TABLE I

NITRILES FROM NITRILE OXIDES[a]

$$R—C\equiv N\rightarrow O\ (I) \longrightarrow R—C\equiv N\ (II)$$

Nitrile oxide I R =	Nitrile II								
	M.p., °C.	Yield, %	Formula	Carbon, %		Hydrogen, %		Nitrogen, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
2,4,6-Trimethylphenyl-[b]	50[c]	98	$C_{10}H_{11}N$	...	...	...	...	9.65	9.56
2,3,5,6-Tetramethylphenyl-[b]	74[d]	91	$C_{11}H_{13}N$	...	...	...	...	8.80	8.81
2,4,6-Trimethoxyphenyl-[b]	143–144[e]	93	$C_{10}H_{11}NO_3$	62.16	61.96	5.74	5.74	7.25	7.28
9-Anthracenyl-[f]	177[g]	98	$C_{15}H_9N$	88.65	88.64	4.46	4.70	6.89	6.81
2,3,5,6-Tetramethylphenylen-1,4[b]	208–209[e,h]	80	$C_{12}H_{12}N_2$	78.22	78.07	6.57	6.52	15.21	15.12

[a] All reductions with trimethyl phosphite, as described in the Experimental section. [b] C. Grundmann and J. M. Dean, *Angew. Chem.*, **76**, 682 (1964); *Angew. Chem., Intern. Ed. Engl.*, **3**, 585 (1964). [c] F. W. Küster and A. Stallberg, *Ann.*, **278**, 212 (1893). [d] O. Jacobsen, *Ber.*, **22**, 1224 (1889). [e] See Experimental section for preparation by another route. [f] Prepared by the procedure described in *b;* yellow needles (from methanol), m.p. 127–128°. *Anal.* Calcd. for $C_{15}H_9NO$: C, 82.19; H, 4.12; N, 6.39; mol. wt., 219. Found: C, 82.39; H, 3.91; N, 6.17; mol. wt., 219. [g] P. Karrer and E. Zeller, *Helv. Chim. Acta*, **2**, 485 (1919). [h] Berl-Block, sealed capillary.

prepared by dehydration of the oxime. The results are summarized in Table I.

This reduction of nitrile oxides to the corresponding nitriles can be of value in establishing the structure, especially in cases where rapid dimerization to the furoxan makes molecular weight determinations difficult. Since, under the applied conditions, the furoxans are reduced no further than to the furazans, the rate of dimerization of a nitrile oxide can be conveniently determined by measuring the consumption of trivalent phosphorus compound by the mixture of nitrile oxide–furoxan,[10] according to eq. 1 and 2.

Experimental[11]

Reduction of Nitrile Oxides to Nitriles.—One millimole of the nitrile oxide was dissolved, if necessary with gentle warming, in 10 ml. of benzene, and 0.4 mmole of trimethyl or triethyl phosphite (practical, Eastman) was added. After heating for 5–10 min. on the steam bath, the reduction was terminated.[12] The cooled reaction mixture was diluted with 10 ml. of benzene, and shaken with 25 ml. of 5% sulfuric acid until the odor of the alkyl phosphite had disappeared. The organic layer was then washed four times with 25 ml. of water each to extract the formed trimethyl or triethyl phosphate and then evaporated *in vacuo* to dryness. The yields of the remaining nitriles are given in Table I, the melting points were generally no more than 1–2° below those given in the table. Except for VI which was purified by vacuum sublimation (110–130° at 0.1 mm) the crude products yielded pure samples by a single recrystallization from methanol or ethanol. **2,4,6-Trimethoxybenzonitrile** (V) and **tetramethylterephthalobisnitrile** (VI) were independently synthesized by refluxing the corresponding oximes with acetic anhydride for 7 hr. From 2,4,6-trimethoxybenzaldoxime,[13] the nitrile V was obtained directly in 92% yield, while tetramethylterephthalodialdoxime (prepared from tetramethylterephthalodialdehyde[14] and hydroxylamine hydrochloride in the usual manner yielding prisms, from ethanol, m.p. 240° dec.) gave a crude product which yielded pure VI only after chromatography from benzene on alumina, followed by vacuum sublimation, 27% (for melting point and analysis of V and VI, see Table I).

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(10) In this case triphenylphosphine is preferred, because of stability towards autoxidation and ease of preparation of an analytically pure standard.

(11) Melting points were determined with the Fisher-Johns melting point apparatus and are uncorrected. Microanalyses are by Galbraith Laboratories, Knoxville, Tenn.

(12) In batches of 0.01 mole and above the reaction becomes quite exothermic and leads to vigorous boiling of the solvent; dropwise addition of the phosphite and a reflux condenser are recommended.

(13) J. Herzig and H. Gehringer, *Monatsh.*, **23**, 868 (1903).

(14) L. A. Mikeksa and D. R. Koennecke, U. S. Patent 2,806,883 (to Esso Research & Engineering Co.) (1958); *Chem. Abstr.*, **52**, 5407*g* (1958).

Optical Rotatory Dispersion of Some Deuterium Compounds[1]

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Many compounds are now known having substantial and useful optical activity due only to hydrogen–deuterium asymmetry. Fickett[3] showed how this optical rotatory power can result from the anharmonicity of the C–H vibrations; *i.e.*, the effective polarizability along a C–D bond differs from that of a C–H bond. According to this theory the optical activity of H–D compounds does not differ in principle from that of normally asymmetric compounds. A corollary is that deuterium compounds should show normal optical rotatory dispersion (O.R.D.).

Little data on this point are available in the literature. The ratio of rotations of 1-butanol-1-*d* and several esters at the mercury green line and the sodium line were reported to be similar to those of other simple alcohols and esters.[4] A recent attempt to measure the O.R.D. curve of cyclopentanone-3-*d* failed when the compound showed insufficient optical activity.[5]

In the course of various studies with optically active deuterium compounds we have had occasion to determine several O.R.D. curves. Earlier measurements were made on a Rudolph photoelectric polarimeter modified with a Beckman monochromator.[6] Rotations on this instrument were taken at selected wave lengths from 650 mμ down to just below 400 mμ. The long path lengths required precluded accurate work at shorter wave lengths. More recently, a number of samples were examined with a Cary 60 recording spectropolarimeter. This instrument has allowed us to measure directly the O.R.D. curves of several deu-

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(1) Stereochemistry of the Primary Carbon. XIV. Paper XIII: A. Streitwieser, Jr., and L. Reif, *J. Am. Chem. Soc.*, **86**, 1988 (1964). This work was supported in part by grants from the Petroleum Research Fund of the American Chemical Society and by the National Science Foundation.

(2) (a) U. S. Public Health Service Postdoctoral Fellow, 1963–1964; (b) National Science Foundation Predoctoral Fellow, 1957–1958.

(3) W. Fickett, *J. Am. Chem. Soc.*, **74**, 4204 (1952).

(4) A. Streitwieser, Jr., *ibid.*, **77**, 1117 (1955).

(5) C. Djerassi and B. Tursch, *ibid.*, **83**, 4609 (1961).

(6) Rudolph spectropolarimeter, Model S-80, O. Rudolph and Sons, Caldwell, N. J.

terated compounds well into the ultraviolet. On its most sensitive mode the Cary 60 has a precision of ±0.0002°. Measurements were again taken neat. Zero readings were obtained using the corresponding undeuterated and inactive compounds. The instrument was checked by comparison of the O.R.D. of 2-butanol with that reported by Lowry and Allsopp.[7]

The data for each compound were fitted to a single-term Drude equation by a plot of $1/\alpha$ *vs.* λ^2 using values read from the O.R.D. curves at 10-mμ intervals. In general, excellent linear plots resulted from which λ_0 could be obtained by extrapolation. In the example shown in Figure 1 a slight tailing is evident at low wave lengths. In Table I are summarized the experimental values of α at a few wave lengths and the derived values of λ_0.

Table I

Compd.	λ_0, mμ	Obsd. rotation, α, in deg.[a] 589 mμ	500 mμ	400 mμ	300 mμ
1-Propanol-1-*d*[b]	205	0.0097	0.0154	0.0262	0.0593
1-Butanol-1-*d*[c]	200	−0.0164	−0.0234	−0.0423	−0.0935
Methyl 1-propyl-1-*d* xanthate[b]	268	−0.0727	−0.1140	...	...
1-Butyl-1-*d* acetate[d,e]	190	0.071	0.104	0.180	...
Benzyl alcohol-α-*d*[f]	245	0.0254	0.0384	0.0736	0.1960[g]
Ethylbenzene-α-*d*[h]	248	0.0462	0.0698	0.1365	0.4350
Benzylamine-α-*d*[i]	263	0.0066	0.0102	0.0208	0.0603[g]
1-Phenylbutane-1-*d*[d,j]	250	−0.103	−0.180	−0.366	...

[a] Rotations were measured on the Cary 60 on the neat liquids at 26° using a 0.1-dm. quartz cell except where noted otherwise. [b] Prepared by V. Sarich (unpublished results) by reduction of propionaldehyde by isobornyloxymagnesium-2-*d* bromide. [c] Older work using a sample prepared by Andreades [A. Streitwieser, Jr., and S. Andreades, *J. Am. Chem. Soc.*, **80**, 6553 (1958)] agreed with that using a different recent preparation of Verbit [A. Streitwieser, Jr., L. Verbit, and R. Bittman, to be published; see Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, p. 50N]. [d] The Rudolf polarimeter was used. [e] Prepared by Andreades[c]; 2-dm. tube. [f] Prepared by Wolfe [A. Streitwieser, Jr., and J. R. Wolfe, Jr., *J. Am. Chem. Soc.*, **79**, 903 (1957)]. [g] At 310 mμ. [h] Prepared by Reif [A. Streitwieser, Jr., and L. Reif, *ibid.*, **86**, 1988 (1964)]. [i] Prepared by Wolfe [A. Streitwieser, Jr., and J. R. Wolfe, Jr., *J. Org. Chem.*, **28**, 3263 (1963)]. [j] A. Streitwieser, Jr., J. R. Wolfe, Jr., and W. D. Schaeffer, *Tetrahedron*, **6**, 338 (1959); 1-dm. tube. A graph of $1/\alpha$ *vs.* λ^2 gave a curve. An approximate extrapolation was made using a few points at the lowest wave lengths.

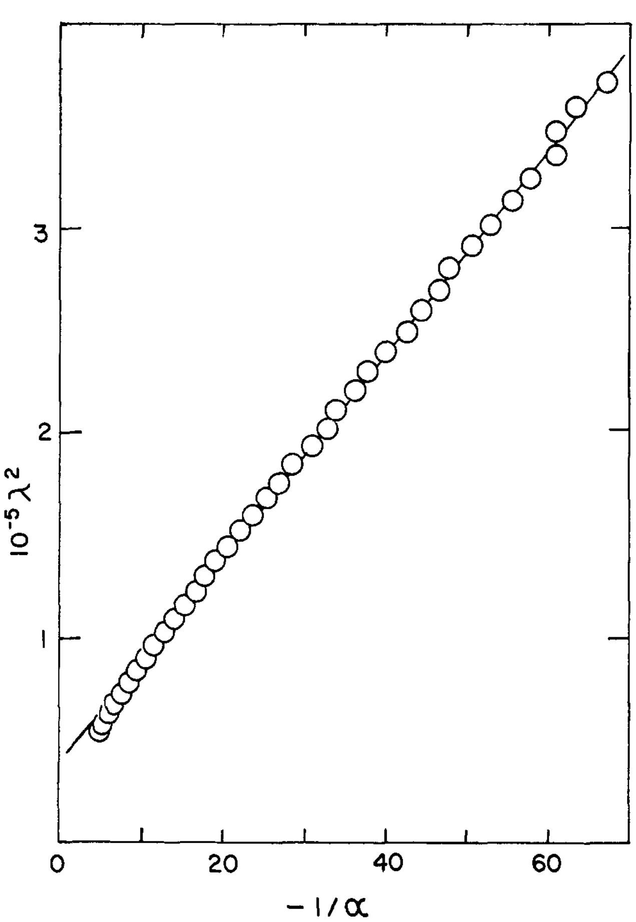

Figure 1.—Drude plot for (−)-1-butanol-1-*d*.

The λ_0 parameter should correspond to the wave length of the nearest optically active absorption band, but only approximate agreement may be expected in cases such as ours in which only a single-term Drude equation is used.[8] For 1-butanol-1-*d* and 1-propanol-1-*d*, the λ_0 values of about 200 mμ are substantially higher than the λ_0 values of 157[9] and 154[10] mμ obtained for 2-butanol and 2-octanol, respectively, but are close to an absorption band at 185 mμ in primary alcohols.[11] The aromatic compounds all show λ_0 of approximately 250 mμ. For comparison, 2-phenylbutane has λ_0 = 233 mμ.[12] In other examples it has been shown that the aromatic ring may function as an optically active chromophore.[13]

The results of the present work confirm the point of view that deuterium behaves as an ordinary substituent so far as optical activity is concerned.

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[7] T. M. Lowry and C. B. Allsopp, *Proc. Roy. Soc.* (London), **A146**, 313 (1934).

[8] See the discussion by W. Heller, "Technique of Organic Chemistry," Vol. I, Part III, A. Weissberger, Ed., 3rd Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 2319 ff.

[9] Obtained with the Cary 60 instrument in the present work.

[10] Calculated from the data of T. M. Lowry and E. M. Richards, [*J. Chem. Soc.*, 1593 (1924)].

[11] A. J. Harrison, B. J. Cederholm, and M. A. Terwilliger, *J. Chem. Phys.*, **30**, 355 (1959).

[12] Calculated from the data of P. W. Benson, J. Kenyon, and J. R. Shepherd [*J. Chem. Soc.*, 658 (1926)].

[13] E. W. Foltz, A. E. Lippman, and C. Djerassi, *J. Am. Chem. Soc.*, **77**, 4359 (1955); G. G. Lyle, *J. Org. Chem.*, **25**, 1779 (1960); L. Verbit, unpublished results.

Tetra-O-methylscutellarein in Orange Peel

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Tangeretin (5,6,7,8,4′-pentamethoxyflavone),[1,2] nobiletin (5,6,7,8,3′,4′-hexamethoxyflavone),[3,4] 3,5,6,7,8,-

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[1] E. K. Nelson, *J. Am. Chem. Soc.*, **56**, 1392 (1934).

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