

HOMOLYTIC METHOXYLATION OF STILBENES BY  
ANODIC OXIDATION OF METHANOL

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Recently, we have found that methoxy radicals which were formed by the electrolytic oxidation of methanol were able to abstract hydrogen atoms from alkylaromatics<sup>1</sup> and hydroaromatics<sup>2</sup> under modified conditions.

This communication deals with the anodic oxidation of methanol in the presence of stilbenes in order to study on the addition of methoxy radicals to olefinic double bonds and also to discuss it stereochemically.

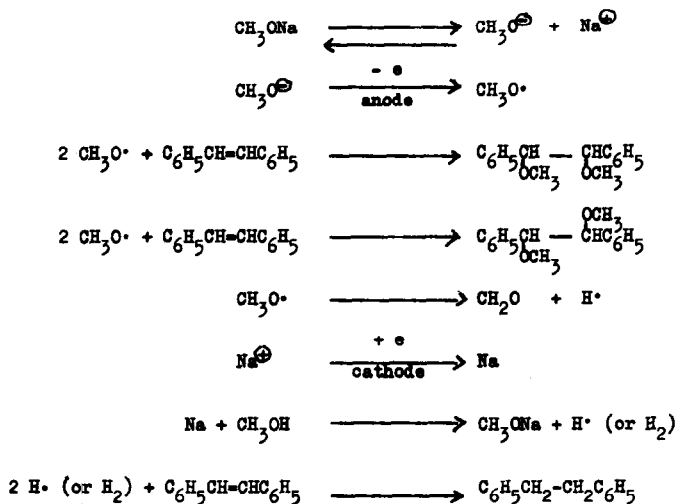
The electrolyses were carried out by using two platinum foil electrodes in cylindrical glass cell as described previously. A current was controlled at 0.3 amp., temperature being kept at 35°C. Electrolysis of methanol in the presence of trans-stilbene for 45 hr. gave meso-hydrobenzoindimethyl ether, I (20%), dl-hydrobenzoindimethyl ether, II (44%) and bibenzyl (trace) respectively, unreacted trans-stilbene (2%) being recovered.

On the contrary, I (26.3%), II (17.5%) and bibenzyl (6.5%) were obtained from cis-stilbene for 72 hr. and 3.8% of unreacted cis-stilbene was recovered.

The separation of these compounds was performed by column-chromatographic technique. I; m.p. 139-139.5°C (Found: C, 79.51; H, 7.60; Calcd. for C<sub>16</sub>H<sub>18</sub>O<sub>2</sub>: C, 79.31; H, 7.49%) and II; m.p. 90.5 - 91°C (Found: C, 79.22; H, 7.28; Calcd. for C<sub>16</sub>H<sub>18</sub>O<sub>2</sub>: C, 79.31; H, 7.49%) were identified by mixed melting point determination

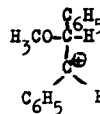
with authentic specimens. The infrared spectra of these compounds showed C-O-C absorption band at  $1104\text{ cm}^{-1}$  (I),  $1092\text{ cm}^{-1}$  (II) respectively and were also identical with those of authentic samples.

Considering from the experimental results reported here and before, it may be said that these reactions may proceed by the homolytic addition to double bond via electrode process as indicated below:



If we suppose that these reactions proceed according to an ionic mechanism as proposed in the case of olefin oxidation with lead tetraacetate<sup>3</sup>, carbonium ion III must be formed as an intermediate. But it is quite unreasonable to consider the formation of III in this system.

In this case I and II are produced in fair yield without giving  $\alpha$ -methoxybibenzyl.



III

Of particular interest is the fact that addition of methoxy radicals to stilbenes proceed stereospecifically under these conditions. The stereochemical pictures of these addition reactions are shown hereunder:

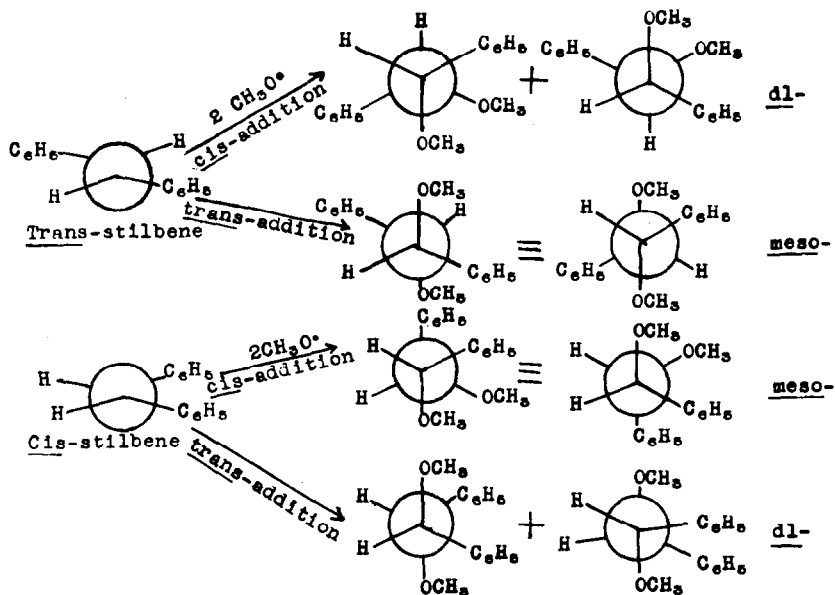


Chart 1 Stereochemistry of addition reaction of methoxy radicals to stilbenes

As indicated above, it seems to be sure that cis-addition to stilbenes takes place in preference to trans-addition.

Further studies on the behavior of free-radicals generated by electrode processes are now being undertaken and detailed description of these results will be published elsewhere.

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