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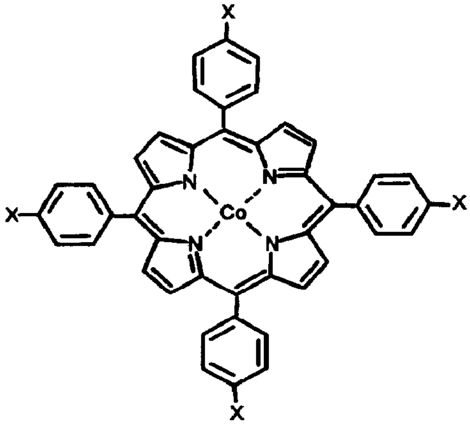
Cobalt(II)-Porphyrin Catalyzed Selective Functionalization of Alkanes with sulfurylchloride: A Remarkable Substituent Effect

Vibha Khanna, Pitchiah Tamilselvan, Swinder Jeet Singh Kalra and Javed Iqbal*
Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, INDIA

Abstract: *Cobalt(II)-porphyrin complex 1* and **2** *catalyses the chlorination and sulfochlorination respectively of n-alkanes and cycloalkanes with sulfuryl chloride in benzene. The p-substituent of the benzene ring in the porphyrin complex* **1** and **2** *shows a remarkable chemoselectivity in these reactions.*

The historical belief regarding the chemical inertness of paraffins has lately been proved to be a myth by the pioneering exemplary studies from the group of Barton and others[1]. Their studies have indicated that paraffins display a rich variety of chemical reactions when confronted by appropriate reactive species whose reactivity profile may be subtly tuned by a judicious choice of the activating reagent. Metal centers have proven to be ideal candidates for inducing reactivity in carbon-hydrogen sigma bond via their "activated form" which is readily achievable on encounter with activating agents like dioxygen, hydroperoxides, halogens etc. The endeavor of these workers in this exciting area of research has laid foundation for the future growth of the syntheses of organic chemicals based on hydrocarbon feed stocks. This communication describes our preliminary results on selective chlorination or sulfochlorination of alkanes with sulfuryl chloride catalyzed by 5,10,15,20-Tetrakis (4-methoxy phenyl)- 21H,23H porphyrin cobalt(II) **1** complex and 5,10,15,20-Tetrakis (4-methyl phenyl)-21H, 23H



$X = -OCH_3$ (**1**)
$X = -CH_3$ (**2**)

porphyrin cobalt(II) 2.

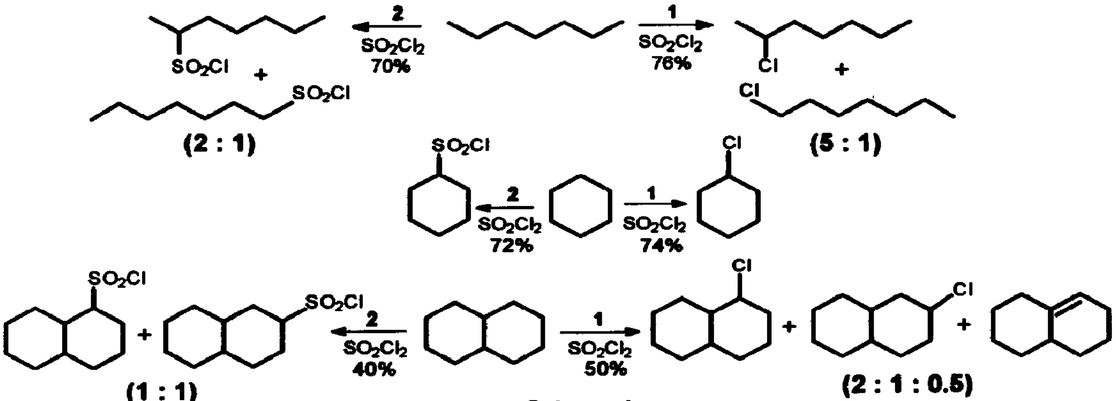
The readily available cobalt complexes[2] 1 and 2 exhibits a remarkably selective and efficient catalytic activity in the chlorination or sulfochlorination of n-alkanes and cycloalkanes with sulfuryl chloride in benzene at 85° C. Thus in the presence of 1 the straight chain alkanes can be converted to the corresponding 2-chloroalkanes[3] in high yields under these conditions[4] (table I, entries 1-3). The 2-chloroalkanes are accompanied by ∼15% of the corresponding 1-chloroalkanes along with some polychlorinated products. Similarly monochlorination of cyclohexane and cyclooctane can be accomplished (table I, entries 4 and 5) in high chemical yields following the protocol as described for n-alkanes. Efficient chlorination of alkanes can be achieved only with two equivalent of sulfuryl chloride as the use of one equivalent or less amount of the later resulted in poor yields of chloroalkanes. The chlorination of isooctane is comparatively slower than n-alkanes and it afforded a mixture of products, however, one of the products found was the primary chloride resulting from the chlorination of one of the tertiary methyl groups (table I, entry 6). Surprisingly, the alkyl aromatic compounds i.e. ethyl benzene and isopropyl benzene did not undergo any appreciable chlorination under these conditions, however, small quantity (∼10-15%) of styrene and methyl styrene were found to be present in the reaction mixture (table I, entries 7 and 8). An equal mixture of cis-and trans-decalin were also chlorinated under these conditions to give a mixture of chlorinated compounds and alkene (scheme I).

Table I :Co (II)-TMPP (1) Catalysed Chlorination of Alkanes with Sulfuryl Chlorides

Entry	Alkane	Products (% yield)[a,b]
		1-chloroalkane :2-chloroalkane
1.	n-hexane	15:85 (75)
2.	n-octane	15:85 (72)
3.	n-nonane	15:85 (76)
4.	cyclohexane	chlorocyclohexane (74)
5.	cyclooctane	chlorocyclooctane (76)
6.	2,2,4-trimethyl pentane	1-chloro-2,2,4-trimethyl pentane (20)
7.	ethylbenzene	styrene (15)
8.	isopropylbenzene	1-methylstyrene (~15-20)

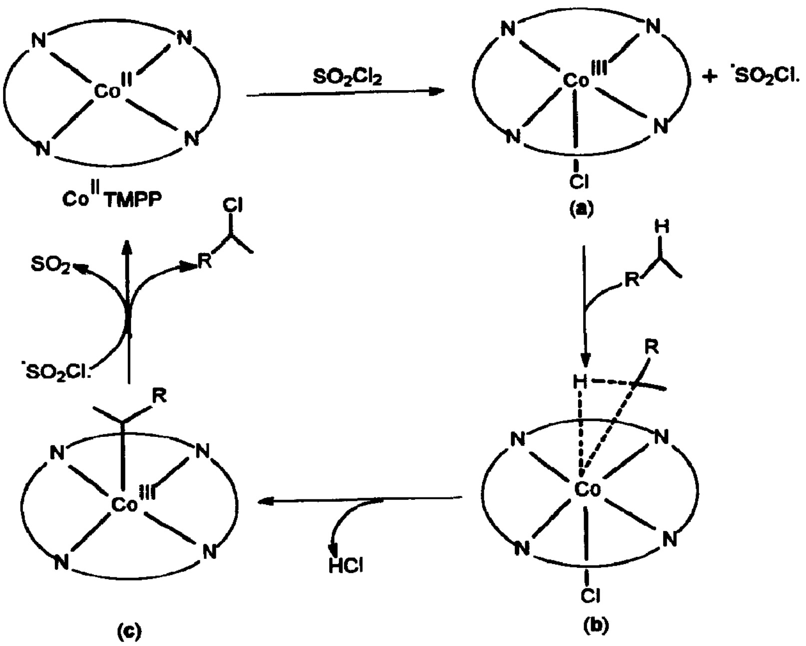
a) Isolated yields of the products. b) The ratio of 1-chloroalkanes and 2-chloroalkanes was obtained from the ^1H NMR of the crude reaction product.

Interestingly, when catalyst 2 is used for these reactions, the chlorosulfonated compounds are obtained as the major product. These reactions are also accompanied by small amount of the corresponding monochlorinated compounds. The chlorosulfonation is also C-2 selective, however, this selectivity is not as high as compared with chlorination reaction catalyzed by 1. Thus n-heptane can be converted in the presence of catalyst 1 to corresponding 2-chloroheptane along with the 1-isomer as a minor product, whereas the reaction catalyzed by 2 leads to 2-chlorosulfonyl product as the major product. This reaction is also accompanied by other regioisomers in small amounts. Similarly cyclohexane can be smoothly transformed in the presence of 2 to the corresponding monochlorosulfonate derivative in good yields (scheme I). A similar treatment on mixture of decalin afforded a mixture of chlorosulfonated compounds as the major products. This diversity in the chemoselectivity is presently unclear. Also this reactivity profile is at variance with a mechanism involving a homolytic cleavage of carbon-hydrogen bond. Thus the unusual C-2 selectivity during chlorination of n-alkanes can not be easily explained by a mechanism involving hydrogen abstraction by a free radical. Therefore this reaction may involve reversible formation of alkyl radicals by direct reaction of the alkane carbon-hydrogen bond with the cobalt(III) species generated during the course of the reaction. Thus, the catalytic cycle for the reaction may be explained by an initial interaction between catalyst 1 or 2 and sulfuryl chloride which will result in a ligand atom transfer to give chlorosulfonyl radical and a cobalt(III)-species (a) (scheme II). The later species may undergo electrophilic substitution[5] of C-H -bond via a three-center transition state (b) to give an alkyl-cobalt(III) intermediate (c). A SH[2] displacement on (c) by chloride or chlorosulfonyl radical may afford the chlorides or chlorosulfonated products respectively and catalyst 1 or 2 will be regenerated to complete the catalytic cycle. Also the high C-2 selectivity may be understood if we invoke the chloride attack on an alkyl-cobalt complex, instead on a free radical, as the steric factor



Scheme I

associated with the former will be responsible for the high regioselectivity. Thus cobalt-porphyrin catalysed reaction of alkanes with sulfuryl chloride provides a very efficient route to selective carbon-hydrogen activation under mild conditions.



Scheme - II

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4. A mixture of catalyst **1** or **2** (~30mg), alkane (30 mmol) and sulfuryl chloride (60 mmol) was stirred at 85°C for 8-15 h. The solvent was removed under reduced pressure and the chloroalkanes were obtained by direct distillation (using the vigreux column) under vacuum from the reaction mixture.

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