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MIXTURES OF CaO–KOH and CaH_2–KOH AS SOLID BASES IN REACTIONS OF INTERPHASE TRANSFER

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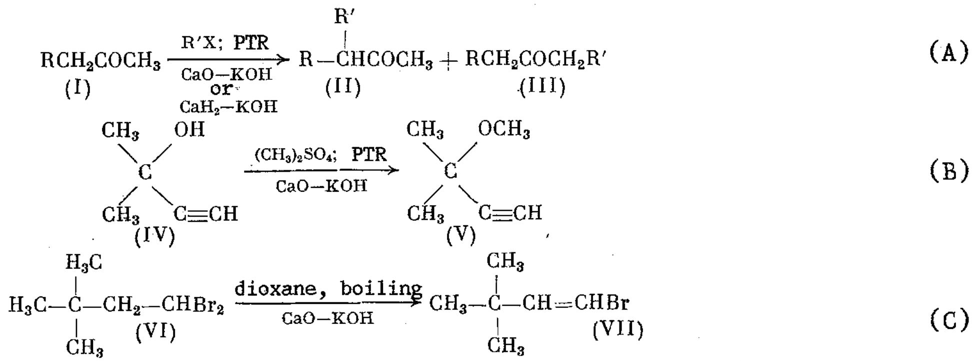
Reactions of interphase alkylation are carried out under standard conditions with an excess of the solid alkali metal hydroxide or its concentrated aqueous solution and catalytic amounts of the phase transfer reagent (PTR). The base thereby simultaneously plays the role of the source of the hydroxide ion and the "drying agent." Its latter property is very important since the activity of the hydroxide ion decreases sharply with the increase of the aqueous solvate cover [1].

The alkylation of butan-2-one (Ib) (Scheme A, Table 1) utilizing solid KOH (15% water content) proceeded without the PTR, and was stopped by the addition of CaO or CaH_2 to the mixture. In the latter case, some initial release of H_2 was noted. The introduction of PTR (crown or polyether) into this dehydrated mixture initiated a vigorous exothermic reaction. It followed from this that the water may act as a phase carrier. In other words, water is a reagent which assists the noncatalytic reaction route.

In the given work, a system with CaO or CaH_2 as the water absorbent is proposed for the alkylation or dehydrohalogenation reactions. The quantity of the absorbent (CaO or CaH_2) is calculated both for the water present in the initial hydroxide, and the water which is separated in the course of the reaction. Polypropylene glycol-250 (PPG) and 15-crown-5 were utilized as the PTRs. The standard reactions studied were the alkylation of acetone (Ia) or butan-2-one (Ib) with allyl bromide or butyl iodide (cf. Scheme A, Table 1).



R = H (Ia), Me (Ib); R = H, R' = *n*-Bu (IIa), (IIIa); R = Me, R' = All (IIb), (IIIb);
R = Me, R' = *n*-Bu (IIc), (IIIc).

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TABLE 1. Conditions of the Alkylation of Acetone (Ia) and Butan-2-one (Ib); (Ia), 2.0 moles; (Ib), 1.15 moles

Ketone	R′X[a]	Base[b]	Absorbent of water (moles)	PTR (mole percent)	Reaction conditions	Structure of the product (yield, %)[c]
(Ib)	AllBr	KOH[d]	–	–	20°, 24 h	(IIb) (33)[e]
(Ib)	AllBr	KOH	CaO (0,78)	–	20°, 24 h	No reaction
(Ib)	AllBr	KOH	CaO (0,78)	PPG (4,0)	20°, 24 h	(IIb) (47)[e]
(Ib)	BuI	KOH	CaH_2 (0,4)	PPG (4,0)	20°, 24 h	(IIc) (50)[f]
(Ib)	AllBr	KOH	CaH_2 (0,4)	PPG (1,6)	70°, 5 h	(IIb) (47)[e]
(Ib)	AllBr	NaOH	CaH_2 (0,25)	15-Crown-5 (0,756)	Boiling 5 h	(IIb) (44)[e]
(Ia)	BuI	KOH	CaH_2 (0,4)	PPG (4,0)	20°, 24 h	(IIa) (51)

[a] The compounds AllBr (0.5 mole) and BuI (0.52 mole) were taken into the reaction.

[b] 0.5 mole in the form of 85% tabletted KOH or 97% tabletted NaOH.

[c] The distilled product is indicated.

[d] 1.0 mole of 85% tabletted KOH.

[e] It contains 8% of the isomeric ketone (IIIb).

[f] It contains 3% of the isomeric ketone (IIIc).

The following features were thereby observed. Firstly, CaO or CaH_2 are inactive both in the presence and the absence of the PTR; both reagents show comparable activity in the standard mixture with the hydroxide and the PTR. Secondly, when the standard mixture of $CaO(CaH_2)$–KOH–PTR was utilized for the isolation of the propargyl ether (V) (Scheme B), the reaction proceeded rapidly and with high yields. Products of the C-alkylation at the acetylene carbon were not observed. On the other hand, this mixed base is too strong for the dehydrohalogenation (Scheme C), and some quantity of tert-butylacetylene is formed together with the halogenoolefin (VII) (56%). The tert-butylacetylene is preferred when the CaO–KOH mixture was obtained in a ball mill. The inactivity of the CaO as a base may be associated with the lack of specificity in the PTRs tested. It can be assumed that this oxide will be active as a base with the specific PTRs on the Ca ion.

EXPERIMENTAL

3-Methylhex-5-en-2-one (IIb). To the well stirred mixture of 103 ml (1.15 moles) of (Ib), 33 g (0.5 moles) of KOH, 44 g (0.78 moles) of CaO (calculated for the water present in the commercial KOH, and the water from the reaction), and 44 ml (0.5 moles) of allyl bromide were added 10 ml of PPG-250. The temperature was maintained below 65-70°C with intensive cooling. The mixture was then stirred without cooling for 24 h; it was decomposed by 150 ml of conc. HCl in 200 ml of H_2O with stirring and cooling. The organic layer was dried over K_2CO_3. The fraction with the bp 69-73°C (60 mm) gave 26.4 g (47%) of the mixture of the two regioisomers (IIb) and (IIIb); the content of (IIIb) was 8% according to GLC. Both the isomers were identified from the GLC and the mass spectra with known samples [2].

3-Methyl-3-methoxybut-1-yne (V). To the well-stirred mixture of 33 g (0.5 moles) of KOH, 44 g (0.78 moles) of CaO, 53 ml (0.5 moles) of (IV), 2 ml of PPG-250, and 100 ml of ether were added 50 ml (0.5 moles) of dimethyl sulfate. The temperature of 30-35°C was maintained with cooling. At the end of the exothermic reaction (1 h), the mixture was stirred for 1 h more; it was decomposed by 150 ml of conc. HCl in 200 ml of water with cooling. The organic layer was dried over solid KOH. The ether (V) was distilled; it had the bp 70-78°C and the yield of 41.5 g (84%). The compound (V) was identical to the known compound, obtained according to [3], on the basis of the GLC and the PMR spectrum.

1-Bromo-3,3-dimethylbut-1-ene (VII). The mixture of 15.5 g (63.5 mmoles) of (VI), 4.2 g (63.3 moles) of 85% tabletted KOH, 2.1 g (50 mmoles) of CaH_2, 15 ml of dioxane, and 0.5 ml of PPG-250 was stirred with boiling. When the dehydrohalogenation was over (H_2 was not released), the mixture was treated with 25 ml of conc. HCl in 60 ml of water. The organic layer was separated and dried over K_2CO_3. Distillation gave 5.8 g (57%) of the olefin (VII), which had the bp 63-67°C (85 mm). The PMR spectrum [δ, ppm, $(CD_3)_2CO$] was as follows: 1.05 s (9H), 6.13 d (1H, J = 14 Hz), and 6.26 d (1H, J = 14 Hz) (cf. [4]). The initial dibromide (1.5 g, 10%) with the bp 92°C (82 mm) was isolated from the high-boiling fraction.

CONCLUSIONS

The KOH—CaO or KOH—CaH_2 mixtures block the uncatalyzed hydrate transfer of the base in the alkylation reactions with phase transfer reagents.

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REACTIONS OF α-HALO-α,β-UNSATURATED ALDEHYDES WITH SECOND AMINES — NOVEL METHOD FOR THE PREPARATION OF N-DISUBSTITUTED α-AMINOCROTONALDEHYDES

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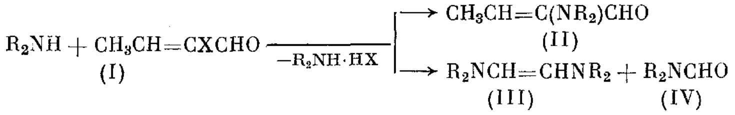
In contrast to N-disubstituted β-amino-α,β-unsaturated carbonyl compounds, for which synthetic methods have been well reported [1], enamine derivatives, containing a carbonyl group and amino group on the same carbon atom, have received very little attention. Unsaturated aliphatic aminoaldehydes have been prepared only by the reaction of organomagnesium compounds with formylated enediamines [2].

As part of our continuing study of the mutual effects of geminal functional groups at sp^2-hybridized carbon atoms we have examined the feasibility of synthesizing α-amino-α,β-unsaturated aldehydes via the reactions of the ipso-substituted halogen atoms in 2-halo-2-butenals. Nucleophilic substitution of halogen atoms located in α-positions to electron withdrawing groups are known to proceed only with great difficulty [3], and lead to the formation of unexpected reaction products [4-7]. By way of example, the reactions of α-bromocinnamic, α,β-dibromocinnamic, or α,β-dibromocrotonic aldehyde with secondary amines lead to the formation of N,N'-tetrasubstituted 1,2-diaminoethylenes [8].

We have found that secondary amines react with α-halocrotonaldehyde via two pathways, which lead to the formation of N-disubstituted α,β-unsaturated α-aminoaldehydes and N,N'-tetrasubstituted 1,2-diaminoethenes, respectively. Which pathway predominates depends on the nature of the amine and the reaction conditions [9]. The results are summarized in Table 1.



$$R_2NH + \underset{(I)}{CH_3CH{=}CXCHO} \xrightarrow[-R_2NH\cdot HX]{} \begin{cases} \longrightarrow \underset{(II)}{CH_3CH{=}C(NR_2)CHO} \\ \longrightarrow \underset{(III)}{R_2NCH{=}CHNR_2} + \underset{(IV)}{R_2NCHO} \end{cases}$$

X = Cl, Br, $R_2N = (CH_2)_5N$ (a), $O(CH_2CH_2)_2N$ (b), $(CH_2)_6N$ (c), Bu_2N (d), Et_2N (e), PhMeN (f).

Maximum yields of N-disubstituted α-aminocrotonaldehydes (II) are obtained with piperidine or morpholine in the presence of Et_3N. Surprisingly, hexamethyleneimine does not give the expected aminoaldehyde, and the reaction is complicated by a significant amount of resin formation. With acyclic dialkylamines (Et_2NH, Bu_2NH) the dominant pathway is the one that leads to the formation of the corresponding enediamines (III).

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