

CYCLIC CROSS-CONJUGATED HYDROCARBONS HAVING INSERTED *p*-QUINOID RING—I¹

DIPHENYL-*p*-TROPYLPHENYLMETHYL CATION FORMED ON AN ATTEMPTED PREPARATION OF 1-CYCLOHEPTATRIENYLIDENE-4- DIPHENYLMETHYLIDENE-2,5-CYCLOHEXADIENE

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Abstract—In connection with the synthetic studies of the cross-conjugated system 2, *p*-(diphenylhydroxymethyl)phenyltropolidene (13)^{*} was prepared. On treatment with CF₃COOH, 13 transformed to an aryltropylium ion (15) via an unstable blue colored compound. Based on NMR spectroscopy and some chemical properties the structure of the pigment is assumed to be diphenyl-*p*-tropylyphenylmethyl cation (16) rather than the primarily anticipated cross-conjugated hydrocarbon 9,9-diphenyl[1.6.7]quinarene (6).

In the area of fulvene or fulvalene type of cross-conjugated non-alternant hydrocarbon chemistry, very little is known concerning with the properties of the long conjugated system such as 1 and 2.

We have attempted the preparation of 1-cycloheptatrienylidene-4-diphenylmethylidene-2,5-cyclohexadiene (6), a diphenyl derivative of 2, starting with the carbinol (13). For this purpose, 13 was treated with acid and we obtained a tropylium ion derivative (15) via an unstable blue pigment. The structure of the pigment is discussed in this paper.

After we had started this work, dicyano derivative of 1 was synthesized by Gompper *et al.*² by direct cyclopropenylation of phenylmalononitrile. The dicyano derivative 5³ has recently been reported to be quite stable in dilute polar solvent solution and in monomeric solid absorbed on silica gel, while it polymerizes immediately with ease in concentrated solution. For the polycyclic cross-conjugated hydrocarbons such as 1, 2, 3, or 4, possessing a quinoid structure inserted between two rings of fulvene, fulvalene type hydrocarbons,

we propose the name "Quinarene" for convenience. The term "Quinarene" suggests the conjugated hydrocarbon (arene) carrying a quinoid structure, and the size of ring is shown in the number in a bracket—1 being [1.6.3]quinarene, 2 being [1.6.7]quinarene, 3 being [5.6.7]quinarene and 4 being [3.6.5]quinarene.

For the synthesis of cross-conjugated system 2, the direct condensation reaction of active methylene compounds with *p*-benzoquinone-tropide (7)^{4†} was unsuccessful, because 7 carries a positive charge in a 7-membered ring rather than in a carbonyl carbon in its polarized structure. Therefore, we planned to prepare the [1.6.7]quinarene structure by the Grignard reaction of *p*-tropylyphenylmagnesium bromide.

p-Aminophenyltropolidene^{1,5} (8) easily obtainable by treatment of aniline with 7-alkoxytropolidene in the presence of acid,⁶ was first converted into *p*-halophenyltropolidene (10a,b,c)^{*} by means of the Sandmeyer reaction of diazonium salt (9) in aqueous dioxane. *p*-Bromophenyltropolidene (10b) reacted with magnesium metal in tetrahydrofuran solution, but did not in ether solution, to give *p*-tropylyphenylmagnesium bromide (11a). *p*-Tropylyphenyllithium (11b) was also obtained upon treatment of 10c with *n*-butyllithium at 0° in ether solution. Addition of benzophenone to an ether solution of 11b or a tetrahydrofuran solution of 11a at room temperature and subsequent work-up and chromatographic purification afforded *p*-(diphenylhydroxymethyl)phenyltropolidene (13) as a colorless oil, in 46% yield. An analogous treatment of 11b with acetone gave *p*-isopropenylphenyltropolidene (12) as a colorless oil.

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^{*}When no notation is made, troyl or tropilidene means 3-substituted cycloheptatriene containing 10–20% of 1-substituted isomer. The detailed components of each compound are given in the NMR spectra in the Experimental.

[†]Compound 7 can also be named as 1-oxa[1.6.7]quinarene.

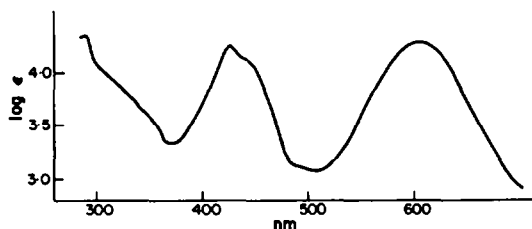
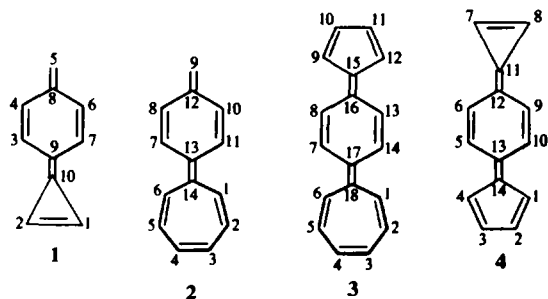
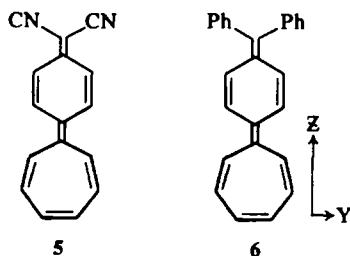


Fig 1. Electronic absorption spectrum of the deep blue colored solution of *p*-(diphenylhydroxymethyl)phenyl-tropylidene (13) in trifluoroacetic acid.



methylene), 5.44–6.80 ppm (m: vinyl) for 13 decreased with time and simultaneously new three signals consisting of a singlet at 5.69 ppm (methine), a quartet centered at 7.67 ppm ($J = 8.5$ Hz) and a multiplet at 9.07 ppm (tropylium) gradually appeared and increased in intensity to give the same spectrum as that for 15.

The process of 13 → blue color species → 15 probably involves the initial formation of diphenyl-*p*-tropyliumphenylmethyl cation, which would stabilize by the distribution of the positive charge into 7-membered ring to give an extensive conjugated system (16). This might be the species of blue color and is stable for a while in acidic media, although intermolecular hydride transfer (17) would proceed

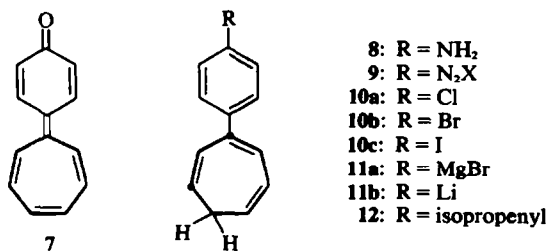


CHART 1.

Upon treatment with a strong acid such as conc H₂SO₄, conc HCl, trifluoroacetic acid, or with aluminum chloride in an organic solvent, 13 was converted to the intensely blue soln with absorption maximum at 605 nm, as shown in Fig. 1. The soln of the pigment in trifluoroacetic acid however, was unstable and gradually changed to a yellow soln within a few hours, and more quickly in mineral acidic media. Yellow needles, which precipitated out on addition of perchloric acid to the above yellow soln, showed the IR and NMR bands entirely identical to those found for tropylium perchlorate (15), which was stepwise prepared from 13 by LAH reduction in presence of aluminum chloride leading to 14 and subsequent hydride abstraction using trityl perchlorate. Transformation of 13 into 15 in trifluoroacetic acid via the blue pigment was also observed by following NMR spectrum of the blue colored soln. The OH signal at 2.87 ppm and troyl signals at 2.26 ppm (t:

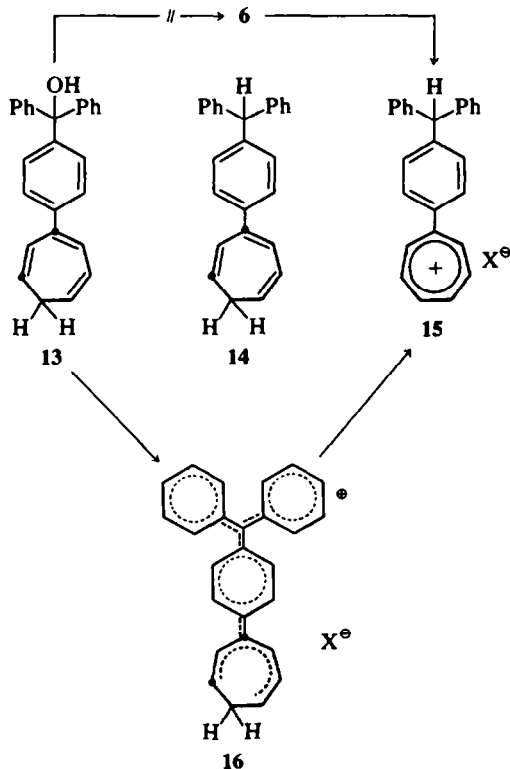


CHART 2.

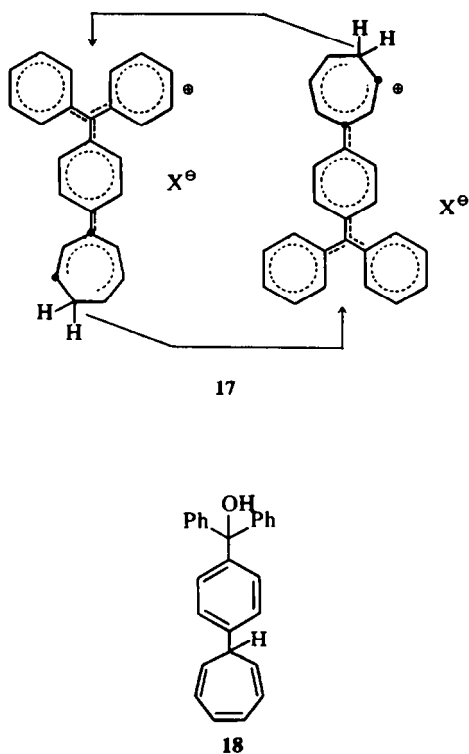


CHART 3.

to give 15. An alternative mechanism for 13 to 15 could be a proton abstraction from the tropylium methylene of 16 to give [1.6.7]quinarene hydrocarbon (6) which is subsequently protonated on triarylmethyl carbon of its dipolar structure affording 15. In the latter process 6 could be in favor for the structure of blue color species. In order to differentiate between these two possibilities, a more careful NMR spectral examination was carried out especially on the methylene region on the blue colored soln by repeating the sweeps for each one minute. However, the methylene proton triplet at 2.26 ppm exists in blue colored soln, at least within initial 10 min, and then gradually decreased with a disappearance of the blue color. If the blue pigment is [1.6.7]quinarene (6) itself, tropylium methylene protons should disappear with appearance of the blue color. In addition, if the distribution of a positive charge into 7-membered ring as shown in 16 is the reason for the blue color, unconjugated hydrocarbon (18) should not give the blue color on treatment with acid. The isomer (18), prepared by Grignard reaction of *p*-(7-tropylium)phenylmagnesium bromide with benzophenone,

Further details of this calculation are to be published together with the results on other cross-conjugated hydrocarbons.

gave in fact only yellow soln on treatment with trifluoroacetic acid showing absorption maxima at nm (log ϵ): 418 (4.41) and 451 (4.38), which are similar to those of triphenylcabinol in trifluoroacetic acid at nm (log ϵ): 402 (4.59) and 426 (4.59). Moreover the stability of the blue color depends on the concentration of the soln, e.g., the blue color changed actually to yellow within a few hours in 3.5×10^{-2} M solution of 13 in trifluoroacetic acid, but was kept unchanged for over one week in 1.1×10^{-4} M solution. This fact suggests that the intermolecular hydride transfer of the pigment (17) causes the disappearance of the color to form 15. According to the evidence of an immediate protonation of dicyano derivative (5) on C-9 position not only in trifluoroacetic acid but also in formic acid³ it is also difficult to assume that the compound (6) remains unprotonated so long while in trifluoroacetic acid. Furthermore, a mixture of 13 and phenyltropyliene or *p*-methoxyphenyltropyliene gave a mixture of 15 and phenyltropylium ion or *p*-methoxyphenyltropylium ion on treatment with trifluoroacetic acid via an unstable blue color indicates that intermolecular hydride abstraction occurred during this process. An attempted isolation of 16 was made by treating the acetic anhydride soln of 13 with hexachloroplatinic acid, however, the resulting blue black precipitates changed to yellow needles (15) during filtration.

Table 1. Calculated transition energies of 1-cycloheptatrienyldiene - 4 - diphenylmethylidene - 2,5 - cyclohexadiene (6) and observed spectrum of *p*-(diphenylhydroxymethyl)phenyltropyliene (13) in trifluoroacetic acid (blue pigment)

Calculated		Observed	
ΔE (ev)	f	ΔE (ev)	(log ϵ)
2.05	0.012 (y)		
2.25	2.46 (z)	2.05	(4.28)
3.69	0.004 (z)	2.92	(4.27)
3.84	0.001 (y)		

While the observed first absorption maximum of 2.05 ev (610 nm) seems to be reasonable for the structure of 6, the observed second absorption maximum of 2.92 ev (log $\epsilon = 4.27$) was not found in the transition energies for 6 calculated by the variable bond-length SCF- π -MO-CI procedure,⁷ as shown in Table 1.*

On the basis of these chemical and spectral evidences, we assume that 16 is essential for the blue color species. Further attempts to isolate and identify the compound 6 are currently underway.

EXPERIMENTAL

All m.ps and b.ps are uncorrected. The instruments used for spectral data are Shimadzu-IR-27G-spectrophotometer (IR), Varian Associates A-60 spectro-

meter (NMR, TMS as internal standard) and Hitachi EPS-2U spectrometer (UV).

p-Aminophenyltropilidene (8). Aniline (60 g, 0.644 mol), 7-ethoxytropilidene (60 g, 0.444 mol) and EtOH (180 ml) were mixed and warmed on a water bath. After a gentle refluxing had started, conc HCl (2–3 ml) was added to the mixture. After refluxing for 2 h, the product was cooled and poured into water and extracted with ether. The ether extract was washed with sat NaHCO₃ aq and dried over Na₂SO₄. The solvent was removed and the product obtained was distilled to give a colorless liquid (64.4 g, 80%), b.p. 132–142°/1 mmHg. NMR showed it to be a mixture of 1- and 3-(*p*-aminophenyl)tropilidene in the ratio of 1:4; ν_{\max} (neat) 3460, 3380, 3320, 2840, 1620, 1515, 1290, 1180, 826, 768, 706, 708 cm⁻¹; δ (CDCl₃) 7.39 (2H, dd, *J* = 9.0 Hz, phenyl), 6.70 (2H, dd, *J* = 9.0 Hz, phenyl), 7.0–6.2 (3H, m, tropanyl vinyl), 5.8–5.35 (2H, m, tropanyl vinyl), 3.62 (2H, s, NH₂), 2.78 (2/5H, d, *J* = 7.0 Hz, tropanyl methylene), 2.35 (8/5H, t, *J* = 6.5 Hz, tropanyl methylene).

p-Iodophenyltropilidene (10c). To a vigorously stirred solution of *p*-aminophenyltropilidene (20 g, 0.11 mol) in dioxane (120 ml), a soln of conc H₂SO₄ (20 ml) in water (100 ml) was added. After cooling below –15° a soln of NaNO₂ (7.8 g, 0.113 mol) in water (14 ml) was added over a period of 40 min. The resulting yellowish orange soln was stirred for further 30 min and was maintained below –15° until just before its use.

Diazonium sulfate (9) thus obtained was added with stirring into a soln of KI (18.2 g, 0.11 mol) in water (30 ml) and dioxane (180 ml) over 2–3 h at +7°. After being stirred overnight at room temp, a black ppt which separated was removed by filtration. The heterogeneous mixture was then concentrated to one half of its original volume, diluted with water, and extracted with benzene. The benzene extracts were washed (sat NaHCO₃ aq), dried (Na₂SO₄), and filtered through (chromatographed) an alumina column (5 × 30 cm) with benzene as eluent. After solvent removal *in vacuo*, the residue was distilled to afford a slightly yellow viscous oil of 10c (9.16 g, 28.1%) b.p. 130–140°/1.1 mmHg; ν_{\max} (neat) 3040, 2960, 2870, 2830, 1480, 1430, 1060, 1000, 817, 760, 730, 706 cm⁻¹; δ (CCl₄) 7.55 (2H, dd, *J* = 8.5 Hz, phenyl), 7.26 (2H, dd, *J* = 8.5 Hz, phenyl), 6.85–6.1 (3H, m, tropanyl vinyl), 5.65–5.2 (2H, m, tropanyl vinyl), 2.62 (2/5H, d, *J* = 7.1 Hz, tropanyl methylene), 2.27 (8/5H, t, *J* = 6.8 Hz, tropanyl methylene); λ_{\max} (MeOH) nm (log ϵ), 234 (4.18), 285 (3.86); (Found: C, 53.15; H, 3.82. C₁₁H₁₁I requires: C, 53.07; H, 3.77%).

p-Bromophenyltropilidene (10b). Diazonium sulfate (9), prepared in the same fashion as above by using *p*-aminophenyltropilidene (10 g, 0.0545 mol) was added with stirring into a soln of cuprous bromide (15.8 g, 0.055 mol) in 47% HBr (20 ml) and dioxane (80 ml) over 1–2 h at +7°. Subsequent work-up, but extracted with light petroleum instead of benzene, afforded a slightly yellow oil (10b; 5.54 g, 41%) b.p. 128–133°/1.1 mmHg; ν_{\max} (neat) 3012, 2825, 1490, 1070, 1005, 820, 780, 760, 732, 715 cm⁻¹; δ (CDCl₃) 7.5–7.0 (4H, m, phenyl), 6.59 (1H, m, tropanyl vinyl), 6.35–5.98 (2H, m, tropanyl vinyl), 5.42–5.09 (2H, m, tropanyl vinyl), 2.61 (1/5H, d, *J* = 7.0 Hz, tropanyl methylene), 2.25 (9/5H, t, *J* = 6.8 Hz, tropanyl methylene).

p-Chlorophenyltropilidene (10a). Diazonium sulfate (9), prepared by using *p*-aminophenyltropilidene (20 g), was added with stirring into a soln of cuprous chloride (28 g, 0.14 mol) in conc HCl (20 ml) and dioxane (150 ml) over 2–3 h at +7°. The mixture was worked up as is described for 10b, and afforded a slightly yellow oil 10a (12.2 g,

55%), b.p. 113–118°/1 mmHg; ν_{\max} (neat) 3040, 2833, 1486, 1062, 1004, 821, 760, 737, 712 cm⁻¹; δ (CCl₄) 7.29 (4H, s, phenyl), 6.90–6.08 (3H, m, tropanyl vinyl), 5.65–5.15 (2H, m, tropanyl vinyl), 2.65 (1/5H, d, *J* = 7.0 Hz, tropanyl methylene), 2.31 (9/5H, t, *J* = 6.8 Hz, tropanyl methylene).

p-Tropylphenyllithium (11b). To a soln of *n*-BuLi (29 mmol) in ether (20 ml) a soln of *p*-iodophenyltropilidene (4.0 g, 13.6 mmol) in ether (20 ml) was added dropwise with stirring at –30–20° under N₂. The resulting soln was stirred at –30–20° for a further 1 h and then at 0° for additional 1 h. The yellowish-orange soln thus obtained contain about 10.0 mmol of *p*-tropylphenyllithium (11b).

p-Tropylphenylmagnesium bromide (11a). Finely cut Mg ribbon (0.177 g, 7.28 mmol) was heated on a luminous flame for 30 min under N₂. A few drops of a soln of *p*-bromophenyltropilidene (2.0 g, 7.29 mmol) in THF (8 ml) was then added with a trace of I₂. When reaction commenced, stirring was started, and the remaining soln of *p*-tropylphenyl bromide was added dropwise. The mixture was then heated at 45° until the Mg metal had dissolved (about 30–40 min). The dark yellow soln thus obtained contained about 5.80 mmol of *p*-tropylphenylmagnesium bromide.

Preparation of p-(diphenylhydroxymethyl)phenyltropilidene (13). (a) To an ether soln of *p*-tropylphenyllithium, prepared by treating *p*-iodophenyltropilidene (4.0 g, 13.6 mmol) with *n*-BuLi (29 mmol), was added dropwise a soln of benzophenone (2.02 g, 11.1 mmol) in ether (100 ml) with stirring at room temp. After being stirred at room temp for 5 h, the resulting soln was hydrolyzed with 2N H₂SO₄ and extracted with ether. The combined organic soln was washed (sat NaHCO₃ aq), dried (Na₂SO₄), and concentrated. The residual yellow semi-solid was subsequently chromatographed on alumina column with light petroleum and benzene as the eluent. The later chromatographic fractions from light petroleum–benzene (1:1) were rechromatographed to separate carbinol (13) (1.78 g, 46%), as colorless viscous oil; ν_{\max} (KBr) 3460, 3012, 2933, 1488, 1443, 1328, 1152, 1005, 897, 829, 763, 702 cm⁻¹; δ (CDCl₃) 7.23 (4H, s, phenyl), 6.95–6.1 (3H, m, tropanyl vinyl), 5.66–5.2 (2H, m, tropanyl vinyl), 2.87 (1H, s, OH), 2.68 (1/5H, d, *J* = 7.0 Hz, tropanyl methylene), 2.26 (9/5H, t, *J* = 6.8 Hz, tropanyl methylene); λ_{\max} (CHCl₃) nm (log ϵ) 293 (3.97); (Found: C, 88.89; H, 6.71. C₁₅H₁₅O₂ requires: C, 89.11; H, 6.33%).

(b) To a THF solution of *p*-tropylphenylmagnesium bromide, prepared from *p*-bromophenyltropilidene (20 g, 7.29 mmol) and Mg (0.177 g, 7.28 mmol), was added dropwise a soln of benzophenone (1.33 g, 7.28 mmol) in THF (15 ml). After being stirred at 45° for 2 h, the resulting soln was worked up as described for (a), and afforded 13 (0.613 g, 24%).

Preparation of p-isopropenylphenyltropilidene (12). To an ether soln of *p*-tropylphenyllithium, prepared by using *p*-iodophenyltropilidene (2.0 g, 6.8 mmol), was added dropwise a soln of acetone (0.4 g, 7.0 mmol) in ether (30 ml). The mixture was worked up as described for 13. The crude product was distilled *in vacuo* to give 12 (1.00 g, 70.5%) as colorless oil, b.p. 132°/1 mmHg; ν_{\max} (neat) 2985, 2905, 1621, 1508, 1493, 1433, 1370, 889, 838, 743, 731, 700 cm⁻¹; δ (CDCl₃) 7.22 (4H, m, benzene), 6.95–6.05 (3H, m, tropanyl vinyl), 5.65–5.15 (2H, m, tropanyl vinyl), 5.30 (1H, broad s, vinyl), 4.98 (1H, m, vinyl), 2.66 (1/5H, d, *J* = 7.0 Hz, tropanyl methylene), 2.26 (9/5H, t, *J* = 6.8 Hz, tropanyl methylene), 2.08 (3H, broad s, CH₃); λ_{\max} (MeOH) nm (log ϵ) 233 (4.11), 253 sh (4.03); 285

(4-01); (Found: C, 92.46; H, 7.93. $C_{16}H_{16}$ requires: C, 92.26; H, 7.74%).

p-(Diphenylmethyl)phenyltropilidene (14). A mixture of $AlCl_3$ (381 mg, 2.86 mmol) and 13 (1.00 g, 2.86 mmol), in ether (10 ml) was added with stirring to an ice-cooled suspension of LAH (136 mg, 3.57 mmol) and $AlCl_3$ (477 mg, 3.57 mmol) in ether (10 ml). After stirring for 1 h at 0°, the mixture was carefully diluted with 2N H_2SO_4 to destroy the excess reagents and extracted with ether. The ether layer was washed (sat $NaHCO_3$ aq), and dried (Na_2SO_4). After evaporating the solvent, the residue was chromatographed on alumina column with light petroleum as the eluent to separate crude hydrocarbon (14). Recrystallization from light petroleum afforded pure 14 (0.602 mg, 63%) as colorless plates, m.p. 111–112°; ν_{max} (KBr) 3030, 1595, 1495, 1443, 1072, 1030, 914, 868, 813, 759, 732, 702 cm^{-1} ; δ ($CDCl_3$) 7.39 (2H, d, $J = 8.5$ Hz, phenyl), 7.06 (2H, d, $J = 8.5$ Hz, phenyl), 7.16 (10H, s, phenyl), 6.9–6.1 (3H, m, troyl vinyl), 5.6–5.2 (2H, m, troyl vinyl), 5.51 (1H, s, methine), 2.70 (1/5H, d, $J = 7.0$ Hz, troyl methylene), 2.28 (9/5H, t, $J = 6.8$ Hz, troyl methylene); λ_{max} ($CHCl_3$) nm (log ϵ) 295 (4.05); mass spectrum m/e 334 (M^+); (Found: C, 93.08; H, 6.59. $C_{26}H_{22}$ requires: C, 93.37; H, 6.33%).

p-(Diphenylmethyl)phenyltropylium perchlorate (15). To a soln of 14 (100 mg, 0.3 mmol) in dichloromethane (5 ml) was added with stirring triphenylmethyl perchlorate (257 mg, 0.75 mmol) at room temp. After the resulting mixture had been stirred overnight and concentrated under reduced pressure, ether was added to precipitate the cation (15). Recrystallization from acetonitrile–ethyl acetate yielded pure 15 (104 mg, 80%) as brownish-yellow needles, m.p. 208° (dec); ν_{max} (KBr) 3030, 1590, 1520, 1493, 1474, 1442, 1260, 1090, 755, 700 cm^{-1} ; δ (CF_3COOH) 7.87 (2H, d, $J = 8.0$ Hz, phenyl), 7.53 (2H, d, $J = 8.0$ Hz, phenyl), 7.27 (10H, s, phenyl), 5.69 (1H, s, methine); λ_{max} ($CHCl_3$) nm (log ϵ) 275 (4.22), 418 (4.46); (Found: C, 71.83; H, 4.93. $C_{26}H_{21}O_2Cl$ requires: C, 72.17; H, 4.89%).

Preparation of 7-[*p*-diphenylhydroxymethyl]phenyl]tropilidene (18). To a THF soln of *p*-(7-troyl)phenylmagnesium bromide, prepared by treating 7-(*p*-bromophenyl)tropilidene⁵ (2.0 g, 7.29 mmol) with Mg (0.177 g, 7.28 mmol) in a similar manner to that for 11a, was added a soln of benzophenone (1.33 g, 7.28 mmol) in THF (15 ml). The crude product was chromatographed on neutral alumina column with light petroleum and benzene as eluents. The fractions from light petroleum benzene (2:1) were rechromatographed to give a colorless oil (18) (0.53 g, 21%); ν_{max} ($CHCl_3$) 3590, 3060, 3010, 1600, 1490, 1445, 1150, 1010, 825 cm^{-1} ; ν_{max} (CS_2) 825, 754, 698 cm^{-1} ; δ (CCL_4) 7.28 (14H, m, benzene), 6.66 (2H, m, troyl vinyl), 6.15 (2H, m, troyl vinyl), 5.33 (2H, m, troyl vinyl), 2.66 (1H, t, $J = 5.0$ Hz, troyl methine), 2.60 (1H, s, OH); λ_{max} (MeOH) nm (log ϵ) 258 (4.04); mass spectrum m/e 350 (M^+); (Found: C, 88.83; H, 6.29. $C_{26}H_{22}O$ requires: C, 89.11; H, 6.33%).

Reaction of 13 with trifluoroacetic acid. A deep blue soln of 13 (10 mg) in trifluoroacetic acid (0.8 ml) was allowed to stand at room temp for 15 h. The solvent was removed *in vacuo* and a few drops of 35% perchloric acid

were added to the residue. After stirring for 30 min, water (1 ml) and benzene (1 ml) were added to precipitate 15 (5.2 mg, 42%).

Reaction of 16 with phenyltropilidene. To a mixture of 13 (30 mg, 0.085 mmol) and phenyltropilidene (50 mg, 0.29 mmol) in dichloromethane (1 ml) was added with stirring trifluoroacetic acid (0.3 ml) at room temp. While stirring for 2 h, the deep blue color of the soln turned to yellow. The solvents were evaporated *in vacuo* and a few drops of 35% perchloric acid was added with stirring to the residue. When being triturated with a mixture of benzene (0.5 ml) and water (1 ml) the residue gave yellow needles (34 mg), which were shown by NMR signals (in trifluoroacetic acid) to be a 1:1 mixture of phenyltropylium perchlorate and 15.

Reaction of 16 with *p*-methoxyphenyltropilidene. A mixture of 13 (35.04 mg, 0.1 mmol) and *p*-methoxyphenyltropilidene (49.5 mg, 0.25 mmol) in dichloromethane (1 ml) was treated with trifluoroacetic acid (0.3 ml). Subsequent work-up as is mentioned above afforded yellow needles (41 mg), which were shown by NMR (in trifluoroacetic acid) to be a 1.5:1 mixture of *p*-methoxyphenyltropylium perchlorate and 15.

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