CHEMISTRY LETTERS, pp. 147-150, 1979. Published by the Chemical Society of Japan

# A CONVENIENT PREPARATION OF 2-SUBSTITUTED 2-CYCLOPENTENONES FROM CYCLOPENTANONE USING 2-(MORPHOLINOTHIO)BENZOTHIAZOLE

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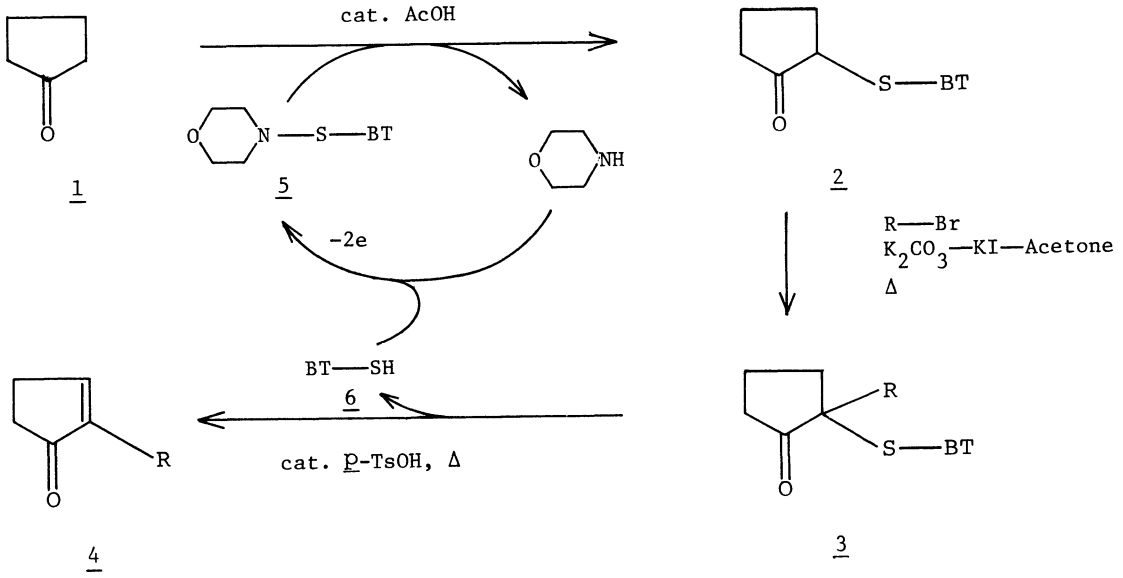
2-Substituted 2-cyclopentenones (4), a precursor of jasmonoids, were prepared in 47-77% overall yields from cyclopentanone (1) via 2-(2-benzothiazolylthio)cyclopentanone (2). Treatment of 1 with 2-(morpholinothio)benzothiazole gave 2 in 98% yield. Alkylation of 2 with RBr-$K_2CO_3$-KI-acetone followed by removal of the 2-mercaptobenzothiazole by thermolysis in benzene containing p-TsOH at 140 °C afforded 4 smoothly.

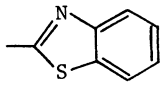
One of the fruitful precursors of jasmonoids synthesis must be 2-substituted 2-cyclopentenones (4) and much effort has been made to prepare 4 by different synthetic procedures.[1] Here, we wish to report a straightforward synthesis of 4 starting from readily available cyclopentanone (1), which comprises following three-step operations: (1) introduction of a 2-benzothiazolylthio group (BT-S) at the α-position of 1, (2) alkylation of the α-sulfenyl ketone 2, and (3) subsequent β-elimination of 2-mercaptobenzothiazole (6) from 3 leading to 4 (Scheme 1).

The introduction of the sulfenyl group at the α-position of alkanones has been carried out by the reaction with disulfides using appropriate bases.[2] The reported procedures, however, seem to be laborious and expensive. In order to find out a more convenient and reactive sulfenylating reagent, we examined various sulfenamides[3] (Table I) and found that 2-(morpholinothio)-benzothiazole (5)[4] was one of the adequate reagents for the present purpose. Moreover, the sulfenylating reagent 5 can be reproduced from the recovered 6 by the electrochemical procedure as shown in the Scheme.[4]

Treatment of 1 (12 mmol) with 5 (12 mmol) in benzene (5 ml) involving acetic acid (6 mmol) at 55-60 °C for 7 h afforded 2 in 98% yield as white crystals (entry 5 in Table I), mp 115-116 °C (from $CCl_4$); IR (Nujol) 1745 $cm^{-1}$; NMR ($CDCl_3$) δ 1.6-3.0 (m, 6, $CH_2$), 4.2 (t, 1, J = 9 Hz, CH). Alkylation of 2 (4 mmol) with 2-pentynyl, allyl, and propargyl bromide (4.5 mmol) in refluxing acetone (15 ml) in the presence of potassium carbonate (40 mmol) and potassium iodide (4 mmol) for 12 h gave the corresponding C-alkylation products 3 in 90-95% yields in contrast to the result with pentyl bromide, which afforded C- and O-alkylation products 3b and 7 in 53% yield in a ratio of 1/5.[5]

The transformation of 3 into 4 was accomplished by the acid-catalyzed thermolysis (Table II). The pyrolysis of 3a in the presence of ca. 10% of




BT = 

| 3, 4 | R |
|---|---|
| a | $-CH_2-C\equiv C-Et$ |
| b | $-(CH_2)_4-Me$ |
| c | $-CH_2-CH=CH_2$ |
| d | $-CH_2-C\equiv CH$ |

Scheme 1

p-toluenesulfonic acid (p-TsOH) at 115 °C for 5 min under nitrogen followed by distillation under reduced pressure afforded olefins 4a and 2-(2-pentynylidene)-cyclopentanone 8[6] in 73% yield in a ratio of 3/1 (entry 1). The prolonged heating favors the formation of the endo-isomer 4a, but the total yield of olefins decreased (entries 2 and 3). As shown in entry 4, the dropping of a mixture of 3a and p-TsOH (ca. 10%) on the preheated glass sand at 250-300 °C under removal of the products by continuous distillation (ca. 3 mmHg) gave 4a and 8 in an equal amount. The results indicate that in the initial stage of the reaction thermal decomposition of 3a would occur competitively to give endo- and exo-olefins via path (a) and (b) in a ratio of 1/1 and subsequent isomerization of the exo-olefin 8 into endo-olefin 4a would proceed by acid-catalyzed reaction[1e] (Scheme 2). Actually, heating a mixture of 4a and 8 (3/1) in benzene containing p-TsOH (ca. 10%) at 140 °C for 1 h gave 4a as a sole product. On the other hand, thermolysis of 3 in benzene containing p-TsOH (ca. 10-20%) in a sealed tube at 140-170 °C for 10-15 min afforded the desired 4 in 51-84% yields (entries 5-8).[7]

Table I. α-Sulfenylation of Cyclopentanone with Sulfenamides

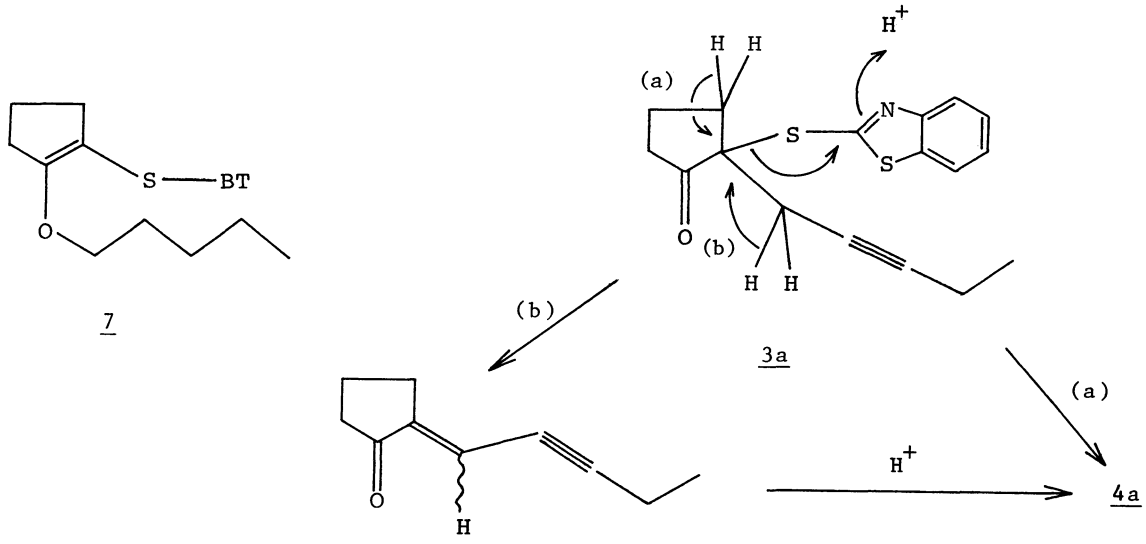
| Entry | Sulfenamide Y—S—N$<^{R^1}_{R^2}$ | | | AcOH | Solvent | Temp. | Time | Product |
|---|---|---|---|---|---|---|---|---|
| | Y[a] | $R^1$ | $R^2$ | %[b] | | °C | h | Yield, %[c] |
| 1 | Ph | $-(CH_2)_2O-(CH_2)_2-$ | [d] | — | $CH_2Cl_2$ | 20-25 | 10 | 0[e] |
| 2 | N-(Phenylthio)phthalimide | | | — | " | 20-25 | 10 | 0[e] |
| 3 | BT | $-(CH_2)_2-O-(CH_2)_2-$ | | — | " | 15-20 | 10 | 63 |
| 4 | " | " | | — | Benzene | 50-60 | 7 | 72 |
| 5 | " | " | | 50 | " | 55-60 | 7 | 98 |
| 6 | " | $-(CH_2)_5-$ | [d] | 50 | " | 55-60 | 7 | 85 |
| 7 | " | Cyclohexyl | H[d] | 50 | " | 55-60 | 7 | 65 |
| 8 | " | iso-Pr | iso-Pr[d] | 100 | " | 55-60 | 7 | trace |

a) Ph = phenyl; BT = 2-benzothiazolyl. b) Mol/mol, based on the sulfenamides. c) Isolated yields after column chromatography ($SiO_2$, benzene/AcOEt, 10/1). d) Electrosynthesized according to the reported procedure: reference 4. e) Unchanged sulfenamides were recovered in 85-90%. f) Electrosynthesized from diphenyl disulfide and phthalimide: S. Torii, H. Tanaka, and M. Ukida, J. Org. Chem., in contribution.

Table II. Thermolysis of 2-Substituted 2-(2-benzothiazolylthio)cyclopentanones

| Entry | Substrate 3 | p-TsOH % (W/W) | Solvent | Temp. °C | Time min | Product, %[a] 4 | 8 |
|---|---|---|---|---|---|---|---|
| 1 | 3a | 10 | Neat | 115[c] | 5 | 55 | 18 |
| 2 | 3a | 10 | " | 115 | 10 | 65 | 13 |
| 3 | 3a | 10 | " | 115 | 15 | 34 | 6 |
| 4 | 3a | 10 | " | 250-300 | —[d] | 36 | 36 |
| 5 | 3a | 10 | Benzene | 140[c] | 10 | 51 | trace[e] |
| 6 | 3b | 15 | " | 140 | 10 | 84 | trace[e] |
| 7 | 3c | 20 | " | 140 | 15 | 81 | trace[e] |
| 8 | 3c | 15 | " | 170 | 10 | 81 | trace[e] |

a) Isolated yields after column chromatography ($SiO_2$, hexane). b) Without addition of p-TsOH 3a was recovered. c) The decomposition did not occur below 100 °C. d) The products were removed by continuous distillation. e) The thiol 6 was obtained in 85-97% yields as white crystals when the reaction mixture was extracted with aqueous 1 M NaOH and the aqueous solution was acidified with aqueous 1 M HCl.




Scheme 2

References and Notes

1) (a) S. Torii and H. Tanaka, Koryo, 114, 41 (1976); (b) T.-L. Ho, Synth. Commun., 4, 256 (1974); (c) R. A. Ellison, Synthesis, 1973, 397; (d) P. Bakuzis and M. L. F. Bakuzis, J. Org. Chem., 42, 2362 (1977); (e) R. F. Abdulla and K. H. Fuhr, ibid., 43, 4248 (1978) and references cited therein.

2) B. M. Trost, Chem. Rev., 78, 363 (1978) and references cited therein.

3) Sulfenylation of active methylene compounds with sulfenamides has been reported: T. Kumamoto, S. Kobayashi, and T. Mukaiyama, Bull. Chem. Soc. Jpn., 45, 866 (1972) and see also reference 2. Similar sulfenylation of alkanones, however, has not yet been reported.

4) S. Torii, H. Tanaka, and M. Ukida, J. Org. Chem., 43, 3223 (1978).

5) Satisfactory elemental analyses and spectral data were obtained in the products, 3a: IR (neat) 3050 (HC=C), 1740 $cm^{-1}$ (C=O); NMR ($CDCl_3$) δ 1.1 (t, 3, J = 7 Hz, $CH_3$), 1.6-2.8 (m, 8), 2.9 (m, 2, $CH_2C{\equiv}C$), 7.0-8.0 (m, 4, HC=C), 3b: IR (neat) 3060 (HC=C), 1740 $cm^{-1}$ (C=O); NMR ($CDCl_3$) δ 0.9 (t, 3, J = 4 Hz, $CH_3$), 1.1-3.0 (m, 14), 7.0-8.0 (m, 4, HC=C), 3c: IR (neat) 3060 (HC=C), 1737 (C=O), 1640, 1625 (C=C), 990, 920 $cm^{-1}$ (HC=C); NMR ($CDCl_3$) δ 1.6-3.0 (m, 6), 4.7-6.2 (m, 3, HC=C), 7.0-8.0 (m, 4, HC=C), 3d: IR (neat) 3285 (HC≡C), 3050, 3030 (HC=C), 2120 (C≡C), 1740 $cm^{-1}$ (C=O); NMR ($CDCl_3$) δ 1.9 (m, 1, HC≡C), 1.8-3.0 (m, 6), 3.0 (m, 2, $CH_2C{\equiv}C$), 7.0-8.0 (m, 4, HC=C), 7: IR (neat) 3070, 3040 (HC=C), 1625 $cm^{-1}$ (C=C); NMR ($CDCl_3$) δ 0.8 (t, 3, J = 6 Hz, $CH_3$), 1.1-2.9 (m, 12), 4.1 (t, 2, J = 6 Hz, $CH_2O$), 7.0-7.9 (m, 4, HC=C).

6) IR and NMR spectra and elemental analysis were in agreement with the assigned structure 8: bp 61-62 °C/0.15 Torr; IR (neat) 2230 (C C), 1710 (C=O), 1620 $cm^{-1}$ (C=C); NMR ($CDCl_3$) δ 1.2 (t, 3, J = 7 Hz, $CH_3$), 1.6-3.0 (m, 8), 6.3 (m, 1, HC=C).

7) The products 4 were identical in all respects with the reported ones: reference 1.

(Received December 4, 1978)