

Synthesis of 1,1-dihalo-2,2-dialkyl Olefins

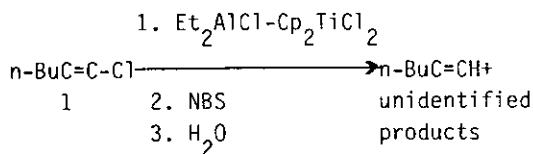
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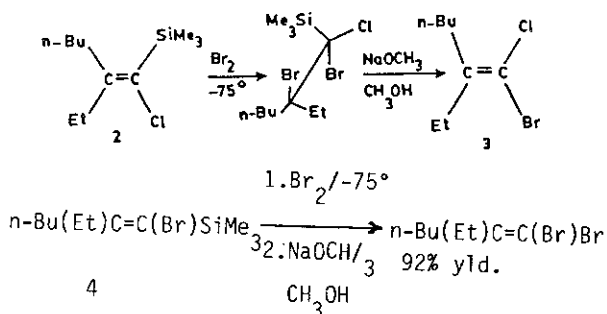
Recently, we have developed a new method for preparing 1-halo-1-(trimethylsilyl)-2,2-dialkyl olefins [1]. The usefulness of such olefins for preparing substituted olefins has been reported [2]. On the other hand, 1,1-dihalo-2,2-dialkyls have not yet played a major role in synthetic methodology. This is probably due to the difficulty of making such compounds. We believe that the availability of mixed 1,1-dihalo-2,2-dialkyl olefins might open new vistas into the methodology for synthesis of substituted olefins. This promoted us to search for convenient procedures for their preparation.

An attempt to prepare 1-bromo-1-chloro-2-ethyl-1-hexene(3) from 1-chloro-1-hexyne(1) via carbometallation-bromination procedure [1] led mainly to the metallated product which upon hydrolysis gave 1-hexyne.



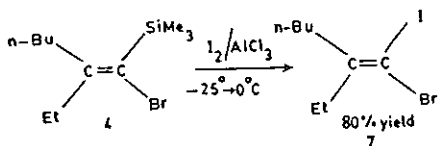
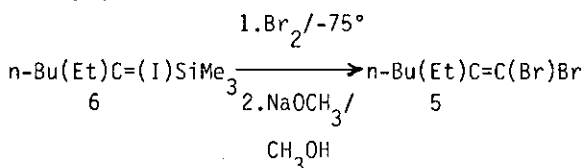
Therefore, attention was turned to the halogenation-desilicohalogenation procedure of the readily available 1-halo-1-(trimethylsilyl)-2,2-dialkylolefins [1]. This procedure proved to be successful. It was found that bromination-desilicobromination of 1-chloro-1-(trimethylsilyl)-2-ethyl-1-hexene(2) led to an excellent yield of (3). Besides bromination-desilicobromination of 1-bromo-1-(trimethyl-

silyl)-2-ethyl-1-hexene(4) led to an excellent yield of 1,1-dibromo-2-ethyl-1-hexene(5). However, attempts to prepare (3) via chlorination-desilicobromination of (4) led to a mixture of unidentified products including the desired product. This is probably due to the high reactivity of chlorine as compared to bromine. Attempts to determine the E/Z ratio of (3), even on capillary GLPC proved unsuccessful; however, it has been shown that trans and cis-1-(trimethylsilyl)-1-olefin undergo trans halogenation and anti-desilicohalogenation, when treated with halogens and base to give the corresponding cis and trans vinylhalides, respectively [3,4]. Therefore bromination-desilicobromination of (2) should afford the (E) isomer of (3).



An attempt to prepare 1-bromo-1-iodo-2-ethyl-1-hexene(6) using iodination-desilicoidination procedure led to no reaction with (4). Besides bromination-desilicobromination of 1-iodo-1-(trimethylsilyl)-2-ethyl-1-hexene (6) led only to (5). Fortunately, the desired product was obtained via electrophilic cleavage of C-Si bond by treating (4) with I₂ in the presence

of anhydrous AlCl_3 . This new method of introducing iodine to double bond may open new vistas into the methodology for synthesis of different compounds of vinyl iodides. Once again, an attempt to determine the E/Z ratio of (7) even on capillary GLPC proved unsuccessful; however electrophilic cleavage of C-Si bond by electrophiles using AlCl_3 , in general, led to a retention of stereochemistry [5]; therefore such reaction should afford the (Z) isomer (7).



Preparation of 2-bromo-2-ethyl-1-hexene(3):

To 0.437g (2mmol) of 1-chloro-1-(trimethylsilyl)-2-ethyl-1-hexene (2) in 2ml CH_2Cl_2 was added dropwise 2.6ml of 1M Br_2 in CH_2Cl_2 (1.3 eq, 2.6 mmol) at -75°C followed by the addition of 4 ml of 1M sodium methoxide in methanol (2eq, 4mmol). The mixture was stirred for 5 min at -75°C , allowed to warm to room temperature, and then stirred for an hour. At the end of this time, the resulting mixture was poured in water and extracted with hexane. After drying over Na_2SO_4 ,

the solvent was removed to afford a residue which was chromatographed on 30 g of silica gel. Elution with hexane gave 0.406g (1.8 mmol, 90% yield) of colorless product: ir (neat) 2980(s), 1600 cm^{-1} (w, C=C), no 1250 cm^{-1} ;

nmr (CCl_4 , internal reference TMS), 0.93 (multiplet, 6H, 2CH_3^-), 1.33 (multiplet, 4H, $-(\text{CH}_2)_2^-$), and 2.22ppm (multiplet, 4H, $2\text{CH}_2-\text{C}=\text{C}$); high resolution mass spectrum, (m/z) 223.9952; calculated for $\text{C}_8\text{H}_{14}^{79}\text{Br}^{35}\text{Cl}$: 223.9968.

Preparation of 1,1-dibromo-2-ethyl-1-hexene(5):

In the same manner as described above, 0.526g (2mmol) of 1-bromo-1-(trimethylsilyl)-2-ethyl-1-hexene(4) in 2ml CH_2Cl_2 was treated with 2.6 ml of 1M Br_2 in CH_2Cl_2 (1.3 eq, 2.6 mmol) at -75°C followed by treatment with 4ml of 1M NaOCH_3 in methanol.

Work-up and evaporation afforded a residue which was chromatographed on 30 g of silica gel. Elution with hexane gave 0.497g(1.84mmol, 92% yield) of colorless product: ir (neat) 2980 (s), and 1595 cm^{-1} (w, C=C), no 1250 cm^{-1} ; nmr (CCl_4 , internal reference TMS), 0.93 (multiplet, 6H, 2CH_3^-), 1.33 (multiplet, 4H, $-(\text{CH}_2)_2^-$), and 2.22 ppm (multiplet, 4H, $2\text{CH}_2-\text{C}=\text{C}$); high resolution mass spectrum, (m/z) 267.9486; calculated for $\text{C}_8\text{H}_{14}^{79}\text{Br}_2$: 267.9462.

Preparation of 1-bromo-1-iodo-2-ethyl-1-hexene(7):

To 0.640g (4.8mmol, 1.2 eq.) of AlCl_3 suspended in 9.6 ml of CH_2Cl_2 at -25°C was added 4.8 ml (4.8 mmol, 1M, 1.2 eq) of iodine in CH_2Cl_2 followed by slow addition of 1.052g (4mmol)

of 1-bromo-1-(trimethylsilyl)-2-ethyl-1-hexene (4). The resulting mixture was stirred at -25°C for an hour and allowed to warm to 0°C . Work-up and evaporation afforded a residue which was chromatographed on 45 g of silica gel. Elution with hexane gave 1.059 g (3.2 mmol, 80% yield) of colorless product:ir (neat) 2980 (s) and 1590 cm^{-1} (w, C=C), no 1250 cm^{-1} ; nmr (CCl_4 , internal TMS), 0.93 (multiplet, 6H, 2CH_3 -), 1.33 (multiplet, 4H, $-(\text{CH}_2)_2$), and 2.22 ppm (multiplet, 4H, $2\text{CH}_2\text{-C=C}$), high resolution mass spectrum, (m/z) 331.0453; calculated for $\text{C}_8\text{H}_{14}^{79}\text{Br}$ I: 331.0499.

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