Synthesis and Purification of Quinquiphenyl for Scintillator

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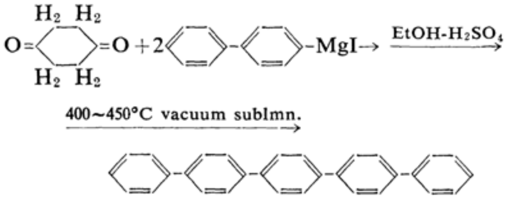
It has been pointed out that quinquiphenyl and sexiphenyl are interesting organic semi-conductors and promissing scintillators for charged particles[1]. Previously, we reported on the synthesis and purification of sexiphenyl[2]. Preparation of a large crystal of high-purity quinquiphenyl, however, has not been substantiated owing to the difficulty in the synthesis by older methods and in the purification. A convenient process for preparing quinquiphenyl of high purity is presented in this paper.

Mayer and Schiffner[3] briefly reported that *p*-terphenyl was formed when a reaction product of cyclohexanedione-1, 4 with phenylmagnesium bromide was sublimed under reduced pressure. A similar process has been found to be convenient for the synthesis of quinquiphenyl:



Cyclohexanedione-1, 4 is highly soluble in benzene, which keeps the compound mostly in keto-form. When the reaction product of cyclohexanedione-1, 4 in benzene with the etherial Grignard reagent is treated with a mineral acid, pale yellow powder containing quinquiphenyl precipitates gradually from the solution. None of the intermediates such as 1, 4-bisbiphenylylcyclohexanediol-1, 4 and 1, 4-bisbiphenylylcyclohexadiene has separated in pure state. They must be quite unstable and convert themselves into quinquiphenyl. The conversion is very slow at an ordinary temperature, but much faster at a higher temperature or in the presence of a mineral acid. Therefore, a rapid synthesis of quinquiphenyl can be substantiated by heating the Grignard reaction product to 400~450°C afterteatmeat with a boiling mixture of sulfuric acid and ethanol.

This heat treatment serves also for the purification, since most of the impurity by-products suffer thermal decomposition more easily than quinquiphenyl to give products which are easily removed. Too high a temperature or a prolonged heating, however, causes considerable decomposition of quinquiphenyl itself. Three other processes are also useful for the purification: i. e. vacuum sublimation, recrystallization and segregation. Slow sublimation at about 300°C (ca. 10^{-3} mmHg) is much more effective than rapid sublimation at a higher temperature. Since quinquiphenyl is quite sparingly soluble in any solvent under 100°C, a large quantity of a solvent having a high boiling point, such as nitrobenzene, tetraline or diethyl succinate should be used for recrystallization. Segregation with a Bridgeman-type furnace is especially effective for further purification of the sample already purified by other methods. The same process is also useful for single-crystal preparation. Yield of the purified quinquiphenyl was about 20% based on cyclohexanedione-1, 4 or 15% based on 4-iodobiphenyl.

A large crystal of purified quinquiphenyl is completely colorless, transparent, hard and tough, and gives an intense violet fluorescence. It has no marked habit to cleave into thin plates. It melts at 388°C into liquid crystal, which becomes transparent at 423°C. (These constants in literature[4] are 401°C (observed, 375°C) and 445°C (observed, 413°C) respectively, while in another literature[5] the melting point is 388.5°C). Specific gravity of quinquiphenyl at 25°C is 1.284 (terphenyl, 1.236; quarterphenyl, 1.262; sexiphenyl, 1.287).

Physical properties of pure quinquiphenyl, such as infrared, ultraviolet and fluorescence spectrum and scintillator efficiency are now under measurement. The results will be reported with those of quarterphenyl and sexiphenyl.

Experimental

Synthesis.—To a warm solution of 4-iodobiphenyl (40 g.) in diethyl ether (250 ml.) containing magnesium ribon (ca. 10 g.) was added a crystal or two of iodine, and the mixture refluxed for 3 hr. and filtered through asbestos fibers.

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

[2] T. Nozaki et al., This Bulletin, **33**, 1329 (1960).

[3] F. Mayer et al., *Ber.*, **65**, 1337 (1932).

[4] D. Vorländer, *Z. phys. Chem.*, **126**, 472 (1927).

[5] O. Gerngross et al., *Ber.*, **57**, 745 (1924).

Cyclohexanedione-1, 4 (5 g.) in benzene (100 ml.) was slowly stirred into the Grignard solution during 10 min., and the mixture refluxed for 20 min. and treated with hydrochloric acid. Most part of the solvent being removed, the residue was boiled in a mixture of sulfuric acid (50 ml.) and ethanol (50 ml.) for 30 min., cooled, collected by filtration and sublimed in vacuo to give two kinds of sublimate: (1) yellowish powder (7 g.) melting at ca. 300°C, (2) colorless material of a higher vapor pressure, melting at 180~185°C, which seemed to be a derivative of biphenylylcyclohexane. Sublimate 1 was placed in a narrow-necked glass tube and heated to 400°C in a furnace. Gas evolved vigorously form the molten product. When the evolution became feeble, the temperature was gradually raised to 450°C during 20 min. The dark grey massive product was sublimed (10^{-3} mmHg, 300°C) to give yellowish powder with black residue. The heat treatment and the vacuum sublimation of this sublimate were repeated once again to give crude quinquiphenyl (4 g.) in almost colorless powder, which melted at 350~360°C into liquid crystal.

Purification.—The crude quinquiphenyl (ca. 4g.) was recrystallized from diethyl succinate (800 ml.) into thin plates, which were sealed in an evacuated Telex-glass tube (9 mm. diameter) and purified by segregation with a Bridgeman-type furnace as in the case of sexiphenyl²⁾ (maximum temperature, 405°C; rate of downward movement, 8 mm. per hr.). The brownish segregate was removed, and the yellowish mass slowly sublimed in vacuo (10^{-3}~10^{-4} mmHg, 290~300°C) into colorless fluorescent powder, which was again subjected to the segregation and sublimation. The sublimate was recrystallized from tetralin, sublimed in vacuo and submitted to single-crystal formation by the same technique used for the segregation. Large colorless crystals were obtained (10×5×2 mm.) with a small amount of faintly yellowish segregate. Found: C, 94.26; H, 5.90. Calcd. for $C_{30}H_{22}$: C, 94.20; H, 5.85%.

Measurement of Melting Point and Specific Gravity.—The sample in a glass capillary was placed along the central axis of a transparent quartz tube (3.5 cm. diameter) together with an Almel-Chromel thermocouple. The tube was heated from outside with nichrome wire, and the temperature was read with a calibrated millivoltmeter. Melting point was measured with the sample obtained as mentioned above and also after further purification; no difference was observed. For the measurement of specific gravity, the crystal was immersed in water, to which a concentrated solution of a heavy metal salt was added until specific gravity of the liquid became equal to that of the crystal, and the former was measured.

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