

This article was downloaded by:

On: 27 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Organic Preparations and Procedures International

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t902189982>

### 1-ETHOXYMETHYLENEAZULENIUM PERCHLORATES

E. C. Kirby

**To cite this Article** Kirby, E. C.(1974) '1-ETHOXYMETHYLENEAZULENIUM PERCHLORATES', *Organic Preparations and Procedures International*, 6: 5, 215 – 216

**To link to this Article:** DOI: 10.1080/00304947409355107

**URL:** <http://dx.doi.org/10.1080/00304947409355107>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

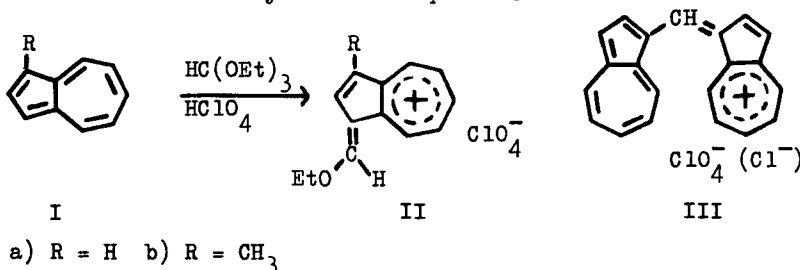
The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## 1-ETHOXYMETHYLENEAZULENIUM PERCHLORATES

E. C. Kirby

Balrobin, Pitlochry, SCOTLAND

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.<sup>1</sup> Azulene itself, however, was reported to give only the dye-salt III under these conditions.<sup>1-3</sup> Similar behavior was noted for 1-methylazulene.<sup>1</sup> A route to 1-formylazulene via 1-ethoxymethyleneazulenium fluoborate has since been described,<sup>5</sup> 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.



## 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-

E. C. KIRBY

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.<sup>4,5</sup> 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.<sup>4</sup> mp. 72-73°.

#### REFERENCES

1. E. C. Kirby and D. H. Reid, *J. Chem. Soc.*, 1724 (1961).
2. N. A. Aldanova and F. N. Stepanov, *Zh. Obshch. Khim.*, 29, 339 (1959).
3. G. Bach, E. J. Poppe and W. Treibs, *Naturwissenschaften* 45, 517 (1958).
4. K. Hafner and C. Bernhard, *Ann.*, 625, 108 (1959).
5. W. Treibs, *Tetrahedron Letters* 47, 4707 (1967).

(Received May 6, 1974; in revised form August 13, 1974)