TRIPHENYLSTANNYL RADICAL OR BENZENETHIYL RADICAL PROMOTED TRANSFORMATION OF 1,1-DIALKOXYCARBONYL-2-(1,3-BUTADIENYL)CYCLOPROPANES INTO 2-ETHENYL-3-CYCLOPENTENES

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Abstract: Dimethyl 2-(1,3-butadienyl)cyclopropane-1,1-dicarboxylate reacts with catalytic amount of Ph₃SnH in benzene at 80 °C to provide dimethyl 2ethenyl-3-cyclopentene-1,1-dicarboxylate in good yield. The transformation of N-tosyl-2-(1,3-butadienyl)aziridine into N-tosyl-2-vinyl-3-pyrroline is also described.

The vinylcyclopropane-cyclopentene rearrangement has attracted much attention from the mechanistic and synthetic points of view.¹ Previously we have reported that 1,3-butadienylcyclopropanes activated by two electron-withdrawing groups smoothly rearrange to vinylcyclopentene derivatives in the presence of Pd(0) catalyst under mild conditions.² Here we wish to report the same type of rearrangements induced by Ph₃Sn or PhS radical.

Free radical reactions have been used increasingly in recent years for the synthesis of organic molecules. 3 The cis-trans isomerization of olefins by the addition-elimination sequence of PhS radical⁴ or Ph₃Ge radical⁵ has been reported. This methodology has been applied to the title rearrangement reaction. Triphenyltin hydride (0.14 g, 0.4 mmol) was added to a solution of dimethyl 2-(3-methyl-1,3-butadienyl)cyclopropane-1,1-dicarboxylate (1) (0.22 g, 1.0 mmol) and azobisisobutyronitrile (AIBN, 66 mg, 0.4 mmol) in benzene (20 ml) under an argon atmosphere. The mixture was heated at $60\degree$ C for 4 h. The resulting mixture was concentrated and the residual oil was submitted to silica-gel column chromatography to give dimethyl 2-isopropenyl-3-cyclopentene-1,l-dicarboxylate (2) (0.18 g) in 82% yield. The use of triphenylgermyl hydride or benzenethiol instead of triphenyltin hydride also gave satisfactory results. For instance, treatment of ${f l}$ with Ph₃GeH-AIBN or PhSH⁶ provided **2** in 54% or 75% yield, respectively. The other results are summarized in Table 1.



Entry	Substrate	Radical Source	Yield (%)	Product (cis:trans)
1	Сооме	Ph ₃ SnH Ph ₃ GeH PhSH n-Bu ₃ SnH	70 58 65 65	C00Me (65:35)
2	COOMe COOMe	Ph ₃ SnH	20	Сооме
3	Ph COOMe COOMe	Ph ₃ SnH PhSH	83 60	COOMe b)
4	COOEt	≻ _{Ph3} snH	90	S02-C-
5	COOEt	Ph ₃ SnH PhSH	98 79	S02-C)-°'
6	Ph CODEt	Ph ₃ SnH n-Bu ₃ SnH	92 80	Ph SO ₂ COOEt
7	COOMe	PhSH	73	COOMe (62:38)
8	0 COOEt	Ph ₃ SnH PhSH	89 80	COOEt

Table 1. Triphenylstannyl (or benzenethiyl) radical induced rearrangement of 1,1-dialkoxycarbonyl-2~(1,3-butadienyl)cyclopropanes^a)

a) A benzene solution of Ph₃SnH (0.4 mmol) (n-Bu₃SnH (0.4 mmol) or Ph₃GeH (0.4 mmol)), AIBN (0.4 mmol), and substrate (1.0 mmol) was heated at 60°C for 1-4 h, or a benzene solution of PhSH (0.4 mmol) and substrate (1.0 mmol) was heated at 60°C for 1-4 h. b) See ref. 7. c) See ref. 8.

Exposure of ethyl 3-(3-methyl-1,3-butadienyl)-2,2-dimethylcyclopropanecarboxylate, which was derived from ethyl crysanthemate to the rearrangement reaction (Ph3SnH-AIBN, 60°C or PhSH, 60°C) resulted in the formation of desired cyclopentene derivative in only 14% or 16% yield after prolonged heating (15 h).⁹ In contrast, treatment of diethyl 3-(3-methyl-1,3-butadienyl)-2,2-dimethylcyclopropane-1,1-dicarboxylate with Ph3SnH-AIBN or PhSH gave diethyl 2-isopropenyl-5,5-dimethyl-3-cyclopentene-1,1-dicarboxylate in 63% or 55% yield, respectively. Moreover, the reaction of dimethyl 2vinylcyclopropane-1,l-dicarboxylate yielded dimethyi 5-triphenylstannyl-3pentene-1,1-dicarboxylate in 70% yield along with no trace of cyclopentene derivatives upon treatment with Ph_3SnH and AIBN at 60°C for 2 h.¹⁰ Thus, the presence of two electron-withdrawing groups and dienic moiety is essential for the rearrangement. The reaction of dimethyl 2-(1,3-pentadienyl)cyclopropane-1,1-dicarboxylate or dimethyl 2-(4-phenyl-1,3-butadienyl)cyclopropane-1,1-dicarboxylate gave the expected cyclopentene derivative in only 20% or <5% yield, respectively.⁹ The use of Et_3B^5 instead of AIBN as a radical initiator was not effective for the title transformation.

We are tempted to assume following reaction mechanism for the rearrangement: (1) the attack of Ph_3Sn radical on the dienic group forms a radical **A** which has a dienylstannyl group, and (2) this collapses to form the respective cyclopentene derivative with new C-C bond formation exclusively producing a five-membered ring and not a seven-membered one.¹¹



The reaction was easily extended to the rearrangement of N-tosyl-2-(1,3-butadienyl)aziridine into N-tosyl-2-vinyl-3-pyrroline. 12,13



References and Notes

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- 6. In the case of PhSH, the reaction proceeded in the absence of AIBN.
- 7. Bp 150°C (1 Torr, bath temp); IR (neat) 3056, 2950, 1734, 1433, 1257, 1224, 1160, 1076, 978, 909 cm⁻¹; NMR (CDCl₃) & 2.70 (dm, <u>J</u> = 18 Hz, 1H), 3.13 (s, 3H), 3.43 (dm, <u>J</u> = 18 Hz, 1H), 3.70 (s, 3H), 4.90 (m, 1H), 5.00 (s, 1H), 5.43 (s, 1H), 5.50-5.85 (m, 2H), 7.13-7.60 (m, 5H). Found: C, 71.03; H, 6.28%. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34%.
- 8. Cis and trans isomeric mixture: Bp 200°C (1 Torr, bath temp); IR (neat) 3064, 2978, 1733, 1598, 1446, 1370, 1320, 1242, 1142, 1083, 900 cm⁻¹; NMR (CDCl₃) δ 1.14 (t, \underline{J} = 7.1 Hz, 0.9H), 1.22 (t, \underline{J} = 7.1 Hz, 2.1H), 1.60 (s, 2.1H), 1.95 (s, 0.9H), 2.45 (s, 3H), 3.25 (dm, \underline{J} = 17 Hz, 1H), 3.45 (dm, \underline{J} = 17 Hz, 1H), 4.12 (m, 2H), 4.22 (m, 0.7H), 4.35 (m, 0.3H), 4.72 (s, 0.7H), 4.86 (s, 0.7H), 5.13 (m, 0.6H), 5.47 (m, 0.7H), 5.60 (m, 0.3H), 5.75 (m, 0.7H), 5.88 (m, 0.3H), 7.15-7.90 (m, 4H). Found: C, 64.41; H, 6.74%. Calcd for C₁₈H₂₂O₄S: C, 64.65; H, 6.63%.
- 9. Starting material was recovered (10-15%) along with unidentified complex by-products.
- 10. The reaction of dimethyl 2-vinylcyclopropane-1,1-dicarboxylate with PhSH gave 5-phenylthio-3-pentene-1,1-dicarboxylate in 25% yield along with unidentified complex by-products.
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