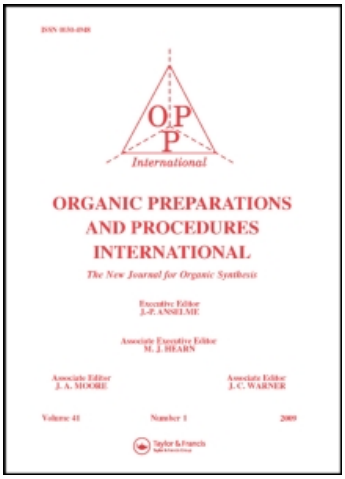

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1-ETHOXYMETHYLENEAZULENIUM PERCHLORATES

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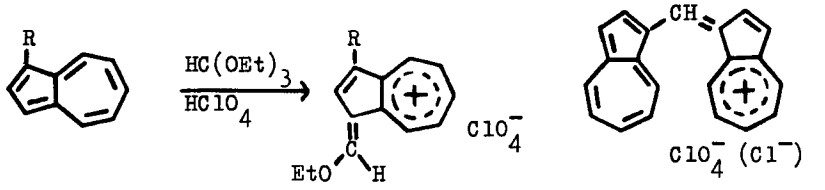
Alkylated azulenes such as 4,6,8-trimethylazulene and guaiazulene (1,4-dimethyl-7-isopropylazulene) readily form 1-ethoxymethyleneazulenium salts of type II when they are treated in ethanol with a large excess of ethyl orthoformate in the presence of a strong acid.[1] Azulene itself, however, was reported to give only the dye-salt III under these conditions.[1-3] Similar behavior was noted for 1-methylazulene.[1] A route to 1-formylazulene via 1-ethoxymethyleneazulenium fluoborate has since been described,[5] but the salt was not isolated. We have found that the use of ethanol in the previous cases has a critical effect on less alkylated azulenes. When ethanol is omitted, the method is of general use and 1-ethoxymethyleneazulenium (IIa) and 1-ethoxymethylene-3-methylazulenium (IIb) perchlorates for example, can be isolated as moderately stable compounds.



I II III

a) R = H b) R = CH_3

EXPERIMENTAL

Ethyl orthoformate and diethyl ether were May & Baker R grade, and were redistilled before use. The ether was dried with and stored over sodium wire. Perchloric acid was B.D.H. AnalaR grade, 70-72% w/w. Melting points are uncorrected and were determined on a Kofler type of heating block. Elemental analyses were performed by the National Physical Laboratory, Teddington, U.K., for which samples were dried at ca. 30°/0.1 mm. for 15 hrs.

1-Ethoxymethyleneazulenium perchlorate (IIa).- A mixture of perchloric acid (0.25 ml.) and ethyl orthoformate (10 ml.) was added to a solut-

ion of azulene (117 mg.) in ethyl orthoformate (10 ml.), both solutions being kept at 7°- 8°. 1-Ethoxymethyleneazulenium perchlorate (250 mg., 96%) precipitated at once as an olive green powder which was washed several times with ether. When heated from room temperature this compound slowly decomposed above 100°. On a block preheated to 110°, it melted at 113°- 116°(dec.). The product tends to decompose in hot solvents and was analyzed without recrystallisation.

Anal. Calcd for $C_{13}H_{13}ClO_5$: C, 54.85; H, 4.60; Cl, 12.45%
Found : C, 54.10; H, 4.55; Cl, 12.16%

Hydrolysis of the product with cold aqueous acetone (1:1, v:v) gave 1-formylazulene (84%) as a purple oil. Its semicarbazone melted at 215°- 217°, lit.[4,5] 217°, 235°.

1-Ethoxymethylene-3-methylazulenium perchlorate (IIb).- A solution of 1-methylazulene (24 mg.) in ethyl orthoformate (5 ml.) was treated with a mixture of perchloric acid (0.2 ml.) and ethyl orthoformate (4 ml.) at 7°- 8°. A golden brown precipitate of 1-ethoxymethylene--3-methylazulenium perchlorate (26 mg., 51%) formed at once, and was washed with ether, mp. 162-165°(dec.) on a block preheated to 110°.

Anal. Calcd for $C_{14}H_{15}ClO_5$: C, 56.29; H, 5.06; Cl, 11.87%
Found : C, 55.42; H, 5.03; Cl, 11.74%

Hydrolysis with cold aqueous acetone (1:1, v:v) gave 1-formyl-3-methylazulene (78%) as violet needles, mp. 70.5°- 71°, lit.[4]mp. 72-73°.

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