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A CONVENIENT METHOD FOR THE SYNTHESIS OF 2-(1-ALKENYL)-2-CYCLOPENTENONES

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It was found that 2-(1-alkenyl)-2-cyclopentenones were synthesized in good yields from β-alkoxy-γ-bromoketones formed by the $TiCl_4$-promoted reaction of α-bromoacetals with 1-trimethylsiloxy-1-cyclopentene.

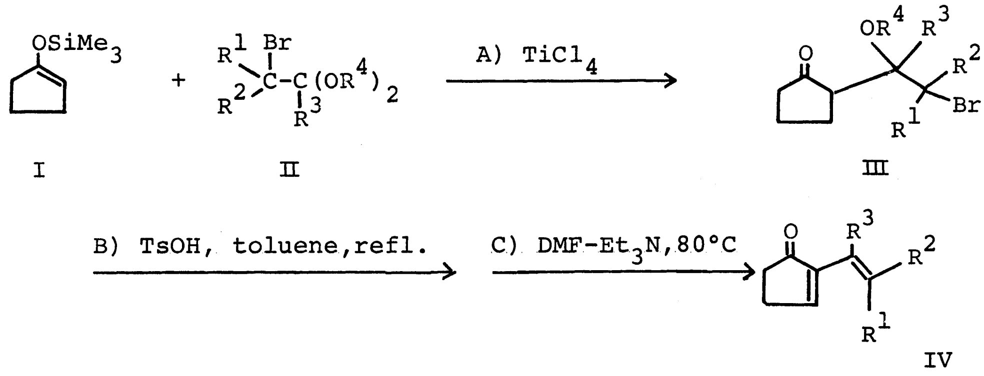
In the preceding paper[1)], it was reported that γ-bromo-β-methoxyketones, formed by the $TiCl_4$-promoted reaction of α-bromoacetals with silyl enol ethers, were easily converted to furans in good yields. Different from the above result, it was found by the present experiment that β-alkoxy-γ-bromoketones(III), derived from the reaction of 1-trimethylsiloxy-1-cyclopentene(I) with α-bromoacetals(II), were converted to the corresponding cyclopentenone derivatives(IV) in good yields.

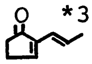
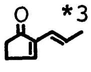
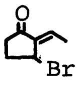
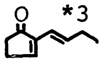
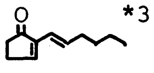
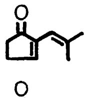
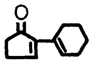
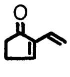
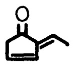
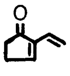
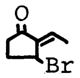
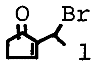
The typical procedure is described for the reaction of the silyl enol ether(I) with 2-bromobutyraldehyde dimethyl acetal (II b). To a methylene chloride(10 ml) solution of the acetal(197 mg, 1.0 mmol) was added dropwise a methylene chloride solution (0.5 ml) of $TiCl_4$ (1.0 mmol) at -78°C under an argon atmosphere. Then a methylene chloride (3 ml) solution of the silyl enol ether (172 mg, 1.1 mmol) was added drop by drop and the resulting mixture was stirred for an additional hour at -78°C. The solution was treated with a cold saturated aqueous $NaHCO_3$ and an organic layer was extracted with ether. After removal of the solvent, 10 ml of toluene was added to the residue. The solution was refluxed for 30 minutes under an argon atmosphere in the presence of a catalytic amount of p-toluenesulfonic acid (TsOH). Further, after removal of toluene under reduced pressure, a DMF-Et_3N solution(5 : 3) of the residue was heated at 80°C for 5 hours under an argon atmosphere. It was cooled, diluted with ether, and washed with three 50 ml portions of cold water. The organic layer was combined with the ether extract from the aqueous washings and washed with

50 ml cold 1N HCl and then with water. After removal of ether, the residue was separated by tlc. Thus, 2-(1-butenyl)-2-cyclopentenone(IVa) was isolated in 70% yield.

In a similar manner, various cyclopentenone derivatives were prepared from the silyl enol ether(I) and α-bromoacetals in good yields as listed in the following Table.

Table. The Synthesis of 2-Cyclopentenone Derivatives.



	II				Time (hr)			Yield^{*2} (%)			
	R^1	R^2	R^3	R^4	A	B	C	cyclopentenone^{*1} IV		other products	
a	H	CH_3	H	C_2H_5	1	0.5	5	 *3	63		
a'	H	CH_3	H	C_2H_5	1	0.5	-	 *3	43	 Va	21
b	H	C_2H_5	H	CH_3	1	0.5	5	 *3	70		
c	H	n-C_4H_9	H	CH_3	1	1	2	 *3	72		
d	CH_3	CH_3	H	CH_3	1	5	5		71		
e	H	$-(CH_2)_4-$		CH_3	1	1	1		91		
f	H	H	H	CH_3	1	3	7		13		18
f'	H	H	H	CH_3	1	3	-		19	 8 	14

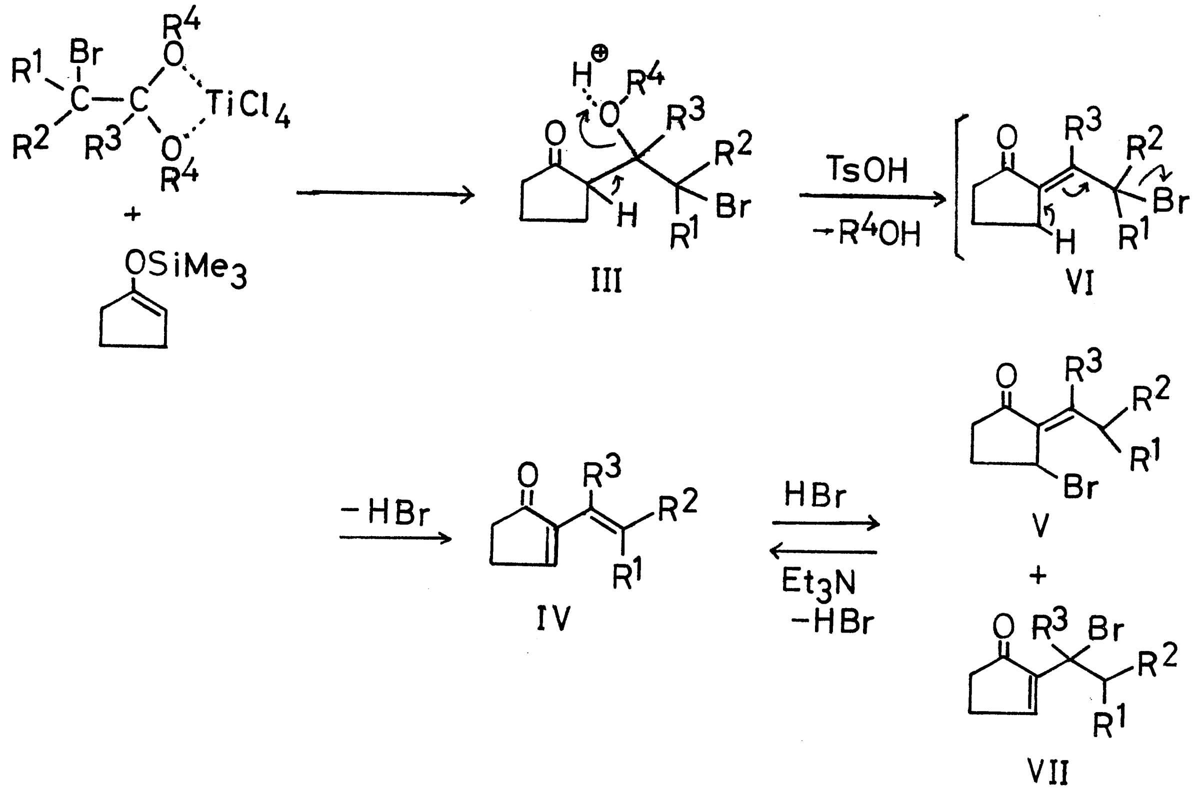
*1 All compounds exhibited ir and nmr spectral data in accordance with assigned structures.

*2 Yield of isolated products

*3 Trans form (ex. IVa, ir: 970 cm^{-1}(trans olefin); nmr: δ 5.97(-CH=, d(J=16.9), 1H), 6.64 (=<u>CH</u>-CH_3-, d × q, 1H)).

As shown in the Table(a'), 3-bromo-2-propylidenecyclopentanone(Va) and IVa were produced in 21% and 43% yields, respectively, when IIIa was refluxed in toluene in the presence of a catalytic amount of TsOH. Contrary to the result, IVa was obtained in good yield on heating Va in DMF-Et_3N.

The reaction can be explained by assuming an initial formation of β-alkoxy-γ-bromoketones(III) by $TiCl_4$-promoted reaction of α-bromoacetals with silyl enol ethers as described in the previous reports.3) On treatment with TsOH, III is converted to an intermediate(VI) with elimination of alcohol, and VI is subsequently changed into the cyclopentenone(IV) with 1,4-conjugate elimination of HBr. Under these reaction conditions, a part of cyclopentenone(IV) reacts with HBr to give adducts, 2-alkylidene-3-bromocyclopentanone(V) and 2-(1-bromoalkyl)-2-cyclopentenone (VII) as shown in the examples of the Table(a', f'). Finally, the cyclopentenone of the type IV is produced by the loss of HBr from the adducts (V, VII) on treating with triethylamine.



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1) T. Mukaiyama, H. Ishihara, and K. Inomata, Chem. Lett., 527(1975).

2) The structure of IVa was identified by the spectral data.
ir: 1700 (νC=O), 1655, 1610, 1590 (νC=C), 967 cm^{-1}(trans olefin);
nmr: δ 1.80 ($-CH_3$, d, 3H), 2.4($-CH_2-$, m(broad), 4H), 5.97(-CH= (side chain), d, 1H),
6.64($=CHCH_3$, d × q, 1H), 7.19(-CH=, t, 1H).

3) T. Mukaiyama and M. Hayashi, Chem. Lett., 15 (1974).
T. Mukaiyama, T. Izawa, and K. Saigo, Chem. Lett., 323 (1974).

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