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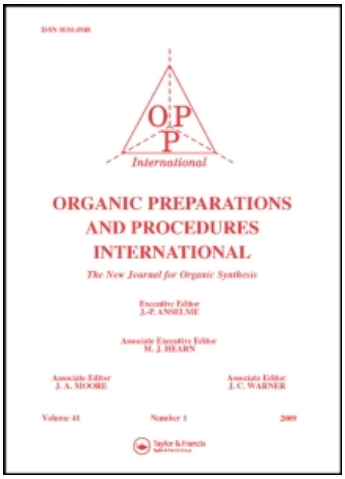

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

SYNTHESIS OF CYCLOPROPANES USING S-ETHENYLSULFILIMINES

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To cite this Article Ikeda, Katsuya , Satoh, Hiroshi and Yamamoto, Tamotsu(1992) 'SYNTHESIS OF CYCLOPROPANES USING S-ETHENYLSULFILIMINES', Organic Preparations and Procedures International, 24: 5, 548 — 551
To link to this Article: DOI: 10.1080/00304949209356727
URL: http://dx.doi.org/10.1080/00304949209356727

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4. The *J* values for the anomeric hydrogen (H-1', assigned by COSY) of steroidal β-glucuronides or β-glucuronates lie between 5.5 and 10 Hz, c.f. T. Nambara, T. Niwa and K. Shimada, *J. Steroid Biochem.*, **21**, 199 (1984); T. Nambara, K. Shimada, T. Ohkubo and T. Niwa, *ibid.*, **16**, 533 (1982); H. Hosoda, W. Takasaki, H. Miura, M. Tohkin, Y. Maruyama and T. Nambara, *Chem. Pharm. Bull. Jpn.*, **33**, 4281 (1985).

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SYNTHESIS OF CYCLOPROPANES USING S-ETHENYLSULFILIMINES†

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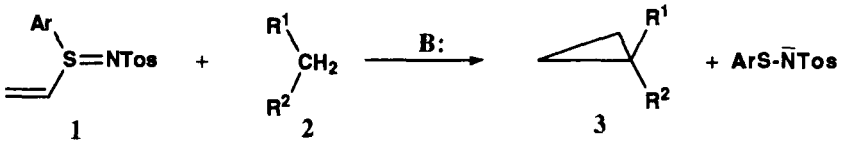
Cyclopropanes are useful compounds for transforming and enlarging carbon skeleton.[1] The main methods for their preparation involve the reaction of olefins with carbene and carbenoid sources,[2] of active methylene compounds with 1,2-dihaloalkanes[3] and with S-ethenylsulfonium compounds,[4] and of olefins with dimsyl anion and its analogues.[5] In recent years, heterogeneous reactions under PTC condition have been reported to give cyclopropanes in higher yields.[6] In a series of studies on the synthesis of ethenyl[7] and cyclic compounds[8] using S-ethenylsulfilimines, we have developed an efficient preparation of cyclopropanes using S-ethenylsulfilimines (**1**).

The method comprises three steps, Michael-type addition, prototropy (γ to α) followed intramolecular substitution.



1 **2** **3**

a) Ar = C_6H_5 b) Ar = 4-MeC_6H_4

S-Ethenyl-S-phenyl- (**1a**) and S-ethenyl-S-(4-methylphenyl)-N-tosylsulfilimines (**1b**) were used as S-ethenylsulfilimines. Seven compounds, whose pKa's values are different, were selected as active methylene compounds (**2**). The reaction of compounds **2** (in slight excess) with **1a** or **1b** were carried out in the presence of equimolar amount of sodium hydride in tetrahydrofuran (THF) at room temperature. The results are listed in Table 1. The reactions of both **1a** and **1b** with **2** gave the corresponding cyclopropanes (**3**) and the highest yields were obtained with **1b**. Moreover, the present method yields the target molecule **3e** from **1** and **2e**, while the PTC method[7] which affords the

comparatively high yield of compounds **3**, gives the hydrolyzed product of **3e**, namely 1-ethoxycarbonyl cyclopropane carboxylate, from **2e** and ethylene dibromide.

Compared with other methods, the present route gives useful yields and provides specific access to the desired cyclopropanes. Further, it could be considered to be a generalized method for the synthesis of cyclopropanes from active methylene compounds in a wide range of pKa values.

EXPERIMENTAL SECTION

Melting points are uncorrected. IR spectra were determined on a Shimazu IR-435 spectrophotometer. ^1H and ^{13}C NMR spectra in $CDCl_3$ were recorded on a JNM-PMX60 and a JNM-GSX270 spectrometer using TMS as an internal standard, respectively. Mass spectra were obtained with a JEOL JMS-D300 spectrometer at 70 eV. All active methylenes (reagents of Tokyo Kasei Ind. Co.) were used after distillation or recrystallization. All solvents were used after drying. S-Ethenylsulfilimines, **1a** and **1b** were obtained in overall yield of about 90% by the reported methods comprising the preparation of aryl 2-hydroxyethyl sulfides followed by their transformation to aryl 2-chloroethyl sulfides and sulfilimination of the latter sulfides with chloramine T[9a] followed by the dehydrochlorination under PTC conditions[9b] [**1a**: mp.111-112°, lit.[9a] 111-113°; **1b**: mp. 128-129°, lit.[9a] 128.5-129.5°]

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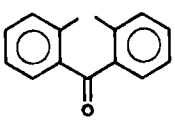
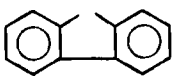
TABLE 1. Preparation of Cyclopropanes **3** using **1**[a]

Run No.	1	(mmol)	2	R^1	R^2	(mmol)	NaH (mmol)	Temp (°C)	Time (hrs)	Yield[b] (%)
1	**1a**	2.0	**2a**	PhCO	PhCO	2.1	2.1	rt 35-40	24 4	77
2	**1b**	2.0	**2a**	PhCO	PhCO	2.1	2.1	rt	24	95
3	**1b**	2.0	**2b**	MeCO	MeCO	2.1	2.1	rt	24	83
4	**1a**	2.0	**2c**	MeCO	EtO_2C	2.1	2.1	rt 35-40	24 4	30
5	**1a**	2.0	**2c**	MeCO	EtO_2C	2.1	2.1	rt	72	35
6	**1b**	2.0	**2c**	MeCO	EtO_2C	2.1	2.1	rt	24	75
7	**1a**	2.0	**2d**	EtO_2C	EtO_2C	2.1	2.1	rt 35-40	24 4	35
8	**1b**	2.0	**2d**	EtO_2C	EtO_2C	2.1	2.1	rt	24	76
9	**1b**	2.0	**2e**	CN	EtO_2C	2.1	2.1	rt	24	82
10	**1a**	2.0	**2f**			2.1	2.1	40-45	1.0	75
11	**1b**	2.0	**2f**			2.1	2.1	rt	12	91
12	**1a**	2.0	**2g**			2.1	2.1	rt	30	60

a) Solvent: THF. b) Yields were determined by NMR for the mixtures composed of cyclopropanes and disulfides

General Procedure.- To a stirred solution of 2.0 mmol of **1** and 2.1 mmol of **2** in 35 ml of THF was added 2.1 mmol of sodium hydride at room temperature. After stirring under the conditions given in Table 1, the solvent was removed by vacuum distillation. The resulting residue was extracted with ether (10ml x 4) and from the combined ethereal extract was evaporated to give an oil or a semi-solid residue of **3**. The structure was confirmed after purification by a suitable method [in the case of column chromatography, silica gel C200 (Wako Chemical Co. Ltd.) and benzene were used].

1,1-Dibenzoylcyclopropane (3a), mp . 94.5-95.5° (from ether-hexane), lit.[10] 87-88°. IR (KBr): 1660 (C=O), 1030(Δ) cm^{-1}. ^1H NMR: δ 1.75 (s, 4H), 7.2-7.8 (m, l0H). ^{13}C NMR: δ 16.62, 40.71, 128.44, 128.52, 132.80, 137.63, 197.51. MS (M/z) : 250 (M^+ 19), 105 (100).

1,1-Diacetylcyclopropane (3b), oil, lit.[11] 74.0-74. 5°/8mm. IR (neat): 1685 (C=O), 1030 (Δ) cm^{-1}. ^1H NMR: 1.41 (s, 4H), 2.16 (s, 6H). MS (m/z) : 126 (M^+ 6.4), 43 (100) .

1-Acetyl-1-ethoxycarbonylcypropane (3c), oil. lit.[5] 72-75°/12mm. IR (neat): 1725 (C=O), 1690 (C=O), 1185 (COC), 1025(Δ) cm^{-1}. ^1H NMR: δ 1.30 (t, 3H, J = 6.8Hz), 1.47 (s, 4H), 2.48 (s, 3H) 4.21 (q, 2H, J = 6.8Hz). MS (m/z): 156 (M^+ 17), 43 (100).

1,1-Diethoxycarbonylcyclopropane (3d), oil, lit.[12] 214-216°/748mm. IR (neat): 1722 (C=O), 1210 (COC), 1023 (Δ) cm^{-1}. ^1H NMR: 1.28 (t, 6H, J = 7.0Hz), 1.43 (s, 4H), 4.20 (q, 4H, J = 7.0Hz). MS (m/z): 186 (M^+ 15), 141 (100).

Ethyl 1-Cyanocyclopropanecarboxylate (3e), oil, lit.[3] 212-216°/760mm. IR (neat): 2240 (C≡N), 1725 (C=O), 1185 (COC), 1019(Δ) cm^{-1}. ^1H-NMR: δ 1.32 (t, 3H, J = 7.3Hz), 1.67 (s, 4H), 4.31 (q, 2H, J = 7.3Hz). MS (m/z): 13 9(M^+ 4.5), 111 (100).

Spiro[anthrone-10,1´-cyclopropane] (3f), mp . 152-153° (from benzene), lit.[13] 152°. IR (KBr): 3060, 3010, 1645 (C=O), 1600, 1480, 1460, 1315, 1175, 1095, 1060, 1035(Δ), 932, 800, 745, 680 cm^{-1}. ^1H NMR: δ 1.83 (s, 4H), 6.8-7.1 (m, 2H), 7.1-7.7 (m, 4H), 8.2-8.6 (m, 2H) .

Spiro[fluorene-9,1´-cyclopropane] (3g), mp. 69-70° (from hexene), lit.[14] 70.5°. IR (KBr): 3040, 3000, 1605, 1435, 1340, 1320, 1217, 1080, 1050, 1020(Δ), 940, 756, 726 cm^{-1}. ^1H NMR: δ 1.59 (s, 4H), 6.8-8.0 (m, 8H).

REFERENCES

† Part I of "*The Studies on the Syntheses Using S-Ethenylsulfilimines*".

1. J. M. Stewart and H. H. Westberg, *J. Org. Chem.*, **30**, 1951 (1965) .
2. a) E. V. Dehmlow and J. Schonefeld, *Ann.*, **746**, 41 (1971); b) S. Siegel and C. G. Bergstrom, *J. Am. Chem. Soc.*, **72**, 3815 (1950).
3. L. W. Jones and A. W. Scott, *ibid.*, **44**, 413 (1922).
4. J. W. Batty, P. D. Howes and C. J. M. Stirling, *J. Chem. Soc Perkin 1*, 65 (**1973**).
5. a) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1353 (1965); b) C. R. Johnson, M.

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Haarke, and C. W. Schroeck, *ibid.*, **92**, 6594 (1970).

6. R. L. Goaller, S. Slaoui, J. L. Pierre and J. L. Luche, *Synth. Commun.*, 1163 (**1982**).

7. a) T. Yamamoto and M. Okawara, *Chemistry Lett.*, 581 (**1975**); b) For the preparation of allyl vinyl ethers, T. Yamamoto, I. Koyama and K. Sugawara, The 42nd Annual Meeting of Chem. Soc. Jpn., Preprint II, 621 (**1980**).

8. a) For the preparation of S,S-, S,O- and S,N-diheterocyclic compounds, see T. Takahashi, T. Atsumi, H. Yamauchi and T. Yamamoto, Chugoku-Shikoku-Kyushu, Local Meeting of Chem. Soc. Jpn., Preprint, 115 (**1986**); b) For the preparation of S,N,N- and O,N,N-triheterobicyclic compounds, see T. Takahashi, Y. Shimizugawa, H. Inoue and T. Yamamoto, The 57th Annual Meeting of Chem. Soc. Jpn., Preprint, II, 584 (**1988**).

9. a) T. Yamamoto and D. Yoshida, *Org. Prep. Proced. Int.*, **20**, 271 (1988); b) Y. Shimizugawa, T. Takahashi, M. Ishii and T. Yamamoto, *ibid.*, **22**, 522 (1990).

10. Beilstein's, **7**, E1, 426.

11. K. Ichikawa, O. Itoh, T. Kawamura, M. Fujiwara and T. Ueno, *J. Org. Chem.*, **31**, 447 (1966).

12. A. W. Dox and L. Yoder, *J. Am. Chem. Soc.*, **43**, 2097 (1921).

13. A. Mustafa and M. K. Hilmy, *J. Chem. Soc.*, 1434 (**1952**).

14. E. J. Greenhow, D. McNeil and E. N. White, *ibid.*, 3204 (**1956**).

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