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The Reaction of Cobalt(III) Porphyrins with α-Diazo-β-Dicarbonyl Compounds

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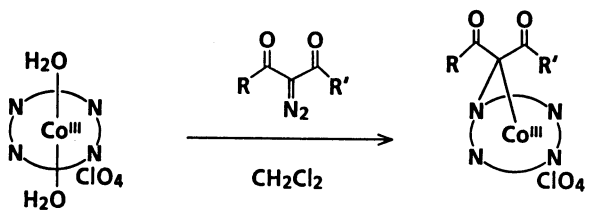
Cobalt(III) porphyrins reacted with α-diazo-β-dicarbonyl compounds to give N,Co-methano bridged Co(III) porphyrins in good yields. The axial ligand and the peripheral substituents have great influence on the insertion of the carbenes and on the subsequent transformation to Co(III) N-alkylporphyrins with a $\overline{\text{N-C=C-O-Co}}^{III}$ linkage.

Organometallic chemistry of metalloporphyrins has recently been recognized to be important in understanding biochemical processes of metalloenzymes and in developing new organometallic reactions.[1] The reaction of metalloporphyrins with carbene precursors leads to the N-alkylation of porphyrin by way of organometalloporphyrins with the carbene bound to the metal or inserted into a metal-nitrogen bond.[2] Mansuy and co-workers have recently reported that Fe^{II}, Fe^{III}, and Co^{III} porphyrins react with phenyl iodonium ylide of dimedone to afford Fe^{II}-carbene complexes and $\overline{\text{N-C=C-O-Fe}}^{II}$, $\overline{\text{N-C=C-O-Fe}}^{III}$ and $\overline{\text{N-C=C-O-Co}}^{III}$ metallacycle complexes.[3] We are interested in these novel metallacycle complexes and this work was directed to elucidate the reactivity and reaction pathway of Co(III) porphyrins with α-diazo-β-dicarbonyl compounds including diazodimedone.

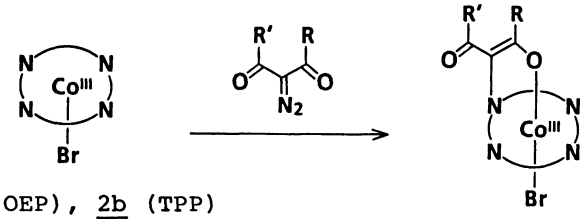
Whereas Mansuy's group obtained the $\overline{\text{N-C=C-O-Co}}^{III}$ metallacycle complex (6b) by the reaction of (TPP[4])$Co^{III}Br$ (2b) with phenyl iodonium ylide of dimedone (10 fold molar excess) at room temperature for 48 h, the corresponding N,Co-methano bridged complex (3b) has been formed immediately in 86% yield through the treatment of $(TPP)Co^{III}(H_2O)_2ClO_4$ (1b) with diazodimedone (1.5 fold molar amount) in CH_2Cl_2. The inequivalency of two methyl groups at the 4-position and the equivalency of two methylene groups at the 3- and 5-position of dimedone moiety in the ^1H NMR spectrum and the normal non-conjugated carbonyl stretching frequencies in the IR spectrum provide evidence in support of the N,Co-methano bridged structure for 3b.[5] Similar N,Co-methano bridged complexes,[6] 3a, 4a, and 5a, have been prepared



R, R' = $-CH_2C(CH_3)_2CH_2-$ 3a, 3b
CH_3 OC_2H_5 4a
OCH_3 OCH_3 5a

1a (OEP), 1b (TPP)

quantitatively and immediately by the reaction of (OEP[4])$(H_2O)_2ClO_4$ (1a) with slightly excess amount of diazodimedone, ethyl diazoacetoacetate, and dimethyl diazomalonate, respectively. 3a is especially stable in comparison with the reported N,Co-methano bridged Co^{III} porphyrins derived from ethyl diazoacetate and diazoacetaldehyde.[2d-f] However, 3a was decomposed by heating for 5 h at reflux in 1,2-dichloroethane solution, with concomitant formation of the $\overline{N\text{-}C\text{=}C\text{-}O\text{-}Co}^{III}$ metallacycle complex (6a, X=Cl) in only 10% yield. Treatment of 3a with $AlCl_3$ (2 fold molar amount) in CH_2Cl_2 solution resulted in the formation of 6a (X = Cl) in a low yield (23%). One of the authors (J.-i. S) pointed out that the sixth axial ligand makes considerable trans labilizing effect on the Co-C σ-bond of N,Co-formylmethano(OEP)Co^{III} complexes.[2f] Accordingly, exchange of the axial ligand of 3a with NaBr followed by refluxing for 2 h in 1,2-dichloroethane afforded 6a in much better yield (58%). As the reaction of diazo compounds with Co^{III} porphyrins is regarded as nucleophilic attack of diazonium ylide on the cationic metal center, the rates of the reaction of bromides, (OEP)Co^{III}Br (2a) and 2b, are much slower than those of perchlorates, 1a and 1b. Furthermore, the initially formed N,Co-methano bridged bromo complexes are much more labile than the corresponding perchlorates. Therefore, the reaction conditions under which 2a and 2b react with α-diazo-β-dicarbonyl compounds inevitably facilitate the transformation of the N,Co-methano bridged complexes to the $\overline{N\text{-}C\text{=}C\text{-}O\text{-}Co}^{III}$ metallacycle complexes. Thus, treatment of 2a and 2b with diazodimedone, ethyl diazoacetoacetate (1.2 - 1.5 fold molar amount) at reflux temperature in 1,2-dichloroethane for 1 - 5 h afforded $\overline{N\text{-}C\text{=}C\text{-}O\text{-}Co}^{III}$ metallacycle complexes,[7] 6a, 7a, 6b, and 7b, in 88, 94, 53, and 66% yield, respectively. As the reaction of 2a and 2b with more nucleophilic dimethyl diazomalonate than the other α-diazo-β-dicarbonyl compounds proceeded faster and the products have proved to be thermally unstable, 2a and 2b were allowed to react with dimethyl diazomalonate at room temperature in dichloromethane for 18 h. While the $\overline{N\text{-}C\text{=}C\text{-}O\text{-}Co}^{III}$ metallacycle TPP complex (9b)[8] was obtained in 69% yield, a mixture of the N,Co-methano bridged OEP complex (5a, X = Br) and the $\overline{N\text{-}C\text{=}C\text{-}O\text{-}Co}^{III}$ metallacycle OEP complex (9a) was formed in 66% total yield with a ratio of 6 : 1. This ratio did not change upon prolonged reaction time and these products were decomposed by heating at reflux in 1,2-dichloroethane to lead to (OEP)Co^{II}.



2a (OEP), 2b (TPP)

R	R'	Yield/% OEP	TPP
$-CH_2C(CH_3)_2CH_2-$		6a (88),	6b (53)
CH_3	OC_2H_5	7a (94),	7b (66)
OCH_3	OCH_3	9a (9*),	9b (69)

* as a mixture with 5a (X = Br, 57%)

Both a ketone enolate form and an ester enolate form are possible for the N-C=C-O-Co^{III} metallacycle structure derived from ethyl diazoacetoacetate. In fact, two isomers, 7b and (7b'), have been formed in 1 : 3 ratio in 64% total yield when 2b was allowed to react with ethyl diazoacetoacetate in dichloromethane at room temperature for 14 h. The reaction of 2b with t-butyl diazoacetoacetate at room temperature for 18 h gave similar two isomeric products, 8 and 8', in 46% total yield with 1 : 6 ratio as summarized in Table 1. The major isomers, 7b' and 8', could be completely rearranged to 7b and 8, when a 1,2-dichloroethane solution of a mixture of the two isomers was heated at reflux for 1 - 3 h. Because the acetyl protons of 8' resonate at by 1.34 ppm lower magnetic field than those of 8 and the t-butyl protons of 8' resonate at by 1.86 ppm higher magnetic fields than those of 8, the t-butyl group of 8' and the acetyl group of 8 are in the strongly shielding region caused by the porphyrin ring current. Similar ^{1}H chemical shift differences were observed for 7b and 7b'.[9] The carbonyl stretching frequencies in the IR spectrum of 8 (1665 cm^{-1}) and 8' (1600 cm^{-1}) are consistent with a conjugated ester carbonyl and a conjugated ketone carbonyl, respectively. Therefore, 7b and 8 are ketone enolate forms and 7b' and 8' are ester enolate forms. The facts that the selectivity between these two isomers was increased by using the bulky carboalkoxy group and an OEP analogue of 7b' has never been obtained even at room temperature suggest that, although a ketone enolate form is thermodynamically preferred, an ester enolate form is kinetically favored due to smaller steric hindrance of a meso phenyl group with the acetyl group than with the carboalkoxy group when β-dicarbonyl group rotates around the N-C$_\alpha$ bond by 90° degree upon going from the N,Co-methano bridged complexes to the N-C=C-O-Co^{III} metallacycle complexes.

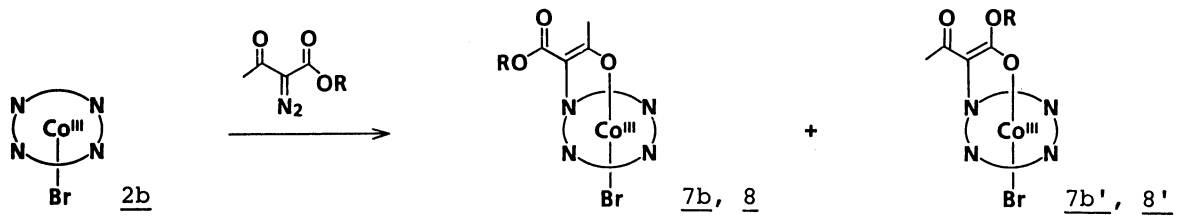


Table 1. Yield and Products Ratio of the Reaction of 2b with Alkyl Diazoacetoacetate

R	Solv.	Temp °C	Time h	Yield %	Ratio 7b,8		7b',8'
C_2H_5	$C_2H_4Cl_2$	80	1	66	1	:	0
C_2H_5	CH_2Cl_2	20	14	64	1	:	3
t-C_4H_9	$C_2H_4Cl_2$	80	2	78	1	:	0
t-C_4H_9	CH_2Cl_2	20	18	46	1	:	6

In conclusion, the reaction of Co(III) porphyrins with α-diazo-β-dicarbonyl compounds gives the N,Co-methano bridged Co(III) porphyrins which are analogues to the complexes derived from ethyl diazoacetate and diazoacetaldehyde,[2d-f] but subsequently rearrange to the N-C=C-O-Co^{III} metallacycle complexes due to the easily enolizable β-dicarbonyl structure.

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4) TPP and OEP denote meso-tetraphenylporphin dianion and octaethylporphyrin dianion, respectively.

5) 3b: ^{1}H NMR (δ, $CDCl_3$, 270 MHz) H_{py} 9.78 (s), 8.89 (s), 8.85 (d), 8.64 (d); PhH 8.2 - 7.7 (m); 3,5-CH_2 -0.45 (d), -3.18 (d); 4-CH_3 -0.67 (s), -0.77 (s) ppm. IR (KBr) C=O 1715, 1685; ClO_4 1085, 620 cm^{-1}. UV-Vis (CH_2Cl_2) λ_{max}(log ε) 357 (4.35), 416 (4.87), 434 (sh, 4.76), 576 (sh, 4.42), 653 (3.66) nm.

6) 3a: ^{1}H NMR (δ, $CDCl_3$, 270 MHz) H_{meso} 10.43 (s), 10.18 (s); CH_2 4.5 - 3.9 (m); CH_3 2.03 (t), 1.84 (t)(x2), 1.83 (t); 3,5-CH_2 -0.89 (d), -3.83 (d); 4-CH_3 -0.94 (s), -1.02 (s) ppm. IR (KBr) C=O 1710, 1680; ClO_4 1085, 620 cm^{-1}. UV-Vis (CH_2Cl_2) λ_{max}(log ε) 359 (sh, 4.43), 401 (4.81), 477 (sh, 4.09), 566 (sh, 3.72) nm. 4a: ^{1}H NMR (δ, $CDCl_3$, 270 MHz) H_{meso} 10.35 (s), 10.28 (s), 10.15 (s), 10.14 (s); CH_2 4.4 - 3.9 (m); CH_3 2.1 - 1.8 (m); OCH_2CH_3 2.07 (m), -0.14 (t); $COCH_3$ -2.13 (s) ppm. IR (KBr) C=O 1725; ClO_4 1085, 620 cm^{-1}. UV-Vis (CH_2Cl_2) λ_{max}(log ε) 403 (4.77), 478 (sh, 4.08), 570 (sh, 3.75) nm. 5a: ^{1}H NMR (δ, $CDCl_3$, 270 MHz) H_{meso} 10.34 (s), 10.11 (s); CH_2 4.4 - 3.8 (m); CH_3 1.99 (t), 1.90 (t), 1.87 (t), 1.84 (t); OCH_3 1.62 (s) ppm. IR (KBr) C=O 1730; ClO_4 1085, 625 cm^{-1}. UV-Vis (CH_2Cl_2) λ_{max}(log ε) 403 (4.61), 568 (sh, 3.71) nm.

7) 6a: ^{1}H NMR (δ, $CDCl_3$, 270 MHz) H_{meso} 10.17 (s), 10.07 (s); CH_2 4.0 - 3.7 (m); CH_3 1.87 (t), 1.86 (t), 1.73 (t), 1.41 (t); 3,5-CH_2 0.75 (s), -0.67 (s); 4-CH_3 -0.44 (s) ppm. IR (KBr) C=O 1635 cm^{-1}. UV-Vis (CH_2Cl_2) λ_{max}(log ε) 394 (4.57), 441 (4.64), 532 (3.93), 578 (3.85) nm. 7a: ^{1}H NMR (δ, $CDCl_3$, 270 MHz) H_{meso} 10.07 (s), 9.99 (s); CH_2 4.0 - 3.65 (m); CH_3 1.88 (t), 1.84 (t), 1.77 (t), 1.23 (t); OCH_2CH_3 3.59 (q), 0.98 (t); $COCH_3$ -0.64 (s) ppm. IR (KBr) C=O 1675 cm^{-1}. UV-Vis (CH_2Cl_2) λ_{max}(log ε) 392 (4.55), 438 (4.64), 532 (3.94), 580 (3.84) nm.

8) 9b: ^{1}H NMR (δ, $CDCl_3$, 270 MHz) H_{py} 8.87 (d), 8.80 (d), 8.77 (s), 8.42 (s); PhH 8.5 - 7.7 (m); OCH_3 3.26 (s), 1.19 (s) ppm. IR (KBr) C=O 1650 cm^{-1}. UV-Vis (CH_2Cl_2) λ_{max}(log ε) 357 (4.36), 400 (sh, 4.43), 455 (4.86), 615 (3.89), 670 (sh, 3.63) nm.

9) ^{1}H NMR data (δ, $CDCl_3$, 270 MHz). 7b: H_{py} 8.84 (d), 8.80 (d), 8.71 (s), 8.41 (s); PhH 8.5 - 7.7 (m); OCH_2CH_3 3.77 (q), 0.97 (t); $COCH_3$ -0.39 (s) ppm. 7b': H_{py} 8.91 (d), 8.81 (d), 8.76 (s), 8.34 (s); PhH 8.5 - 7.7 (m); OCH_2CH_3 1.53 (q), -0.62 (t); $COCH_3$ 0.97 (s) ppm. 8: H_{py} 8.86 (d), 8.80 (d), 8.70 (s), 8.39 (s); PhH 8.5 - 7.8 (m); OC_4H_9 1.15 (s); $COCH_3$ -0.42 (s) ppm. 8': H_{py} 8.89 (d), 8.77 (d), 8.75 (s), 8.37 (s); PhH 8.6 - 7.7 (m); OC_4H_9 -0.71 (s); $COCH_3$ 0.92 (s) ppm.

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