On a New Group of Catalysts for Benzoin Condensation.

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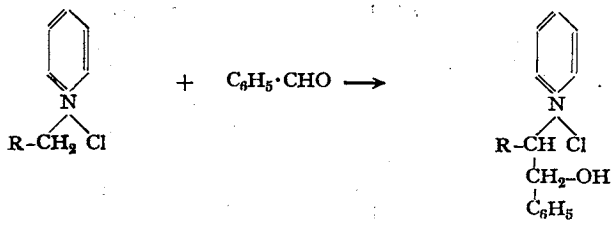
(A) The action of thiaxoliumbases.

As far as we know, cyanides are the only catalysts of benzoin condensation, which takes place in alkaline solution.

We happened to have found a new group of catalysts of benzoin condensation.

According to F. Kraenke, a sort of ethanolamine is produced when a salt, obtained from $R-CH_2-Cl$ and pyridine, is treated with benzaldehyde in alkaline solution.



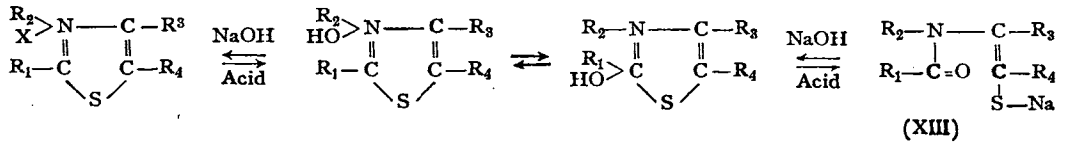
we substituted thiaxolium salt instead of pyridinium salt in this reaction, expecting to obtain the corresponding ethanolamine, but we unexpectedly found that benzoin was crystallized out.

Following derivatives of thiazolium were investigated:

N-Benzylthiazoliumbromide	(I)
N-Ethylthiazoliumbromide	(II)
N-Dethylthiazoliumiodide	(III)
N-Benzyl-4-methylthiazoliumbromide	(IV)
Vitamin B_1	(V)
N-Ethyl-4-methyethiazoliumiodide	(VI)
N-Benzyl-2,4-dimethylthiazoliumbromide	(VII)
N-Phcenacylthiazoliumbromide	(VIII)
N-p-bromophenacylthiazoliumbromide	(X)
N-Benzyl-4-pheylthiazoliumbromipe	(IX)
N-Phenyl-4-methylthiazoliumperchlorate	(XI)
Thiazol	(XII)

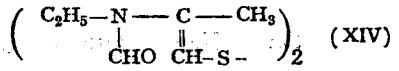
Compounds from (I) to (VI) were proved to have the catalytic action upon benzoincondensation. If furfural is used as an aldehyde, furoin can be obtained.

When a thiazolium salt reacts with an alkali, it is supposed that the following reaction takes place.



So we wondered if the real catalyst of this reaction might be the cleavaged product of the ring (XIII).

As it is difficult to prepare (XIII) we have made its oxidation-product, i. e. disulphide (XIV).

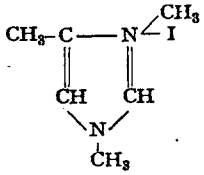


(XIV)

This disulphide was also proved to be a catalyst of benzoin condensation.

(B) The action of imidazoliumbase.

The following compounds were investigated concerning catalytic action upon benzoin condensation.



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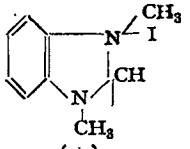

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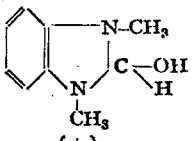

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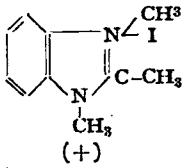

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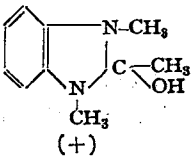

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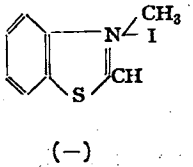

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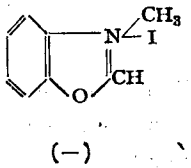

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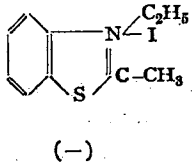

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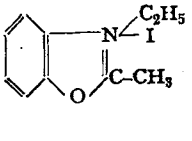

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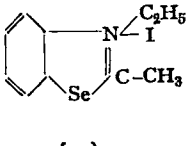

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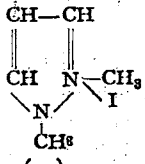

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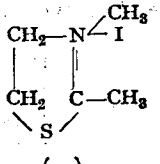

(−)

(+) indicates the catalytic action.

Judging from the above result, it is clear that imidazoliumbases have the same action with thiazoliumbases.