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SYNTHESIS OF VINYLCYCLOPENTANES FROM VINYLCYCLOPROPANES AND ALKENES PROMOTED BY BENZENETHIYL RADICAL

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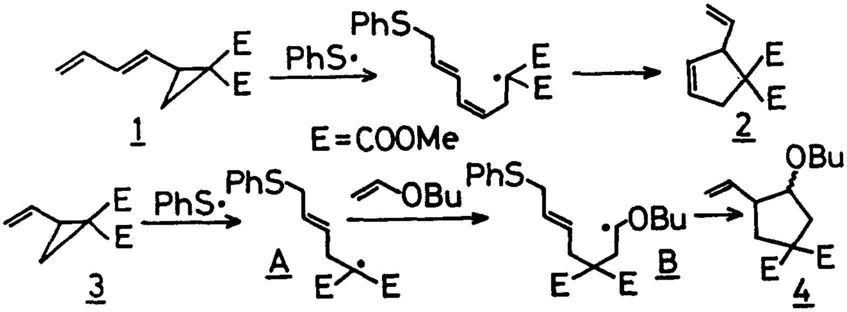
Abstract: The reaction of dimethyl 2-vinylcyclopropane-1,1-dicarboxylate with butyl vinyl ether in the presence of a catalytic amount of PhSH provides dimethyl 3-butoxy-4-vinylcyclopentane-1,1-dicarboxylate in 82% yield.

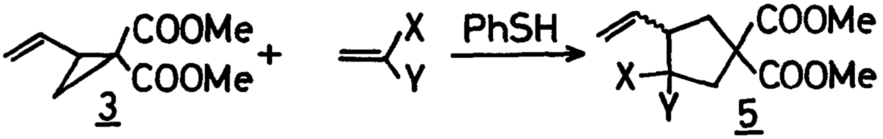
Recently we reported[1] that benzenethiyl radical (or triphenyltin radical) promotes the transformation of 2-(1,3-butadienyl)cyclopropane-1,1-dicarboxylate **1** into 2-vinyl-3-cyclopentene-1,1-dicarboxylate **2**. Here, we wish to report an application of this methodology to the title reaction which presumably proceeds as follows: (1) the attack of thiyl radical[2] on the vinyl group of cyclopropane **3** forms a radical **A** under cyclopropane ring cleavage, (2) radical **A** adds to an alkene intermolecularly to give a radical **B**, and (3) this collapses to form the respective cyclopentane derivative **4** and regenerate benzenethiyl radical.[3]



Benzenethiol (44 mg, 0.4 mmol)[4] was added to a solution of dimethyl 2-vinylcyclopropane-1,1-dicarboxylate **3** (0.18 g, 1.0 mmol) in butyl vinyl ether (50 mmol, 6.5 ml) under an argon atmosphere. The mixture was heated at 60 °C for 40 min. The resulting mixture was concentrated and the residual oil was submitted to preparative tlc on silica gel to give dimethyl 3-butoxy-4-vinylcyclopentane-1,1-dicarboxylate 4^5 (0.23 g) in 82% yield.[6]

The results of the reaction of vinylcyclopropane **3** with various alkenes are summarized in Table 1. Whereas electron rich olefins such as vinyl ether (entries 1, 2, 3, and 4) and vinyl ester (entry 5) provided cyclopentanes in good yields, alkenes containing electron-withdrawing sub-

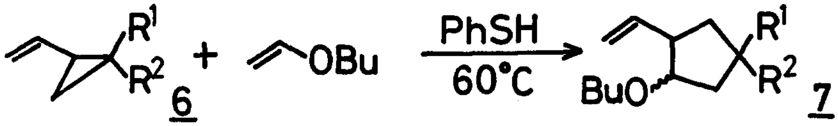
Table 1. Synthesis of cyclopentane derivatives from dimethyl 2-vinylcyclopropane-1,1-dicarboxylate and various alkenes[a]



Entry	Alkene		Reaction		Yield of 5	Isomeric
	X	Y	Temp (°C)	Time (h)		Ratio[b]
1	H	$O-C_4H_9$	60	0.7	82	65:35
2	Me	OMe	25	16	71[c]	100: 0
3	H	$OSiMe_3$	60	3	65	81:19
4	OEt	OEt	60	2	79	——
5	Me	$OCOCH_3$	60	3	74	80:20
6	H	$n-C_5H_{11}$	60	3	54	69:31
7	H	CH_2SiMe_3	60	3	63	79:21
8	H	COOMe	60	48	38[d]	76:24
9	H	CN	60	22	21[d]	64:36
10	$HC{\equiv}C-n-C_4H_9$		60	16	6	——

a) Alkenes (50 eq) were used as solvents unless otherwise noted.
b) See ref. 7. c) See ref. 8. d) See ref. 9.

Table 2. Synthesis of cyclopentane derivatives from several vinylcyclopropanes and butyl vinyl ether[a]



Entry	Vinylcyclopropane 6		Reaction	Yield of 7[b]
	R^1	R^2	Time (h)	
1	COMe	COOMe	2	77
2	COMe	COMe	11	14
3	CN	CN	6	21
4	SO_2Ph	SO_2Ph	9	20
5	COOEt	H	0.5	57
6	COPh	H	5	50
7	SO_2Ph	H	6	17
8			6	0

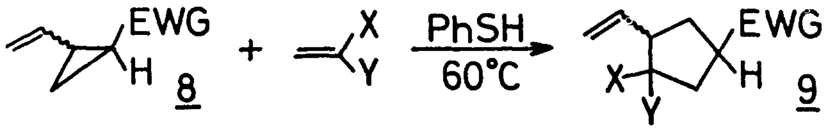
a) Vinylcyclopropane (1.0 mmol), butyl vinyl ether (50 mmol), and PhSH (0.4 mmol) were employed. b) Isomeric mixtures.

stituents such as acrylonitrile and methyl acrylate gave poor yields.[10] 1-Heptene and allyltrimethylsilane also afforded satisfactory results.

Various vinylcyclopropanes bearing a variety of functional groups were prepared and the radical induced reactions of these compounds with butyl vinyl ether were studied (Table 2). Several facts are worth noting. (1) Ketoester **6** (R^1 = COMe, R^2 = COOMe) gave the cyclopentane **7** in good yield as well as diester **3**. In contrast, diketo-, dicyano-, and disulfonylcyclopropanes afforded the corresponding vinylcyclopentanes in poor yields. (2) The presence of two electron-withdrawing groups was not essential for the reaction. For instance, cyclopropanes having one electron-withdrawing group such as ethyl 2-vinylcyclopropanecarboxylate or 1-benzoyl-2-vinylcyclopropane gave **7** in fair yields. Moreover, the reaction was completed in a short period (<30 min) in the case of ethyl 2-vinylcyclopropanecarboxylate. (3) Treatment of a solution of 1,2-dimethyl-1-butyl-2-vinylcyclopropane in butyl vinyl ether with benzenethiol gave 3,5-dimethyl-1-phenylthio-2-nonene in 80% yield (based on the PhSH employed) and no trace of the desired cyclopentane derivative was detected in the reaction mixture (entry 8). 1,1-Bis(phenylthio)-2-vinylcyclopropane also gave no cyclopentane **7** but 1,5,5-tris(phenylthio)-2-pentene in 82% yield.

The reaction of vinylcyclopropane **8** having one electron-withdrawing group with alkenes in the presence of a catalytic amount of benzenethiol was examined (Table 3). Not only electron rich olefins but also electron poor alkenes such as methyl acrylate or acrylonitrile afforded the respective cyclopentanes **9** in good yields.[11]

Table 3. Synthesis of cyclopentane derivatives from vinylcyclopropanes and various alkenes



Entry	Vinylcyclopropane **8** EWG	Alkene X	 Y	Reaction Time (h)	Yield of **9**
1	COOEt	Me	OAc	1	77
2	COOEt	H	COOMe	16	76
3	COOEt	H	CN	16	48
4	COPh	Me	OAc	6	71
5	COPh	H	COOMe	11	63
6	SO_2Ph	Me	OAc	6	54

a) Vinylcyclopropane **8** (1.0 mmol), isopropenyl acetate (50 mmol), and PhSH (0.4 mmol) were employed. Benzene was used as a solvent in the case of methyl acrylate and acrylonitrile. See ref. 9.

References and Notes

1. K. Miura, K. Fugami, K. Oshima, and K. Utimoto, Tetrahedron Lett., **29**, 1543 (1988).
2. K. Griesbaum, Angew. Chem., Int. Ed. Engl., **9**, 273 (1970); Y. Ichinose, K. Wakamatsu, K. Nozaki, J-Ł. Birbaum, K. Oshima, and K. Utimoto, Chem. Lett., **1987**, 1647.
3. Allylsulfides have been used for the synthesis of C-C bonds. Y. Ueno, S. Aoki, and M. Okawara, J. Am. Chem. Soc., **101**, 5415 (1979); Y. Ueno, K. Chino, and M. Okawara, Tetrahedron Lett., **23**, 2575 (1982).
4. The reaction proceeded without a radical initiator such as AIBN. Sufficient amount of PhSH (20-40 mol%) was required for obtaining reasonable reaction rates and yields of the cyclopentanes. A part of thiyl radical directly attacked alkenes to provide $PhSCH_2CH_2OBu$.
5. **4** (Stereoisomeric mixture, 65:35): Bp 135 °C (bath temp, 1 Torr); IR (neat) 3076, 2954, 2870, 1735, 1637, 1458, 1437, 1254, 1198, 1170, 1099 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.90 (t, J = 6.7 Hz, 3H), 1.23-1.60 (m, 4H), 1.75-1.95 (m, 0.7H), 2.10-2.75 (m, 4.3H), 3.23 (dt, J = 9.0, 6.0 Hz, 0.35H), 3.40 (t, J = 6.7 Hz, 2H), 3.60 (dt, J = 6.5, 6.5 Hz, 0.65H), 3.73-3.77 (m, 6H), 4.98 (m, 2H), 5.78 (ddd, J = 17.5, 10.5, 7.0 Hz, 0.65H), 5.93 (ddd, J = 17.2, 10.0, 7.8 Hz, 0.35H). Found: C, 63.39; H, 8.78%. Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51%.
6. Ph_3SnH-AIBN system was not as effective as PhSH. For instance, the use of Ph_3SnH (0.4 mmol) and AIBN (0.4 mmol) instead of PhSH provided **4** in 39% yield along with unidentified products.
7. Structure of the isomers (cis or trans) could not be determined.
8. **5** (X = Me, Y = OMe, single isomer): Bp 120 (bath temp, 1 Torr); IR (neat) 3074, 2976, 2950, 2826, 1735, 1638, 1458, 1377, 1264, 1199, 1163, 1115, 1065, 919 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.13 (s, 3H), 2.00 (dd, J = 16.4, 10.8 HZ, 1H), 2.28 (d, J = 14.1 Hz, 1H), 2.60 (d, J = 14.1 Hz, 1H), 2.69-2.80 (m, 2H), 3.18 (s, 3H), 3.73 (s, 3H), 3.75 (s, 3H), 5.02-5.12 (m, 2H), 5.73 (ddd, J = 17.4, 9.8, 7.5 Hz, 1H). Found: C, 61.14; H, 7.93%. Calcd for $C_{13}H_{20}O_5$: C, 60.92; H, 7.87%.
9. Without benzene, polymerization of methyl acrylate (or acrylonitrile) took place and the desired cyclopentanes were not produced at all. Benzenethiol (0.4 mmol) was added to a solution of vinylcyclopropane **3** (1.0 mmol) and methyl acrylate (or acrylonitrile, 30 mmol) in benzene (10 ml) and the resulting mixture was heated at 60 °C.
10. The reaction of **3** with α,β-unsaturated ester or ketones in the presence of palladium catalyst has been reported. I. Shimizu, Y. Ohashi, and J. Tsuji, Tetrahedron Lett., **26**, 3825 (1985).
11. Financial support by the Ministry of Education, Science, and Culture of Japan (Grant-in-Aid for Scientific Research No. 63470074) is acknowledged.

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