the Synthesis of Aliphatic Nitro Compounds[1,2]

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RECEIVED SEPTEMBER 8, 1955

A simple new synthesis of primary and secondary nitro compounds which involves treating alkyl halides with sodium nitrite in dimethylformamide is described; 55–62% yields of pure nitro compounds are obtained.

To date the principal method of preparing nitroparaffins has been the reaction of an alkyl halide with silver nitrite.[3] A recent study has demonstrated, however, that this reaction is really useful only for the synthesis of primary nitroparaffins. With secondary halides the yields of nitroparaffins are about 15% while with tertiary halides they fall to 0–5%.[4] A synthesis developed by Iffland and his co-workers, which involves the conversion of ketones into secondary nitroparaffins, is extremely valuable in certain instances, *e.g.*, the synthesis of nitrocyclobutane, but it cannot be regarded as a method of general utility.[5]

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(1) Paper XII in the series, "The Chemistry of Aliphatic and Alicyclic Nitrocompounds." A preliminary account of this work appeared in *Chemistry and Industry*, 443 (1955).

(2) This research was supported, in part, by grants from The Explosives Department of E. I. du Pont de Nemours and Co., and, in part, by the United States Air Force under Contract No. AF 18(600)-310 monitored by the Office of Scientific Research, Air Research and Development Command.

(3) Industrially, of course, the vapor phase nitration process due to Hass is employed on a large scale for the preparation of nitromethane, nitroethane and the two nitropropanes. But despite its great commercial importance this cannot be regarded as a laboratory procedure, especially since complex mixtures of products are formed.

(4) N. Kornblum, B. Taub and H. E. Ungnade, THIS JOURNAL, **76**, 3209 (1954); N. Kornblum, R. A. Smiley, H. E. Ungnade, A. M. White, B. Taub and S. A. Herbert, *ibid.*, **77**, 5528 (1955).

(5) D. C. Iffland, G. X. Criner, M. Koral, F. J. Lotspeich, Z. B. Papanastassiou and S. M. White, *ibid.*, **75**, 4044 (1953); D. C. Iffland and G. X. Criner, *ibid.*, **75**, 4047 (1953); D. C. Iffland and Teh-Fu Yen, *ibid.*, **76**, 4083 (1954).