5-OXOTETRAHYDROTHIO- AND 5-OXOTETRAHYDROCHROMYLIUM SALTS

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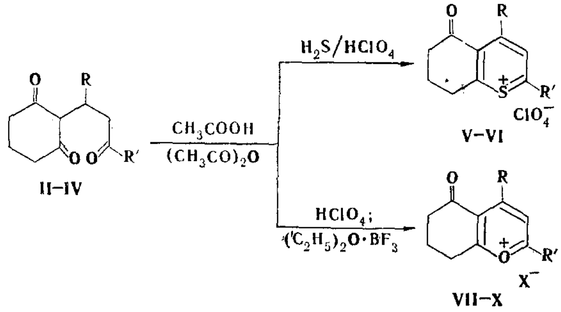
It is known that 2-[3-(1,3-diphenylpropan-1-onyl)]cyclohexane-1,3-dione (I) is not capable of undergoing conversion to 5-oxotetrahydrothiochromylium salts under the influence of hydrogen sulfide under acid catalysis conditions [1].

We have observed for the first time that oxo-1,5-diketones that contain methoxy groups in the phenyl substituents, viz., 2-{3-[1-(p-methoxyphenyl)-3-phenylpropan-1-onyl]}- (II) and 2-{3-[1,3-di(p-methoxyphenyl)propan-1-onyl]}cyclohexane-1,3-dione (III), are converted to the corresponding 5-oxo-5,6,7,8-tetrahydrothiochromylium salts (V, VI), with mp 148-150 and 116-119°C, in 37 and 38% yields on treatment with $H_2S/HClO_4$ in a mixture of glacial acetic acid with acetic anhydride (8:2).

We found that triketones II and III and 2-{3-[1-phenyl-3-(p-methoxyphenyl)propan-1-onyl]}cyclohexane-1,3-dione (IV) react with boron trifluoride etherate, and triketone II reacts with perchloric acid in a mixture of glacial acetic acid with acetic anhydride (8:2) to give 5-oxo-5,6,7,8-tetrahydrochromylium salts (VII-X), with mp 114-116, 203-205, 200-203, and 175-178°C, in 31, 39, 13, and 48% yields, respectively.



II, V, VIII, IX $R=C_6H_5$, $R'=C_6H_4-OCH_3$-*p*; III, VI, X $R=R'=C_6H_4-OCH_3$-*p*; IV, VII $R=C_6H_5-OCH_3$-*p*, $R'=C_6H_5$; VII, IX, X $X=BF_4$, VIII $X^-=ClO_4$

Thus for the first time we have obtained tetrahydrothiochromylium (V, VI) and tetrahydrochromylium (VII-X) salts that contain a carbonyl group in the 5 position. The methoxyphenyl groups in the 2 and 4 positions of the intermediately formed 5-oxotetrahydrothiochromenes and their isoelectronic analogs apparently increase the electron density in these positions of the heterocycles, thereby promoting salt formation. The new reaction of oxo-1,5-diketones opens up extensive possibilities for syntheses based on tetrahydrochromylium and tetrahydrothiochromylium salts.

The results of elementary analysis of V-X for their C, H, Cl, and S content are in agreement with the calculated values, and the IR spectra confirm the adopted structures.

LITERATURE CITED

1. V. G. Kharchenko, L. I. Markova, and K. M. Korshunova, Zh. Org. Khim., No. 3, 663 (1976).

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