line product which melted at 92–94° which corresponds to the melting point of ethyl 3,5-dinitrobenzoate.

In another run, the Grignard reagent was prepared from 33.4 g. (0.2 mole) of γ-ethoxypropyl bromide, 4.8 g. (0.2 gram atom) of magnesium turnings and 80 ml. of anhydrous ether. The reagent was refluxed for one hour, and only a trace of liquid was condensed in the cooling trap.

Forty milliliters of ether was removed by distillation from the reaction mixture and 50 ml. of dry benzene was added to give approximately the original volume. An additional 28 ml. of solvent was distilled, 50 ml. of dry benzene was added and 22 ml. more of solvent was removed. The Grignard reagent was stirred and then refluxed for one hour. At this point, 8 ml. of distillate had collected in the cooling trap; 4 ml. of this material boiled below 0° and it was removed. The mixture was refluxed for another two hours and an additional 3 ml. of a liquid was obtained which boiled below 0°. The reaction mixture was treated with 18.34 g. (0.1 mole) of anhydrous cadmium chloride and heated at reflux for one hour. Only a trace of low boiling liquid was collected.

The low boiling material (7 ml.) was allowed to distil into a mixture of 50 ml. of carbon tetrachloride, 6.1 g. of bromine and 1 ml. of water which was contained in a 100-ml. pressure bottle. After standing at room temperature for 36 hours, the mixture was poured into a sodium bisulfite solution. The organic layer was separated, washed with water, dried over calcium chloride and concentrated. The residue was distilled to give 4 g. of material which boiled at 59–63° (20 mm.), 162–164° (746 mm.), $n^{19}{}_{\mathrm{D}}$ 1.5198, $d^{35}{}_{4}$ 1.97. The following physical properties are recorded for trimethylene dibromide: b.p. 165°, $n^{15}{}_{\mathrm{D}}$ 1.5249, $d^{17}{}_{\mathrm{D}}$ 1.9736.

Reaction of 11-Bromohendecanoyl Chloride with the Supposed Di-(γ-phenoxypropyl)-cadmium.—A mixture of 2.27 g. (0.094 gram atom) of magnesium turnings and 15 ml. of anhydrous ether was treated, under nitrogen, with a solution of 20.0 g. (0.094 mole) of γ-phenoxypropyl bromide in 50 ml. of anhydrous ether. It was observed that a gas was being evolved during this period. To the reaction mixture was added 7.25 g. (0.049 mole) of anhydrous cadmium chloride and the ether then was removed by distillation and replaced with 50 ml. of dry benzene. The mixture was refluxed for an additional hour.

A solution of 22.6 g. (0.08 mole) of 11-bromohendecanoyl chloride in 20 ml. of dry benzene was introduced over a period of 25 minutes. The reaction mixture was heated to reflux for two hours and then decomposed with dilute sulfuric acid. The benzene layer was washed with water, 5% sodium carbonate solution and dried over anhydrous sodium sulfate. The sodium carbonate extracts were acidified and yielded only a trace of an oily material.

The benzene solution was concentrated and the residual oil was distilled *in vacuo*. A fraction was obtained at approximately 50° (0.5 mm.) which solidified in the receiver and appeared to be phenol. A sample of this material was treated with bromine and 2,4,6-tribromophenol resulted, m.p. 93–94°. A higher boiling fraction (10.5 g.) was collected from the distillation at 206–207° (1 mm.). It solidified upon cooling below room temperature and was recrystallized from petroleum ether (b.p. 28–38°). The compound crystallized in the form of leaflets which melted at 23–24°.

Anal. Calcd. for $C_{17}H_{25}OBr$: C, 59.82; H, 7.38. Found: C, 60.06; H, 7.67.

This compound was shown to be phenyl 11-bromohendecanoate.

A 2-g. sample of the ester was hydrolyzed by boiling it with a 10% solution of hydrochloric acid in Cellosolve for six hours. There was obtained 0.2 g. of 11-bromohendecanoic acid, m.p. 40–42°. This was converted to the corresponding amide which melted at 83–85° and did not depress the melting point of an authentic sample of 11-bromohendecanamide.

Hydrolysis of 7.7 g. of the phenyl ester by means of aqueous alcoholic sodium hydroxide gave phenol, identified as 2,4,6-tribromophenol, and 5.1 g. of 11-phenoxyhendecanoic acid, m.p. 74.5–75.5° (from dilute alcohol), neut. equiv. 278.

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Note on the Ultraviolet Absorption Spectra of Some *p*-Substituted D-*threo*-2-Dichloroacetamido-1-phenyl-1,3-propanediols

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In the course of another investigation[1] the absorption spectra of two *p*-substituted D-*threo*-2-dichloroacetamido-1-phenyl-1,3-propanediols were studied in 95% ethanol, water, 0.01 *N* hydrochloric acid and 0.01 *N* sodium hydroxide solutions and compared with the spectra of chloramphenicol.[2] The effects of changing the solvent are very small, the spectra of each compound remaining essentially the same when determined in any of the above solvents (*cf.* Table I) indicating absence of prototropic rearrangements.

The spectra of the 4-nitro-,[2] 4-methylmercapto- and the 4-methylsulfonyl-substituted compounds in water are shown in Fig. 1. The less electrophilic methylmercapto group causes an expected hypsochromic shift when it is substituted for the $-NO_2$ group of chloramphenicol while the sulfone group

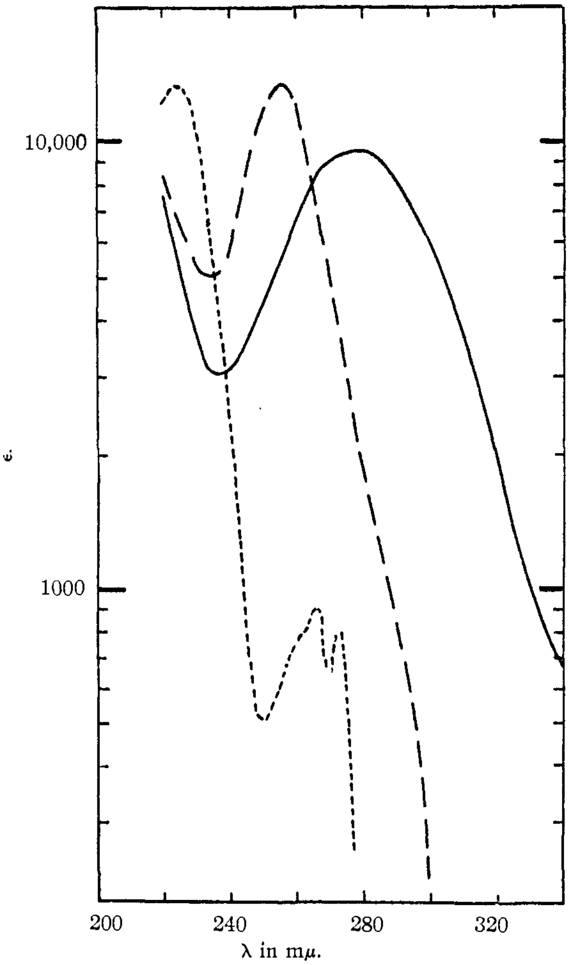

Fig. 1.—Absorption spectra of: —, *p*-NO_2-C_6H_4-R; ---, *p*-CH_3S-C_6H_4-R; ...., *p*-CH_3SO_2-C_6H_4-R in H_2O. R = D-*threo*-2-dichloroacetamido-1,3-propanediol.

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[1] R. A. Cutler, R. J. Stenger and C. M. Suter, THIS JOURNAL, **74**, 5475 (1952).

[2] M. C. Rebstock, H. M. Crooks, Jr., J. Controulis and Q. R. Bartz, *ibid.*, **71**, 2458 (1949).

Table I

Ultraviolet Absorption Spectra of *p*-Substituted D-*threo*-2-Dichloroacetamido-1-phenyl-1,3-propanediols in Different Solvents

Compound	95% EtOH λ	95% EtOH $\epsilon \times 10^{-3}$	H_2O λ	H_2O $\epsilon \times 10^{-3}$	0.01 *N* HCl λ	0.01 *N* HCl $\epsilon \times 10^{-3}$	0.01 *N* NaOH λ	0.01 *N* NaOH $\epsilon \times 10^{-3}$
D-*threo*-2-Dichloroacetamido-(4-nitrophenyl)-1,3-propanediol	274	9.8	278	9.5	279	9.2	279	9.2
D-*threo*-2-Dichloroacetamido-(4-methylmercapto)-1,3-propanediol	258	13.1	256	13.2	255	13.1	256	13.2
D-*threo*-2-Dichloroacetamido-(4-methylsulfonyl)-1,3-propanediol	224	13.7	224	13.4	224	13.3	224	13.2
	266	0.8	266	0.9	266	0.9	266	0.95
	274	0.7	274	0.8	274	0.8	274	0.8

produces a further hypsochromic shift with the appearance of a "memory" of the benzene envelope. As would be expected, the spectra of these latter two compounds approximate quite closely those obtained for thioanisole[3] and methyl phenyl sulfone,[4] respectively. However in the latter case the D-*threo*-2-dichloroacetamido-1,3-propanediol portion of the molecule quenches the benzene resonance to a slight degree and only a shoulder at 260 mμ and a doublet at 266 and 274 mμ are now in appearance. The successive hypsochromic shifts for $-SMe$ and $-SO_2Me$ indicate decreased resonance interaction between the nucleus and the *p*-substituent as the original planarity of chloramphenicol with the *p*-NO_2 group planar to the aromatic ring is destroyed.

The spectra were determined with a Cary recording instrument, slit schedule 20, dynode voltage 4, and 1-cm. quartz cells. The assistance of Mrs. M. Becker is gratefully acknowledged.

(3) E. A. Fehnel and M. Carmack, This Journal, **71**, 2889 (1949).

(4) E. A. Fehnel and M. Carmack, *ibid.*, **71**, 231 (1949); *cf.* E. A. Fehnel and M. Carmack, *ibid.*, **72**, 1292 (1950).

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The Ultraviolet-induced Isomerization of Tiglic Acid to Angelic Acid

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Tiglic acid (I) and angelic acid (II) are the *trans*- and *cis*-modifications of 2-methyl-2-butenoic acid.[2] Although tiglic acid is usually considered as a *cis*-isomer, it has a higher melting point, a lower heat of combustion and a lower acid dissociation constant than angelic acid. It is also the less heat labile of the two isomers.

I
m.p. 65°
627 kcal./mole
$K_a = 9.6 \times 10^{-6}$

II
m.p. 45°
635 kcal./mole
$K_a = 50 \times 10^{-6}$

Because of the unusual relationship between the steric configurations and the physical properties of these isomers it was of interest to investigate the possibility of converting tiglic acid (I) to angelic acid (II) by ultraviolet irradiation. It has been reported that no detectable isomerization occurred when an aqueous solution of tiglic acid was exposed to sunlight for 75 days.[3] We have found, however, that irradiation of tiglic acid does effect a partial inversion to angelic acid. From the semi-liquid mixture which resulted from irradiating a 13-g. sample of powdered tiglic acid for 43 days there was obtained 8.2 g. of tiglic acid, 0.36 g. of angelic acid and 1.5 g. of what appeared to be a mixture of tiglic and angelic acids. The angelic acid was isolated from the irradiated mixture by a fractional crystallization of the calcium salts.

For this study, it was desirable to have suitable derivatives available for differentiating tiglic and angelic acids. None of those described is entirely satisfactory either because of the difficulty of preparation (*e.g.*, the anilide of angelic acid[4]) or because the melting point difference is too small. The *p*-phenylphenacyl esters were readily prepared in good yields and found to possess suitable melting points.

Experimental

Irradiation of Tiglic Acid.—Samples of powdered tiglic acid in quartz test-tubes were exposed to the direct rays of a 500-watt Hanovia ultraviolet lamp until almost completely liquefied. After such exposure, the irradiated material was dark brown and evidently contained some polymeric material. The neutralization equivalent obtained on a sample which had been irradiated 50 hours agreed with the theoretical value calculated for $C_5H_8O_2$ and indicated no appreciable decarboxylation had occurred.

Isolation of Angelic Acid from Irradiated Mixture.—A 13-g. sample of tiglic acid which had been irradiated 43 days was refrigerated several hours and the tiglic acid (m.p. 63–65°, 3.6 g.) which separated was washed with light petroleum ether. All mother liquors were combined, treated with Norite and diluted with an equal volume of petroleum ether. After cooling, oily crystals separated which yielded another 1.13 g. of tiglic acid when recrystallized. Two repetitions of the process of dilution of the mother liquors with petroleum ether, followed by cooling and recrystallization of the solid which separated, furnished an additional 3.4 g. of tiglic acid, m.p. 63–65°. When further processing failed to yield any more tiglic acid, the solvent was removed *in vacuo*. A brown oil remained which melted below room temperature. This material was dissolved in 10% potassium carbonate and decolorized with Norite. The filtrate was freed of non-acidic impurities by extraction with chloroform

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(1) The Rockefeller Institute for Medical Research, New York 21, N. Y.

(2) Notwithstanding Pfeiffer's conclusive body of evidence (*Z. physik. Chem.*, **48**, 58 (1904)) supporting the above configurations and also the evidence of Sudborough and Davies (*J. Chem. Soc.*, **95**, 976 (1909)), Auwers and Wissebach (*Ber.*, **56**, 723 (1923)), and Hey (*J. Chem. Soc.*, 2321 (1928)), some contemporary textbooks of organic chemistry still assign the old and incorrect Wislicenus configurations (*Ann.*, **250**, 224 (1889)) to these acids, *e.g.*, G. Wittig, "Stereochemie," Akademische Verlagsgesellschaft, Leipzig, 1934, pp. 134–135, and P. Karrer, "Organic Chemistry," 4th English Edition, Elsevier Publ. Co., Inc., New York, 1950, p. 208.

(3) B. K. Malaviya and S. Dutt, *Proc. Acad. Sci. United Provinces Agra Oudh, India*, **4**, 319 (1935); *C. A.*, **30**, 1056[6] (1936).

(4) E. Blaise and P. Bagard, *Ann. chim.*, [8] **11**, 119 (1907).