SYNTHETIC EXPERIMENTS IN THE BENZOPYRONE SERIES

Part LXVII. Synthesis of α-Methyl Dihydrofurano-Chromeno-Chromone

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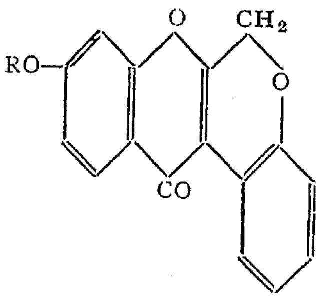
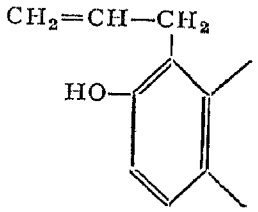
Received February 24, 1958

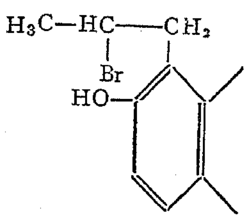
In a number of earlier publications have been described experiments relating to a new approach to the synthesis of rotenone and its derivatives. They have been developed on the basis that an isoflavone skeleton provides the core and the pyran and dihydrofuran rings are subsequently formed. Hence as stages in the synthetic attempt, the tetracyclic systems, (*a*) isoflavonofurans [1,2] and (*b*) chromeno-chromones[3–5] were prepared from the appropriate isoflavones. There are two ways of eventually building up the five-ring structure starting with either (*a*) or (*b*). The second route has now been explored and a furan ring has been successfully built on a chromeno-chromone unit. The steps involved are indicated in the following formulæ.



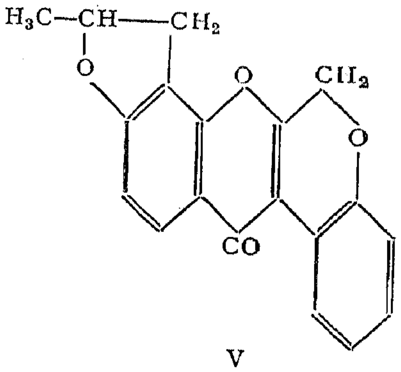
I R=H
II R= $-CH_2\text{-}CH{=}CH_2$



III



IV



V

7-Hydroxy chromeno-chromone (I) needed for the synthesis could be made in two ways: (1) by the N-bromosuccinimide method of Seshadri and Varadarajan[3] and (2) by the ethoxyacetyl chloride method of Mehta and Seshadri.[4] The latter is more convenient. By boiling compound (I) with allyl bromide and potassium carbonate in acetone solution is obtained the 7-allyloxy compound (II) which undergoes Claisen migration to yield 7-hydroxy-8-allyl chromeno-chromone (III). The change, however, is not very smooth and is accompanied by the formation of a large quantity of resinous products. Alteration of temperature and the time of heating within small ranges did not improve the quality of the product. The 7-hydroxy-8-allyl compound (III) on heating with aqueous hydrobromic acid gives 7-hydroxy-8-(β-bromopropyl)-chromeno-chromone (IV) which undergoes furan ring closure with pyridine to yield the pentacyclic compound, 5″: 4″-dihydro-5″-methylfurano (2″: 3″: 7: 8)-chromeno-(3′: 4′: 2: 3)-chromone (V).

EXPERIMENTAL

7-Allyloxy chromeno-chromone (II).—7-Hydroxy chromeno-chromone[3,4] (I, 1 g.) was dissolved in dry acetone (200 c.c.) and treated with allyl bromide (1·4 c.c.) and ignited potassium carbonate (15 g.). The mixture was refluxed on a water-bath for 8 hours. The solvent was then distilled off, ice-cold water (300 c.c.) added to the residue and the contents left in the refrigerator for 16 hours. The solid product was filtered, washed with water (50 c.c., 4 times), dried and crystallised first from alcohol and then from ethyl acetate-petroleum ether mixture when it came out as colourless plates, m.p. 140–41°; 0·75 g. (Found: C, 74·3; H, 4·8; $C_{19}H_{14}O_4$ requires C, 74·5; H, 4·6%).

7-Hydroxy-8-allyl chromeno-chromone (III).—The allyloxy compound (II, 0·75 g.) was heated in an oil-bath at 180° for 2 hours. The compound melted at first and gradually solidified during the course of one hour. It was then cooled and extracted with 1% aqueous sodium hydroxide. The solution was filtered and the clear filtrate acidified with cold dilute hydrochloric acid when a red coloured solid separated out. It was filtered, washed, dried and crystallised from ethyl acetate and petroleum ether mixture yielding colourless short prisms, m.p. 206–8°; 0·26 g. (Found: C, 74·6; H 4·6; $C_{19}H_{14}O_4$ requires C, 74·5; H, 4·6%).

7-Hydroxy-8-(β-bromopropyl)-chromeno-(3′: 4′: 2: 3)-chromone (IV).—A solution of the 8-allyl chromeno-chromone (III, 0·25 g.) in glacial acetic acid (18 c.c.) was heated with hydrobromic acid (8 c.c., 48%) in a water-bath at 50° C. for 8 hours, cooled and poured over crushed ice (75 g.) and stirred when a solid gradually separated out. It was filtered, washed, dried and crystallised from ethyl acetate and petroleum ether mixture when it appeared as small cubic crystals, m.p. 120–22°; 0·11 g. (Found; Br, 20·2%; $C_{19}H_{15}O_4$ Br requires Br 20·7%).

5″ : 4″-*Dihydro-5″-methyl-furano-*(2″ : 3″ : 7 : 8)-*chromeno-*(3′ : 4′ : 2 : 3)-*chromone* (*V*).—A solution of the above compound (IV, 0·1 g.) in dry and redistilled pyridine (6 c.c.) was heated in a boiling water-bath for 2 hours. It was then cooled and poured over crushed ice (50 g.) and acidified with excess of dilute hydrochloric acid. The solid product was filtered, washed with water, dried and crystallised from a mixture of ethyl acetate and petroleum ether yielding short needles, m.p. 158–60°; 0·025 g. (Found: C, 74·4; H, 4·5; $C_{19}H_{14}O_4$ requires C, 74·5; H, 4·6%). It gave no test for the presence of bromine. It did not dissolve in aqueous sodium hydroxide or concentrated hydrochloric acid but dissolved in concentrated sulphuric and nitric acids to give reddish brown solutions; the Durham test was negative.

SUMMARY

Starting from 7-hydroxy chromeno-chromone, the 8-allyl derivative has been prepared as intermediate and the α-methyl furan ring closed by means of hydrogen bromide and pyridine, yielding the five-ring structure of α-methyl dihydro-furano-chromeno-chromone.

REFERENCES

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3. Seshadri and Varadarajan .. *Proc. Ind. Acad. Sci.*, 1953, **37 A**, 784.
4. Mehta and Seshadri .. *Ibid.*, 1955, **42 A**, 192.
5. Sehgal and Seshadri .. *Ibid.*, 1955, **42 A**, 36.