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HIGHER ALKYLDIMETHYLBENZYLAMMONIUM CHLORIDES (CATAMINE AB) AS AN EFFECTIVE PHASE TRANSFER CATALYST IN THE DIHALOCYCLOPROPANATION OF OLEFINS

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Triethylbenzylammonium and n-hexadecyltrimethylammonium chlorides are the most common phase transfer catalysts in the generation of dihalocarbenes from haloforms by the action of alkali in two-phase systems [1, 2].

We have shown the high efficiency of a technical mixture of higher alkyldimethylbenzylammonium chlorides with alkyl groups containing from 10 to 18 carbon atoms (catamine AB) as a catalyst for the dihalomethylenation of unsaturated compounds by $CHCl_3$ and $CHBr_3$ in a two-phase system. We should note that catamine AB was used by Kurginyan [3] for the preparation of unsaturated chlorides by the dehydrochlorination of polychlorohydrocarbons.

The experiments were carried out at about 40° C usually by the addition of excess haloform to a mixture of 50% aq. NaOH, unsaturated acceptor (1-hexene, cyclohexene, cis,cis,1-5-cycloocadiene, allyl chloride and allyl bromide) and the catalyst in 2-4:5:1:0.02 mole ratio. When 0.1-0.2 mole olefin was used, the reactions were completed in 40-60 min and virtually unaccompanied by the formation of side-products (the yields of the corresponding gem-dihalocyclopropanes were up to 95%).



It is interesting that the yields of 7,7-dihalonorcaranes in the case of cyclohexene increase significantly upon the addition of an apolar aprotic solvent (hexane), while there is virtually no such effect in the case of 1-hexene.

The dichloromethylenation of 1,5-cyclooctadiene gives a $\sim 50\%$ total yield of a mixture of monoadduct (I) and diadduct (II) in about 2:5 mole ratio. Gas-liquid chromatography indicated that the same ratio is found 10 min after the onset of chloroform addition.



In the case of allyl halides also having two reaction sites, the yields of the corresponding halomethylgem-dihalocyalopropanes (III) and (IV) do not exceed 40-45%. The combined addition of allyl chloride and chloroform to NaOH and catamine AB gave better results than the usual order for the mixing of the reagents. In addition, in the case of allyl bromide with CHCl₃, the allylic bromine is exchanged by chlorine with the formation of chloromethyl analog (III) along with bromomethyl-gem-dichlorocyclopropane (IV).

 $CH_2 = CHCH_2CI \xrightarrow{CHCI_3, aq. NaOH} CI \xrightarrow{CI} CI \\ catamine AB \\ (III) \xrightarrow{CH_2CI} CH_2CI$

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$$CH_2 = CHCH_2Br \xrightarrow{CHCl_3, aq, NaOH} AB \xrightarrow{CI} Cl_{CH_2Br} + (III)$$

We should note that the use of catamine AB often gives higher yields of the products of gem-dihalomethylenation of unsaturated compounds than other similar phase transfer catalysts. Thus, the adduct of CCl_2 to 1-hexene was preparatively isolated in 73% yield as compared to a 60% yield obtained using tricaprylmethylammonium chloride [1]. The yield of 7,7-dibromonorcarane using catamine AB was 90% as compared to 72-76% yields obtained using other catalysts [1].

The purity and structure of the gem-dihalocyclopropanes obtained were established by gas-liquid chromatography, elemental analysis and IR and PMR spectroscopy using reference samples.

EXPERIMENTAL

The starting haloforms and unsaturated compounds were freshly distilled technical samples. Catamine AB is a technical product in the form of a 50% aqueous solution (TU 6-01-816-75).

The gas-liquid chromatographic analysis was carried out at 100-200°C on an LKhM-72 chromatograph using a 150 \times 0.3 cm column packed with 5% silicone SE-30 on Celite 545 and 3% OV-17 on Chromatone N. The helium gas carrier flow rate was 40-45 ml/min. The IR spectra were taken neat on a UR-20 spectrometer. The PMR spectra were taken on a Tesla BS-467 spectrometer at 60 MHz for solutions in CCl₄ with TMS as the internal standard.

<u>7,7-Dichloronorcarane</u>. A sample of 47.8 g (0.4 mole) CHCl₃ was added over 50 min to a stirred mixture of 8.2 g (0.1 mole) cyclohexene, 40 ml 50% aq. NaOH, 2 g catamine AB (as a 50% aqueous solution) and 20 ml hexane at 36-40°C. Then, 0.5 liter water and 100 ml ether were added and the layers were separated. The organic layer was combined two 100-ml ethereal extracts of the aqueous layer, dried over MgSO₄, evaporated and distilled to give 15.8 g (95%) dichloronorcarane with bp 40-41°C (2 mm) nD²⁰ 1.5040 [4].

Under the same conditions but in the absence of hexane, the yield of dichloronorcarane was 78%, while the yield with hexane and a double amount of NaOH was 75%.

<u>7,7-Dibromonorcarane</u> was obtained by analogy to the previous experiment at 40-42°C. The yield was 23 g (90%), bp 84-85°C (3 mm), n_D^{20} 1.56.12 [4] (the yield in the absence of hexane was only 42%).

<u>1-Butyl-2,2-dichlorocyclopropane</u> was obtained by an analogous procedure. The yield was 14 g (73%), bp 76-77°C (25 mm), n_D^{20} 1.4525 [4] (the yield in the absence of hexane was 70%).

<u>2,2-Dichloro-1-chloromethylcyclopropane (III)</u> was obtained analogously from 0.2 mole allyl chloride, 0.4 mole CHCl₃, 1 mole NaOH and 2 g catamine AB (without hexane) to give 6.4 g product (20%), bp 52°C (20 mm), n_D^{20} 1.4865 [5]. The combined addition of CHCl₃ and allyl chloride to a mixture of the other reagents under the same conditions gave 11.5 g (36%) (III).

<u>2,2-Dichloro-1-bromomethylcyclopropane (IV)</u> was obtained by the addition of 0.2 mole over 40 min at $36-40^{\circ}$ C to a mixture of 0.1 mole allyl bromide, 0.5 mole NaOH and 2 g catamine AB. Stirring for 4 h at 40-42°C gave 8.5 g of a mixture of (III) and (IV) with bp 35-40°C (3 mm) in 10 and 32% yields, respectively. Redistillation gave (IV) in 95% purity, bp 72-74°C (20 mm), n_D^{20} 1.5143 [5].

<u>9,9-Dichlorobicyclo[6.1.0]non-4-ene (I) and 5,5,10,10-tetrachlorotricyclo[7.1.0.0^{1,8}]decane (II).</u> A sample of 47.8 g (0.4 mole) CHCl₃ was added over 1 h to a mixture of 10.8 g (0.1 mole) 1,5-cyclooctadiene, 40 ml 50% aq. NaOH, 2 g catamine AB and 20 ml hexane at 36-44°C and stirred for an additional 1 h at 40-42°C. The mixture was cooled to ~20°C and 1 liter water was added. The crystalline precipitate of (II) was filtered off. The filtrate was extracted with two 100-ml portions of ether. The ethereal extracts were combined with the crystals and maintained for 24 h at 0-5°C to give 10 g (36%) (II), mp 174-176°C (from methanol) [6]. Distillation of the mother liquor gave 3 g (15%) (I), bp 95-96°C (4 mm), np²⁰ 1.5225 [6].

CONCLUSIONS

A technical mixture of higher alkyldimethylbenzylammonium chlorides (catamine AB) has been proposed as an efficient catalyst for the dihalomethylenation of unsaturated compounds by haloforms in two-phase systems.

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C-ALKYLATION OF 3-METHYL-1-PHENYL-5-PYRAZOLONE BY HEXAFLUOROACETONE AND ITS IMINES

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Some aromatic amines and heteroaromatic compounds react in the absence of catalyst with hexafluoroacetone [1-5] and its imines [6-8] to form C-alkylation products. In the present work, results are given for a study of the reactions of hexafluoroacetone and its imines with 3-methyl-1-phenyl-5-pyrazolone (I).

Pyrazolone (I) reacts with hexafluoroacetone quantitatively to give $4-(\alpha-hydroxyhexafluoroisopropyl)-3-$ methyl-1-phenyl-5-pyrazolone (II).



Thus, the alkylation is directed toward the site of maximum electron density in (I) [9].

Pyrazolone (I) reacts amlogously at 20°C with the trifluoroacetylimine (IIIa) and benzenesulfonylimine (IIIb) of hexafluoroacetone. Imine (IIIa) was found to be more active than (IIIb), which was noted previously in reactions with indole [7]. The only reaction products were pyrazolones (IVa) and (IVb) which are the products of C⁴-alkylation. Hexafluoroacetone imine (IIIc), whose electrophilicity is much less than that for N-acyl derivatives (IIIa) and (IIIb), reacts with (I) at 120°C to give $4-(\alpha-\text{aminohexafluoroisopropyl})-3-\text{methyl}-4-\text{phenyl}-5-$ pyrazolone (IVc) in 68%. Pyrazolone (IIIc) was obtained also by heating trifluoroacetyl derivative (IVa) in a water—ethanol solution of NaOH at reflux.



 $\mathbf{R} = \mathbf{CF_3CO} \text{ (IIIa), (IVa); } \mathbf{R} = \mathbf{C_6H_5SO_2} \text{ (IIIb), (IVb); } \mathbf{R} = \mathbf{H} \text{ (IIIc), (IVc).}$

The structures of (II) and (IVa)-(IVc) were established using ¹³C and ¹⁹F NMR spectroscopy (Table 1) PMR spectroscopy (Experimental) and elemental analysis (Table 2). The multiplicity of the signals in the EMR spectra indicate the C⁴-substitution of 3-methyl-1-phenyl-5-pyrazolone (I).

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