tional crystallization, hydrolysis of the salt, and desulfonation of the acid.

Although 1-methylnaphthalene picrate is listed in reference books as a suitable derivative for identification of the hydrocarbon, the substance cannot be obtained directly from the 1-methylnaphthalene usually available commercially.[4] The constant melting picrate obtained in the regular way is apparently[2] a 1:1 addition product of the picrates of the two isomeric hydrocarbons. Consequently the picrate cannot be used generally for purposes of identification and purification. The styphnate is also unsatisfactory.

In the course of a separate investigation we have shown that this limitation does not apply to the addition products with 1,3,5-trinitrobenzene and 2,4,7-trinitrofluorenone. These derivatives serve well for identification, and yield the pure hydrocarbon by chemical methods or simply by perfusion through alumina The regenerated hydrocarbon gives directly the authentic derivatives with picric or styphnic acid, trinitrobenzene or trinitrofluorenone.

We wish to express our appreciation to the Research Corporation for a grant supporting this work.

Experimental

Treatment of several representative batches of 1-methylnaphthalene[4] with picric acid in methanol or ethanol, in the usual way, gave the 1:1 "compound"[2] of the **mixed picrate**, whose final melting point, 123.5–124°, was unchanged by further recrystallization. The melting point frequently mentioned in the literature[2] is 121–123°. The authenticated melting point of the picrate of 1-methylnaphthalene is 141.5°, and that of the 2-isomer is 116–117°.[2]

Attempts to prepare the **styphnate** from the same hydrocarbon[4] did not give a homogeneous product. In a typical case, equimolar quantities of styphnic acid and the hydrocarbon were boiled in methanol to effect solution. The yellow solid which separated on cooling melted at 114–120° and dissociated with erratic broadening of the melting range (*ca.* 103–145°) on recrystallization from methanol, 95% ethanol, or acetic acid. The recorded[2] melting points of the styphnates of 1- and 2-methylnaphthalene are 134–135° and 129.5°, respectively.

The melting point of the **trinitrobenzene derivative** prepared from 10.7 g. (0.053 mole) of the commercial hydrocarbon[4] and 7.81 g. (0.055 mole) of 1,3,5-trinitrobenzene in 50 ml. of 95% ethanol was constant (153–153.5°) after five recrystallizations from methanol. The melting points in the literature[2] are 147° and 153.5–154.5° for the 1-methyl isomer and 123° and 124° for the 2-methyl isomer.

The same hydrocarbon,[4] 0.90 g. (0.00635 mole), with 2.0 g. (0.00635 mole) of 2,4,7-trinitrofluorenone[5] in hot glacial acetic acid gave the pure **trinitrofluorenone derivative**, constant melting (163–164°) orange needles, after five recrystallizations from glacial acetic acid.

Anal. Calcd. for $C_{24}H_{15}O_7N_3$ (1:1 complex); C, 63.0; H, 3.3; N, 9.2. Found: C, 62.8, 63.0; H, 4.0, 3.9; N, 9.5, 9.2.

The derivative dissociated completely when it was kept for 28 hours at 1 mm. and 80°. The analytical sample was unchanged by drying in vacuum at room temperature for two weeks.

The pure **1-methylnaphthalene** was regenerated from the trinitrofluorenone or trinitrobenzene derivatives by passing a dry benzene solution through a 15-inch column of activated alumina and washing with benzene (to which petroleum ether (35–60°) was added in the case of the trinitrobenzene derivative) until the colored band of the nitro compound moved down near the end of the column. From 0.27 g. of the trinitrofluorenone derivative and 0.18 g. of the trinitrobenzene derivative the regenerated hydrocarbon was obtained in quantitative yield, 0.08 and 0.07 g., respectively.

Another sample of the trinitrobenzene derivative (2.7 g.) was treated with tin and acetic–hydrochloric acids essentially as described by Orchin.[5] The solution was extracted with ether and benzene and the combined extracts after washing successively with dilute hydrochloric acid, strong alkaline sodium hyposulfite, water, dilute hydrochloric acid and water, gave the pure 1-methyl isomer in quantitative yield (1.1 g.).

Samples of the hydrocarbon regenerated from the trinitrobenzene derivative were treated separately in the usual way with picric acid, styphnic acid, and trinitrobenzene in boiling methanol, and with trinitrofluorenone in hot glacial acetic acid. In each case the derivative separated directly in pure condition; the melting points were 141–141.5°, 134.5–135°, 154–154.5° and 163–164°, respectively, and were not changed by recrystallization. The melting point of this trinitrofluorenone derivative was not changed by admixture with the trinitrofluorenone derivative prepared direct from the commercial hydrocarbon.

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Enrichment of Tin Activity Through the Szilard–Chalmers Separation

BY HERTA SPANO[1] AND MILTON KAHN

We wish to report that tetraphenyltin is a suitable compound for the enrichment of tin activity through the Szilard–Chalmers reaction. Solid tetraphenyltin was irradiated with slow neutrons, dissolved in benzene and extracted with various aqueous solutions. In nearly every case a large fraction of the tin activity appeared in the aqueous phase associated with a small amount of inactive tin. The results are summarized in Table I.

TABLE I

Expt.	Aqueous solution	Enrichment factor[a]	Sn activity in aqueous phase, %
1	H_2O	113	4
2	3.0 *f* HCl	2200	40
3	6.0 *f* HCl	2700	48
4	1.0 *f* NaOH	2800	50

[a] Specific activity of tin in aqueous phase divided by specific activity of tin in tetraphenyltin before extraction.

Experimental

Tetraphenyltin obtained from Eastman Kodak Co. was used without further purification. Eight hundred-milligram samples of tetraphenyltin were irradiated in the thermal column of the Los Alamos Fast Reactor for two hours. Each sample was transferred to a 150-ml. beaker, and dissolved in 100 ml. of thiophene-free benzene. This solution was then transferred to a 125-ml. separatory funnel and shaken for five minutes at room temperature with 20 ml. of an aqueous solution. The aqueous phase was washed with 50 ml. of benzene. The tin activity in both the extracted benzene phase and the aqueous solution was determined. Also, the aqueous phase was analyzed for total tin. In each instance no more than 0.04 mg. of tin was found in the aqueous phase. It turned out that the amount of tin detected in the aqueous phase, in each case, was independent of whether or not the tetraphenyltin had been irradiated.

In all experiments the fraction of the total tin activity recovered in each phase was computed on the basis of the tin activity found in a 36-mg. sample of tetraphenyltin

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[4] Eastman Kodak Co., Rochester, N. Y.

[5] M. Orchin and E. O. Woolfolk, THIS JOURNAL, **68**, 1727 (1946); M. Orchin, L. Reggel and E. O. Woolfolk, *ibid.*, **69**, 1225 (1947).

[1] This paper is a portion of the dissertation presented by Herta Spano in fulfillment of the requirements for the Master's Degree in the Graduate School of the University of New Mexico, June, 1951.

which was alongside the 800-mg. samples during each irradiation.

Since the success of the Szilard–Chalmers reaction is known to be dependent on the level of the γ-radiation in the pile it was desirable that all samples be irradiated under the same conditions.[2] The tetraphenyltin samples used in experiments 1 and 2 were alongside each other in the pile during the irradiation as were the samples used in experiments 3 and 4. It is believed that the γ-fluxes during these two irradiations were approximately the same because the beta activity of the samples used in experiments 3 and 4 was only 15% higher than that of the samples used in experiments 1 and 2.

The β-activity of the 1.1-day Sn^{121} was detected in all experiments. During the two-hour irradiation the activities of Sn^{113} and Sn^{123} produced are negligible compared to that of Sn^{121}. The 2.7-year Sb^{125} activity that is produced through decay of the 10-minute Sn^{125} is also negligible compared to the Sn^{121} activity. The tin was precipitated as stannic phenylarsonate,[3] suspended in 5 ml. of 95% alcohol and then prepared for counting by filtration on a tared, 24 mm. diameter, Whatman #50 filter paper, dried for 30 minutes at 110°, and weighed. The counting samples measured 14 mm. in diameter and were mounted on 2 × 2.5 in. cardboard cards with scotch tape placed directly over the sample. These cards were placed in a holder which fixed the position of the sample relative to an Amperex #100 C Geiger–Muller tube. All counting samples had activities within the range from 600 to 6000 counts per minute, and in this range the response of the counter was linear. The thickness of the samples, which was of the order of 28 mg./cm.^{2}, varied as much as 2 mg./cm.^{2}, necessitating corrections for self-absorption of the β-particles. The self-absorption correction amounted to a 1.15% increase in the total counting rate of a sample for each milligram increase in sample weight.

In order to determine the tin activity in the aqueous phase a 5-ml. aliquot was warmed slightly to remove traces of benzene, and then treated with a drop of liquid bromine so that all the tin present would be in the stannic state. The excess bromine was removed by gentle heating, and 1 ml. of a solution of stannic chloride containing 10 mg. of tin per ml. was added. The tin was precipitated as stannic hydroxide which was then dissolved in a minimum of 6 *f* hydrochloric acid. One-half ml. of 6 *f* hydrochloric acid was added in excess, and the sample diluted to 5 ml. with water. The sample was heated to 90° and then 5 ml. of a saturated aqueous solution of phenylarsonic acid was added. After a digestion period of ten minutes at 90°, the sample was cooled, allowed to stand at room temperature for 15 minutes, and then mounted for counting. The percentage of tin in the precipitate formed under these conditions was equal to that calculated from the formula of stannic phenylarsonate within a probable error of 1%.

The tin activity in the benzene phase was determined by evaporating an aliquot to dryness, ashing the tetraphenyltin residue with concentrated sulfuric acid and 30% hydrogen peroxide, and finally precipitating the tin as stannic phenylarsonate which was then mounted for counting. The tin activity in the 36-mg. sample of tetraphenyltin was determined in the same way.

In all the experiments only about 80% of the total tin activity was recovered. It turned out that approximately 80% of the activity lost was adsorbed on the walls of the beaker in which the irradiated solid tetraphenyltin was originally dissolved. In one experiment[4] an irradiated sample of tetraphenyltin was dissolved directly in a separatory funnel prior to extraction with 3 *f* hydrochloric acid and accordingly a larger enrichment factor (3400) and a higher yield (61%) were obtained. These results suggest the formation of tin radiocolloids in benzene.

The total tin present in the aqueous phase was determined colorimetrically by observing the molybdenum-blue color produced by the action of stannous tin on a molybdate reagent.[5] After reduction to the stannous state the color produced by the tin present in an aliquot of the aqueous phase was compared, visually, with that produced in several standard solutions of tin.

Acknowledgment.—We wish to express our appreciation to Dr. Roderick W. Spence and Mr. James E. Sattizahn, Jr., of the Los Alamos Scientific Laboratories for irradiation of the samples of tetraphenyltin.

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(2) R. R. Williams, *J. Phys. Colloid Chem.*, **52**, 603 (1948).

(3) E. G. Meyer, Ph.D. Thesis, University of New Mexico, 1950.

(4) On the basis of the β-activity of this irradiated sample, the γ-flux during the irradiation of this sample was the same as that during the irradiation of the samples used in experiments 3 and 4.

(5) F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," 3rd. ed., D. Van Nostrand Co., New York, N. Y., 1949, p. 217.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NEW MEXICO
ALBUQUERQUE, NEW MEXICO

RECEIVED AUGUST 9, 1951

COMMUNICATIONS TO THE EDITOR

THE SYNTHESIS OF BUTATRIENE[1]

Sir:

Butatriene has been synthesized in high yield by the action of powdered zinc on 1,4-dibromobutyne in purified diethylene glycol diethyl ether at 70°. The reaction product was collected as a low boiling liquid in a Dry Ice–acetone trap, or as a solid in a liquid nitrogen trap. The material polymerized upon being warmed to room temperature in the absence of air and with hydroquinone or other inhibitors present. The monomer showed negative tests with acetylenic hydrogen reagents such as alkaline mercuric iodide. With bromine in carbon tetrachloride it gave 1,2,3,4-tetrabromobutene-2 (80% yield), m.p. 68–69.5°, identical with an authentic sample prepared by bromination[2] of 1,4-dibromobutyne-2.

The butatriene exhibited the following physical properties: C/H ratio on two different samples, 92.29/7.71 and 91.82/8.18; mol. wt. (Dumas method at 250 mm. pressure), 52.6; mass spectrum (relative intensities): mass 52 (100), mass 51 (72), mass 50 (54); u.v. max. (95% ethanol), 241 mμ (20,300), apparent max. 310 mμ (250). In the infrared[3] (gas, 100 mm., 10 cm. cell), strong bands were shown at 2990, 1708, 1610, and 860 cm.$^{-1}$ (broad); medium bands at 2030, 1358, 1206, and 1065 cm.$^{-1}$ (broad).

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RECEIVED NOVEMBER 23, 1951

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(1) Supported in part by the Research Corporation.

(2) A. Valette, *Ann. chim.*, [12] **3**, 644 (1948).

(3) For aiding in obtaining the data we wish to thank Dr. David Eggers, who is now working on a more detailed interpretation of the infrared spectrum.