

Reaction of hexachloropropene with dihydroxy aryl aldehydes, ketones and acids

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ABSTRACT

The reaction of hexachloropropene with dihydroxy aryl aldehydes, ketones and acids has been explored to synthesise substituted 3, 4-dichlorocoumarins. The structures of the latter have been deduced from their spectral-analytical data.

THE present paper describes the synthesis of substituted 3, 4-dichlorocoumarins by condensation of hexachloropropene (I) with different dihydroxy aryl aldehydes, ketones and acids. This work was prompted by the fact that Newman and co-workers¹ have observed that the reaction of I with resorcinol is not successful and the latter is recovered unchanged.

Instead of resorcinol, we carried out condensation of I with β -resorcyaldehyde in the presence of anhydrous aluminium chloride, when a dichlorocoumarin (II) with a free hydroxy group was isolated in 25% yield. The presence of the latter was confirmed by deep brown colouration with alcoholic FeCl_3 , which disappeared as soon as its acetyl derivative was prepared. The mass spectrum of II showed molecular ion peaks at m/e 258 and 260, and its analytical data indicated that only one -OH group (in position 4) was involved in the coumarin formation. The OH group in '2' position is strongly chelated and does not take part in the ring formation. The NMR ($\text{CF}_3\text{CO}_2\text{H}$) spectrum of II was fully consistent with its structure as 7-hydroxy-6-formyl-3, 4-dichlorocoumarin. The IR (nujol) of the latter showed bands at 1720 (>C=O coumarin) and 1680 (CHO) cm^{-1} .

Similarly, resacetophenone afforded 7-hydroxy-6-acetyl-3, 4-dichlorocoumarin (III) whose structure was evident from its spectral data. Mass spectrum showed molecular ion peaks at m/e 272 and 274. The NMR

spectrum showed signals at δ 2.9 (3H, s, CO-CH₃), δ 7.1 (1H, s, C₈H) and δ 8.6 (1H, s, C₅H). The IR (nujol) showed bands at 1740 (>C=O) coumarin and 1670 (>C=O) cm⁻¹. The presence of a free -OH was confirmed by deep brown colouration with alcoholic FeCl₃ and preparing the acetyl derivative which showed molecular ion peaks at m/e 314 and 316 in the mass spectrum. The NMR (CF₃COOH) spectrum showed signals at δ 2.35 (3H, s, O-COCH₃), δ 2.9 (3H, s, CO-CH₃), δ 7.1 (1H, s, C₈H) and δ 8.6 (1H, s, C₅H).

The above reaction was found to be of general applicability and was extended to the other dihydroxy aryl aldehydes, ketones and acids in which one of the -OH groups was strongly chelated. Their structures were established on the basis of spectral data. The yields of the dichlorocoumarins ranged from 20–30%. We also carried out the reaction of I with II and III but both were recovered unchanged.

As a point of interest the reaction of I with 5, 7-dihydroxy-2, 2-dimethylchroman-4-one was studied in which the -OH group in position '5' is hydrogen bonded with the carbonyl group. In this case, a crystalline compound was isolated whose mass spectrum and analysis showed it to be a benzo-tri-pyran derivative (XII).

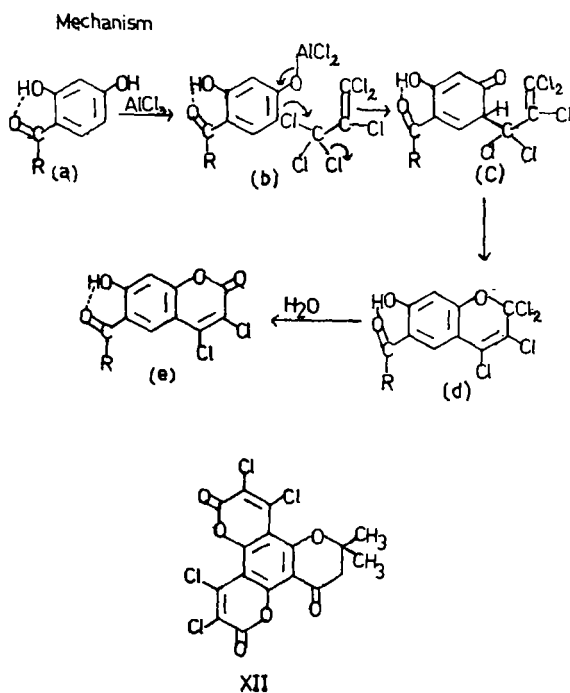


Table 1

No.	Phenolic Compound**	Substituted 3, 4-dichloro-coumarin	Nature of crystals	M.P.	Analysis	Spectral data
II	β -Resorcylic aldehyde ^a	7-Hydroxy-6-formyl	Yellow needles	218-19°	Calcd. for $C_{10}H_6O_4Cl_2$ C, 46.3; H, 1.54; Found C, 46.7; H, 2.0%.	I.R. (nujol) 1680, 1720 cm^{-1} . M ⁺ 258 and 260. NMR δ 7.15 (1H, s, C ₆ H), δ 8.6 (1H, s, C ₃ H).
III	Resacetophenone ^a	7-Hydroxy-6-acetyl	Yellow needles	218°	Calcd. for $C_{11}H_6O_4Cl_2$ C, 48.3; H, 2.2; Found: C, 48.6; H, 2.6%.	I.R. (nujol) 1670, 1740 cm^{-1} . M ⁺ 272 and 274, NMR δ 2.9 (3H, s, COCH ₃), δ 7.1 (1H, s, C ₆ H), δ 8.6 (1H, s, C ₃ H).
IV	2, 4-Dihydroxy-3-methyl-acetophenone ^a	7-Hydroxy-6-acetyl-8-methyl	Colourless needles	223-24°	Calcd. for $C_{12}H_6O_4Cl_2$ C, 50.2; H, 2.8; Found: C, 49.8; H, 2.9%.	I.R. (nujol) 1680, 1740 cm^{-1} . NMR δ 2.4 (3H, s, Ar-CH ₃); 2.95 (3H, s, COCH ₃); M ⁺ 286 and 288. δ 8.6 (1H, s, C ₃ H).
V	Respropionophenone ^a	7-Hydroxy-6-propionyl	Yellow needles	148-49°	Calcd. for $C_{13}H_6O_4Cl_2$ C, 50.2; H, 2.8; Found C, 49.8; H, 2.9%.	I.R. (nujol) 1680, 1740 cm^{-1} . M ⁺ 286 and 288. NMR δ 1.4 (3H, t, -CH ₃), δ 3.4 (2H, q, -CH ₂), δ 7.1 (1H, s, C ₆ H), δ 8.6 (1H, s, C ₃ H).

VI	2, 4-Dihydroxy 3-methyl propiophenone ^a	7-Hydroxy- 6-propionyl- 8-methyl	Colourless plates	191-92°	Calcd. for C ₁₁ H ₁₀ O ₄ Cl ₄ C, 51.8; H, 3.3; Found: C, 52.2; H, 3.7%.	I.R. (nujol) 1680, 1740 cm ⁻¹ . M ⁺ 300 and 302. NMR δ 1.4 (3H, t, -CH ₃), δ 2.4 (3H, s, Ar-CH ₃), δ 3.3 (2H, q, -CH ₂), δ 8.6 (1H, s, C ₆ H).
VII	Orcin aldehyde ^a *	7-Hydroxy- 5-methyl- 6-formyl	Yellow needles	245-46°	Calcd. for C ₁₁ H ₆ O ₄ Cl ₄ C, 48.3; H, 2.2; Found: C, 48.1; H, 2.5%.	I.R. (nujol) 1680, 1740 cm ⁻¹ . M ⁺ 272 and 274.
VIII	Orcaceto- phenone ^a	7-Hydroxy- 5-methyl- 6-acetyl	Yellow needles	198-99°	Calcd. for C ₁₁ H ₆ O ₄ Cl ₄ C, 50.2; H, 2.8; Found: C, 49.8; 2.5%.	I.R. (nujol) 1670, 1740 cm ⁻¹ . M ⁺ 286 and 288. NMR δ 2.7 (3H, s, Ar-CH ₃), δ 2.85 (3H, s, CO-CH ₃), δ 6.95 (1H, s, C ₆ H).
IX	2-Acetyl- resorcinol ^a , ¹¹	7-Hydroxy- 8-acetyl	Yellow needles	201-2°	Calcd. for C ₁₁ H ₆ O ₄ Cl ₄ C, 48.3; H, 2.2; Found: C, 48.8; H, 2.6	I.R. (nujol), 1680, 174 m ⁻¹
X	β-Resorcylic acid ¹¹	7-Hydroxy- 6-carboxy	Colourless needles	267-68°	Calcd. for C ₁₀ H ₄ O ₆ Cl ₄ C, 43.6; H, 1.5; Found: C, 43.1; H, 1.7%	I.R. (KBr) broad band around 3000 (OH of CO ₂ H) 1745 (C=O; Coumarin) cm ⁻¹
XI	2, 4-Dihydroxy- 3-methyl- benzoic acid ¹¹	7-Hydroxy- 6-carboxy- 8-methyl	Colourless needles	276°	Calcd. for C ₁₁ H ₆ O ₆ Cl ₄ C, 45.7; H, 2.1; Found: C, 45.2; H, 2.0%.	

* NMR spectra of all the compounds were taken in CF₃COOH.

** The numbers in superscript relate to reference.

It thus appears that in the chroman-4-one the OH group in '5' position is not as strongly chelated as in case of resacetophenone and other compounds.

MECHANISM

The phenol (*a*) reacts with aluminium chloride to yield the salt (*b*). The position '5' is considerably electron rich, since it is ortho to free-OH and para to hydrogen bonded -OH group. So a nucleophilic displacement of chlorine of the trichloromethyl group on hexachloropropene by the anion of salt (*b*) (reacting at position '5') yields the cyclohexadienone intermediate (*c*). The latter by an attack of the Lewis acid (AlCl_3) on the benzylic chlorine affords (*d*). Hydrolysis of (*d*) with water furnishes the final product (*e*).

EXPERIMENTAL

GENERAL PROCEDURE: The dihydroxy aryl aldehyde, ketone or acid (0.02 mole) in dry dichloromethane (25 ml) was slowly allowed to react with a stirred slurry of anhydrous aluminium chloride (0.06 moles) in the same solvent (25 ml). The stirring was continued till the evolution of HCl gas ceased or slowed down considerably (3 hr). Then hexachloropropene (0.02 moles) was added dropwise during 10 minutes and the reaction mixture was stirred for 3 more hours. The solvent was removed on the steam bath and the dark tarry mass was decomposed by ice and dilute sulphuric acid. The solid obtained was washed with water and then with a little alcohol and crystallised from acetone in shining needles.

PREPARATION OF BENZO-TRIPYRAN DERIVATIVE (XII)

5, 7-Dihydroxy-2, 2-dimethylchroman-4-one (2.08 g, 0.01 moles) in dry dichloromethane (25 ml) was slowly allowed to react with a stirred slurry of anhydrous aluminium chloride (7.98 g, 0.03 moles) in the same solvent (25 ml). After stirring the reaction mixture for 3 hr hexachloropropene (2.5 g, 0.01 moles) was added slowly during 10 minutes. The reaction mixture was stirred for 3 more hours and worked up as described above. The solid obtained was crystallised from acetone in shining brownish needles (1 g), m.p. 269-70° (Found: C, 45.8; H, 1.9; $\text{C}_{17}\text{H}_8\text{O}_6\text{Cl}_4$ requires C, 45.4; H, 1.8%).

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