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METHOXYMERCURATION/DEMERCURATION REACTIONS OF CYCLOPROPANES IN THE PRESENCE OF ACRYLONITRILE

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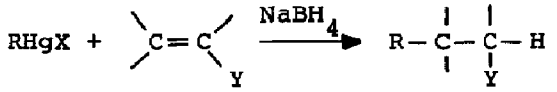
Summary: Methoxymercuration/demercuration reactions of cyclopropanes 4 in the presence of acrylonitrile yield products 5 in a carbon-carbon bond formation reaction.

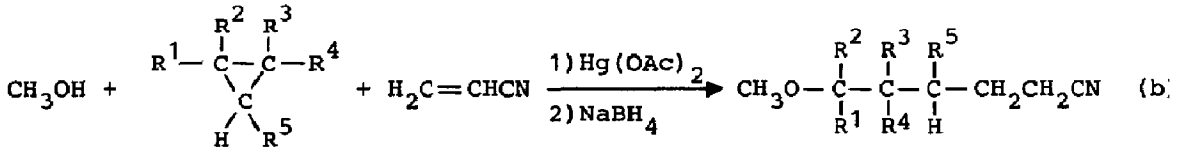
Reductions of alkylmercuric salts 1 with $NaBH_4$ in the presence of electron deficient alkenes 2 yield products 3 in a radical chain reaction (eq.a)[1].



(a)

1 2 3

We now have observed that cyclopropanes 4, which are precursors for 3-methoxyalkyl mercuric salts[2], can undergo carbon-carbon bond formation reactic with acrylonitrile in one flask syntheses (eq.b).



(b)

4 5

Equimolar amounts of cyclopropanes 4 and $Hg(OAc)_2$ are treated with CH_3OH at 20-65°C. After 1-3 d CH_3OH is distilled off and acrylonitrile, dissolved in CH_2Cl_2 (30% solution), is added in 20 molar excess. After reduction with $NaBH_4$ (0.5-1.0 h) filtration and distillation yield products 5 (Table I).

Table I

Overall yields and spectra of products 5 in methoxymercuration/demercuration reactions of cyclopropanes 4 in the presence of acrylonitrile.

Cyclopropanes 4					Products 5	^{1}H-NMR(δ)	IR(cm^{-1})
R^1	R^2	R^3	R^4	R^5	(Yield,%)	OCH_3	C=O
C_6H_{13}	H	H	H	H	50	3.33	2250
C_6H_5	H	H	H	H	87	3.21	2255
C_2H_5	C_2H_5	H	H	H	65	3.10	2250
H	$-(CH_2)_4-$		H	H	82	3.31	2250
CH_3	H	CH_3	H	CH_3	20[a]	3.30	2245
CH_3	CH_3	CH_3	H	H	81	3.15	2255
CH_3	CH_3	CH_3	CH_3	H	56	3.17	2250

a) $Hg(OCOCF_3)_2$ is used; with isolated organomercuric salts the yield is 93%.

The overall yields of one flask syntheses (b) with cyclopropanes 4 that are unsubstituted at one carbon atom (R^5 = H) are between 50 and 87%. Because of the difficult mercuration[3] the yield decreases with 1,2,3-trimethylcyclopropane although the carbon-carbon bond formation reactions occurs with 93%.

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References

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3) C.H. De Puy and R.H. Mc Girk, J. Am. Chem. Soc. 96, 112 (1974).

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