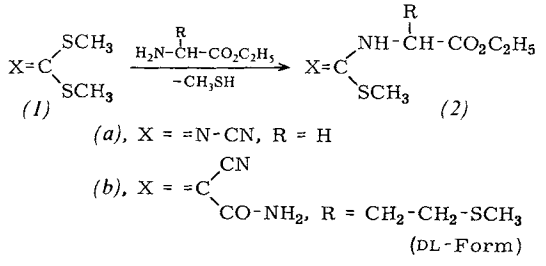
New Amino Acid Derivatives from Cyanamide and Cyanacetamide

By *Joachim Gante* and *Günther Mohr*[*]

Six to eight hours' refluxing of dimethyl cyanimidodithiocarbonate *(1a)*[1] and dimethyl (α-cyanocarbamoylmethylene)dithiocarbonate *(1b)*[2] with glycine ethyl ester or DL-methionine ethyl ester hydrochloride, respectively, and sodium ethoxide (molar ratio 1:1:1) in anhydrous ethanol afforded the hitherto unknown amino acid derivatives *(2a)* (yield 50%, m. p. 98—99 °C) and *(2b)* (yield 91%, oil).



(1) *(2)*

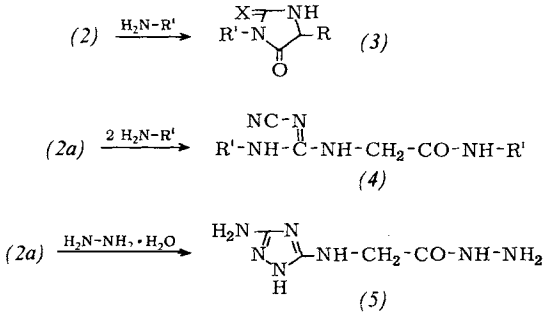
(a), X = =N-CN, R = H

(b), X = =C(CN)-CO-NH$_2$, R = CH$_2$-CH$_2$-SCH$_3$ (DL-Form)

On refluxing for several hours with equimolar amounts of primary amines in ethanol or with an excess of concentrated ammonia/ethanol (2:1), *(2a)* and *(2b)* were converted into the respective hydantoin analogs *(3)* (see Table).

Cpd.	R	R'	X	Yield (%)	M. p. (°C)
(3a$_1$)	H	CH$_2$—CH(CH$_3$)$_2$	=N—CN	28	244–247
(3a$_2$)	H	(CH$_2$)$_5$—CH$_3$	=N—CN	32	168–170
(3a$_3$)	H	CH$_2$—CH$_2$—OH	=N—CN	38	195–196
(3a$_4$)	H	CH$_2$—C$_6$H$_5$	=N—CN	47	239
(3a$_5$)	H	CH$_2$—CH$_2$—C$_6$H$_5$	=N—CN	40	243–245
(3a$_6$)	H	cyclo-C$_6$H$_{11}$	=N—CN	20	229–230
(3b$_1$)	CH$_2$—CH$_2$—SCH$_3$	H	=C(CN)CONH$_2$	46	290
(3b$_2$)	CH$_2$—CH$_2$—SCH$_3$	CH$_3$	=C(CN)CONH$_2$	71	171–172
(4a$_1$)		CH$_3$		93	165–167
(4a$_2$)		CH(CH$_3$)$_2$		60	128–131
(4a$_3$)		(CH$_2$)$_7$—CH$_3$		31	155
(4a$_4$)		CH$_2$—C$_6$H$_5$		82	210

Reaction of *(2a)* with a two- to four-fold excess of amine under otherwise identical conditions gave the urea analogs *(4)*.



(3)

(4)

(5)

(2a) and hydrazine hydrate (molar ratio 1:1.8; 2 hours' refluxing in ethanol) furnished *N*-(5-amino-1,2,4-triazol-3-yl)glycine hydrazide *(5)* (yield 79%, m. p. 227—228 °C).

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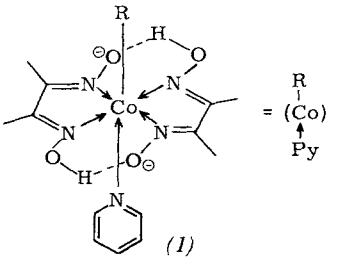
Novel Degradation Reactions of Halomethyl Derivatives of Bis(diacetyldioximato)cobalt[**]

By *Gerhard N. Schrauzer*, *Anthony Ribeiro*, *Lian P. Lee*, and *Raymond K. Y. Ho*[*]

Unsubstituted alkylcobaloximes[1] *(1)* with, *e.g.*, R = CH$_3$, which are of interest as model compounds of organocobalt derivatives of vitamin B$_{12}$, generally exhibit a high resistance to attack by alkali. In contrast, studies on halomethyl-

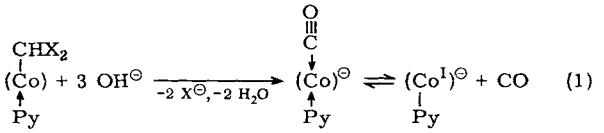


(1)

(1a), R = CHX$_2$ (X=Cl, Br, I)
(1b), R = CH$_2$X (X=Cl, Br, I)
(1c), R = CX$_3$ (X=Cl, Br, I)
(1d), R = CF$_3$
(1e), R = CH$_2$OCH$_3$
(1f), R = COOCH$_3$

cobaloximes *(1a)*—*(1c)* revealed evidence for a surprisingly high alkali sensitivity. Nucleophilic attack of the cobalt-bonded halomethyl group by OH$^\ominus$ ion causes initial Co—C bond cleavage to give halomethanols and cobaloxime(I). The interesting reactions that ensue are reported in the present communication.

In 0.1 N NaOH dihalomethylcobaloximes *(1a)*[2] undergo rapid, quantitative decomposition (no isolable intermediate) into carbonylcobaloxime(I), the carbon monoxide complex of cobaloxime(I), which is at equilibrium with free CO and cobaloxime(I) [eq. (1)].



(1a) (1)

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