Neopentyl iodide was prepared according to Landauer and Rydon; b.p. 70–72° (100 mm.), n^{20}D, 1.4893–1.4898, 63–72% yield. *Anal.*[6] Calcd. for $C_5H_{11}I$: C, 30.32; H, 5.60; I, 64.08. Found: C, 30.44; H, 5.74; I, 64.07. This product gave an immediate precipitate with 0.1 *N* aqueous silver nitrate and produced an acidic solution when shaken with distilled water. Hydrolysis in 80% aqueous ethanol was complete in 1 to 1.5 hr. and the acidity developed corresponded to 5 to 6% *t*-amyl iodide. Under the same conditions hydrolysis of *pure* neopentyl iodide was less than 0.1% complete after 12 hr. and the hydrolysis of *t*-amyl iodide was over in 45 min.

Using matched cells, the difference between the infrared spectrum of this neopentyl iodide and neopentyl iodide obtained according to Whitmore was determined with a Perkin–Elmer double-beam spectrophotometer (model 21). Strong absorption bands at 8.8 and 12.71 μ, as well as weaker bands at 7.50, 7.85, 9.57, 11.00 and 13.13 μ, were observed in the Landauer and Rydon product. All these bands are present in the spectrum of *t*-amyl iodide and are absent from the infrared spectrum of pure neopentyl iodide. Finally, the infrared spectra of neopentyl iodide prepared and purified according to Landauer and Rydon and that of a synthetic mixture consisting of 5% *t*-amyl iodide and 95% neopentyl iodide (prepared according to Whitmore) showed no significant difference.

In order to obtain pure neopentyl iodide, the Landauer–Rydon procedure is followed up to, but not including, the final distillation. At this point the product is mechanically tumbled for five hours with *ca.* three volumes of water after which the organic phase is tumbled for one hour with an equal volume of 0.1 *N* aqueous silver nitrate. The organic layer is isolated, washed with water, dried and rectified. After a small forerun (b.p. 70–71° (100 mm.), n^{20}D 1.4840–1.4888), there is collected a 53–57% yield of pure neopentyl iodide (b.p. 71° (100 mm.), n^{20}D 1.4888), spectrophotometrically identical with the iodide prepared by Whitmore's procedure.

Neopentyl iodide prepared according to Landauer and Rydon gives a brownish-violet coloration when run on to a column of silica gel. The same color is produced when pure neopentyl iodide to which 1% of *t*-amyl iodide has been added is used. However, neither the neopentyl iodide prepared by the Landauer–Rydon reaction and purified as described herein nor that prepared according to Whitmore imparts a color to a column of silica gel.

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[6] Microanalyses by Galbraith Laboratories, Knoxville, Tennessee.

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PURDUE UNIVERSITY
LAFAYETTE, INDIANA

The Reaction of Silver Nitrite with α-Haloesters[1,2]

BY NATHAN KORNBLUM, MARY E. CHALMERS AND RALPH DANIELS

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The reaction of silver nitrite with α-haloesters has been examined in order to determine its usefulness for the synthesis of α-nitroesters and, also, to test the mechanism proposed for the reaction of silver nitrite with organic halides.[3]

The reaction of α-bromoesters with silver nitrite proves to be so slow as to be completely impractical. Thus, after 6.5 days at room temperature ethyl bromoacetate and ethyl-α-bromopropionate have only reacted to the extent of 12–15%. This is to be contrasted with the fact that when primary alkyl bromides are employed the reaction is complete in two to three days. Since it is wise to operate at or close to room temperature when working with silver nitrite,[4] attention was turned to the use of α-iodoesters. At room temperature these react with silver nitrite at a reasonable rate and give excellent yields of pure α-nitroesters (Table I).

TABLE I

PREPARATION OF α-NITROESTERS FROM α-IODOESTERS

Ethyl α-nitroester	Yield, %	Reacn. time, hours	B.p. °C.	Mm.	n^{20}D
Nitroacetate	77	48	71–72	3	1.4245
α-Nitropropionate	80	48	75–76	9	1.4210[a]
α-Nitrobutyrate	75	54	82–83	8	1.4233[b]
α-Nitrocaproate	84	144	80–81	3	1.4302[c]

[a] *Anal.* Calcd. for $C_5H_9O_4N$: C, 40.81; H, 6.17; N, 9.52. Found: C, 40.91; H, 5.82; N, 9.31. [b] *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. [c] *Anal.* Calcd. for $C_8H_{15}O_4N$: N, 7.41. Found: N, 7.54.

The reaction of silver nitrite with organic halides has recently been described as a "pull–push" process involving the development of an electron deficiency at the carbon atom undergoing substitution.[3] Among other things, it has been shown that the greater the carbonium character of the transition state the greater is the yield of nitrite ester and the less that of the nitro compound. Adjacent charge considerations leave no doubt that in the reaction of silver nitrite with α-haloesters the carbonium component in the transition state will be distinctly smaller than when alkyl halides are employed. Consequently, it was anticipated that the rate of reaction of an α-haloester with silver nitrite would be slower than for the corresponding alkyl halide and that a larger fraction of the α-haloester would be converted to the nitro compound than when an alkyl halide is employed.

It has now been found that at 0° the reaction of 2-iodopropane is half over in 8 minutes whereas with ethyl α-iodopropionate the half-life of reaction is 4,860 minutes. Furthermore, the reaction of 2-iodopropane with silver nitrite gives but 15–23% yields of 2-nitropropane[5] while ethyl α-iodopropionate gives an 80% yield of ethyl α-nitropropionate. These facts provide further support for the proposed mechanism.[3]

Experimental[6]

Silver nitrite was prepared as described previously.[7] The requisite α-iodoesters were readily obtained from α-bromoesters in 75–85% yields by treatment with sodium iodide in dry acetone at room temperature for 12 hours (*cf.* Table II).

Ethyl α-Nitropropionate.—Except for variations in reaction time (*cf.* Table I) this preparation is typical of the procedure employed. Ethyl α-iodopropionate (68.7 g., 0.3 mole) was added dropwise to a stirred suspension of silver nitrite (0.6 mole, 92.4 g.) in 500 ml. of absolute ether cooled to 0° in an ice-bath; this addition required 1.5 hours. The ice-bath was removed and the reaction mixture was stirred at room temperature until a negative Beilstein test was obtained (total time 48 hours). The silver salts were removed by filtration, washed with absolute ether. The

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[1] Paper X 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. AF18(600)-310 monitored by the Office of Scientific Research, Air Research and Development Command.

[3] N. Kornblum, R. A. Smiley, R. K. Blackwood and D. C. Iffland, THIS JOURNAL, **77**, 6269 (1955).

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

[5] N. Kornblum, R. A. Smiley, H. E. Ungnade, A. M. White, B. Taub and S. A. Herbert, *ibid.*, **77**, 5528 (1955).

[6] Analyses by Galbraith Microanalytical Laboratory, Knoxville, Tenn.

[7] N. Kornblum, B. Taub and H. E. Ungnade, THIS JOURNAL, **76**, 3209 (1954)

TABLE II

α-IODOESTERS

Ester	B.p. °C.	B.p. Mm.	$n^{20}D$	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Ethyl iodoacetate[a]	60	3	1.5045				
Ethyl α-iodopropionate	49	7	1.4963	26.33	26.21	3.98	3.93
Ethyl α-iodobutyrate	46	1	1.4923	29.77	30.04	4.55	4.74
Ethyl α-iodocaproate	84	4	1.4873	35.37	35.87	5.60	5.90

[a] W. H. Perkin [*J. Chem. Soc.*, **65**, 402 (1894)] reports b.p. 142.5–143.5° (250 mm.), $n^{12.7}D$ 1.5079.

filtrate and washings were concentrated *in vacuo* and the residual pale blue oil was distilled; yield 35.3 g. (80%) of pure ethyl α-nitropropionate (b.p. 75–76° (9 mm.), $n^{20}D$ 1.4210).

This α-nitroester dissolves readily in saturated aqueous sodium bicarbonate solution and from the resulting yellow solution ethyl α-nitropropionate ($n^{20}D$ 1.4210) is recovered in 90% yield by acidification with aqueous acetic acid containing urea.[8] The other α-nitroesters listed in Table I also dissolve readily in saturated aqueous bicarbonate and, of course, they are also easily soluble in 10% aqueous sodium hydroxide.

Rate Measurements.—A solution consisting of 5.95 g. (0.035 mole) of 2-iodopropane and 200 ml. of anhydrous diethyl ether was stirred and cooled in an ice-bath. After one hour duplicate 1-ml. samples were withdrawn to give the initial concentration of iodide. Then 53.9 g. (0.35 mole) of silver nitrite was added as rapidly as possible and the reaction followed by withdrawing 1-ml. samples. The unreacted 2-iodopropane was converted to ionic iodide by the use of Raney nickel and alkali[9] and titrated as such with silver nitrate. The reaction of ethyl α-iodopropionate was followed in exactly the same way using 7.98 g. (0.035 mole) of the ester. Duplicate runs gave times of half-reaction which agreed within 1%.

The rates with α-bromoesters were determined as above (except for operating at room temperature) and also by recovery of the α-bromoesters. In a typical experiment 50.1 g. (0.30 mole) of ethyl bromoacetate was treated, at 25–28°, with 48.5 g. (0.315 mole) of silver nitrite. After 6.5 days 40.1 g. (80%) of the ethyl bromoacetate was recovered.

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DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
WEST LAFAYETTE, INDIANA

Triolein-H^3

DAVID KRITCHEVSKY,[a] R. F. J. MCCANDLESS,[a] JOSEPH E. KNOLL[b] AND MAXWELL L. EIDINOFF[b]

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To obtain a triglyceride of an unsaturated acid labeled with tritium, which was required for other studies, we undertook the preparation of triolein-H^3 by isotope exchange involving a sealed-tube reaction of the fat with labeled water in the presence of reduced platinum and a small quantity of base.[1] Although the over-all yield of isotopic exchange was low, it was possible to obtain tritium-labeled triolein in good yield and of a specific activity (16.9 μc./g.) sufficient for our further work.

Upon saponification, the oleic acid moiety was found to contain 14.8 μc./g. and the glycerol 0.10 μc./g., using calculations correcting for the hydrogen atoms gained during saponification. About 16% of the activity was lost during the saponification. Heating the triolein-H^3 with dilute base for a short time resulted in no loss of activity.

To ascertain that none of the activity was due to hydrogenation of the double bonds present in triolein, the acid recovered after saponification was subjected to paper chromatography using the method of Savary[2] which gives wide separation of oleic and stearic acids. No stearic acid could be detected by spray with Rhodamine B solution and activity was recovered only from the oleic acid area when the strips were subjected to radioactive assay in a windowless counter.[3] Additional proof of the absence of stearic acid was the demonstration that the iodine number of the radioactive product was identical with that of the starting material.

Experimental

Triolein-H^3.—One gram of platinum oxide and 1 ml. of tritiated water were introduced into a glass tube and the catalyst was reduced in a stream of hydrogen gas. After the tube had been thoroughly flushed with nitrogen, 6 g. of triolein (hydroxyl value 0.7, free fatty acid content 0.15%, iodine number 85.3 (theory 86),[4] 15 mg. of KOH and an additional 5 ml. of tritiated water (8.8 mc./ml.)) were added, the tube was evacuated and sealed, then maintained at 130° for 28 hours with constant shaking. After the shaking period the organic layer was taken up in ether and the acidic material separated from the neutral triolein on an IRA-400 ion exchange column.[5] The specific activity of the eluted triolein (5.2 g.) measured by gas counting[6] was 16.9 μc./g. The iodine number of the eluted material was 85.0. It is possible that some of the triglyceride was hydrolyzed during the course of the isotopic exchange, but any appreciable amounts of mono- or diglyceryl oleate would cause considerable lowering of the iodine number; the d^{20}_4 0.915 $\frac{20°}{4°}$ (lit. 0.915 (15°),[7] 0.9152 (20°)[8]). Since the specific gravity of glyceryl monoöleate is 0.947, appreciable quantities of this material in our final product would have resulted in an elevation of the observed value.

Saponification.—The radioactive triolein was saponified by refluxing with concd. alcoholic KOH for 5 hours in an atmosphere of nitrogen. After acidification and extraction, the ether solution was passed over a column of IRA-400 resin, the oleic acid being eluted with alcoholic HCl. The aqueous layer was distilled to dryness at reduced pressure and the residual salt extracted with hot acetone to obtain the glycerol. The corrected activity of the oleic acid was 14.8 μc./g. (4.2×10^3 μc./mole) and that of the glycerol was 0.10 μc./g. (9 μc./mole). Partial saponification was carried out using dilute alcoholic KOH and only 1 hour reflux. There was no change in the activity of the recovered triolein.

Paper Chromatography.—Descending chromatography on single strips of Whatman No. 1 paper was used, with methanol–water 8:2 as the developing solvent. In model experiments with mixtures of oleic and stearic acids, the stearic acid remained at or near the origin (R_f 0.00–0.05) and the oleic acid had an R_f of 0.60–0.90, measuring from the origin to the foremost point of the spot. The spots were actually wide streaks about 6 cm. in length, but showing no overlap if the solvent front was allowed to travel at least 25 cm. In two representative runs, 150 c.p.m. were applied to the origin. After development of the chromatogram no color and no counts were found at the origin. The oleic acid gave R_f values of 0.58 and 0.93, respectively, with recovery of most of the counts from the area detected using the Rhodamine B spray.

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