PYRYLIUM SALTS FROM TRICYCLOHEXANONOL β-KETOLS

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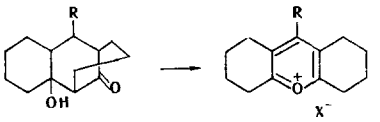
UDC 547.815.07

We have found that β-ketols of the 4 R-2,3-tetramethylene[1,3,3]bicyclononan-9-on-2-ol series readily form pyrylium salts upon reaction with iodine, tropylium perchlorate, or perchloric acid in acetic acid:



I, II III-VI

I, III, V R=H; II, IV, VI R=CH_3; III, IV X=ClO_4; V, VI X=I_3

This reaction opens up new possibilities for the synthesis of 9-R-sym-octahydroxanthylium salts.

EXPERIMENTAL

1) A 0.95-g (0.005 mole) sample of tropylium perchlorate was added to 1.04 g (0.005 mole) of ketol I in 20 ml of acetic acid, and the mixture was then stirred for 48 h. Ether was then added to precipitate 1.31 g (91%) of colorless crystals of sym-octahydroxanthylium perchlorate (III) with mp 172-173° [1].

9-Methyl-sym-octahydroxanthylium perchlorate (IV), with mp 130-131° [1], was similarly obtained in 80% yield.

2) A 5.2-g sample of ketol I was refluxed in 50 ml of acetic acid for 2 h, after which the mixture was cooled, and 5.4 g of 70% perchloric acid was added in the course of 1 h. After 2 h, the mixture was diluted with ether and worked up in the usual way to give 0.5 (8%) of salt III with mp 172-174° [1].

3) An ether solution of 19.95 g (0.075 mole) of iodine was added to 5.2 g of ketol I in 50 ml of acetic acid, after which the mixture was stirred for 8 h, and the resulting crystals of pentaiodide V were isolated as described above to give 10.8 g (51%) of a product with mp 112-114° (from acetonitrile). 9-Methyl-sym-octahydroxanthylium pentaiodide (VI) with mp 103-104° (from acetonitrile) was similarly obtained from ketol II in 50.7% yield.

The results of elementary analysis of pentaiodides V and VI for carbon, hydrogen, and iodine were in agreement with the calculated values.

LITERATURE CITED

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