

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 $28 \pm 5^{\circ}$. 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., $^{\circ}\text{C}$.	% CO_2	% N_2O	% N_2
$\text{O}_2\text{NCH}_2\text{CO}_2\text{Et}$	Orsat	28 ± 5	38.3	33.0	28.7
$\text{O}_2\text{NCH}_2\text{CO}_2\text{Et}$	Mass spec.	29 ± 1^a	$\dots^b$	59.3	40.7
$\text{O}_2\text{NCH}_2\text{CO}_2\text{Et}^c$	Orsat	28 ± 1	$\dots^b$	64.0	36.0
$\text{O}_2\text{NCH}_2\text{CO}_2\text{Et}^c$	Mass spec.	28 ± 1	$\dots^b$	65.1	34.9
$\text{BrCH}_2\text{CO}_2\text{Et}$	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_D^{20} 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_D^{20} 1.4050, d_4^{20} 1.1148, d_4^{30} 1.0947. *Anal.* Calcd. for $\text{C}_4\text{H}_7\text{O}_4\text{N}$: 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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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

(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).

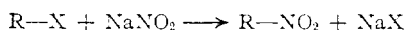
(2) This research was supported, in part, by grants from The Explosives Department of E. I. du Pont de Nemours and Co., and, in part, by the United States Air Force under Contract No. AF 18(600)-310 monitored by the Office of Scientific Research, Air Research and Development Command.

(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).

A rather obvious way of synthesizing nitroparaffins would appear to be the reaction of an alkyl halide with sodium nitrite



However, it is widely accepted that the reaction of alkyl halides with alkali metal nitrites produces nitrite esters rather than nitro compounds.⁶

To add to the confusion, there is an old and well known preparation of nitromethane (35-38% yield) in which the sodium salt of chloroacetic acid is treated with sodium nitrite after which the unstable α -nitroacetic acid is decarboxylated.⁷ What is not so well known, however, is that this method, which is due to Kolbe, is worthless for the preparation of higher nitroparaffins.⁸ Finally, the reaction of sulfonate esters with alkali metal nitrites has been reported, time and again, to be without merit as a means of synthesizing nitroparaffins.⁹

The present investigation shows that, contrary to general opinion, the reaction of sodium nitrite with alkyl halides is a simple and effective way of obtaining nitro compounds. The usefulness of this reaction can be gauged from the yields of *pure* aliphatic and alicyclic nitro compounds given in Table I.

TABLE I
REACTION OF ALKYL AND CYCLOALKYL HALIDES WITH SODIUM NITRITE

Halide	Yield, %	
	Nitro compound	Nitrite ester
1-Bromoheptane	60	29
1-Iodoheptane	61	31
1-Bromooctane	60	29
1-Iodooctane	60	31
1-Iododecane	57	25
1-Iodo-3-phenylpropane	58	26
Benzyl bromide	55	33
2-Bromooctane	58	..
2-Iodooctane	60	28
4-Bromoheptane	61	..
4-Iodoheptane	62	25
Bromocyclopentane	57	..
Iodocyclopentane	55	..
Bromocycloheptane	55	..
Iodocycloheptane	58	..

The success of this reaction hinges upon the use of dimethylformamide (DMF) as the solvent. Unless appreciable amounts of *both* the alkali metal nitrite and the alkyl halide are in solution no reaction occurs (*cf.* Experimental). With this restriction in mind it is apparent why only in DMF and ethylene glycol, of the common solvents, does a reaction occur: only these two solvents have the ability to dissolve sodium or potassium nitrite.^{10,10a}

(6) Although statements to this effect occur in most textbooks and monographs we have not been able to find any support for this view in the original literature.

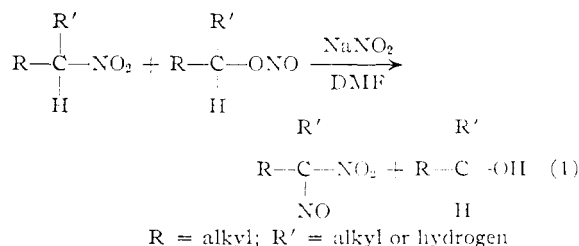
(7) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., Second Edition, 1941, p. 401.

(8) W. Treibs and H. Reinheckel, *Ber.*, **87**, 341 (1954); L. Henry, *Rec. trav. chim.*, **24**, 352 (1905); V. Auger, *Bull. soc. chim.*, [3] **23**, 333 (1900).

(9) F. Drahowzal and D. Klamann, *Monatsh.*, **82**, 970 (1951); P. C. Ray and P. Neoig, *J. Chem. Soc.*, **69**, 1900 (1906); V. M. Rodionov, *Bull. soc. chim.*, [4] **39**, 324 (1920); F. Kaufler and C. Pomeranz, *Monatsh.*, **22**, 492 (1901).

(10) ADDED IN PROOF.—Mr. D. E. Hardies of this laboratory has now found that the reaction of 2-iodooctane with sodium nitrite in dimethyl sulfoxide occurs rapidly under the identical conditions used

A second reason for using DMF is that the reaction of alkali nitrites with alkyl halides is exceptionally fast in this medium.^{11,12} This great speed of reaction in DMF makes it possible to minimize a side reaction (1), whose existence has been established recently¹³



Even in DMF sodium nitrite has a rather limited solubility and this prevents realization of the reaction of nitrite ion with an alkyl halide at a rate which would be anticipated from the kinetics in dilute solution.¹¹ Nonetheless, the reaction of a primary bromide or iodide with sodium nitrite at room temperature is so much faster than the competing process that merely working up the reaction mixture promptly prevents intrusion by the reaction of eq. 1.

With secondary bromides and iodides the reaction of eq. 1 would become a serious competitor in the absence of several simple devices. The addition of urea to DMF considerably increases the solubility of sodium nitrite¹⁴ and, in reactions employing secondary alkyl iodides, this is all that is required to provide the yields listed in Table I. With secondary bromides, and also cyclopentyl and cycloheptyl iodides, it becomes desirable not only to add urea but also a nitrite ester scavenger. Compounds such as phloroglucinol, catechol and resorcinol can be used for this purpose; of these phloroglucinol is the most effective.¹⁵

when DMF is the solvent. 2-Nitrooctane is obtained in 58% yield and 2-octyl nitrite in 24% yield; in other words within the experimental error the yields are identical. Since dimethyl sulfoxide is an even better solvent for sodium nitrite than DMF, the use of urea (*vide infra*) appears unnecessary.

(10a) Lithium nitrite is soluble in DMF, ethylene glycol, ethanol and acetone and in these solvents the reaction with alkyl halides also occurs. Intrinsically all three alkali nitrites are equally effective as shown by their reaction with 1-iodooctane in DMF: lithium nitrite gives a 57% yield of pure 1-nitrooctane, sodium nitrite a 60% yield and potassium nitrite a 58% yield. Lithium nitrite is the most soluble in DMF; if it were available, and cheap, it would be the nitrite of choice.

(11) N. Kornblum, R. K. Blackwood and D. D. Mooberry, to be published.

(12) Excellent grounds exist for preferring DMF to the other common solvents except in the case of ethylene glycol. The preference for DMF over ethylene glycol is predicted on work carried out early in this investigation and, although there are definite indications that (a) the reaction in glycol is not nearly so rapid as in DMF and (b) isolation of the nitro compound from glycol is not so easy as from DMF, these points have not been established rigorously.

(13) N. Kornblum, R. K. Blackwood and D. D. Mooberry, *THIS JOURNAL*, **78**, 1501 (1956).

(14) The solubility of potassium nitrite in DMF is also increased by urea, but to a smaller extent.

(15) It reacts rapidly with nitrite esters to form a deeply colored material, presumably nitrosophloroglucinol, which is readily soluble in water and non-volatile, thus making facile the isolation of pure colorless nitro compound. On the other hand, catechol allows nitrosation of the nitro compound a greater chance to compete and the nitro compound obtained is usually highly colored even though it has the correct refractive index. Preliminary experiments using resorcinol indicate that it is more like catechol than phloroglucinol as regards its ability to destroy nitrite esters.

As will be seen from Table I, alkyl bromides and iodides are equally useful for the preparation of primary and secondary nitroparaffins. In contrast, alkyl chlorides react too slowly to be useful.

The reactions employing 1- and 2-bromoöctane have been found to be first order in halide and first order in nitrite ion.¹¹ It is not surprising, then, that this bimolecular displacement process fails with *t*-butyl bromide, *t*-butyl chloride, cyclohexyl bromide and cyclohexyl iodide. Instead of nitro compounds, isobutylene and cyclohexene are obtained.¹⁶

Sulfonate esters may also be employed; *n*-octyl tosylate, for example, gives 1-nitroöctane in 43–46% yield.¹⁷ The use of sulfonates would, of course, be advantageous when dealing with alcohols which are subject to rearrangement on conversion into halides.

Finally it should be pointed out that the reaction of alkyl halides with sodium nitrite in DMF is carried out under very mild conditions. The reaction temperature is maintained at or close to 25° except for a few instances in which it is lowered to –20 to –15° (cf. Experimental).

Experimental¹⁸

Reagents.—Dimethylformamide, du Pont technical grade, is essentially anhydrous and in a number of experiments was used directly. In a number of instances the DMF was dried by allowing it to stand over calcium hydride. Although no attempt was made to study the influence of water on the reaction, it does not appear that rigorously anhydrous conditions are necessary. Analytical grade sodium nitrite, dried at 115°, was used. The urea was dried at 105° for several hours. Ringwood Technical Grade phloroglucinol dihydrate was rendered anhydrous by heating for three hours at 110°.¹⁹

The alkyl halides were carefully rectified²⁰ and only middle cuts of constant *n*_D²⁰ and b.p. were used. Except in the case of cycloheptyl bromide the *n*_D²⁰ values were identical with those in the literature. Our cycloheptyl bromide was obtained from the alcohol in 87% yield, b.p. 50° (3 mm.), *n*_D²⁰ 1.5049; Vogel²¹ reports *n*_D²⁰ 1.4991 and Zelinsky²² *n*_D²⁰ 1.4996. *Anal.* Calcd. for C₇H₁₃Br: C, 47.49; H, 7.40. Found: C, 47.30, 47.48; H, 7.39, 7.48.

The only new iodide is 1-iodo-3-phenylpropane (73% yield), b.p. 98° (3 mm.), *n*_D²⁰ 1.5850. *Anal.* Calcd. for C₉H₁₀I: C, 43.92; H, 4.51. Found: C, 43.94; H, 4.58. *n*-Octyl tosylate was prepared from *n*-octyl alcohol and tosyl chloride by the method of Drahowzal and Klamann²³; b.p. 170° (0.8 mm.), *n*_D²⁰ 1.4946; lit.²³ b.p. 167–168° (0.6 mm.), *n*_D²⁰ 1.4946.

(a) Primary Nitro Compounds.—When primary bromides are used a reaction time of six hours is needed; with primary iodides the reaction time is 2.5 hours. Urea is not needed;

(16) In a recent paper, de la Mare, Hughes, Ingold and Pocker [*J. Chem. Soc.*, 2930 (1954)] claim that the reaction of *t*-butyl bromide with nitrite ions (supplied as either tetraethyl- or tetramethyl-ammonium nitrite) gave *t*-nitrobutane and *t*-butyl nitrite. Since it is reported that nitromethane is used as the solvent, and since it is admitted that dehydrohalogenation occurs, it would, among other things, be of more than passing interest to know how these authors isolated *t*-nitrobutane from such an untidy situation—or even managed to detect it.

(17) Conceivably the use of phloroglucinol will produce a significant increase in the yield.

(18) Analyses are by Galbraith Microanalytical Laboratories, Knoxville, Tenn., and by Dr. C. S. Yeh and Mrs. S. L. Margerum, Purdue University.

(19) We are indebted to the Ringwood Chemical Co., Ringwood, Ill., for a generous gift of phloroglucinol.

(20) All rectifications were carried out using a 60 × 1 cm. externally heated column, packed with 1/4 inch glass helices and equipped with a total reflux variable take-off head.

(21) A. I. Vogel, *J. Chem. Soc.*, 1809 (1918).

(22) N. Zelinsky, *Ber.*, **35**, 2691 (1902).

(23) F. Drahowzal and D. Klamann, *Monatsh.*, **82**, 452 (1951).

if it is added, the only effect is to halve the reaction time. The following procedure is typical of that used with all primary halides except benzyl bromide (see below).

The Preparation of 1-Nitroöctane from 1-Bromoöctane.—1-Bromoöctane (58 g., 0.30 mole) was poured into a stirred mixture of 600 ml. of DMF and 36 g. of sodium nitrite (0.52 mole) immersed in a water-bath maintained at room temperature²⁴; stirring was continued for 6 hours. The reaction mixture was then poured into 1.5 l. of ice-water layered over with 100 ml. of petroleum ether (b.p. 35–37°). The aqueous phase was extracted four more times with 100-ml. portions of petroleum ether after which the extracts were washed with four 75-ml. portions of water and dried over anhydrous magnesium sulfate. The petroleum ether was removed by distillation under reduced pressure through the column²⁰; heat was supplied by a bath whose temperature was gradually raised to ca. 65°. Rectification²⁰ of the residue yielded 13.6 g. (29%) of 1-octyl nitrite (b.p. 37° (2 mm.), *n*_D²⁰ 1.4127; lit. values²⁴ b.p. 56° (9 mm.), *n*_D²⁰ 1.4127), 2.8 g. of interfractions, and 28.2 g. (60%) of 1-nitroöctane (b.p. 60° (1 mm.), *n*_D²⁰ 1.4324; cf. Table II).

With the iodides, the procedure was modified slightly in that the petroleum ether extracts were washed with two 75-ml. portions of 10% aqueous sodium thiosulfate (to remove small amounts of free iodine) and then with two 75-ml. portions of water.

The Preparation of Phenylnitromethane from Benzyl Bromide.—In the special case of benzyl bromide it was necessary to operate at –20 to –15° and to add urea. At room temperature no phenylnitromethane was obtained. The only product isolated, benzoic acid (25% yield), was, presumably, formed *via* the nitrolic acid.

Benzyl bromide (51.3 g., 0.30 mole) was poured into a stirred mixture of 600 ml. of DMF, 36 g. of sodium nitrite (0.52 mole) and 40 g. of urea maintained at –20 to –15°.²⁴ After five hours the reaction mixture was worked up as in the 1-nitroöctane preparation except that 700 ml. of diethyl ether was used for extraction. Rectification²⁰ yielded 13.1 g. (33%) of crude benzyl nitrite (b.p. 44° (5 mm.), *n*_D²⁰ 1.5010–1.5024), 1.7 g. of interfractions and 22.1 g. (55%) of phenylnitromethane (b.p. 76° (2 mm.), *n*_D²⁰ 1.5316; cf. Table II).

(b) Secondary Nitro Compounds.—In reactions employing open-chain secondary iodides, addition of urea is sufficient to prevent the side reaction of eq. 1. If urea is not added there is a ca. 5% drop in yield, presumably because the reaction must then be run ca. 2.5 times longer.

With secondary open-chain and alicyclic bromides, and also cyclopentyl and cycloheptyl iodides, it becomes desirable to add a nitrite ester scavenger such as phloroglucinol. For example, when 2-octyl bromide reacts with sodium nitrite in DMF–urea, the yield rises to a maximum in the range 13–16 hours and then falls; but even after 25 hours unreacted 2-octyl bromide remains. By adding phloroglucinol, however, the yield of 2-nitroöctane, after a 45-hour reaction time, is 58%. The other product, instead of being 2-octyl nitrite, is 2-octanol, presumably a by-product of the nitrosation of phloroglucinol.

When a nitrite ester scavenger is added to these systems, excessive reaction time is no longer critical. The only requirement is that sufficient time be given for the halide to react completely. Urea is employed only for the convenience of reducing the reaction time.

The Preparation of 4-Nitroheptane from 4-Iodoheptane.—This was identical to the preparation of 1-nitroöctane from 1-bromoöctane, except that (a) 40 g. of urea (0.67 mole) was added to the sodium nitrite–DMF mixture before addition of the 4-iodoheptane (67.8 g., 0.30 mole), (b) the reaction time was 5.5 hr. and (c) the petroleum ether extracts were washed with aqueous 10% sodium thiosulfate and then water. Rectification^{25,20} yielded 10.9 g. (25%) of 4-heptyl nitrite (b.p. 44° (18 mm.), *n*_D²⁰ 1.4032) and 26.4 g. (60%) of

(24) This reaction is mildly exothermic. Also, since alkyl nitrites are photochemically unstable (Horswell and Silverman, *Ind. Eng. Chem., Anal. Ed.*, **13**, 555 (1941)) in this, and subsequent operations, exposure to strong light is avoided.

(25) The blue color, which is due to small amounts of 4-nitro-1-nitrosoheptane (pseudonitrole), gradually becomes blue-green, then green and finally yellow as the working up process continues. Usually the last stages of this color sequence occur during the rectification. The pseudonitrole decomposition products are separable without any difficulty from the nitroparaffin.

4-nitroheptane (b.p. 59° (8 mm.), n_D^{20} 1.4219; cf. Table II).

2-Nitrooctane was prepared from 2-iodooctane by the same procedure, except that the reaction time was 4 hr.

The Preparation of 2-Nitrooctane from 2-Bromooctane.—The procedure used to prepare 1-nitrooctane from 1-bromooctane was followed except that (a) 40 g. of urea and 40 g. of anhydrous phloroglucinol (0.3 mole) were added to the stirred DMF-sodium nitrite mixture and (b) the reaction time was 45 hr. Rectification²⁰ yielded 15.0 g. (38%) of 2-octanol (b.p. 45° (1 mm.), n_D^{20} 1.4262; m.p. of the phthalate half-ester 55°, mixed m.p. with known phthalate half-ester 55°) and 27.6 g. (58%) of 2-nitrooctane (b.p. 67° (3 mm.), n_D^{20} 1.4280; cf. Table II).

4-Nitroheptane was obtained from 4-bromoheptane by this procedure (reaction time 60 hours). The urea-phloroglucinol procedure was also used to prepare nitrocyclopentane and nitrocycloheptane from the bromides, the reaction times being 42 and 54 hours, respectively. Finally, even though this urea-phloroglucinol procedure was employed to convert iodocyclopentane and iodocycloheptane to the nitro compounds, the reaction times were those required for secondary iodides, 5 and 6 hours, respectively (cf. Tables I and II).

Relevant data for the nitroparaffins obtained in this study are listed in Table II. All dissolve completely, but not at once, in 10% aqueous alkali. In the case of 4-nitroheptane shaking for ca. 2 hours is required to effect complete solution.

TABLE II
PHYSICAL CONSTANTS OF NITRO COMPOUNDS

Compound	B.p.			Literature		
	°C.	Mm.	n_D^{20}	°C.	Mm.	n_D^{20}
1-Nitroheptane	68	2	1.4284	64	3 ^c	1.4283 ^c
1-Nitrooctane	60	1	1.4324	72	3 ^c	1.4323 ^c
1-Nitrodecane ^a	107	2	1.4391	..	..	..
1-Nitro-3-phenylpropane ^b	123	4	1.5222	..	..	..
Phenylnitromethane	76	2	1.5316	78	1 ^d	1.5315 ^d
2-Nitrooctane	67	3	1.4280	66	2 ^e	1.4280 ^e
4-Nitroheptane	59	8	1.4219	90	25 ^e	1.4200 ^{f,g}
Nitrocyclopentane	58	10	1.4540	90	40 ^e	1.4518 ^{f,g}
Nitrocycloheptane	70	1.5	1.4723	114	20 ^e	1.4722 ^h

^a Anal. Calcd. for $C_{10}H_{21}NO_2$: C, 64.12; H, 11.31; N, 7.48. Found: C, 64.42; H, 11.24; N, 7.66. ^b Anal. Calcd. for $C_9H_{11}NO_2$: C, 65.43; H, 6.71; N, 8.48. Found: C, 65.38; H, 6.88; N, 8.76. ^c Ref. 4a. ^d N. Kornblum, R. A. Smiley, R. K. Blackwood and D. C. Iffland, THIS JOURNAL, 77, 6269 (1955). ^e Ref. 4b. ^f n_D^{25} . ^g Ref. 5. ^h H. Stone, Ph.D. Thesis, Ohio State University, 1950.

Nitrite Esters.—Two new esters were produced as by-products of this synthesis of nitroparaffins: (1) *n*-decyl nitrite, b.p. 95° (4 mm.), n_D^{20} 1.4247. Anal. Calcd. for $C_{10}H_{21}NO_2$: N, 7.48. Found: N, 7.40. (2) γ -Phenyl-*n*-propyl nitrite, b.p. 56° (1 mm.), n_D^{20} 1.4979. Anal. Calcd. for $C_9H_{11}NO_2$: N, 8.48. Found: N, 8.62.

Use of Sulfonate Esters.—In the case of *n*-octyl tosylate, *n*-butyl tosylate and *n*-butyl methanesulfonate the procedure was identical to that for 1-bromooctane, except that 40 g. of urea was added initially to the reaction mixture and the reaction time was extended to 8.5 hours; yields 43–46%.

The Reaction of Cyclohexyl Iodide (and Bromide) with Sodium Nitrite.—(a) The reaction of 63 g. of cyclohexyl iodide with sodium nitrite in DMF was carried out as described above for 4-iodooctane. After 12 hours a 1-ml. sample of the solution was withdrawn, run into water, and extracted with chloroform. The free iodine in the chloroform was titrated with standard thiosulfate. The results showed a 38% yield of free iodine. When the aqueous solution was titrated for iodide ion with silver nitrate it was found that 44% of the iodine in the cyclohexyl iodide had been converted to iodide ion. On working up the product 14.15 g. (57% yield) of cyclohexene (b.p. 80–82°, n_D^{20} 1.4456–1.4462) was obtained. A 1-ml. sample was treated with 2,4-dinitrophenylsulfenyl chloride according to Kharasch.²⁶ There was obtained 1.8 g. (61%) of the adduct, m.p. 117°. A 1-ml. sample of authentic cyclohexene (b.p.

83°, n_D^{20} 1.4463) gave 2.0 g. (64%) of the derivative, m.p. 117°; mixed m.p. 117°. In addition, 5.8 g. (9%) of cyclohexyl iodide was recovered. There was no detectable amount of nitrocyclohexane.

(b) The reaction of cyclohexyl bromide was conducted as for cyclohexyl iodide. After 21 days it was only 80% complete and on working up the dark red solution a 12% yield of cyclohexene (b.p. 83°, n_D^{20} 1.4458–1.4462) was isolated. In addition a 15% recovery of cyclohexyl bromide was made.

The Reaction of *t*-Butyl Bromide (and Chloride) with Sodium Nitrite.—(a) *t*-Butyl bromide (41 g., 0.3 mole) was treated with sodium nitrite in DMF as described for 4-iodooctane, provision being made to trap isobutylene. After 24 hours at room temperature there was obtained 12.3 g. (73%) of a liquid having b.p. –5°; lit. value for isobutylene b.p. –7°. When allowed to evaporate into a solution of bromine in carbon tetrachloride it decolorized the solution. When the experiment was repeated at 0° for 18 hours, 11.5 g. (70% yield) of isobutylene, b.p. –6° was isolated. It decolorized bromine.

(b) The reaction of *t*-butyl chloride (28 g., 0.3 mole) was carried out at 0° for six days. The only product isolated was isobutylene (10.8 g., 65% yield). It had b.p. –4.5°, and decolorized bromine.

The Effect of the Solvent on the Reaction of 1-Iodoctane with Alkali Nitrites.—The reactions were conducted by adding 0.09 mole of the nitrite (4.6 g. of $LiNO_2$, 6.2 g. of $NaNO_2$, 7.6 g. of KNO_2) and 0.05 mole (12 g.) of 1-iodooctane to about 90 ml. of the anhydrous solvent. The mixtures were allowed to stand, stoppered, in the dark at room temperature for 36 hours. At 8-hr. intervals a 5-ml. sample was withdrawn and tested for nitrite ion, iodide ion and nitroparaffin.

The test for nitrite consisted in adding a crystal of potassium iodide to about 2 ml. of the solution and acidifying with 10% nitric acid. A positive test was indicated by the liberation of iodine and was taken to mean the alkali nitrite was soluble. 1-Nitrooctane was detected by use of the Davidson test.²⁸

All three nitrites are soluble in DMF and ethylene glycol and in each nitroparaffin formation occurs. In ethanol, methanol, acetone, 1,2-dimethoxyethane, and pyridine lithium nitrite is soluble and a reaction occurs with the formation of nitro compound; sodium and potassium nitrite are insoluble in these solvents and no reaction occurs. All three nitrites are insoluble in diethyl ether, acetonitrile, dioxane, and tetrahydrofuran and no reaction occurs. With water as a solvent the nitrites are soluble but the halide is insoluble and again no reaction occurs.

The foregoing data were confirmed and extended by pre-

TABLE III
EFFECT OF SOLVENT ON THE REACTION OF 1-IDOOCANE WITH ALKALI NITRITES^a

Solvent	Reaction time, hr.	Nitro, %	Nitrite, %	Unreacted	
				halide, %	LiNO ₂ , %
LiNO ₂					
DMF	2.5	57	26	..	..
Ethanol	108	39	19 ^b	5	..
Acetone	96	37	20 ^b	5	..
Diethyl ether	24	0	0	93	96
Diethyl ether ^d	24	0	0	94	92
NaNO ₂					
DMF	2.5	60	31	..	..
Ethanol	24	0	0	93	96
Ethanol ^d	24	0	0	93	94
Acetone	24	0	0	94	99
Diethyl ether	24	0	0	95	98
Diethyl ether ^d	24	0	0	97	99
Diethyl ether ^e	24	0	0	91	99

^a Carried out at room temperature, in the dark, unless otherwise noted. ^b 1-Octanol. ^c Negative test for iodide ion. ^d At reflux temperature. ^e 1-Iodoethane used.

(26) N. Kharasch, H. L. Wehrmeister and H. Tigerman, THIS JOURNAL, 69, 1612 (1947).

(27) A. V. Grosse, *ibid.*, 59, 2739 (1939).

(28) D. Davidson, *J. Chem. Ed.*, 17, 81 (1940).

parative scale experiments. A mixture of 48 g. (0.20 mole) of 1-iodooctane, 24.2 g. (0.35 mole) of sodium nitrite (or 18.6 g. of lithium nitrite), and 250 ml. of the solvent was stirred at room temperature (or higher if noted). The undissolved solid was isolated by filtration, washed, dried, and weighed. The filtrate was dried and rectified. In this way the data of Table III were obtained.

The Influence of Urea on the "Solubility" of Alkali Nitrites in DMF.—The "solubility" of sodium and potassium nitrite in DMF-urea solutions was determined by placing 10 g. of the alkali nitrite in 100 ml. of DMF containing varying amounts of urea. The mixtures were sealed, shaken for 24 hours at room temperature, the undissolved nitrite isolated by filtration, washed with anhydrous ether, dried and then weighed.

TABLE IV
"SOLUBILITY" OF NITRITES IN DMF

Nitrite	Composition of "solvent"		Grams of nitrite dissolved
	DMF, ml.	Urea, g.	
NaNO ₂	100	...	1.88
NaNO ₂	100	4.35	4.41
NaNO ₂	100	8.7	7.6
NaNO ₂	100	19.4	7.27
KNO ₂	100	...	0.64
KNO ₂	100	7.1	3.49

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Reaction of Aliphatic Nitro Compounds with Nitrite Esters^{1,2}

BY NATHAN KORNBUM, ROBERT K. BLACKWOOD AND DAVID D. MOOBERRY

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Although primary nitroparaffins, secondary nitroparaffins and α -nitroesters are inert toward nitrite esters, the joint action of a nitrite ester and sodium nitrite destroys the nitro compound. Primary nitro compounds give the carboxylic acid, secondary nitroparaffins yield ketones and α -nitroesters are converted to α -oximinooesters. The course of these reactions is described.

In the preceding paper of this series³ it was found that if a nitroparaffin, an alkyl nitrite and sodium nitrite are allowed to stand at room temperature, the nitro compound is destroyed. The nature of the destructive process is the subject of the present communication.

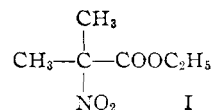
As shown in Table I, when 1-nitrooctane is treated with sodium nitrite it is quantitatively recovered (expt. 1 to 3). Nor is there any reaction when 1-nitrooctane is exposed to nitrite esters (expt. 4 and 5). In contrast, when 1-nitrooctane is exposed to the combined influence of sodium nitrite and an alkyl nitrite it is converted into caprylic acid (expt. 6 to 9).

Table IB summarizes a series of experiments using 2-nitrooctane. Here again the nitro compound is completely stable toward either sodium nitrite or alkyl nitrites but is destroyed by their joint influence, 2-octanone being produced.

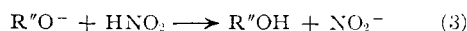
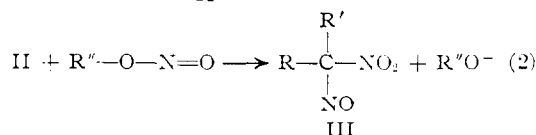
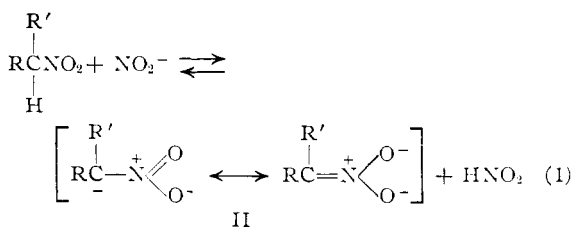
In Table IC are recorded the data of experiments involving ethyl α -nitropropionate. After 24 hours contact with sodium nitrite the α -nitroester is recovered in 93% yield⁴ (expt. 17). And after 45 hours there is no reaction between the α -nitroester and *n*-propyl nitrite (expt. 19). But treatment with both sodium nitrite and *n*-propyl nitrite results in complete destruction of the ethyl α -nitropropion-

ate in 22 hours, ethyl α -oximinopropionate being formed.

Thus, for reaction to occur, all three reagents—the nitro compound, the alkyl nitrite and sodium nitrite—are needed. It is also necessary to have a hydrogen atom on the carbon holding the nitro group as is shown by the failure of ethyl α -nitroisobutyrate (I) to react. From these facts, and the



data which follow, it is apparent that the reaction proceeds first to give nitrosated nitro compounds (III) which, being unstable, break down to form the products isolated. As will be seen, the nitrite ion simply functions as a base.⁵



The reactions of III vary with the nature of the substituents. When R = alkyl and R' = hydro-

(5) Although nitrosation of nitroparaffins by nitrite esters has apparently not been reported previously one would have anticipated that, in the presence of a strong base, e.g., ethoxide ion, nitrosation would take place readily. It is surprising, however, that a base as weak as nitrite ion is able to act as an effective catalyst.

(1) Paper XIII in the Series "The Chemistry of Aliphatic and Alicyclic Nitro Compounds."

(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) N. Kornblum, H. O. Larson, R. K. Blackwood, D. D. Mooberry, E. P. Oliveto and G. E. Graham, *THIS JOURNAL*, **78**, 1497 (1956).

(4) Given 168 hours in which to act, sodium nitrite alone is able to destroy a perceptible amount of the α -nitroester (expt. 18). This is understandable since α -nitroesters are distinctly more acidic than nitroparaffins. It is interesting to note that the conversion of an α -nitroester to the α -oximinooester by the agency of sodium nitrite is much slower in DMF than in aqueous ethanol [N. Kornblum and J. H. Eicher, *THIS JOURNAL*, **78**, 1494 (1956)].