solvent on a flash evaporator. This procedure gave an 85% yield of white crystals, m.p. 219–220° dec. Two crystallizations from ethanol–ethyl acetate gave an analytical sample, m.p. 221–222° dec.

Anal. Calcd. for $C_{11}H_{26}ClNO$: C, 59.03; H, 11.71; N, 6.26. Found: C, 58.90; H, 11.73; N, 6.12.

2-Methyl-2,3-bis(dimethylamino)butane.—A mixture of 15.9 g. (0.085 mole) of 3-dimethylamino-3-methyl-2-chlorobutane hydrochloride and 60 g. (0.53 mole) of 40% aqueous dimethylamine was shaken mechanically for 16 hr. The mixture was then warmed to 50° for 1 hr. after which the temperature was raised to 80° and maintained for 1 hr. The resulting mixture was treated with 8.4 g. (0.21 mole) of sodium hydroxide pellets, then extracted with three 15-ml. portions of ether. The ether extracts were combined and dried with anhydrous potassium carbonate. Distillation from glass wool through a 50-cm. Vigreux column gave 10.1 g. (75% yield) of colorless oil, b.p. 95° (54 mm.), n^{20}D 1.4482. Redistillation gave an analytical sample, b.p. 93° (52 mm.), n^{20}D 1.4482.

Anal. Calcd. for $C_9H_{22}N_2$: C, 68.29; H, 14.01; N, 17.70. Found: C, 68.28; H, 14.20; N, 17.3 (average).

The **methiodide** was precipitated from an ethyl acetate solution of the amine and had m.p. 155°. Attempts to crystallize the sample from ethanol plus ethyl acetate resulted in partial decomposition.

# Optically Active Amines. IV. The Dissymmetric Chromophore in the N-Salicylidene Derivatives of α- and β-Arylalkylamines[1]

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The degradative conversion of (+)-α-phenylneopentylamine to D-α-benzamido-β,β-dimethylbutyric acid definitively establishes the (R) configuration for this amine. This supports the suggestion made earlier that for the N-salicylidene derivatives of α- and β-arylalkylamines, a dissymmetric chromophore, arising from the interaction of the aryl group and the salicylidenimino moiety, is responsible for the observed Cotton effect near 315 mμ in their optical rotatory dispersion curves. In addition, an assessment of the steric requirements for this interaction is now possible. As borne out by optical rotatory dispersion and circular dichroism measurements with (S)-(−)-N-salicylidene-α,β-diphenylethylamine, consideration of these requirements may allow the assignment of the absolute configuration of an optically active α- or β-arylalkylamine from the sign of the Cotton effect near 315 mμ in the optical rotatory dispersion curve of its N-salicylidene derivative.

In the two previous papers in this series,[1b,2] the optical rotatory dispersion curves of a number of N-salicylidene-α- and -β-arylalkylamines (Ia–h) were reported. With the exception of Ih, these Schiff bases in ethanol
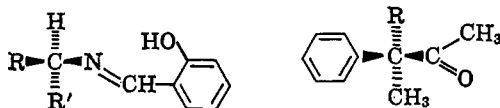
(S)-(+)-Ia, R = 1-$C_{10}H_7$; R′ = CH_3
(S)-(+)-Ib, R = C_6H_5; R′ = CH_3
(R)-(−)-Ic, R = C_2H_5; R′ = C_6H_5
(R)-(−)-Id, R = $CH_2CO_2C_2H_5$; R′ = C_6H_5
(R)-(−)-Ie, R = $C(CH_3)_3$; R′ = C_6H_5
(S)-(+)-If, R = $C_6H_5CH_2$; R′ = CH_3
L-(−)-Ig, R = CO_2CH_3; R′ = p-$HOC_6H_4CH_2$
(S)-(−)-Ih, R = C_6H_5; R′ = $C_6H_5CH_2$

(S)-(+)-IIa, R = H
(R)-(−)-IIb, R = C_2H_5

display Cotton effects near 410 and 315 mμ. With dioxane or hexane as the solvent, only the Cotton effect near 315 mμ was observed, usually enhanced in amplitude. On the basis of a comparison of these curves with those of the N-salicylidene derivatives of (S)-(+)-sec-butylamine and a number of optically active aliphatic α-amino acid esters, for which no complete Cotton effect could be observed, it was suggested that, for the α- and β-arylalkylamine derivatives, the

relatively strong Cotton effects may be due to a dissymmetric chromophore.[3] The latter is thought to arise from an interaction of the π-electrons of the aryl group and the salicylidenimino moiety. It was also suggested that this interaction may be analogous to that between the carbon–carbon π-electrons and the carbonyl group in an optically active β,γ-unsaturated or α-phenyl ketone[4] (II) which sometimes results in a Cotton effect near 300 mμ of much greater amplitude than those displayed by saturated analogs.

For these unsaturated ketones, the rotatory power depends principally on the spatial arrangement of the interacting carbon–carbon double bonds with respect to the carbonyl group. The conformational arrangements for which the interactions arise have been discussed in detail.[4a,b,d] For (S)-(+)-3-phenyl-2-butanone (IIa), the Cotton effect near 300 mμ is positive,[4b] whereas, for (R)-(−)-3-phenyl-3-methyl-2-pentanone (IIb), the effect is negative,[4b] the sign and the amplitude depending on the relative effective size of the R group in II with respect to that of methyl.

For the N-salicylidene derivative of an optically active α-arylalkylamine such as Ia–e, it was suggested that a similar analysis may allow a correlation between its absolute configuration and its rotatory dispersion

(1) (a) Presented at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, Abstracts of Papers, p. 21P. (b) Paper III: M. E. Warren, Jr., and H. E. Smith, *J. Am. Chem. Soc.*, **87**, 1757 (1965).

(2) H. E. Smith, S. L. Cook, and M. E. Warren, Jr., *J. Org. Chem.*, **29**, 2265 (1964).

(3) A. Moscowitz, *Tetrahedron*, **13**, 48 (1961).

(4) (a) R. C. Cookson and J. Hudec, *J. Chem. Soc.*, 429 (1962); (b) A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 1945 (1962); (c) K. Mislow and J. G. Berger, *ibid.*, **84**, 1956 (1962); (d) K. Mislow, *Ann. N. Y. Acad. Sci.*, **93**, 459 (1962); (e) S. F. Mason, *J. Chem. Soc.*, 3285 (1962); *Mol. Phys.*, **5**, 343 (1962).

curve, the sign of the Cotton effect near 315 mμ[5] being dependent on the absolute configuration and not on the relative effective size of the alkyl group. For (S)-(+)-N-salicylidene-α-phenylethylamine[7] (Ib), the Cotton effect is positive,[2] and, for that of (R)-(−)-ethyl N-salicylidene-β-aminohydrocinnamate[9] (Id), it is negative.[1b] Since it is also negative for the N-salicylidene derivative of (+)-α-phenylneopentylamine (Ie),[1b] the (R) configuration was also assigned to this amine, even though an assessment of the effective sizes[10] of the groups attached to the asymmetric center in these derivatives suggests that the preferred conformation of the latter is different from that of the other two.

With the same considerations, the (R) configuration was also assigned to (+)-α-phenyl-n-propylamine and the (S) configuration to (−)-α-(1-naphthyl)-ethylamine.[11] These latter assignments, however, can be made without consideration of a dissymmetric chromophore. Consideration of the effective sizes of the groups attached to the asymmetric centers in Ia–d[10] indicated that for each the conformer composition is similar. It is also reasonable to expect that, for the same configuration, these derivatives should display similar optical rotatory dispersion curves each with a Cotton effect near 315 mμ of the same sign.

We now wish to report degradative work which definitively establishes the (R) configuration for (+)-α-phenylneopentylamine and supports the conclusion that a dissymmetric chromophore is present in the N-salicylidene derivatives of optically active α- and β-arylalkylamines.

Results

Establishment of the (R) configuration for (+)-α-phenylneopentylamine (III) follows from its stepwise conversion to D-α-benzamido-β,β-dimethylbutyric acid[12] (VI) (cf. Chart I[13]) by an ozonolysis procedure.[14] The absolute configuration of the amino acid has been previously established[12] as a result of the action of hog renal amidase on the racemic amide, that isomer preferentially hydrolyzed being assigned the L configuration.[15]

(5) For a N-salicylidene derivative in ethanol, dioxane, or hexane, the absorption band near 315 mμ is attributed to an intramolecularly hydrogen-bonded form of I.[6] In ethanol or dioxane, the band at longer wave length which is very weak or absent in hexane has been assigned to a tautomeric form[6b] or to intermolecularly hydrogen-bonded complexes between the derivative and the solvent.[6a,6c] It has been recently concluded that for these latter complexes the intramolecular hydrogen bond is not present.[6c]

(6) (a) J. Hires and L. Hackl, Acta Univ. Szeged. Acta Phys. Chem., 5, 19 (1959); (b) D. Heinert and A. E. Martell, J. Am. Chem. Soc., 85, 183, 188 (1963); (c) J. Charette, G. Faltlhansl, and Ph. Teyssie, Spectrochim. Acta, 20, 597 (1964).

(7) Prepared[8] from (S)-(−)-α-phenylethylamine. Absolute configuration: W. Leithe, Ber., 64, 2827 (1931).

(8) A. P. Terent'ev and V. M. Potapov, Zh. Obshch. Khim., 28, 1161 (1958).

(9) Prepared[1b] from (R)-(+)-ethyl β-aminohydrocinnamate. Absolute configuration: R. Lukes, J. Kovar, J. Kloubek, and K. Blaha, Collection Czech. Chem. Commun., 23, 1367 (1958).

(10) (a) S. Winstein and N. J. Holness, J. Am. Chem. Soc., 77, 5562 (1955); (b) B. J. Armitage, G. W. Kenner, M. J. T. Robinson, Tetrahedron, 20, 747 (1964); (c) W. F. Reynolds and T. Schaefer, Can. J. Chem., 42, 2119 (1964).

(11) This assignment is a confirmation of that recently made [H. Wolf, E. Bunnenberg, and C. Djerassi, Ber., 97, 533 (1964)] on the basis of the rotatory dispersion curve of the N-phthaloyl derivative.

(12) N. Izumiya, S.-C. J. Fu, S. M. Birnbaum, and J. P. Greenstein, J. Biol. Chem., 205, 221 (1953).

(13) In Chart I, rotatory powers refer to those observed with absolute ethanol as the solvent.

(14) H. Arakawa, Naturwiss., 50, 441 (1963).

Chart I

(R)-III, [α]²⁶D +2.5° (R)-IV, [α]²⁸D +77°

D-V, [α]²⁶D +4° D-VI, [α]²⁷D −30°
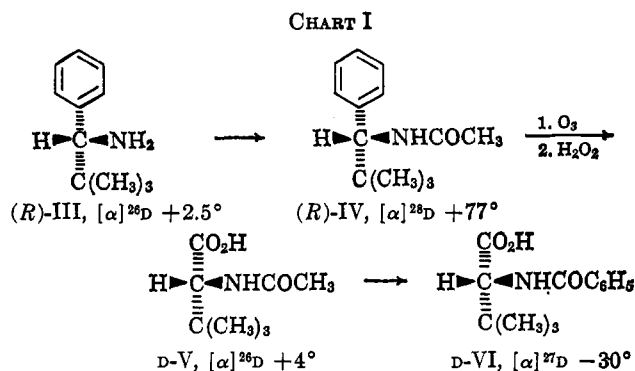
In the present work, (R)-(+)-α-phenylneopentylamine (III) was converted to the corresponding N-acetyl derivative (IV), protection of the amino group being necessary during ozonolysis.[16] Since the rotatory power of neither D- nor L-α-acetamido-β,β-dimethylbutyric acid (V) has been recorded previously and neither the amino acid nor its hydrochloride salt is conveniently purified, the product V from the ozonolysis step was hydrolyzed to the amino acid, and the latter converted directly to the N-benzoyl compound (VI), the rotatory power of which was compared with that reported.[12]

Discussion

The three most stable intramolecularly hydrogen-bonded[5] conformations of a N-salicylidene-α-arylalkylamine are shown for the absolute configuration VII, Ar being a phenyl or a 1-naphthyl group and R an alkyl group. Since hydrogen is smaller
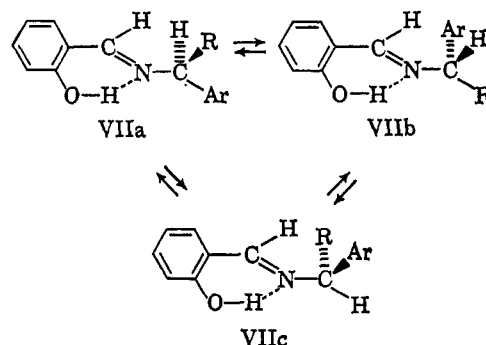
in effective bulk size than both the alkyl and aryl groups, VIIc is of the highest energy. When the alkyl group is methyl or ethyl, smaller than the aryl group,[10c] VIIa is preferred to VIIb. When the alkyl group is t-butyl, larger than the aryl group,[10a] the converse is the case. By analogy to the rotationally significant conformers of an optically active β,γ-unsaturated or α-phenyl ketone,[4b] it is assumed that VIIa is rotationally unimportant and that the sign and magnitude of the Cotton effect near 315 mμ[17] depends on the algebraic sum of the rotatory contributions of VIIb and VIIc, only these conformers having the aryl group and the salicylidenimino moiety properly oriented for rotationally significant interactions. Based on the sign

(15) For a discussion of this method and its reliability, see J. P. Greenstein and M. Winitz, "Chemistry of the Amino Acids," Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1961, p. 1778, and references therein.

(16) W. Strecker and H. Thienemann, Ber., 53, 2096 (1920).

(17) In this discussion the Cotton effect near 410 mμ is not considered since there is some ambiguity as to its origin.[5]

of the Cotton effects displayed by α-arylalkylamine derivatives of certain absolute configurations, Ib[7] and Ie, VIIb is taken to be a positive contributor; VIIc is negative. Since an alkyl group is always larger than hydrogen, VIIb is always preferred to VIIc, and the N-salicylidene derivative of an α-phenyl- or α-(1-naphthyl)alkylamine with the configuration and structure VII will in general display a positive Cotton effect near 315 mμ. For the enantiomorph, the Cotton effect will be negative.

It is to be noted, however, that any prediction concerning the sign of this Cotton effect is limited at the present time to α-phenyl- and α-(1-naphthyl)alkylamine derivatives with a hydrogen attached at the asymmetric center. For an α-arylalkyl amine with two different alkyl groups attached at the asymmetric center, the same considerations may allow a deduction of its configuration, provided that a substantial difference in the effective bulk sizes of the alkyl groups allows a Cotton effect near 315 mμ to be observed. It also appears that, for an amine in which the alkyl group incorporates an alkoxycarbonyl group α to the asymmetric center (Id), a correct correlation is possible. If, however, the alkyl group contains some other chromophoric group, an assessment of its possible interaction with either the aryl or salicylidenimino groups must be made before the shape of its rotatory dispersion curve can be related to its absolute configuration.

For some β-phenylalkylamine derivatives, a similar analysis, restricted to α-benzyl compounds and with the limitations noted above, may be used to predict the sign of the Cotton effect near 315 mμ observed in their optical rotatory dispersion curves. In VII, when the group designated Ar is a benzyl group and R a methyl group, it is found that this compound, (S)-(+)-N-salicylidene-α-benzylethylamine[18] (If), does in fact display a Cotton effect at 315 mμ of the same sign (positive) and comparable in amplitude to that for (S)-(+)-N-salicylidene-α-phenylethylamine.[2] Since the negative Cotton effect at 318 mμ displayed by (−)-methyl N-salicylidene-L-tyrosinate[1b,19] (Ig) is in agreement with the prediction, it may be assumed that an alkoxycarbonyl group attached to the asymmetric center has no rotationally significant interaction with the salicylidenimino group. In both α- and β-arylalkylamine derivatives the alkoxycarbonyl group may be taken to be rotationally similar to an alkyl group.

As borne out for these conclusions, it is to be noted that (S)-(−)-N-salicylidene-α,β-diphenylethylamine[20] (Ih) in ethanol, dioxane, and hexane displays from 600–275 mμ only a plain negative optical rotatory dispersion curve,[1b] the rotatory contributions of the conformers of Ih (VIII) cancelling one another. When circular dichroism measurements[21] were made with this Schiff

VIIIa ⇌ VIIIb

VIIIc
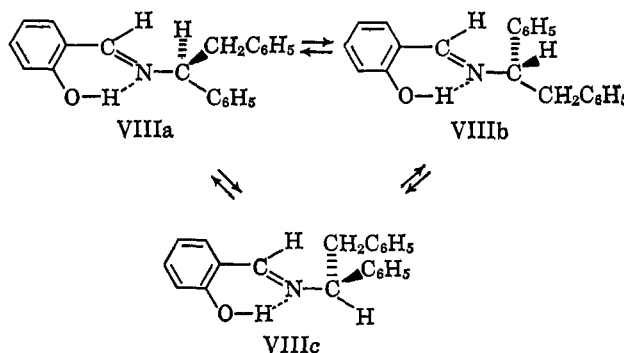
base in EPA[23] at room temperature, only a plain negative curve from 295–270 mμ was observed. On cooling of the sample to −192° the conformational equilibrium is shifted toward VIIIa, the conformer of lowest energy,[10c] and, in agreement with the conclusions outlined above, a negative maximum[24] at 314 mμ ([θ] −5300) was found.

Experiments to assess more accurately the steric requirements for the interaction of an aryl group with a salicylidenimino moiety are now in progress with conformationally more rigid α- and β-arylalkylamine derivatives.

Experimental[25]

(±)-N-Acetyl-α-phenylneopentylamine [(±)-IV].—To 2.29 g. of (±)-α-phenylneopentylamine [(±)-III, 0.0141 mole], b.p. 113–115° (26 mm.), n^{25}D 1.5111, was added 6.32 g. of acetic anhydride (0.0619 mole), and the solution was boiled 20 min. The cooled solution was diluted with water. The acetic acid was neutralized with solid sodium carbonate and the precipitate was collected by filtration. Recrystallization of this solid from ethanol–water gave 2.56 g. of pure (±)-IV (89% yield), white cubes, m.p. 133–134°. Two recrystallizations of the derivative from ethanol–water afforded an analytical sample, m.p. 133–134°.

Anal. Calcd. for $C_{13}H_{19}NO$: C, 76.05; H, 9.33. Found: C, 76.23; H, 8.99.

(R)-(+)-N-Acetyl-α-phenylneopentylamine [(R)-(+)-IV].—Using the procedure outlined above (R)-(+)-α-phenylneopentylamine [(R)-(+)-III], b.p. 105–106° (15 mm.), n^{25}D 1.5111, [α]^{28} D +2.5° (c 7.1), d^{20}_4 0.926, [α]^{20}D +5.2° (neat), was converted to (R)-(+)-IV (89% yield), white cubes on recrystallization from ethanol–water, sublimed without melting at 135° (sealed tube). After sublimation at 100° (0.02 mm.) the derivative had [α]^{28}D +77° (c 2.01) and an infrared spectrum identical with that of (±)-IV.

Anal. Calcd. for $C_{13}H_{19}NO$: C, 76.05; H, 9.33. Found: C, 75.64; H, 9.19.

(±)-α-Acetamido-β,β-dimethylbutyric Acid [(±)-V].—A mixture of dry oxygen–ozone, produced in a standard corona discharge ozonator, was passed for 43 hr. into a solution of 2.14 g. of (±)-N-acetyl-α-phenylneopentylamine [(±)-IV, 0.0104 mole] in 35 ml. of glacial acetic acid at room temperature. To this solution was then added 1.17 g. of 30% hydrogen peroxide (0.0104 mole). After standing at room temperature for 1 hr., the solvent was evaporated at reduced pressure, and on dilution of the pasty residue with water, a yellow solid was precipitated. The solid was collected by filtration and extracted thoroughly with aqueous sodium carbonate. As an insoluble fraction there was obtained

(18) Prepared[2] from (S)-(+)-α-benzylethylamine. Absolute configuration: P. Karrer and K. Ehrhardt, Helv. Chim. Acta, 34, 2202 (1951).

(19) Prepared[1b] from (+)-methyl L-tyrosinate. Absolute configuration: ref. 15, Vol. 1, Chapter 2.

(20) Prepared[1b] from (S)-(+)-α,β-diphenylethylamine. Absolute configuration: P. Pratesi, A. La Manna, and G. Vitali, Farmaco (Pavia), Ed. Sci., 15, 387 (1960).

(21) H. E. Smith and R. Records, unpublished measurements using a Baird-Atomic/Jouan dichrograph operating with a photomultiplier voltage of 1.1 kv., sometimes increased to 1.3 kv. in regions of high absorption, and concentrations such that the slit width was no higher than 1.4 mm. at the circular dichroism maxima and following the procedures[22a] and molecular ellipticity calculations[22b] outlined earlier.

(22) (a) K. M. Wellman, E. Bunnenberg, and C. Djerassi, J. Am. Chem. Soc., 85, 1870 (1963); (b) K. Mislow, E. Bunnenberg, R. Records, K. Wellman, and C. Djerassi, ibid., 85, 1342 (1963).

(23) Ether–isopentane–ethanol mixture in the ratio 5:5:2 by volume.

(24) For circular dichroism nomenclature, see C. Djerassi and E. Bunnenberg, Proc. Chem. Soc., 299 (1963).

(25) Melting points were taken in capillary tubes and are corrected. Boiling points are not corrected. Microanalyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn. Optical rotations were obtained using 1-dm. tubes and, unless otherwise noted, the solvent was absolute ethanol. Infrared spectra were measured with a Perkin-Elmer, Model 137B, spectrophotometer equipped with rock salt optics and using potassium bromide pellets.

0.269 g. of starting material, (±)-IV (12% yield), m.p. 129–131°. The sodium carbonate solution was acidified with hydrochloric acid, and, after complete precipitation, 0.322 g. of crude (±)-V (20% yield), m.p. 227–230°, was collected by filtration. On sublimation of this solid at 130–160° (0.02 mm.) pure (±)-V was obtained, m.p. 234–235°, lit.[26] m.p. 234°.

Anal. Calcd. for C$_8$H$_{15}$NO$_3$: C, 55.73; H, 8.73; N, 8.09; neut. equiv., 173. Found: C, 55.60; H, 8.74; N, 8.04; neut. equiv., 175.

D-(+)-α-**Acetamido-β,β-dimethylbutyric Acid** [D-(+)-V].— Ozonolysis of 0.781 g. of (R)-(+)-N-acetyl-α-phenylneopentyl-amine [(R)-(+)-IV, 3.81 mmoles] in 35 ml. of glacial acetic acid was accomplished as outlined above except that the reaction time was reduced to 35 hr. No unreacted starting material was isolated, and the crude product, D-(+)-V (13% yield), sublimed without melting at 190° (sealed tube), was sublimed at 140–150° (0.02 mm.). Pure D-(+)-V had [α]^{26}D +4° (c 2.06) and an infrared spectrum identical with that of (±)-V.

Anal. Calcd. for C$_8$H$_{15}$NO$_3$: C, 55.73; H, 8.73; N, 8.09; neut. equiv., 173. Found: C, 55.61; H, 8.80; N, 8.30; neut. equiv., 170.

(±)-α-**Benzamido-β,β-dimethylbutyric Acid** [(±)-VI].—A suspension of 0.739 g. of (±)-α-acetamido-β,β-dimethylbutyric acid [(±)-V, 4.27 mmoles] in 20 ml. of 10% hydrochloric acid was boiled for 4 hr. The solvent was then removed at reduced pressure leaving 0.638 g. of a pale yellow solid. To 0.108 g. of this solid (0.647 mmole) in 4 equiv. of 1 N sodium hydroxide was added 0.083 g. of benzoyl chloride (0.54 mmole) over a period of

(26) F. Knoop and N. Okada, *Arch. ges. Physiol.*, **201**, 3 (1923).

30 min. while stirring and cooling in an ice bath. The mixture was stirred for an additional 30 min. at room temperature and then washed with ether. The aqueous solution was acidified with hydrochloric acid and the precipitate was collected by filtration. Recrystallization of this material from ethanol–water gave 0.061 g. of pure (±)-VI [40% yield based on (±)-V], white plates, m.p. 164–165° (ethanol–water), lit.[12] m.p. 165°. The infrared spectrum of the derivative was identical with that of an authentic sample, m.p. 164–165°, prepared from racemic α-amino-β,β-dimethylbutyric acid, sublimed without melting at 240° (sealed tube), obtained from Nutritional Biochemical Co., Cleveland, Ohio.

Anal. Calcd. for C$_{13}$H$_{17}$NO$_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.11; H, 7.30; N, 5.79.

D-(−)-α-**Benzamido-β,β-dimethylbutyric Acid** [D-(−)-VI].— D-(+)-α-acetamido-β,β-dimethylbutyric acid [D-(+)-V] was hydrolyzed and the N-benzoyl derivative was prepared as outlined above. The pure product, D-(−)-VI (33% yield), crystallized with 1 mole of water, m.p. 103–105° (ethanol–water), lit.[12] m.p. 105° for the L isomer. After drying at 78° (1 mm.) for 15 hr. the sample lost the water of crystallization and had m.p. 150–151°, [α]^{27}D −30° (c 1.98), and an infrared spectrum identical with that of (±)-VI; lit.[12] m.p. 151°, [α]^{25}D +26.2° (c 3) for the L isomer.

Anal. Calcd. for C$_{13}$H$_{17}$NO$_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.40; H, 7.16; N, 5.97.

Chemistry of Dichloromaleimides. I. The Reaction of Dichloromaleimides with Tertiary Amines in Hydroxylic Solvents

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The reaction of N-substituted 2,3-dichloromaleimides with tertiary amines in hydroxylic solvents has been found to give N-(N-substituted 2-oxy-3-maleimidyl)ammonium betaines. A reaction path is postulated.

The reaction of 2,3-dichloro-1,4-naphthoquinone (I) with amines has received considerable study. Compound I reacts with primary amines to give 2-amino-3-chloro-1,4-naphthoquinones[2] (III) (see Scheme I). Of further interest is the interaction of I with pyridine in an alcohol or acetic acid, discovered by Ullmann and Ettisch[3] and later extended by Truitt,[4] to give the pyridinium compound II. The reaction of the structurally related dihalomaleimides with amines, on the other hand, has received little study. Dichloromaleimides (IV) react with primary amines to give 2-amino-3-chloromaleimides (V)[5] and with tertiary arylamines, in the presence of sodium cyanide, to give 4-(2-cyano-3-maleimidyl)arylamines.[6]

It was of interest to determine whether dichloromaleimides (IV) would react with a tertiary heteroaromatic amine, such as pyridine, in a fashion analogous to I, to give VI. Treatment of IV (R = H, C$_6$H$_5$CH$_2$, and C$_6$H$_5$CH$_2$CH$_2$) with pyridine in methanol or acetic acid gave yellow solids whose analyses cor-

SCHEME I

Z = tertiary amine
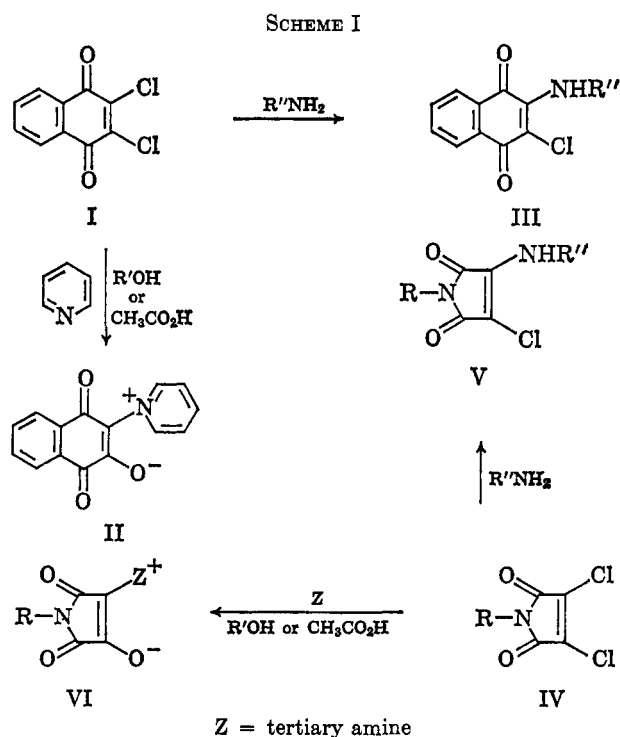
responded to compounds 2, 3, and 4, respectively, in Table I. The absence of halogen was confirmed by a

(1) (a) Author to whom inquires should be addressed. (b) Deceased.

(2) A. Plagemann, *Chem. Ber.*, **15**, 484 (1882).

(3) F. Ullmann and M. Ettisch, *ibid.*, **54B**, 259 (1921).

(4) P. Truitt, F. Mahon, O. Platas, R. L. Hall, and T. Eris, *J. Org. Chem.*, **25**, 962 (1960).

(5) G. Ciamician and P. Silber, *Chem. Ber.*, **22**, 33, 2490 (1889).

(6) E. L. Martin, C. L. Dickinson, and J. R. Roland, *J. Org. Chem.*, **26**, 2032 (1961).