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p-(3,4-Diphenyl-1,3-cyclopentadien-1-yl)phenyltropylium Perchlorate. An Intermediate in the Synthesis of [5.6.7]Quinarene System[1,2]

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Attempt was made to dehydrogenate *p*-(3,4-diphenyl-1,3-cyclopentadien-1-yl)phenyltropilidene, prepared by treating *p*-tropylphenyllithium or *p*-tropylphenylmagnesium bromide[3] with 3,4-diphenylcyclopent-2-enone, to $3'',4''$-diphenyl-1-cycloheptatrienylidene-4-cyclopentadienylidene-2,5-cyclohexadiene, 10,11-diphenyl[5.6.7]quinarene. The resulting blue pigment showed spectral properties in line with those of *p*-(3,4-diphenyl-1,3-cyclopentadien-1-yl)phenyltropylium ion, [5.6.7]quinarenium ion, carrying a delocalized positive charge (VII′), but not those of expected cross-conjugated hydrocarbon.

The chemistry of fulvalene has been developed[4] and shown to be of greate theoretical interest.[5] The chemistry of polycyclic cross-conjugated π-systems such as I,[2,6] II or III having an inserted *p*-quinoid structure between the two dipole centers of heptafulvene, sesquifulvalene or calicene would also be of interest in connection with its aromatic nature. We have used the name "quinarene"[7] for the sake of convenience to designate this type of polycyclic cross-conjugated hydrocarbon possessing quinoid structure inserted between the two rings of fulvalene (fulvene) type structure. The ring size is shown in brackets; II being [5.6.7]-quinarene, III [3.6.5]quinarene and I [1.6.7]quinarene.[2] Numbering systems (I, II, III) are given for the structures.

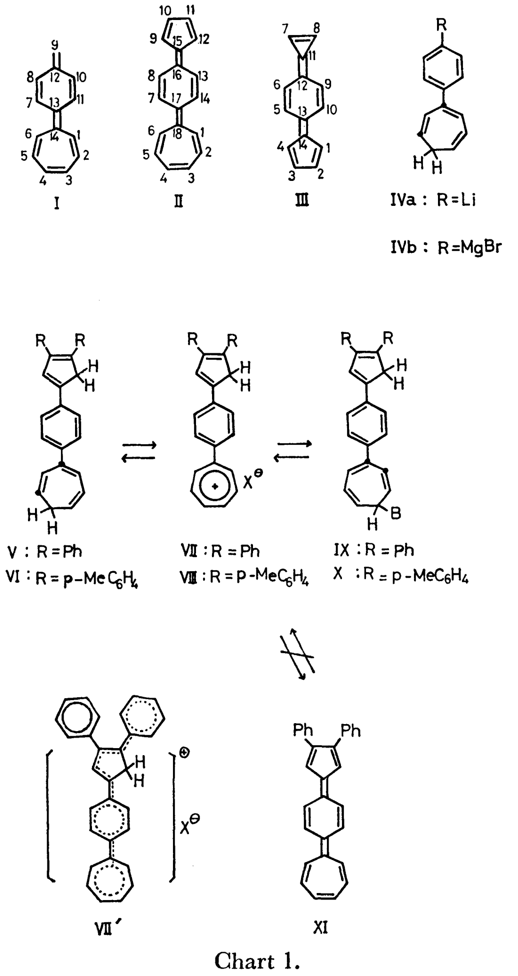

Chart 1.

PPP-type SCF-π-MO calculation[8] suggests that the quinarene (II) should have aromatic character (E_R/π) analogous to sesquifulvalene. In order to determine the ground-state properties of II, the synthesis of 10,11-diphenyl[5.6.7]quinarene (XI) was undertaken.

We reported on a convenient synthetic method of *p*-tropylphenylcarbinol derivative by the reaction of *p*-tropylphenyllithium (IVa) with alkyl or aryl ketones.[2] The reaction was developed for the synthesis of the compounds of type II.

Results and Discussion

Treatment of IVa or the corresponding Grignard reagent (IVb) with 1.7 mol equivalents of 3,4-diphenylcyclopent-2-enone[9] in ether at room temperature followed by hydrolysis with 2 M sulfuric acid gave yellow needles (V), mp 125—126 °C in 33.5% yield. V has no OH band in its IR spectrum and contains one additional singlet methylene proton resonance at 3.84 ppm besides a triplet (at 2.31 ppm) and a doublet (at 2.72 ppm) tropyl[3] methylene proton resonance in NMR spectrum, indicating that the dehydration of primarily formed carbinol had occurred to afford the hydrocarbon (V). V in dichloromethane was allowed to react with 2.5 mol equivalents of triphenylmethyl perchlorate resulting in an intensely blue solution, from which perchlorate VII was isolated as blue black needles in 88% yield. Di-*p*-tolyl derivative (VI), obtained by the treatment of IV with 3,4-di-*p*-tolylcyclopent-2-enone, also afforded blue black needles (VIII)[10] on reaction with triphenylmethyl salt. VII turned to the original tropilidene (V) on lithium aluminum hydride reduction in ether. Perchlorate (VII) was immediately converted into a yellow 3- and 2-aryl-7-ethoxytropilidene (IX: B=OEt) on treatment with sodium bicarbonate in the presence of ethanol, from which salts of the cation (VII) were regenerated by the action of acids such as hydrogen bromide, hydrogen chloride, trifluoroacetic acid, or perchloric acid. The chemical

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Table 1. Solvent effects on the electronic absorptions of 10, 11-diaryl[5.6.7]-quinarenium ions (VII and VIII)

nm (log ε)	CH_3CN	$MeCO_2H$	HCl–MeOH	CH_2Cl_2	$CHCl_3$	CF_3CO_2H
VII	543 (4.2)	550 (4.2)	548 (4.3)	630 (4.3)	617 (4.2)	627 (4.3)
X=ClO_4	352 (4.1)	354 (4.1)	352 (4.1)	364 (4.1)	364 (4.0)	482 (3.9)[a]
	273 (4.3)	—	270 (4.3)	275 (4.2)	276 (4.2)	365 (4.0)
VIII	556 (4.3)	565 (4.2)	565 (4.3)	650 (4.4)	640 (4.3)	639 (4.0)
X=ClO_4	357 (4.1)	358 (4.2)	358 (4.1)	365 (4.2)	371 (4.2)	490 (4.3)[a]
	276 (4.2)	—	270 (4.3)	275 (4.4)	275 (4.3)	350 (4.0)

a) Absorption maxima of dications formed by a protonation at the 5-membered ring of VII and VIII.

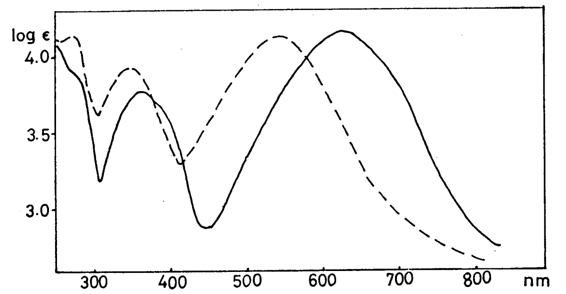


Fig. 1. Electronic absorption spectra of 10,11-diphenyl-[5.6.7]quinarenium ion (VII): (——) in $CHCl_3$, and (------) in CH_3CN.

properties as well as elemental composition of VII ($C_{30}H_{23}ClO_4$) were in line with the *p*-(3,4-diphenyl-1,3-cyclopentadien-1-yl)phenyltropylium ion structure.

However, there is some doubt as to the structure of pigment (VII), as seen from its electronic spectra. The longest wavelength absorption maximum of VII at 543—550 nm in such solvents as acetonitrile, acetic acid, or methanol–hydrochloric acid (violet solutions) shows a large bathochromic shift to 617—630 nm when the solvent is changed to chloroform, dichloromethane, or 9: 1 mixed solvent of chloroform and trifluoroacetic acid (blue solutions) (Table 1 and Fig. 1). The absorption maximum of VII at an extraordinary longer wavelength region of 630 nm is conspicuous as compared with the absorption maxima of phenyltropylium ion[11,12] at 385 nm and *p*-biphenylyltropylium ion at 415 nm. On the other hand, molecular orbital calculation for diphenyl derivative of [5.6.7]quinarene[8] using the variable bond length SCF-π-MO-CI procedure predicted the lowest singlet transition energies of XI to be 2.09 eV: $f=2.96$. The observed absorption maximum (630 nm) of VII and molecular orbital

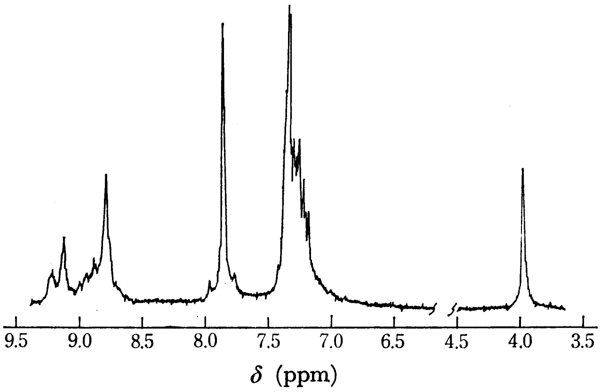


Fig. 2. NMR spectrum of 10,11-diphenyl[5.6.7]quinarenium ion (VII) in a 9: 1 mixture of $CHCl_3$ and CF_3CO_2H.

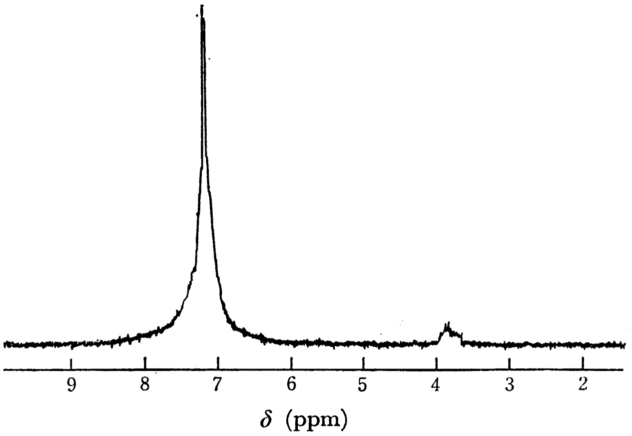


Fig. 3. NMR spectrum of 10,11-diphenyl[5.6.7]quinarenium ion (VII) in $CHCl_3$ at +30 °C.

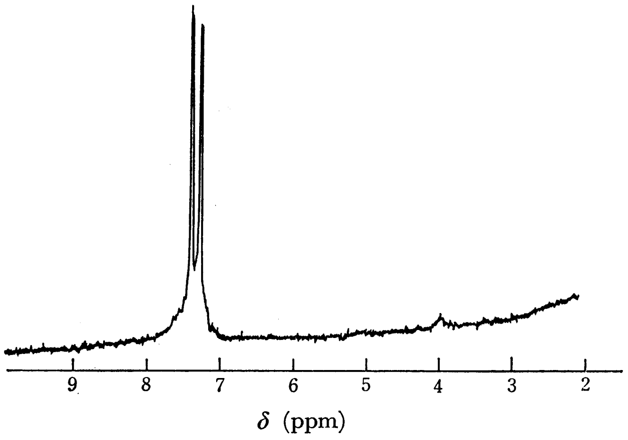


Fig. 4. NMR spectrum of 10,11-diphenyl[5.6.7]quinarenium ion (VII) in $CHCl_3$ at −30 °C.

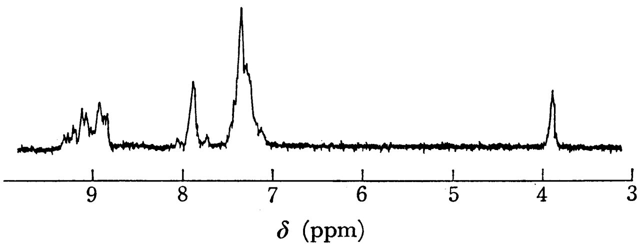
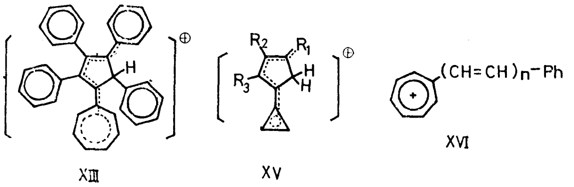


Fig. 5. NMR spectrum of 10,11-diphenyl[5.6.7]quinarenium ion (VII) in liq. SO_2.

calculation would be reasonable if cation (VII) is capable of existing as an equilibrium mixture with quinarene-type hydrocarbon (XI) in chloroform or dichloromethane solution.

NMR spectral studies of VII, however, exclude the possibility of the equilibrium. A deep blue solution of VII in chloroform containing 10% of trifluoroacetic acid shows a multiplet at 8.90 ppm (6H, tropylium ion), AB-type triplet at 7.80 ppm (4H, benzene ring), a multiplet at 7.20 ppm (11H, benzene ring and an olefinic proton of 5-membered ring) and a singlet at 3.96 ppm (2H, methylene), indicating that VII is the structure of the blue pigment (Fig. 2). In non-acidic, pure chloroform, the presumed equilibrium between VII and XI would favor deprotonated species XI. However, the solution showed a small and broad singlet at 3.9—4.0 ppm attributed to the methylene group of the 5-membered ring of VII, besides a broad peak at around 7.20 ppm, at +30 °C (Fig. 3), and two sharp peaks at −30 °C (Fig. 4) where all 7- and 6-membered ring protons appear together, no signal at lower field being observed. Moreover the solution of VII in liq. SO_2, having violet color (λ_{max} at 552 nm) analogous to the acetonitrile solution, showed a spectrum of Fig. 5 clearly attributable to the cation (VII).



XIII XV XVI

Chart 2.

TABLE 2. CALCULATED TRANSITION ENERGIES OF 10,11-DIPHENYL[5.6.7]QUINARENE (XI) AND 10,11-DIPHENYL [5.6.7]QUINARENIUM ION (VII) COMPARED WITH THE OBSERVED SPECTRUM OF VII IN CHLOROFORM

Calculated					Experimental
XI			VII		VII (X=ClO_4)
ΔE (eV)	f		ΔE (eV)	f	ΔE (eV) (logε)
2.00	0.004	(y)	2.02	0.79	2.02 (4.2)
2.08	0.008	(y)	2.52	0.008	
2.09	2.96	(z)	3.10	0.57	3.40 (4.0)
3.33	0.06	(z)	3.45	0.27	
3.81	0.00	(y)	3.60	0.003	

It was concluded that both violet- and blue-colored solutions contain a single species having structure VII excluding the presumed equilibrium with XI. The absorption maximum of VII at a longer wavelength region of 630—617 nm might be due to the contribution of structure VII′ carrying a delocalized positive charge all over the molecule. Prinzbach and his co-workers observed a similar bathochromic effect[13–15] of the conjugated acids XIII and XV as compared with the corresponding cross-conjugated hydrocarbons, sesquifulvalene (XII) and calicene (XIV). Jutz and Voithenleitner[16] presented further examples of the long conjugated tropylium ion derivatives (XVI), stating that XVI (n=3) and XVI (n=4) have absorption maximum at 592 nm in chloroform (539 nm in acetonitrile) and at 646 nm in chloroform (582 nm in acetonitrile), respectively. These values are in fair agreement with the spectral characteristics of VII, if the bathochromic effect of a benzene ring is equivalent to about 1½ ethylenic links.[17]

The calculated electronic spectral data of VII are summarized in Table 2, where the calculated values for VII, rather than those for XI, are in good agreement with the observed values. The deprotonation of VII with a base such as diisopropylamine or pyridine has not been successful so far.

Experimental

Mps and bps are uncorrected. The instruments used for spectral measurements are Shimadzu IR-27-G spectrophotometer (IR), Varian Associates A-60 and HA-100 spectrometers (NMR, TMS as internal standard) and Hitachi EPS-2U spectrometer (UV).

*Preparation of 3-[*p*-(3,4-Diphenyl-1,3-cyclopentadien-1-yl)-phenyl]tropilidene (V).* *a*) To a solution of *p*-tropylphenyllithium[1] (10.0 mmol) in ether (40 ml), prepared from *p*-tropyliodobenzene (4.0 g, 13.6 mmol) and *n*-butyllithium (30.0 mmol), was added dropwise a solution of 3,4-diphenylcyclopent-2-enone (2.58 g, 11.1 mmol) in ether (100 ml) with stirring at room temperature. After being stirred for 5 hr, the mixture was hydrolyzed with 2M-H_2SO_4 and extracted with ether. The combined organic solution was washed (satd. $NaHCO_3$ soln.), dried (Na_2SO_4), and concentrated. The residual yellow semi-solid was chromatographed on an alumina column with light petroleum–benzene as an eluent. The chromatographic fractions from light petroleum–benzene (1: 1) were recrystallized from ether to give V (1.29 g, 33.6%) as yellow needles, mp 125—126 °C; ν_{max} (KBr) 3050, 2930, 1600, 1500, 1440, 1370, 1200, 1070, 1030, 912, 891, 822, 759, 697 cm^{-1}; δ (CCl_4) 7.39 (4H, s, benzene), 7.26 (5H, s, benzene), 7.15 (5H, s, benzene), 6.96 (1H, s, 5-membered ring) 6.60—6.05 (3H, m, tropyl), 5.65—5.15 (2H, m, tropyl), 3.84 (2H, s, 5-membered methylene), 2.72 (4/5H, d, J=7.0 Hz, tropyl methylene), 2.31 (6/5H, t, J=6.8 Hz, tropyl methylene); λ_{max} ($CHCl_3$) nm (log ε) 303 (4.25), 375 (4.57). Found: C, 93.59; H, 6.56%. Calcd for $C_{30}H_{24}$: C, 93.71; H, 6.29%.

b) To a solution of *p*-tropylphenylmagnesium bromide[1] (7.7 mmol) in THF (25 ml), prepared from *p*-tropylbromobenzene (2.4 g, 9.7 mmol) and Mg-ribbon (1.236 g, 9.7 mmol), was added a solution of 3,4-diphenylcyclopent-2-enone (1.96 g, 8.4 mmol) in THF (30 ml) with stirring at room temperature. After being stirred for 5 hr, the mixture was worked up as above to give V (1.19 g, 31%).

*Preparation of 4-Hydroxy-3,4-di(*p*-tolyl)-2-cyclopentenone.* To a suspension of 4,4′-dimethylbenzil (12.5 g, 51.3 mmol) in acetone (10 ml) was added 33% NaOH solution (0.5 ml) and the red solution was stirred for 30 min at room temp. After addition of another NaOH solution (33%, 1.5 ml), the mixture was refluxed for 2 hr and then poured into hot water (50 ml). The crude product (10.3 g, 72.4%) which separated was washed with ether and recrystallized from benzene to give 4-hydroxy-3,4-di(*p*-tolyl)-2-cyclopentenone as colorless needles, mp 171 °C; ν_{max} (KBr) 3440, 2920, 1680, 1590, 1515, 1410, 1333, 1267, 1212, 1183, 1060, 980, 864, 831, 818, 734 cm^{-1}; δ ($CDCl_3$) 7.25 (8H, m, benzene), 6.56 (1H, s, 5-membered ring), 3.51 (1H, s, OH), 2.94, 2.79, (each 1H, AB-q, J=19.0 Hz); λ_{max} (MeOH) nm (log ε)

399 (4.40), 220 (4.37). Found: C, 81.64; H, 6.59%. Calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52%.

*Preparation of 3,4-Di(*p*-tolyl)cyclopent-2-enone.* To a warmed mixture (50 °C) of red phosphorus (3.4 g), 58% hydriodic acid (1.8 ml) and acetic acid (30 ml) was added 4-hydroxy-3,4-di(*p*-tolyl)-2-cyclopentenone (3.2 g, 11.5 mmol). The mixture was stirred for 2 hr at 80 °C and then filtered to remove phosphorus. The filtrate was added to cooled 10% $NaHSO_3$ solution and extracted with ether. After removal of the ether, the residue was distilled *in vacuo* affording the crude product (2.32 g, 76.8%), which was recrystallized to colorless needles, mp 109 °C; ν_{max} (KBr) 2950, 1680, 1590, 1510, 1270, 1190, 935, 813 cm^{-1}; δ ($CDCl_3$) 7.45, 7.12, (each 2H, J=8.2 Hz, benzene), 7.05 (4H, s, benzene), 6.72 (1H, d, J=1.5 Hz, 5-membered ring), 4.57 (1H, ddd, J=7.3, 2.5, 1.5 Hz, benzyl), 3.10 (1H, dd, J=18.5, 7.3 Hz, methylene), 2.37 (1H, dd, 18.5, 2.5 Hz, methylene), 2.29 (3H, s, methyl), 2.25 (3H, s, methyl); λ_{max} (MeOH) nm (log ε) 295 (4.31), 220 (4.18). Found: C, 86.91; H, 7.05%. Calcd for $C_{19}H_{18}O$: C, 86.98; H, 6.91%).

*3-[*p*-(3,4-Di-*p*-tolyl-1,3-cyclopentadien-1-yl)phenyl]tropilidene (VI).* To a solution of *p*-tropylphenyllithium[1] (5.0 mmol) in ether (20 ml) was added dropwise a solution of 3,4-di(*p*-tolyl)cyclopent-2-enone (1.57 g, 6.0 mmol) in ether (80 ml) with stirring at room temperature. After being stirred for 5 hr at the same temp., the resulting mixture was worked up as for V and the residual oil was chromatographed on silica gel column with 5% benzene in *n*-hexane as an eluent. The later chromatographic fraction was recrystallized from light petroleum to give VI (0.94 g, 45.5%) as pale yellow needles, mp 156 °C; ν_{max} (KBr) 3020, 1505, 810, 764, 718 cm^{-1}; δ (CCl_4) 7.37 (4H, s, benzene), 7.17—6.81 (8H, m, tolyl), 6.97 (1H, s, 5-membered ring), 6.46—6.05 (3H, m, tropyl), 5.60—5.18 (2H, m, tropyl), 3.73 (2H, s, 5-membered methylene), 2.68 (1/5H, d, J=7.0 Hz, tropyl methylene), 2.30 (9/5H, t, J=6.8 Hz, tropyl methylene), 2.26 (3H, s, methyl), 2.32 (3H, s, methyl); λ_{max} (MeOH) nm (log ε) 370 (4.51), 298 (4.22), 275 (4.19), 238 (4.35). Found: C, 93.43; H, 6.97%. Calcd for $C_{32}H_{28}$: C, 93.16; H, 6.84%.

p-(3,4-Diphenyl-1,3-cyclopentadien-1-yl)phenyltropylium Perchlorate (VII). To a solution of tropilidene (V) (0.20 g, 0.52 mmol) in dichloromethane (9 ml) was added triphenylmethyl perchlorate (0.45 g, 1.30 mmol) with stirring. After being stirred for 3 hr, the precipitate was filtered and washed with ether to give crude VII (0.22 g, 88%). Recrystallization from acetic acid gave blue black needles, mp>300 °C; ν_{max} (KBr) 3030, 1600, 1517, 1500, 1477, 1260, 1200, 1090, 917, 829, 758, 697 cm^{-1}; δ (10% CF_3CO_2D in $CDCl_3$) 9.25—8.70 (6H, m, tropylium), 7.77 (4H, s, benzene), 7.40—7.17 (10H, m, benzene), 3.98 (2H, s, methylene); λ_{max} ($CHCl_3$) nm (log ε) 617 (4.24), 363 (4.02), 276 sh (4.16). Found: C, 74.27; H, 4.97%. Calcd for $C_{30}H_{23}ClO_4$: C, 74.58; H, 4.85%.

*p-(3,4-Di-*p*-tolyl-1,3-cyclopentadien-1-yl)phenyltropylium Perchlorate (VIII).* Tropilidene (VI) (0.30 g, 0.73 mmol) in dichloromethane (5 ml) was treated with triphenylmethyl perchlorate (0.50 g, 1.46 mmol) as for VII to give crude VIII (0.25 g, 67.3%). Recrystallization from acetic acid afforded blue black needles, mp>300 °C; ν_{max} (KBr) 3003, 1590, 1508, 1490, 1260, 1200, 1090, 917, 813, 765 cm^{-1}: δ (10% CF_3CO_2D in $CDCl_3$) 9.34—8.77 (6H, m, tropylium), 7.84 (4H, s, benzene), 7.34—6.97 (8H, m, benzene), 3.90 (2H, s, methylene), 2.37 (3H, s, methyl), 2.31 (3H, s, methyl); λ_{max} ($CHCl_3$) nm (log ε) 640 (4.32), 371 (4.16), 281 (4.27). Found: C, 75.27; H, 5.44%. Calcd for $C_{32}H_{27}ClO_4$: C, 75.21; H, 5.33%.

Reduction of VII with Lithium Aluminum Hydride. To a suspension of tropylium ion (VII: X=BF_4) (0.10 g, 0.2 mmol) in ether (8 ml) was added dropwise a solution of $LiAlH_4$ (24.5 mg, 0.64 mmol) in ether (3 ml). The solution was stirred for 2 hr at room temperature. Water was then added to decompose the excess reagent and the precipitate was filtered. The precipitate and the filtrate were separately extracted with ether, and the combined extract was evaporated. The residue (82 mg) was chromatographed on a silica gel column and eluted with benzene(3%)–hexane. Yellow needles (30 mg, 37%) obtained showed IR spectrum identical with that of V.

Reaction of VII with Ethanol in the Presence of Sodium Bicarbonate. To a suspension of VII (0.10 g, 0.21 mmol) in chloroform (30 ml) and ethanol (3 ml) was added satd. $NaHCO_3$ soln. (30 ml). The mixture was then shaken vigorously and a yellow chloroform layer was separated, washed (satd. NaCl soln.) and dried (Na_2SO_4). Evaporation of the solvent gave IX: B=OEt (80 mg, 88%) as a yellow powder, mp 108—110 °C; ν_{max} (KBr) 3021, 2857, 1597, 1502, 1441, 1372, 1200, 1109, 912, 889, 820, 757, 696 cm^{-1}; δ ($CDCl_3$) 7.45 (4H, s, benzene), 7.25 (10H, m, benzene), 7.00 (1H, s, 5-membered ring), 6.70—6.05 (m, tropyl), 5.80—5.45 (m, tropyl), 3.85 (2H, s, 5-membered methylene), 3.65 (4/5H, q, J=6.9 Hz, ethyl), 3.51 (6/5H, q, J=6.9 Hz, ethyl), 3.50 (1H, m, methine), 1.26 (6/5H, t, ethyl), 1.23 (9/5H, t, ethyl); λ_{max} ($CHCl_3$) nm (log ε) 275 sh, 290 sh, 370 (4.27).

Reaction of VIII with Ethanol in the Presence of Sodium Bicarbonate. Tropylium perchlorate(VIII) (0.20 g, 0.39 mmol) in chloroform (50 ml) and ethanol (5 ml) was treated with $NaHCO_3$ as above to give X: B=OEt (0.16 g, 90%) as a yellow powder; δ (CCl_4) 7.37 (4H, s, benzene), 7.05 (9H, m, tolyl and 5-membered ring), 6.40—5.90 and 5.80—5.30 (5H, m, tropyl), 3.75 (2H, s, methylene), 3.62 (4/5H, q, J=6.9 Hz, ethyl), 3.58 (6/5H, q, J=6.9 Hz, ethyl), 3.50 (1H, m, methine), 2.32 and 2.16 (each 3H, tolyl methyl), 2.92 (6/5H, t, J=6.9 Hz, ethyl), 2.90 (9/5H, t, J=6.9 Hz, ethyl).

Reaction of IX with Hydrogen Bromide. Dry hydrogen bromide was introduced to a solution of IX: B=OEt (80 mg, 0.186 mmol) in benzene (5 ml). The blue black precipitate was then collected by filtration, washed (with benzene) and dried *in vacuo*, affording VII: X=Br (60 mg, 70.0%). Recrystallization from acetic acid gave blue needles, mp 180 °C (decomp.). Found: C, 77.23; H, 4.99%. Calcd for $C_{30}H_{23}Br$: C, 77.75; H, 5.00%.

Reaction of IX with Hydrogen Chloride. Dry hydrogen chloride was introduced to a solution of IX: B=OEt (100 mg, 0.23 mmol) in benzene (5 ml). The reaction mixture was worked up as above to give a blue black powder of VII: X=Cl (87 mg, 87%), which was recrystallized from acetic acid to give blue black needles, mp 150 °C (decomp.). Found: C, 85.38; H, 5.27%. Calcd for $C_{30}H_{23}Cl$: C, 86.00; H, 5.53%.

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