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 ε × 10⁻³	H_2O λ	H_2O ε × 10⁻³	0.01 *N* HCl λ	0.01 *N* HCl ε × 10⁻³	0.01 *N* NaOH λ	0.01 *N* NaOH ε × 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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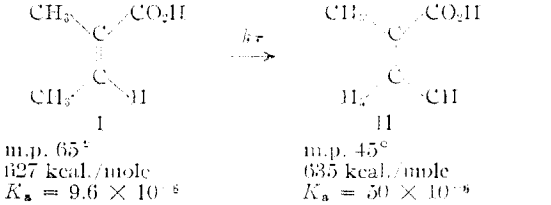
Tiglic acid (I) and angelic acid (II) are the *trans*- and *cis*-modifications of 2-methyl-2-butenoic acid.[2] Although tiglic acid is usually considered as a *cis*-isomer, it has a higher melting point, a lower heat of



I — m.p. 65°; 827 kcal./mole; $K_a = 9.6 \times 10^{-5}$

II — m.p. 45°; 635 kcal./mole; $K_a = 50 \times 10^{-5}$

combustion and a lower acid dissociation constant than angelic acid. It is also the less heat labile of the two isomers.

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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(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)), Anwers and Wisebach (*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**, 1056⁸ (1936).

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

(A); the aqueous phase was acidified to *p*H 1 with 1:1 sulfuric acid and then extracted with four 20-ml. portions of chloroform. The chloroform extracts were washed with water, dried and evaporated *in vacuo* to give 3.66 g. of a yellow oil (B). Evaporation of the solvent from A yielded 2 mg. of an oil with a terpene odor.

Separation of B *via* the Calcium Salts.—B was suspended in 30 ml. of water and treated with 1.37 g. of calcium hydroxide. Vigorous shaking and warming caused a solid to separate from the reaction mixture. After the mixture was diluted with an equal volume of ethanol and heated, most of the solid dissolved. The solution was filtered to remove excess calcium hydroxide, concentrated and the first crop of crystals (C, 0.72 g.) collected. The mother liquor was concentrated to dryness and the residue recrystallized from the minimum of hot 90% ethanol to give 2.0 g. of crystals (D). Dilution of the mother liquor with a large volume of acetone precipitated 1.1 g. of white powder (E). The mother liquors from E were discarded.

C was suspended in water, acidified with 1:1 hydrochloric acid and the solution extracted with chloroform. The extracts were washed, dried and the solvent removed *in vacuo*. The partially crystalline residue was recrystallized from petroleum ether to give 95 mg. of tiglic acid. The mother liquor (F) was reserved.

When D was treated as described for A and the acid residue crystallized from light petroleum ether, 359 mg. of large, flat, lustrous plates separated; m.p. 42–43°. Recrystallization furnished pure angelic acid (II) melting at 44–45.2°. The mother liquors (G) were combined and reserved.

Anal. Calcd. for $C_5H_8O_2$: C, 59.99; H, 8.06. Found: C, 60.12; H, 8.00.

***p*-Phenylphenacyl Angelate (III).**—Angelic acid (187 mg. from D) and *p*-phenylphenacyl bromide (515 mg.) were allowed to react according to the usual procedure.[5] The yellow solid which separated (540 mg.) was decolorized with Norite and recrystallized three times from ethanol to give 200 mg. of beautiful, silver-white leaflets of pure *p*-phenylphenacyl angelate, m.p. 89.0–90.5°.

Anal. Calcd. for $C_{19}H_{18}O_3$: C, 77.54; H, 6.16. Found: C, 77.68; H, 6.22.

***p*-Phenylphenacyl Tiglate (IV).**—Tiglic acid (280 mg.) and *p*-phenylphenacyl bromide (770 mg.) were allowed to react according to the procedure described for III. When processed as described, the reaction mixture yielded large, thin, white leaflets of pure *p*-phenylphenacyl tiglate (456 mg., m.p. 105–106°).

Anal. Calcd. for $C_{19}H_{18}O_3$: C, 77.54; H, 6.16. Found: C, 77.79; H, 6.22.

A 50-50 mixture of the *p*-phenylphenacyl esters of angelic and tiglic acids exhibited a large melting point depression, m.p. 75–84°.

When E was dissolved in water and processed as described for C, 25 mg. of tiglic acid resulted. The mother liquor (H) was combined with F and G and the solvent removed *in vacuo*. The liquid residue (1.54 g.) crystallized when cooled to 0°, but remelted at room temperature. It had an odor characteristic of tiglic or angelic acid and consisted presumably of a mixture of unresolved tiglic and angelic acids.

(5) N. L. Drake and J. P. Sweeney, THIS JOURNAL, **54**, 2059 (1932).

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3-Phenylpyridine[1]

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3-Phenylpyridine has been prepared by a large variety of methods, some of which give only the 3-isomer, but most of which result in a mixture of 2-, 3- and 4-phenylpyridines. In the former group are the procedures involving rearrangement, with ring expansion, of an α- or N-substituted pyrrole.[2-4] The conditions are drastic, the yields are very poor, and the method is of little if any preparative value.[4] Also in this group is the first reported synthesis of 3-phenylpyridine, accomplished from β-naphthoquinoline by oxidation to a dicarboxylic acid and decarboxylation by alkaline fusion,[5] a procedure which is quite lengthy and also gives very poor yields.

The methods which result in mixtures of 2-, 3- and 4-phenylpyridines frequently also give poor yields and suffer from the fact that tedious fractional crystallization of a salt, usually the picrate, is necessary in order to obtain a pure isomer. Variations of the Gomberg (or diazo) reaction in which the decomposition and nitrogen elimination are carried out in pyridine solution have been commonly used. Diazotized *p*-nitroaniline[6] (with subsequent replacement of the nitro group), diazotized aniline,[7] N-nitrosoacetanilide[8] and 3,3-dimethyl-1-phenyltriazene[9] have all been decomposed in pyridine to give the three isomeric phenylpyridines. Similar results are obtained when diphenyliodonium chloride,[10] benzoyl peroxide,[11] or phenylazotriphenylmethane[12] are heated in pyridine.

An obvious alternative which would eliminate the isomer problem would be to use the corresponding aminopyridine derivative and decompose in benzene. This has been tried with 2-aminopyridine but failed due to the difficulty of diazotizing an α-amino group and the inability to nitrosate the N-acetyl derivative,[8] a result which parallels the experience with *o*- and *p*-nitroacetanilide.[13] However, since 3-aminopyridine behaves as an ordinary aromatic amine,[14] there was good reason to believe it could be used for introducing the 3-pyridyl group through some modification of the diazo reaction. 3-Aminoquinoline,[12,15] several 3-amino-chloropyridines[12] and 3-amino-2-*n*-butoxypyridine[12] have been successfully converted to the corresponding 3-phenyl compounds, indicating that 3-aminopyridine itself could be used if the operational difficulties could be overcome.

Although N-(3-pyridyl)-acetamide was easily nitrosated, the high water solubility of the product made it difficult to extract and hence unsuitable. 3,3-Dimethyl-1-(3′-pyridyl)-triazene was readily prepared and in good yield, but it proved to be much too stable, being recovered unchanged from refluxing benzene in the presence of glacial acetic acid or dry hydrogen chloride. An alternative was

(1) Presented in part before the Division of Organic Chemistry, American Chemical Society, Atlantic City, N. J., September 15, 1952.

(2) G. Ciamician and P. Silber, *Ber.*, **20**, 191 (1887).

(3) A. Pictet, *ibid.*, **38**, 1946 (1905).

(4) E. R. Alexander, A. B. Herrick and T. M. Roder, THIS JOURNAL, **72**, 2760 (1950).

(5) Zd. H. Skraup and A. Cobenzl, *Monatsh.*, **4**, 456 (1883).

(6) R. Forsyth and F. L. Pyman, *J. Chem. Soc.*, 2912 (1926).

(7) J. W. Haworth, I. M. Heilbron and D. H. Hey, *ibid.*, 349 (1940).

(8) J. W. Haworth, I. M. Heilbron and D. H. Hey, *ibid.*, 372 (1940).

(9) J. Elks and D. H. Hey, *ibid.*, 441 (1943).

(10) R. B. Sandin and R. K. Brown, THIS JOURNAL, **69**, 2253 (1947).

(11) D. H. Hey and E. W. Walker, *J. Chem. Soc.*, 2213 (1948).

(12) W. J. Adams, D. H. Hey, P. Mamalis and R. E. Parker, *ibid.*, 3181 (1949).

(13) J. W. Haworth and D. H. Hey, *ibid.*, 361 (1940).

(14) E. A. Steck and G. W. Ewing, THIS JOURNAL, **70**, 3397 (1948).

(15) H. Coates, A. H. Cook, I. M. Heilbron, D. H. Hey, A. Lambert and F. B. Lewis, *J. Chem. Soc.*, 401 (1943).