

BIO-ANORGANH
XHMEIA
(Γ)

1926 Έκχυλισματά από κυκλώζι φιλαν



1948

Κρύσταλλοι κατάλληλοι για X-ray ανάλυση

1956

Προσδιορισμός δομής

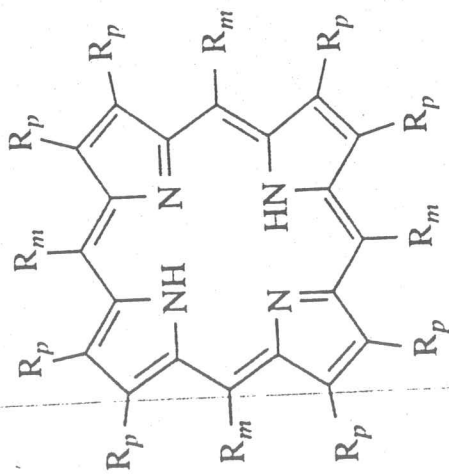
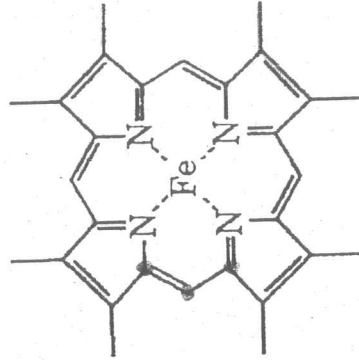


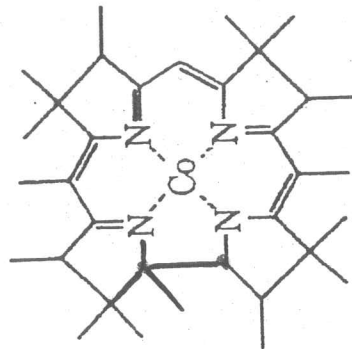
FIGURE 22.2
 The porphyrin skeleton. Note that there are two main types of substituents—those on the pyrrole rings (R_p) and those in the intermediate, meso, positions (R_m). The parent nucleus, porphine, corresponds to $R_p = R_m = H$.



Μη χηρόμορφα
 κέντρα



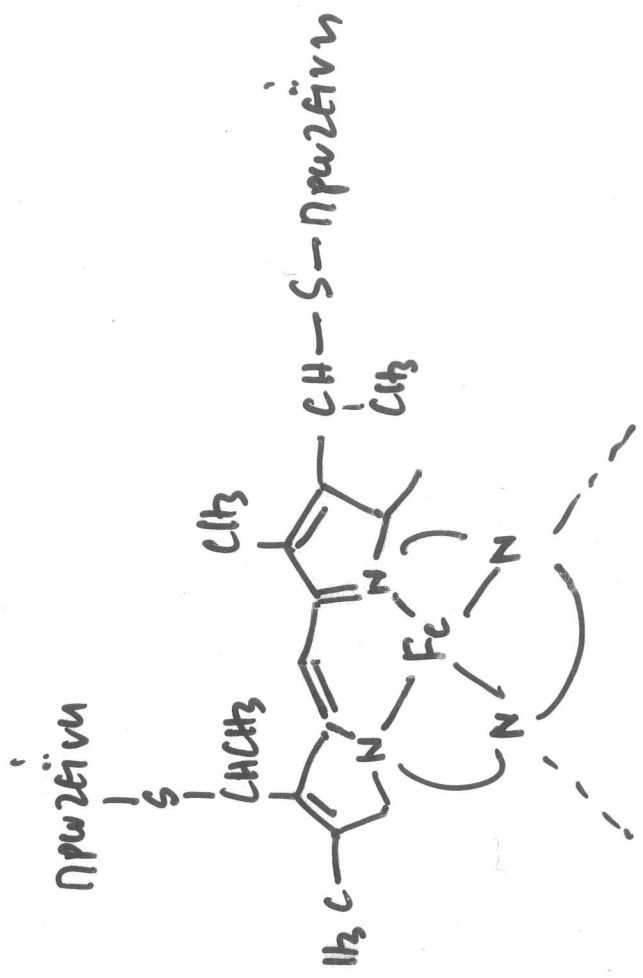
Porphyrin (16 μm)



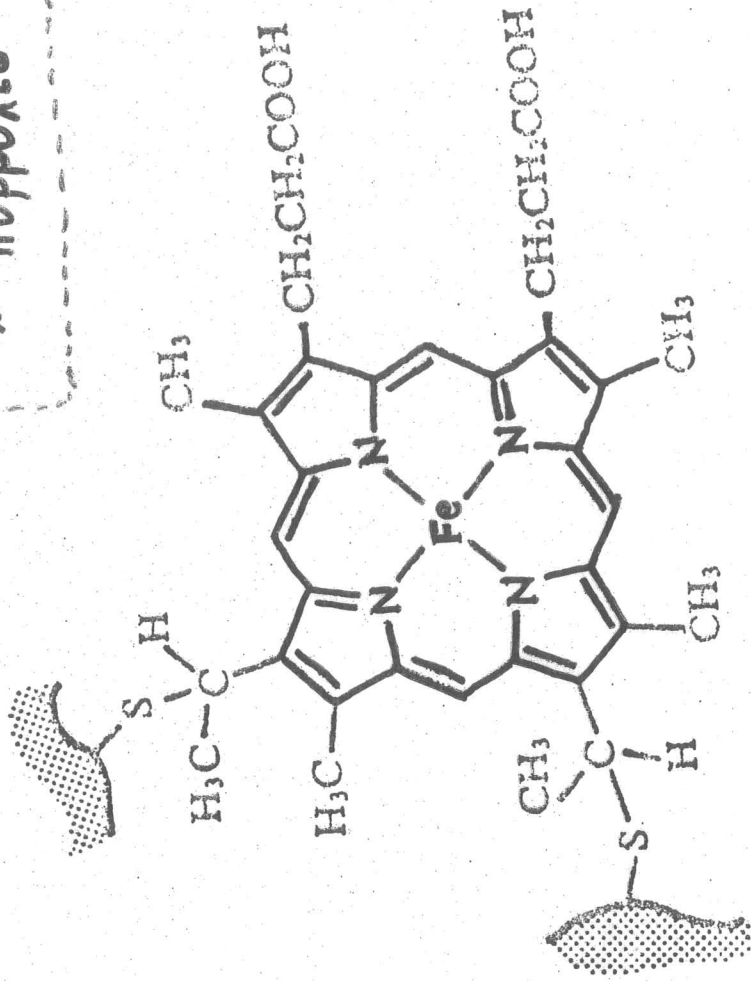
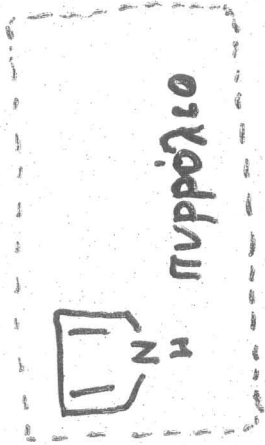
Corrin (15 μm)

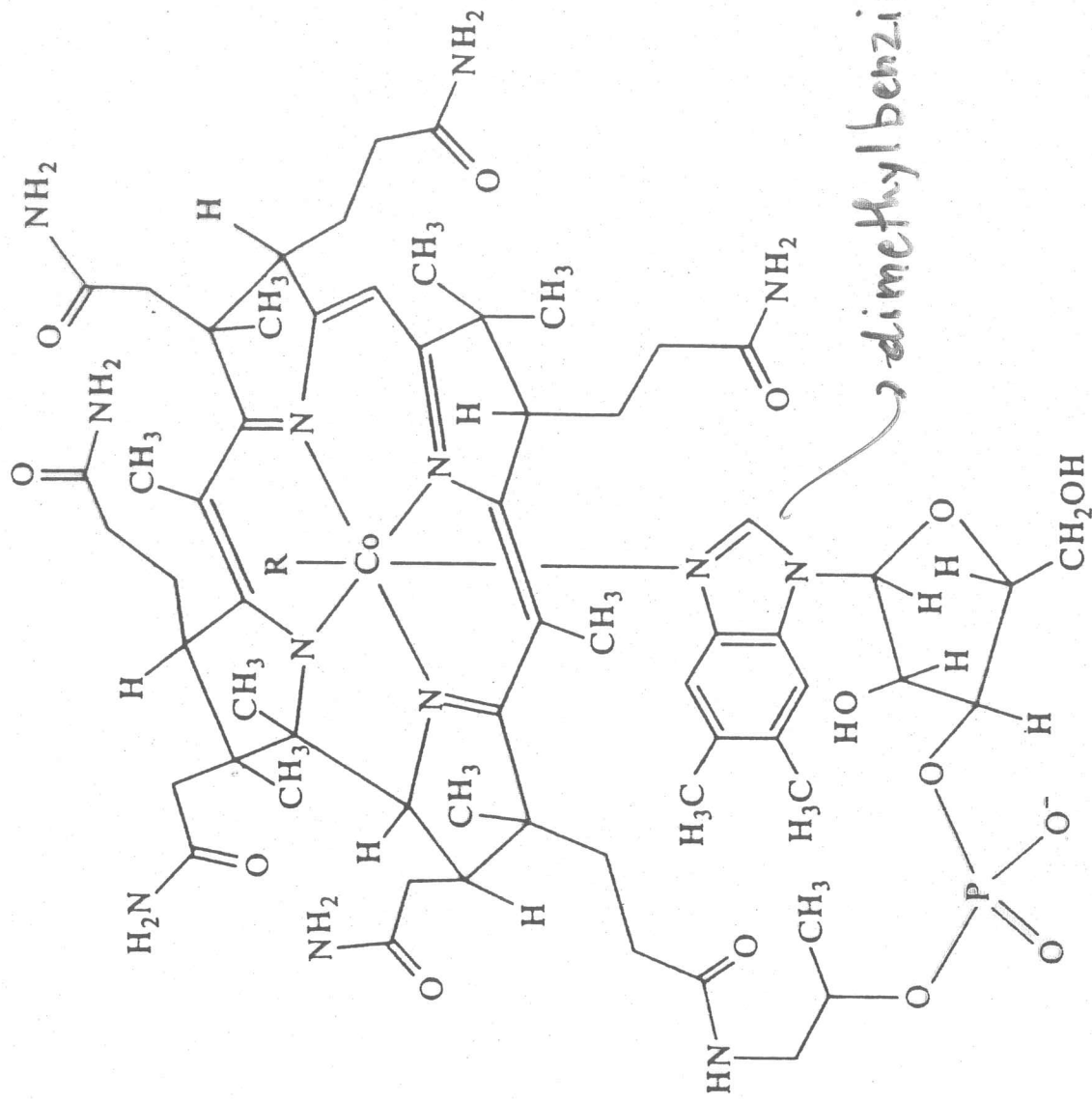
χηρόμορφα
 κέντρα

Figure 1. Corrin and porphyrin. The lines extending from the periphery of the macrocycles represent alkyl or acyl substituent groups. Strictly speaking, the terms "porphyrin" and "corrin" refer to the metal-free macrocycles. For purposes of emphasis, however, the structures are shown containing metals usually associated with them under biological conditions.



Κυρίως πυρην C





dimethyl benzimidazole unit

FIGURE 22.11
General structure of vitamin B₁₂ and its derivatives.

$R = \text{CH}_3$
μιδυλοκοβαλαμιν

$R = \text{CN}$
κυανοκοβαλαμιν
(βιταμιν B₁₂)

$R = \text{OH}$
νιτροκοβαλαμιν

$R = \text{H}_2\text{O}$
νδροκοβαλαμιν

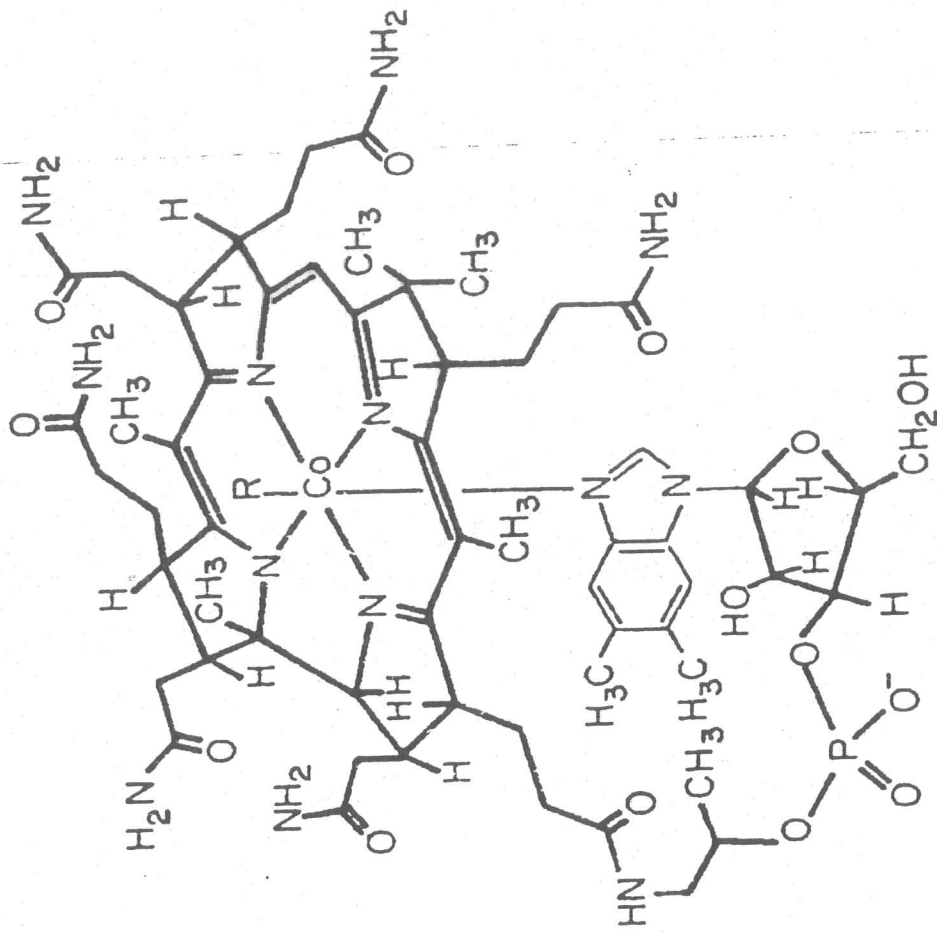
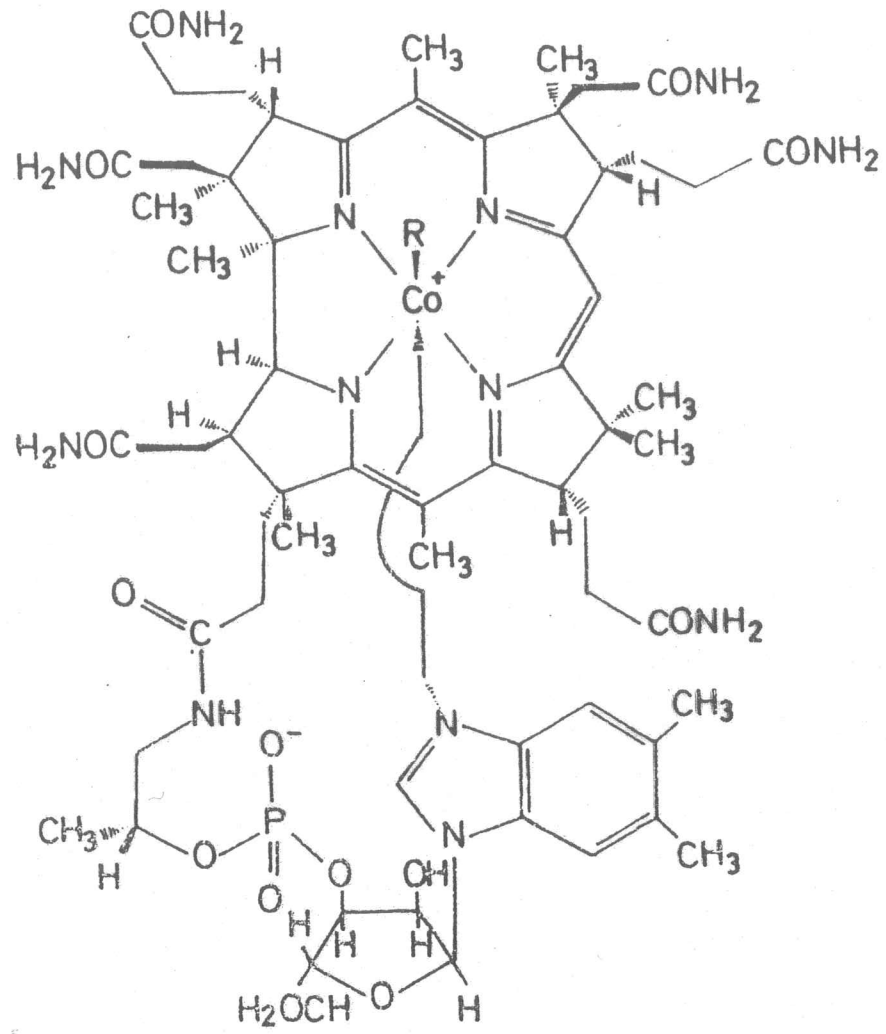
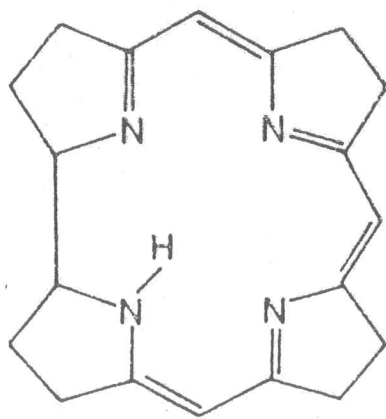


Figure 1.

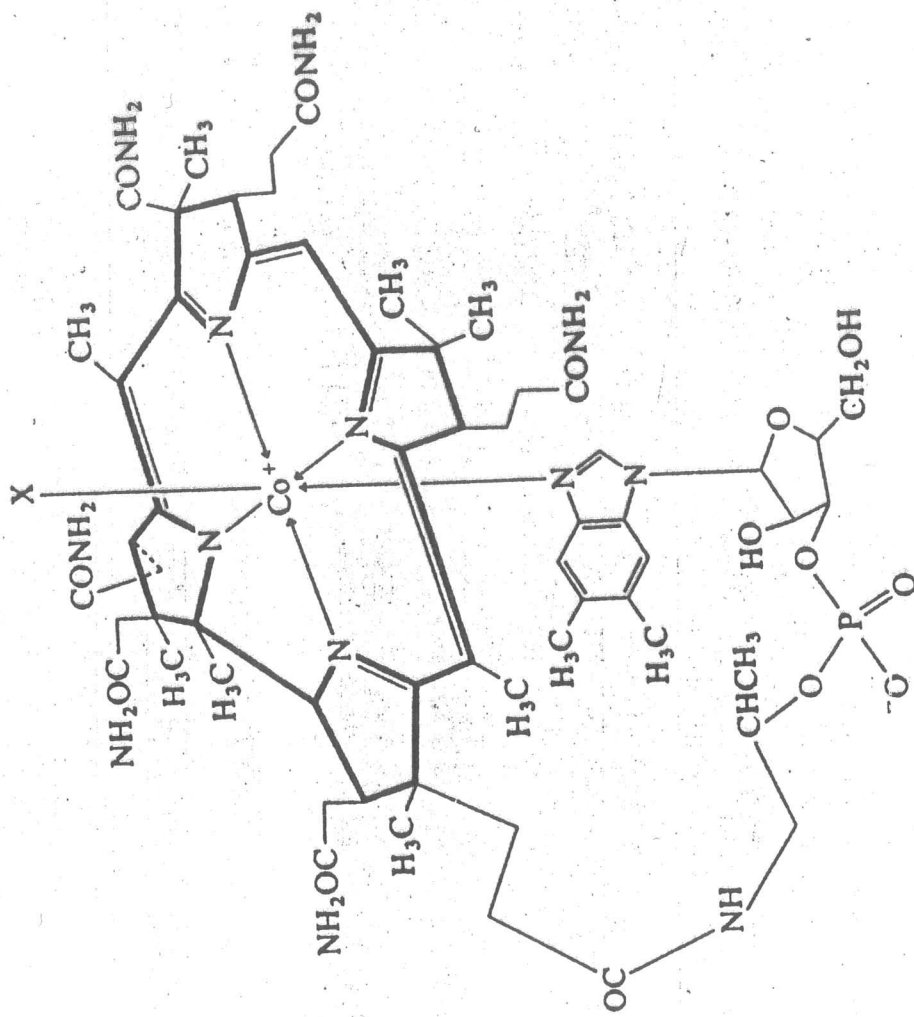


a.



b.

BITAMIN H B₁₂



Σχήμα 3.5.
Δομή της κομπολαμίνης.

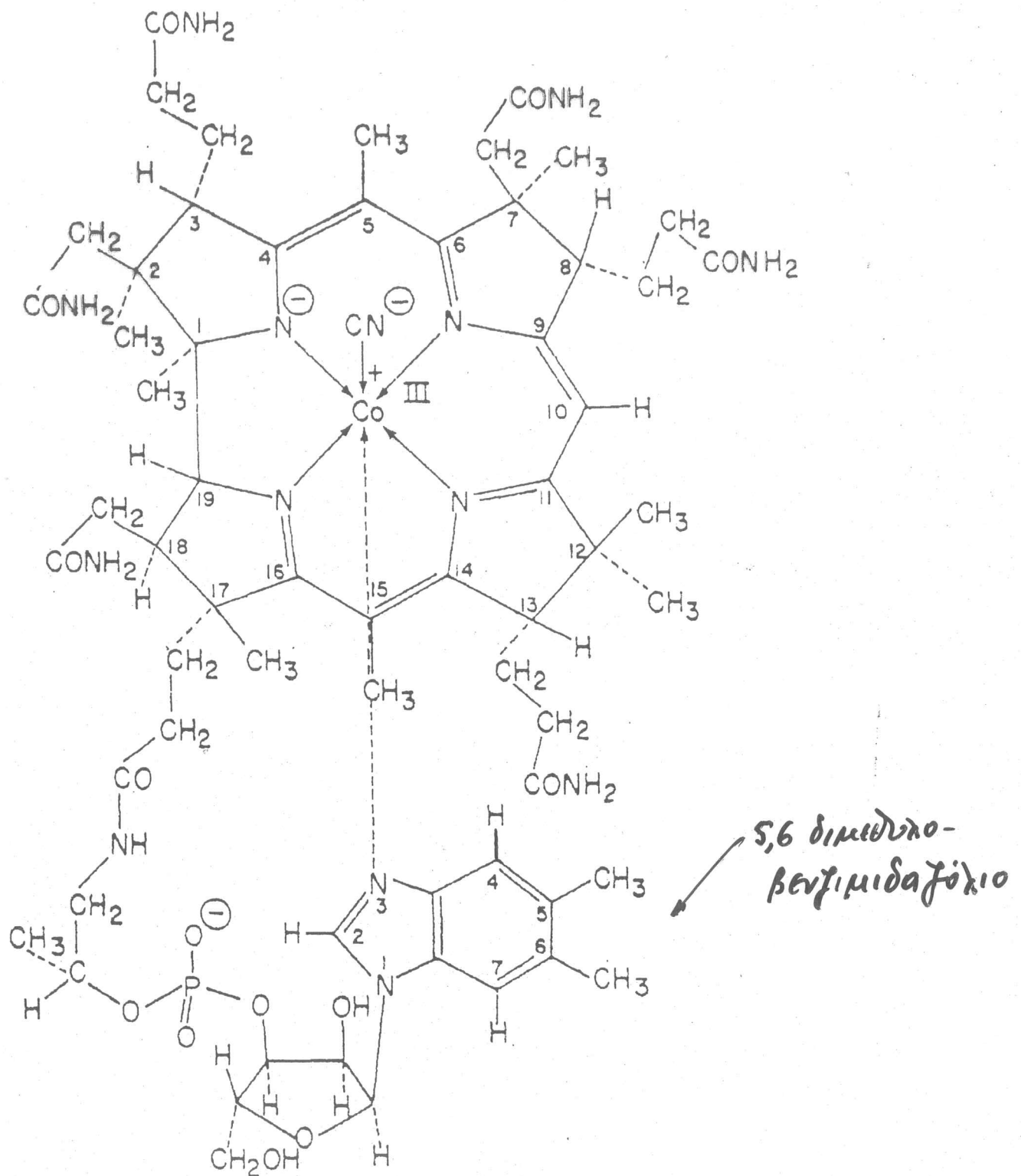
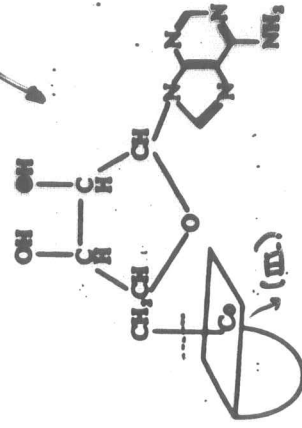
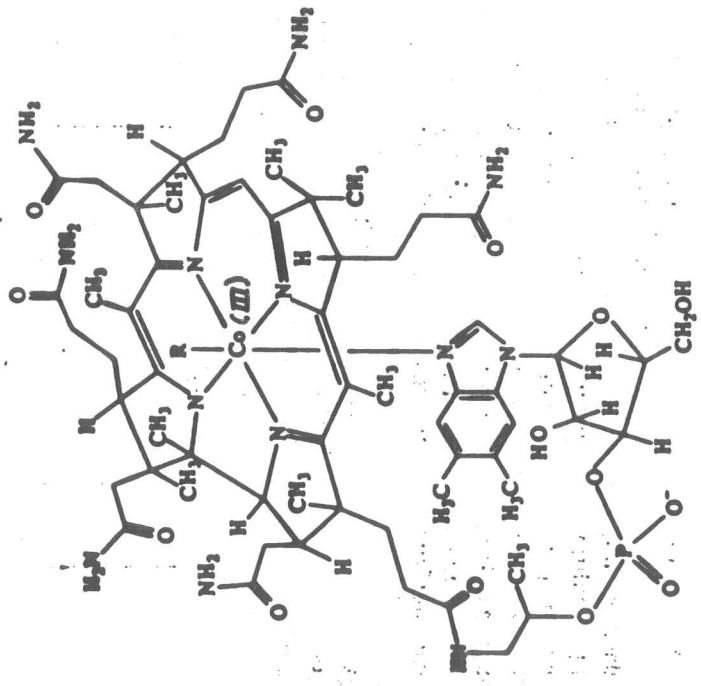


Figure 2. Cyanocobalamin (from J. M. Pratt, "Inorganic Chemistry of Vitamin B₁₂" Academic Press, New York, N.Y., 1972, p 2; reproduced with permission of the author and Academic Press).

5' δροφραδενοσίνη



Schematic structure of vitamin B₁₂ coenzyme, showing the group coordinated at the R site.



General structure of vitamin B₁₂ and its derivatives.

ΚΙΤΡΙΝΟ-ΠΟΡΤΟ ΕΑΛΛΟΧΡΩΜΗ ΔΙΑΜΟΝΗ ΖΙΜΜΗ

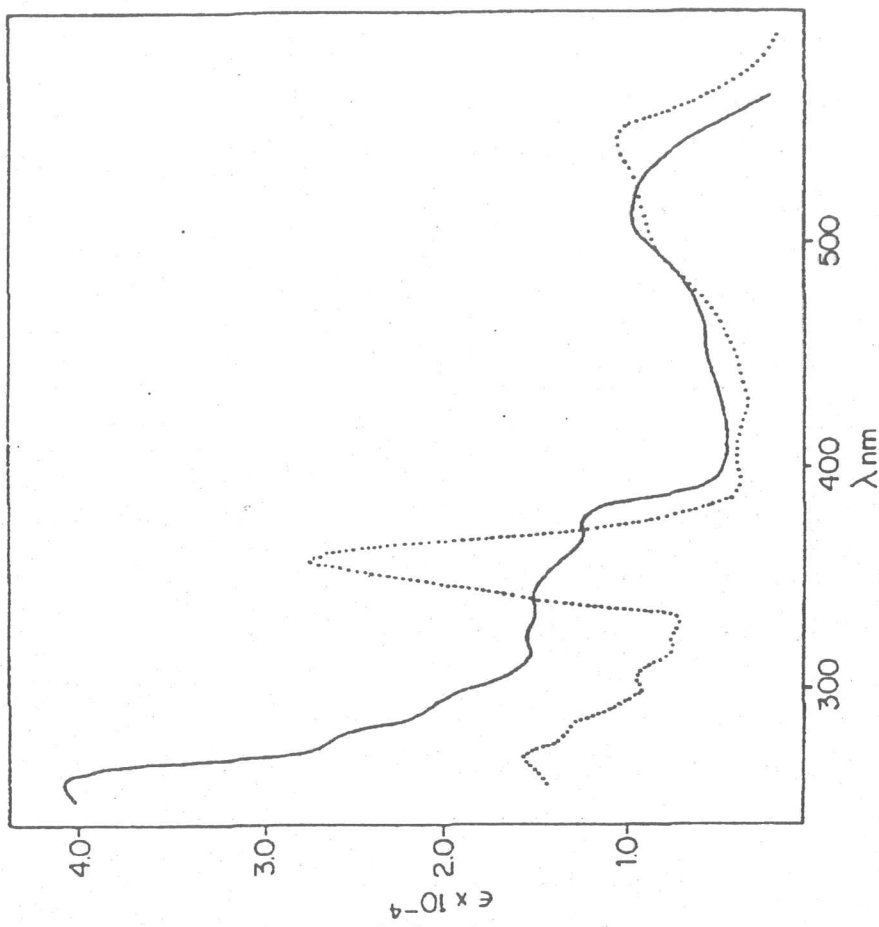


Figure 2. Optical absorption spectra (H₂O) of vitamin B₁₂ (-----) and the vitamin B₁₂ coenzyme (———).

1962

R = 5'-σεαφραδενοσυλ-κοβαλαμιν
(60νινζυμο B₁₂)

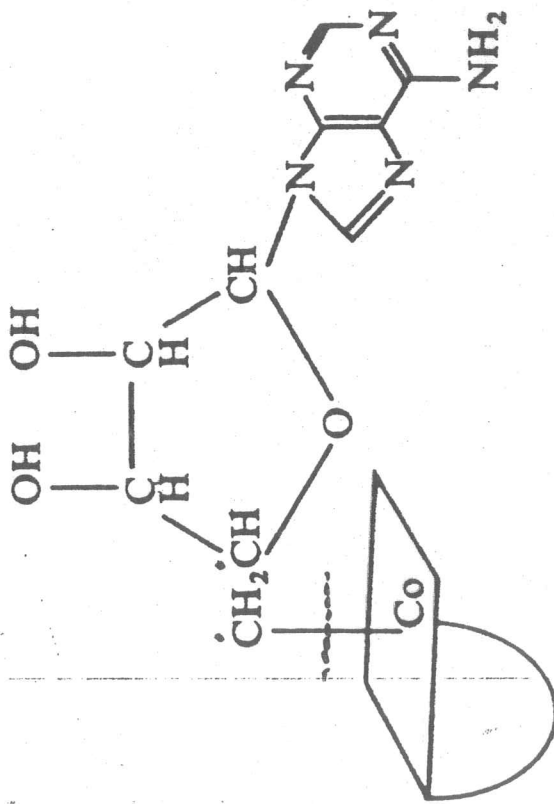


FIGURE 22.12

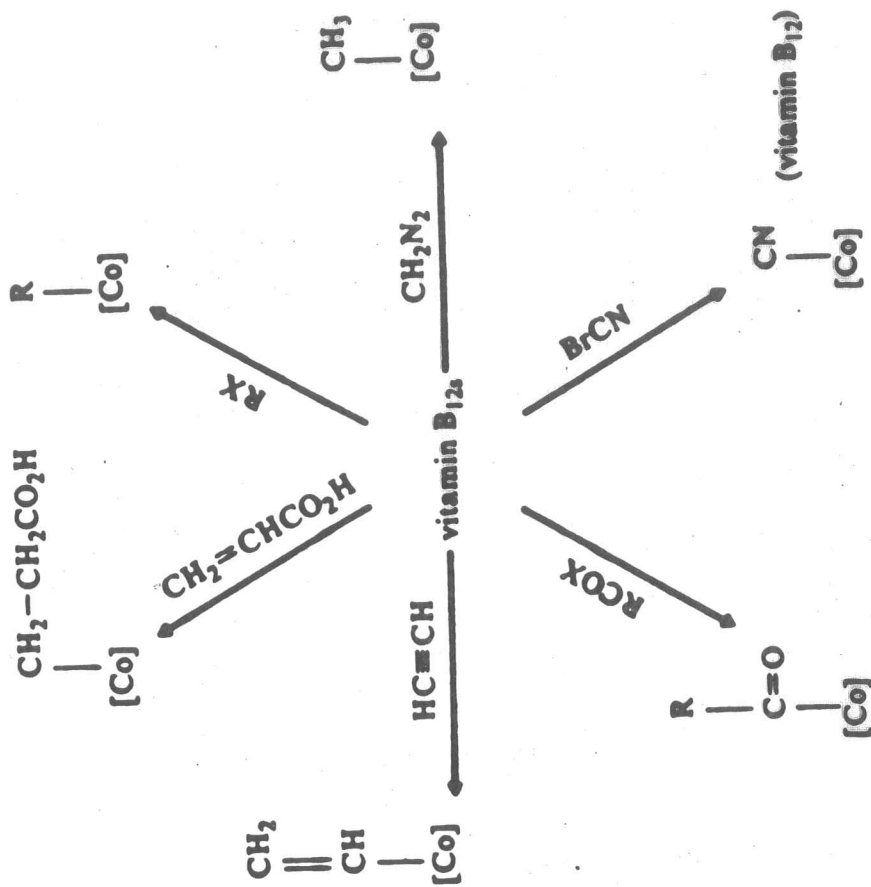
Schematic structure of vitamin B₁₂ coenzyme, showing the group coordinated at the R site.



Τα ένζυμα που περιέχουν το συνένζυμο B_{12}

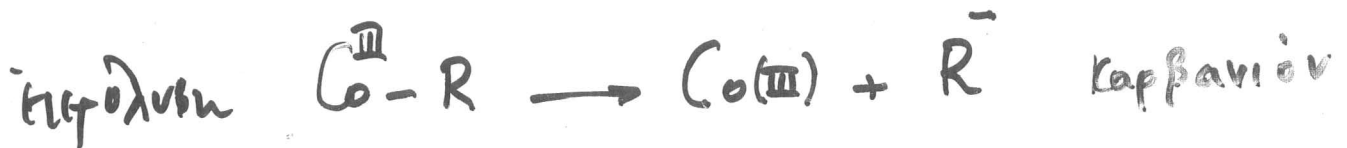
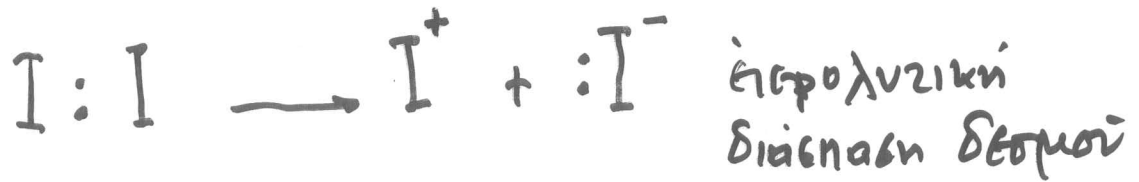
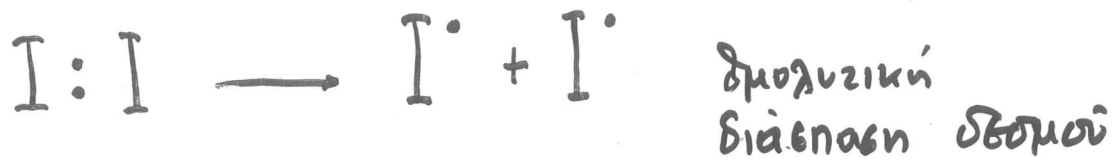
συμμετέχουν σε:

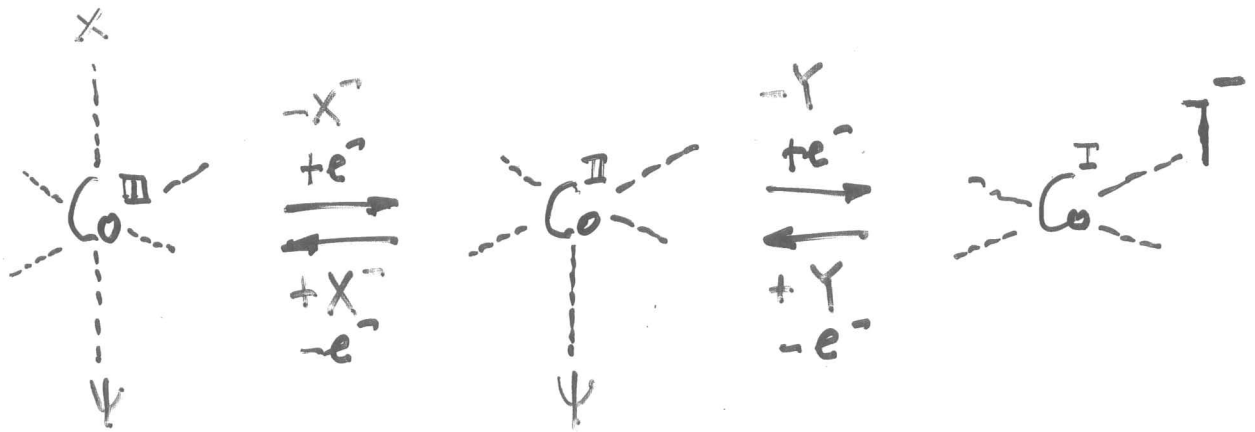
1. Θειδοαναμική αντίδραση
2. Αλκυλιώσεις
3. Αντίδραση επαναβιενθιόσων μέσω ριζών
(ήδη υπεροκυκλητική 1,2 μετατόπιση)
(σε κορεσμένες ενώσεις)



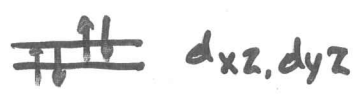
RCOX Ακυλιωτικό μέσο
 CH₂N₂ Διαζωπράξινο

RX Ακυλιωτικό παράγωγο
 CH₂=CHCO₂H Βινυλικό οξύ.





αναγωγική απόσταση
 —————
 οξειδωτική προδιάθεση



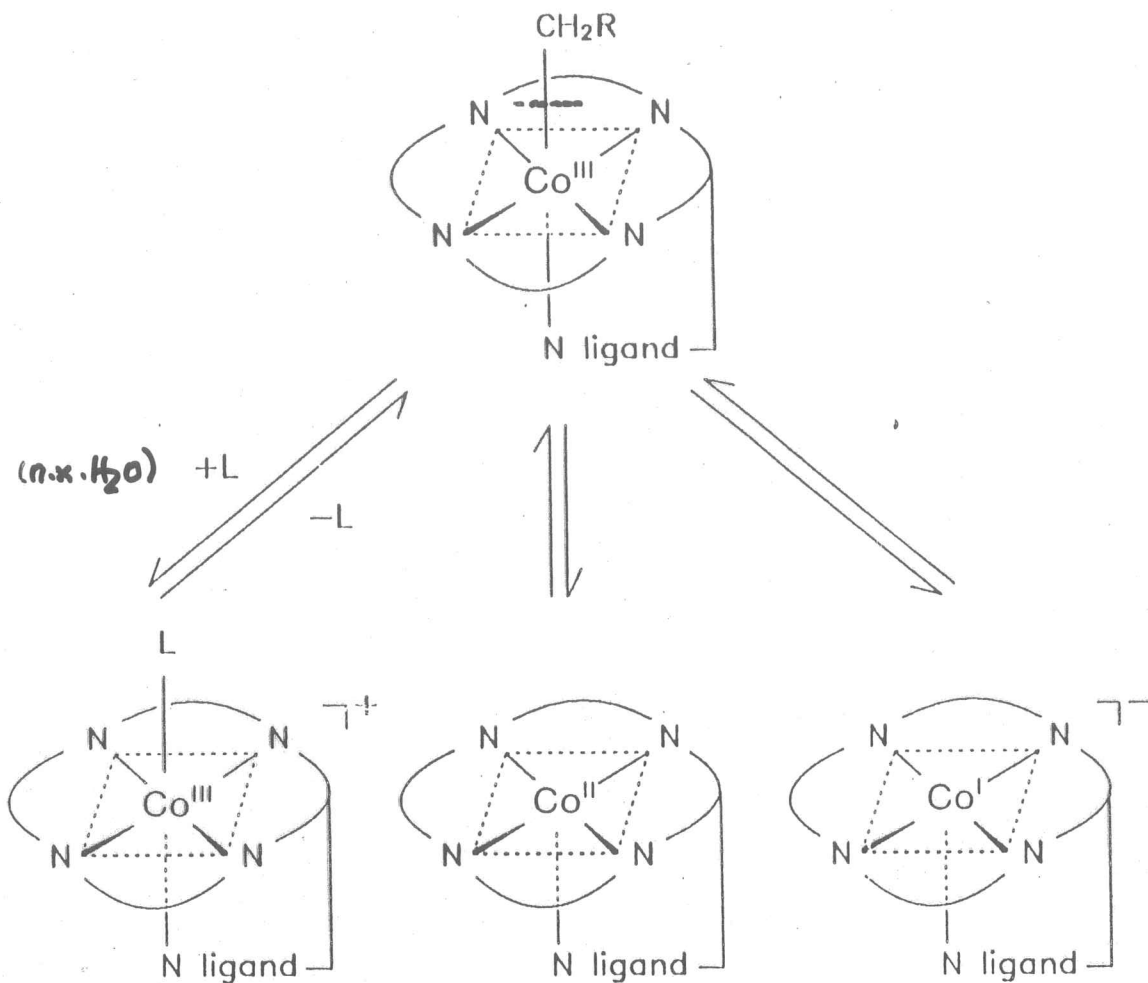
οκταεδρικό πεδίο
 d^6



τετραγωνική πυραμίδα
 d^2



τετραγωνικό πεδίο d^8

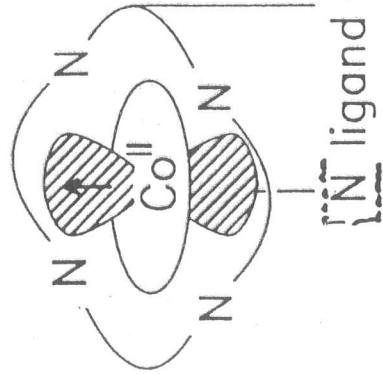


	$+ 3\text{CH}_2\text{R}^-$ καρβαιόν	$+ \cdot\text{CH}_2\text{R}$	$+ \text{CH}_2\text{R}^+$ καρβοκατιόν
type of reaction:	<u>heterolysis</u>	<u>homolysis</u>	<u>heterolysis</u>
metal configuration in the product:	d^6 low-spin; stable, inert	d^7 low-spin, 1 unpaired electron (d_z^2) ¹	d^8 , 'super-nucleophilic' (d_z^2) ²
alkyl ligand, eliminated as:	'carbanion', nucleophilic	1° alkyl radical, very reactive	'carbocation', electrophilic
approximate electrochemical potential equivalent ^a :	$> 0 \text{ V}$	$0 \text{ --- } -0,4 \text{ V}$	$< -0.9 \text{ V}$

^aIn biochemistry, all redox potentials are generally referenced to the normal hydrogen electrode (NHE)

εωλιεετω

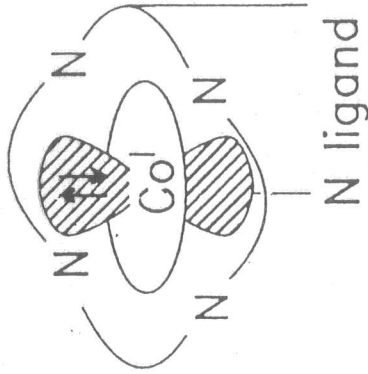
radical scavenger:



$(d_{z^2})^1$

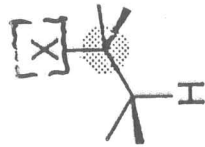
Σύζευξη: spin hyperfine
 $+ {}^{59}\text{Co} \left(I = \frac{7}{2} \right)$
 $+ {}^{14}\text{N} \left(I = 1 \right)$

supernucleophile:

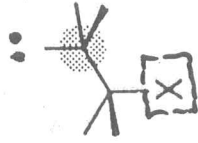


$(d_{z^2})^2$

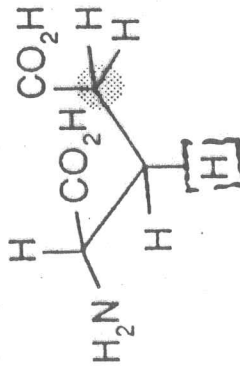
general reaction:



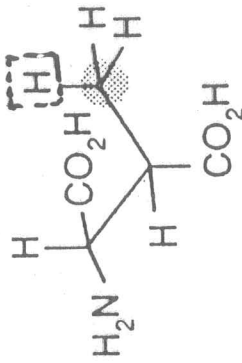
mutase



concrete example:



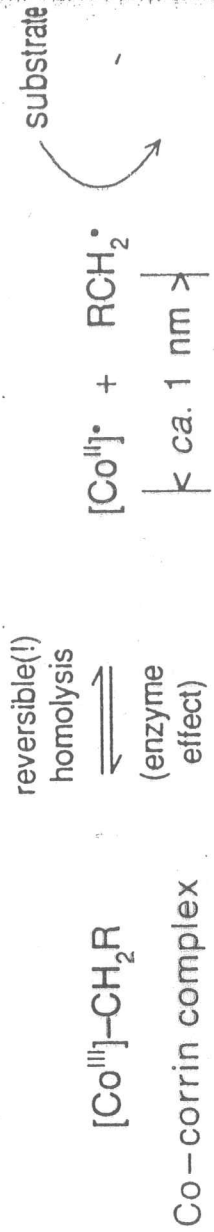
glutamate
mutase



β -methylaspartic acid

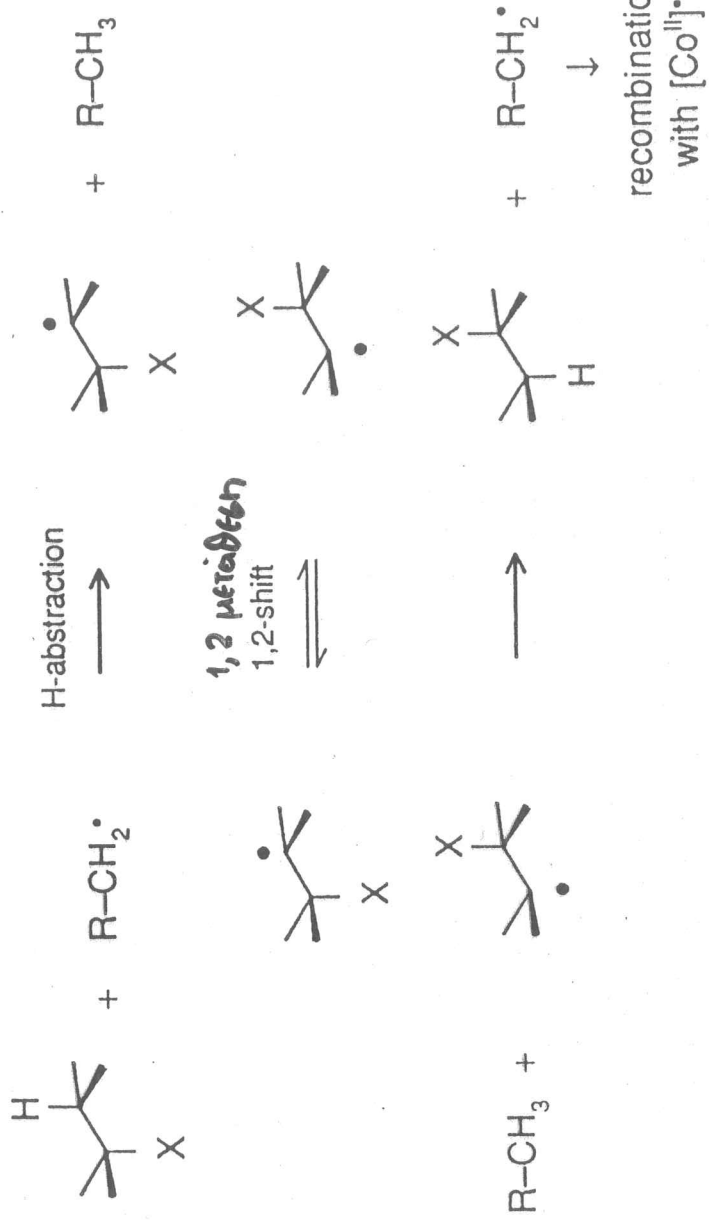
glutamic acid

initiation:



Co-corrin complex

general radical mechanism:





X = O, NH

R = 5'-deoxyadenosyl

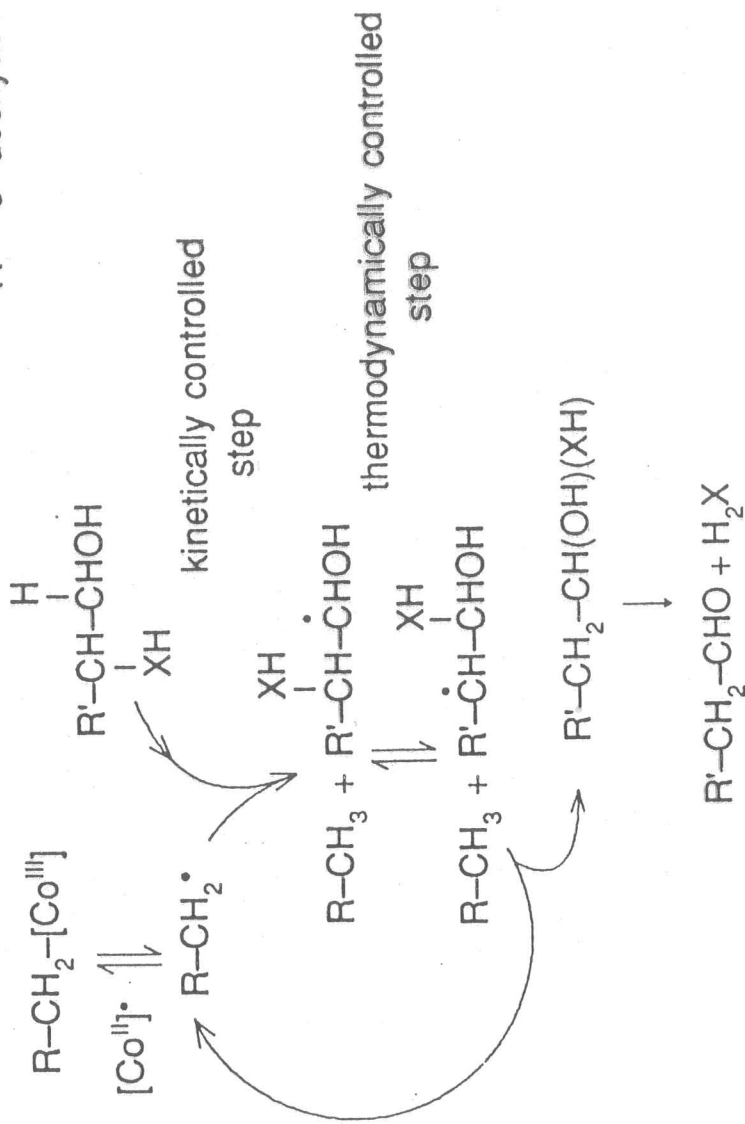
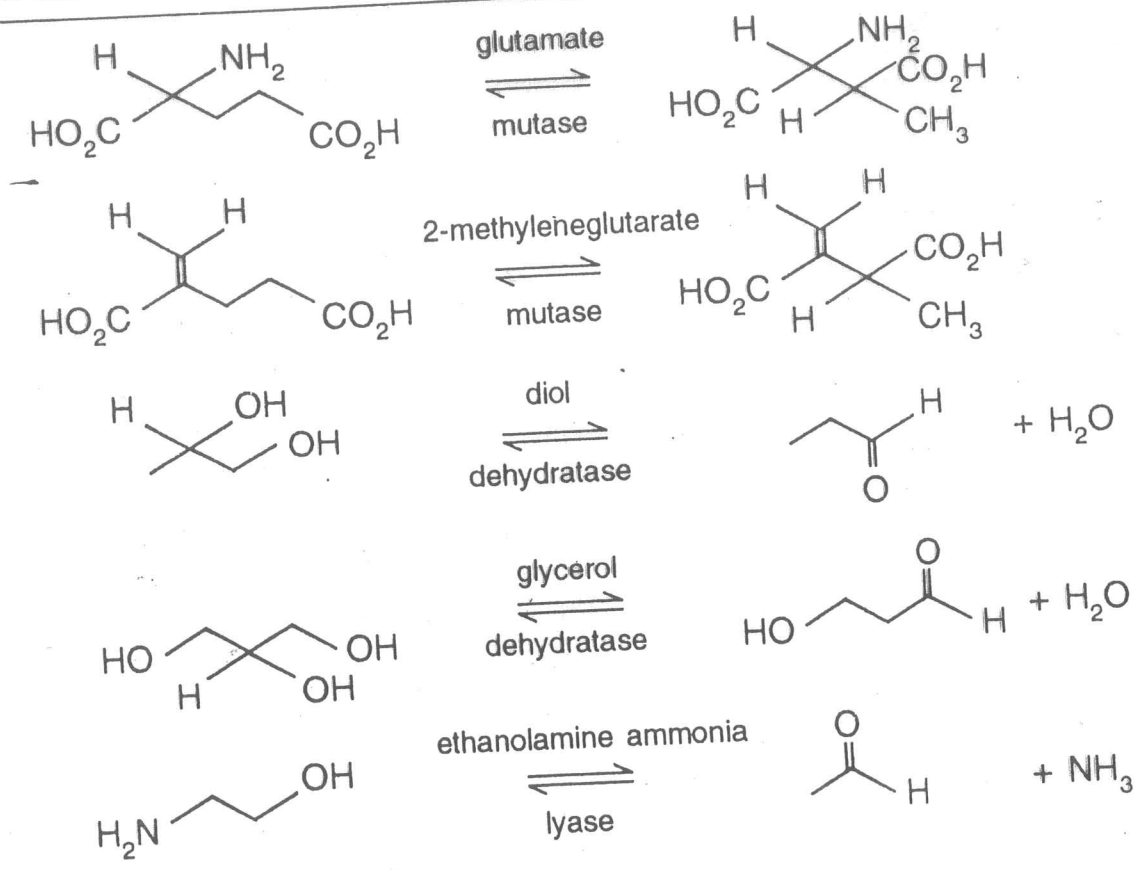
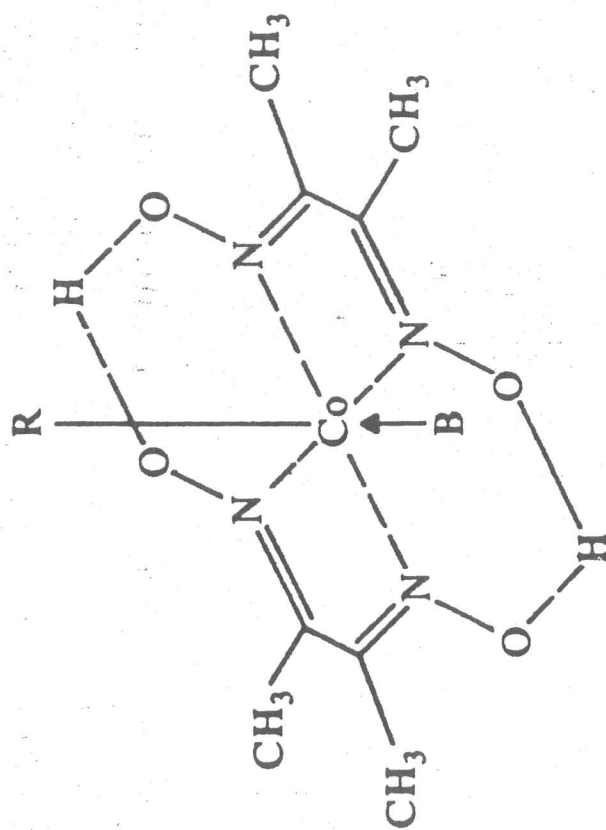


Table 3.1 Reactions requiring coenzyme B₁₂

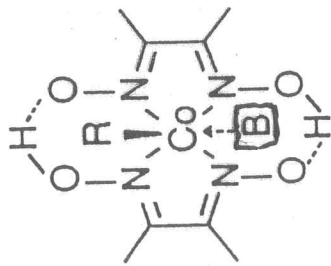


22



R = acid anion,
alkyl, or aryl

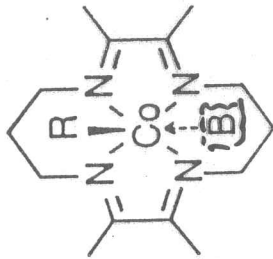
B = base, e.g.,
pyridine



cobaloxime complex

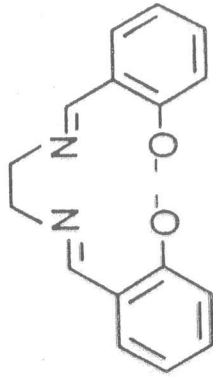
B: base (PPh_3)

δι (διακετυλοδιοφηνιλη)



a CoSta complex

α-διμινιο



salen ligand

δι (σαλικυλ-αλδεϋδη) αιθυλινο-
-διμινιο

· Ενζυμική ενεργοποίηση \Rightarrow Σπασίμο δεσμού $\text{Co} \vdash \text{R}$

- Δεν επηρεάζεται από ηλεκτρονικά φαινόμενα
π.χ. Βασικότητα οργανοφωσφίνης (PR_3)

- αλλά από "στερικά" φαινόμενα (PR_3)