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Reaction of hexachloropropene with hydroxy-coumarins and chromones

AJIT R. DESHPANDE AND J. R. MERCHANT, F.A.Sc.

Department of Chemistry, Institute of Science, Bombay 400032

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ABSTRACT

The reaction of hexachloropropene with hydroxy-coumarins and chromones has been utilized to synthesise dichloro-benzodipyrandiones. The structures of the latter have been deduced from their spectral-analytical data. The reaction with 4-hydroxy-coumarin derivatives affords dichloropyrano-benzpyrandiones.

1. INTRODUCTION

IN a project to synthesise heterocyclic compounds with a possible therapeutic value, we studied the reaction of hexacholoropropene (I) with different hydroxy-coumarins and chromones. Newman and Schiff[1] have reported the formation of 3, 4-dichloro-coumarins by the reaction of substituted phenols with this reagent.

Condensation of different hydroxy-coumarins and chromones with (I) was carried out in the presence of anhydrous aluminium chloride to furnish the corresponding trichloroacrylates which on cyclisation with aluminium chloride afforded the required dichloro-benzodipyrandiones (*see* table 1). The u.v. spectrum of the latter in general showed $\lambda_{max}^{dioxane}$ around 220, 275, 350 nm, whilst their i... spectrum (Nujol) showed the $> C = O$ band in the region 1740–1760 cm^{-1}.

7-Hydroxy-4-methylcoumarin furnished a trichloroacrylate which on cyclisation yielded a crystalline compound. From its analytical data and n.m.r. spectrum showing signals at δ 2·75 (3H, s, CH_3 at C_4), δ 6·66 (1H, s, at C_3), δ 7·66 (1H, s, at C_{10}), and δ 8·51 (1H, s, at C_5), it was assigned the linear structure (II), 2H, 8H-benzo (1, 2-*b*: 5, 4-*b'*) dipyran-4-methyl-6,7-dichloro-2,. 8-dione.

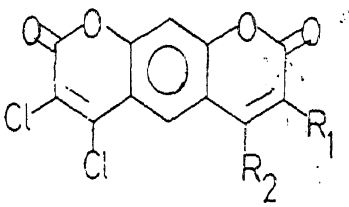
Table 1. Product obtained by reaction of hexachloropropene with hydroxy-coumarins and chromones

No.	Coumarin/ chromone*	Trichloro-acrylate	M.P.	Analysis	Cyclised	M.P.	Analysis
1.	7-Hydroxy-4-methyl coumarin[2]	Colourless needles[a]	182–83°	Calcd. for $C_{13}H_7O_4Cl_3$ C, 46·7; H, 2·09% Found: C, 47·0; H, 2·2%	(II); Pale brown plates[b]	308–09°	Calcd. for $C_{13}H_6O_4Cl_2$ C, 52·5; H, 2·02% Found: C, 52·6; H, 2·4%
2.	7-Hydroxy-coumarin[3]	Colourless needles[a]	180–81°	Calcd. for $C_{12}H_5O_4Cl_3$ C, 45·1; H, 1·6% Found: C, 45·4; H, 1·8%	(III); Brownish needles[c]	265–67°	Calcd.: for $C_{12}H_4O_4Cl_2$ C, 50·9; H, 1·4% Pound: C, 50·5; H, 1·9%
3.	7-Hydroxy-4-methyl-6-ethylcoumarin[4]	Colourless needles[a]	160–61°	Calcd. for $C_{15}H_{11}O_4Cl_3$ C, 49·7; H, 3·0% Found: C, 50·1; H, 3·2%	..	..	..
4.	7-Hydroxy-4, 8-dimethylcoumarin[5]	Colourless needles[a]	198–99°	Calcd. for $C_{14}H_9O_4Cl_3$ C, 48·4; H, 2·6% Found: C, 48·6; H, 2·6%	..	..	..
5.	7-Hydroxy-3-ethyl-4-methylcoumarin[6]	..	..	..	(IV): Pale yellow needles[a]	237°	Calcd.: for $C_{15}H_{10}O_4Cl_2$ C, 55·4; H, 3·1% Found: C, 55·0; H, 3·5%
6.	6-Hydroxy-4-methyl coumarin[7]	Colourless needles[c]	140–41°	Calcd. for $C_{13}H_7O_4Cl_3$ C, 46·7; H, 2·1% Found: C, 47·0; H, 2·1%	..	..	..
7.	5-Hydroxy-4, 7-dimethyl-coumarin[8]	..	..	..	..	..	..

8. 4-Hydroxy-coumarin[9]	..	..	..	(VI); Colourless plates[c]	295–97°	Calcd.: for $C_{13}H_4O_4Cl_2$ C, 50·9; H, 1·6% Found: C, 51·3; H, 2·0%	
9. 4-Hydroxy-8-methyl-coumarin[9]	..	..	..	(VII); Shining colourless needles[c]	265°	Calcd.: for $C_{13}H_6O_4Cl_2$ C, 52·5; H, 2·0% Found: C, 52·6; H, 2·4%	
10. 4-Hydroxy-6-methyl-coumarin[9]	..	..	..	(VIII): Yellow needles[c]	268–70°	Calcd.: for $C_{13}H_6O_4Cl_2$ C, 52·5; H, 2·0% Found: C, 52·3; H, 2·0%	
11. 4-Hydroxy-6, 8-dimethylcoumarin[10]	..	..	..	(IX): Yellow needles[c]	231–32°	Calcd.: for $C_{14}H_8O_4Cl_2$ C, 54·02; H, 2·57% Found: C, 53·9; H, 2·9%	
12. 7-Hydroxy-2-methyl-chromone[11]	Colourless needles[f]	145°	Calcd. for $C_{13}H_7O_4Cl_3$ C, 46·7; H, 2·1% Found: C, 46·8; H, 2·3%	..	..	..	
13. 6-Hydroxy-2-methyl-chromone[12]	Colourless needles[f]	144°	Calcd. for $C_{13}H_7O_4Cl_3$ C, 46·7; H, 2·1% Found: C, 46·3; H, 2·1%	..	..	..	
14. 5-Hydroxy-2-methyl-chromone[13, 14, 15]	..	..	..	(V): Brownish needles[c]	273–74°	Calcd.: for $C_{13}H_6O_4Cl_2$ C, 52·5; H, 2·0% Found: C, 52·9; H, 2·4%	

* Numbers in superscript given in this column relate to references.

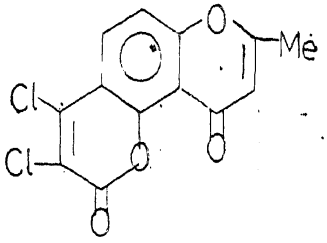
a = Crystallised from benzene.
b = Crystallised from benzene-methanol.
c = Crystallised from methanol.
d = Crystallised from ethylacetate.
e = Crystallised from alcohol.
f = Crystallised from benzene-petrol ether (40–60°).



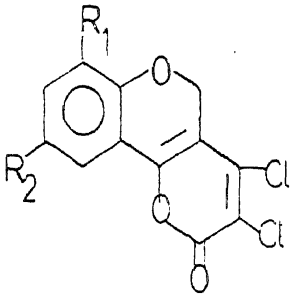
II R_1=H, R_2=Me

III R_1=R_2=H

IV R_1=Et; R_2=Me



V



VI R_1=R_2=H

VII R_1=Me, R_2=H

VIII R_1=H; R_2=Me

IX R_1=R_2=Me

Similarly, 7-hydroxy-coumarin with (I) afforded a trichloroacrylate which cyclised to give the expected 2H, 8H-benzo(1, 2-*b*: 5, 4-*b'*) dipyran-6, 7-dichloro-2, 8-dione (III).

7-Hydroxy-3-ethyl-4-methylcoumarin condensed directly with I when 2H, 8H-benzo (1, 2-*b*: 5, 4-*b'*) dipyran-3-ethyl-4-methyl-6, 7-dichloro-2,8-dione (IV) was obtained. The latter was condensed with piperidine, morpholine and diethylamine respectively, to furnish the 6-piperidino- (m.p 220–21°); 6-morpholino- (m.p. 258–59°) and 6-diethylamino- (m.p. 186–87°) derivatives.

Trichloroacrylate of 7-hydroxy-4-methyl-6-ethylcoumarin failed to cyclise indicating reluctance for angular cyclisation. Also, all attempts to cyclise the trichloroacrylate of 7-hydroxy-4, 8-dimethylcoumarin were futile.

The trichloroacrylates of 6-hydroxy-4-methylcoumarin and 6-hydroxy-2-methylchromone behaved rather unusually. The trichloroacryloxy side chain was ruptured during heating with aluminium chloride giving back the starting hydroxybenzopyrone.

The trichloroacrylate of 7-hydroxy-2-methylchromone also failed to cyclise.

5-hydroxy-2-methylchromone afforded directly (V) whereas 5-hydroxy-4,7-dimethylcoumarin failed to react and was recovered unchanged.

We also studied the reaction of (I) with 4-hydroxy-coumarin, 4-hydroxy-8-methylcoumarin, 4-hydroxy-6-methylcoumarin and 4-hydroxy-6, 8-dimethylcoumarin to obtain the respective 2H, 5H-pyrano (3, 2 *c*) (1) benzopyran-3, 4-dichloro-2,5-diones.

2. EXPERIMENTAL

2 1. GENERAL PROCEDURE FOR THE PREPARATION OF TRICHLOROACRYLATES

The hydroxy-coumarin or chromone (0·03 moles) in dry dichloromethane was added to a stirred slurry of anhydrous aluminium chloride (0·06 moles) in the same solvent. When the addition was complete, the mixture was further stirred till the evolution of HCl had ceased or slowed down considerably (about 3 hours). Hexachloropropene (0·03 moles) was then added dropwise during 10 minutes. The reaction mixture which generally assumed a dark colour was stirred for 3 more hours. After removing the solvent the dark tarry mass was decomposed with ice and sulphuric acid and subjected to steam distillation to remove unreacted hexachloropropene. The residue left behind was filtered and washed with water. It was then triturated with aqueous sodium hydroxide (10 ml., 10%) to remove the unreacted hydroxybenzopyrone, filtered and washed well with water. The residue was dried and crystallised from suitable solvents.

Usually the trichloroacrylates were obtained but in some cases the dichloro-benzodipyrandiones were directly obtained.

2 2. CYCLISATION OF THE TRICHLOROACRYLATES WITH ALUMINIUM CHLORIDE

The trichloroacrylate (1 g) was intimately mixed with anhydrous aluminium chloride (1·5 g) and the mixture heated till it melted and then held at that temperature for 2 hours. It was then cooled and decomposed with ice and dilute sulphuric acid and the product washed with water, dried and crystallised from the appropriate solvents.

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