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REACTIONS OF ORGANIC ANIONS XXXVI. CATALYTIC METHOD OF PREPARATION OF 1-CHLORO-1-PHENYLTHIOCYCLOPROPANE DERIVATIVES IN AQUEOUS MEDIUM[x]

M.Mąkosza and E.Białecka

Institute of Organic Chemistry and Technology,

Technical University /Politechnika/, Warsaw.

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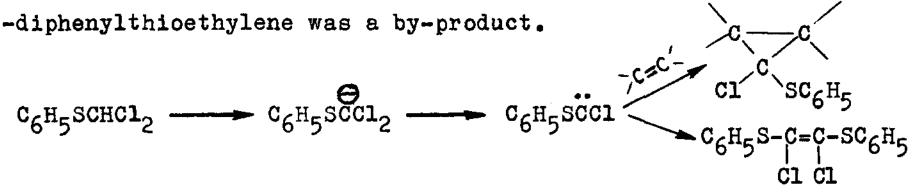
We have observed, that the reaction of chloroform[1] or bromoform[2] with olefins in the presence of 50% aqueous NaOH and triethylbenzylammonium chloride /TEBA/ is a very convenient method for preparation of dichlorocyclopropane derivatives. Carbene is formed in the first stage of the reaction and it reacts after with olefins.

In this work we have tried to form chlorophenylthiocarbene in aqueous medium and synthesize 1-chloro-1-phenylthiocyclopropane derivatives.

Until now chlorophenylthiocarbene was formed in anhydrous conditions by the action of t-C_4H_9OK on dichloromethylphenyl sulphide in petroleum ether[3] or cyclohexane[4] and the addition of this carbene to olefins proceeded with the yield of about 15-20 % /if the olefin was cyclohexene/ or 50-60% /if the olefin was isobutene/.

We have observed that dichloromethylphenyl sulphide reacted exothermically with a slight excess of olefins in the presence of 50% aqueous NaOH and TEBA chloride as catalyst. The 1-chloro-1-phenylthiocyclopropane derivatives were isolated in the yield of about 50%. A little amount of 1,2-dichloro-1,2-diphenylthioethylene was a by-product.



Carbene, which is formed in this reaction, adds to olefin or partly dimerizes.

The following synthesis of 1-phenyl-2-chloro-2-phenylthiocyclopropane may be an illustration of this method:

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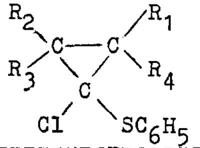
[x] Part XXXV.M.Mąkosza,I.Gajos, Bull.Acad.Polon.Sci.,Sér.sci.chim.,in press.

5,2g /0,05 mole/ of styrene, 7.76g /0.04 mole/ of dichloromethylphenyl sulphide, 15 ml of 50% aq. NaOH and 0.2 g TEBA chloride were stirred at 40-50°C for two hours. Upon dilution with water, separation of the layers and distillation cyclopropane derivative /6.7g 63% yield/ and of 1,2-dichloro-1,2-diphenylthioethylene /0.7g 10% yield/ were obtained.

Similiar results gave other olefins. The yields and the properties of some chlorophenylthiocyclopropane derivatives are collected in the Table:

Table[x]

No	olefin	cyclopropane derivatives 						
		R_1	R_2	R_3	R_4	yield	b.p.°C/mm Hg	n_D^{22}
1[xx]	hexene-1	C_4H_9	H	H	H	20%	103/0.4	1.5499
2	isoprene	$CH=CH_2$	H	H	CH_3	51%	102/0.5	1.5847
3	styrene	C_6H_5	H	H	H	63%	127/0.3	1.6253
4	cyclohexene	$/CH_2/_4$		H	H	44%	115/0.3	1.5980
5	butyl-vinyl ether	C_4H_9O	H	H	H	58%	117-20/0.4	1.5463
6	butyl-vinyl sulphide	C_4H_9S	H	H	H	49%	124/0.4	1.5781

[x] The structures of all compounds were confirmed by analytical data and NMR spectra.

[xx] Lit.[3] b.p. 122°C/0.02 mm Hg

We have supposed, that the mechanism of this reaction is the same as the mechanism of dichlorocarbene formation in aqueous medium[1]. By action of conc. NaOH solution TEBA chloride is transformed into the hydroxide insoluble in aqueous phase. It migrates to the boundary between the aqueous and organic phase where it reacts with dichloromethylphenyl sulphide to yield II, which is transformed into carbene. Carbene reacts with olefin, regenerated TEBA chloride passes again to the phase boundary:

$$C_6H_5SCHCl_2 + Et_3\overset{\oplus}{N}CH_2Ph\ \overset{\ominus}{OH} \rightleftharpoons C_6H_5S\overset{\ominus}{C}Cl_2\ Et_3\overset{\oplus}{N}CH_2Ph\ /II/ + H_2O$$

$$C_6H_5S\overset{\ominus}{C}Cl_2\ Et_3\overset{\oplus}{N}CH_2Ph \longrightarrow C_6H_5S\overset{\cdot\cdot}{C}Cl + Et_3\overset{\oplus}{N}CH_2Ph\ \overset{\ominus}{Cl}$$

The presented method provides a convenient route for the synthesis of chlorophenylthiocyclopropane derivatives.

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