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SYNTHESIS OF 1-(DIMETHYLAMINOMETHYLENE)-6(1H)-AZULENONE, A 1,6-AZULENEQUINONE 1-METHIDE DERIVATIVE

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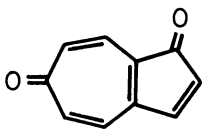
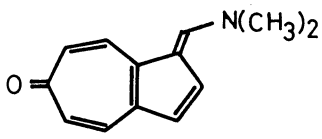
Reaction of 6-hydroxyazulene with DMF-$POCl_3$ followed by treatment with aq $HN(CH_3)_2$ gave 1-(dimethylaminomethylene)-6(1H)-azulenone (2) in 100% yield. Treatment of 2 with Ac_2O generated 6-acetoxy-1-formylazulene (3) which was hydrolyzed with aq $HN(CH_3)_2$ at room temp to give 1-formyl-6-hydroxyazulene (4). Upon heating of 3 with aq $HN(CH_3)_2$, 2 was obtained. Alkaline hydrolysis of 2 afforded 4.

Azulenequinones are of much current interests in their properties.[1,2] Reports of syntheses of 2,6-azulenequinone 2-,[3] and 6-methide[4] derivatives have been published. We now report the synthesis and some reactions of 1-(dimethylaminomethylene)-6(1H)-azulenone (9-dimethylaminofulveno[1,2-d]tropone) (2), a 1-methide derivative of 1,6-azulenequinone (1).

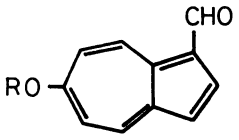
The Vilsmeier-Haack reaction is the most useful method for the synthesis of formylazulenes.[5] During the course of an investigation on the formylation of 6-hydroxyazulene and its derivatives, we have found a facile method for the synthesis of 2. Reaction of 6-acetoxyazulene[6] with dimethylformamide-phosphoryl chloride at



(1)



(2)



(3) R=Ac

(4) R=H

0 °C for 30 min followed by treatment with water at room temp gave a mixture of the products which was separated by successive extraction under the controlled pH's to give 6-acetoxy-1-formylazulene (3) (red-violet, mp 98-100 °C), 1-formyl-6-hydroxyazulene (4)[7] [yellow, mp 184 °C (dec)], and 2 [yellow, mp 233 °C (dec)], in 13.1, 6.9, and 34.3% yields, respectively. On acetylation with acetic anhydride the crude mixture gave 3 in 88% yield based on 6-acetoxyazulene. On the other hand, the treatment of 6-hydroxyazulene[6] with DMF-$POCl_3$ at 0 °C for 30 min followed by treatment with 40% aq dimethylamine afforded 2 in 100% yield.

Treatment of 2 with acetic anhydride in the presence of pyridine at 80 °C for 4.5 h gave 3 in 89% yield, and hydrolysis of 2 with aq sodium hydroxide in ethanol

at room temp overnight produced 4 in 96% yield. Treatment of 3 with 40% $HN(CH_3)_2$ at room temp overnight gave 4 in 95% yield. Heating of 3 with aq $HN(CH_3)_2$ in ethanol at 80 °C for 1 h gave 2 in 82% yield.

The structures of 2, 3, and 4 were determined on the basis of their spectral data (given in Table 1). Further, the mass spectrum of 2 shows peaks at m/e 199 (M^+, 86.7%) and 171 (M^+-CO, 100), and the IR spectrum of 2 shows very strong absorption bands at 1590 and 1625 cm^{-1}, comparable to those of tropones.[8] The stereochemistry of the dimethylaminomethylene moiety in 2 was determined by Nuclear Overhauser effect (NOE) experiment. Irradiations of the $N(CH_3)_2$ peaks induced 6.3 and 8.3% NOE's on the methine and H-2 signals, respectively, but no effect was observed on the H-8 signal. When the H-8 peak was irradiated, a 7.3% NOE was observed on the methine proton signal. These data indicate that the dimethylamino group of 2 locates in an E-conformation relative to the seven-membered ring.

Table 1. The Spectral Data of 2, 3, and 4.

2 UV: λ_{max} (MeOH) nm (log ε), 230.5 (4.12), 236sh(4.10),263 (4.89), 275sh (3.88), 285 (3.92), 295.5 (3.88), 355(4.65), 390 (4.47), and 403sh (4.43); IR (KBr): 1625 (vs) and 1590 cm^{-1} (vs); NMR ($CDCl_3$, at 200 MHz, and at 23 °C): δ 3.44 and 3.49 (two singlets, $N(CH_3)_2$), 6.89 (d, J=5.0 Hz, H-3), 6.87 (dd, J=2.5, 11.5 Hz, H-5 or 7), 6.90 (dd, J=2.5, 11.5 Hz, H-7 or 5), 7.05 (d, J=5.0 Hz, H-2), 7.58 (d, J=11.5 Hz, H-4 or 8), 7.59(d,J=11.5 Hz, H-8 or 4), and 7.79 (s, =CH-).

3 UV: λ_{max} (MeOH) nm (log ε), 216 (4.41), 236sh (4.16), 258sh (3.90), 267 (3.96), 312 (4.59), 348 (3.98), 376 (4.01), 392sh (3.86), and 520 (2.71); IR (KBr): 2740, 1770, and 1645 cm^{-1}; NMR ($CDCl_3$, at 60 MHz): δ 2.35 (s, CH_3CO), 7.10-7.38 (m, H-5 & 7), 7.27 (d, J=4.0 Hz, H-3), 8.10 (d, J=4.0 Hz, H-2), 8.37 (d, J=11 Hz, H-4), 9.45 (d, J=11 Hz, H-8), and 10.25 (s, CHO).

4 UV: λ_{max} ($CHCl_3$) nm (log ε), 266 (3.87), 327 (4.60), 364 (3.88), 375 (3.86), 385 (3.84), 396 (3.84), and 476 (3.90); NMR (acetone-d_6, at 60 MHz): δ 7.15 (d, J=4.0 Hz, H-3), 7.18 (dd, J=2, 11 Hz, H-5 or 7), 7.24 (dd, J=2, 11 Hz, H-7 or 5), 7.84 (d, J=4 Hz, H-2), 8.40 (d, J=11 Hz, H-4), 9.30 (d, J= 11 Hz, H-8), and 10.20 (s, CHO); IR ($CHCl_3$): 3200, 1642 (vs), and 1581 (vs) cm^{-1}.

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