filtered and basified with NH_4OH. The oily product was taken up in ether, dried with K_2CO_3 and distilled. The product was a pale yellow oil boiling at 140–145° at 15 mm., yield 0.3 g., 9%.

7-Bromo-1-ethyl-2-methyl-6,7-dihydro-4H-pyrano(4,3d)thiazolium Iodide.—The base (0.3 g., 1 mol) and excess ethyl iodide were refluxed for 6 hr. The oily brown precipitate crystallized on standing overnight. The crystals were collected, washed with acetone and recrystallized from absolute ethanol. The pale orange crystalline product melted at 164–168° dec., yield 50 mg., 10%.

Anal. Calcd. for $C_9H_{13}BrINOS$: N, 3.59; S, 8.22. Found: N, 3.69; S, 8.40.

2-Methyl-6,7-dihydro-4-H-thiopyrano(4,3d)thiazole (III).—Twenty grams of tetrahydro-1-thio-4-pyrone,[4] 30.5 g. of N-bromosuccinimide and 50 ml. of dry CCl_4 were gently warmed under reflux on the steam-bath until a violent reaction set in. The mixture was chilled in an ice-bath, filtered from succinimide and the filtrate was evaporated under water-pump vacuum until the CCl_4 was removed. The crude 3-bromo-tetrahydro-1-thio-4-pyrone thus obtained is unstable and must be used at once.

The product from the above reaction was diluted with 25 ml. of absolute ethanol, 12 g. of thioacetamide was added and the mixture was kept at 0° for 24 hr. followed by standing at room temperature for 3 days. The alcohol was distilled off under water-pump vacuum and the brown residue was extracted with 3% hydrochloric acid. After extracting the acid solution with ether to remove tarry impurities, the solution was made alkaline with $NaHCO_3$ and the oily base was taken up in ether. The ether solution was dried with anhydrous K_2CO_3, evaporated and the product was distilled under reduced pressure. The product was a pale yellow oil boiling at 125–135° at 8 mm. The yield was 5.0 g., 17%.

2-Methyl-6,7-dihydro-4H-thiopyrano(4,3d)thiazole Hydrochloride.—The base (16 g.) in absolute ether (500 ml.) was saturated with dry hydrogen chloride at 0°. The solvent was decanted from the sticky precipitate, and the latter was stirred with 150 ml. of acetone until crystallization occurred. After filtration and washing with acetone, the product was recrystallized from 100 ml. of absolute ethanol. The pale yellow crystals had m.p. 180–181°, yield 12.0 g., 62%.

Anal. Calcd. for $C_7H_{10}ClNS_2$: C, 40.43; H, 4.85; N, 6.74; S, 30.87. Found: C, 40.65; H, 4.88; N, 6.70; S, 31.00.

1-Ethyl-2-methyl-6,7-dihydro-4H-thiopyrano(4,3d)thiazolium Ethyl Sulfate (QS2).—For use in the dye syntheses, equimolecular proportions of the base and freshly distilled ethyl sulfate were heated at 110 to 115° for 5 minutes. The viscous product was used without purification.

2-Methyl-6,7-dihydro-5H-thiopyrano(3,2d)thiazole (IV).—Twenty-five grams (1 mol) of tetrahydro-1-thio-3-pyrone[5] was added to a mixture of 38.2 g. (1 mol) of N-bromosuccinimide and 50 ml. of dry carbon tetrachloride. After the initial vigorous reaction, the mixture was refluxed for 5 minutes. The mixture was chilled, the succinimide filtered and the filtrate evaporated as far as possible under reduced pressure. The product was mixed with 15.0 g. (1 mol) of thioacetamide and 100 ml. of absolute ethanol and allowed to stand at 0° for 3 hr., then overnight at room temperature and finally refluxed for 2 hr. The base was isolated and purified the same as IV above and was obtained as a pale yellow oil, b.p. 90 to 92° at 0.5 mm. The product crystallized on chilling. The yield was 13.4 g., 36%.

1-Ethyl-2-methyl-6,7-dihydro-5H-thiopyrano(3,2d)thiazolium Ethyl Sulfate (QS3).—The base was heated with ethyl sulfate the same as in the preparation of QS2 and the crude product was used in the dye syntheses.

1-Ethyl-2-methyl-6,7-dihydro-5H-thiopyrano(3,2d)thiazolium Iodide (QS5).—The base (10.0 g., 1 mol) was refluxed with ethyl iodide (20 g., 100% excess) for 16 hr. The crystalline product was crushed under ether, washed on the filter with acetone and dried. The yield of light tan crystals was 13.0 g., 68%. For analysis the product was recrystallized twice from absolute ethanol (10 ml. per g.). The pure material had m.p. 150–153° dec. *Anal.* Calcd. for $C_9H_{14}INS_2$: I, 38.80; N, 4.28; S, 19.60. Found: I, 38.51; N, 4.11; S, 19.52.

Absorption data for the new dyes are given in Table II.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Some Methyl Derivatives of *p*-Quaterphenyl[1]

BY HENRY GILMAN AND EUGENE A. WEIPERT

RECEIVED SEPTEMBER 17, 1956

Condensation of *p*-terphenyl-4-yllithium and 4,4′-biphenylenedilithium with 2-, 3- and 4-methylcyclohexanone, followed by dehydration, has been used to synthesize monomethyltetrahydro-*p*-quaterphenyls and dimethyloctahydro-*p*-quaterphenyls, respectively. The corresponding *p*-quaterphenyl derivatives are formed by dehydrogenation with chloranil. The effect of structure on melting points and on solubilities is discussed.

Chain-type polyaryls have been shown to be superior solutes in liquid solution scintillators.[2-4] The use of hydrocarbons as solutes reaches a limit with *p*-terphenyl because those of higher molecular weight are limited by their sparing solubility in the commonly employed aromatic solvents. The introduction of methyl groups on the terminal rings of *p*-quaterphenyl seemed a direct method of surmounting this limitation in view of an expected decrease in melting point and increase in solubility corresponding to the reduction of symmetry. Also, of significance is the conclusion of Hayes, Ott and Rogers[3] that methyl groups do not generally cause an appreciable change in the scintillation ability of the solute.

Table I shows that this expectation was justified. It is interesting to note the marked correspondence of melting point and solubility in toluene through this series. Among the completely aromatic compounds the one outstanding increase in melting point occurs with the 4,4‴-dimethyl compound (125° higher than the 3,3‴-isomer), and this is accompanied by a drop to nearly complete insolubility. The 4-methyl derivative is rather unusual in that it melts higher than the more symmetrical parent hydrocarbon (320°) while it is slightly more soluble. The series of compounds containing cyclohexene rings exhibits the same trends but in more pronounced fashion. While the melting points are somewhat unreliable because of decomposition of those melting above 200°, it is evident that the close grouping of melting points in the three monomethylated compounds is a reflection of a similar situation in the completely aro-

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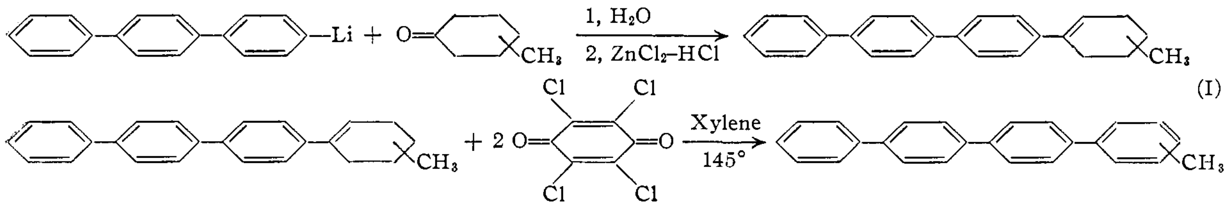
[1] This work was supported by the United States Atomic Energy Commission under Contract No. AT(11-1)-59.

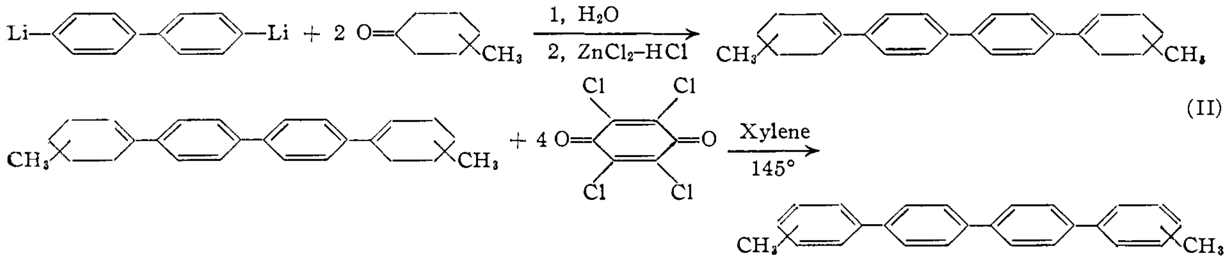
[2] H. Kallman and M. Furst, *Nucleonics*, **8**, No. 3, 32 (1950).

[3] F. Hayes, D. Ott and B. Rogers, *ibid.*, **13**, No. 12, 38 (1955).

[4] F. Hayes, D. Ott and V. Kerr, *ibid.*, **14**, No. 1, 42 (1956).



(I)



(II)

matic series. The melting points of the monomethyl-*p*-quaterphenyls proceed from 172 to 330° and the solubilities drop from 26 g./l. to only 1 g./l. In the partially saturated series the span of melting points is only between 184 and 208° while the solubilities drop from 48 to 4 g./l. With methyl groups on both terminal rings the scope of these variations is greatly magnified: the 4,4‴-derivatives being very high melting and comparatively insoluble, while the 2,2‴-dimethyl compounds have surprisingly low melting points and high solubilities in view of their molecular weight and symmetry.

TABLE I

MELTING POINTS AND SOLUBILITIES OF SOME METHYLATED *p*-QUATERPHENYLS

	p-Quaterphenyl derivative		Tetrahydro (or octahydro) derivative	
Substituent	M.p., °C.	Solubility in toluene, g./l.	M.p., °C.	Solubility in toluene, g./l.
2-Methyl	172–173	26.0	184–185	48.0
3-Methyl	244–245	3.0	200 dec.	10.7
4-Methyl	328–330	1.2	208 dec.	3.8
2,2‴-Dimethyl	150–151	36.0	108–109	86.0
3,3‴-Dimethyl	214–215	6.3	149–150	35.0
4,4‴-Dimethyl	338–340	0.2	225 dec.	2.7
Unsubstituted	320[a]	0.8		

[a] F. Ullmann and G. M. Meyer, *Ann.*, **332**, 52 (1904).

The monomethyl derivatives were prepared by condensation of *p*-terphenyl-4-yllithium with the appropriately substituted methylcyclohexanone, followed by dehydration of the intermediate carbinol and dehydrogenation of the olefin according to scheme I. In analogous fashion the symmetrically dimethylated quaterphenyls were prepared from 4,4′-dilithiobiphenyl according to scheme II.

Of the numerous methods available for dehydration of the intermediate cyclohexanol derivatives, vigorous stirring with Lucas reagent as prescribed by Crawford and Nelson[5] was clearly superior. Most of the more common acid catalysts require conditions that afford poor contact between these intractable carbinols and the reagent. In using the Lucas reagent it is not even necessary to isolate the crude carbinol, since it is dehydrated in the benzene solution resulting directly from the organometallic-ketone reaction.

Dehydrogenation to the aromatic system with sulfur and selenium gave poor yields and led to difficulties in purification. The method of Arnold and Collins[6] employing chloranil as the oxidant in refluxing xylene proved to be much cleaner and provided satisfactory yields. Isolation and purification of the product from this oxidation was more conveniently carried through as suggested by Crawford and Nelson[5] since the products could not be distilled under reasonable conditions.

The compounds described at this time were prepared incidental to a study concerned with organic liquid solution scintillators. Evaluation of the compounds for this purpose is being made by Drs. Wright H. Langham, F. Newton Hayes and Donald G. Ott of the Los Alamos Laboratories who will report the results later.

Experimental[7]

4-(Methyl-1-cyclohexen-1-yl)-*p*-terphenyl.—To a stirred solution of 0.040 mole of *p*-terphenyl-4-yllithium[8] in 130 ml. of ether was added 4.71 g. (0.042 mole) of 2-methylcyclohexanone in 60 ml. of benzene. The suspension was stirred at gentle reflux for 30 minutes, then cooled and hydrolyzed with 50 ml. of 10% hydrochloric acid. An additional 150 ml. of benzene was added, and the layers were separated. The organic layer was distilled until the temperature reached 60° and the remaining benzene suspension stirred at gentle reflux for 2 hr. with 60 ml. of Lucas reagent. The layers were separated and the organic layer washed with water, sodium bicarbonate and water again. Evaporation of the benzene solution left a gummy residue which was crystallized from 150 ml. of 1:1 benzene–ethanol to give 8.70 g. (68%) of white powder, melting over the range 168–174°. After seven recrystallizations from benzene–ethanol there remained 5.50 g. (43%) of white plates, melting at 184–185°. The product turned pale yellow upon exposure to direct sunlight.

Anal. Calcd. for $C_{25}H_{24}$: C, 92.59; H, 7.41. Found: C, 92.50; H, 7.67.

2-Methyl-*p*-quaterphenyl.—A mixture of 3.24 g. (0.010 mole) of 4-(methyl-1-cyclohexen-1-yl)-*p*-terphenyl and 4.96 g. (0.020 mole) of chloranil was heated in 50 ml. of refluxing xylene for 12 hr. The mixture was cooled and diluted with 150 ml. of petroleum ether (b.p. 60–70°). The precipitated brown solid was filtered and extracted with 50 ml. of hot ethyl acetate. This extract was diluted with

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[5] H. M. Crawford and H. B. Nelson, THIS JOURNAL, **68**, 134 (1946).

[6] R. T. Arnold and C. Collins, *ibid.*, **61**, 1407 (1939).

[7] All melting points are uncorrected. Reactions involving organolithium reagents were carried out under an atmosphere of dry, oxygen-free nitrogen in sodium-dried solvents.

[8] H. Gilman and E. A. Weipert, *J. Org. Chem.*, **22**, in press (1957).

50 ml. of benzene and combined with the xylene–ligroin filtrate. The combined organic solution was extracted with three 60-ml. portions of 5% potassium hydroxide, then evaporated to dryness. The residue was crystallized twice from a 1:3 benzene–ethanol mixture to give 1.24 g. (38.7%) of pale yellow material melting at 170–172°. Sublimation of this material at 160° (0.01 mm.) and recrystallization of the sublimate from the same solvent mixture afforded white needles melting at 172–173°.

Anal. Calcd. for $C_{25}H_{20}$: C, 93.75; H, 6.25. Found: C, 93.57; H, 6.39.

4-(Methyl-1-cyclohexen-1-yl)-*p*-terphenyl.—Using the same quantities and conditions as described for the 2-methyl isomer, there was obtained 6.25 g. (49%) of shiny plates from benzene which melted at 200° with decomposition.

Anal. Calcd. for $C_{25}H_{24}$: C, 92.59; H, 7.41. Found: C, 92.31; H, 7.72.

3-Methyl-*p*-quaterphenyl.—Chloranil oxidation as above and recrystallization from benzene afforded a 62% yield of nearly white plates melting at 244–245.5°. The analytical sample was obtained by sublimation at 210° (0.01 mm.) and melted at 245–246°.

Anal. Calcd. for $C_{25}H_{20}$: C, 93.75; H, 6.25. Found: C, 93.43; H, 6.51.

4-(4-Methyl-1-cyclohexen-1-yl)-*p*-terphenyl.—Once again the same quantities and conditions were employed; however, the crude product after treatment with Lucas reagent melted over the range 205–235° and resisted purification by recrystallization. The crude material was sublimed at 200° (0.01 mm.) to provide 3.15 g. (32%) of white material with a melting range of 204–208°. Recrystallization from benzene raised this to 208° with decomposition.

Anal. Calcd. for $C_{25}H_{24}$: C, 92.59; H, 7.41. Found: C, 92.69; H, 7.42.

4-Methyl-*p*-quaterphenyl.—4-(4-Methyl-1-cyclohexen-1-yl)-*p*-terphenyl (1.62 g., 0.005 mole) was dehydrogenated with 2.48 g. (0.010 mole) of chloranil in 25 ml. of xylene by refluxing for 8 hr. Upon dilution of the xylene solution with petroleum ether as before, both the product and the dihydrochloranil precipitated. This mixture was extracted continuously with hot ethanol to remove dihydrochloranil and then with toluene which dissolved the desired product. When cooled, the toluene extract deposited 1.05 g. (65.6%) of nearly white plates having a melting range of 322–329°. Sublimation at 210° (0.01 mm.), followed by recrystallization from toluene, afforded 0.64 g. (38%) of clear plates melting at 328–330°.

Anal. Calcd. for $C_{25}H_{20}$: C, 93.75; H, 6.25. Found: C, 94.04; H, 5.98.

4,4′-Bis-(methyl-1-cyclohexen-1-yl)-biphenyl.—To a solution of 0.025 mole of 4,4′-biphenylenedilithium[9] in 100 ml. of 1:1 benzene–ether was added, over a period of 30 minutes, a solution of 5.72 g. (0.051 mole) of 2-methylcyclohexanone in 50 ml. of benzene. The resulting gray-green suspension was stirred at gentle reflux for 3 hr., then hydrolyzed with 50 ml. of 10% hydrochloric acid. The layers were separated and the organic layer washed with water and filtered from a trace of solid material. This solution was distilled until the temperature had reached 60° and the remaining benzene solution stirred at gentle reflux with 60 ml. of Lucas reagent for 2 hr. The oily solid obtained from the organic layer was crystallized from 100 ml. of ethanol to give 1.51 g. (18%) of shiny plates having a melting range of 98–103°. Two recrystallizations from ethanol raised the melting point to 107–108°. The analytical sample melted at 108.5–109°.

Anal. Calcd. for $C_{26}H_{30}$: C, 91.23; H, 8.77. Found: C, 91.07; H, 8.86.

2,2′′′-Dimethyl-*p*-quaterphenyl.—The octahydro derivative (1.37 g., 0.004 mole) was treated with 3.94 g. (0.016 mole) of chloranil in 25 ml. of refluxing xylene for 12 hr. to give 0.59 g. (44%) of crude product melting over the range 125–134°. Sublimation at 120° (0.01 mm.) gave white needles having a melting range of 142–146°. Four recrystallizations from ethanol produced a pure sample melting at 150–151°.

Anal. Calcd. for $C_{26}H_{22}$: C, 93.41; H, 6.59. Found: C, 93.45; H, 6.58.

4,4′-Bis-(methyl-1-cyclohexen-1-yl)-biphenyl.—Employing quantities and conditions identical to those used for the 2-methyl isomer there was obtained 3.32 g. (39%) of pale yellow material melting at 144–146°. After four recrystallizations from 1:1 ethanol–benzene the shiny, white plates melted at 149–150°.

Anal. Calcd. for $C_{26}H_{30}$: C, 91.23; H, 8.77. Found: C, 91.31; H, 8.77.

3,3′′′-Dimethyl-*p*-quaterphenyl.—Chloranil oxidation of 1.67 g. (0.005 mole) of 4,4′-bis-(methyl-1-cyclohexen-1-yl)-biphenyl produced 0.41 g. (24%) of nearly white material having a melting range of 210–215°. Sublimation at 210° (0.01 mm.) left 0.30 g. (19%) of clear plates melting at 214–215°.

Anal. Calcd. for $C_{26}H_{22}$: C, 93.41; H, 6.59. Found: C, 93.24; H, 6.64.

4,4′-Bis-(4-methyl-1-cyclohexen-1-yl)-biphenyl.—Again using the same quantities and conditions as in the preparation of the 2-methylcyclohexenyl derivative, there was recovered 2.70 g. (31%) of shiny white plates which gradually melted to a yellow-orange liquid over the range of 215–223°. Two recrystallizations from benzene left 2.20 g. (26%) which decomposed at 225°.

Anal. Calcd. for $C_{26}H_{30}$: C, 91.23; H, 8.77. Found: C, 90.77; H, 8.91.

4,4′′′-Dimethyl-*p*-quaterphenyl.—Oxidation of 1.67 g. (0.005 mole) of the bis-cyclohexene compound prepared above with chloranil gave 0.81 g. (58%) of gray powder which charred slowly above 320°. After sublimation at 210° (0.01 mm.) and recrystallization from toluene there was recovered 0.26 g. (18%) of white powder melting at 338–340°. Pummerer and Seligsberger[10] reported 334° for this compound.

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[9] H. Gilman, W. Langham and F. W. Moore, THIS JOURNAL, **62**, 2327 (1940).

[10] J. Pummerer and F. Seligsberger, *Ber.*, **64B**, 2485 (1931).

AMES, IOWA

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, VETERANS ADMINISTRATION HOSPITAL]

Studies in the Naphthalene Series. III. Synthesis of Apogossypol Hexamethyl Ether[1]

BY J. D. EDWARDS, JR., AND J. L. CASHAW

RECEIVED NOVEMBER 16, 1956

Apogossypol hexamethyl ether, the primary degradation product of gossypol, the pigment and toxic principle in cottonseed, formulated by Adams as 2,2′-bi-5-isopropyl-1,6,7-trimethoxy-3-methylnaphthyl has been synthesized by the oxidative coupling of 5-isopropyl-1,6,7-trimethoxy-3-methyl-1-naphthol and methylation of the resulting binaphthol.

Gossypol, the yellow pigment of cottonseed, has been the subject of extensive work[2] and was for-

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[1] Preliminary communication: J. D. Edwards, Jr., and J. L. Cashaw, THIS JOURNAL, **78**, 3224 (1956).

[2] For a review of these studies see F. Mayer and A. H. Cook, "The Chemistry of Natural Coloring Matters," Reinhold Publishing Corp., New York, N. Y., 1943, pp. 114–117; R. D. Haworth, *Ann. Repts. Progr. Chem.* (Chem. Soc. London), **36**, 284 (1939); C. H. Boatner "Cottonseed and Cottonseed Products," edited by A. E. Bailey, Interscience Publishers, Inc., New York, N. Y., 1948, Chap. VI, pp. 213–363.