

It has thus been proved for the first time with the complexes (1) and (2) that the EDA-CT band in EDA complexes with an optically active component can develop circular dichroism and contribute to optical activity.

As stated above, the optically active part of a charge transfer is extremely small. Accordingly, this effect could not be detected with another EDA complex, (+)-methylcyclohexanone tetracyanoethylene (3), in heptane.

Plain dispersion curves [2] with a superimposed positive Cotton curve were obtained for the EDA complexes of methyl (-)- α -[2,4,5,7-tetranitrofluorenylideneaminoxy]propionate as optically active acceptor with 2-methylnaphthalene (4) or stilbene (5) in benzene and carbazole (6) in dioxan. Methyl(+)- and (-)- α -[2,4,5,7-tetranitrofluorenylideneaminoxy]propionates with anthracene (7) in benzene yielded plain dispersion curves with a superimposed positive or negative Cotton curve, respectively. Circular dichroism could not be observed, within the limits of accuracy, for the EDA complexes (4)–(7). The effect referred to under 1. above, viz. change in the absorption band of the optically active component responsible for the optical activity, comes into play in the case of complexes (4)–(6). This leads to a change in the rotatory dispersion in the appropriate frequency range of the CT band.

As regards complex (7), it is a moot point whether its positive Cotton curve is a result of the effect referred to under 1. above or is due to a partial contribution of the CT band.

While effect 1. is clearly in operation in the case of complexes (4)–(7), it is not noticeable, within the limits of experimental accuracy, for (1)–(3). This may however be explained by the octant rule [2], since tetracyanoethylene lies in one of the planes of symmetry of the carbonyl orbital and should therefore have only a minor effect on the optical activity of the carbonyl band.

Received, January 17th, 1964 [Z 647/481 IE]
German version: Angew. Chem. 76, 228 (1964)

[1] Summary on EDA interaction, cf. G. Briegleb: Elektronen-Donator-Acceptor-Komplexe. Springer, Berlin-Göttingen-Heidelberg 1961.

[2] Definitions and nomenclature, cf. F. S. Mason, Molecular Physics 5, 343 (1962); W. Moffit and A. Moscowitz, J. Chem. Physics 30, 648 (1959); C. Djerassi; Optical Rotatory Dispersion. McGraw-Hill, New York 1960.

[M] is the molecular rotation. The circular dichroism is the difference in the molecular absorption coefficients of left and right circularly polarized light, respectively.

[*] ϵ = decadic extinction coefficient.

μ_m = magnetic dipole-transition moment.

ν_e = electric dipole-transition moment.

[3] The contribution made to rotation by the EDA band is the difference $\Delta[M] = [M_{EDA}] - [M_{opt. act.}]$, where $[M_{EDA}]$ and $[M_{opt. act.}]$ are the [M]-values of the EDA complex and of the pure, optically active component, respectively, within the range of the EDA band. The strength (R) of rotation is the imaginary part of the product of electrical and magnetic charge-transition moments.

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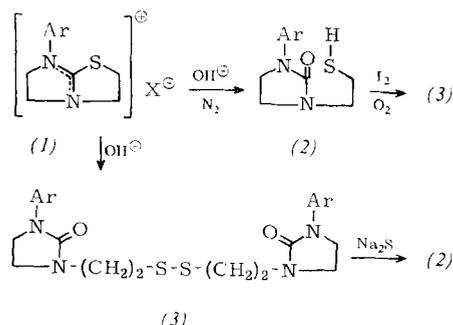
Formation and Behavior of 2,3,5,6-Tetrahydro-7-arylimidazo[2,1-b]thiazolium Salts [1]

By Dr. H. Dorn

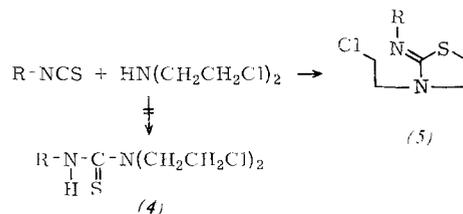
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The bicyclic system imidazo[2,1-b]thiazole [2] and 6,7-dihydro-5H-imidazo[2,1-b]thiazolium salts [3] are accessible from 2-mercaptoimidazole or imidazoline-2-thione and α -halogeno ketones. Aryl isothiocyanates and bis-(β -chloroethyl)amine react in benzene at room temperature to give

2,3,5,6-tetrahydro-7-arylimidazo[2,1-b]thiazolium chlorides, which are convertible into other salts, e.g. (1), Ar = C₆H₅, X = Cl: m.p. 96–97°C [*]; (1), Ar = C₆H₅, X = HSO₄: m.p. 168–169°C; (1), Ar = C₆H₅, X = ClO₄: m.p. 145–146°C. The structure of (1) is supported by the absence of non-ionic chlorine, by C=N absorption in the infrared, and by its degradation reactions. The salts (1) react with a small excess of alkali on contact with air to yield the thiol (2) and, as a by-product, the disulfide (3), e.g. Ar = C₆H₅: m.p. 157°C.



Under nitrogen, however, the only product is 1-(β -mercaptoethyl)-3-arylimidazolid-2-one (2), e.g. Ar = C₆H₅: m.p. 71.5°C, which is oxidized by air or iodine quantitatively to (3). The disulfide (3) is reducible under nitrogen to the thiol (2).



The claim [4] that thioureas (4) arise from isothiocyanates and bis-(β -chloroethyl)amine must be treated with reserve. We succeeded in isolating an intermediate of the bicyclic product (1), viz. the 2-iminothiazolidine derivative (5), R = 2,3,4,6-tetra-*O*-acetyl-1- β -D-glucosyl, and its salts.

Received, January 20th, 1964 [Z 673/497 IE]
German version: Angew. Chem. 76, 301 (1964)

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[2] E. Ochiai, Ber. dtsh. chem. Ges. 69, 1650 (1936); H. Andersog and K. Westphal, Ber. dtsh. chem. Ges. 70, 2044 (1937).

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[*] (1), Ar = C₆H₅, X = Cl, crystallizes with 1 H₂O. On heating to 75–77°C, water is lost and three modifications melting at 96–97°C, 124–125°C and 138–139°C are obtained.

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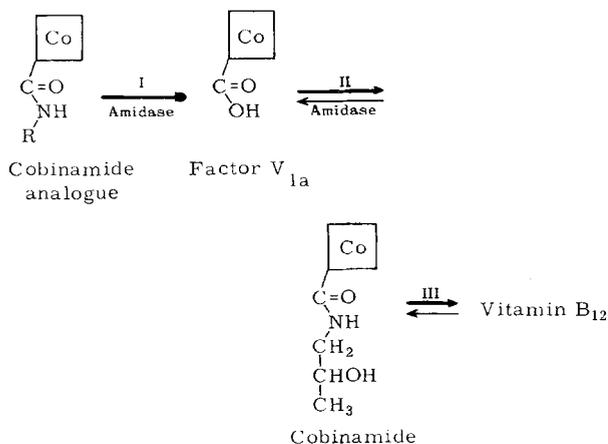
Cleavage of the f-Amide Bond in Cyanocobalamin Analogues by Propionibacterium shermanii

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In the biosynthesis of vitamin B₁₂ analogues [1] by *Propionibacterium shermanii* from cobinamide analogues, whose alkanolamine residues are fluorinated, often practically all the starting material is converted into vitamin B₁₂ if cobalt-free media are used. This is especially noticeable when the alkanolamine residue is 1-amino-2-hydroxy-2-(*o*-fluorophenyl)ethane, 1-amino-2-hydroxy-2-(*p*-fluorophenyl)ethane, or 1-amino-2-hydroxy-3,3,4,4,5,5,5-heptafluoropentane.

P. shermanii obviously produces an amidase, which splits the amide link of the cobinamide analogue giving factor V_{1a} [2] and which then converts this into vitamin B₁₂.



The conversion of factor V_{1a} into cobinamide and vitamin B₁₂ has already been observed [3]. In order to find out whether the amidase can also convert cobinamide into factor V_{1a}, *i.e.* whether Reaction II is reversible, we added factor V_{1a} and [⁶⁰Co]cobinamide to fermentation flasks with *P. shermanii*, and interrupted the experiments at various times. Reversibility of Reaction II should cause factor V_{1a} to become radioactive. The fermentation flasks each contained 7.2 g of corn steep liquor, 10 g of glucose, and ca. 90 ml of tap water. After fermenting for 5 days, 2 mg of factor V_{1a} and 30 nC of [⁶⁰Co]cobinamide were added. After further 12, 24, 36, 48, and 60 h, the fermentation products were worked up; the corrinoids were separated by paper chromatography [4] and their radioactivity measured.

At first the ⁶⁰Co appears principally in the vitamin B₁₂, *i.e.* Reactions II and III go to the right. Later most of the radioactivity appears in factor V_{1a} [5]; this indicates the reversibility of Reactions II and III. The results show moreover that both [⁶⁰Co]cobinamide and [⁶⁰Co]vitamin B₁₂ (and unlabelled factor V_{1a}) can serve as precursors for the production of [⁶⁰Co]factor V_{1a} [6].

Received, January 30th, 1964 [Z 662/494 IE]

Publication deferred until now at the authors' request

German version: *Angew. Chem.* 76, 272 (1964)

[1] For reviews on the chemistry and biochemistry of vitamin B₁₂ and its analogues, see *W. Friedrich and K. Bernhauer* in [4]; *K. Bernhauer, O. Müller, and F. Wagner*, *Angew. Chem.* 75, 1145 (1963); *Angew. Chem. internat. Edit.* 3, 200 (1964); *R. Bonnett*, *Chem. Reviews* 63, 573 (1963).

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[4] *W. Friedrich and K. Bernhauer*, in *K. F. Bauer: Medizinische Grundlagenforschung*. Thieme, Stuttgart 1959, Vol. II, p. 661.

[5] Ca. 10000 counts/min per mg of factor V_{1a}.

[6] Our thanks are due to the Deutsche Forschungsgemeinschaft for supporting the above work and to Dr. *E. E. Gabbe* for the radioactivity measurements.

Differentiation of Primary, Secondary, and Tertiary Alcohols by Near Infrared Spectroscopy

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Primary, secondary, and tertiary alcohols are normally distinguished by infrared spectroscopy on the basis of the vibrational band due to C–O valence vibration, which occurs

near 1050 cm⁻¹ for primary alcohols, near 1100 cm⁻¹ for secondary alcohols, and near 1150 cm⁻¹ for tertiary alcohols [1]. However, since these bands lie in the same region of the spectrum as the vibrational bands of the carbon skeleton of the molecule, their allocation is sometimes difficult. The range from 7000 to 7080 cm⁻¹ has been assigned to the first overtone of the OH valence vibration [2–4], but here primary, secondary, and tertiary alcohols have not previously been differentiated.

Now it was found that primary alcohols absorb in the range from 7090 to 7115 cm⁻¹, secondary alcohols from 7067 to 7078 cm⁻¹, and tertiary alcohols from 7042 to 7053 cm⁻¹, independent of whether the hydroxylated carbon atom is substituted with either methyl or phenyl groups (Table I). The small frequency differences involved demand very careful recording at low speed in the region of the band, in order to pin-point the correct frequency of the band maximum. The exact value of the band maximum has to be read from the frequency counter, otherwise errors of 5–10 cm⁻¹ can occur. The recorded frequencies were measured in 1–5% solution in spectroscopically pure CCl₄. The concentration of the solutions had no effect on the recorded position of the bands.

Table I. Absorption of some alcohols in the near infrared [5].

	Frequency [cm ⁻¹]
<i>Primary alcohols</i>	7090–7115
Methanol	7115
Ethanol	7090
1-Propanol	7095
1-Butanol	7095
1-Pentanol	7095
Isoamyl alcohol	7105
2-(N-Methylamino)ethan-1-ol	7100
2-Amino-2-methylpropanol	7100
<i>Secondary alcohols</i>	7067–7078
2-Propanol	7070
2-Butanol	7075
Cyclohexanol	7075
1-Aminopropanol	7078
Sedamine	7067
Samandarine	7074
Cholesterol	7070
<i>Tertiary alcohols</i>	7042–7053
t-Butanol	7050
Triphenylmethanol	7051
1-Phenylcyclohexanol	7042
1-Phenylcyclopentanol	7043
1-Methyl-1-phenylpropanol	7049
1,1-Dimethylpropanol	7053

Received, February 3rd, 1964 [Z 664/493 IE]

German version: *Angew. Chem.* 76, 271 (1964)

[1] *L. J. Bellamy: The Infrared Spectra of Complex Molecules*. Methuen, London 1958, p. 96.

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[5] Perkin-Elmer Model 125.

Pyrolysis of Benzyl Azide in the Gas Phase

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The thermal decomposition of azides is significantly affected by the solvent [1]. We have investigated the pyrolysis of benzyl azide (1) in the gas phase at 360°C/0.1 mm with nitrogen as diluent, and have so far succeeded in isolating by chromatography, *N*-benzylideneaniline (2), m. p. 53 to