Synthesis and Purification of Sexiphenyl for Scintillator

By Tadashi NOZAKI, Michiko TAMURA, Yuhei HARADA* and Kazuo SAITO

(Received March 21, 1960)

It has been believed that sexiphenyl is an interesting organic semi-conductor and a promising scintillator for charged particles¹⁾. However its preparation was made only on a small scale²⁻⁴⁾, and an attempt to obtain this compound in sufficient quality and quantity for scintillator met with little success¹⁾. The present authors have found a favorable condition for the production of 4-nitroterphenyl from *p*-terphenyl (1, 4-diphenylbenzene) and succeeded in obtaining several tens of grams of sexiphenyl in a moderate yield. Although its purification involved a great difficulty, repeated vacuum sublimation and zone refining followed by recrystallization from tetralin afforded this compound in high purity. Its almost colorless single crystal gives an intense violet fluorescence and is satisfactorily used as a scintillator and wavelength shifter for Čerenkov radiation.

Preparation of Sexiphenyl.—The process is shown in Table I. Two methods have so far been presented for the synthesis: 1) the Ullmann condensation of 4-iodoterphenyl with the aid of silver powder at 320°C²⁾; 2) the same condensation of a mixture of 4-iodobiphenyl and 4, 4′-diiodobiphenyl with copper powder³⁾. According to the present authors' re-examination, both gave a very poor yield. Especially the latter provided a product containing as much as 0.7% iodine, after repeated vacuum sublimation and recrystallization from tetralin and dibutylphthalate. Contrary to the description in the literature, the Ullmann condensation of 4-iodoterphenyl with copper gave a good yield (more than 40%), provided that the iodoterphenyl was sufficiently pure and the condensation was carried out on a small scale. It appears as if the exothermic reaction, when carried out on a large scale, raises the temperature so remarkably that both the yield and the purity of the product were lowered.

4-Iodoterphenyl was obtained from 4-aminoterphenyl hydrochloride by diazotization and Sandmeyer's reaction, made free from phenols and the remaining amines by extraction with xylene and further purified by vacuum distillation and recrystallization from isoamyl acetate. Although both the amine and the diazonium salt are sparingly soluble in dilute hydrochloric acid, the diazotization proceeds in a good yield in suspension. This process compares favorably with that in concentrated sulfuric acid²⁾.

For obtaining pure 4-aminoterphenyl, preparation of pure 4-nitroterphenyl is essential. Nitration of terphenyl usually gives polynitro

TABLE I. SYNTHESIS OF SEXIPHENYL

Raw material	Product	Process	Remarks
p-terphenyl (I)	4-nitroterphenyl (II) (ca. 60%) 2-nitroterphenyl (15 to 20%) 2′-nitroterphenyl (15 to 25%)	HNO_3 in acetic acid and acetic anhydride	new process
4-nitroterphenyl (II)	4-aminoterphenyl hydrochloride (III) (almost 100%)	$SnCl_2$ in ethanol and HCl	Ref. 2 (slightly modified)
4-aminoterphenyl hydrochloride (III)	4-iodoterphenyl (IV) (ca. 40%)	$NaNO_2$ in HCl suspension; urea and KI	Ref. 2 (modified)
4-iodoterphenyl	sexiphenyl (V) (40 to 80%)	Cu at 280°C	Ref. 2 (modified)

---

[*] Present address, Kitazono High School, Itabashi-ku, Tokyo.

1) R. C. Sangstar et al., *J. Chem. Phys.*, **24**, 713 (1956).

2) R. Pummerer and K. Bittner, *Ber.*, **57**, 84 (1924).

3) R. Pummerer and L. Selingsberger, ibid., **64**, 2477 (1931).

4) A. E. Gillam and D. H. Hey, *J. Chem. Soc.*, **1939**, 1170.

compounds[5]. Allen et al. obtained 4-nitroterphenyl in 72% yield in glacial acetic acid in the presence of a small excess of nitric acid[6]; they gave, however, no information on the other 28% portion. The present authors have found that at temperatures exceeding 100°C and in glacial acetic acid containing about 10% of acetic anhydride and a trace of sulfuric acid, the rate of mono-nitration of *p*-terphenyl is significantly greater than the decomposition of nitric acid, which is in turn much greater than the rate of nitration of mononitroterphenyls. Higher temperature and greater concentration of acetic anhydride and sulfuric acid increase the solubility of *p*-terphenyl, but facilitates the decomposition of nitric acid, resulting in incomplete nitration of *p*-terphenyl. On the other hand, the amount and the concentration of nitric acid affected the result to a less extent. When the reaction mixture was cooled, fairly pure 4-nitroterphenyl separated as light yellow needles. Column chromatography of the mother liquor gave pure 2-nitro- and 2′-nitroterphenyl.

Purification of Sexiphenyl.—Crude sexiphenyl obtained by vacuum sublimation from the condensation product was yellow in color and contained significant amounts of copper and iodine. Most copper was removed by digesting the sublimate in aqueous potassium cyanide solution. Extremely low solubility of sexiphenyl in any organic solvent (e. g. less than 0.1 g. in one litre of boiling tetralin) makes recrystallization and chromatographic purification very laborious or even impracticable. It was further disclosed by neutron activation analysis that vacuum sublimation and recrystallization from various organic solvents were less effective for the removal of iodine-containing compounds. On the other hand, a cycle consisting of zone refining and vacuum sublimation was very useful for this purpose. (Table II) It appears as if the iodine-containing substance suffers thermal decomposition during zone refining to give compounds that are more easily removed through these processes. However, too high a temperature caused considerable decomposition of sexiphenyl itself, especially when the purity was low. Since the thermal decomposition of sexiphenyl becomes marked over 480°C, the zone refining was best effected at a maximum temperature between 440 and 450°C.

After a vacuum sublimation and a recrystallization from tetralin, the crystalline product gave the correct carbon and hydrogen content. Nevertheless the melting point rose with repeated zone refining and vacuum sublimation, until it reached a constant value after four times' repetition of the cycle, a recrystallization from tetralin and a vacuum sublimation. The final product becomes a translucent fluid at 428~429°C; it appears to be present in a liquid crystalline state until the translucent phase becomes transparent sharply at 543°C. Further purification brought about no change in these constants. Formation of a nematic or a smectic state is quite probable for such a long molecule. The melting point seems to be very sensitive toward impurity and the low values (465°C[3] and 475°C[2]) given by former authors appear to be due to insufficient purity.

TABLE II. IODINE CONTENT OF SEXIPHENYL PURIFIED BY ZONE REFINING AND VACUUM SUBLIMATION

Repetition of the cycle	Location of sample piece (cm. from the bottom)	I content (p.p.m.)
2	0	6.5
	2	3.0
	4	1.6
	6	5.2
	7.5 (top)	2.0
	residue on sublimation	2.5
4	0	<0.15
	2	<0.08
	4	<0.3
	6	<0.05
	7 (top)	<0.06
5	after recrystaln. and sublimation (final product)	<0.04

The quantity decreased to one sixth of that of the crude compound through the purification process, but the purity was so high that no impurity element was detected by chemical and neutron activation analysis. The low iodine content (less than 0.04 p.p.m.) compares with that of silicon for semi-conductor, which is regarded as one of the purest substance available. The final product is evaporated onto the window of a photomultiplier tube in vacuo and used as wavelength shifter. It is also converted into a large single crystal ($10\times5\times2$ mm.) and used as scintillator for alpha- and beta-rays. The photomultiplier pulse obtained with this scintillator is higher than that with quaterphenyl or anthracene, which has been regarded the best organic scintillator. The result will be reported elsewhere together with the optical properties of sexiphenyl.

Experimental

Preparation of Sexiphenyl. — *Mono-nitration of p-Terphenyl.*—Chemically pure *p*-terphenyl (I) (m. p.

---

[5] H. France, I. M. Heilbron and D. H. Hey, *J. Chem. Soc.*, **1938**, 1364.

[6] C. F. A. Allen and D. M. J. Burness, *J. Org. Chem.*, **14**, 177 (1949).

205~210°C, 500 g.) was dissolved in a boiling mixture of glacial acetic acid (18 l.) and acetic anhydride (2 l.) containing 6 N sulfuric acid (1 ml.). The solution was cooled to 105°C and treated with small portions of nitric acid (*d*, 1.42; total 200 ml.) with good stirring, the temperature being kept below 110°C. When the evolution of brown gas ceased, the solution was heated to boiling and then cooled to give small pale yellow needles of 4-nitroterphenyl (II), which were recrystallized from isoamyl acetate. M. p. 213°C, yield 290 g., corresponding to 60% of I.

Found: C, 78.46; H, 4.71; N, 5.02. Calcd. for $C_{18}H_{13}O_2N$: C, 78.53; H, 4.76; N, 5.01%.

The mother liquor was evaporated to remove most of the acetic acid and acetic anhydride, the orange residue dissolved in a mixture of benzene and petroleum benzine and submitted to column chromatography by the use of activated alumina (10 g.). Only a small amount of dark resinous substance remained on the column and further chromatographic separation of the effluent afforded two sorts of crystalline compound.

1) Colorless small plates melting at 129~130°C gave 4, 2′, 4′-trinitroterphenyl and thus was identified as 2′-nitroterphenyl. Yield ca. 20%.

Found: N, 5.03, 5.15. Calcd. for $C_{18}H_{13}O_2N$: N, 5.01%.

2) Clear yellow plates melting at 126~127°C were identified as 2-nitroterphenyl. The corresponding amine, and acetylated amine gave the same melting points with those in the literature. Yield, 15 to 20%.

Found: N, 5.00, 5.12. Calcd. for $C_{18}H_{13}O_2N$: N, 5.01%.

Reduction of 4-Nitroterphenyl.—II (250 g.) in hot isoamyl acetate (8 l.) was gradually added to a warm mixture of ethanol (8 l.) and 11 N hydrochloric acid (2 l.) containing stannous chloride (dihydrate, 2 kg.) with a good stirring. The mixture was boiled for 30 min.; the almost colorless 4-aminoterphenyl hydrochloride (III) was filtered off, washed with ethanol, suspended in 0.1 N hydrochloric acid. boiled to remove ethanol and filtered off. The reduction was almost quantitative.

Diazotization and the Sandmeyer Decomposition.—To a freshly prepared suspension of III in water (20 l.) containing 11 N hydrochloric acid (250 ml.) and zinc chloride (dihydrate 50 g.), was dripped sodium nitrite (80 g.) in water (1 l.) with good stirring. This was continued for 3 hr. after the addition of nitrite, the temperature being kept at 10°C. No apparent change was observed. The excess of nitrite having been decomposed with urea, the suspension was treated with potassium iodide (200 g.) solution and heated to nearly boiling. When the suspension became colorless and the evolution of nitrogen ceased, the precipitate was filtered off, washed with sodium sulfite solution and dried. Powder of crude 4-iodoterphenyl (IV) was dissolved in hot xylene filtered and shaken first with hot 6 N sodium hydroxide solution and then with hot 6 N sulfuric acid containing stannous chloride and filtered. The filtrate was evaporated to remove most of the xylene and treated with ethanol to give pure IV, which was further distilled in vacuo (240°C, 10^{-2} mmHg) and recrystallized from isoamyl acetate. Yield, 40% based on II, m.p. 247~248°C.

Found: C, 60.74, 60.60; H, 3.67, 3.62; I, 35.64, 35.60. Calcd. for $C_{18}H_{13}I$: C, 60.69; H, 3.68; I, 35.63%.

The Ullmann Condensation.—In a small test tube, the powder of IV was mixed with copper (1 to 4 by weight), freshly prepared from copper sulfate and zinc dust and dried in vacuo, and placed in a potassium hydrogen sulfate bath at 280°C for 15 min. The reaction mixture was extracted with xylene and the residue sublimed in vacuo (400°C, 10^{-3} mmHg) to give crude sexiphenyl (V). The yield of this crude product was 0.25 g. from 1 g. of IV, corresponding to 10% based on I.

Purification of Sexiphenyl.—The crude V (12 g.) was boiled in potassium cyanide solution (10%, 500 ml.) for 30 min., sublimed in vacuo and further purified by recrystallization or by zone refining.

Recrystallization.—Since V is very sparingly soluble in organic solvents, only those with high boiling points are useful. Tetralin and dibutyl phthalate were passed through a column (diameter, 25 mm.; length, 600 mm.) of activated alumina, distilled in vacuo and used for recrystallization in a nitrogen atmosphere. Sublimed V (0.1 g.) was dissolved in boiling tetralin (1 l.), filtered, and the filtrate gradually cooled to give fluorescent platelets, which were filtered off, washed with ethanol, and dried. The product melted to a translucent fluid at 420°C.

Found: C, 94.04, 93.96; H, 5.75, 5.74. Calcd. for $C_{36}H_{26}$: C, 94.29; H, 5.71%.

Zone Refining.—A Bridgemann type furnace (diameter, 35 mm.) was set up to give a narrow region (ca. 2 cm.) of the maximum temperature (450°C) and have a suitable temperature gradient. A Telex tube containing V in vacuo (10^{-4} mmHg) was caused to move downward at a rate of 3 cm. per hr. in the furnace. After this process a pale yellow mass with many dark brown stripes was obtained with a brown segregate on the top. The solid was taken out of the tube, the separable colored part removed and the yellowish mass was sublimed in vacuo. Almost colorless V came out, preceded by a small amount of yellowish substance, and a small amount of dark yellow residue remained. The sublimate consisted of almost pure V.

Since organic iodine compounds quench the fluorescence of organic scintillators to a marked extent[7], the removal of iodine was studied by repeated zone refining and vacuum sublimation. The sublimed V was submitted to zone refining and the iodine content of the solid determined by neutron activation analysis at various locations. The solid was then sublimed in vacuo and a similar cycle repeated. The results are summarized in Table II. It is seen that the difference in iodine content at varying locations in one lot is not marked but there appears to be an overall trend toward a lower iodine content with repetition of the cycle.

Examination of the Purity of Sexiphenyl.—The purity of V was examined by the usual chemical analysis and the neutron activation analysis.

Neutron Activation Analysis.—This is suitable for the determination of more than 0.005 μg. of iodine.

---

[7] W. H. Helhuish and W. S. Metcalf, *J. Chem. Soc.*, **1958**, 480.

The sample (10 mg.) was sealed in a polyethylene envelope and irradiated with thermal neutrons in a water-boiler type reactor for 1 hr. under a neutron flux 6×10^{11} neutrons per cm^2 per sec., together with a standard potassium iodide. The irradiated sample was swiftly taken out of the reactor and the counting rate due to iodine-128 (half life, 25 min.) was determined with a G. M. counter. A known portion of the standard was converted into silver iodide together with a known amount of carrier iodine and the counting rate similarly measured under the same condition. The radioisotope was identified by the measurement of the half life; carbon, hydrogen, oxygen and nitrogen give no appreciable amount of radioisotope.

A similar method was also useful for the determination of copper (more than 0.02 μg.) by the use of copper acetate as a standard. The irradiated sample was set aside until radioactive iodine decayed and submitted to scintillation spectrometry for the counting rate due to 0.51 MeV annihilation peak of copper-64 (half life, 12.8 hr.) to be measured. No appreciable amount of copper was found in sublimed V.

Measurement of the Melting Point.—This involved some experimental difficulty, because V melts at a very high temperature and sublimes to a significant extent at more than 350°C. The sample was sealed in a glass capillary in vacuo and placed in a quartz tube together with an Almel-Chromel thermocouple. The tube was heated from outside with nichrom wire and the temperature was read on a calibrated millivoltmeter. A fused sodium nitrate bath was also useful for the same purpose.

Summary

1) Mononitration of *p*-terphenyl is satisfactorily effected at 100 to 110°C in glacial acetic acid containing about 10% acetic anhydride and a trace of sulfuric acid, and 4-nitro- (ca. 60%), 2′-nitro- (20 to 25%) and 2-nitroterphenyl (15 to 20%) are obtained.

2) Sexiphenyl is formed in a fairly good yield (more than 40%) by the Ullmann condensation of 4-iodoterphenyl and copper.

3) Sexiphenyl is satisfactorily purified by repeated zone refining and vacuum sublimation. The final product melts at 428~429°C to form an apparent liquid crystalline state and becomes tranparent at 543°C (475°C in literature). It contains an appreciable amount of neither iodine nor copper and can be converted into a fairly large single crystal to be used as scintillator.

A part of the expenses was defrayed by a grant from the Ministry of Education, to which the authors' thanks are due.

Institute for Nuclear Study
The University of Tokyo
Tanashi, Tokyo
(M. T. and K. S.)

The Electrical Communication
Laboratory, Musashino, Tokyo
(T. N.)