and V_3Ge[2] have been prepared and are all isomorphous. It seemed of interest to attempt the preparation of Mo_3Ge.

Samples of molybdenum and germanium powders in atomic ratios of approximately three to one were heated for several hours near 1000° to effect equilibrium. X-Ray diffraction patterns were then obtained with a General Electric powder camera. Filtered copper Kα radiation was used (α_1 = 1.540522 Å., α_2 = 1.544367 Å.). A sample having the over-all composition $MoGe_{0.33}$ gave a very faint molybdenum pattern and the strong pattern of a cubic phase. A sample of composition $MoGe_{0.37}$ gave a strong pattern of the cubic phase and faint lines of a phase that we have shown to be $MoGe_{0.67 \pm 0.03}$. The composition of the cubic phase, therefore, is $MoGe_{0.35 \pm 0.03}$, or Mo_3Ge, with no observable solid solution range.

Values of the cell constant a obtained from different values of d/n (the distance between crystallographic planes) were plotted against $\cos^2 \theta \cot \theta$, where θ is the angle of reflection of the X-ray beam. The plot was extrapolated to $\theta = 90°$ to obtain the best value of a from each photograph. The diffraction patterns of two different samples containing Mo_3Ge in equilibrium with molybdenum yielded $a = 4.9330 \pm 0.0003$ Å. and $a = 4.9329 \pm 0.0006$ Å. A pattern of Mo_3Ge in equilibrium with $MoGe_{0.67}$ yielded $a = 4.9332 \pm 0.0003$ Å. Variation of the lattice constant with composition is within the uncertainties in the measurements, strengthening the conclusion that Mo_3Ge has no appreciable solid solution range.

The density of a small, porous sample of Mo_3Ge was determined from measurements of its apparent weight in air and in water. This experimental density was 9.7 ± 0.4 g. cm.$^{-3}$; the density calculated assuming six molybdenum atoms and two germanium atoms per unit cell of the cubic lattice was 9.97 ± 0.01 g. cm.$^{-3}$.

Values for d/n calculated for lines from the diffraction pattern of Mo_3Ge corresponded very closely to those reported by Templeton and Dauben[4] for Mo_3Si, although six of the weaker lines of the Mo_3Si pattern were missing from the Mo_3Ge pattern. The two phases are obviously isomorphous. Table I lists the *hkl* assignments, d/n values, and calculated and visual intensities for Mo_3Ge. The calculated intensities were reduced to the same arbitrary scale used by Templeton and Dauben in their determination of the structure of Mo_3Si, and their values for Mo_3Si were included in the table for comparison. The intensities calculated for Mo_3Ge agree satisfactorily with the intensities observed. The six lines observed in the Mo_3Si pattern, but not observed in the Mo_3Ge pattern, all have very low calculated intensities for Mo_3Ge. Thus Mo_3Ge, like Mo_3Si, belongs to space group O_h^3–Pm3n and has the β-tungsten[7] structure. The positions of the atoms are: two Ge in (a) at 0, 0, 0; $^1/_2$, $^1/_2$, $^1/_2$; and six Mo in (c) at $^1/_4$, 0, $^1/_2$; $^1/_2$, $^1/_4$, 0; 0, $^1/_2$, $^1/_4$; $^3/_4$, 0, $^1/_2$; $^1/_2$, $^3/_4$, 0; 0, $^1/_2$, $^3/_4$.

Each germanium atom in Mo_3Ge is surrounded by 12 molybdenum atoms at 2.75 Å. Each molybdenum atom has two molybdenum atoms at 2.46 Å., four germanium atoms at 2.75 Å. and eight molybdenum atoms at 3.02 Å.

TABLE I

DIFFRACTION DATA FOR Mo_3Ge

vs, very strong; s, strong; m, medium; w, weak.

	Mo_3Ge	Mo_3Ge		Mo_3Si (T + D)[4]
hkl	*d*	Visual	Calcd.	Calcd.
110	3.4724	w$^-$	5	36
200	2.4557	w	45	25
210	2.1993	vs	163	183
211	2.0031	s	96	58
220	....	Absent	<1	3
310	....	Absent	1	7
222	1.4215	w	17	25
320	1.3663	w$^+$	34	26
321	1.3167	m	44	26
400	1.2323	w$^-$	21	16
330 411	....	Absent	1	4
420	1.1024	w	13	7
421	1.0755	m	34	33
332	1.0506	w$^-$	12	7
422	....	Absent	<1	2
431 510	....	Absent	<1	6
432 520	0.9158	s	46	43
521	0.9004	m$^-$	23	13
440	0.8720	m$^+$	30	22
433 530	....	Absent	<1	5
442 600	0.8221	w$^+$	20	12
610	0.8110	m	25	27
532 611	0.8002	s	63	39

DEPARTMENT OF CHEMISTRY
PURDUE RESEARCH FOUNDATION
AND DEPARTMENT OF PHYSICS
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

RECEIVED JULY 26, 1951

---

[7] H. Hartmann, F. Ebert and O. Bretschneider, *Z. anorg. Chem.*, **198**, 116 (1931).

The Purification and Identification of 1-Methylnaphthalene

BY MILTON D. SOFFER AND ROBERTA A. STEWART[1]

The inefficacies of conventional methods for the liberation of 1-methylnaphthalene from its usual impurity, the 2-methyl isomer, have been pointed out recently by Morrell, Pickering and Smith.[2] The best method in the literature[2,3,3b] involves a rather tedious process, *i.e.*, sulfonation, conversion of the sulfonic acids to their *p*-toluidine salts, frac-

---

[1] Department of Chemistry, Wellesley College, Wellesley, Mass.

[2] S. H. Morrell, G. B. Pickering and J. C. Smith, *J. Inst. Petroleum*, **34**, 677 (1948).

[3] (a) G. T. Morgan and E. A. Coulson, *J. Soc. Chem. Ind.*, **53**, 73 (1934); (b) after this article was submitted it was brought to our attention that a method involving distillation of the hydrocarbon under special conditions in the presence of 5-ethylnonanol as an azeotropic agent was reported by J. Feldman and M. Orchin; Abstracts of Papers, 117th Meeting, American Chemical Society, Chicago, Ill., September 3 to 8, 1950.

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.

SMITH COLLEGE
NORTHAMPTON, MASSACHUSETTS AND
DYSON PERRINS LABORATORY
OXFORD UNIVERSITY
OXFORD, ENGLAND

RECEIVED MAY 18, 1951

---

(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).

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

---

(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.