TABLE I

ETHERS OF VANILLIN

Ether	Yield, %	M.p., °C.	B.p., °C.	B.p., Mm.	$n^{25}D$	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Isopropyl	71		122[a]	0.3	1.5561					
Propyl	84	61–62[b]								
Isobutyl	72		130[c]	0.3	1.5459	$C_{12}H_{16}O_3$	69.21	69.35	7.74	7.89
Butyl	91	30–31	136[d]	1.0	1.5525					
s-Butyl	87		125	0.3	1.5483	$C_{12}H_{16}O_3$	69.21	69.17	7.74	7.78
Amyl	79		145[e]	.1	1.5423	$C_{13}H_{18}O_3$	70.24	70.22	8.16	8.15
Hexyl	100	42–43[f]	142–143	.25		$C_{14}H_{20}O_3$	71.16	71.28	8.53	8.57
Heptyl	100	39–40[g]	155	.5		$C_{15}H_{22}O_3$	71.97	72.02	8.86	8.87
Methylene-bis	55	157–158[h]				$C_{17}H_{16}O_6$	64.55	64.59	5.10	5.22

[a] Kubiczek, *et al.*,[3] recorded a b.p. of 141–142° (5 mm.) for this compound. [b] Kubiczek, *et al.*, recorded a m.p. of 59–60°. [c] Kubiczek, *et al.*, reported a b.p. of 147° (7 mm.). [d] Kubiczek, *et al.*, reported a b.p. of 140.5–141° (2 mm.). [e] Z. I. Kanevska [*Arch. Pharm.*, **271**, 462 (1933)] reported a b.p. of 185–186° (17 mm.). [f] From petroleum ether (b.p. 65–110°). [g] From petroleum ether (b.p. 30–60°). [h] From ethanol or methanol.

ethers of vanillic acid had been recorded. Kubiczek, Pohl and Smahel[3] prepared a number of aliphatic ethers of vanillin as intermediates in the preparation of analogous amines, but these authors reported no analyses for their compounds.

A number of aliphatic ethers of vanillin have been prepared by treating the potassium salt of vanillin with an equivalent of alkyl iodide in absolute ethanol. These ethers were oxidized in substantially quantitative yield to their respective vanillic acids by means of potassium permanganate in acetone. Data for ethers and acids are given in Tables I and II, respectively.

TABLE II

ETHERS OF VANILLIC ACID

Ether	M.p., °C.[a]	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Isopropyl	146–147	$C_{11}H_{14}O_4$	62.84	63.13	6.71	6.77
Propyl	183–184[b]	$C_{11}H_{14}O_4$	62.84	62.91	6.71	6.78
Isobutyl	142–143	$C_{12}H_{16}O_4$	64.27	64.37	7.19	7.22
Butyl	155–156	$C_{12}H_{16}O_4$	64.27	64.32	7.19	7.23
s-Butyl	99–100	$C_{12}H_{16}O_4$	64.27	64.37	7.19	7.21
Amyl	132–133	$C_{13}H_{18}O_4$	65.53	65.55	7.61	7.69
Hexyl	118–119	$C_{14}H_{20}O_4$	66.64	66.72	7.99	8.01
Heptyl	118–119	$C_{15}H_{22}O_4$	67.64	67.66	8.33	8.34
Methylene-bis	269–270	$C_{17}H_{16}O_8$	58.62	58.48	4.63	4.78

[a] All ethers except isopropyl and methylene-bis were recrystallized from dilute methanol. The isopropyl ether was recrystallized from methanol and the methylene-bis ether was recrystallized from either methanol or ethanol. [b] A. Cahours [*Compt. rend.*, **84**, 152 (1877)] reported this compound but gave no m.p.

Experimental

All melting and boiling points are uncorrected.

General Etherification Procedure. Preparation of Vanillin Isopropyl Ether.—A solution of 8 g. (0.2 atom) of potassium in 500 cc. of absolute ethanol was treated with 30.4 g. (0.2 mole) of vanillin. The mixture, containing a yellow precipitate, was treated with 42 g. (0.25 mole) of isopropyl iodide, and the resulting mixture was boiled under reflux with magnetic stirring for 7 hours. The yellow precipitate disappeared after short boiling and was replaced with a little potassium iodide. The reaction mixture was distilled under reduced pressure with magnetic stirring until most of the ethanol was removed, and the residue was diluted with water and extracted with ether. The ether was washed with dilute potassium hydroxide solution and then with water and finally dried and distilled to leave 27.3 g. (71%) of yellow oil. The oil was fractionated under reduced pressure to give vanillin isopropyl ether as an almost colorless oil, b.p. 122° (0.3 mm).

All ethers of Table I were prepared in the same manner. In the case of the methylene bis-vanillin ether the molar ratio of methylene iodide was halved.

General Oxidation Procedure. Preparation of Vanillic Acid Ethyl Ether.—A solution of 5 g. of vanillin ethyl ether in 250 cc. of dry acetone was heated to boiling and treated with potassium permanganate crystals until a permanent violet color resulted. The mixture was boiled for 30 minutes, and then diluted with water. Boiling was continued until most of the acetone had distilled, and the mixture was then filtered. The residue was washed with hot water, and the combined filtrate and washings were acidified with sulfur dioxide. The resulting white precipitate was filtered, washed with water, and dried. The yield was 5.5 g. (100%). Recrystallization from methanol gave white needles of vanillic acid ethyl ether melting at 194–195°. This corresponds with the melting point of 195–196° for this compound reported by Nomura.[4]

The ethers listed in Table I were oxidized in the same manner to give substantially quantitative yields of their respective acids listed in Table II.

Acknowledgment.—The author wishes to thank Mr. Harold Willemsen for the analyses reported in this paper.

---

[3] G. Kubiczek, M. Pohl and A. Smahel, *Monatsh.*, **77**, 52 (1947).

[4] H. Nomura, *J. Chem. Soc.*, **111**, 774 (1917).

THE INSTITUTE OF PAPER CHEMISTRY
APPLETON, WISCONSIN

The Ultraviolet Absorption Spectra of Some Highly Chlorinated Aromatic Systems

BY WILLIAM L. MOSBY

RECEIVED SEPTEMBER 3, 1954

It is well known that substituents, whose interference radii overlap as do those in the "hindered" positions[1] of certain aromatic nuclei, may have a pronounced effect upon the ultraviolet absorption spectrum. In general, compared to the unsubstituted nucleus, this effect is characterized by bathochromic and hyperchromic displacements of the longer wave length maxima, and a diminution of fine structure in these regions. The effect becomes much more pronounced in highly substituted nuclei, particularly as additional substituents force the system to deviate from coplanarity. In this regard octamethylnaphthalene[2] and other polymethylnaphthalenes[2,3] were discussed recently.

Completely substituted aromatic systems, such as would be most useful in studying these effects,

---

[1] *Inter alia*, M. S. Newman, THIS JOURNAL, **62**, 2297 (1940); F. Bell and D. H. Waring, *J. Chem. Soc.*, 2689 (1949); H. Brockmann and R. Randelbrock, *Ber.*, **84**, 533 (1951); E. Clar and D. G. Stewart, THIS JOURNAL, **74**, 6235 (1952).

[2] B. J. Abadir, J. W. Cook and D. T. Gibson, *J. Chem. Soc.*, 8 (1953).

[3] W. L. Mosby, THIS JOURNAL, **75**, 3348 (1953).

are quite rare, since synthetic difficulties increase rapidly with increasing substitution. For two reasons chlorine would be an ideal substituent for this investigation. First, it is readily introduced into most aromatic systems and, second, while possessing a smaller interference radius than the methyl group, chlorine as a substituent usually produces a greater bathochromic shift than does a methyl group.

Few highly chlorinated, and apparently only two completely chlorinated polycyclic nuclei have been described. No reference was found to the ultraviolet spectrum of a perchlorinated compound, but Grinbaum and Marchlewski[4] have published the ultraviolet spectrum of an octachlorophenanthrene, m.p. 280°. The compound was not precisely identified, nor further characterized, but would seem to be the same product described by Zetter.[5] The spectrum, as obtained by these authors, shows a slight hyperchromic displacement of the 251 mμ maximum (Clar's β-bands[6]) present in phenanthrene but, surprisingly, no bathochromic shift is evident. A suppression of fine structure and fusion of the *para*- and α-bands of phenanthrene are visible, and a very large (log ε 4.0 *vs.* 2.4 in phenanthrene) hyperchromic shift of the α-bands is conspicuous. Unfortunately, these data are of only general qualitative value since positions occupied by the chlorine atoms cannot be assigned with certainty.

The absorption spectra of some chlorinated naphthalenes, anthracenes and naphthacenes have been discussed by Clar and Marschalk.[7] Octachloronaphthalene was described long ago[8] but was not well known until the work of Schwemberger and Gordon.[9] It is the major constituent of the commercial product "Halowax 1051," and has been of recent interest.[10] In contrast to octamethylnaphthalene[2] (electron attracting *vs.* electron donating substituents), octachloronaphthalene does not form addition complexes with picric acid or trinitrofluorenone, nor does it show any deepening of color on admixture of solutions of the reactants. The color test[9] with a 30% solution of antimony pentachloride in carbon tetrachloride was confirmed, but as similar colors are given by other chloronaphthalenes, the test is of limited value. The ultraviolet absorption spectrum of octachloronaphthalene is compared in Fig. 1 with the spectra of octamethylnaphthalene[2] and 1,4,5,8-tetrachloronaphthalene[7] given in the literature. A considerable broadening of the β-bands and a strong bathochromic shift of the whole curve are evident.

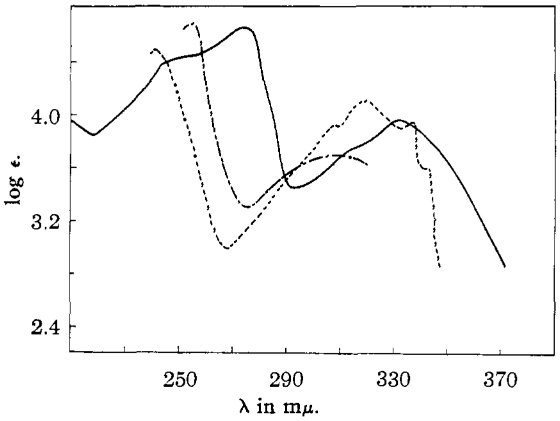

Fig. 1.—The ultraviolet absorption spectra of: ——, octachloronaphthalene; —·—·—, octamethylnaphthalene; -·-·-·, 1,4,5,8-tetrachloronaphthalene.

The only other perhalogenated aromatic polycycle which has been described is decachloropyrene. By stepwise chlorination, pyrene is ultimately converted[11] to decachloropyrene *via* the intermediate product 3,5,8,10-tetrachloropyrene. Neither of these compounds forms an addition complex with picric acid or trinitrofluorenone. The ultraviolet spectra of these two compounds are shown in Fig. 2. A progressive bathochromic shift with respect to pyrene and 3-chloropyrene[12] is the most noticeable feature of the spectrum of 3,5,8,10-tetrachloropyrene. In addition there is a change in the appearance of the bands in the 360–390 mμ region (Clar's α-bands[6]).

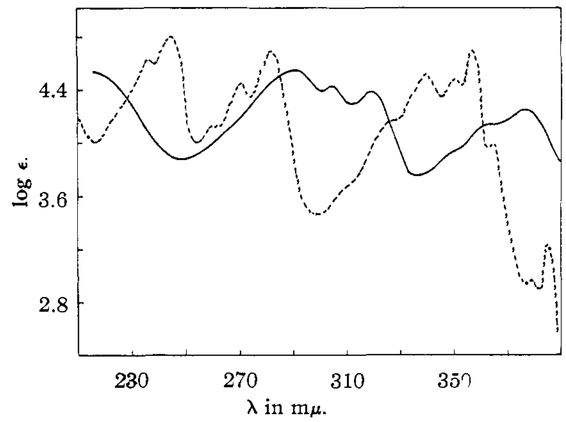

Fig. 2.—The ultraviolet absorption spectra of: ——, decachloropyrene; ------, 3,5,8,10-tetrachloropyrene.

A surprising alteration is evident in the spectrum of decachloropyrene (Fig. 2), and it is scarcely recognizable as that of a pyrene derivative. The three peaks in the 290–320 mμ range show an order of intensity exactly the reverse of either the β- or the β′-bands in pyrene. The broad group from 350–

---

[4] R. Grinbaum and L. Marchlewski, *Bull. intern. acad. polon. sci. Classe sci. math. nat.*, **A**, 171 (1937).

[5] G. Zetter, *Ber.*, **11**, 164 (1878).

[6] The three principal regions of ultraviolet absorption exhibited by aromatic hydrocarbons have variously been referred to, respectively, as the β-, *para*- and α-bands by E. Clar ["Aromatische Kohlenwasserstoffe." 2nd Ed., Springer Verlag, Berlin, 1952, pp. 25–37], the I, II and III bands by E. A. Braude [*Ann. Reports*, **42**, 122 (1945)] and the ^1B_b, ^1L_a and ^1L_b bands by H. B. Klevens and J. R. Platt [*J. Chem. Phys.*, **17**, 470 (1949)]. For the sake of convenience, Clar's nomenclature is arbitrarily adhered to here.

[7] E. Clar and C. Marschalk, *Bull. soc. chim. France*, **17**, 433 (1950).

[8] For a summary of early work see G. Ruoff, *Ber.*, **9**, 1483 (1876).

[9] W. Schwemberger and W. Gordon, *J. Gen. Chem.* (*U.S.S.R*), **2**, 921 (1932); **4**, 695 (1934); *Chem. Zentr.*, **105**, **I**, 215 (1934); **106**, **II**, 514 (1935).

[10] R. Roedig, *Chem. Ber.*, **80**, 207 (1947); J. Bernimolin, *ibid.*, **87**, 640 (1954).

[11] H. Vollmann, H. Becker, M. Corell and H. Streeck, *Ann.*, **531**, 1 (1937).

[12] R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, curves 472 and 492.

390 $m\mu$ probably represents Clar's "*para*" bands. The α-bands are either non-existent, or have been shifted beyond the ultraviolet range of the instrument.

It seems probable that the abnormalities exhibited by the spectra of octachloronaphthalene and decachloropyrene may to a large extent derive from the non-coplanar nature of these molecules, which are analogous to other systems shown to be noncoplanar.[1-3,13]

Acknowledgment.—The author is indebted to the Bakelite Company for a generous supply of "Halowax 1051."

Experimental

Octachloronaphthalene was prepared by the repeated recrystallization of "Halowax 1051" from cyclohexane or benzene, followed by vacuum sublimation and recrystallization from cyclohexane. The product crystallized in small, nearly colorless needles, m.p. 196–197° (lit.[9] 197.5–198°). 3,5,8,10-Tetrachloropyrene and decachloropyrene were prepared by Vollmann's method.[11]

The ultraviolet spectra were obtained from solutions of the compounds in 95% ethanol (denatured with methanol) using a Cary Automatic Recording Spectrophotometer, Model 10. The positions of the absorption maxima (in $m\mu$) are given below, followed in parentheses by the corresponding approximate intensity (log ϵ). The slight partial insolubility of the two pyrene derivatives prevented obtaining precise values of log ϵ. Asterisks indicate points of inflection or shoulders.

Octachloronaphthalene: 243 (4.38); 275 (4.67); 318* (3.77); 332 (3.87) and 345* (3.79).

3,5,8,10-Tetrachloropyrene: 236.5 (4.62); 245 (4.80); 260–263* (4.13); 270.5 (4.45); 279* (4.56); 282 (4.69); 310* (3.71); 326.5 (4.17); 335* (4.34); 340 (4.51); 349.5 (4.47); 357 (4.69); 364.5 (3.99); 379 (2.97) and 385 (3.23).

Decachloropyrene: 245* (3.90); 258* (4.00); 268* (4.20); 279* (4.40); 291.5 (4.55); 305 (4.42); 319.5 (4.38); 345* (3.88); 363* (4.14) and 376.5 (4.25).

---

[13] W. L. Mosby, *J. Org. Chem.*, **19**, 294 (1954).

RESEARCH DIVISION
AMERICAN CYANAMID COMPANY
BOUND BROOK, NEW JERSEY

The Reaction of Methanol with 3-Methylphthalic Anhydride

BY NORMAN RABJOHN AND H. H. FARMER[1]

RECEIVED SEPTEMBER 27, 1954

We have had occasion to examine the reaction of methanol with 3-methylphthalic anhydride and have found that a mixture of the isomeric half-esters is produced. The 1- and 2-methyl acid esters appear to be formed in the ratio of about 59 to 41%, respectively.

These results are in conflict with the work of Hayashi, *et al.*,[2] who state that 3-methylphthalic anhydride and methanol give the 1-methyl ester of melting point 114.5–115°. They also obtained this same material from the reaction of 3-methylphthalic acid with methanol in the presence of hydrogen chloride. Since Hayashi, *et al.*,[2] did not report analytical data on their compound, it appears that they mistook 3-methylphthalic anhydride for the 1-methyl ester. The former melts at 114–115° and is formed readily from the mixture of the 1- and 2-methyl esters upon drying. Hayashi, *et al.*,[2] stated that the original product of the reaction of 3-methylphthalic anhydride and methanol melted at 74–89° which corresponds closely with the properties of the mixture of half-esters which we isolated.

We determined the percentages of the isomeric half-esters in the mixture by converting them to the mixture of silver salts and decarboxylating to give a mixture of methyl *o*-toluate and methyl *m*-toluate. This was hydrolyzed to a mixture of *o*- and *m*-toluic acids which melted at 65–85°. Melting point data indicate[3] that the latter mixture was composed of 42% *o*- and 58% of *m*-toluic acid, respectively. The ultraviolet absorption spectra of *o*- and *m*-toluic acid, mixtures of these acids (25:75, 50:50 and 75:25) and of the mixture of acids from the half-esters were determined in cyclohexane solutions. Plots of the molar extinction coefficients for these compositions against the percentage of *o*-toluic acid at various wave lengths indicated the unknown mixture consisted of 41% of *o*- and 59% of *m*-toluic acid.

The yields of methyl *o*- and *m*-toluate obtained on decarboxylation of the mixture of the silver salts of the half-esters was low and it is recognized that the proportion of *o*- and *m*-toluic acids may not correspond quantitatively to those of the half-esters. However, the results agree quite well with the findings of Newman and Muth,[4] who have shown that 3-methylphthalic anhydride reacts with aromatic hydrocarbons in the presence of aluminum chloride, or Grignard reagents to give mixtures of products corresponding to attack at either the 1- or 2-carbonyl group of the anhydride.

Experimental[5]

3-Methylphthalic Anhydride.—3-Methyl-1,2,3,6-tetrahydrophthalic anhydride was prepared according to the method of Frank, Emmic and Johnson[6] and dehydrogenated by the procedure of Newman and McCleary[7] to the desired anhydride, m.p. 114–115°.

Reaction of 3-Methylphthalic Anhydride with Methanol.—A mixture of 12 g. (0.074 mole) of 3-methylphthalic anhydride and 3.6 g. (0.11 mole) of methanol was heated to reflux for 3 hours. The crystalline mass, which was obtained upon cooling, was air-dried and recrystallized from 500 ml. of hot petroleum ether (b.p. 60–68°). There was obtained 9 g. of a white solid which melted at 74–84° after four recrystallizations.

Anal. Calcd. for $C_{10}H_{10}O_4$: C, 61.84; H, 5.19; neut. equiv., 194. Found: C, 62.11; H, 5.30; neut. equiv., 192.

Conversion of the Half-esters to a Mixture of *o*- and *m*-Toluic Acids.—The mixture of half-esters from the previous experiment was treated with an ammoniacal silver nitrate solution to give a mixture of the silver salts. Three grams of the latter was placed in a test-tube which was equipped with a short glass tube leading to a gas trap immersed in a Dry Ice–acetone mixture. The silver salts were decomposed by heating cautiously with a bunsen burner. From the material which deposited in the trap, there was obtained 0.6 g. of 3-methylphthalic anhydride (m.p. 113–115°) and a small amount of a liquid. The latter was dis-

---

[1] Abstracted in part from the M.A. thesis of H. H. Farmer.

[2] M. Hayashi, S. Tsuruoka, I. Morikawa and H. Namikawa, *Bull. Chem. Soc. Japan*, **11**, 184 (1936).

[3] H. Lettre, H. Barneck, W. Fuhst and F. Hardt, *Ber.*, **70**, 1410 (1937).

[4] M. S. Newman and C. W. Muth, THIS JOURNAL, **72**, 5191 (1950).

[5] All melting points are uncorrected. The authors are indebted to P. D. Strickler and R. E. Bolin for the semi-micro carbon and hydrogen analyses.

[6] R. L. Frank, R. D. Emmic and R. S. Johnson, THIS JOURNAL, **69**, 2315 (1947). The authors would like to thank R. L. Frank for supplying the needed piperylene.

[7] M. S. Newman and C. D. McCleary, *ibid.*, **63**, 1542 (1941).