A Novel Synthesis of Spirocyclopropenes from the Haloallene Derivatives with Alkanethiolate Ions

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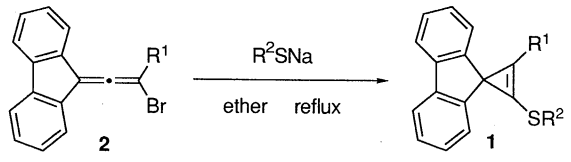
Reactions of 1-bromo-1-substituted-2-(9-fluorenylidene)-ethenes with alkanethiolate ions gave spiro[1-alkylthio-cyclopropene-3,9'-fluorenes]. The bromoallene derived from 2,3-diphenylindene also afforded the corresponding spiro-cyclopropene compound.

Spirocyclopropene compounds have been investigated with regard to spiroconjugation system[1-3] and used for the preparation of photochromic spirodihydroindolizines.[4,5] General methods of spirocyclopropenes synthesis were addition of appropriate carbene species to unsaturated bonds and also rearrangement of vinyl carbenes.[2] However, the yield of the desired compounds was not always satisfactory, because of difficulty in preparing appropriate carbene species such as diazo compounds.



R^1=Ar, *t*-Bu, TMS R^2=Et, Pr, *i*-Pr, Bu, Hex

Scheme 1.

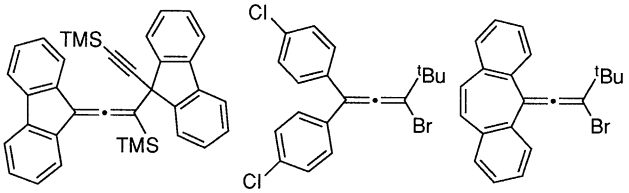
In the course of our studies on the reactivities of haloallenes,[6,7] we found that spiro[1-alkylthiocyclopropene-3,9'-fluorenes] (**1**) were obtained from 1-bromo-2-(9-fluorenylidene)ethenes (**2**) by treating with alkanethiolate ions (Scheme 1). Present paper deals with the unique and facile spirocyclopropene synthesis from bromoallenes readily obtained from 2-propynol derivatives.[7]

A typical experimental procedure is as follows (Table 1, Entry 4): To a solution of ethanethiol (624 mg, 10 mmol) in ether (10 ml), NaH (60% in paraffin, 402 mg, 10 mmol) was added at 0 °C and the mixture was stirred at room temperature for 15 min. Bromoallene **2** (R^1=*t*-Bu, 323 mg, 1.0 mmol) was added to the above solution and the reaction mixture was refluxed for 24 h. After quenching, crude products were chromatographed on silica gel to give spirocyclopropene **1** (R^1=*t*-Bu, R^2=Et, 268 mg, 88% yield). The structures of the spirocyclopropenes **1** were confirmed by the spectral data.[8]

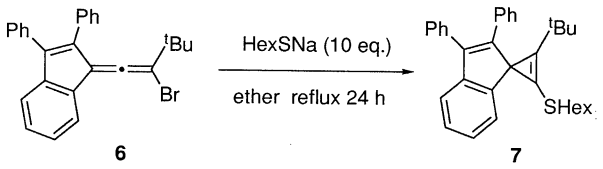
Table 1. The synthesis of the spirocyclopropenes **1**

Entry	R^1	R^2	Anion/eq	Time/h	Yeild[a]/%	Recovd/%
1	Ph	Et	1.2	1	51	35
2	Ph	Bu	1.2	1	74	
3	Ph	Hex	1.2	1	71	
4	*t*-Bu	Et	10	24	96(88)[b]	
5	*t*-Bu	Pr	10	3	95	
6	*t*-Bu	Bu	10	1	89	10
7	*t*-Bu	Hex	10	1	93	6
8	*t*-Bu	*i*-Pr	10	24	14	55
9	TMS	Et	10	1	53	(40)[c]
10	TMS	Hex	10	1	66	(32)[c]

[a]Determined by ^{1}H NMR. [b]Isolated yield. [c]Dimeric product **3**.

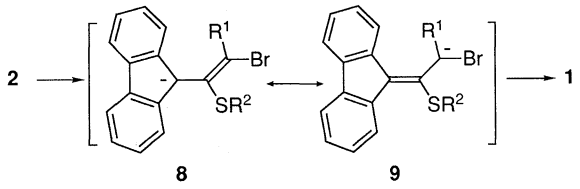


Trimethylsilyl substituted **2** also gave **1** accompanied by the dimerized compound (**3**).[9] The allenes **2** having substituted *tert*-butyl group needed longer reaction time than phenyl substituted **2**. The reaction rate depended upon the length of the alkyl chain of the thiol (Entry 4-7). The reaction was sluggish when the alkyl group in the thiolate ion was a branched one (Entry 8). The reaction of the chloroallene in place of the bromoallene **2** gave spirocyclopropene **1** (R^1=*t*-Bu, R^2=Hex) only in a yield of 33% under the same reaction conditions as Entry 7, presumably due to lower leaving-group ability of the chlorine atom. The bromoallenes (**4**, **5**) having no fluorene subunit did not give any cyclopropene derivatives, but only resulted in recovery of the starting material quantitatively under the same reaction conditions



Scheme 2.

as Entry 4. On the other hand, the indene derivative (**6**) reacted with hexanethiolate ion gave the corresponding cyclopropene (**7**) in a yield of 72% (Scheme 2). Cyclopentadiene structure which stabilizes the anion seems to be essential for the cyclopropene formation reaction. This supposition is supported by the result that the bromoallene (R^1=*t*-Bu) substituted by electron-withdrawing chlorine atoms at the 2,7-position of the fluorene moiety reacted with ethanethiolate anion under the same conditions as Entry 4 to give the corresponding spiro-cyclopropene in a yield of 93% after the reaction time of only 1 hour. Thiolate anion was also necessary for the reaction because



Scheme 3.

the reactions with amine or alcohol instead of thiol gave products entirely different from cyclopropene.[10]

Concerning the reaction mechanism, the first stage of the reaction should be the attack of the alkanethiolate anion to the central carbon of the allene bond to form the ambident anion expressed by the resonance structures **8** and **9** (Scheme 3). But these anions cannot react to the neighboring vinyl groups in view of their geometry.[11] We believe that the spirocyclopropene was formed by intramolecular addition reaction of the carbene generated by elimination of the bromo anion from **9**. The bromine atom of **9** is readily eliminated due to neighboring group participation of the alkylthio group. The length of the alkyl chain on the thiol should contribute to appropriately directing the lone pair of the sulfur atom to the back side of the bromine atom of **9**.

The mechanistic aspect is not clear yet, but the cyclopropene formation from the haloallene derivatives with alkanethiolate anions reported here is a new type reaction. Further mechanistic experiments are in progress.

References and Note

1 H. E. Simmons and T. Fukunaga, *J. Am. Chem. Soc.*, **89**, 5208 (1967).
2 H. Durr and R.Gleiter, *Angew. Chem., Int. Ed. Engl.*, **17**, 559 (1978).
3 W. E. Billups, W. Luo, and M. Gutierrez, *J. Am. Chem. Soc.*, **116**, 6463 (1994).
4 H. Durr, *Angew. Chem., Int. Ed. Engl.*, **28**, 413 (1989).
5 H. Durr, Y. Ma, and G. Cortellaro, *Synthesis*, **1995**, 294.
6 T. Toda, N. Shimazaki, H. Hotta, T. Hatakeyama, and T. Mukai, *Chem. Lett.*, **1978**, 523.
7 M. Minabe, M. Yoshida, S. Saito, K. Tobita, and T. Toda, *Bull. Chem. Soc. Jpn.*, **61**, 2067 (1988).
8 Typical data of **1** (R^1=*t*-Bu, R^2=Et): mp 74-76 °C; IR (KBr) 1818 cm^{-1} (C=C of the cyclopropene); ^1H NMR (300 MHz, $CDCl_3$) δ 0.98 (3H, t, *J*=7.5 Hz), 1.18 (9H, s), 2.47 (2H, q, *J*=7.5 Hz), 7.26-7.29 (4H, m, H-1', H-2', H-7', H-8'), 7.30-7.37 (2H, m, H-3', H-6'), 7.83 (2H, dt, *J*=7.2, 1.2 Hz, H-4', H-5'); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.25 (CH_3), 27.62 (CH_2), 29.36 (CH_3 of *t*-Bu), 33.38 (C of *t*-Bu), 42.90 (spiro C), 104.26 (=C-S), 119.61 (C-4', C-5'), 120.80 (=C-*t*-Bu), 120.99 (C-1', C-8'), 125.83 (C-3', C-6'), 126.16 (C-2', C-7'), 139.48 (C-4a', C-4b'), 148.11 (C-8a', C9a'). Anal. Found: C, 82.29; H, 7.19%. Calcd for $C_{21}H_{22}S$: C, 82.30; H, 7.24%.
9 **3**: mp 163-166 °C; IR (KBr) 2163, 1920 cm^{-1}: ^{13}C NMR (75 MHz, $CDCl_3$) δ -0.92, -0.25, 53.93 (C-9), 87.26 (TMS-C≡), 105.20, 111.40 (TMS-C=), 119.97, 120.04, 122.08, 125.51, 126.70, 126.89, 128.07, 128.45, 137.81, 138.67, 140,23, 147.17, 204.90 (=C=).
10 The reaction with amines gave complicated mixture, while with alcohols it afforded 9-alkoxy-9-ethynylfluorene derivatives in good yields.
11 Z. Rappoport, *Acc. Chem. Res.*, **25**, 474 (1992).

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