Formation of Allenes by Reaction of 1,4-Dibromobut-2-ene with Dialkyl Ketones and Base

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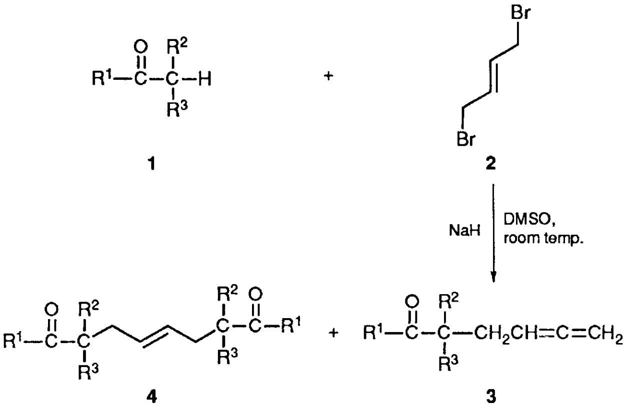
By reaction of 1,4-dibromo-(*E*)-but-2-ene with dialkyl ketones and sodium hydride the allenic ketones **3** were obtained as the main products, in addition to the symmetrical unsaturated 1,8-diketones **4**.

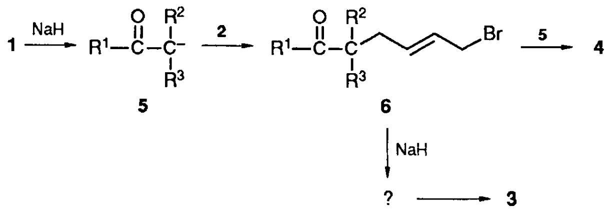
We have been investigating the reaction of 1,4-dibromo-(*E*)-but-2-ene with compounds containing two acidic geminal hydrogens, under basic conditions, which afforded 2-vinylcyclopropane derivatives.[1] Formation of vinylcyclopropane derivatives involves two reactions: (*i*) simple alkylation of active methylene compounds, and (*ii*) intramolecular addition of a carbanion to the double bond with concerted elimination of bromide anion from the allylic position.[1–3] However, by treatment of 1,4-dibromo-(*E*)-but-2-ene **2** with dialkyl ketones **1a–e** and sodium hydride as a base, instead of the expected 2-vinylcyclopropane derivatives we obtained the allenic ketones **3**, and the unsaturated symmetrical 1,8-diketones **4**, as products of simple alkylation of the ketones by **2** (Scheme 1).

Reactions were performed by using equimolar amounts of dialkyl ketones **1** and 1,4-dibromobut-2-ene **2**, while a 2.5 molar excess of sodium hydride as a base was required. Dimethyl sulphoxide (DMSO) or tetrahydrofuran (THF) were used as solvents. Reactions were carried out at room temperature (3–8 h) and the products were isolated by column chromatography (Table 1). The allenic ketones **3**, chain-extended by four carbon atoms, show characteristic spectroscopic data for the $-CH=C=CH_2$ group: ν_{max} (film) 1955–1960 cm^{-1} and ^1H NMR: δ 4.50–5.00 (m, 2H, $=C=CH_2$) and 5.40–5.60 (m, 1H, $-CH=C=$). All other signals were consistent with the proposed structures.

The principal products were the allenic ketones **3** (yields: 34–40%) (see Table 1), in addition to the unsaturated 1,8-diketones **4**, the ratio of **3** to **4** being about 1.6 : 1. When



Scheme 1



Scheme 2

Table 1 Reaction of dialkyl ketones **1** with 1,4-dibromobut-2-ene **2** under basic conditions

Starting ketones				Products (%)[a,b]	
1	R^1	R^2	R^3	**3**	**4**
a	Pr^n	H	Et	38	24
b	Pr^i	Me	Me	40	25
c	Et	H	Pr^n	39[c]	24[d]
d	Bu^n	H	Pr^n	34	20
e	Et	H	Bu^n	37[c]	23[d]
f	$–[CH_2]_{13}–$		H	—	45[e]

[a] Yields of **3** and **4** are for isolated products. Products were isolated from the neutralized reaction mixture, solvent was removed, and from the residual oil compounds **3** and **4** were isolated by column chromatography on silica gel using light petroleum–acetone (90 : 10 and 95 : 5) as eluant. [b] Satisfactory spectroscopic data, together with microanalytical and/or mass spectroscopic data, were obtained for compounds **3a–e** and **4a–f**. [c] Mixture of two isomers. [d] Mixture of three isomers. [e] 2-(4-Bromobut-2-enyl)cyclopentadecanone, the product of monoalkylation, was isolated in 20% yield.

symmetrical starting ketones **1a**, **1b** and **1d** were used a single allenic ketone and 1,8-diketone were obtained. However, by using unsymmetrical ketones **1c** and **1e**, which can give two different carbanions, two or more isomeric allenic ketones **3** and 1,8-diketones **4** were formed. Chromatographic separations were not successful, and the ratio of isomers has not been determined, but we believe that it depends on the stability of the corresponding carbanions.

The ratio of allenic ketones **3** to 1,8-diketones **4** decreased when a two molar excess of ketones **1** to dibromobutene **2** was used. However, with less than an equimolar ratio of **1** to **2** lower yields of compounds **3** and **4** were obtained, but monoalkylation occurred, and the alkylated ketones **6** were isolated. Also, when more than a 2.5 molar excess of sodium hydride was used, yields of allenic ketones were not increased. The allenic ketone **3** was not formed in the reaction of cyclopentadecanone **1f** with **2** under the same conditions, and only mono- and di-alkylation took place (Table 1).

Formation of allenic ketones **3** involves the intermediary monoalkylkated compound **6** (Scheme 2). The existence of the monoalkylkated ketone **6**, as an intermediate was proved by reaction of 1-bromo-5-ethylnon-2-en-6-one, separately prepared,† with sodium hydride which also afforded the allenic ketone **3**. The mechanism of formation of the allenic group from the monoalkylated intermediate **6** is not clear but probably involves a carbanion or carbenoid intermediate.[4,5] It was also proved, in a separate experiment, that dehydrobromination of the starting 1,4-dibromobut-2-ene does not occur, and $CH_2{=}C{=}CHCH_2Br$ was not detected as an intermediate.

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† 1-Bromo-5-ethylnon-2-en-6-one was prepared by reaction of di-n-propyl ketone with an equimolar amount of sodium hydride and 1,4-dibromobut-2-ene in THF.