

444. *The Relation between Configuration and Conjugation in Diphenyl Derivatives. Part VI.* Some Alkyldiphenyls.*

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A number of dialkyldiphenyls have been prepared and their ultraviolet absorption spectra studied. In the series of 2 : 2'-dialkyldiphenyls, contributions from a discrete conjugation band are still apparent when the alkyl groups are ethyl or isopropyl but are no longer evident when they are *tert.*-butyl.

A RE-EXAMINATION of the ultraviolet absorption spectrum of 2 : 2'-ditolyl (Part III) ¹ has shown that slight conjugation between the two benzene rings is still apparent, in spite of the steric effect of the *o*-methyl groups, the inflection at *ca.* 227 m μ being regarded as a vestigial conjugation band displaced to shorter wavelength.

We have now prepared 2 : 2'-diethyl- and 2 : 2'-diisopropyl-diphenyl; 2 : 2'-di-*tert.*-butyldiphenyl (Lesslie and Turner, unpublished work) has also been available and we have examined the absorption spectra of these three compounds (Fig. 1, Table 1). The spectra

TABLE 1. *Ultraviolet absorption spectra of 2 : 2'-dialkyldiphenyls.*

Diphenyl compound	$\lambda_{\text{inf.}}$	ϵ	$\lambda_{\text{min.}}$	ϵ	Long-wave fine structure	
					$\lambda_{\text{max.}}$	ϵ
2 : 2'-Dimethyl ¹	(<i>ca.</i> 227)	6800	260.5	770	263.5 271	800 600
2 : 2'-Diethyl	(<i>ca.</i> 227)	6000	258.5	685	263.5 271	730 560
2 : 2'-Diisopropyl	(<i>ca.</i> 227)	5500	254	630	(258) 263.5	640 720
2 : 2'-Di- <i>tert.</i> -butyl	—	—	249.5	290	271 (258) 263.5 270	560 380 430 330

Solvent, 95% ethanol; wavelengths (m μ) in parentheses denote inflections.

show a progressive decrease in conjugation with increasing size of the alkyl groups until with 2 : 2'-di-*tert.*-butyldiphenyl no trace of a discrete conjugation band remains. In the other three compounds the inflection at *ca.* 227 m μ is apparent, its intensity decreasing slightly from methyl to isopropyl. Considering the compounds in the reverse order, it is seen that the absorption at the minimum (between the short-wave band and the long-wave fine structure) at 249.5 m μ ($\epsilon_{\text{min.}}$ 290) in di-*tert.*-butyldiphenyl moves to progressively longer wavelengths ($\lambda_{\text{min.}}$ 254, 258.5, 260.5 m μ in diisopropyl-, diethyl- and dimethyl-diphenyl respectively) and is of correspondingly greater intensity as the contribution from the vestigial conjugation band becomes more important and overlaps the long-wave band. In diethyl- and dimethyl-diphenyl this overlapping has obliterated one of the fine-structure

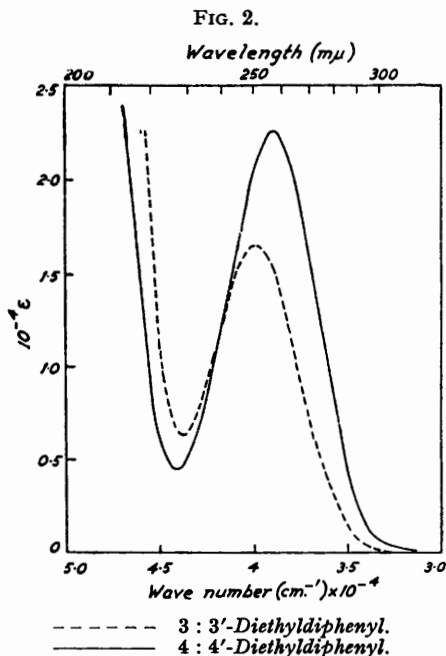
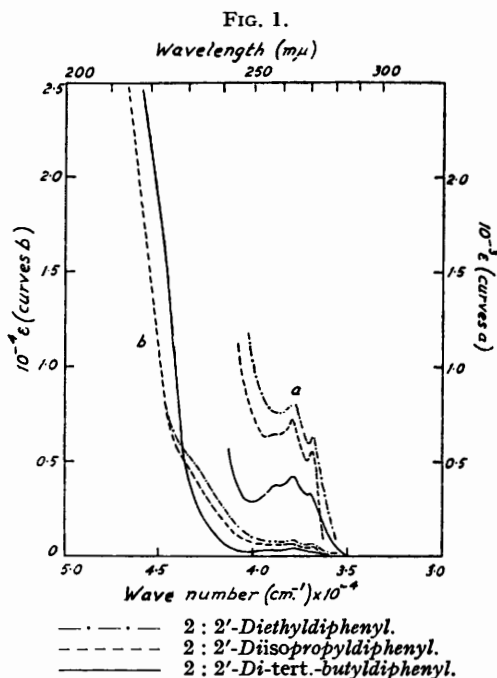
* Part V, *J.*, 1955, 2708.

¹ Beaven, Hall, Lesslie, Turner, and Bird, *J.*, 1954, 131.

bands of the alkylbenzene partial chromophore which is present as an inflection at 258 m μ in the other two compounds.

All four compounds show at least two bands of the alkylbenzene partial chromophores at 263.5 and 270–271 m μ . The intensities of these bands are slightly reduced for the diethyl and diisopropyl compounds in comparison with those for 2:2'-dimethyldiphenyl and much reduced for the di-*tert.*-butyl compound (in which they are rather more than twice those of *tert.*-butylbenzene). Thus, except perhaps in di-*tert.*-butyldiphenyl, the long-wave band system is overlapped by the vestigial conjugation band.

The data for the alkylbenzenes are taken from Stair,² the Catalogue of the Ultraviolet Spectral Data of the American Petroleum Research Institute Project No. 44, and, in the case of ethylbenzene, from our own work.



3:3'- and 4:4'-Diethyl-diphenyl show the expected light-absorbing properties (Fig. 2; Table 2). Both are typical conjugated diphenyls, the second compound showing the

TABLE 2. Ultraviolet absorption spectra of 3:3'- and 4:4'-di-alkyldiphenyls.

Diphenyl compound	Minimum		Conjugation band	
	$\lambda_{min.}$	ϵ	$\lambda_{max.}$	ϵ
Diphenyl	222	4300 *	249	17,300 *
3:3'-Diethyl	228.5	6200	251	16,500
4:4'-Diethyl	226.5	4500	256.5	22,500
4:4'-Diisopropyl	226	4600	256.5	23,500

Solvent, 95% ethanol.

* Amended values, means of three determinations each.

long-wave shift and the increased intensity of absorption characteristic of 4:4'-disubstituted diphenyls (cf., for example, Williamson and Rodebush³); similar behaviour is exhibited by 4:4'-diisopropyldiphenyl (Table 2). For none of these compounds was long-wave fine

² Stair, *J. Res. Nat. Bur. Stand.*, 1949, **42**, 587.

³ Williamson and Rodebush, *J. Amer. Chem. Soc.*, 1941, **63**, 3018.

structure observed. The 3 : 3'-diethyl compound is thus in marked contrast to 3 : 3'-dimethoxydiphenyl where an intense long-wave band is present.³ The effect of *mm'*-substituents on the absorption spectrum of diphenyl has been considered by Wenzel⁴ (cf. Platt⁵), who suggests that the "hidden" contribution from the phenyl partial chromophores in diphenyl itself becomes evident when the system is strongly perturbed by appropriate substituent groups which interact (by mesomerism) with the phenyl groups. However alkyl groups (unlike alkoxy-groups) exhibit only weak interactions with a benzene ring and in any case the absorption contributions from the alkylphenyl partial chromophores occur at shorter wavelengths than those from the alkoxyphenyl partial chromophores, so that overlapping by the conjugation band will be much greater in 3 : 3'-dialkyl- than in 3 : 3'-dialkoxy-diphenyls.

2 : 2'-Diethyldiphenyl* was prepared by three methods. It was obtained in 45—50% overall yield from *o*-ethylaniline *via* *o*-ethyliodobenzene and an Ullmann reaction (cf. Mascarelli and Longo⁶). Reduction with iron and water and the use of sulphuric acid instead of hydrochloric acid for diazotisation avoided the formation of the 4-chloro-2-ethyl-1-iodobenzene obtained by these authors as a by-product. Treatment of *o*-ethylphenylmagnesium bromide with anhydrous cupric chloride gave 2 : 2'-diethyldiphenyl in 13—14% overall yield from *o*-ethylaniline (method of Krizewsky and Turner⁷). *cyclo*Hexanone was ethylated with ethyl iodide and sodamide. Some 2-ethyl*cyclo*hexanone was obtained, together with 2 : 2'-diethyl*cyclo*hexanone, identified as the semicarbazone. 2-Ethyl*cyclo*hexanone was treated with *o*-ethylphenylmagnesium bromide, and the alcohol obtained was dehydrated with formic acid. Dehydrogenation of the resulting 2 : 2'-diethyl-3 : 4 : 5 : 6-tetrahydrodiphenyl gave 2 : 2'-diethyldiphenyl.

For the preparation of 2 : 2'-diisopropyldiphenyl an Ullmann reaction was carried out on methyl 3-iodo-4-isopropylbenzoate, made from the corresponding 3-amino-compound. The resulting methyl 6 : 6'-diisopropyldiphenyl-3 : 3'-dicarboxylate was hydrolysed and the acid decarboxylated.

3 : 3'-Diethyldiphenyl was obtained by the deamination of 3 : 3'-diethylbenzidine with hypophosphorous acid. 4 : 4'-Diethyldiphenyl was prepared by the Krizewsky-Turner method⁷ from *p*-bromoethylbenzene or, better, by an Ullmann reaction on *p*-ethyliodobenzene.⁸

4 : 4'-Diisopropyldiphenyl was made by an Ullmann reaction on *p*-iodoisopropylbenzene; it has been described as existing in two forms^{8, 9, 10} with melting points 49° and 65—66°. We obtained only the higher-melting form.

EXPERIMENTAL

o-Ethylaniline.—*o*-Ethylnitrobenzene and *o*-ethylaniline were available commercially but initially were obtained from 1-ethyl-2 : 4-dinitrobenzene.¹¹ This was reduced either with disodium disulphide or with ammonium hydrogen sulphide^{12, 13} to 4-amino-1-ethyl-2-nitrobenzene. Deamination by the action of hypophosphorous acid on the diazo-compound gave *o*-ethylnitrobenzene. Cline and Reid¹³ record that reduction of this nitro-compound by iron and hydrochloric acid gave a poor yield of *o*-ethylaniline. By carrying out a similar reduction

* *Added, May 25th, 1956.*—The 2 : 2'-diethyldiphenyl has now been examined by gas chromatography and found to contain appreciable quantities of impurities. A sample was purified by three crystallisations from ethanol at *ca.* -35° and redistilled; the spectral data now given in Table I were determined on this specimen. We are indebted to Dr. E. A. Johnson, who carried out this work, and to Dr. A. T. James for use of the gas chromatography apparatus.

⁴ Wenzel, *J. Chem. Phys.*, 1953, **21**, 403.

⁵ Platt, *ibid.*, 1951, **19**, 101.

⁶ Mascarelli and Longo, *Gazzetta*, 1941, **71**, 397.

⁷ Krizewsky and Turner, *J.*, 1919, **115**, 559.

⁸ Schreiner, *J. prakt. Chem.*, 1910, **81**, 422.

⁹ Bert and Dorier, *Bull. Soc. chim. France*, 1925, **37**, 1398.

¹⁰ Boedtke, *ibid.*, 1929, **45**, 645.

¹¹ Weisweiler, *Monatsh.*, 1900, **21**, 39.

¹² Schultz, *Ber.*, 1909, **42**, 2633.

¹³ Cline and Reid, *J. Amer. Chem. Soc.*, 1927, **49**, 3150.

in presence of alcohol¹⁴ a 68–70% yield of pure base was obtained. The crude base was steam-distilled and the total steam-distillate treated with acetic anhydride (102 g.). The acetyl derivative was filtered off and crystallised from aqueous ethanol: it had m. p. 112–113° (126 g. from 151 g. of nitro-compound). By hydrolysis with 20% hydrochloric acid *o*-ethylaniline (85 g., 70%) was obtained, having b. p. 210–211°, n_D^{25} 1.5598.

2 : 2'-*Diethylidiphenyl*.—(a) *o*-Ethylaniline was diazotised in sulphuric acid, and aqueous potassium iodide added. *o*-Ethyl iodobenzene, b. p. 90°/12 mm., was obtained in 80% yield. The iodo-compound (150 g.) was heated with an equal weight of copper bronze in a bath kept at ca. 240° for 3 hr. The organic product was extracted with boiling chlorobenzene and, after removal of solvent, the residue was fractionated under reduced pressure. 2 : 2'-Diethylidiphenyl was finally distilled from sodium (yield 42.5 g., 60%) and had b. p. 142–143°/14–15 mm., n_D^{25} 1.5624 (Found : C, 91.4, H, 8.5. Calc. for $C_{16}H_{18}$: C, 91.4; H, 8.6%).

(b) *o*-Bromoethylbenzene (b. p. 63–64°/8–9 mm., n_D^{25} 1.5476) was best prepared by a Sandmeyer reaction, the base being diazotised in hydrobromic acid. A Grignard reagent was made from it and anhydrous cupric chloride gradually added, giving 2 : 2'-diethylidiphenyl in 28% yield.

2-Ethylcyclohexanone. *cycloHexanone* (98 g., 1 mole) was added gradually during 1 hr. to sodamide (43 g., 1.1 mole) in boiling benzene (800 c.c.). The mixture was heated for 1½ hr. and ethyl iodide (156 g., 1 mole) then added during 1 hr. After further heating (2½ hr.) of the mixture, water was added and the benzene layer separated. Solvent was removed and the residue was twice distilled under reduced pressure. The first fraction (33 g.), b. p. 68°/16 mm., was predominantly 2-ethylcyclohexanone, the second (17 g.), b. p. 84–90°/13 mm., mainly 2 : 2-diethylcyclohexanone. The high-boiling residue (42 g.) probably consisted of self-condensation products of cyclohexanone. A semicarbazone made from the second fraction had m. p. 202–203° after four crystallisations from ethanol (Meerwein¹⁵ gives m. p. 202–203° for 2 : 2-diethylcyclohexanone semicarbazone). The first fraction was also converted into the semicarbazone, m. p. 163° (lit., 161–162°) after four crystallisations from ethanol (yield 25 g.). By hydrolysis with dilute hydrochloric acid pure 2-ethylcyclohexanone (14 g., 12%) was obtained.

(c) 2-Ethylcyclohexanone (14 g.) in ethereal solution was added to a Grignard reagent prepared from magnesium (3.2 g.) and *o*-bromoethylbenzene (20.6 g.), and the mixture heated under reflux for 20 hr. The product was worked up in the usual way, the ethereal solution dried (Na_2SO_4), and the ether distilled off. The residue was dehydrated by formic acid (75 c.c.) under reflux for 4 hr. The product was extracted with benzene, and the benzene solution washed and dried. After removal of the benzene the residue was distilled under reduced pressure, giving 4 g. (17%) of a hydrocarbon (or mixture of isomeric hydrocarbons), b. p. 132–133°/11 mm., n_D^{25} 1.5261 (Found : C, 89.3; H, 10.6. Calc. for $C_{16}H_{22}$: C, 89.7; H, 10.3%). Dehydrogenation by heating with sulphur for 4 hr. at 240° gave 2 : 2'-diethylidiphenyl (2 g.).

Methyl 3-Amino-4-isopropylbenzoate.—Methyl 3-nitro-4-isopropylbenzoate was obtained in almost quantitative yield by nitration of *p*-isopropylbenzoic acid, followed by treatment with thionyl chloride and then methanol.¹⁶ Attempted reduction of the acid with iron and acetic acid, ammonium sulphide, or ammoniacal ferrous sulphate was unsuccessful. The ester was largely unchanged after being shaken with hydrogen in the presence of catalysts (platinum or palladium). However, reduction in 88% yield was achieved by using tin and hydrogen chloride in a methanolic solution of the ester (cf. Abenius¹⁷). The *benzoyl* derivative of the amino-ester had m. p. 118° (Found : C, 72.6; H, 6.3; N, 4.9. $C_{18}H_{19}O_3N$ requires C, 72.7; H, 6.4; N, 4.7%).

Methyl 3-Iodo-4-isopropylbenzoate was obtained in 66% yield by the diazo-process. It had b. p. 140–142°/7 mm., n_D^{25} 1.5780 (Found : C, 43.7; H, 4.2; I, 41.6. $C_{11}H_{13}O_2I$ requires C, 43.4; H, 4.3; I, 41.8%). A little was hydrolysed to the *acid*, m. p. 173–174° (Found : I, 44.0. $C_{10}H_{11}O_2I$ requires I, 43.8%).

6 : 6'-*Diisopropylidiphenyl-3 : 3'-dicarboxylic Acid*.—The above iodo-ester (76 g.) was treated with copper bronze in a bath at 270–275° for 50 min. The product was extracted with chlorobenzene, the solvent removed, and the residue treated with light petroleum. The solid so precipitated, after two crystallisations from methanol, gave *methyl 6 : 6'-diisopropylidiphenyl-3 : 3'-dicarboxylate* as prisms, m. p. 143–144° (36 g., 81%) (Found : C, 74.7; H, 7.5. $C_{22}H_{26}O_4$ requires C, 74.6; H, 7.4%). Hydrolysis with ethanolic sodium ethoxide gave 6 : 6'-*diisopropylidiphenyl-3 : 3'-dicarboxylic acid* with m. p. 285–290°, which was raised to 323–324° by two

¹⁴ West, *J.*, 1925, 127, 494.

¹⁵ Meerwein, *Annalen*, 1913, 396, 225.

¹⁶ Bryan and Foote, *J. Amer. Pharm. Assoc.*, 1949, 38, 572; 1950, 39, 644.

¹⁷ Abenius, *J. prakt. chem.*, 1889, 40, 425.

crystallisations from acetic acid (Found: C, 69.0; H, 6.7. $C_{20}H_{20}O_4 \cdot CH_3 \cdot CO_2H$ requires C, 68.8; H, 6.8%). The solvent-free acid was obtained by crystallisation from ethanol (Found: C, 73.4; H, 6.9. $C_{20}H_{20}O_4$ requires C, 73.2; H, 6.7%) (m. p. unchanged).

2: 2'-*Diisopropylidiphenyl*.—A solution of the above acid (10 g.) in quinoline containing copper bronze was heated for 10 hr. Most of the quinoline was distilled off and the residue poured into water and acidified with hydrochloric acid. The oil which separated was extracted with ether; the extract was washed, dried, and distilled. The fraction, b. p. 150—160°/12 mm., solidified and two crystallisations from ethanol gave pure 2: 2'-*diisopropylidiphenyl*, m. p. 67—68° (4.2 g.) (Found: C, 90.6; H, 9.1. $C_{18}H_{22}$ requires C, 90.8; H, 9.2%).

3: 3'-*Diethylbenzidine* was prepared from *o*-ethylnitrobenzene.¹⁸ The dibenzylidene derivative had m. p. 129—130° (Schultz and Flachsländer¹⁸ give 124—125°). The *disalicylidene* derivative crystallised from cyclohexane or from light petroleum (b. p. 100—120°) and had m. p. 157—158° (Found: C, 79.6; H, 6.3; N, 6.8. $C_{30}H_{28}O_2N_2$ requires C, 80.4; H, 6.3; N, 6.3%).

3: 3'-*Diethylidiphenyl*.—A solution made from 3: 3'-diethylbenzidine dihydrochloride (47 g., 1 mol.), concentrated hydrochloric acid (45 c.c., 3 mol.), and water (600 c.c.) was diazotised at -4° to -2° with sodium nitrite (22.8 g., 2.2 mol.) in water (75 c.c.). Hypophosphorous acid (50%; 300 c.c., 15 mol.), pre-cooled to 0°, was added and the solution stirred at 0° for 1 hr., then kept overnight at 5°. The oily layer was separated and the aqueous layer thrice extracted with ether. The combined extracts were washed several times with 30% sodium hydroxide solution, then with water, and dried (CaCl₂). Removal of the ether, followed by distillation and redistillation, gave 21 g. (63%) of crude material. Small amounts of phenolic impurities were eliminated by distillation over sodium, whence pure 3: 3'-*diethylidiphenyl*, b. p. 154—155°/9—10 mm., n_D^{25} 1.5768, was obtained (Found: C, 91.5; H, 8.5. $C_{18}H_{18}$ requires C, 91.4; H, 8.6%).

p-*Ethylidobenzene*.—*p*-Ethylnitrobenzene was reduced with zinc and hydrochloric acid.¹³ *p*-Ethylacetanilide had m. p. 91° (lit., 94°). *p*-Ethylidobenzene, b. p. 87—88°/8—9 mm., n_D^{25} 1.5888, was prepared by a modification of Willgerodt and Bergdolt's method,¹⁹ the *p*-ethylaniline being diazotised in sulphuric acid solution.

4: 4'-*Diethylidiphenyl*.—(a) *p*-Ethylidobenzene was heated with copper bronze,⁸ and the resulting 4: 4'-diethylidiphenyl distilled under reduced pressure; it crystallised from methanol or ethanol in flakes, m. p. 83° (Schreiner⁸ gives m. p. 81°) (Found: C, 91.6; H, 8.5%).

(b) *p*-Bromoethylbenzene, b. p. 93—94°/23 mm., n_D^{25} 1.5449, was obtained in 42% yield by a Sandmeyer reaction, the base being diazotised in hydrobromic acid. A Grignard reagent was prepared from it and treated with anhydrous cupric chloride, giving 4: 4'-diethylidiphenyl, m. p. 83°, after crystallisation as above.

p-*Iodoisopropylbenzene*.—*p*-Nitroisopropylbenzene was reduced in ethanolic solution by hydrogen and Adams platinum oxide. The acetyl and the benzoyl derivative had m. p.s 104—105° (Newton²⁰ gives 105.8—106.6°) and 162.5—163° (lit., 161.4—162°)²⁰ respectively. *p*-Iodoisopropylbenzene, b. p. 86—92°/5—6 mm., n_D^{25} 1.5725, was obtained by diazotising the amine in sulphuric acid and adding the diazo-solution to aqueous potassium iodide.

4: 4'-*Diisopropylidiphenyl*.—*p*-Iodoisopropylbenzene (5 g.) was heated with copper bronze (8 g.) at 260—270° for 45 min. The mixture was extracted with hot chlorobenzene; the solvent was removed and the residue distilled, giving 2 g. of 4: 4'-*diisopropylidiphenyl*, b. p. 155—160°/4.5 mm. It was redistilled from sodium and crystallised twice from ethanol, forming plates, m. p. 65—66° (Found: C, 90.8; H, 9.3%).

Absorption Spectra.—Spectra were measured on a Unicam S.P. 500 spectrophotometer.

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¹⁸ Schultz and Flachsländer, *J. prakt. chem.*, 1902, **66**, 153.

¹⁹ Willgerodt and Bergdolt, *Annalen*, 1903, **327**, 286.

²⁰ Newton, *J. Amer. Chem. Soc.*, 1943, **65**, 2434.