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The Reaction of 2,4,6-Trihalophenols with Tropylium Perchlorate. A New Route for Triphenylmethane-Type Pigments

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Synopsis. The reaction of 2,4,6-tribromo- and triiodophenols with tropylium perchlorate in the presence of triethylamine gave 4-(3,5-dihalo-4-hydroxy-α-phenylbenzylidene)-2,6-dihalo-2,5-cyclohexadien-1-ones, respectively.

Reactions of the tropylium(cycloheptatrienylium) ion[1] with various nucleophilic reagents have been well-known.[2,3] Although, the tropylation of various phenols has been used as a key step in the synthesis of quinarenones,[4] no reports on concerning the tropylation of trihalophenols with tropylium has been reported up to date.

While studing the tropylation of 2,6-dihalophenols[5] with the tropylium ion we found that 2,6-dihalophenols containing a small amount of 2,4,6-trihalophenols (**1**) as an impurity reacted with the tropylium ion to give violet pigments. We have carefuly studied this reactions and have finally disclosed that the 7-cycloheptatrienyl skeleton rearranged to benzylidene moiety via a norcaradiene-type intermediate to give triphenylmethane-type pigments (**3**). We present herein our result, since the new approach is different from the reported methods for the preparation of **3**.

Results and Discussion

When 2,4,6-tribromophenol (**1a**) was treated with tropylium perchlorate (**2**) in the presence of triethylamine, a violet color was displayed, thus suggesting the formation of a pigment which could be easily isolated as a Na-salt (**3a**) from the reaction mixture by a treatment with aqueous sodium hydrogencarbonate. In the case of triiodophenol (**1b**), although the reaction is slightly slower than that of **1a** (see experimental section), Na salt (**3b**) was finally obtained. On the other hand, trichlorophenol (**1c**) did not react with **2**, even under heating for another 4 h (Chart 1).

The electronic spectra of **3a** and **3b** were quite similar with each other (see Experimenal section). The acidification of **3a** and **3b** with dilute hydrochloric acid gave free phenols, (**4a**)[6] and (**4b**), respectively. Acetylation of **3a** with acetic anhydride in the presence of a catalytic amount of pyridine afforded acetate (**5**). The catalytic hydrogenation of **3b** consumed 5 molar equivalents of hydrogen to give 4, 4′-dihydroxytriphenylmethane (**6**)[7] in moderate yield, so that the structure could be well confirmed by the ^{1}H NMR spectrum (Chart 2).

The mechanism for this rearrangement of cycloheptatriene to a six-membered ring seems to involve a norcaradiene intermediate (**B**) (Scheme 1). An intermediate (**A**) generated by the reaction of a phenolate ion of **1** with the tropylium ion (**2**) could be isomerized to a valency tautomer (**B**), which rearranged to the benzylidene moiety[8] along with an elimination of the HX molecule to give a quinonemethide (**C**). Another phenolate ion molecule attacks the methylene carbon of intermediate **C** to generate **D**, from which the HX molecule eliminates to result **3**.

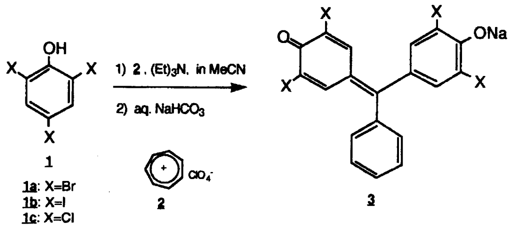


Chart 1.

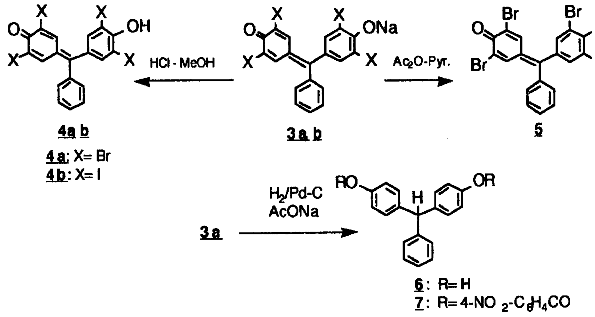
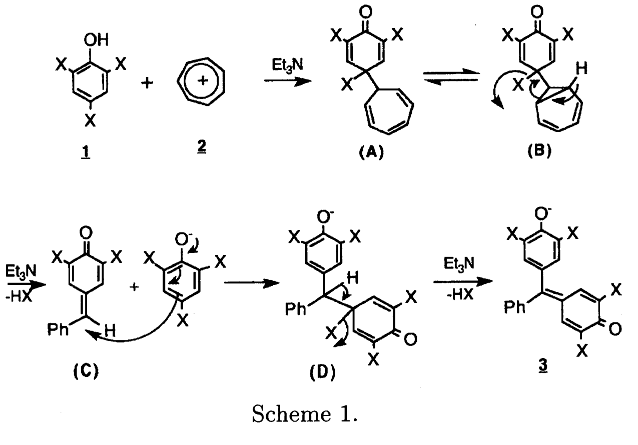


Chart 2.



Scheme 1.

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Experimental

All of melting points are uncorrected. The IR spectra were recorded on a Shimadzu IR-27 Spectrometer and the electronic spectra on a Hitachi EPS-3 Spectrometer. The NMR spectra were measured using a Varian A-60 D Spectrometer. The mass spectra were recorded on a Hitachi RMU-6 mass spectrometer at 25 eV.

Na Salt of 4-(3,5-Dibromo-4-hydroxy-α-phenylbenzylidene)-2,6-dibromo-2,5-cyclohexadien-1-one (3a). To a stirred solution of 2,4,6-tribromophenol (6.6 g, 0.020 mol) and triethylamine (6.1 g, 0.060 mol) in 30 ml of acetonitrile, tropylium perchlorate (**2**) (5.1 g, 0.026 mol) was added and then heated on a water bath under reflux for 2 h; it was then cooled to room temperature. The reaction mixture was transferred into an Erlenmeyer flask, together with 150 ml of ethyl acetate and 150 ml of saturated aqueous sodium hydrogencarbonate. After stirring for 30 min, black crystals were precipitated from the solution. The precipitates were collected by filtration, washed with ethyl acetate and water, and then dried under vacuum. Yield: 364 mg, 24% (based on the reacted tribromophenol). Recrystallization from a mixture of methanol and acetone gave black-violet needles with a metallic luster, mp of which could not be observed up to 300°C. IR (KBr) 3430 (weak), 1587 and 1550 cm^{-1} (anion of conjugated enol); UV-vis, $\lambda_{\max}$ (MeOH) 315 (log ε=3.98), 402 (3.88), 595 (4.52) nm; UV, $\lambda_{\max}$ (alkaline MeOH) 320 (3.98), 364 (2.94) nm. Found: C, 36.32; H, 1.95; Br, 50.95%. Calcd for $C_{19}H_9O_2Br_4Na\cdot H_2O$: C, 36.23; H, 1.74; Br, 50.75%. From the filtrate, 4.5 g of the unreacted **1a** was recovered.

4-(3,5-Dibromo-4-hydroxy-α-phenylbezylidene)-2,6-dibromo-2,5-cyclohexadien-1-one (4b). To a solution of **3a** (30 mg, 0.049 mmol) in 1 ml of methanol, two drops of 2 mol dm^{-3} hydrochloric acid was added. The mixture was diluted with water and extracted with ethyl acetate. The organic layer was washed with brine, and dried over anhydrous sodium sulfate. Evaporation of the solvent gave brownish red prisms (from chloroform), mp 300—303°C (decomp) (lit, decomp, over 270°C).[6] Yield: 28 mg, 96%. IR (KBr) 3330 (OH), 1632 (C=O) cm^{-1}. Found: C, 38.50; H, 1.98%. Calcd for $C_{19}H_{10}O_2Br_4$: C, 38.67; H, 1.71%.

4-(3,5-Dibromo-4-acetoxy-α-phenylbenzylidene)-2,6-dibromo-2,5-cyclohexadien-1-one (5). A mixture of **3a** (38 mg), 0.5 ml of acetic anhydride, and a drop of pyridine was heated at 80°C for 30 min. The usual workup gave 45 mg of yellow prisms (from a mixture of benzene and ethanol), mp 267—268°C. IR (KBr) 1773 (acetate C=O), 1639 (C=O) cm^{-1}. Found: C, 40.86; H, 2.39%. Calcd for $C_{21}H_{12}O_3Br_4$: C, 40.66; H, 1.95%.

4,4′-Dihydroxytriphenylmethane (6). A solution of 200 mg (0.32 mmol) of **3a** and 100 mg of sodium acetate in 10 ml of methanol was shaken in an atmosphere of hydrogen in the presence of Pd–C at room temperature for 7 h; 50 ml (2.2 mmol) of hydrogen was absorbed to give a colorless solution. After removing the catalyst by filtration, the filtrate was diluted with water and extracted with ether. The extracts were washed with water and then dried over anhydrous sodium sulfate. The solvent was evaporated to give a reddish-orange solid (85 mg), which was recrystallized from chloroform to produce colorless needles (61 mg, 69.1%), mp 161—162°C (lit, mp 161°C).[7] IR (KBr) 3240 (OH), 3030 (aromatic CH), 1600, 1513 cm^{-1}; UV $\lambda_{\max}$ (MeOH) 234 (log ε=4.11), 281 (3.60) nm; ^{1}H NMR (acetonitrile-d_3, at 60 MHz) δ=5.35 (1H, s, methine), 6.69 (4H, d, J=9.0 Hz, *ortho* of phenol), 6.35 (2H, br.s, OH), 6.98 (4H, d, J=9.0 Hz, *meta* of phenol), 7.15 (5H, m, phenyl). MS m/z 276 (M^+, 100%). Found: C, 82.46; H, 5.84 %. Calcd for $C_{19}H_{16}O_2$: C, 82.67; H, 5.80%.

Bis(4-nitrobenzoate) (7) was obtained from the reaction of **6** (10 mg) with 4-nitorobenzoyl chloride (20 mg) in pyridine (1 ml). White fine crystals (from methanol), mp 178—179°C. Yield (14 mg, 67.7%). IR (KBr) 1754 cm^{-1}. Found: C, 68.61; H, 3.66; N, 4.98%. Calcd for $C_{33}H_{22}O_8N_2$: C, 68.98; H, 3.86; N, 4.88%.

Na Salt of 4-(3,5-Diiodo-4-hydroxy-α-phenylbenzylidene)-2,6-diiodo-2,5-cyclohexadien-1-one (3b). To a solution of triiodophenol (1.0 g, 2.1 mmol) and triethylamine (0.62 g, 6.1 mmol), **2** (0.420 g, 2.2 mmol) was added; the mixture was then heated at 60—65°C for 2h. The usual workup carried out in a similar manner to that described above to give 110 mg (15% yield, based on the reacted triiodophenol) of (**3b**). Metalic luster deep-violet fine crystals (from ethyl acetate), mp of which could not be observed up to 300°C. IR (KBr) 1570^{sh} and 1536 cm^{-1} (anion of conjugated enol); UV-vis $\lambda_{\max}$ (MeOH) 240^{sh} (logε=4.25), 312 (3.96), 406 (3.98), 602 (4.54) nm; $\lambda_{\max}$ (alkaline MeOH) 255^{sh} (log ε=4.34), 312 (3.76), 370 (3.20) nm. Found: C, 27.96; H, 1.52; I, 62.28%. Calcd for $C_{19}H_9O_2I_4Na\cdot H_2O$: C, 27.90; H, 1.34; I, 62.06%. From the filtrate, 0.15 g of the unreacted triiodophenol was obtained by sublimation.

4-(3,5-Diiodo-4-hydroxy-α-phenylbenzylidene)-2,6-diiodo-2,5-cyclohexadien-1-one (4b). A solution of **3b** (21 mg) in methanol (1 ml) was treated with diluted hydrochloric acid, and then extracted with ethyl acetate. The extract was worked up to give 19 mg of **4b**. Brownish red prisms (from chloroform), mp 227—228°C. IR (KBr) 3410 (OH), 1638 (C=O), 1565 cm^{-1}. Found: C, 29.57; H, 1.46; I, 65.47%. Calcd for $C_{19}H_{10}O_2I_4$: C, 29.34; H, 1.28; I, 65.26%.

Reaction of Trichlorophenol (1c) with 2. A solution of **1c** (0.79 g), triethylamine (1.2 g) and **2** (0.94 g) in acetonitrile (3 ml) was heated at 90—98°C for 6 h. After cooling, the mixture was acidified with dilute hydrochloric acid, and then extracted with ether. When the extract was treated with aqueous sodium hydrogencarbonate, no color change by a pigment was observed. Finally, the extract was worked up to recover white crystals (0.75 g) of unchanged **1c**.

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