4-Chloro-7-*p*-tolylmercaptoquinoline.—A solution of 10.88 g. of 4-hydroxy-7-*p*-tolylmercaptoquinoline (0.041 mole), m.p. 233–239° (expt. 2), was gently refluxed with 41 ml. of phosphorus oxychloride for two hours. Then the excess of oxychloride was removed by distillation at reduced pressure (20 mm.) and the residue was treated with cold dilute ammonia and extracted with ether. On removal of the solvent, 10.30 g. of a crude, tan-colored product was obtained, m.p. 54–57°. For the purification, it was dissolved in 150 ml. of dry petroleum ether (b.p. 30–50°) and filtered from any undissolved material. The solution was applied on an alumina column (18 × 150 mm.) which was eluted with another 350 ml. of the same solvent. From the evaporation of the combined petroleum ether fractions (500 ml.), a residue of 9.74 g. of a white solid, m.p. 58.5–60°, was obtained (83.8%). On recrystallization from petroleum ether (b.p. 52–63°), the melting point was raised to 59.5–60°.

Anal. Calcd. for $C_{16}H_{12}ClNS$: S, 11.22. Found: S, 11.48.

On continuing elution with chloroform, 0.61 g. of a brown-colored, impure residue was obtained after removing the solvent from the eluate. Previous examples of this efficient purification of chloroquinolines by adsorption can be found in the literature.[8]

As a proof of structure, a sample of the 4-chloro-7-*p*-tolylmercaptoquinoline thus obtained was allowed to react with *p*-thiocresol in toluene solution with a concentration about one tenth molar in both reactants. The solution was kept at 80° for a day or so and yellow crystals, m.p. 182.5–191°, separated on cooling. This product was shown to be the hydrochloride of the 4,7-di-(*p*-tolylmercapto) derivative (IV) since by treatment with sodium hydroxide solution, extraction with ether and removal of the solvent, pure crystals of compound IV, m.p. 100.5–101.5°, were obtained.

Acknowledgments.—A preliminary attempt of reaction between compound II and the thiol was run by one of us (G. I.) in Prof. Gilman's Laboratory. The authors are grateful to Profs. V. Caglioti and H. Gilman for helpful discussion. Thanks are also due to Dr. G. Bonola for the duplication of some of the experiments.

[8] B. Riegel, G. R. Lappin and B. H. Adelson, This Journal, **68**, 1264 (1946).

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Neopentyl Iodide

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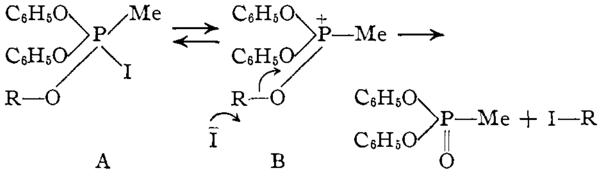
Although the synthesis of neopentyl iodide from neopentane by Whitmore, Wittle and Harriman[2] provides this compound in a high state of purity it is time consuming and not well adapted to the synthesis of even moderate amounts (100–200 g.) of the iodide. In contrast, the method recently reported by Landauer and Rydon,[3] by which neopentyl iodide is obtained in 74% yield when neopentyl alcohol is treated with a mixture of methyl iodide and triphenyl phosphite, seems well suited to the preparation of substantial quantities of the iodide.[4]

It has now been found, however, that although the yield and properties of the product described by Landauer and Rydon may be duplicated routinely, the product is not pure neopentyl iodide but is contaminated with *ca.* 6% of *t*-amyl iodide.

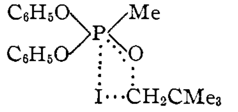
This note describes a modification of the Landauer and Rydon procedure which gives pure neopentyl iodide in 53–57% yield. Direct infrared comparison, using the matched-cell technique, shows that the product is identical with that obtained according to Whitmore, Wittle and Harriman.[2] The present procedure, therefore, constitutes the most convenient method of preparing neopentyl iodide in a high state of purity.

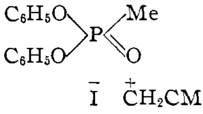
While recognizing that the available evidence is not sufficient to enable a definite conclusion to be reached regarding the mechanism of the reaction of triphenyl phosphite methiodide with alcohols, Landauer and Rydon suggest an SN2 mechanism:



The evidence cited by them[3] for reactions employing primary and secondary alcohols supports this view. But the suggestion that neopentyl iodide is formed by the SN2 mechanism leans heavily on the claim that rearrangement does not occur and, in light of the present finding, loses much of its force.

Actually, we incline to the view that neopentyl iodide is formed by a "frontal attack" which can be envisioned in several ways. In one, the covalent form (A) undergoes "*cis* elimination" thus giving rise to a cyclic transition state (a). Alternatively, the ionic form (B) breaks up to give an ion pair (b) which collapses to neopentyl iodide before rearrangement occurs. (The iodide ion is suitably located because of the equilibrium between the covalent form (A) and the ionic form (B) and also because of the electrostatic attraction of the positively charged phosphorus for the iodide ion). When combination of the ions is delayed rearrangement occurs and *t*-amyl iodide is formed.[5]


a


b

Acknowledgment.—Our thanks are due to Dr. J. W. Amy of this Department for determining the infrared spectra and for assisting us in their interpretation.

Experimental

Neopentyl alcohol was obtained in 85–90% yield by reducing trimethylacetic acid with lithium aluminum hydride: b.p. 110–111°, m.p. 55–56°. Eastman Kodak Co. triphenyl phosphite was used directly. Neopentyl iodide, prepared for reference, according to Whitmore, *et al.*,[2] had b.p. 70° (100 mm.), $n^{20}D$ 1.4887. *t*-Amyl iodide from *t*-amyl alcohol and 58% hydriodic acid had b.p. 53° (50 mm.), $n^{20}D$, 1.4976–1.4980.

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[1] 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.

[2] F. C. Whitmore, E. L. Wittle and B. R. Harriman, This Journal, **61**, 1585 (1939).

[3] S. R. Landauer and H. N. Rydon, *J. Chem. Soc.*, 2224 (1953).

[4] Whitmore, Wittle and Harriman (ref. 2) found that the reaction of neopentyl alcohol with phosphorus and iodine gives only a 4–9% yield of neopentyl iodide

[5] The material balance has never exceeded 80% and the deficiency may well be due to olefin formation.

Neopentyl iodide was prepared according to Landauer and Rydon; b.p. 70–72° (100 mm.), $n^{20}\mathrm{D}$, 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.), $n^{20}\mathrm{D}$ 1.4840–1.4888), there is collected a 53–57% yield of pure neopentyl iodide (b.p. 71° (100 mm.), $n^{20}\mathrm{D}$ 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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The Reaction of Silver Nitrite with α-Haloesters[1,2]

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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.	$n^{20}\mathrm{D}$
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).