TABLE I

Cinnamylidenemalonic Acids

	Yield, %	M.P.[a]	M.P. (Cor.)[a] for Anal.	Compound	Calcd.		Found	
					C	H	C	H
3-CH_3O	100	189–196	201.6–202.0[b]	$C_{13}H_{12}O_5$	62.91	4.88	62.88	4.72
3-$C_6H_5CH_2O$	89	162–176	192.0[c]	$C_{19}H_{16}O_5$	70.36	4.97	70.71	5.01
2-$C_6H_5CH_2O$-3-CH_3O	95	130–139	162.3–163.9[d]	$C_{20}H_{18}O_6$	67.79	5.12	68.05	5.15
4-$C_6H_5CH_2O$-3-CH_3O	75	140–154	195.0–195.5[e]	$C_{20}H_{18}O_6$	67.79	5.12	68.10	5.03
Phenylvaleric Acids								
3-HO	81.5	89–112	115.2–117.0[f]	$C_{11}H_{14}O_3$	68.02	7.27	68.21	7.27
3-CH_2O	79	B.p. 200–220 (1 mm.-bath)	B.p. 142–143 (0.17 mm.)	$C_{12}H_{16}O_3$	69.20	7.75	70.22	7.79
2-HO-3-CH_3O	42	81–88	86.2–88.2[g]	$C_{12}H_{16}O_4$	64.27	7.19	64.61	7.24
4-HO-3-CH_3O	74	86–89	90.5–92.5[h]	$C_{12}H_{16}O_4$	64.27	7.19	63.66	7.31
4-$C_6H_5CH_2O$-3-CH_3O	81[i]	93.5–100	100.5–102[j]	$C_{19}H_{22}O_4$	72.59	7.06	72.62	7.17
Benzosuberones								
2-HO	18[k]	156.5–163.5	164.4–166.1[l]	$C_{11}H_{12}O_2$	74.97	6.87	75.06	6.95
2-CH_3O	94	54–58	58.9–60.3[m]	$C_{12}H_{14}O_2$	75.76	7.42	75.81	7.42
1-$C_6H_5CO_2$-2-CH_3O	51	124–139	138.0–141.4	$C_{19}H_{18}O_4$	73.53	5.85	73.39	5.89
1-HO-2-CH_3O	(82)[n]	88–95	98.4–100.6	$C_{12}H_{14}O_3$	69.88	6.84	69.83	6.84
3-$C_6H_5CO_2$-2-CH_3O	42[o]	119–124	126–127.4[p]	$C_{19}H_{18}O_4$	73.53	5.85	73.65	5.68
3-HO-2-CH_3O	30	106–109	112.0–113.2[q]	$C_{12}H_{14}O_3$	69.88	6.84	70.24	7.04

[a] All cinnamylidenemalonic acids melted with gas evolution. [b] From benzene–ethyl acetate, canary yellow. [c] Instantaneous; from benzene–ethyl acetate, canary yellow. [d] From benzene–ethyl acetate, canary yellow. [e] Golden yellow clumps of spears from methanol. [f] From benzene. [g] From cyclohexane–acetone or aqueous methanol; dark green ferric chloride test. The *benzoate* melted at 98–99.6° (cor.). Calcd. for $C_{19}H_{20}O_5$: C, 69.50; H, 6.14. Found: C, 69.39; H, 6.10. [h] From cyclohexane; green ferric chloride test. The *acetate*, from benzene–petroleum ether (b.p. 65–110°) melted at 76.5–78.1° (cor.). Calcd. for $C_{14}H_{18}O_5$: C, 63.14; H, 6.81. Found: C, 63.27; H, 6.85. [i] From the catalytic reduction of the cinnamylidenemalonic acid followed by heating at 180° and extraction with hot cyclohexane. [j] From cyclohexane. [k] Cyclization time 30 min. (95°). [l] From benzene-cyclohexane; identical to the compound obtained (by Mr. Irwin Schmeltz) from 2-methoxybenzosuberone by cleavage with aluminum chloride. The *benzoate* from methanol melted at 60.2–61.2° (cor.). Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.24; H, 5.65. [m] From cyclohexane and sublimed at 0.16 mm. (90° bath). The *oxime*, from cyclohexane and sublimed at 0.12 mm. (140° bath) melted at 127.0–128.8° (cor.). Calcd. for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37. Found: C, 70.35; H, 7.55. [n] By saponification of the benzoate; deep green ferric chloride test. [o] Cyclization time 25 mins. (90°). [p] From benzene-petroleum ether (b.p. 60–71°). Saponification of the benzoate gave 3-hydroxy-2-methoxybenzosuberone which was methylated to 2,3-dimethoxybenzosuberone, identical to known material.[4] [q] From benzene-petroleum ether (b.p. 60–71°); green ferric chloride test. The *acetate* from petroleum ether (b.p. 90–110°) melted at 104.8–106.4° (cor.). Calcd. for $C_{14}H_{16}O_4$: C, 67.72; H, 6.50. Found: C, 67.96; H, 6.57.

lated prior to decarboxylation in virtually quantitative yield m.p. 112–119° (gas evol.). From benzene–petroleum ether (b.p. 65–110°) and ethyl acetate–petroleum ether, material melting at 122.8–124.0° (gas evol.) was obtained.

Anal. Calcd. for $C_{13}H_{16}O_6$: C, 58.20; H, 6.01. Found: C, 58.15; H, 6.01.

The catalytic reduction of 4-benzyloxy-3-methoxycinnamylidenemalonic acid in alcohol over platinum gave a malonic acid with retention of the benzyl group. Decarboxylation gave the benzyl ether of the valeric acid (Table I). Debenzylation[9] gave δ-4-hydroxy-3-methoxyphenylvaleric acid (93.2%) identical to the material produced *via* Raney alloy–sodium hydroxide.

δ-4-Benzoyloxy-3-methoxyphenylvaleric acid. The dried mixture of the benzoate and benzoic acid, m.p. 89–102°, obtained by treatment with benzoyl chloride in aqueous sodium hydroxide was either (a) sublimed 24 hr. at 70° (0.3 mm.) to yield material (76%) m.p. 118–123° which depressed the melting point of benzoic acid or (b) digested three times with water at 90°, filtering after each digestion, to yield product (77%) m.p. 121–124°, similarly depressing the melting point of benzoic acid. By repeated crystallization from benzene–petroleum ether (b.p. 90–110°) 1:10, colorless material m.p. 126.0–127.8° was obtained.

Anal. Calcd. for $C_{19}H_{20}O_5$: C, 69.50; H, 6.14. Found: C, 69.51; H, 6.13.

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2,4′-Diphenylbiphenyl

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Of the nine possible $C_{24}H_{18}$ hydrocarbons consisting of four linked benzene rings, eight are recorded.[1–8] We now report the synthesis of the re-

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maining compound, 2,4′-diphenylbiphenyl (IV). 2,4′-Dinitrobiphenyl (I)[9] was reduced to 2,4′-diaminobiphenyl (II)[10] and tetrazotized. The tetrazonium hydroxide was decomposed in the presence of benzene[11] to give 2,4′-diphenylbiphenyl (IV), m.p. 209–210° in less than 1% yield. In an alternative synthesis 2,4′-diacetamidobiphenyl (III) was nitrosated and the *N*-nitroso compound was decomposed in benzene solution[12] to give a 3% yield of 2,4′-diphenylbiphenyl.

The availability of 2,4′-diphenylbiphenyl makes possible some further correlations of the ultraviolet absorption characteristics of the quaterphenyls. Ultraviolet absorption data for quaterphenyls and related compounds are recorded in Table I.

TABLE I

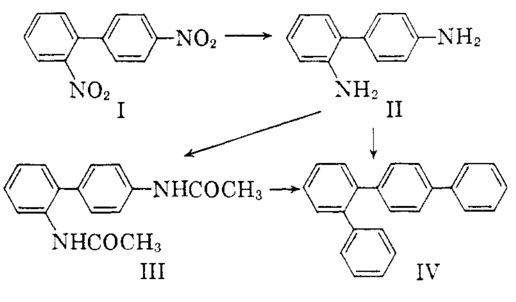
ULTRAVIOLET ABSORPTION DATA FOR QUATERPHENYLS AND RELATED COMPOUNDS

Compound	λ_{max}, mμ	Log ε	Solvent[a]	Ref.
Biphenyl	248	4.3	C	13
p-Terphenyl	276	4.54	H	14
p-Quaterphenyl	292	4.75	H	14
3,4′-Diphenylbiphenyl	~267	4.54	C	3
3,3′-Diphenylbiphenyl	250	4.74	C	3
2,4′-Diphenylbiphenyl	257	4.55	M	
	274	4.55	M	
2,3′-Diphenylbiphenyl	235	4.65	C	3
	255sh.	—	C	3
2,2′-Diphenylbiphenyl	<230	>4.5	E	15
1,3,5-Triphenylbenzene	251	4.76	H	16

[a] The letters stand for the following solvents: C, cyclohexane; H, hexane; M, methanol; E, ethanol.

Two generalizations have been drawn[14] from the spectra of the polyphenyls: For all *p*-polyphenyls, both λ_{max} and ε increase with the number of nuclei present; and for all *m*-polyphenyls, the λ_{max} remains constant (approx. 250 mμ), while ε increases with the number of nuclei present. It has also been observed[3] that an *o*-configuration in a polyphenyl interferes with through-conjugation. The data given in Table I confirm these postulates for the quaterphenyl series. In *p*-quaterphenyl the maximum is at the longest wave length for the series and presumably the chromophore covers the entire molecule. Where *m*- or *o*- configurations are present, the chromophore is broken at that point. Thus, 3,4′-diphenylbiphenyl, in which a *p*-terphenyl structure is found, shows absorption similar to that of *p*-terphenyl, and 3,3′-diphenyl shows absorption at the same wave length as biphenyl, but with almost three times the intensity. 2,4′-Diphenylbiphenyl shows absorption corresponding to both biphenyl and *p*-terphenyl chromophores. 2,3′-Diphenylbiphenyl shows mainly absorption corresponding to single benzene nuclei with a shoulder in the region corresponding to the biphenyl chromophore, and 2,2′-diphenylbiphenyl shows only end absorption in the 230–300 mμ region. 1,3,5′-Triphenylbenzene shows absorption at the same wave length as biphenyl with almost three times the intensity. Presumably each pair of linked rings contributes to the absorption in this case. The spectra of the other two triphenylbenzenes are not recorded.

2,4′-Diphenylbiphenyl shows possibilities as a scintillation solute. It shows a pulse height relative to terphenyl of 1.06 at 3 g./1 in toluene[17] and a solubility of 3% in toluene at 27°.



EXPERIMENTAL

2,4′-Diaminobiphenyl. 2,4′-Dinitrobiphenyl, obtained as a by-product from the nitration of biphenyl,[9] was reduced with tin and hydrochloric acid[10] to give the diamine in 65% yield.

2,4′-Diacetamidobiphenyl. Fifteen g. of 2,4′-diaminobiphenyl was heated on the steam bath for 2 hr. with 25 g. of acetic anhydride. The solution was poured into 400 ml. of ice water. The resulting suspension was warmed on a steam bath for 30 min., cooled, and filtered. The crude product was recrystallized from aqueous ethyl alcohol to give 10 g. (61%, from dinitrobiphenyl) of 2,4′-diacetamidobiphenyl, m.p. 198–200°. Reported[10] m.p. 202°.

2,4′-Diphenylbiphenyl. 1. From 2,4′-diaminobiphenyl. Six g. of 2,4′-diaminobiphenyl was tetrazotized at 0° in hydrochloric acid. The solution was allowed to warm to 5–6° as 100 ml. of benzene was added. The solution was kept at 5–6° as excess 5*N* sodium hydroxide was added over 1 hr., with rapid stirring. The stirring was continued at 5–6° for 1 hr. and then at room temperature for 20 hr. The benzene layer was separated and dried, and the benzene was removed by distillation to leave 5 g. of a black tar. Sublimation gave 15 mg. of a white solid, m.p. 190–192°. On recrystallization from benzene the m.p. was raised to 208–210°.

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2. *From 2,4'-diacetamidobiphenyl.* Ten g. of 2,4'-diacetamidobiphenyl was dissolved in 150 ml. of glacial acetic acid and 75 ml. of acetic anhydride. Ten g. of anhydrous potassium acetate and 1 g. of phosphorus pentoxide were added, and the solution was cooled to −5°. The solution was stirred and a solution of 5.5 g. of redistilled nitrosyl chloride in 10 ml. of acetic anhydride was added at −20°. Stirring was continued for 15 min., the mixture was poured onto 500 g. of ice and water and the solution was extracted twice with 200 ml. of benzene. The benzene extract was washed twice with 50 ml. of ice water and dried over anhydrous sodium sulfate. The solution was warmed to 35–40° until no more nitrogen was evolved (1 hr.), filtered, and the benzene removed by distillation to leave 10 g. of a black tar. The black tar was chromatographed on acid alumina (Woelm, Grade I), using benzene as eluant. The eluate coming through the column before the colored material was evaporated to dryness to give 0.3 g. (3%) of 2,4'-diphenylbiphenyl, m.p. 209–210° from benzene or toluene. Ultraviolet absorption: λ_{max} 257 mμ (log ϵ, 4.55); 274 mμ (log ϵ, 4.55) in methanol (Beckman DK-2 spectrophotometer). Infrared absorption: 1605(w), 1529(w), 1484(m), 1456(w), 1403(w), 1350(w), 1170(w), 1076(w), 1005(m), 908(w), 839(s), 748(v.s.), 686(s) cm.$^{-1}$ All bands attributable to *o*-, *p*- or monosubstituted benzenes. (KBr pellet; Baird recording double-beam spectrometer).

Anal.[18] Calcd. for $C_{24}H_{18}$: C, 94.08; H, 5.92. Found: C, 93.90; H, 6.20.

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[18] Analysis by Micro Tech Laboratories, Skokie, Ill.

Application of the Equilibrium Theory of Solvent Isotope Effects to Deoxymercuration

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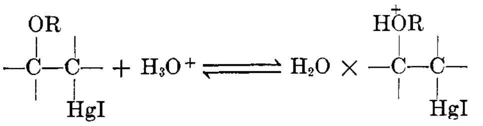
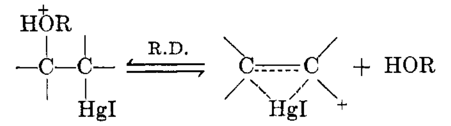
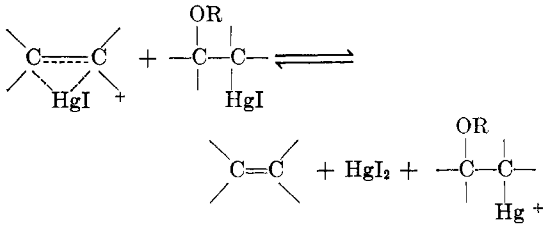
In previous papers[1,2] the mechanism of deoxymercuration induced by nonhalogen acids has been discussed, and evidence favoring a prototropic equilibrium followed by a rate-determining reaction of the protonated substrate was presented. The suggested mechanism is shown in Equations 1–3.



(1)



(2)



(3)

For such a mechanism it would be expected that the equilibrium theory of solvent isotope effects[3] would successfully predict the dependence of rate on solvent deuterium content in partially deuterated water when R is an alkyl group. Although the precision was inadequate for a definite conclusion, the work on 2-methoxy-1-iodomercuripropane (I) suggested that there were systematic differences between observed and predicted rates.[1]

The reason for the lack of precision in the earlier work was that I is deoxymercurated at an inconveniently high rate. The dependence of rate on solvent deuterium content has now been examined for 2-methoxy-1-iodomercuriethane (II). Deoxymercuration of II is slower than deoxymercuration of I by a factor of about 10, so that considerably better precision could be obtained. The present results are in accord with the predictions of the equilibrium theory of solvent isotope effects.[3]

Rates were obtained spectrophotometrically at 25° by following the build-up of the mercuric iodide absorption at 2800 Å. The initial substrate concentration was 3 × 10^{-5} and the acid was always in large excess. Reactions were followed to 50–80% of completion. With a large excess of acid the mechanism shown in Equations 1–3 leads to the rate law shown in Equation 4,

$$k_1 = \frac{2.303}{2(t - t_0)} \log \frac{(D_\infty - D_0)}{(D_\infty - D_t)} \tag{4}$$

where k_1 is the pseudo first-order rate constant and D_t is the optical density at time t.[1] The quantity log $[(D_\infty - D_0)/(D_\infty - D_t)]$ was evaluated from semilogarithmic plots of $(D_\infty - D_t)$ *vs.* t. A typical example of such a plot is shown in Fig. 1. None of the present plots showed the negative curvature mentioned previously,[1] but such curvature was not specifically sought.

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