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# Introduction of Different Groups to α- and β-Positions of Cyclic α,β-Unsaturated Ketones via [2π + 2π] Photocycloaddition with Ketene Silyl Acetals Followed by Electrode Reaction

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The photoadducts of cyclic conjugated enones with ketene silyl acetals and silyl enol ether were subjected to electrolysis to bring about the oxidative cleavage of the Si-O bond, which induced the collapse of the cyclobutane ring to perform the introduction of the different groups to both positions of the ene moieties of the enones.

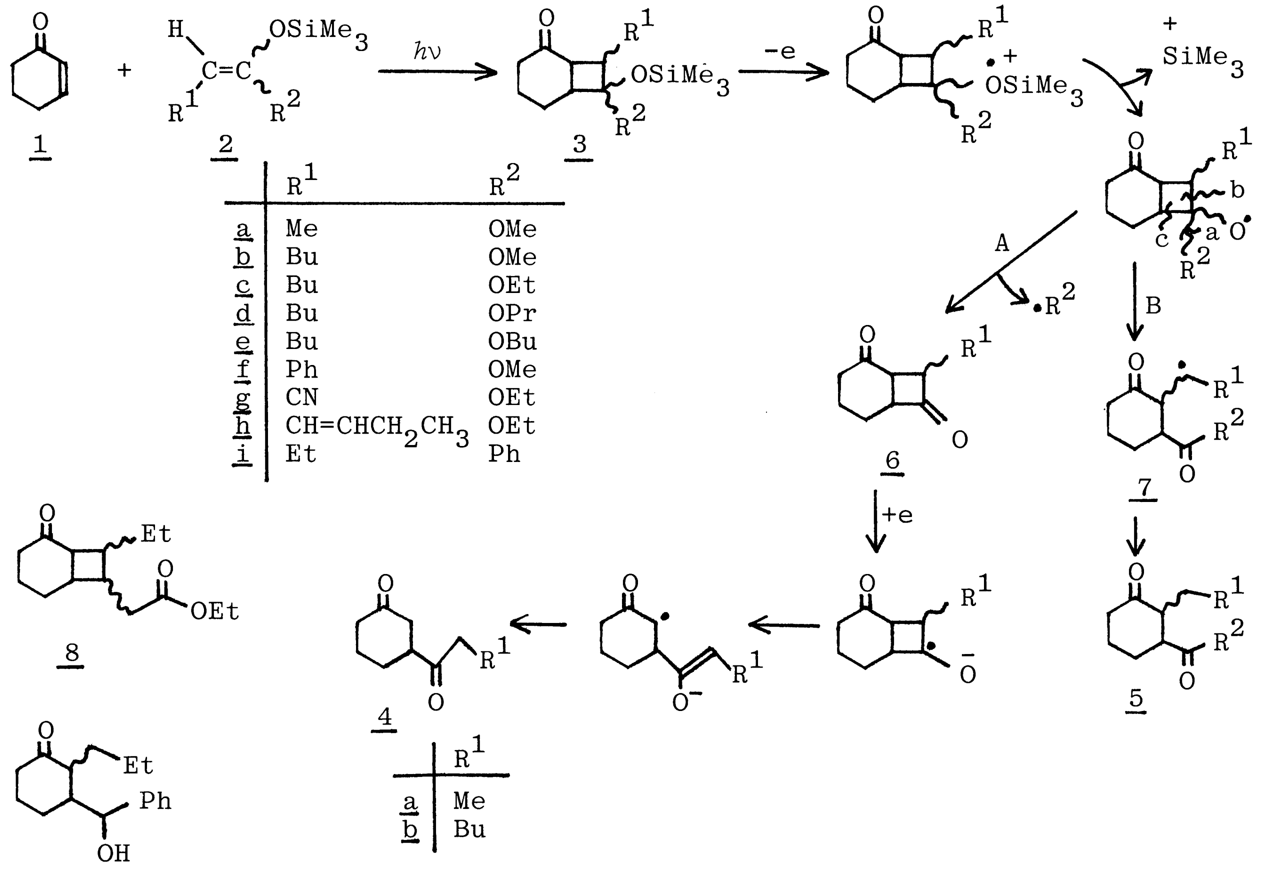
As with the reaction of silyl enol ethers with electron-deficient olefins, the formation of the Michael adducts under photo-irradiation(1) or the action of the Lewis acids(2) has been well-known. The introduction of the different groups, however, to the each position of the olefin by the cleavage of the bond coming from the silyl enol ether after the cycloaddition has not been so far reported to our knowledge although the arynes were reacted with ketene silyl acetals to afford o-substituted aromatic carboxylic acids via the cycloaddition followed by hydrolysis(3) and the silyl enol ethers from the cyclic ketones afforded the ring expanded products by the radical reaction following hydrolysis of the cycloadducts.(4) In this paper, we wish to present the introduction of the different groups to the α- and β-positions of cyclic α,β-unsaturated ketones through the photoreaction with ketene silyl acetals and silyl enol ether followed by the electrode reaction.

At first, the photoreaction of 2-cyclohexenone 1 (2 mmol) with 1-methoxy-1-trimethylsiloxy-1-propene 2a (4 mmol) in acetonitrile or pentane (5 $cm^3$, respectively) was performed using high-pressure Hg lamp for 20 h under $N_2$ atmosphere to afford the adduct. The adduct was assigned as 7-methoxy-8-methyl-7-trimethylsiloxybicyclo[4.2.0]-

octan-2-one 3a from the subsequent transformation of it to 4a (vide infra) and the analogy with the regiochemistry of the photoaddition of 1 with vinyl ethers5) although GC-MS spectra suggested that it was composed of a mixture of four stereoisomers. The yield of 3a was higher in pentane (85%) than that in acetonitrile (50%). An acetonitrile solution containing 3a and tetraethylammonium p-toluenesulfonate (0.2 mol $\text{dm}^{-3}$) as a supporting electrolite was electrolized using carbon-rod electrodes as anode and cathode in an undivided cell until electricity of 3.6 F $\text{mol}^{-1}$ had been passed. 3-Propionylcyclohexanone 4a, which is considered to be apparently derived by the overall action of 2a as the propionyl anion equivalent, was formed as a sole product. Thus, this reaction furnishes a new method for the acyl anion equivalent. Next, the adducts 3b-e formed by the photoreaction of 1 with the hexanoate ketene silyl acetals 2b-e were subjected to the electrode reaction to afford 3-carboalkoxy-2-pentylcyclohexanones 5 as a stereoisomeric mixture, along with 3-hexanoylcyclohexanone 4b. The yield of 5 was highest in the case of 3c, the ketene silyl acetal from the ethyl ester, and decreased with those from the shorter or longer esters (Table 1, Entry 2-5).

The mechanism for the formation of 4 and 5 from the reaction of 1 with 2 may be presumed as Scheme 1. The pathway for the formation of 4 via the intermediate 6 as revealed by route A may be supported by electrolysis of 3a in a THF solution containing tetrabutylammonium perchlorate using an undivided cell in which 6a was furnished as a product. The formation of 5 by enlargement of $R^1$ group from Me to Bu might be reasoned in terms of the strain release from the adduct 3. It was ascertained by the Norrish II photoreaction of the product to bring about elimination of the pentyl group that the product is 5 by way of the b-bond cleavage of the cyclobutane ring, not that via the c-bond cleavage. Then, the ketene silyl acetals bearing the phenyl, cyano, or vinyl groups as $R^1$ were explored with expectation that stabilization of the intermediate 7 by those groups would facilitate the b-bond cleavage to form preferentially 5 following route B. Thus, 3f, the ketene silyl acetal from methyl phenylacetate, was subjected to the photo-addition with 1 followed by the electrode reaction, giving 3-carbomethoxy-2-phenylmethylcyclohexanone 5f as a mixture of stereoisomers. Noteworthily, 3g, the ketene silyl acetal from ethyl cyanoacetate, afforded the expected product 5g in a single stereoisomer under photo-irradiation possibly due to the stereoelectronic factor. The reaction of 3h, in which $R^1$ is the 1-butenyl group, with 1 brought about only the cycloaddition with a carbon-carbon double bond of $R^1$ to effect 8. The photo- and electrochemical reaction sequence of 1-phenyl-1-trimethylsiloxybutene 2i with 1 afforded 9 as a mixture of stereoisomers, which was possibly derived by the further electrochemical reduction of the expected product 5i. On the other hand, the silyl enol ether of the aliphatic ketone such as 4-hexanone failed to perform the desired reaction.

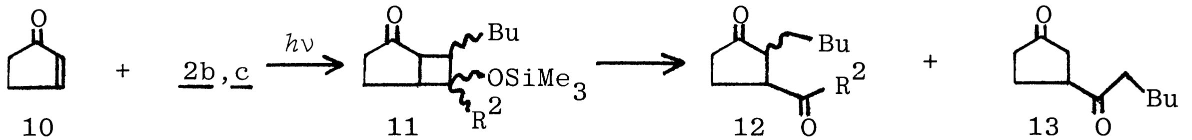
When 2-cyclopentenone 10 was used, the results were somewhat differed from those with 1. The reaction with 2b effected selectively 3-carbomethoxy-2-pentylcyclopentanone 12b without competitive formation of the 3-acylated product 13, whilst that with 2c afforded the desired product 12c along with 13. Similarly to the reaction with 1, both of 12 and the intermediate 11 were consisted of a mixture of stereoisomers.



| 2 | $R^1$ | $R^2$ |
|---|---|---|
| a | Me | OMe |
| b | Bu | OMe |
| c | Bu | OEt |
| d | Bu | OPr |
| e | Bu | OBu |
| f | Ph | OMe |
| g | CN | OEt |
| h | $CH=CHCH_2CH_3$ | OEt |
| i | Et | Ph |

| 4 | $R^1$ |
|---|---|
| a | Me |
| b | Bu |

Scheme 1.



Scheme 2.

Table 1. Consecutive Photo- and Electrochemical Reaction of Ketene Silyl Acetals and Silyl Enol Ether with Enones[a]

| Entry | Enone | Silyl Enol Ether | Photoreaction Product | Electroreaction Product |
|---|---|---|---|---|
| | | | Yield/%[b] | Yield/%[b,c] |
| 1 | 1 | 2a | 3a (85) | 4a (90) |
| 2 | 1 | 2b | 3b (83) | 4b (45), 5b (35) |
| 3 | 1 | 2c | 3c (74) | 4c (36), 5c (54) |
| 4 | 1 | 2d | 3d (72) | 4d (50), 5d (41) |
| 5 | 1 | 2e | 3e (61) | 4e (17) |
| 6 | 1 | 2f | 3f (82) | 5f (92) |
| 7 | 1 | 2g | 5g (52) | |
| 8 | 1 | 2i | 3i (63) | 9 (51) |
| 9 | 10 | 2b | 11b (86) | 12b (50) |
| 10 | 10 | 2c | 11c (82) | 12c (21), 13 (36) |
| 11 | 10 | 2f | 11f (83) | 12f (92) |

a)Reaction procedure; the reaction mixture after evaporation of pentane following the photoreaction in a pentane solution was directly electrolyzed in an acetonitrile solution. b)Determined by GLC. c)Based on the photoadduct (3 or 11).

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