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Violet dyes of the 1860s: Hofmann, Britannia, violet de Paris, Wanklyn's, and Crystal violet (1883)

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Abstract

Two 19th-century historical violet dyes from the Historische Farbstoffsammlung, Technical University of Dresden, have been analysed by liquid chromatography–mass spectrometry (LC-MS). The data are presented as charts with retention time and two scales: electron spray mass spectrometry counts (*m/z*) and milli-absorption units (UV). These dyes are complex mixtures as anticipated from the synthetic methods involving partial alkylation of rosaniline or synthesis using mixtures of *N*-methylaniline and *N,N*-dimethylaniline. The charts typically show chromophores separated by CH_2 units which have separated well. Hofmann's violet is presumably made by Hofmann's method of synthesis, but the analyses do not verify with certainty who the inventors are because of the complexity of the dye mixtures.

Keywords

aniline red, aniline violet, fuchsin, liquid chromatography-mass spectrometry, rosaniline

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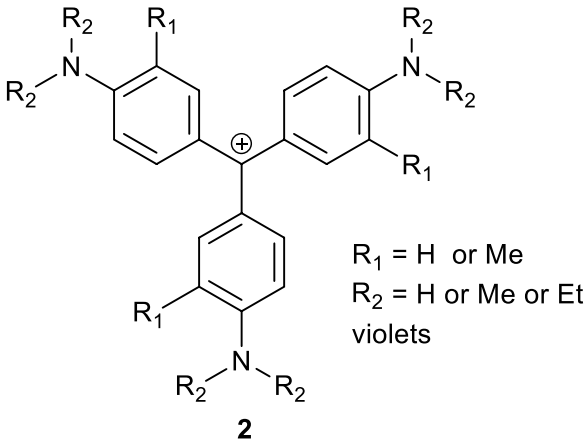

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Introduction

Mauveine was the first aniline dye from which many others followed.[1–4] Benzene and toluene and other aromatics were by-products from coal-tar distillation which produced illuminating gas.[5] Benzene was difficult to distil free from toluene so after nitration and reduction aniline contained small amounts of toluidine.[6] Caro's mauve in the Deutsche museum is mainly pseudomauveine suggesting that pure aniline was available from 1860.[7] However, Perkins-Museum-stored mauveine is rich in two homologues: mauveine A and mauveine B, suggesting it was made from aniline enriched with toluidine, which gives a better yield.[6] In line with these studies, other aniline dyes, such as reds, blues, greens and violets, might be expected to be mixtures.[8,9] Our work on triphenylrosaniline showed it to be a complex mixture of homologues which separated

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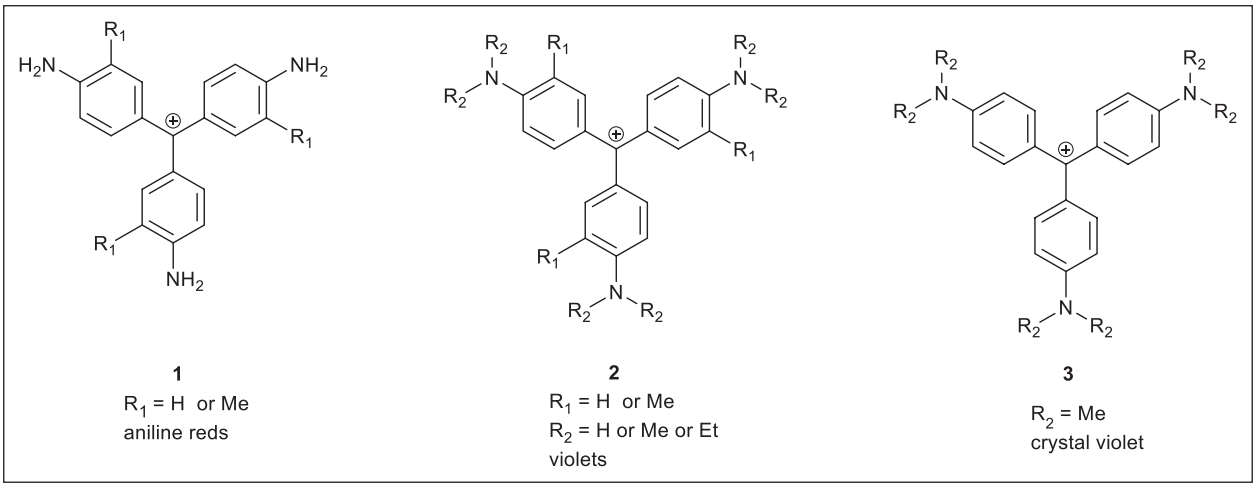

Figure 1. Drawing illustrating the complex mixtures of aniline red, also known as fuchsin or rosaniline, the violets and the simpler structure of crystal violet. The rosaniline was made by oxidative condensation of p-toluidine, which provides the middle carbon, with two units selected from aniline and *o*-toluidine.

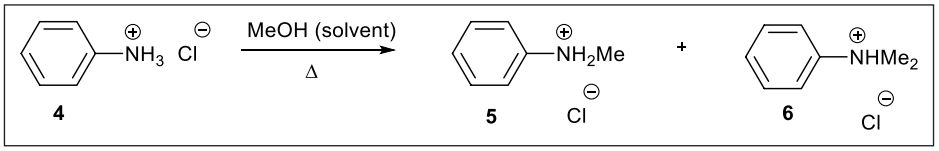

Figure 2. Bardy's alkylation of aniline hydrochloride with methanol.[21]

beautifully by liquid chromatography–mass spectrometry (LC-MS).[10] There are a number of different historic violet dyes made by different investigators which should have different isomers and homologues because of their method of synthesis.[11] The Hofmann violets, patented in 1863, were made by alkylating rosaniline (also known as fuchsin or aniline red)[12–16] with methyl and ethyl iodides or bromides in methylated spirit in a sealed iron boiler at up to 150°C (Figure 1).[17]

Perkin's Britannia violet,[2] patented in 1864, was made by alkylating rosaniline in alcohol with aqHBr, prepared by treating turpentine with bromine, and heating in a closed vessel for 8 h at 150°C.[18,19] Perkin was not able to purchase a source of aqHBr so it was made in house. Lauth[20] discovered violet de Paris and its method of synthesis, but did not commercialise it apparently because of restrictions in France over the use of rosaniline. The synthesis was commercialised in 1866 by A Poirrier and C Chappat who alkylated aniline hydrochloride with methanol to give a mixture of *N*-methylaniline and *N,N*-dimethylaniline which was then oxidised with Sn(II) and Hg(II) salts into a violet dye heating by heating at 175°C–300°C (Figure 2).[21] The acid is the catalyst and appears on both sides of the equation in Figure 2. The question arose as to whether violet de Paris was the same as rosaniline violet. Lauth considered that they were the same noting that pure aniline was used. Wanklyn patented a violet dye in 1864 by alkylating rosaniline with an oil, made from treating manna sugar with HI and phosphorous, at 120°C.[22] This is reported to be a mistake, and he used glycerol instead of manna sugar which liberates 2-iodopropane as the alkylating agent.[23–27] 2-Iodopropane is an oil, with a boiling point of 89°C, which would distil from the reaction mixture as reported. The reaction mixture was an alcohol with a large excess of HI (1:30), which boils as an azeotrope (57% HI:43% H_2O) at 127°C. Alky iodides from reducing manna sugar would have much higher boiling points (>170°C). Crystal violet was patented by Caro in 1883 and was prepared by treating *N,N*-dimethylaniline with phosgene and $AlCl_3$.[28] He named it Crystal Violet because of its crystallinity and brilliant shades.

Discussion

LC-MS data for the analysis of two historic violet dyes (**A** and **B**) from the Technical University of Dresden are reported. These were called Rotviolet and Hofmann violet, respectively, and pictures of the bottles are in the Supplemental Material. Figures 3 and 4, Tables 1 and 2 report data for the first violet dye **A** (Rotviolet) and Figure 5, Table 3 report data for the second violet dye **B** (Hofmann Violet). The charts have two scales. One is for the mass spectrum in electrospray mass spectrometry (ESMS) counts and the other is for the ultraviolet (UV) spectrum in milli Atomic Units (mAU). The horizontal scale is the retention time and larger chromophores stay for longer in the polymer pores. In Figures 3 and 4, there is a pattern as each peak is separated by an *m/z* of 14 which corresponds to a CH_2 or methylene group. The method does not distinguish methyl groups attached to carbon or nitrogen, but we can tell the total number of methylene groups. Some ethyl groups might also be included because some methods of alkylation used mixtures of methylating and ethylating agents (Hofmann's method). The possible methylated fuchsin

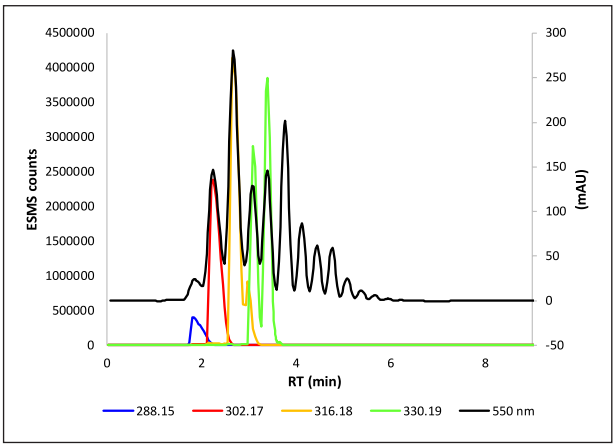

Figure 3. UV at 550 nm, EIC of M^+ ions for compounds.

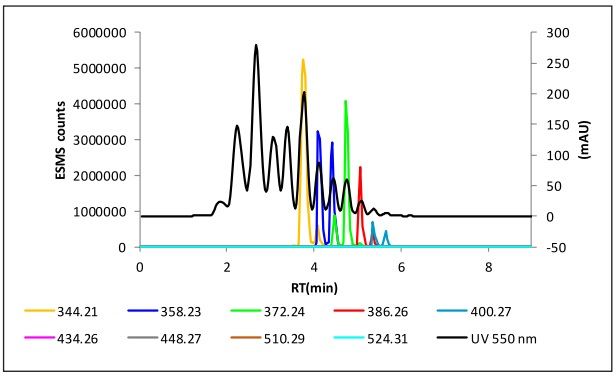

Figure 4. UV at 550 nm, EIC of M^+ ions for compounds.

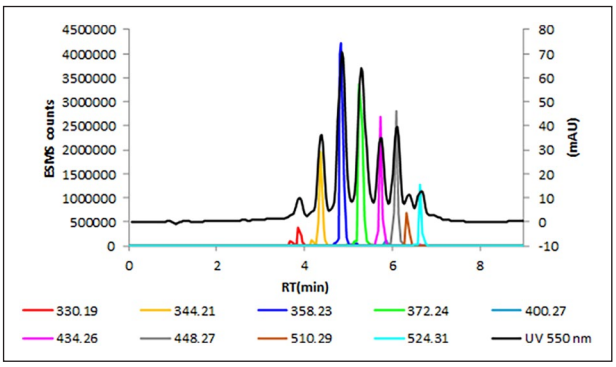

Figure 5. UV at 550 nm, EIC of M^+ ions for compounds.

derivatives are drawn in Figure 1 and the colour coded *m/z* with the number of methyl groups are listed here. Figure 3: *m/z* 288 (fuchsin)-302(Me)-316(2Me)-330(3Me). Figure 4: *m/z* 344(4Me)-358(5Me)-372(6Me)-386(7Me)-400(8Me). These data show the complex mixture of partially alkylated dyes that was present including the possibility of crystal violet as a minor component. Each *N*-methyl alkylation causes a slight bathochromic shift of the absorption maximum so that the dye turns from red to violet.

Figure 5 shows LC-MS data for the second historic violet dye **B**. The first four peaks follow a pattern of molecular weights as in Figures 3 and 4. *m/z* 330(3Me)-344(4Me)-358(5Me)-372(6Me). These compounds are likely to appear

Table 1. Compound peak areas for Figure 3 relative to the total peak area.

min	*m/z* 288	*m/z* 302	*m/z* 316	*m/z* 330
1.8	2.3			
2.2		12.3		
2.7			18.0	
3			1.6	
3.1				8.5
3.4				10.8

Table 2. Compound peak areas for Figure 4 relative to the total peak area.

min	*m/z* 344	*m/z* 358	*m/z* 372	*m/z* 386	*m/z* 400
3.8	15.0				
4.1	1.1	7.8			
4.4		6.0			
4.5			2.9		
4.8			7.1		
5.1				3.7	
5.3				0.7	
5.4					1.3
5.6					0.8

in Figure 1. However, Hofmann was reported to use a mixture of methyl and ethyl iodide to alkylate rosaniline so two methylene groups could be combined and inserted to form an ethyl group. However, the next four *m/z* peaks for compounds **7-10** do not follow the same pattern. *m/z* 434-448-510-524. These are likely to arise because some partially phenylated rosaniline was mixed in with the fuchsin or rosaniline to be alkylated to deepen the hue. Fuchsin was reacted with aniline to give the blue dye triphenylrosaniline.[10,29] Suggested structures for the dyes are shown in Figure 6. Dyes **7** and **8** of *m/z* 434 and 448 will contain one phenyl substituent and dyes **9** and **10** of *m/z* 510 and 524 will contain two phenyl substituents and an appropriate number of methylene groups. These studies give an insight into the manufacturing practice and once again the complexity of the chromophores.

The early dye chemists developed some interesting chemistry for which the mechanisms may not have been fully explained to date. Turpentine contains α-Pinene. WH Perkin used its reaction with bromine commercially to liberate aqHBr as he was not able to buy aqHBr.[2] The by-product is cymene so the driving force of aromaticity along with the molecular strain of pinene facilitates the reaction. A mechanism for this reaction is proposed here in Figure 7. The alkene will brominate forming a bromonium ion **13** which is ring opened by relief of the strain in the four membered ring. Carbocation **14** can rearrange into carbocation **16**, then liberate the first proton forming the precursor to cymene. Loss of HBr forming cymene **12** liberate the second proton. This reaction has frequently been studied by Lewis acid catalysis.[30,31]

Figure 8 proposes a mechanism for the reaction of glycerol with HI and phosphorous to form 2-iodopropane **25** used by Wanklyn in a commercial violet synthesis.[22] This reaction was topical with Berthelot, Hofmann, and Cahours

Table 3. Compound peak areas for Figure 5 relative to the total peak area.

min	*m/z* 330	*m/z* 344	*m/z* 358	*m/z* 372	*m/z* 400	*m/z* 434	*m/z* 448	*m/z* 510	*m/z* 524
5.2									
4.4	2.1	10.3							
4.8			23.3						
5.3				21.8					
5.4									
5.6									
5.7						12.3			
5.9					0.6				
6.1							14.2		
6.3								2.9	
6.6									5.3

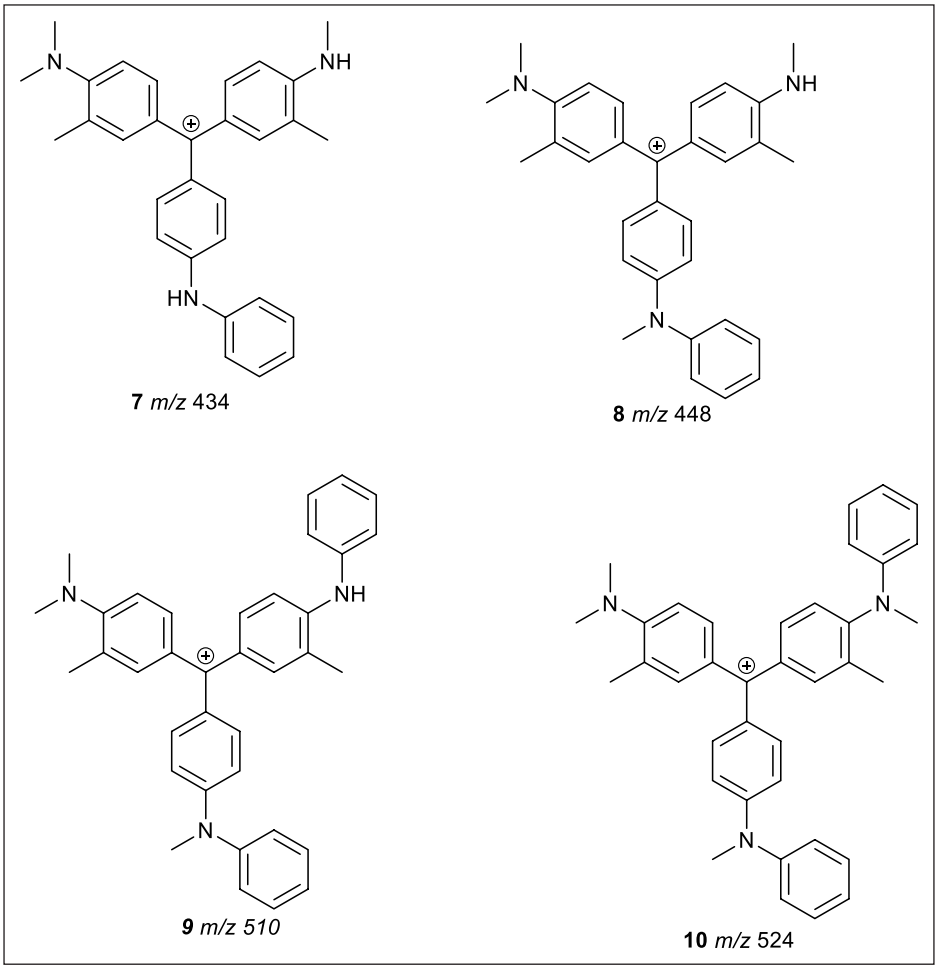

Figure 6. Possible structures of the higher molecular weight dyes appearing in Figure 5.

in the 1850s where it was studied first.[26,27] Formally glycerol is converted into 1,2,3-triiodopropane **19** and is then subjected to a series of addition elimination reactions leading to propene **23**. If the vessel is sealed, propane is converted to 2-iodopropane **25** used by Wanklyn.

Conclusion

Two historical violet dyes from the Technical University of Dresden have been analysed by LC-MS. Both are complex mixtures of chromophores which separated effectively into individual components. The first mixture **A** (Rotviolet) contained 11-12 chromophores of molecular weights 288 (fuchsin)-302(Me)-316(2Me)-330(3Me)-344(4Me)-358(5Me)-372(6Me)-386(7Me) and 400(8Me). The second mixture **B** (Hofmann violet) contained chromophores of molecular weight 330(3Me)-344(4Me)-358(5Me)-372(6Me)-434(5Me:Ph)-448(6Me:Ph)-510(5Me:2Ph)-524(6Me:2Ph). Ethyl groups are also expected, but the data show an initial stepwise increase in one CH_2 only. The analytical method separates chromophores based on size and a single CH_2 group difference is enough to separate two very similar large polar chromophores. Mixture B is believed to have included a partially phenylated chromophore,

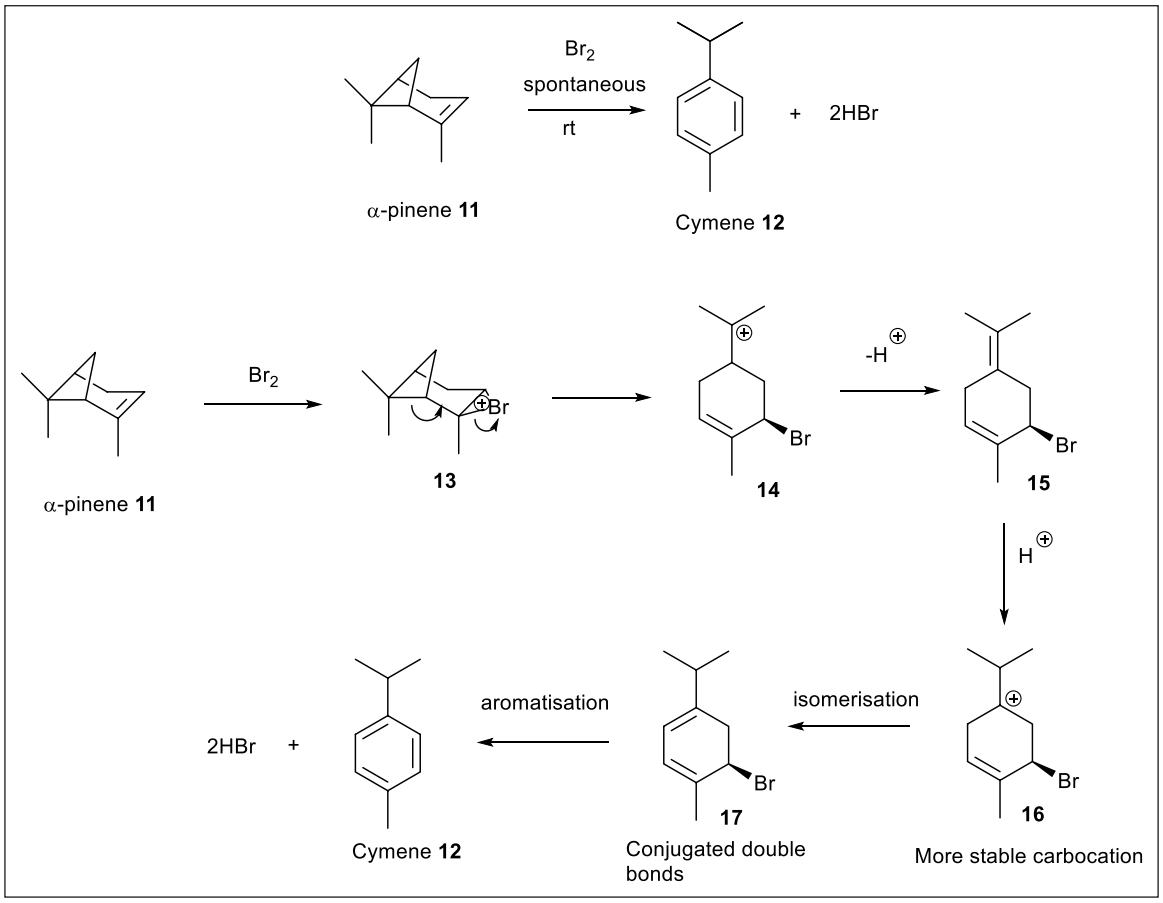

Figure 7. Proposed α-Pinene to cymene conversion with aqueous bromine generating HBr.

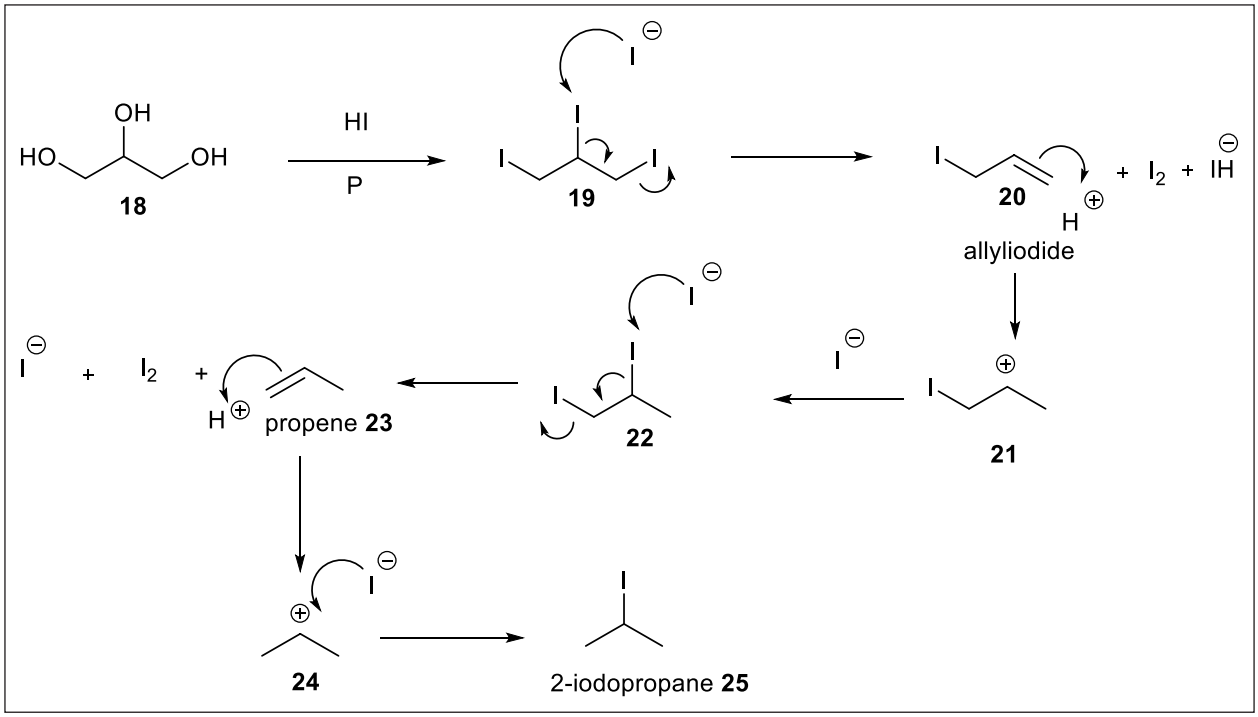

Figure 8. Proposed *sealed* reaction of glycerol with HI and phosphorous. The phosphorous mops up the iodine.

mono- or diphenylated, in the synthesis.[10,29] It might also be rosaniline alkylated with a mixture of methyl and ethyl groups since its provenance is Hofmann violet.[11] The phenylated chromophores were probably made by Girard's method reacting rosaniline or fuchsin with aniline.[29] Mechanisms are suggested for some of the early industrial chemistry, which was used in the synthesis of these dyes, turpentine with bromine,[18] and glycerol with HI/P.[26,27]

Experimental

For analytical separation, an Agilent 1290 Infinity high-performance liquid chromatography (HPLC) system consisting of a quaternary HPLC pump, cooled auto sampler compartment, column compartment, and diode array UV-visible detector was used. A Gold C-18 column (2.1 mm × 150 mm, Thermo Scientific, UK) was used for separation with a water/methanol gradient (both 0.1% v/v formic acid) from 40% to 100% MeOH in 7 min. The flow rate was 0.5 mL min^{-1}, column temperature 40°C and sample volume 5 μL. The mass spectrometer (ESMS) used was a MAXIS II Ultra-High Resolution Time-Of-Flight (UHR TOF) LC-MS System (Bruker UK Ltd, England) with electro spray ionisation (ESI) source connected to the UV-visible detector by a short length of polyether ether ketone (PEEK) tubing. The ESMS was operated in positive ion mode with a capillary voltage of 4.5 kV using sodium formate clusters for calibration and methyl stearate as lock mass. Mass spectra were recorded automatically.

Sample preparation

Samples of two dyes were provided in small plastic bags. These were cut open with scissors, and a grain or two of dye was removed with a spatula and placed in a small sample vial (2 cm × 4 cm). The spatula was cleaned each time to avoid cross-contamination. The grains were dissolved in MeOH and sent for analysis in a sealed sample vial.

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Declaration of conflicting interests

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Supplemental Material

The proton and carbon NMR data for all compounds in the experimental section is reported in the Supplemental Material (Figure SI).

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