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# Synthesis of 1-, 2-, and 6-Azulenethiols

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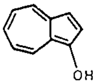
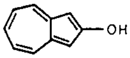
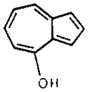
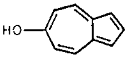
Summary: 1-Azulenethiol was synthesized by reductive cleavage of di-1-azulyl disulfide, and 2- and 6-azulenethiols were synthesized by the conversion of the corresponding hydroxyl group to mercapto group via dimethylthiocarbamates.

Several reports of the attachment of sulfur atom to azulene nucleus have been found in the literature in the chemistry of azulene.$^{1)}$ However, no report on the synthesis of azulenethiols has been appeared, although some efforts have been devoted;$^{2)}$ acid or base catalyzed hydrolysis of *S*-acetyl-1-azulenethiol, and reductive cleavage of di-1-azulyl disulfide to prepare 1-azulenethiol. Whereas, syntheses and tautomeric properties of 1-, 2-, 4-, and 6-hydroxyazulenes have been reported.$^{3)}$



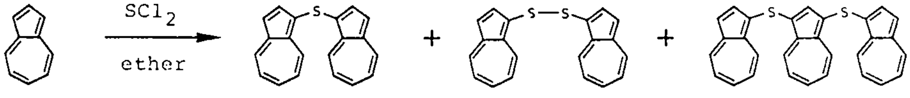




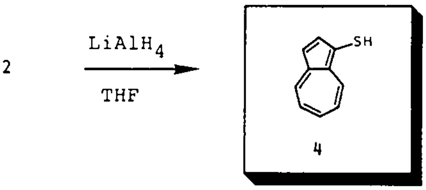


In this communication, synthesis of 1-, 2-, and 6-azulenethiols by the following methods will be reported; 1-azulenethiol was synthesized by the reductive cleavage of di-1-azulyl disulfide, and 2- and 6-azulenethiols were synthesized via the corresponding dimethylthiocarbamates derived from the reaction of hydroxyazulenes with dimethylthiocarbamyl chloride.$^{4)}$

Replogle et al. have reported that the reaction of azulene with sulfur dichloride yielded di-1-azulyl sulfide (1) in 18% (net 28%) yield.$^{5)}$ According to the paper, we followed the same reaction, and isolated three kinds of products, including 1, di-1-azulyl disulfide (2), and tri-azulene derivative (3) in 28, 17, and 7.3% yields, respectively.$^{6)}$ The compound (2) has already been obtained$^{2a)}$ by the treatment of 1-thiocyanoazulene with zinc or by alkaline treatment of 2,4-dinitrophenyl-1-azulyl sulfide. Reductive cleavage of 2 with $LiAlH_4$ in anhydrous THF afforded 1-azulenethiol (4)$^{7)}$ as unstable blue oil, bp 105-107 °C (0.01 mmHg) in 90% yield.

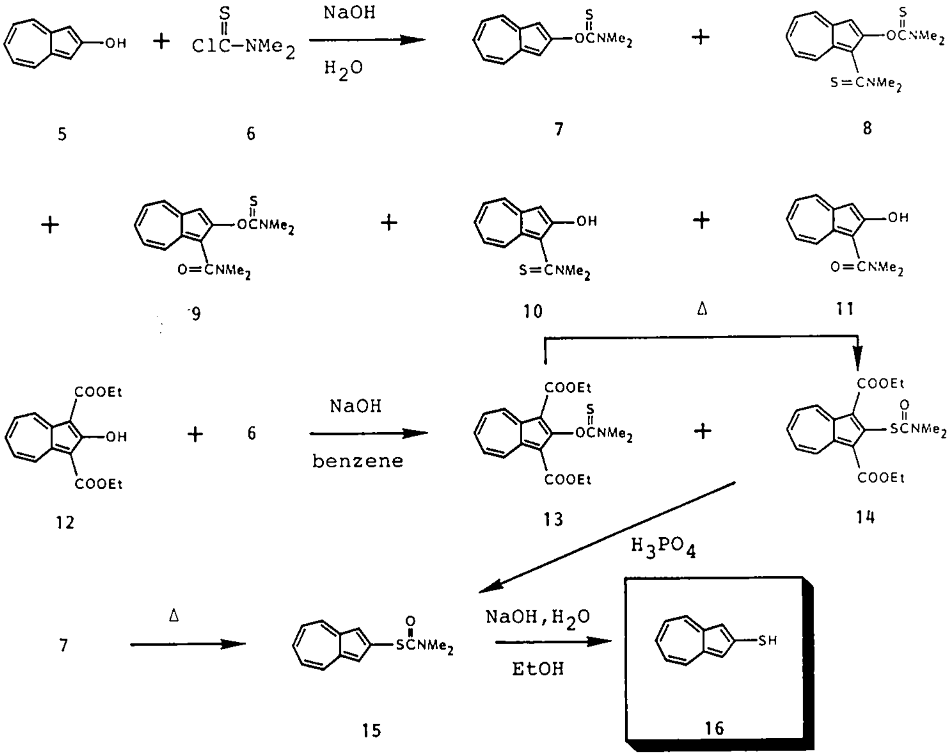


1 2 3



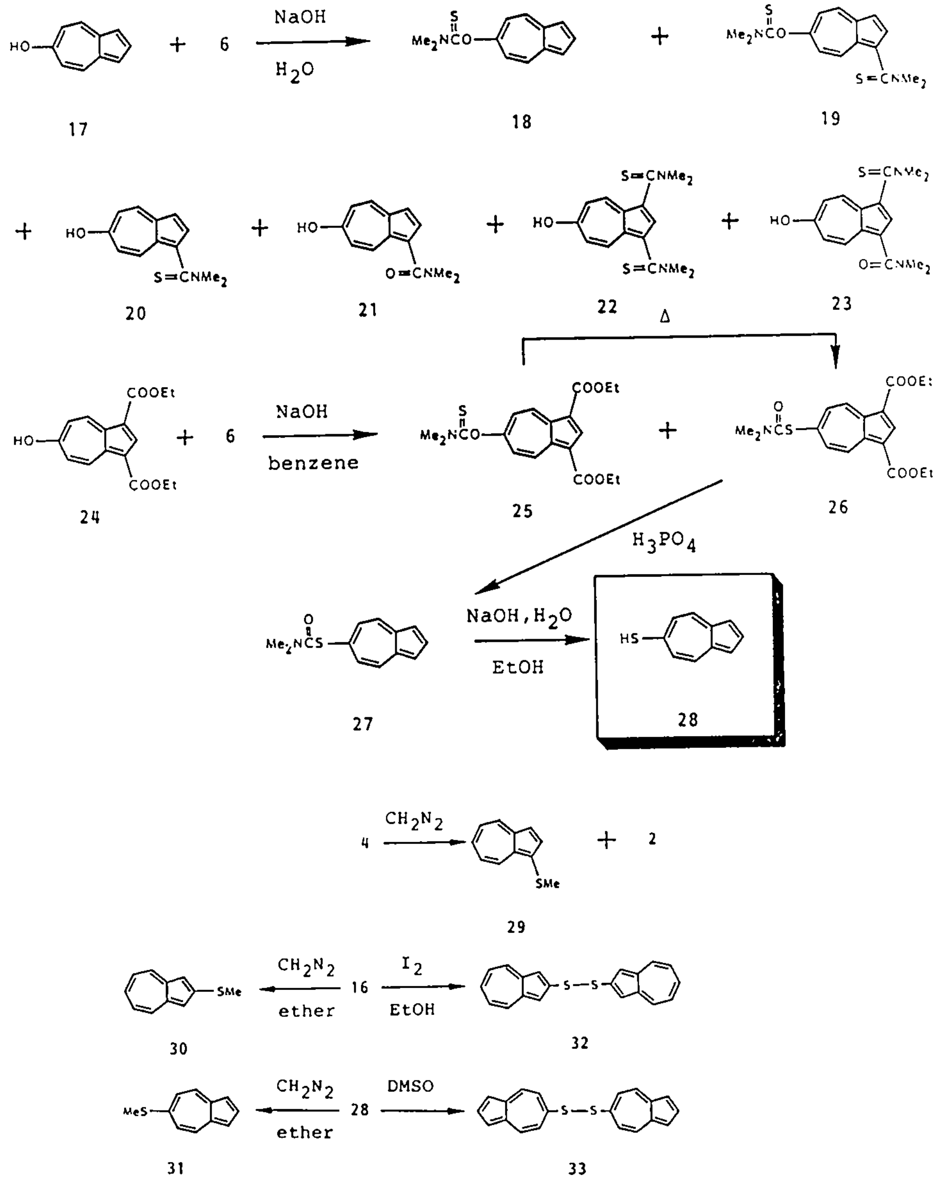
4

Reaction of 2-hydroxyazulene (5)[8] with dimethylthiocarbamyl chloride (6) in the presence of sodium hydroxide afforded a complex mixture, from which five kinds of products (7 - 11), involving electrophilic substitutions at 1-position of 5 with 6, were isolated in 23, 30, 3.2 2.3, and 0.6% yields, respectively.[6] A similar reaction of diethyl 2-hydroxyazulene-1,3-dicarboxylate (12)[9] with 6 in the basic condition yielded a mixture of *O*-dimethylthiocarbamate (13) and *S*-dimethylthiocarbamate (14) in 23 and 48% yields, respectively.[6] Heating of 13 in molten state afforded 14 in quantitative yield. Heating of 14 with 100% $H_3PO_4$ gave decarboxylation product; *S*-2-azulyldimethylthiocarbamate (15) in 86% yield, which was also obtained from 7 by heating in quantitative yield. Hydrolysis of 15 with aqueous solution of potassium hydroxide yielded 2-azulenethiol (16)[10] in quantitative yield as reddish violet prisms, mp 119.8-121.1 °C.



Similarly, the reaction of 6-hydroxyazulene (17)[7] with 6 afforded six kinds of products (18 - 23), in 2.4, 2.8, 44. 15, 12, and 2.7% yields, respectively.[6] Diethyl 6-hydroxyazulene-1,3-dicarboxylate (24)[11] was reacted with 6 to give *O*- and *S*-dimethylthiocarbamates (25 and 26) in 46 and 17% yields, respectively.[6] The compound (25) was quantitatively converted to 26 by heating. Decarboxylation of 26 with $H_3PO_4$ followed by alkaline hydrolysis of the resulted *S*-6-azulyldimethylthiocarbamate (27)[6] afforded 6-azulenethiol (28)[12] in 43% yield from 26 as blue needles, mp 112.5-114.9 °C.

Methylation of these new azulenethiols (4, 16, and 28) with diazomethane yielded the corresponding methylthio derivatives (29,[13] 30,[6] and 31[6]), respectivley, in addition of disulfide (2) from 4. Oxidation of 16 and 28 with iodine and DMSO yielded the corresponding disulfides 32 and 33, respectively.[6]



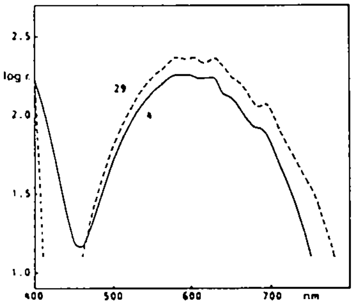


Fig. 1 Visible spectra of 4 and 29 in hexane

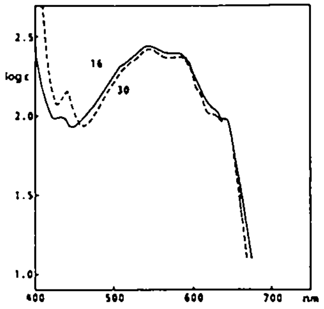


Fig. 2 Visible spectra of 16 and 30 in hexane

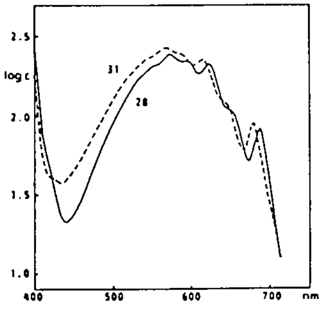


Fig. 3 Visible specrra of 28 and 31 in hexane

Visible absorption spectra of these azulenethiols and the corresponding methylthioazulenes in hexane are shown in Figs. 1 - 3, indicating similar patterns, respectively. Furthermore, the $^{1}$H-NMR of these azulenethiols in $CDCl_3$[7, 10, 12] indicate that they do not exist in the equilibrium with their thioketone structures, but exist in their thiol structures.

## References and Notes

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4) The method was applied from the literature [M. S. Newman and F. W. Hetzel, Org. Synth., 51, 139 (1971)].

5) L. L. Replogle, G. C. Peters, and J. R. Maynard, J. Org. Chem., 34, 2022 (1969).

6) All new compounds gave satisfactory elemental analyses and/or correct mass spectra, and also showed reasonable spectroscopic data (IR, $^{1}$H-NMR and/or $^{13}$C-NMR).
3; yellowish blue prisms, mp 114 °C, MS m/z 444 ($M^+$ base peak), 7; reddish violet needles, mp 133 °C, MS m/z 231 ($M^+$ base peak), 8; reddish violet plates, mp 164 °C (dec), MS m/z 318 ($M^+$ 17%), 9; violet needles, mp 117 °C, MS m/z 302 ($M^+$ 89%), 10; MS m/z 231 ($M^+$ base peak), 11, orange needles, mp 164 °C (dec), MS m/z 215 ($M^+$ 69%), 13; orange needles, mp 127 °C, Ms m/z 375 ($M^+$ base peak), 14; reddish needles, mp 150 °C, MS m/z 375 ($M^+$ 64%), 15; blue needles, mp 156 °C, MS m/z 231 ($M^+$ base peak), 18; blue needles, MS m/z 231 ($M^+$ base peak), 19; green needles, MS m/z 318 ($M^+$ 85%), 20; purple needles, mp 171 °C (dec), MS 231 ($M^+$ base peak), 21; reddish needles, mp 181 °C, MS m/z 215 ($M^+$ 41%), 22; orange needles, mp 168 °C (dec), MS m/z 318 ($M^+$ base peak), 23; orange solid, MS m/z 302 ($M^+$ base peak), 25; orange needles, mp 157 °C (dec), MS m/z 375 ($M^+$ base peak), 26; blue needles, mp 210 °C, MS m/z 375 ($M^+$ base peak), 27; blue needles, mp 151 °C, MS m/z 231 ($M^+$ base peak), 30; blue needles, mp 105 °C, MS m/z 174 ($M^+$ base peak), 31; blue plates, mp 140 °C, MS m/z 174 ($M^+$ base peak), 32; blue needels, mp 153 °C, MS m/z 318 ($M^+$ base peak), 33; brownish blue needles, mp 187 °C (dec), MS m/z 318 ($M^+$ 66%).

7) 4; Blue oil, $^{1}$H-NMR ($CDCl_3$) $\delta$ = 3.31 (s, SH), 7.15 (dd, J=9.9, 9.5, H-7), 7.24 (dd, J=9.8, 9.5, H-5), 7.32 (d, J=3.9, H-3), 7.62 (dd, J=9.8, 9.8, H-6), 7.88 (d, J=3.9, H-2), 8.25 (d, J=9.5, H-4), 8.55 (d, J=9.5, H-8).

8) K. Takase, T. Asao, Y. Takagi, and T. Nozoe, Chem. Commun., 1968, 368.

9) T. Nozoe, K. Takase, and N. Shimazaki, Bull. Chem. Soc. Jpn., 38, 247 (1965).

10) 16; Reddish violet prisms, $^{1}$H-NMR ($CDCl_3$) $\delta$ = 3.88 (s, SH), 7.13 (s, H-1,3), 7.14 (dd, J= 9.2, 9.0, H-5,7), 7.47 (t, J=9.2, H-6), 8.05 (d, J=9.0, H-4,8).

11) T. Nozoe, T. Asao, H. Susumago, and M. Ando, Bull. Chem. Soc. Jpn., 47, 1471 (1974).

12) 28; Blue needles, $^{1}$H-NMR ($CDCl_3$) $\delta$ = 3.94 (s, SH), 7.08 (d, J=10.7, H-5,7), 7.31 (d, J=3.6, H-1,3), 7.74 (t, J=3.6, H-2), 8.04 (d, J=10.7, H-4,8).

13) L. L. Replogle, R. M. Arluck, and J. R. Maynard, J. Org. Chem., 30, 2715 (1965).

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