explanations. It is hoped that further work now in progress in this Laboratory will contribute toward the solution of this and several other related general problems pertaining to hyperconjugation.

Experimental

Kinetic Procedure.—The kinetic method, the analyses for bromide ion and for olefin have been described previously.[13]

All bath temperatures were set by Beckmann thermometers standardized in the baths at the exact temperature desired against the same platinum resistance thermometer and Mueller bridge arrangement, sensitive to a few thousandths of a degree. The temperature accuracy, not limited by the calibration standard should be of the order of ±0.01° or less.

For the isopropyl bromide kinetic runs the bromide ion was extracted in an aqueous solution and titrated with silver nitrate solution directly using a potentiometer arrangement with a silver electrode as the indicator. The details of this procedure will be published later.

Preparation of Organic Compounds.—A sample of 62.5 g. (0.55 mole) of 4,4-dimethyl-2-pentanone,[14] b.p. 124–125° (760 mm.), n^{25}D 1.4018, was added slowly to a slurry of 7.6 g. (0.2 mole) of lithium aluminum hydride in 600 ml. of dry ether under dry nitrogen. The excess hydride was decomposed with water and the mixture was poured on 500 ml. of ice-cold 10% sulfuric acid. The ether layer and the ether extracts of the water layer were combined, washed, dried with anhydrous potassium carbonate and distilled. 4,4-Dimethyl-2-pentanol, 40 g. (0.34 mole), was collected at 137–138° (751 mm.); n^{25}D 1.4168; yield 62%.

4,4-Dimethyl-2-bromopentane, 24.9 g. (0.14 mole), b.p. 59.3–59.8° (33 mm.), n^{25}D 1.4439, was prepared by the slow addition of excess gaseous hydrogen bromide to 42.5 g. (0.37 mole) of 4,4-dimethyl-2-pentanol at about 60°.

4-Methyl-2-pentanol, 41.2 g. (0.41 mole), b.p. 132°, was prepared following the usual Grignard technique from 137 g. (1.0 mole) of isobutyl bromide and 50 g. (1.1 moles) of acetaldehyde, b.p. 20.5–21°. 4-Methyl-2-bromopentane, 45 g. (0.27 mole), b.p. 33° (mm.), was prepared from 41 g. (0.41 mole) of the corresponding alcohol and gaseous hydrogen bromide.

4,4-Dimethylpentene-1, 105 g. (1.07 mole), b.p. 71.0–71.8° (755 mm.), n^{25}D 1.3902, was prepared by the addition of 5.0 moles of *t*-butylmagnesium chloride to an ice-cold solution of 605 g. (5.0 moles) of allyl bromide in ether. This material was redistilled in a 75-plate Wheeler concentric tube column and separated into 14 fractions. The infrared spectra of fractions 6 to 12, recorded parallel to one another on the same chart, using a Perkin–Elmer Model 21 infrared recording spectrophotometer, showed no differences between fractions. A cooling curve taken on a portion of the mixture of these fractions with a two-junction copper–constantan thermocouple calibrated at four points showed f.p. (initial) −137.62°, f.p. (half-frozen) −137.70°.

4,4-Dimethylpentene-2, b.p. 76.7–76.8°, n^{25}D 1.3960, was prepared by the dehydration of 4,4-dimethyl-2-pentanol and was purified by distillation through the 75-plate concentric tube column. The infrared spectra of successive fractions again showed a good "flat" and a cooling curve on the fraction used gave f.p. (initial) −118.86°; f.p. (half-frozen) −119.04°.

4-Methylpentene-1 was prepared by the addition of isopropylmagnesium bromide to allyl bromide and was purified by distillation through a 40 × 0.9 cm. column packed with phosphorbronze screen helices and equipped with a partial take-off head. All other organic compounds used, except solvents, were carefully purified by distillation through a 50 × 1.0 cm. vacuum-jacketed column packed with $^3/_{32}''$ glass helices and equipped with a partial take-off head.

Preparation of Kinetic Mixture of Olefins.—A sample of 9.7 g. (0.54 mole) of 4,4-dimethyl-2-bromopentane was thoroughly mixed with 100 ml. of about 1 *N* sodium ethoxide in absolute ethanol and allowed to react at 45° for about ten half-lives. The contents were then mixed in a separatory funnel with 800 ml. of water and fifty ml. of fractionally distilled petroleum ether (b.p. 28°). The organic layer was separated and the aqueous layer was washed with two more portions of petroleum ether. The combined petroleum ether extracts were dried over anhydrous potassium carbonate and most of the petroleum ether was removed through a 40 × 0.9 cm. total reflux, partial take-off column packed with phosphorbronze screen helices. The residue was then distilled through a 20 × 0.6 cm. straight-tube column and 3.0 g. (0.031 mole) of olefin was collected, b.p. 69–78°. The olefin composition of this sample was determined by comparison of infrared spectrum with that of synthetic mixtures of known concentration.

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[13] V. J. Shiner, Jr., THIS JOURNAL, **74**, 5285 (1952).

[14] W. A. Mosher and J. C. Cox, *ibid.*, **72**, 3701 (1950).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Reaction of Silver Nitrite with Secondary and Tertiary Alkyl Halides[1,2]

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Treatment of secondary halides with silver nitrite gives nitroparaffins in *ca.* 15% yields. The reaction of tertiary halides with silver nitrite is even less useful as a means of preparing nitroparaffins (0 to 5% yields). The complex mixtures produced have been shown to contain, in addition to the anticipated nitroparaffins and nitrite esters, olefins, nitrate esters and adducts of olefins with oxides of nitrogen.

In the preceding paper[3] it was shown that the reaction of primary bromides and iodides with silver nitrite gives excellent yields of primary nitroparaffins. The present study is concerned with the utility of this reaction for the synthesis of secondary and tertiary nitro compounds. Furthermore, our interest in the mechanism of these reactions has led us to determine how much alkyl nitrite is formed.

It transpires that when secondary and tertiary halides react with silver nitrite a rather complex mixture is produced. In addition to the anticipated nitroparaffin and nitrite ester, a number of other compounds have been isolated and identified.

Secondary Halides.—As is clear from the data of Table I, the yields of nitro compounds obtained on treating secondary bromides and iodides with silver

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[1] Paper VI in the series "The Chemistry of Aliphatic and Alicyclic Nitro Compounds."

[2] This research was supported 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, B. Taub and H. E. Ungnade, THIS JOURNAL, **76**, 3209 (1954); *cf.* also C. W. Plummer and N. L. Drake, *ibid.*, **76**, 2720 (1954).

TABLE I

THE REACTION OF SILVER NITRITE WITH SECONDARY HALIDES

Halide	Nitro-paraffin, %	Nitrite ester, %	Olefin, %	Nitrate ester, %
2-Chloropropane[a]	0	0		
2-Bromopropane[b]	19–26	24–34[c]		[d]
2-Iodopropane[e]	15–23	25–35[c]		[d]
2-Chlorobutane[f]	0	0		
2-Bromobutane	19–24	27–37[c]		1[g]
2-Iodobutane	10–15	30–35[c]		2[h]
4-Bromoheptane	7–15	22–29	12–20	8–10[i]
4-Iodoheptane	9	27	25	9[j]
2-Chlorooöctane[k]	0	0		
2-Bromooöctane	17–23	18–25	10[l]	[d]
2-Iodooöctane	15–20	17–25	5–11[m]	[n]
2-Me-5-bromooöctane	11	34	30[o]	9[p]
2-Me-5-iodooöctane	14	30	23[q]	9[p]
1-Ph-2-bromopropane	18	33		[d]
1-Ph-2-iodopropane	[r]	26		[d]

[a] After one day at 0° and six days at room temperature only 2% of the theoretical amount of AgCl had formed. [b] Reaction 98% complete as shown by amount of AgBr isolated. [c] Determined spectrophotometrically (ultraviolet). [d] Shown to be present spectrophotometrically (infrared). [e] Reaction 99% complete as shown by amount of AgI isolated. [f] After one day at 0° and six days at room temp. only 3% of the theoretical amount of AgCl had formed. The yield of recovered 2-chlorobutane was 73%. [g] *Anal.* Calcd. for $C_4H_9NO_3$: C, 40.33; H, 7.62; N, 11.77. Found: C, 40.60, 40.40; H, 7.52, 7.68; N, 11.78, 11.86. This colorless liquid had b.p. 68.5–69° (100 mm.), n^{20}D 1.4012. N. Kornblum, J. T. Patton and J. B. Nordmann (THIS JOURNAL, **70**, 748 (1948)) report b.p. 59° (80 mm.), n^{20}D 1.4015 for 2-butyl nitrate. [h] *Anal.* Calcd. for $C_4H_9NO_3$: C, 40.33; H, 7.62; N, 11.77. Found: C, 40.21, 40.29; H, 7.41, 7.76; N, 11.70, 11.92; colorless liquid, b.p. 68–69° (100 mm.), n^{20}D 1.4014. [i] *Anal.* Calcd. for $C_7H_{15}NO_3$: C, 52.15; H, 9.38; N, 8.69. Found: C, 52.30, 52.12; H, 9.45, 9.58; N, 8.75, 8.79; colorless liquid, b.p. 75–76° (3 mm.), n^{20}D 1.4208. [j] *Anal.* Calcd. for $C_7H_{15}NO_3$: C, 52.15; H, 9.38; N, 8.69. Found: C, 52.35, 52.37; H, 9.61, 9.41; N, 8.62, 8.54; colorless liquid, b.p. 57–58° (20 mm.), n^{20}D 1.4203. [k] After 12 hours at 0° and 60 hours at room temperature 94% of the 2-chlorooöctane was recovered and no AgCl had been produced. [l] The "octene" isolated was presumably a mixture of 1- and 2-octene, b.p. 119°, n^{20}D 1.4128. *Anal.* Calcd. for C_8H_{16}: C, 85.71; H, 14.29. Found: C, 85.45, 85.64; H, 14.42, 14.65. [m] Presumably a mixture of 1- and 2-octenes, b.p. 122–125°, n^{20}D 1.4122. *Anal.* Calcd. for C_8H_{16}: C, 85.71; H, 14.29. Found: C, 85.84, 85.51; H, 14.31, 14.55. [n] No effort was made to detect nitrate ester in these experiments. [o] The olefin, presumably a mixture of 2-methyl-4-octene and 2-methyl-5-octene, reacts rapidly with potassium permanganate and decolorizes bromine in carbon tetrachloride; b.p. 35–38° (13 mm.), n^{20}D 1.4166–1.4170. M. Tuot [*Compt. rend.*, **211**, 561 (1940)] reports n^{20}D 1.4181 for 2-methyl-4-octene; *cf.* also footnote *q*. [p] The nitrate ester fractions from the 2-methyl-5-bromooöctane and 2-methyl-5-iodooöctane runs were combined and purified. *Anal.* Calcd. for $C_9H_{19}NO_3$: C, 57.10; H, 10.11; N, 7.40. Found: C, 57.23, 57.05; H, 10.10, 10.15; N, 7.60, 7.47; colorless liquid, b.p. 92–93° (25 mm.), n^{20}D 1.4279. [q] This olefin (presumably a mixture of 2-methyl-4-octene and 2-methyl-5-octene) had b.p. 41–42° (20 mm.), n^{20}D 1.4168–1.4170. *Anal.* Calcd. for C_9H_{18}: C, 85.63; H, 14.37. Found: C, 85.84; H, 14.10. [r] Because of inadvertent loss of material it is only possible to give an estimated yield (15–20%).

nitrite are poor.[4] There are several reasons for this. Here nitrite ester formation is a distinctly more important process than in reactions employing primary halides. Of even greater significance is the formation of olefins. Thus, when 2-methyl-5-bromooöctane is treated with silver nitrite a 30% yield of 2-methyloctenes is obtained, while from 4-heptyl iodide a 25% yield of 3-heptene is isolated. These, and other results summarized in Table I, demonstrate that, in contrast to primary halides, secondary bromides and iodides on treatment with silver nitrite undergo significant amounts of dehydrohalogenation.[5]

Dehydrohalogenation is responsible for two additional side reactions: (a) the "low temperature" formation of nitrate esters and (b) the formation of olefin–oxide of nitrogen adducts. The reaction of silver nitrite with alkyl halides at elevated temperatures previously has been shown to produce nitrate esters[3,6] in consequence of the thermal instability of silver nitrite. This silver salt readily undergoes oxidation–reduction according to eq. 1 and the silver nitrate produced reacts with alkyl halides to form nitrate esters. However, by working in the

$$2AgNO_2 \longrightarrow AgNO_3 + Ag + NO \qquad (1)$$

temperature range 0 to 28° the reaction of eq. 1 is averted and excellent yields of pure nitroparaffins are obtained from primary bromide and iodides with no evidence of nitrate ester formation.[3]

The device of operating at low temperatures proves, however, not to be successful with secondary alkyl bromides and iodides. Even when the reaction with silver nitrite is conducted at 0 to 28° the product contains nitrate ester. This can only mean that with secondary halides there exists a "low temperature" path to nitrate ester formation.

The following sequence accounts for the "low temperature" production of alkyl nitrates, is consistent with all the available facts,[7] and only invokes reactions known to occur under the conditions employed

$$\textit{sec}\text{-alkyl iodide} + AgNO_2 \longrightarrow \text{olefin} + AgI + HNO_2 \qquad (2)$$

$$2HNO_2 \rightleftharpoons H_2O + N_2O_3 \qquad (3)$$

$$N_2O_3 \rightleftharpoons NO_2 + NO \qquad (4)$$

$$AgNO_2 + NO_2 \longrightarrow AgNO_3 + NO \qquad (5)$$

$$\textit{sec}\text{-alkyl iodide} + AgNO_3 \longrightarrow \textit{sec}\text{-alkyl nitrate} \qquad (6)$$

Reaction 5, which is rather less well known than the others, has been shown by Oswald[8] to take place readily at room temperature.[9]

Actually, the yields of nitrate esters are not large (*cf.* Table I), but they are not easy to remove from the nitro compounds by distillation. Recourse to chemical separation gives the pure nitroparaffin but further diminishes the yield.

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[4] Secondary chlorides fail to react not only under our, rather mild, conditions but also upon considerably more vigorous treatment. Thus, after six hours of refluxing, a benzene solution of 2-chlorooöctane was not attacked by silver nitrite to any significant extent as shown by the 81% recovery of the 2-chlorooöctane (M. Cenker, Ph.D. Thesis, Purdue University, February, 1949).

[5] In the isopropyl and 2-butyl series the material balances always fall short by *ca.* 25%, presumably because of the formation of propylene and butylenes, the isolation of which has not been attempted.

[6] N. Kornblum, N. N. Lichtin, J. T. Patton and D. C. Iffland, THIS JOURNAL, **69**, 307 (1947).

[7] For example, oxides of nitrogen are never observed in the reactions of primary straight chain halides with silver nitrite but they are regularly noted in reactions involving secondary bromides and iodides.

[8] M. Oswald, *Ann. chim.*, [9] **1**, 85 (1914).

[9] The possibility that nitrite esters are oxidized to nitrate esters by NO_2 is not excluded, especially in light of British Patent 586,344 [C. W. Scaife, H. Baldock and A. E. W. Smith, *C. A.*, **41**, 6893 (1947)].

The second side reaction induced by dehydrohalogenation derives from the simultaneous production of olefins and oxides of nitrogen. Nitrogen trioxide and nitrogen tetroxide readily add to olefins giving nitrosites, nitrosates, nitro-nitrites, nitro-nitrates and dinitrocompounds.[10] It is not surprising, then, that part of the product from reactions involving secondary bromides and iodides is high boiling and the presumption that this is composed of olefin–N_2O_3 (and N_2O_4) adducts is supported by the isolation, in several instances, of crystalline compounds having the composition and properties of such N_2O_3 adducts (see Experimental).

In light of the foregoing it becomes apparent why the reaction of secondary halides with silver nitrite is not a good way to obtain secondary nitro compounds.

Tertiary Halides.—In contrast to primary and secondary chlorides, tertiary chlorides react with silver nitrite. However, the yields of nitroparaffins are very low (*ca.* 5%), the principal products being nitrite esters (*cf.* Table II). Significant amounts of high boiling, blue-green liquids also are obtained which dissolve in aqueous alkali and liberate brown fumes on treatment with 85% phosphoric acid, properties characteristic of olefin–N_2O_3 (and N_2O_4) adducts.

From the mixtures produced on treating tertiary bromides with silver nitrite no nitro compounds could be isolated, but nitrite esters were obtained in 50–64% yield (Table II). Here again, blue-green adducts of olefins with oxides of nitrogen are formed in appreciable amounts.

It is conceivable that the *t*-butyl nitrite arises from hydrolysis of the halide followed by the reaction of *t*-butyl alcohol with nitrous acid; *i.e.*

$$(CH_3)_3CX + AgNO_2 \longrightarrow (CH_3)_2C{=}CH_2 + HNO_2 + AgX$$

$$2HNO_2 \rightleftarrows H_2O + N_2O_3$$

$$(CH_3)_3C{-}X + H_2O \longrightarrow (CH_3)_3C{-}OH + HX$$

$$HX + AgNO_2 \longrightarrow AgX + HNO_2$$

$$(CH_3)_3C{-}OH + HNO_2 \longrightarrow (CH_3)_3C{-}ONO + H_2O$$

To test this possibility, 0.5 mole of *t*-butyl chloride was treated with 0.65 mole of silver nitrite in the presence of 100 g. of Drierite. The yield of *t*-butyl nitrite was 63%, identical with the yield in the absence of Drierite. A reaction was then run using 0.5 mole of *t*-butyl bromide and 0.65 mole of silver nitrite in the presence of 0.6 mole of calcium hydride. The yield was 63%, exactly the same as in the absence of calcium hydride. From these experiments, it appears that the above sequence is not the path by which *t*-butyl nitrite is produced.

TABLE II

THE REACTION OF SILVER NITRITE WITH TERTIARY HALIDES

Halide	Nitroparaffin, %	Nitrite ester, %
t-Butyl chloride	4–6	63–64[b]
t-Butyl bromide	0[a]	63–64[b]
t-Butyl iodide	0	0[b]
t-Amyl chloride	5–6	57–58[b]
t-Amyl bromide	0	50–60[b]
2-Me-2-chlorooöctane	[c]	49[d]
2-Me-2-bromoöctane	0	33[e]

[a] In an early experiment (by B. T.) an 8% yield of *t*-nitrobutane was obtained, but this could not be repeated by R. A. S. [b] Determined spectrophotometrically (ultraviolet). [c] A small yield (*ca.* 5%) of what appears to be impure 2-methyl-2-nitroöctane was obtained. [d] B.p. 58° (4 mm.), n^{20}_{D} 1.4189. [e] B.p. 53° (3 mm.), n^{20}_{D} 1.4188. In addition, a 28% yield of 2-methyl-2-octanol (n^{20}_{D} 1.4280) was isolated.

One run was made using *t*-butyl iodide. Contact with silver nitrite at 0° for fifteen minutes resulted in a rapid reaction. However, the product was found to contain molecular iodine (50% yield) as well as a colorless gas which boils below room temperature; no *t*-nitrobutane was isolated nor did the reaction product possess the characteristic ultraviolet absorption spectrum of *t*-butyl nitrite. Although further study is needed before this reaction can be said to be understood, it is obvious, even at this juncture, that this is not a useful way to make *t*-nitrobutane.

In summary, the reaction of tertiary iodides and bromides with silver nitrite is worthless for the synthesis of *t*-nitro compounds and the situation is not much better when *t*-chlorides are employed.

Experimental[11]

The silver nitrite employed was prepared as described[3] except for a number of runs in which Mallinckrodt silver nitrite was used. Mallinckrodt anhydrous diethyl ether, analytical reagent, was employed throughout.

Rectifications were either carried out with a 20-inch modified Widmer column[12] fitted with a variable take-off head, or with a small (50 cm. × 1 cm.) glass-helices packed column.

Alcohols.—With the exceptions noted below, the alcohols employed were commercial samples which were rigorously dried and rectified; only middle cuts of constant b.p. and n^{20}_{D} were taken.

4-Heptanol was prepared in two ways: (a) the action of *n*-propylmagnesium bromide on butyraldehyde which gave a 47% yield of the pure alcohol, b.p. 83° (45 mm.), n^{20}_{D} 1.4200; (b) reduction of 4-heptanone (b.p. 143°, n^{20}_{D} 1.4070) with lithium aluminum hydride (60–75% yield); b.p. 155°, 84° (45 mm.), n^{20}_{D} 1.4202; lit. values[13]; b.p. 155–155.4°, n^{20}_{D} 1.4205.

2-Methyl-5-octanol was synthesized by treating *n*-butyraldehyde with isoamylmagnesium bromide; yield 71%, b.p. 72° (8 mm.), n^{20}_{D} 1.4262; lit. values[14]: b.p. 89° (18 mm.), n^{20}_{D} 1.426.

Reduction of phenylacetone with lithium aluminum hydride gave 1-phenyl-2-propanol in 91% yield, b.p. 110° (20 mm.), n^{20}_{D} 1.5210; lit. values: b.p. 116° (25 mm.), n^{25}_{D} 1.5195[15a]; n^{20}_{D} 1.5190.[15b]

2-Methyl-2-octanol was obtained in 67% yield by the action of *n*-hexylmagnesium bromide on acetone; b.p. 65° (2 mm.), n^{20}_{D} 1.4280. Kirrmann[16] reports b.p. 81° (13 mm.), n^{19}_{D} 1.4299.

Halides.—2-Chloropropane (b.p. 35°, n^{20}_{D} 1.3776), 2-chlorobutane (b.p. 67.7°, n^{20}_{D} 1.3967), *t*-butyl chloride (b.p. 51°, n^{20}_{D} 1.3856) and *t*-amyl chloride (b.p. 85°, n^{20}_{D} 1.4054) were commercial samples which had been purified carefully. 2-Chloroöctane was prepared from 2-octanol (purified *via* the acid phthalate) by treatment with thionyl chloride and pyridine, and then rectifying (b.p. 63° (14 mm.), n^{20}_{D} 1.4259).

2-Bromopropane (b.p. 59°, n^{20}_{D} 1.4246) and 2-bromobutane (b.p. 90°, n^{20}_{D} 1.4367) were obtained by washing commercial samples with concentrated hydrochloric acid, water, 10% aqueous sodium bisulfite, 10% aqueous sodium carbonate and then with water. After drying over sodium sulfate the bromides were rectified. *t*-Butyl bromide (b.p.

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[10] H. Baldock, N. Levy and C. W. Scaife, *J. Chem. Soc.*, 2627 (1949); A. Michael and G. H. Carlson, *J. Org. Chem.*, **5**, 1 (1940).

[11] Microanalyses by Galbraith Laboratories, Knoxville, Tenn.

[12] M. Smith and H. Adkins, THIS JOURNAL, **60**, 657 (1937).

[13] M. L. Sherrill, *ibid.*, **52**, 1982 (1930).

[14] M. Tuot, *Compt. rend.*, **202**, 1339 (1936).

[15] (a) H. H. Zeiss and M. Tsutsui, THIS JOURNAL, **75**, 898 (1953); (b) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **105**, 1115 (1914).

[16] A. Kirrmann, *Compt. rend.*, **184**, 1463 (1927).

TABLE III

CONSTANTS AND ANALYSES OF ALKYL HALIDES

Halide	B.p., °C.	Mm.	$n^{20}\mathrm{D}$	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found
2-Me-2-chlorooöctane	86	27	1.4290	66.44	66.72	11.77	11.54
2-Me-2-bromooöctane	59	3	1.4533	52.16	52.35	9.24	9.35
2-Me-5-bromooöctane	45	2	1.4528	52.16	52.41	9.24	9.23
1-Ph-2-bromopropane[a]	89	3	1.5436	54.24	54.56	5.54	5.89
t-Amyl bromide	49	105	1.4406	39.80	39.58	7.28	7.60
4-Iodoheptane	93	30	1.4920	37.16	37.34	6.65	6.85
2-Me-5-iodooöctane[b]	72	4	1.4871	42.52	42.68	7.48	7.68
1-Ph-2-iodopropane[c]	93	2	1.5850	43.90	43.59	4.47	4.75

[a] Prepared by treating the tosylate of 1-phenyl-2-propanol with anhydrous lithium bromide in dry acetone at room temperature for two days. *Anal.* Found: Br, 40.20, 40.01; calcd. Br, 40.14. [b] Prepared by G. E. Graham of this Laboratory. [c] Prepared by treating the tosylate of 1-phenyl-2-propanol with sodium iodide in anhydrous acetone for two days at room temperature.

73°, $n^{20}\mathrm{D}$ 1.4276) was prepared from the alcohol by treatment with a mixture of 48% aqueous hydrobromic acid and 96% sulfuric acid at a temp. below 5°. 2-Bromooöctane (b.p. 60–61° (5 mm.), $n^{20}\mathrm{D}$ 1.4502) and 4-bromoheptane (b.p. 72° (34 mm.), $n^{20}\mathrm{D}$ 1.4498) were obtained from the corresponding alcohols and phosphorus tribromide. Sherrill[13] reports b.p. 64° (16 mm.), $n^{20}\mathrm{D}$ 1.4495 for 4-bromoheptane.

2-Iodopropane (Columbia) was washed with aqueous sodium bisulfite, with water, dried over anhydrous magnesium sulfate and then rectified (b.p. 88.9°, $n^{20}\mathrm{D}$ 1.4987). All the other secondary iodides used in this study (except 1-phenyl-2-iodopropane) were prepared by treating the alcohols with red phosphorus and iodine: 2-iodobutane (b.p. 118.2°, $n^{20}\mathrm{D}$ 1.4995), 2-iodooöctane (b.p. 83° (10 mm.), $n^{20}\mathrm{D}$ 1.4886). *t*-Butyl iodide was prepared according to Norris[17]; the product after washing with aqueous sodium bisulfite was dried quickly over anhydrous sodium sulfate and distilled (b.p. 99°, $n^{20}\mathrm{D}$ 1.4899).

The remaining halides employed in this investigation are either new compounds or have been inadequately characterized heretofore. Their properties are given in Table III.

Alkyl Nitrites.—The secondary and tertiary nitrite esters needed as reference compounds were prepared from the corresponding alcohols; Table IV summarizes their properties. The following procedure[18] exemplifies the method of synthesis employed, unless otherwise stated in Table IV.

TABLE IV

CONSTANTS AND ANALYSES OF ALKYL NITRITES

Nitrite	B.p., °C. (mm.)	$n^{20}\mathrm{D}$	Nitrogen, % Calcd.	Found
Isopropyl[a,b]	39.9–40	1.3520	15.7	14.9
2-Butyl	68.2–68.5	1.3712[c]		
4-Heptyl[b,d]	71 (62)	1.4038	9.67	9.66
2-Octyl[a]	63 (16)	1.4090[e]		
2-Me-5-octyl	63 (10)	1.4140	8.09	7.97
1-Ph-2-propyl[a]	57 (1)	1.4892	8.48	8.84[f]
2-Ph-1-propyl[a]	58 (2)	1.4946	8.48	8.35[g]
t-Amyl	69 (338)	1.3890[h]		
2-Me-2-octyl	56 (3)	1.4186	8.09	8.18

[a] Obtained by treating the alcohol with nitrosyl chloride according to N. Kornblum and E. P. Oliveto (THIS JOURNAL, **69**, 465 (1947)). [b] Obtained by treating the alcohol with sodium nitrite and sulfuric acid (W. A. Noyes, *ibid.*, **55**, 3888 (1933)). [c] N. Kornblum, J. T. Patton and J. B. Nordmann (THIS JOURNAL, **70**, 749 (1948)) report b.p. 68°, $n^{20}\mathrm{D}$ 1.3710. [d] The procedure of ref. 18 gave 4-heptyl nitrite of $n^{20}\mathrm{D}$ 1.4041. [e] N. Kornblum and E. P. Oliveto (ref. *a*) report $n^{20}\mathrm{D}$ 1.4082. [f] *Anal.* Calcd. for $C_9H_{11}NO_2$: C, 65.45; H, 6.66. Found: C, 65.52; H, 6.51. [g] *Anal.* Calcd. for $C_9H_{11}NO_2$: C, 65.45; H, 6.66. Found: C, 65.20, 65.66; H, 6.98, 6.94. [h] Lit. value: b.p. 63° (345 mm.), $n^{17}\mathrm{D}$ 1.3904 (S. D. Wilson and E. F. Yang, *Chinese J. Physiol.*, **4**, 391 (1930)).

Preparation of 2-Methyl-2-octyl Nitrite.—In a three-necked flask fitted with a stirrer and dropping funnel were placed 43.2 g. (0.3 mole) of 2-methyl-2-octanol and 41.4 g. (0.6 mole) of sodium nitrite dissolved in a minimum amount of water. The mixture was cooled to 0° and then, with continuous stirring, 71 g. (0.12 mole) of aluminum sulfate ($18H_2O$) dissolved in sufficient water to give a 40% solution was added over a period of one hour. After addition was complete, the reaction mixture was stirred at ice temperatures for two more hours and poured into a separatory funnel; the aqueous layer was removed, and the yellow organic layer was washed three times with water and dried over anhydrous sodium sulfate. Rectification[12] gave 37.8 g. (72% yield) of 2-methyl-2-octyl nitrite having a constant b.p. and $n^{20}\mathrm{D}$ (*cf.* Table IV).

The Reaction of 4-Bromoheptane with Silver Nitrite.—With minor variations the following is typical of the experiments on which the data of Table I are based: In a 3-necked flask fitted with a stirrer, dropping funnel and reflux condenser protected with a drying tube were placed 116 g. (0.75 mole) of silver nitrite and 200 ml. of anhydrous ether. The mixture was cooled to 0° by an ice-bath and with continuous stirring (in the absence of light) 89.5 g. (0.5 mole) of 4-heptyl bromide dissolved in 50 ml. of ether was added over a period of two hours. After the addition was complete the mixture was stirred at 0° for 24 hours and then allowed to come to room temperature and stirred for 22 hours more. At this time the supernatant ether solution gave a negative Beilstein test and no precipitate was obtained when a saturated solution of silver nitrate in acetonitrile was added to two drops of the ether solution which had been diluted with an equal volume of methanol.

The silver salts were removed by filtration and thoroughly washed with ether. The filtrate and extracts were combined and the ether was removed by pumping at 55 mm. for three hours, a train of three traps cooled to −80° (Dry Ice) being employed as receivers. Only the first trap had any contents (I). The material which had not volatilized then was distilled under reduced pressure (first at 53 mm. and then, gradually down to 15 mm.). The distillate was divided into four portions: (a) the most volatile fraction which condensed in the Dry Ice trap interposed between the system and the pump. This was combined with I and from the resulting ethereal solution II 3-heptene was isolated as described below: (b) 20.9 g. of material boiling from 40° (53 mm.) to 70° (15 mm.); all these fractions were yellow and had $n^{20}\mathrm{D}$ 1.4043–1.4145: (c) 14.1 g. of material b.p. 70–80° (15 mm.), $n^{20}\mathrm{D}$ 1.4189–1.4234; the first fractions were yellow, the last colorless: (d) 5.76 g. of b.p. 80–82° (15 mm.), $n^{20}\mathrm{D}$ 1.4241–1.4310; the first part of this material was colorless, the last yellow. The residue from this distillation weighed 2.3 g. and was a deep yellow liquid.

3-Heptene.—When the ethereal solution II was dried over anhyd. magnesium sulfate and rectified, 6.2 g. (13% yield) of 3-heptene was isolated, b.p. 95–96°, $n^{20}\mathrm{D}$ 1.4049; lit. value[19]: b.p. 94°, $n^{20}\mathrm{D}$ 1.4049. *Anal.* Calcd. for C_7H_{14}: C, 85.63; H, 14.37. Found: C, 85.53, 85.86; H, 14.15, 14.29. The olefin decolorized bromine in carbon tetrachloride solution and reacted instantaneously with potassium permanganate.

4-Heptyl Nitrite.—Upon rectification the 20.9 g. of (b) gave 15.2 g. (22% yield) of 4-heptyl nitrite, b.p. 67° at 50 mm., $n^{20}\mathrm{D}$ 1.4041 (*cf.* Table IV).

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(17) J. F. Norris, *Am. Chem. J.*, **38**, 640 (1907).

(18) A. Chretien and Y. Longi, *Compt. rend.*, **220**, 746 (1945).

(19) V. Ipatieff and A. Grosse, THIS JOURNAL, **57**, 1616 (1935).

TABLE V

CONSTANTS AND ANALYSES OF NITROPARAFFINS

Compound	B.p., °C. (mm.)	$n^{20}D$	Analyses, % Calcd. C	H	N	Found C	H	N
2-Nitrobutane	78 (100)	1.4043	46.53	8.79	13.58	46.72	8.83	13.51
4-Nitroheptane	86 (20)	1.4240	57.93	10.4	9.65	57.76	10.25	9.87
						57.82	10.28	9.54
2-Nitroöctane	66 (2)	1.4280			8.80			8.73
2-Me-5-nitroöctane	75 (8)	1.4320	62.38	11.05	8.09	62.63	11.11	8.10
						62.45	11.24	7.93
1-Ph-2-nitropropane	96 (2)	1.5159	65.45	6.66	8.48	65.45	6.75	8.76
2-Me-2-nitropropane	125–127	1.4022						
2-Me-2-nitrobutane	78 (65)	1.4142			11.96			12.01

4-Heptyl Nitrate.—The 14.1 g. of (c) was shaken with four 10-ml. portions of 10% sulfuric acid for a few minutes and then overnight with 32 ml. of 10% aq. sodium hydroxide. Ten ml. remained undissolved and further shaking with aqueous alkali caused no further volume change. The combined aqueous alkaline solutions were washed with petroleum ether (b.p. 35–37°), the petroleum ether phase was added to the alkali-insoluble layer, washed with water and dried over anhyd. magnesium sulfate. The petroleum ether solution (100 ml.) then was passed through a column of 50 g. of activated alumina and the column then was eluted with 500 ml. of petroleum ether. Distillation gave 6.3 g. (8% yield) of colorless 4-heptyl nitrate, b.p. 85° (25 mm.), $n^{20}D$ 1.4207. *Anal.* Calcd. for $C_7H_{15}NO_3$: C, 52.15; H, 9.38; N, 8.69. Found: C, 52.32, 52.41; H, 9.40, 9.53; N, 8.87, 8.72. Infrared analysis showed the complete absence of –OH (2.68–2.84) and the characteristic covalent nitrate bands were present at 6.15, 7.85 and 11.5 μ.

4-Nitroheptane.—The aqueous alkaline solution obtained in the isolation of 4-heptyl nitrate was acidified with an ice-cold saturated water solution of hydroxylamine hydrochloride and allowed to stand at 0° overnight. After extracting with petroleum ether and drying over magnesium sulfate the 4-nitroheptane was isolated by distillation; yield 5.4 g. (7%), b.p. 67° (7 mm.), $n^{20}D$ 1.4247. *Anal.* Calcd. for $C_7H_{15}NO_2$: C, 57.93; H, 10.4; N, 9.65. Found: C, 57.95, 58.15; H, 10.44, 10.32; N, 9.46, 9.68. Infrared analysis showed the typical nitro bands at 6.45 and 7.37 μ.

The 5.76 g. of material labeled (d), b.p. 80–82° (15 mm.), probably contained considerable 4-nitroheptane since 75% of it dissolves in aqueous alkali.

In some runs appreciable amounts of alcohols are obtained. These presumably arise from the hydrolysis of nitrite esters.

Olefin–Oxide of Nitrogen Adducts. (a) From the Reaction of 1-Phenyl-2-iodopropane with Silver Nitrite.—After conducting the reaction in the usual way the silver salts were removed by filtration and the ether solution of products was placed in a refrigerator. After two days a small amount of white crystals had appeared. These were recrystallized from acetone; m.p. 130–133° dec. These crystals are insoluble in ethanol and in water. Their acetone solution is blue. *Anal.* Calcd. for $C_9H_{10}N_2O_3$: C, 55.60; H, 5.15; N, 14.43. Found: C, 55.79, 55.73; H, 5.31, 5.09; N, 14.39.

The ether solution from which the white crystals had separated was pumped at 0° until most of the ether had been removed and then the residual material was distilled at 3 mm. Soon after the distillation was started, it was noted that blue liquid and blue solid were condensing in the Dry Ice trap maintained between the still and the vacuum pump. After the distillation was complete the trap was allowed to come to room temperature; it was found to contain about 1 ml. of water, 2 ml. of yellow liquid and about 0.5 g. of white crystals. After filtration and drying, these crystals melted at 141–143° to a blue melt with decomposition. *Anal.* Calcd. for $(C_9H_{10}N_2O_3)_2$: C, 55.60; H, 5.15; N, 14.43. Found: C, 55.85, 55.73; H, 5.11, 5.29; N, 13.91, 13.88.

These two crystalline compounds are, presumably, the diastereoisomeric nitroso nitro compounds produced by adding N_2O_3 to 1-phenyl-1-propene but, of course, this has not been established.[20] The isomeric 1-phenyl-2-nitroso-2-nitropropane (1-phenyl-2-propyl pseudonitrole) melts at 89–90° (*vide infra*).

(b) From the Reaction of 2-Iodobutane with Silver Nitrite.—The reaction was conducted as usual and then the silver salts were removed by filtration. The ether solution of products, after standing overnight in a refrigerator, deposited 0.21 g. of white crystals which consisted of needles (m.p. 127–129°) and plates (m.p. 131–134°). Both melt to blue liquids. The higher melting form was analyzed. *Anal.* Calcd. for $(C_4H_8N_2O_3)_2$: C, 36.37; H, 6.10; N, 21.21. Found: C, 36.96; H, 6.14; N, 21.35.

It is noteworthy that 2-nitroso-2-nitrobutane has m.p. 58–59°.[21]

In the 2-propyl and the 2-butyl series the nitrite esters and nitroparaffins were removed from high boiling materials by high-vacuum distillation at temps. below 30°. It was found repeatedly that the residual liquids spontaneously decompose on standing at room temperature for a few hours; brown fumes are evolved and dark colored liquids are produced. Such instability is characteristic of olefin–N_2O_3 adducts.[22]

The Reaction of *t*-Butyl Chloride with Silver Nitrite.—With the small variations the following is representative of the experiments employing tertiary halides. Furthermore, it provides an example of the ultraviolet spectroscopic procedures used to determine the yields of nitrite esters (both secondary and tertiary) which cannot be separated quantitatively from the diethyl ether used as a reaction solvent.

The ultraviolet spectrum of *t*-butyl nitrite in diethyl ether solution between 300–400 mμ is a series of well-defined absorption maxima. Furthermore, in this region absorption is so intense that using a Cary recording spectrophotometer, readings can be made only with *colorless* solutions of the yellow *t*-butyl nitrite. However, nitrogen dioxide, nitrogen trioxide and the compounds formed by addition of these oxides to isobutene, all show absorption in this region and conceivably might have interfered with the determination of *t*-butyl nitrite. Clean separation of *t*-butyl nitrite from the relatively non-volatile isobutene–oxide of nitrogen adducts was achieved readily at room temperature and a vacuum of 10 mm. But nitrogen trioxide and nitrogen tetroxide cannot be removed from an ether solution of *t*-butyl nitrite in this way. Fortunately, a mixture of nitrogen trioxide and nitrogen tetroxide gives a yellow solution in diethyl ether whose ultraviolet spectrum has absorption peaks at 388, 373 and 360 mμ, wave lengths which are absorption minima for *t*-butyl nitrite. When this yellow solution is diluted until *colorless*, it has no absorption at 395 mμ, a principal peak for *t*-butyl nitrite, and there is negligible adsorption at the other *t*-butyl nitrite maxima employed (379 and 365 mμ). As a further precaution against the possibility of interference, plots of absorbance *vs.* concentration were made for diethyl ether solutions of pure *t*-butyl nitrite using the absorption maxima at 365, 379 and 395 mμ. Since in subsequent determinations of *t*-butyl nitrite in reaction products the concentrations given by using these three plots were the same, it is exceedingly unlikely that there was any interference. In the event of interference the three peaks would likely have been displaced by different amounts, and thus readings at the three different wave lengths would have given three different concentrations.

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[20] A Referee kindly has pointed out that one of these N_2O_3 adducts may be the nitrosite of α-methylstyrene.

[21] E. Piloty, *Ber.*, **35**, 3095 (1902).

[22] N. Levy and C. W. Scaife, *J. Chem. Soc.*, 1094 (1946); A. Michael and G. H. Carlson, *J. Org. Chem.*, **5**, 1 (1940).

A slurry of 100 g. of silver nitrite and 250 ml. of anhydrous ether in a 500-ml. three-necked flask fitted with a drying tube, dropping funnel and glass paddle stirrer was cooled in a salt–ice-bath and 46.25 g. (0.5 mole) of *t*-butyl chloride was added dropwise over a period of an hour. After stirring at ice temperature for a total of 28 hours, the silver salts were removed by filtration, washed with ether and the washings were added to the green filtrate. The ether solution of products was placed in a flask fitted to a 4-ft. glass helix packed column, the column head being cooled by circulating brine and set for total reflux. Two Dry Ice traps were placed between the head of the column and the vacuum pump. Without application of heat, the pressure was reduced to 200 mm., then to 50 mm. and finally to 10 mm. and distillate was collected until it started to freeze in the first trap as it came over. (The material which had not distilled amounted to 10.53 g. of a blue liquid; it was treated as described below.) The distillate, consisting of ether and nitrite, was diluted to 500 ml. with ether and one ml. of this was further diluted to 50 ml. From the absorbance at 365, 379 and 395 mμ it was found that 32.7 g. of *t*-butyl nitrite (64% yield) had been produced.

Rectification of the diethyl ether–*t*-butyl nitrite solutions manifestly failed to give complete separation. The ether distilling off was yellow and it had a distinct odor of *t*-butyl nitrite. Despite this, there was obtained 20.8 g. (40% yield) of *t*-butyl nitrite, b.p. 63°, n^{20}_D 1.3687.

The 10.53 g. of blue liquid left after *t*-butyl nitrite and diethyl ether were removed from the reaction product (see above) was diluted with an equal volume of 35–37° petroleum ether, washed with water, then with 10% sodium hydroxide until the aqueous layer remained colorless, then with 85% phosphoric acid, and finally with water. After drying over anhydrous magnesium sulfate, the petroleum ether solution was distilled. This gave 2.2 g. (4% yield) of *t*-nitrobutane, b.p. 125–127°, n^{20}_D 1.4022; lit. values[23]: n^{20}_D 1.4015, b.p. 126°.

Duplication of this experiment, except for the addition of 100 g. of Drierite to the reaction mixture, gave a 63% yield of *t*-butyl nitrite and a 5% yield of *t*-nitrobutane.

1-Phenyl-2-nitro-2-nitrosopropane (**1-Phenyl-2-propyl Pseudonitrole**).—An aqueous alkaline solution of 1-phenyl-2-nitropropane containing sodium nitrite was acidified with hydrochloric acid. The product was taken up in diethyl ether, the blue solution was washed with water, dried over anhydrous magnesium sulfate and placed in a refrigerator. The white crystals obtained were recrystallized from a mixture of acetone and ether; m.p. 89–90° (to a blue liquid). *Anal.* Calcd. for $C_9H_{10}N_2O_3$: C, 55.60; H, 5.15; N, 14.43. Found: C, 55.81, 55.68; H, 5.26, 5.33; N, 14.65, 14.28.

LAFAYETTE, INDIANA

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[23] R. H. Wiswall and C. P. Smyth, *J. Chem. Phys.*, **9**, 356 (1941).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Reactions of Alkyl Iodides with Halogens[1]

BY F. MARSHALL BERINGER AND HERMAN S. SCHULTZ

RECEIVED APRIL 7, 1955

Optically active 2-iodoöctane reacted with chlorine or with bromine in a cold inert solvent to give as a main product 2-chloroöctane or 2-bromoöctane of predominantly inverted configuration. Similar reaction with iodine monochloride yielded predominantly inverted 2-chloroöctane, optically inactive 2,3-dichloroöctane and an optically inactive iodochlorooctane.[2] Under similar conditions neopentyl iodide reacted with chlorine and bromine to give *t*-amyl halides and the halogen adducts of trimethylethylene. Possible mechanisms for these reactions are discussed.

Introduction

Currently it appears that there are three mechanisms by which alkyl halides can exchange with free halogens. First, exchange may be initiated by iodine atoms produced thermally or by photolysis.[3] With allyl iodide another mechanism is apparently operating, namely, coördination of molecular iodine with the olefinic bond followed by loss of a different pair of adjacent iodine atoms.[4] Finally there seems to be a third, non-radical path available for exchange with chlorine, bromine or iodine monochloride.[5–7] It has been suggested[7] that these last exchanges proceed through the formation and breakdown of alkyl iodide–halogen complexes, which may be precipitated at low temperatures[6] and which exist in appreciable amount at room temperature.[8]

TABLE I

REACTIONS OF OPTICALLY ACTIVE 2-IODOÖCTANE: R = 2-OCTYL

Reaction	Conditions	RI	RX[a]	k_i/k_r[b]
RI + Cl_2	1:1 $HCCl_3$–pet. ether,	d_4 1.3164 (26°)	0.8663 (26°)	6.0
↓ 70.6%	−78°, 1.5 hr.; 0°, 1.5 hr.	n_D 1.4877 (22°)	1.4251 (24°)	
RCl + ICl		$[\alpha]_D$ +46.33 (26°) b.p. 94° (16 mm.)	−24.93 (26°) 61° (14 mm.)	
RI + ICl	CCl_4, 25°, 74 hr.	n_D 1.4782 (26°)	1.4224 (23°)	2.1
↓ 33.4%[c]		$[\alpha]_D$ −45.47 (28°)	+12.4 (24°)	
RCl + I_2		b.p. 93 °(16 mm.)	64° (16 mm.)	
RI + Br_2	Pet. ether,	d_4 1.3157 (27°)	1.1010 (26°)	3.5
↓ 85%[d]	−78°, 2 hr. 0°, 1 hr.	n_D 1.4864 (25°)	1.4485 (26°)	
RBr + IBr		$[\alpha]_D$ +45.0 (27°) b.p. 95° (17 mm.)	−21.0 (26°) 79° (17 mm.)	
RI + Br_2	Pet. ether,	n_D 1.4857 (26°)	1.4492 (25°)	2.3
↓ 55%[d]	25°, 5 hr.	$[\alpha]_D$ +45.7 (25°)	−15.4 (25°)	
RBr + IBr		b.p. 72° (5 mm.)	77° (16 mm.)	

[a] X = Cl in reactions with Cl_2, ICl; X = Br in reactions with Br_2. [b] See definition and discussions in footnotes 9 and 10. [c] For other products see Experimental section. [d] Yield was obtained with *dl*-2-iodoöctane.

At the inception of this work in 1950, it was felt that useful information might be obtained concern-

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[1] This paper is taken from the Ph.D. dissertation of Herman S. Schultz, June, 1956. The reaction of optically active 2-iodoöctane with chlorine to give 2-chloroöctane of inverted configuration was reported earlier in the B.S. thesis of David Goland, June, 1951.

[2] The conversion of optically active 2-iodoöctane to 2-chloroöctane of inverted configuration has been independently confirmed recently: E. J. Corey and W. J. Wechter, THIS JOURNAL, **76**, 6040 (1954).

[3] For leading papers see R. M. Noyes and D. J. Sibbett, *ibid.*, **75**, 761, 767 (1953).

[4] D. J. Sibbett and R. M. Noyes, *ibid.*, **75**, 763 (1953).

[5] A. Geuther, *Ann.*, **123**, 124 (1862); C. Friedel, *ibid.*, **135**, 206 (1865); F. Viebock and A. Schwappach, *Ber.*, **63B**, 2818 (1930).

[6] J. Thiele and W. Peters, *ibid.*, **38**, 3842 (1905); *Ann.*, **369**, 149 (1909).

[7] R. M. Keefer and L. J. Andrews, THIS JOURNAL, **75**, 543 (1953); **76**, 253 (1954).

[8] R. M. Keefer and L. J. Andrews, THIS JOURNAL, **74**, 1891 (1952).