tated. This was identified as unchanged starting material (ethane-1-diethylamino-2-triethylammonium iodide).

Preparation of ethylenebis(triethylammonium bromide). Eight and six-tenths grams (0.05 mole) *N, N, N', N'*-tetraethylethylenediamine,[9] 13 g. (0.12 mole) ethyl bromide, and 8 ml. ethanol were refluxed for 12 hr. The solid material which formed on cooling was filtered and the precipitate washed with ethanol and dried *in vacuo*, m.p. 228–235° (dec.). After several recrystallizations from ethanol, 2.2 g. (11.3%) ethylenebis(triethylammonium bromide) were obtained, m.p. 243–244° (dec.). A mixed melting point with the product obtained according to the procedure of Lucius[4] showed a depression, m.p. 225–230° (dec.).

Anal. Calcd. for $C_{14}H_{34}Br_2N_2$: C, 43.08; H, 8.78; Br, 40.95; N, 7.18. Found: C, 42.93; H, 8.89; Br, 40.82; N, 7.31.

After concentrating the alcoholic mother liquor of ethylenebis(triethylammonium bromide) and subsequent cooling, 0.5 g. (2.8%) ethane-1-diethylammonium-2-triethylammonium dibromide precipitated. This salt was purified by recrystallization from propanol-acetone and had a m.p. 204–205° (dec.).

Anal. Calcd. for $C_{12}H_{30}Br_2N_2$: Br, 44.13. Found: Br, 43.83.

Upon adding aqueous picric acid to this dibromide, ethane-1-diethylammonium-2-triethylammonium dipicrate, m.p. 186–188°, was formed. It was identified by a mixed melting point with the sample prepared above.

Ethane-1-diethylamino-2-triethylammonium bromide. All the solvent from the ethanolic mother liquor which remained after filtration of ethane-1-diethylammonium-2-triethylammonium dibromide was removed *in vacuo*. The oily residue did not solidify on cooling. Yield was 11.9 g. (84.5%). This oil was soluble in acetone, insoluble in ether and gave a positive Br^- test. A picrate was prepared in ethanol which was identified by a mixed melting point, as ethane-1-diethylammonium-2-triethylammonium dipicrate, m.p. 186–188°.

Preparation of ethane-1-diethylammonium-2-triethylammonium dibromide. By adding the theoretical amount of hydrobromic acid to an aqueous solution of this oily residue, evaporating the water *in vacuo*, and recrystallizing the residue from propanol-acetone, a white crystalline material was obtained, m.p. 205–206° (dec.). This product was shown to be ethane-1-diethylammonium-2-triethylammonium dibromide. The oil was therefore ethane-1-diethylamino-2-triethylammonium bromide.

Preparation of ethylenebis(triethylammonium chloride). A solution of ethylenebis(triethylammonium bromide) was chromatographed over the cation exchange resin DOWEX 50-WX8, 200–400 mesh, used in hydrogen form. The column was eluted with $3N$ hydrochloric acid, the effluent collected, the solvent evaporated *in vacuo*, and the residue crystallized from propanol-acetone. Ethylenebis(triethylammonium chloride) had a m.p. 278–279° (dec.).

Anal. Calcd. for $C_{14}H_{34}Cl_2N_2$: Cl, 23.53. Found: Cl, 23.42.

This dichloride gave with picric acid ethylenebis(triethylammonium picrate), m.p. 244–245°.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ANDHRA UNIVERSITY]

Synthesis of Chromones. II. Some Derivatives of 7-Hydroxy-2-methylchromone

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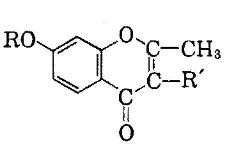
7-Hydroxy-2-methylchromone has been synthesized by an improved method and a number of its derivatives have been prepared.

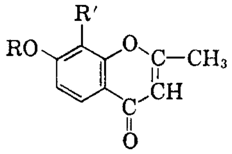
An earlier publication[1] which may be considered as Part I of this series deals with the chemistry of some naturally occurring chromones and reports the synthesis of 5-methoxy-, and 5,8-dimethoxy-2-methylchromones. The present communication deals with the synthesis of a number of derivatives of 7-hydroxy-2-methylchromone.

7-Hydroxy-2-methylchromone[2] (I) has been synthesized by an improved method using the Kostanecki reaction, with the intermediate, 7-acetoxy-3-acetyl-2-methylchromone (II), isolated in good yield and characterized by the ready formation of its 2,4-dinitrophenylhydrazone. Hydrolysis of II using aqueous sodium carbonate gave rise to I, which gave its 2,4-dinitrophenylhydrazone during twenty four hours.

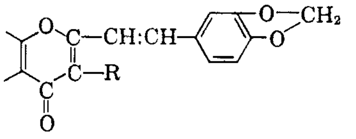
Methylation of I using excess diazomethane gave its methyl ether (III) which yielded its 2,4-dinitrophenylhydrazone during twenty-four hours.



I. R = R' = H
II. R = R' = $COCH_3$
III. R = CH_3; R' = H
VI. R = $COCH_3$; R' = H



IV. R = H; R' = CHO
V. R = $COCH_3$; R' = CHO
VII. R = H; R' = $COCH_3$



VIII. R = H or $COCH_3$

Condensation of I using hexamine in glacial acetic acid produced 8-formyl-7-hydroxy-2-methylchromone (IV), as pale yellow rectangular plates, characterized by an intense red ferric color and the ready formation of its 2,4-dinitrophenylhydrazone. Its acetate V was prepared, which was further characterized by the ready formation of its 2,4-dinitrophenylhydrazone. Acetylation of I using

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(1) C. Ramachandra Rao and V. Venkateswarlu, *Rec. trav. chim.*, **75**, 1321 (1956).

(2) St. V. Kostanecki and A. Rozycki, *Ber.*, **34**, 106 (1901).

acetic anhydride and pyridine gave its acetoxy derivative[2] VI which underwent smooth migration when heated with anhydrous aluminum chloride giving rise to 8-acetyl-7-hydroxy-2-methylchromone (VII), characterized by the ready formation of its 2,4-dinitrophenylhydrazone.

A number of piperonylidene derivatives of the type VIII of 2-methylchromones, just reported, have been synthesized.

EXPERIMENTAL

7-Hydroxy-2-methylchromone (I). A mixture of reacetophenone (5 g.), acetic anhydride (15 ml.), and anhydrous sodium acetate (10 g.) was boiled under reflux at 180–185° for about 6 hr. The cooled reaction mixture was then decomposed with ice water and the brown solid that had separated out crystallized from methanol, when it appeared as yellow plates, m.p. 126–127°, identified as *7-acetoxy-3-acetyl-2-methylchromone* (II), by its insolubility in alkali and the ready formation of its 2,4-dinitrophenylhydrazone, which on crystallization from ethyl acetate–petroleum ether (b.p. 40–60°) appeared as yellow needles, m.p. 268–269°. Yield, 3.5 g.

Anal. Calcd. for $C_{20}H_{16}N_4O_8$: C, 54.5; H, 3.6. Found: C, 54.6; H, 3.8.

Five g. of II were boiled gently under reflux using sodium carbonate solution (50 ml., 10%), during 1 hr. The clear solution thus obtained was acidified with concentrated hydrochloric acid and the precipitated solids filtered and dried. The dry solids were macerated with methanol when a crisp solid, mainly consisting of I, was obtained. This type of separation was found to be advantageous as it removed traces of 7-hydroxy-3-acetyl-2-methylchromone during alcoholic treatment. Yield: 2 g. A sublimed sample of I (245°/0.01 mm.) melted at 254–255°.

Anal. Calcd. for $C_{10}H_8O_3$: C, 68.2; H, 4.5. Found: C, 68.3; H, 4.8.

The 2,4-dinitrophenylhydrazone of I appeared as deep red rectangular prisms, m.p. 320° (from ethyl acetate).

Anal. Calcd. for $C_{16}H_{12}N_4O_6$: C, 53.9, H, 3.4. Found: C, 54.2; H, 3.5.

7-Hydroxy-2(3′,4′-methylenedioxystyryl)chromone. I (1 mole) was condensed with piperonal (1 mole) using alcoholic sodium ethoxide by gentle boiling on a water bath for about 1 hr. On working up the reaction product, the compound appeared as yellow rectangular plates (from methanol), m.p. 225–226°. A sublimed sample (220°/0.01 mm.), however, melted at 227–228°. In alcoholic and concentrated sulfuric acid solutions, the compound exhibited a blue fluorescence.

Anal. Calcd. for $C_{18}H_{12}O_5$: C, 70.1; H, 3.9. Found: C, 70.4; H, 4.1.

7-Methoxy-2-methylchromone (III). This compound, prepared by methylating I, using excess diazomethane in ether, melted at 112–13° and formed its 2,4-dinitrophenylhydrazone during 24 hr., which appeared as orange-red prisms (from ethyl acetate), m.p. 173–74°.

Anal. Calcd. for $C_{17}H_{14}N_4O_6$: C, 55.1; H, 3.7. Found: C, 55.4; H, 3.9.

7-Methoxy-2(3′,4′-methylenedioxystyryl)chromone. Prepared by the condensation of III with piperonal using alcoholic sodium ethoxide, it appeared as bright yellow rectangular plates (from ethyl acetate), m.p. above 300°. In alcoholic and concentrated sulfuric acid solutions, it exhibits a pale blue fluorescence.

Anal. Calcd. for $C_{19}H_{14}O_5$: C, 70.8; H, 4.3. Found: C, 71.1; H, 4.6.

8-Formyl-7-hydroxy-2-methylchromone (IV). To a solution of I (1 g.) in glacial acetic acid (40 ml.), hexamine (4 g.) was added and the resulting solution heated on a boiling water bath for 6 hr. The reaction mixture was then decomposed by the addition of hot hydrochloric acid (20 ml., 1:1) and heating continued for another 0.5 hr. It was then diluted with water to about 200 ml. and extracted with a large volume of ether, and the ether extract washed with a solution of sodium bicarbonate to remove acid impurities. Removal of the solvent left a yellow residue which appeared as pale yellow rectangular plates, m.p. 171–172°, after one crystallization from petroleum ether (b.p. 40–60°). A sublimed sample (165°/0.01 mm.), however, melted at 173–174°. In alcoholic solution, it gave an intense red ferric color.

Anal. Calcd. for $C_{11}H_8O_4$: C, 64.7; H, 3.9. Found: C, 65.0; H, 4.2.

IV readily gave its 2,4-dinitrophenylhydrazone during 15 min., which on crystallization from ethyl acetate appeared as deep red short rectangular plates, m.p. 306°.

Anal. Calcd. for $C_{17}H_{12}N_4O_7$: C, 53.1; H, 3.1. Found: C, 53.5; H, 3.1.

8-Formyl-7-hydroxy-2(3′,4′-methylenedioxystyryl)chromone. This was prepared using IV and piperonal following the procedure adopted earlier. It appeared as bright yellow rectangular plates and prisms (on crystallization from methanol), m.p. 262–263°. A sublimed sample (250°/0.01 mm.) had the same m.p. It exhibits a blue fluorescence in alcoholic and concentrated sulfuric acid solutions.

Anal. Calcd. for $C_{19}H_{12}O_6$: C, 67.8; H, 3.6. Found: C, 67.9; H, 3.8.

8-Formyl-7-acetoxy-2-methylchromone (V). This was prepared from IV using acetic anhydride and pyridine and crystallized from methanol as colorless rectangular plates, m.p. 159–160°.

Anal. Calcd. for $C_{13}H_{10}O_5$: C, 63.5; H, 4.1; Found: C, 63.6; H, 4.2.

It readily gave its 2,4-dinitrophenylhydrazone, which appeared as red needles, m.p. 301–302° after one crystallization from ethyl acetate.

Anal. Calcd. for $C_{19}H_{14}N_4O_8$: C, 53.5; H, 3.2. Found: C, 53.9; H, 3.5.

8-Formyl-7-acetoxy-2(3′,4′-methylenedioxystyryl)chromone. This was prepared using V and piperonal adopting the procedure described earlier. It appeared as bright orange-yellow prisms (from alcohol), m.p. above 300°. In alcoholic and concentrated sulfuric acid solutions, it exhibits a blue fluorescence.

Anal. Calcd. for $C_{21}H_{14}O_7$: C, 66.6; H, 3.7. Found: C, 67.0, H, 4.1.

8-Acetyl-7-hydroxy-2-methylchromone (VII). A mixture of 7-acetoxy-2-methylchromone (1 g.) and powdered anhydrous aluminum chloride (2 g.) was heated on a metal bath at 120° and when the reaction mixture had melted, the temperature was raised slowly to 140° and kept at that temperature for 10 min. Decomposition of the cooled reaction product using hydrochloric acid, while cooling, gave the compound as a pale yellow solid, which appeared as colorless stout needles when recrystallized from methanol, m.p. 191–192°. A sublimed sample had the same melting point. With alcoholic ferric chloride, it gave an intense red color.

Anal. Calcd. for $C_{12}H_{10}O_4$: C, 66.1; H, 4.6. Found: C, 66.3; H, 4.8.

This readily gave its 2,4-dinitrophenylhydrazone, which appeared as yellow needles on crystallization from ethyl acetate–petroleum ether (b.p. 40–60°), m.p. 284–285°.

Anal. Calcd. for $C_{18}H_{14}N_4O_7$: C, 54.3, H, 3.5. Found: C, 54.6; H, 3.7.

WALTAIR, INDIA