REACTION OF DIAZOACETONE WITH TRIMETHYLSILYLACETYLENES AND CONVERSION OF 1-TRIMETHYLSILYL-3-ACETYLCYCLOPROPENES TO 3-ACETYLCYCLOPROPENES

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A new method was proposed previously [1] for the synthesis of the 1-H- and 1,2-di-Hcyclopropene-3-carboxylic acids by the hydrolysis of the esters of the corresponding trimethylsilylcyclopropenecarboxylic acids, which are obtained by the reaction of trimethylsilylacetylenes with ethyl diazoacetate. It seemed expedient to determine if this same procedure can be used to obtain the 1-unsubstituted 2-alkyl-3-acetylcyclopropenes, the synthesis of which by the direct addition of acetylcarbene to the multiple bond of monosubstituted acetylenes is problematical, in particular due to the ease of inserting carbenes at the acetylenic C-H bond.

The reaction of diazoacetone with **alky1**(trimethy1sily1)acetylenes (I) was run at 100-130°C and a diazoacetone:(I) mole ratio equal to 1:8-10, in the presence of copper bronze as the catalyst. Here the corresponding 1-(trimethy1sily1)-2-alky1-3-acety1cyclopropenes (II) were formed in 15-35% **yields**.

 $RC \equiv CSi(CH_3)_{3} + N_2CHCOCH_3 \xrightarrow{Cu} R - C = C - Si(CH_3)_{3} \xrightarrow{KOH} R - C = C - H$ (II) $R = CH_3 (a), n - C_4H_9 (b), n - C_5H_{11} (c), n - C_8H_{17} (d)$

The treatment of (II) with dilute aqueous-alcohol alkali solution at 20°, i.e., hydrolysis under the conditions used to obtain the 1-unsubstituted cyclopropene-3-carboxylic acids in a similar manner [1], led to the formation of the 1-unsubstituted 2-alkyl-3-acetylcyclopropenes (III) in only 5-15% yields, with marked tarring of the reaction products. When (II) was hydrolyzed with alkali solution at -20° , followed by neutralization of the reaction mass with dilute H₂SO₄ solution at -70° , the tar formation decreased substantially and we were able to obtain the 1-unsubstituted cyclopropenes (III) in up to 70% yields. As a result (III), in contrast to (II) and other 1,2-disubstituted 3-acetylcyclopropenes [2], is much less stable when heated, especially in the presence of inorganic bases.

The structure of the synthesized (III) was confirmed by the elemental analysis, IR, and NMR spectral data. The attention is attracted to the lower value of the frequency of the intracyclic double **bond** in the IR spectra of (III) (1800 cm⁻¹) when compared with (II) (1825-1830 cm⁻¹), which indicates the electron-donor character of the trimethylsilyl group in cyclopropenes.

High-molecular products were obtained exclusively when we attempted the aldol-crotonic condensation of (III) using alkaline and alkaline-earth catalysts, even under mild conditions (for example, in a solvent), which, like the marked tarring of the reaction mass under the alkaline hydrolysis conditions for (II), can also be explained by the low stability of (III).

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H COCH

) H

TABLE 1. Properties of 3-Acetylcyclopropenes R-G

NMR spectrum (ô, ppm)	CO R R	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c ccccc} 0 & s & 0.90 & \text{m} & \text{(CH3)} \\ 1,50 & \text{m} & (3\text{CH3}), & 2,35 & \text{m} \\ 1,50 & \text{m} & (3\text{CH3}), & 2,35 & \text{m} \\ \end{array}$	1 s $\begin{pmatrix} 0.438 \\ 0.88 \\ 1.65 \\ 0.465 \\ 0.6CH_2 \end{pmatrix}$, 2,45 m 0,20 s	$ \begin{array}{c cccc} 0 & d & 2,20 & p(CH_8) \\ 5 & d & 0,98 & m & (CH_3), & 1,25- \\ 1,70 & m & (2CH_3), & 2,55 & m \\ 1,70 & m & (2CH_3), & 2,55 & m \\ \end{array} $	8 d $\begin{pmatrix} 0.013 & -7 \\ 0.87 & m & (CH_8), 1,07- \\ 1,75 & m (3CH_8), 2,55 & m \\ \end{pmatrix}$ 6,38 m
	COCH4 CI	1,83 s 2, 1,83 s 2,	1,80 s 2,	1,83 s 2,5	1,85 s 2,3 1,87 s 2,3	1,88 \$ 2,5
Infrared spectrum (u, cm ⁻¹)	כ≕כ	1840 1830	1825	1826	1805 1800	1800
	c=0	1685 1685	1680	1685	1690 1690	1690
d 4 0.		0,9161 0,8879	0,8870	0,8786	0,9279 0,8960	0,8996
n ²⁰		1,4555 1,4584	1,4609	1,4613	1,4640 1,4561	1,4584
bp, °C (p, mm of Hg)		64-66 (8) 101-104 (6)	108—110 (8)	122124 (5)	11	67-70 (12)
Yield, % of theory		13 23	33	17	40 † 72 †	22
Values of	Ŕ	Si(CH3)3 Si(CH3)3	Si(CH ₃)3	Si(CH3)3	Н	н
	R	CH_3 $n-C_4H_9$	n-C5H11	<i>n</i> -C ₈ H ₁₇	CH_8 n - C_4H_9	n-CsH11
Com- pound		(11 a) (11b)	(11c)	(IId)	(1111 a) (1111 b)	(IIIc)

*The methylene group is α to the ring. †Based on the GLC data.

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EXPERIMENTAL

The GLC analysis was run on an LKhM-8MD instrument (using a 300×0.2 cm column packed with Silicone SE-30 deposited on silanized Chromatone, a katharometer as the detector, helium as the carrier gas, and a flow rate of 30 ml/min).

The NMR spectra were obtained on a Varian DA-60-1 instrument for solutions in CHCl₃ (in the case of (II)) or CCl₄ (in the case of (III)), with TMS as the internal standard. The IR spectra were recorded on a UR-20 spectrophotometer (as a film of the substance on KBr).

<u>Methyl(trimethylsilyl)acetylene (Ia)</u>. To a solution of C_2H_5MgBr (from 12 g of Mg and 55 g of ethyl bromide) in 250 ml of THF was added an excess of methylacetylene at 0° in 2.5 h. Then 55 g of $(CH_3)_3SiCl$ was added at 20°. After stirring for 8 h at 65-67° the reaction mass was decomposed with aqueous $(NH_4)_2SO_4$ solution. From the organic layer we isolated 37 g (65%) of (Ia); bp 94-97° (750 mm); $n_D^{2°}$ 1.4200; $d_4^{2°}$ 0.7549; cf. [3].

In a similar manner were obtained n-butyl(trimethylsilyl)acetylene (Ib); 63% yield; bp 59-62° (27 nm); $n_D^{2^\circ}$ 1,4310; $d_4^{2^\circ}$ 0.7724, cf. [3]; n-amyl(trimethylsilyl)acetylene (Ic); 49% yield; bp 68-71° (10 mm); $n_D^{2^\circ}$ 1.4334; $d_4^{2^\circ}$ 0.7850, cf. [3]; n-octyl(trimethylsilyl)acetylene (Id); yield 54%; bp 80-81° (3 mm); $n_D^{2^\circ}$ 1.4423; $d_4^{2^\circ}$ 0.7904.

<u>1-Trimethylsilyl-2-n-butyl-3-acetylcyclopropene (IIb)</u>. To 96 g of (Ib) and 0.04 g of copper bronze at 130° was added in 3.5 h a solution of 5.3 g of diazoacetone in 10 g of (Ib). When the N₂ evolution had ceased the catalyst was filtered. From the filtrate we distilled 95.5 g (90%) of the starting (**Ib**) with bp 66-69° (31 mm), while from the residue we isolated 1.4 g (23%) of cyclopropene (IIb).

The other (II) compounds were obtained in a similar manner. Their yields and properties are given in Table 1.

<u>2-n-Butyl-3-acetylcyclopropene (IIIb).</u> To 2.1 g of 5% KOH solution in methanol, cooled to -68° , was added 1 g of (IIb). After stirring for 3 h at -20 to -22° the mass was cooled to -68° and 2.94 g of 5% H₂SO₄ solution, cooled to 0°, was added. The precipitate was filtered and the methanol was distilled from the filtrate. The residue was extracted with ether. The extract was dried over MgSO₄ and then evaporated in vacuo. We obtained 0.48 g (72%) of cyclopropene (IIb).

Compounds (IIIa), (IIIb), and (IIIc) were synthesized in a similar manner (see Table 1).

CONCLUSIONS

1-Trimethylsily1-2-alky1-3-acetylcyclopropenes were synthesized by the thermocatalytic reaction of diazoacetone with alky1(trimethylsily1)acetylenes, which by alkaline hydrolysis under mild conditions were converted to the corresponding 1-unsubstituted 2-akly1-3-acety1-cyclopropenes.

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