Reaction of Tris(*t*-butylthio)cyclopropenylium Perchlorate with Arylmagnesium Bromides

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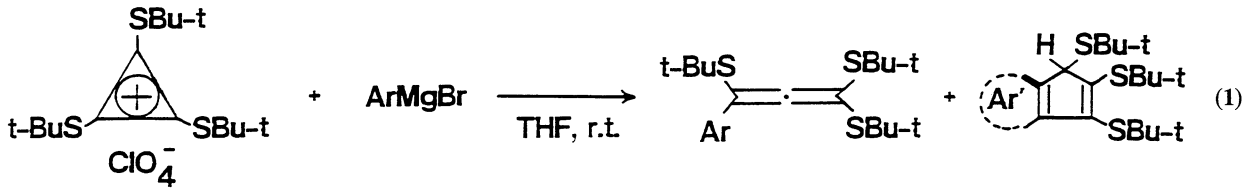
Synopsis. The reaction of tris(*t*-butylthio)cyclopropenylium perchlorate with phenyl-, *o*-tolyl-, or 1-naphthylmagnesium bromide in tetrahydrofuran at room temperature gave *t*-butylthio-substituted allenes and indenes. The reaction with 2,6-xylylmagnesium bromide gave only the corresponding allene derivative.

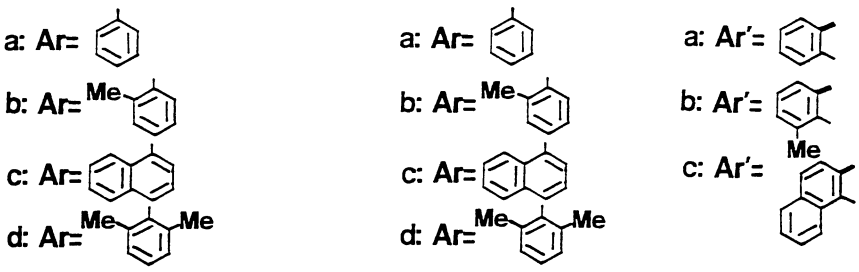
The cyclopropenyl cations are interesting from the viewpoint of their applications to synthetic reactions. Recently, we reported that tris(isopropylthio)cyclopropenyl cation reacts with pyrrole and indoles in the presence of sodium hydride in dimethyl sulfoxide to give pyrrolizine and fluorazene derivatives, respectively, in good yields.[1] On the other hand, recent studies have shown that the 1-(methylthio)- and 1-(diphenylamino)-2,3-diphenylcyclopropenyl cations react with phenylmagnesium bromide in tetrahydrofuran (THF) at room temperature to give 1-(methylthio)- and 1-(diphenylamino)-2,3,3-triphenylcyclopropenes, and the resulting cyclopropenes are converted into the 1-(methylthio)- and 1-(diphenylamino)-2,3-diphenylindenes, respectively, on heating at 50-70 °C.[2,3] In the course of our studies on the reactivity of the tris(alkylthio)cyclopropenyl cations, we examined the reactions of tris(*t*-butylthio)cyclopropenylium perchlorate (**1**) with phenyl-, *o*-tolyl-, 1-naphthyl-, and 2,6-xylylmagnesium bromides (**2a**—**d**). The reaction was carried out under argon in dry THF at room temperature for 4 h. In the cases of **2a**—**c**, *t*-butylthio-substitutd allenes (**3a**—**c**) and indenes (**4a**—**c**) were obtained (reaction 1 and Table 1). The reaction with **2d** gave only the allene **3d**. Thus, we found that the cyclopropenyl cation **1** reacts with arylmagnesium bromides to bring about the formation of *t*-butylthio-substituted allenes. The reactions proceeded more readily than those using 1-(methylthio)- and 1-(diphenylamino)-2,3-diphenylcyclopropenyl cations,[2,3] indicating that the cyclopropene ring with three *t*-butylthio groups undergoes ring opening much more readily than the ring with two phenyl groups. It has been reported that the conversion of 1-(methylthio)-2,3,3-triphenylcyclopropene into the corresponding indene derivative proceeds through the formation of a vinylcarbene intermediate, followed by the C-H insertion of the carbene into the benzene ring.[2] From these results, it is reasonable to believe that the reaction proceeds through the formation of a vinylcarbene intermediate (**5a**—**d**) to give allenes (**3a**—**d**) by rearrangement of the *t*-butylthio group and indenes (**4a**—**c**) by intramolecular cyclization, as shown in Scheme 1.

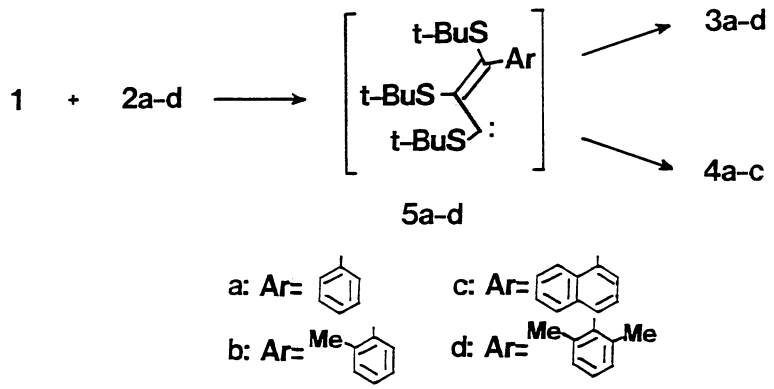
Table 1. Reaction of **1** with Arylmagnesium Bromides[a]

ArMgBr[b]	Yield[c]/%	
	Allenes	Indenes
2a	**3a** (29)	**4a** (47)
2b	**3b** (20)	**4b** (65)
2c	**3c** (14)	**4c** (67)
2d	**3d** (77)	—[d]

a) THF, r.t., and 4 h. b) The ArMgBr/**1** molar ratio= 3:1. c) Isolated yields based on **1**. d) Not detected.







Scheme 1.

Experimental

IR spectra were measured on a Hitachi 215 spectrophotometer. All ^{1}H NMR spectra (270 MHz) and ^{13}C NMR spectra (68 MHz) were determined on a JEOL JNM-GX 270 FT NMR spectrometer in $CDCl_3$ using TMS as an internal standard. Mass spectra were recorded on a Shimadzu LKB-9000 spectrometer operating at an ionization potential of 70 eV. Elemental analysis data (C and H) agreed within ±0.3% with the calculated values.

General Procedure for the Reaction of Tris(*t*-butylthio)cyclopropenylium Perchlorate (1) with Arylmagnesium Bromides. To a solution of arylmagnesium bromides (**2a**—**d**) (1.5 mmol) in dry THF (5 ml) was added the compound **1** (0.5 mmol) in one portion. The mixture was stirred under argon at room temperature for 4 h. A saturated aqueous ammonium chloride solution was then added, and the mixture was extracted with dichloromethane (100 ml). The organic layer was washed with water (100 ml) and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the residual oil was chromatographed over silica gel using hexane-dichloromethane (5:1) as the eluent to give the products (**3a**—**d** and **4a**—**c**). The structures of all products described above were determined by ^{1}H and ^{13}C NMR, IR, mass spectra, and elemental analyses.

3a: Colorless oil; IR (neat) 2970, 2930, 2870, 1900, 1495, 1450, 1395, 1370, 1160, 825, 770, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.40 (s, 18H), 1.41 (s, 9H), 7.24—7.38 (m, 3H), and 7.67—7.70 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=31.4, 31.8, 48.6, 48.7, 94.9, 100.1, 122.7, 127.7, 128.0, 128.3, 136.7, and 213.8; MS *m*/*z* 380 (M^+).

3b: Colorless oil; IR (neat) 3075, 2970, 2930, 2870, 2350, 1920, 1460, 1370, 1165, 835, 760, and 725 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.30 (s, 9H), 1.38 (s, 18H), 2.47 (s, 3H), 7.15—7.17 (m, 3H), and 7.47—7.49 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=20.8, 31.1, 31.6, 48.1, 48.4, 93.8, 99.4, 125.5, 127.8, 129.4, 130.7, 135.8, 136.3, and 211.1; MS *m*/*z* 394 (M^+).

3c: Colorless oil; IR (neat) 3050, 2960, 2925, 1920, 1475, 1460, 1395, 1370, 1165, 840, 805, and 780 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.32 (s, 9H), 1.36 (s, 18H), 7.42—7.56 (m, 3H), 7.72—7.85 (m, 3H), and 8.49 (d, 1H); ^{13}C NMR ($CDCl_3$) δ=31.2, 31.7, 48.5 (2C), 94.6, 98.4, 125.1, 126.0, 126.2 (2C), 127.2, 128.3, 128.5, 134.0, 134.5, 137.6, and 211.8; MS *m*/*z* 430 (M^+).

3d: Colorless oil; IR (neat) 3060, 2930, 2720, 1910, 1460, 1395, 1365, 1220, 1160, 875, 830, and 765 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.38 (s, 18H), 1.44 (s, 9H), 2.48 (s, 6H), and 6.98—7.10 (m, 3H); ^{13}C NMR ($CDCl_3$) δ=20.8, 31.1, 31.4, 47.4, 48.2, 97.5, 100.0, 127.8, 127.9, 134.2, 136.8, and 207.0; MS *m*/*z* 408 (M^+).

4a: Colorless oil; IR (neat) 3070, 2950, 2900, 2860, 1475, 1455, 1395, 1365, 1250, 1220, 1160, 1020, 975, 760, and 720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.34 (s, 9H), 1.38 (s, 18H), 1.47 (s, 9H), 4.53 (s, 1H), 7.26—7.34 (m, 2H), and 7.55—7.64 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=32.2 (2C), 32.4, 44.9, 50.1 (2C), 56.5, 122.7, 124.1, 126.5, 127.2, 144.6, 144.7, 147.3, and 152.9; MS *m*/*z* 380 (M^+).

4b: Yellow crystals, mp 117.5—118.0 °C (decomp); IR (KBr) 3050, 2950, 2900, 1595, 1500, 1470, 1455, 1395, 1365, 1265, 1220, 1170, 1150, 1075, 1035, and 790 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.20 (s, 9H), 1.38 (s, 9H), 1.40 (s, 9H), 2.62 (s, 3H), 4.58 (s, 1H), 7.03 (d, 1H), 7.26 (t. 1H), and 7.51 (d, 1H); ^{13}C NMR ($CDCl_3$) δ=19.2, 32.2, 32.3, 32.4, 46.2, 49.2, 50.1, 56.8, 120.3, 127.6, 128.3, 134.0, 142.3, 142.9, 144.9, and 154.8; MS *m*/*z* 394 (M^+).

4c: Yellow crystals, mp 146.0—146.5 °C; IR (KBr) 3050, 2960, 2920, 1475, 1460, 1400, 1375, 1165, 1095, 830, and 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.10 (s, 9H), 1.41 (s, 9H), 1.44 (s, 9H), 4.89 (s, 1H), 7.42—7.59 (m, 2H), 7.86—7.89 (m, 3H), and 8.72 (d, 1H); ^{13}C NMR ($CDCl_3$) δ=32.3, 32.4 (2C), 47.0, 49.4, 50.4, 56.7, 121.2, 124.6, 125.3, 126.0, 128.5, 128.8, 129.6, 132.6, 140.2, 142.7, 143.0, and 155.9; MS *m*/*z* 430 (M^+).

References

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