

## Synthesis and Rearrangement of Azulenesulfonium Salts

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Dedicated to Professor Rolf Huisgen on the occasion of his 60th birthday

Rearrangement reactions of azulenes with retention of the bicyclic system have hardly been studied so far; just a few thermally induced or acid-catalyzed isomerizations of 1-alkyl-, 1-aryl-, and 1-acylazulenes to the corresponding 2-substituted azulenes are known<sup>[1]</sup>. We have now found that *S,S*-dimethyl-4-azulenylmethylsulfonium salts of type (3) not only provide a facile entry to numerous 4-functionalized azulene derivatives, but also undergo a mechanistically and preparatively interesting rearrangement.

Compound (3) (blue platelets) can be prepared by reaction of sodium (6,8-dimethyl-4-azulenyl)methanide (1)<sup>[2]</sup> with di-

methylsulfane to give 6,8-dimethyl-4-(methylthiomethyl) azulene (2) (blue crystals) followed by methylation of (2). On reaction with nucleophiles (dimethylamine, aqueous sodium acetate, sodium azide, lithium chloride or bromide), compound (3)—a potential umpolung product of (1)—affords the hitherto inaccessible compounds (4a–e) (blue crystals or oils, see Table 1). Reaction of (3) with triphenylphosphane gives the phosphonium salt (4f) (blue crystals) which is capable of undergoing Wittig reactions with aldehydes<sup>[3]</sup> (see Table 1).

Contrary to initial expectations, deprotonation of (3) with sodium methoxide (in methanol, room temperature) fails to yield the resonance-stabilized sulfonium ylide (5a). Instead, a fast, and for non-benzenoid, cyclically conjugated  $\pi$ -electron systems previously unknown, [2,3]sigmatropic rearrangement of (5b)—which is presumably in equilibrium with (5a)—with loss of the 10 $\pi$ -electron system apparently takes

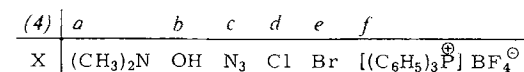
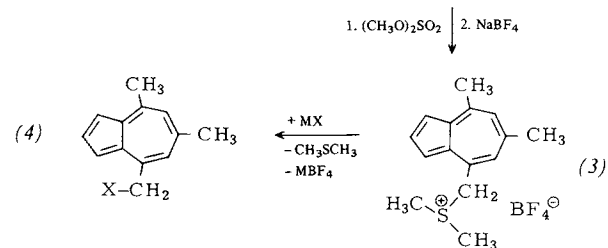
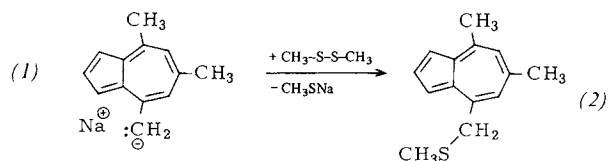
Table 1. Selected physical data of compounds (3), (4a–f), (6), (7), (8).

Cpd.	Yield [%]	M. p. [°C]	UV ( <i>n</i> -hexane) $\lambda$ [nm] (log $\epsilon$ )	100 MHz- <sup>1</sup> H-NMR (CDCl <sub>3</sub> ), $\delta$ values
(2)	75	35	245 (4.42), 290 (4.73), 332 sh (3.48), 337 (3.54), 349 sh (3.61), 352 (3.64), 363 sh (3.02), 550 (2.69), 563 (2.69), 587 (2.66), 610 sh (2.66), 640 (2.28)	7.68 (t, $J = 4$ Hz, 1H, H-2), 7.43, 7.38 (dd, $J = 4$ Hz, $J = 1.4$ Hz, 2H, H-1, 3), 7.16, 7.06 (br. s, 2H, H-5, 7), 4.19 (s, 2H, —CH <sub>2</sub> —), 2.85 (s, 3H, 8-CH <sub>3</sub> ), 2.62 (s, 3H, 6-CH <sub>3</sub> ), 2.04 (s, 3H, —SCH <sub>3</sub> )
(3)	77	145 (dec.)	248 (4.39), 289 (4.65), 309 sh (3.39), 342 (3.50), 356 (3.54), 370 sh (2.74), 572 (2.69), 597 sh (2.64), 665 sh (2.20) [a]	7.88–7.71 (m, 2H, H-2; H-1 or H-3), 7.55 (dd, $J = 3.8$ Hz, $J = 2$ Hz, 1H, H-1 or H-3), 7.50, 7.38 (br. s, 2H, H-5, 7), 5.39 (s, 2H, —CH <sub>2</sub> —), 3.16 (s, 6H, —S(CH <sub>3</sub> ) <sub>2</sub> ), 2.93 (s, 3H, 8-CH <sub>3</sub> ), 2.70 (s, 3H, 6-CH <sub>3</sub> ) [b]
(4a)	81		244 (4.42), 287 sh (4.62), 290 (4.66), 304 sh (3.93), 323 sh (3.40), 330 sh (3.48), 335 (3.55), 346 sh (3.60), 350 (3.66), 360 sh (3.04), 367 sh (2.54), 387 sh (1.43), 530 sh (2.61), 548 (2.67), 566 (2.66), 589 (2.63), 613 sh (2.44), 642 (2.24), 678 sh (1.56)	7.64 (t, $J = 4$ Hz, 1H, H-2), 7.49, 7.30 (dd, $J = 4$ Hz, $J = 1.8$ Hz, 2H, H-1, 3), 7.35, 6.98 (br. s, 2H, H-5, 7), 3.87 (s, 2H, —CH <sub>2</sub> —), 2.77 (s, 3H, 8-CH <sub>3</sub> ), 2.56 (s, 3H, 6-CH <sub>3</sub> ), 2.27 (s, 6H, 4-N(CH <sub>3</sub> ) <sub>2</sub> )
(4b)	75	144	234 sh (4.21), 248 (4.38), 288 (4.67), 291 sh (4.66), 297 sh (4.59), 329 sh (3.51), 335 (3.59), 345 sh (3.63), 350 (3.70), 550 (2.68), 581 sh (2.63), 635 sh (2.22) [c]	7.78–7.61 (m, 1H, H-2), 7.44–7.27 (m, 3H), 7.13 (s, 1H, H-5 or H-7), 5.20 (s, 2H, —CH <sub>2</sub> —), 4.66 (br. s, 1H, —OH), 2.88 (s, 3H, 8-CH <sub>3</sub> ), 2.66 (s, 3H, 6-CH <sub>3</sub> )
(4c)	65		246 (4.37), 286 (4.67), 290 (4.66), 307 sh (3.85), 336 (3.53), 352 (3.63), 390 sh (1.46), 538 sh (2.57), 557 (2.63), 571 (2.63), 593 (2.58), 619 sh (2.44), 650 sh (2.17), 681 sh (1.76)	7.70 (t, $J = 4$ Hz, 1H, H-2), 7.38, 7.32 (dd, $J = 4$ Hz, $J = 1.6$ Hz, 2H, H-1, 3), 7.06 (s, 2H, H-5, 7), 4.73 (s, 2H, —CH <sub>2</sub> —), 2.79 (s, 3H, 8-CH <sub>3</sub> ), 2.57 (s, 3H, 6-CH <sub>3</sub> )
(4d)	75	50	215 (3.45), 247 (4.38), 288 sh (4.64), 291 (4.65), 311 sh (3.81), 330 sh (3.40), 340 sh (3.50), 343 (3.52), 353 (3.55), 394 sh (1.74), 563 sh (2.61), 575 (2.62), 595 sh (2.58), 622 sh (2.48), 653 sh (2.22), 683 sh (1.92)	7.76 (t, $J = 4$ Hz, 1H, H-2), 7.48, 7.42 (dd, $J = 4$ Hz, $J = 1.8$ Hz, 2H, H-1, 3), 7.19, 7.13 (s, 2H, H-5, 7), 5.06 (s, 2H, —CH <sub>2</sub> —), 2.87 (s, 3H, 8-CH <sub>3</sub> ), 2.63 (s, 3H, 6-CH <sub>3</sub> )
(4e)	56	70	250 (4.39), 294 (4.59), 314 sh (3.86), 348 (3.50), 356 (3.50), 578 (2.65), 598 sh (2.61), 624 sh (2.53), 658 sh (2.26), 688 sh (2.01)	7.68 (t, $J = 3.9$ Hz, 1H, H-2), 7.50, 7.41 (dd, $J = 3.9$ Hz, $J = 1.8$ Hz, 2H, H-1, 3), 7.15, 7.10 (s, 2H, H-5, 7), 4.95 (s, 2H, —CH <sub>2</sub> —), 2.86 (s, 3H, 8-CH <sub>3</sub> ), 2.61 (s, 3H, 6-CH <sub>3</sub> )
(4f)	89	219	227 (4.57), 251 (4.49), 279 sh (4.43), 290 (4.58), 309 sh (4.00), 341 (3.52), 356 (3.58), 566 (2.71), 600 sh (2.65), 657 sh (2.23) [a]	7.84–7.13 (m, 17H), 6.96 (br. s, 1H), 6.83–6.60 (m, 2H), 5.10 (d, $J_{P,H} = 15$ Hz, 2H, —CH <sub>2</sub> —), 2.80 (s, 3H, 8-CH <sub>3</sub> ), 2.26 (s, 3H, 6-CH <sub>3</sub> )
(6)	78	< 15	219 (4.04), 261 (4.22), 290 sh (3.22), 370 (3.66)	6.77 (dd, $J_{2,3} = 5.4$ Hz, $J_{1,3} = 1.4$ Hz, 1H, H-3), 6.64 (dd, $J_{2,3} = 5.4$ Hz, $J_{1,2} = 2.2$ Hz, 1H, H-2), 6.44 (~t, $J \approx 1.8$ Hz, 1H, H-1), 5.90, 5.86 (br. s, 2H, H-5, 7), 5.71, 4.72 (br. s, 2H, —CH <sub>2</sub> —), 2.81, 2.18 (d, $J = 13$ Hz, 2H, —CH <sub>2</sub> —), 2.12 (br. s, 3H, 8-CH <sub>3</sub> ), 2.01 (s, 3H, —SCH <sub>3</sub> ), 1.96 (br. s, 3H, 6-CH <sub>3</sub> ) [d]
(7)	10	58	249 (4.46), 293 sh (4.69), 296 (4.70), 308 sh (3.99), 331 sh (3.47), 346 sh (3.65), 352 (3.75), 368 (3.52), 493 sh (2.64), 558 (2.69), 521 sh (2.67), 600 (2.63), 657 (2.21)	7.67 (t, $J = 4$ Hz, 1H, H-2), 7.51, 7.32 (dd, $J = 4$ Hz, $J = 1.8$ Hz, 2H, H-1, 3), 7.17 (s, 2H, H-5, 7), 3.95 (s, 2H, —CH <sub>2</sub> —), 3.12 (s, 3H, 8-CH <sub>3</sub> ), 2.83 (br. s, 6H, 4,6-CH <sub>3</sub> ), 2.18 (s, 3H, —SCH <sub>3</sub> )
(8)	45	54	247 (4.41), 292 (4.67), 296 (4.67), 301 sh (4.64), 332 sh (3.50), 345 sh (3.64), 352 (3.76), 355 sh (3.52), 369 (2.65), 563 (2.57), 600 sh (2.57), 658 (2.11)	7.55 (d, $J_{2,3} = 4$ Hz, 1H, H-2), 7.27 (d, $J_{2,3} = 4$ Hz, 1H, H-3), 6.95 (s, 2H, H-5, 7), 4.31 (s, 2H, —CH <sub>2</sub> —), 3.16 (s, 3H, 4-CH <sub>3</sub> ), 2.81 (s, 3H, 8-CH <sub>3</sub> ), 2.55 (s, 3H, 6-CH <sub>3</sub> ), 2.07 (s, 3H, —SCH <sub>3</sub> )

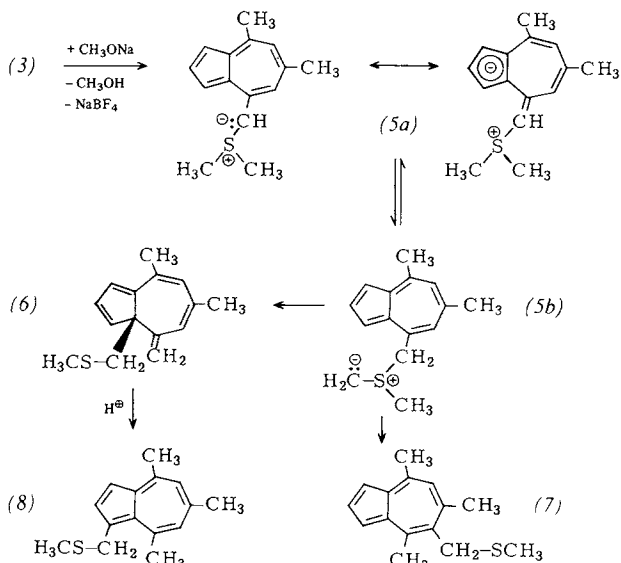
[a] In CH<sub>3</sub>OH. [b] In [D<sub>6</sub>]-acetone. [c] In dioxane. [d] 25.2 MHz-<sup>13</sup>C-NMR (CDCl<sub>3</sub>),  $\delta$  values: 149.6 (quart. C), 144.9 (=C—H), 144.1, 132.6, 131.9 (3 quart. C), 130.5, 129.2, 126.9, 123.4 (each 1 =C—H), 111.5 (=CH<sub>2</sub>), 62.0 (quart. C), 42.4 (—CH<sub>2</sub>—), 27.3, 24.1, 18.4 (each 1 CH<sub>3</sub>).

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place, giving a 78% yield of the readily isolable, stable 6,8-dimethyl-4-methylene-3a,4-dihydroazulene derivative (6) (yellow crystals), along with 10% of the isomeric 4,6,8-trimethyl-



azulene derivative (7) (blue needles). The structure of (6) was established primarily by analysis of the <sup>1</sup>H-coupled <sup>13</sup>C-NMR spectrum. Formation of compound (6) corresponds to that of the methylenecyclohexadiene intermediates detected in the Sommelet-Hauser rearrangement of *o,o'*-disubstituted benzyl-dimethylsulfonium and -trimethylammonium salts<sup>[4]</sup>.



Unlike these intermediates, (6) does not undergo thermal rearrangement; however, acid-catalyzed rearrangement (1% HClO<sub>4</sub> in CH<sub>3</sub>OH) regenerates the azulene system to give 4,6,8-trimethyl-1-(methylthiomethyl)azulene (8) (blue needles).

Physical data of the new compounds are compiled in Table 1.

Received: April 28, 1980 [Z 514 IE]  
German version: Angew. Chem. 92, 635 (1980)

CAS Registry numbers:

(2), 74465-56-8; (3), 74465-58-0; (4a), 74465-59-1; (4b), 74465-60-4; (4c), 74465-61-5; (4d), 74465-62-6; (4e), 74465-63-7; (4f), 74465-65-9; (6), 74465-66-0; (7), 74465-67-1; (8), 74465-68-2

[1] S. Kurokawa, T. Sato, T. Noguchi, K. Yano, Bull. Chem. Soc. Jpn. 48, 1559 (1975); V. B. Mochalin, Yu. N. Porshner, Usp. Khim. 46, 1002 (1977); Russ. Chem. Rev. 46, 530 (1977), and further references therein; K. Hafner, W. Rieper, unpublished.

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[3] (4f) reacts with sodium methoxide in methanol to give a bright red phosphonium ylide, which yields, e.g., with benzaldehyde a chromatographically separable 1:1 mixture of (*E*)- and (*Z*)-6,8-dimethyl-4-styrylazulene (yield 69%).  
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## Dimerization of Propylene with Catalysts Exhibiting Activities Like Highly-Active Enzymes

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In 1963 we discovered soluble catalysts which dimerize ethylene and propylene with high activity, even at  $-20^{\circ}\text{C}$  at normal pressure<sup>[1]</sup>. As catalysts we have employed, *inter alia*,  $\pi$ -allylnickel halides in combination with Lewis acids such as EtAlCl<sub>2</sub>. The dimerization of propylene can be controlled within wide limits by addition of phosphanes having different electronic and, especially, steric properties, so that dimers of various structures can be prepared at will<sup>[1]</sup>. The olefin dimerizations were performed in CH<sub>2</sub>Cl<sub>2</sub> or C<sub>6</sub>H<sub>5</sub>Cl. We have quoted the activity of the catalysts in the dimerization of propylene at normal pressure and  $-20^{\circ}\text{C}$  for 3–6 kg product/(g Ni · h).

In later experiments we established that the previously found, but nevertheless considerable activity was apparently exclusively determined by the reaction conditions such as stirring, cooling, and gas feed, even though relatively small amounts of catalyst were employed. As we have now found, the activity is in fact about one thousand times higher. The experiments for determining such high activities were performed as follows:

100 ml of C<sub>6</sub>H<sub>5</sub>Cl, 350 g (8.33 mol) of 99.8% propylene, and 0.6 g (4.72 mmol) of EtAlCl<sub>2</sub> are mixed at temperatures between  $-45$  and  $-75^{\circ}\text{C}$ . The relatively large amount of EtAlCl<sub>2</sub> should ensure that traces of impurities are trapped (under the conditions given, EtAlCl<sub>2</sub> does not react with propylene). The vigorously stirred mixture is then treated with a solution of 0.0023 g (5  $\mu\text{mol}$ ) of  $\pi$ -C<sub>3</sub>H<sub>5</sub>NiBrP(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub> in 1 ml C<sub>6</sub>H<sub>5</sub>Cl (prepared by multiple dilution of aliquot amounts). A strongly exothermic reaction immediately sets in, so intensive cooling is necessary to keep the temperature of the reaction mixture constant. After 30 min the reaction is terminated by passage of gaseous NH<sub>3</sub>, excess propylene (250–300 g) is bubbled off, and the product worked up. Table 1 lists the results of experiments at various temperatures.

Table 1. Catalytic dimerization of propylene.

<i>T</i> [°C]	g Product/ (5 $\mu\text{mol}$ cat. × 30 min)	kg Product/ (g Ni · h)	mol C <sub>3</sub> H <sub>6</sub> / (mol Ni · h)	Turnover number/s [a]
-75	22	152	209 524	60
-65	47	324	447 619	130
-55	84	580	800 000	230

[a] Turnover number = reaction steps at the active center; here: molecules of propylene/atom Ni (approx. values).

As expected, in the temperature range quoted the amount of product/30 min doubles on increasing the temperature by 10 °C. The composition of the products is practically independent of the temperature, in contrast to catalysts in which

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[\*\*] Activity = amount of reacted substrate/(catalyst unit × unit time).