In agreement with this postulate, it has been found that optically active nitrate esters are converted by either hydrazine or ammonium sulfide to optically active alcohols with a high degree of retention of configuration.

Cristol, *et al.*,[4] demonstrated by hydrogenolysis that (+)-2-octyl nitrate and (+)-2-octanol have the same configuration, and, further, that alkaline hydrolysis of (+)-2-octyl nitrate gave 2-octanol with some retention of configuration, but with considerable racemization. It has been found in this Laboratory that (+)-2-octyl nitrate reacts with hydrazine at room temperature to give (+)-2-octanol having 84% of the activity of the alcohol from which the nitrate was prepared, and that the (−)-nitrate is converted by ammonium polysulfide to (−)-alcohol with 99% of the original activity. The high degree of retention of configuration shows that the nitrogen–oxygen bond is cleaved rather than the alkyl–oxygen bond, although this evidence does not distinguish between the two modes of nucleophilic attack[2] (*i.e.*, at the alkoxy oxygen or at nitrogen) which would lead to heterolysis of this bond. However, the formal positive charge on the nitrogen atom makes it a more likely site for nucleophilic attack than the oxygen atom.

The reduction of *trans*-1,2-cyclohexanediol dinitrate with hydrazine gave only the *trans*-glycol, while only the *cis*-glycol could be isolated from the ammonium sulfide reduction of the *cis*-dinitrate. These results indicate that, in both types of reduction, O–N cleavage occurs in both nitrate groups.

Experimental

The optically active 2-octanols, resolved by the method of Kenyon,[5] were converted to the nitrates with mixed acid, according to the procedure of Shriner and Parker.[6] *cis*- and *trans*-cyclohexanediol dinitrates were prepared by the reaction of the respective glycols in chloroform solution with mixed nitric and sulfuric acids at −5 to −10°.[7]

Optical rotations were measured with a Rudolph high-precision polarimeter, using the pure liquids in 1-dm. tubes, except where noted otherwise. Infrared spectra were run on a Perkin–Elmer model 21 instrument.

Reductions of 2-Octyl Nitrate. A. With Hydrazine.—Two milliliters (1.90 g., 0.011 mole) of (+)-2-octyl nitrate, $[\alpha]^{25}_{\mathrm{D}}$ +17.51°, prepared from (+)-2-octanol having $[\alpha]^{25}_{\mathrm{D}}$ +9.63°, was mixed with 5 ml. of 95% hydrazine and just enough ethanol to make the mixture homogeneous. Gas evolution and yellowing of the solution began at once. After standing at room temperature for 6 days, no further gassing was visible. The ethanol was removed by distillation at reduced pressure, and the two layers of the residual liquid were separated. The top layer was dissolved in ether and washed with dilute hydrochloric acid and with water, and the ether solution was dried over sodium sulfate. On evaporation of the ether, there remained 1.20 g. (0.0075 mole) of (+)-2-octanol, $[\alpha]^{25}_{\mathrm{D}}$ +8.11°. This was characterized by comparison of its infrared absorption spectrum with that of authentic 2-octanol, and with that of the nitrate.

B. With Ammonium Sulfide.—Two grams (0.0114 mole) of (−)-2-octyl nitrate, prepared from (−)-2-octanol having $[\alpha]^{25}_{\mathrm{D}}$ −8.54°, was treated with 5 ml. of commercial 20% ammonium sulfide solution (containing 5–6% free sulfur) and 10 ml. of ethanol. The mixture became very red after four hours, and then became lighter as sulfur precipitated out. After 3 days the sulfur was filtered and the pale yellow filtrate extracted with ether and the extract dried with sodium sulfate. The ether and ethanol were distilled off, leaving 1.5 g. of a reddish-yellow oil which smelled strongly of 2-octanol. Distillation yielded 0.4 g. (0.003 mole) of (−)-2-octanol. This was made up to 5 ml. with ethanol and placed in a 4-dm. polarimeter tube. This gave α^{25}_{D} −2.70°, $[\alpha]^{25}_{\mathrm{D}}$ −8.44°. The product obtained from the *dl*-nitrate in similar, larger-scale runs was characterized as 2-octanol by its infrared spectrum.

Reductions of Cyclohexanediol Dinitrates. A. *trans*-Dinitrate with Hydrazine.—Two and one-half grams (0.012 mole) of *trans*-1,2-cyclohexanediol dinitrate and 5 ml. of 95% hydrazine were allowed to stand together at room temperature with occasional shaking. After two days, when the mixture was homogeneous and no more gas evolution was observed, the mixture was distilled until all of the hydrazine was removed. The residual yellow oil was crystallized to an oily solid by freezing with Dry Ice. When sucked dry on a sintered glass disk, it weighed 0.5 g. and melted at 93–94°. A mixed m.p. with authentic *trans*-1,2-cyclohexanediol, m.p. 103–104°, was not depressed but a mixed m.p. with the *cis* isomer showed considerable depression. Recrystallization of the crude product from ethyl acetate gave 0.4 g. (0.0035 mole) of pure *trans*-1,2-cyclohexanediol, m.p. and mixed m.p., 103–104°. No *cis*-glycol was found.

B. *cis*-Dinitrate with Ammonium Sulfide.—Two and one-half grams (0.012 mole) of *cis*-1,2-cyclohexanediol dinitrate, 10 ml. of ammonium sulfide solution and 10 ml. of ethanol were allowed to stand for 24 hours. The precipitated sulfur was filtered, and the ethanol was removed from the filtrate by distillation. The remaining aqueous solution was extracted with five 10-ml. portions of chloroform. On evaporation of the solvent, the extract yielded a mass of yellowish-white crystals from which, by recrystallization from carbon tetrachloride, was obtained 0.6 g. (0.005 mole) of *cis*-1,2-cyclohexanediol, m.p. 93–94°. A mixed m.p. with the authentic *cis*-glycol, m.p. 97°, was 95–96°, and with authentic *trans*-glycol was 76–77°. There was also obtained a trace of solid melting at 84–85° which was apparently mainly *cis*-glycol, as a mixed m.p. with *trans*-glycol was depressed but a mixed m.p. with pure *cis* was not depressed.

The infrared spectrum of the product melting at 93–94° was identical with that of the authentic *cis* glycol.

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[4] S. J. Cristol, A. Shadan and B. Franzus, Abstracts of Papers, 125th National Meeting of the American Chemical Society, Kansas City, Mo., Spring, 1954, p. 20N.

[5] J. Kenyon in H. Gilman and A. H. Blatt, "Organic Syntheses," Coll. Vol. I, 2nd Edition, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 418.

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Reactions of Vanillin and Its Derived Compounds. XXIV.[1] Some Ethers of Vanillin and Vanillic Acid[2]

BY IRWIN A. PEARL

RECEIVED AUGUST 30, 1954

In connection with other studies in our laboratories a number of aliphatic ethers of vanillin and vanillic acid were required. A literature search indicated that many of the ethers of vanillin had been prepared, but only the methyl, ethyl and *n*-propyl

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[1] For paper XXIII of this series, see THIS JOURNAL, **76**, 3635 (1954).

[2] The results reported here are from a research program at this Institute, sponsored by the Sulphite Pulp Manufacturers' Research League; acknowledgment is made for their permission to publish these results.

TABLE I

ETHERS OF VANILLIN

Ether	Yield, %	M.p., °C.	B.p., °C.	B.p., Mm.	$n^{25}\text{D}$	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.

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

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

The Ultraviolet Absorption Spectra of Some Highly Chlorinated Aromatic Systems

BY WILLIAM L. MOSBY

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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,

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[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).