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HOMOLYTIC SUBSTITUTION OF 2-METHYLQUINOLINE BY CROWN ETHERS

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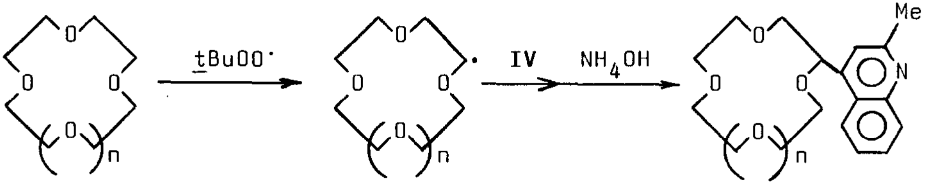
Summary: The paper describes the reactions of crown ethers with 2-methylquinolinium hydrogen sulfate in the presence of the redox system tert-butylhydroperoxide+$FeSO_4$, giving substituted products in yields of 65-69%.

Crown ethers substituted by heteroaromatic rings are synthesized by the cyclization of orthodihydroxy derivatives of aromatic heterocycles with α,ω dichloro derivatives of linear polyethers[1], or by the condensation of substituted benzo crown ethers with acetic anhydride, followed by O-N exchange[2]. No data are available in the literature concerning the direct introduction of heterocycles into crown ethers. However, it is known that heteroaromatic compounds can be substituted by simple ethers, and by the simplest analogue of crown ethers, 1,4-dioxane[3].

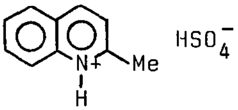
On the basis of this observation, we have undertaken a study of the adaptation of this method to crown ethers and we report here the successful direct substitution of crown ethers by a heterocycle.



I-III **V-VII**

n= 1 (I, V); 2 (II, VI);
3 (III, VII)

IV=



In the reactions of crown ethers I-III with the protonated 2-methylquinoline IV, the α-oxyalkylated products **V-VII** are formed with high selectivity. Mechanistic considerations based on literature data[3] indicate that the tert-butylperoxy radical, formed by the homolytic decomposition of tert-butylhydroperoxyde, transforms substrates I-III to the corresponding radicals by hydrogen abstraction. These nucleophilic radicals, participate in substitution by displacing the γ-hydrogen of protonated, electron-deficient 2-methylquinoline (**IV**). Under the reaction conditions employed, the ring size of the crown ether has practically no effect on the product yield. Compounds **V-VII** were formed in yields of 69, 65 and 65%, respectively. These values are slightly lower than the yield in the similar transformation of 1,4-dioxane (74%)[3].

Experimental

To a stirred solution of 0.01 mole of crown ether, 0.013 mole of 2-methylquinolinium hydrosulfate **IV** and 0.01 mole of $FeSO_4 \cdot 7H_2O$ in dimethylsulfoxide, 0.015 mole of <u>tert</u>-butylhydroperoxide is added in one hour under an argon atmosphere. The reaction mixture is diluted with an equal volume of water, neutralized with aqueous ammonia solution and extracted with chloroform. Chloroform and unreacted starting materials are steam-distilled off, and the residual products are purified by column chromatography (Al_2O_3, hexane-chloroform 3:1) and characterized by NMR spectroscopy (Table).

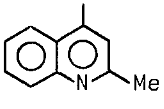
Table

NMR data on synthesized substituted crown ethers

Products[1]	$-CH_3$	$-CH_2-O-$	$-O-\underset{\vert}{C}H-Ar$[2]	$-Ar$[2]
(2-methylquinolinyl-4)-12-crown-4 (**V**)	s 2.5 3H	m 3.44-3.78 14H	m 5.20-5.33 1H	m 7.20-8.13 5H
(2-methylquinolinyl-4)-15-crown-5 (**VI**)	s 2.59 3H	m 3.45-3.78 18H	m 5.20-5.33 1H	m 7.20-8.15 5H
(2-methylquinolinyl-4)-18-crown-6 (**VII**)	s 2.61 3H	m 3.40-3.71 22H	m 5.21-5.34 1H	m 7.20-8.10 5H

[1] Yellow oils of high viscosity.

[2] Ar=



References

1. F. Vögtle, K. Frensch: Angew. Chem., Int. Ed. Eng., <u>15</u>, 685 (1976).
2. V. I. Dulenko, S. L. Bogza, Yu. A. Nikolyukin: Khim. Geterotsikl. Soed., 1283 (1984).
3. W. Buratti, G. P. Gardini, F. Minisci, F. Bertini, R. Galli, M. Perchinunno: Tetrahedron, <u>27</u>, 3655 (1971).

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