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The Dehydrogenation of *ortho*-Tropylphenols and the Synthesis of Furano-*p*-benzoquinonetropides[1]

Tetsuo Nozoe and Kazuko Takahashi

Department of Chemistry, Faculty of Science, Tohoku University, Katahira-cho, Sendai

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The intermolecular disproportionation reaction between 2-methoxy-10*aH*-cyclohepta-[*b*]benzofuran (4) and 2-acetoxy-3-methoxyphenyltropylium ion (2) occurred upon the treatment of 2 with 2 N hydrochloric acid, thus affording 3'-methoxy-2', 2-epoxyphenyltropylium ion (5) and 3-(2-acetoxy-3-methoxyphenyl)tropilidene (6). 3*H*-Cyclohepta[*b*]benzofuran-3-one (furano-*p*-benzoquinonetropide) (25), its ethyl (30), chloro (35), acetyl (40) and hydroxy (48) derivatives were synthesized by the application of this disproportionation reaction to the dehydrogenation products of 4-tropyl, 6-ethyl-4-tropyl, 6-chloro-4-tropyl, 6-acetyl-4-tropyl resorcinol and 4-tropylphroglucinol triacetate respectively. The electronic spectra of these furano-*p*-benzoquinonetropides (25), (30), (35), and (40), in water showed their long wavelength absorption maxima at mμ (lcg ε) values of 540 (3.74), 568 (3.57), 512 (3.83) and 512 (3.51) respectively. However the spectra of these compounds in chloroform showed the peaks at mμ (log ε) values of 635 (3.03), 685 (3.61), 665 (3.56) and 600 (3.50) respectively, the peaks had shifted to wavelengths longer by 100—150 mμ than those in water. This solvent effect, the reverse of the case of *p*-benzoquinonetropides, may be interpreted in terms of an increased contribution by the polar structure to the ground state as a result of the formation of the furan ring.

It has previously been reported[2-5] that phenols and polyhydric phenols react with ethyl tropyl ether at the ortho and para positions. The dehydrogenation of para-tropylphenols led to the corresponding *p*-hydroxyphenyltropylium ions, which could then be converted to purple-colored pigments on neutralization in an aqueous sodium bicarbonate solution; the pigments formed were named *p*-benzoquinonetropide.[6,7]

In the present study the dehydrogenation of ortho-tropylphenol derivatives will be discussed. An English group[4] has recently reported the transformation of 8 to 12 and its subsequent dehydrogenation to benzofuranotropylium ions. We have already got the same result independently and, furthermore, found that the acidic hydrolysis of 2-acetoxyphenyltropylium ions gives benzofuranotropylium ions directly. This reaction is applicable for the synthesis of furano-*p*-benzoquinonetropides, which are a new tropide system.

The reaction product of 6-tropylguaiacol acetate (1)[5] with phosphorus pentachloride in carbon tetrachloride was isolated in a 62% yield as the perchlorate salt of 2. The acid hydrolysis of 2 in 2 N hydrochloric acid on a boiling water bath for 5 min gave 5 and an oily residue. The infrared spectrum of 5 did not show any band due to the carbonyl group or the hydroxy group, but it did show bands at 1099—1081 cm^{-1} (ClO_4) and 763 cm^{-1} (in-phase CH out-of plane bending of the tropylium ion).

The molecular formula of 5 was $C_{14}H_{11}O_2 \cdot ClO_4$, and a stretching band of the ether group in the furan ring appearing at 1052 cm^{-1} might be comparable to those for benzofuranotropones.[8] On the basis of the above considerations, compound 5 might be a benzofuranotropylium ion. The product 6 which was obtained at the same time was concluded to be an isomer of compound 1 with respect to the location of the saturated or unsaturated carbon atom of the tropyl group. The reaction process might be represented in chart 1, and disproportionation between 4 and 2 might have given rise to the two products 5 and 6.

1) A part of the Ph. D. Thesis of Kazuko Takahashi, Tohoku University (1963); presented at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April (1963); T. Nozoe, "Kagaku no Ryoiki," Vol. 17, No. 12, Nankodo, Tokyo (1963), p. 77.

2) T. Nozoe and K. Kitahara, *Chem. & Ind.*, **1962**, 1192; A part of the Ph. D. Thesis of Kazuo Kitahara, Tohoku University (1963).

3) R. Van Helden, A. P. ter Borg and A. F. Bickel, *Rec. Trav. Chim.*, **81**, 599 (1962); T. Nozoe, *J. Chinese Chem. Soc.*, 156 (1962).

4) P. Bladon, P. L. Pauson, G. R. Proctor and W. J. Rodger, *J. Chem. Soc.*, **1966**, 926.

5) K. Takahashi, This Bulletin, **40**, 1461 (1967).

6) T. Nozoe and K. Kitahara, to be published; presented at the 15th Annual Meeting of the Chemical Society of Japan, Kyoto, April (1962); T. Nozoe, "Kagaku no Ryoiki," Vol. 17, No. 12, Nankodo, Tokyo (1963), p. 77.

7) T. Nozoe and K. Takahashi, This Bulletin, **40**, 1473 (1967).

8) S. Seto and Y. Ikegami, *Bull. Chem. Research Inst. Non-Aqueous Solns., Tohoku Univ.*, **11**, No. 2, 1 (1962).

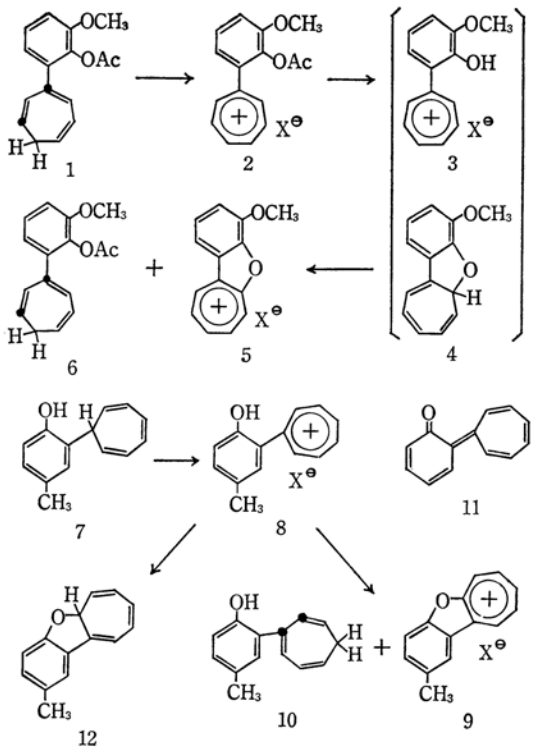

Chart 1

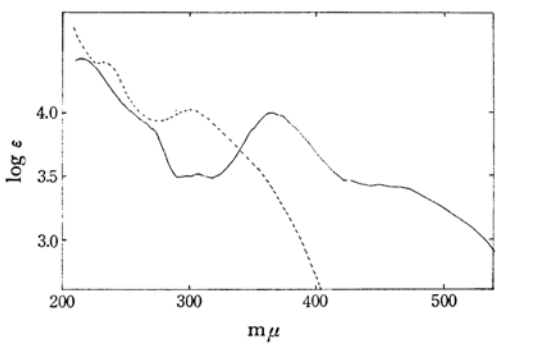

Fig. 1. UV spectra of 8 (in CH_3CN) and 9 (in MeOH).
—— 8 ---- 9

The fact that the addition of tropylium bromide in the reaction system in 2 N hydrochloric acid enhanced the formation of 5 supported the above reaction mechanism, since tropylium bromide might be regarded as a hydride acceptor in this reaction.

With the purpose of isolation of 2-hydroxyphenyltropylium ions such as 8, we caused the reaction of *p*-cresol with ethyl tropyl ether, this, followed by treatment with triphenylmethyl perchlorate in dichloromethane, formed deep orange plates, 8,[4] the structure of which was confirmed by infrared spectral measurements and the results of micro analysis. On heating in 2 N hydrochloric acid, the compound 8 immediately bear turned yellow and gave yellow needles, 9,[4] and an oily residue, 10. The infrared spectrum of 10 was quite similar to that of 7 and the infrared spectrum of 9 exhibits no hydroxyl band, showing that a furan ring was closed. The ultraviolet spectra of 8 and 9 are shown in Fig. 1. The neutralization of 8 in an aqueous sodium bicarbonate solution did not lead to *o*-benzoquinonetropide, 11, but it did produce an oily stuff; the infrared and NMR spectra indicate the formation of 12[4].

With the purpose of obtaining a pyrrole ring containing compounds from 2-aminophenyltropilidenes, 3-acetoamidophenol was treated with ethyl tropyl ether to yield the compound 13 in a 90% yield. The structure of 13 was clarified by the formation of 2-amino-4-methoxybenzoic acid on the oxidation of the methylated product. The dehydrogenation of 13 is still under consideration.

We applied this reaction to 4-tropylresorcinol,[5] expecting furano-*p*-benzoquinonetropide to be formed. For this reason, we examined the dehydrogenation reaction of the several tropylresorcinols. The acetylation of 14 with acetic anhydride yielded the diacetylated product, 15. On heating[9,10] 15 at 180—185°C for 1 hr, a viscous oily product, 16, was formed. Since the compound 16 showed absorption bands at 2857 and 2907 cm^{-1} assignable to the methylene of the tropyl group,[11] it was evident that 15 underwent thermal isomerization; the isomerization product is believed to be a mixture of 1-tropyl and 3-tropyl derivatives.[10] The dehydrogenation of 16 with phosphorus pentachloride in carbon tetrachloride, followed by the addition of chloroplatinic acid, led to the formation of 17 ($X=\frac{1}{2}PtCl_6$) in a 55% yield. The treatment of 17 with 4 N hydrochloric acid in a boiling water bath gave rise to 18 in a 23% yield and an oily residue, 19. 19 showed absorption bands at 2837 and 2872 cm^{-1}; these were almost identical with those of 16, so compounds 18 and 19 were formed by a disproportionation reaction similar to that observed for 2. The infrared spectrum of 18 showed a sharp band for the hydroxy group at 3472 cm^{-1}, a C–O stretching band for the furan ring at 1046 cm^{-1}, and a CH out-of-plane bending of the tropylium ion at 748 cm^{-1}. Furthermore, to confirm the structure, 18 was then hydrogenated to absorb 3 mol of hydrogen, giving 21. The ultraviolet spectrum of 21 was similar to that of benzofuran, and 21 gave

9) In general, substituted tropilidenes having substituents at positions other than 7 (such as 3, or 2, or 1) were dehydrogenated with phosphorus pentachloride in a better yield than were 7-substituted tropilidenes.
10) A. P. ter Borg and H. Kloosteriziel, *Rec. Trav. Chim.*, **82**, 741 (1963).
11) T. Nozoe, T. Mukai, T. Tezuka and K. Osaka, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **84**, 662 (1963).

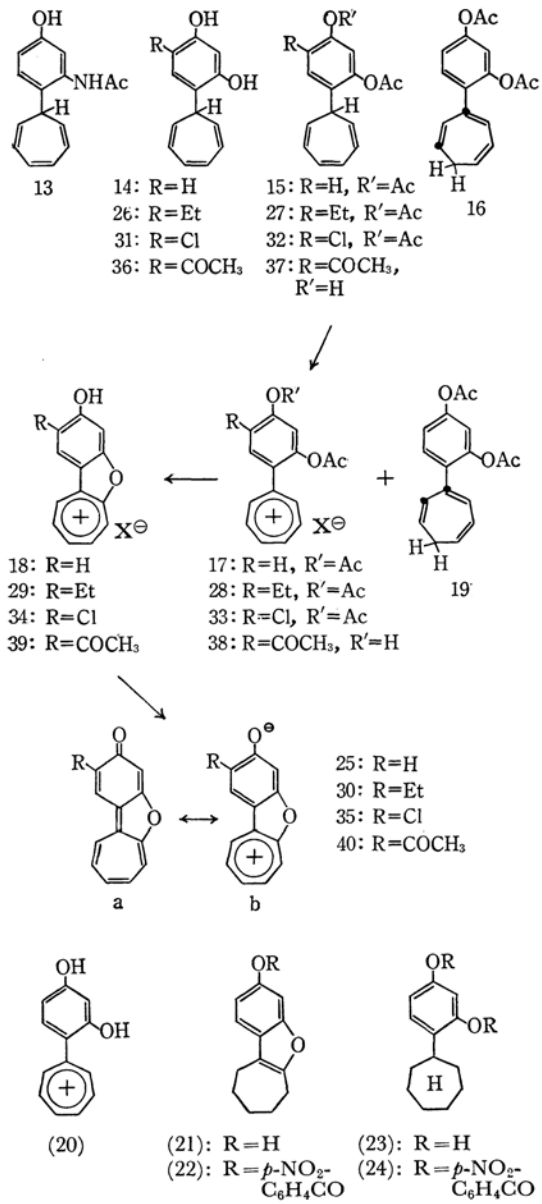

Chart 2

a mono-*p*-nitrobenzoate. On the other hand, 23 obtained by the hydrogenation of 4-tropylresorcinol gave quantitatively di-*p*-nitrobenzoate, 24. From these facts, it was confirmed that 18 was the hydroxybenzofuranotropylium ion.

When the aqueous solution of 18 was treated with sodium bicarbonate, it immediately turned purple and 25 was formed. Although the *p*-benzoquinonetropide was slightly soluble in water and separated out as black needles, furano-*p*-benzoquinonetropide, 25, did not separated out from the water layer but was extracted with chloroform to give a black solid, 25.

In a similar manner, 30, 35, and 40 were prepared from 26, 31, and 36[5] respectively by the reaction course shown in Chart 2, however, 36 resisted giving a diacetylated compound and only gave the monoacetate of 37 because of the strong hydrogen bond between acetyl carbonyl and the hydroxy group. In order to prepare *o*-benzoquinonetropide, the oxidation of 14 with silver oxide was investigated, but 25 was formed in a low yield.

The electronic spectra of 18, 29, 34, and 39 in 1 N sulfuric acid are shown in Fig. 2, in which

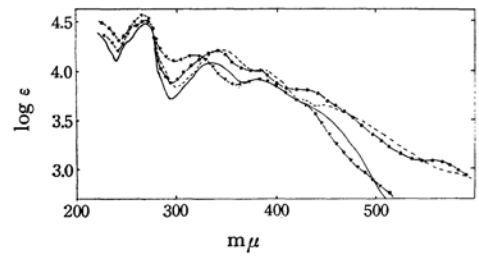

Fig. 2. Electronic spectra of 18, 29, 34 and 39 in 1 N sulfuric acid.
—— 18 ---- 29 -●- 34 -◀- 39

the spectrum of 5 is also included. In the spectra of *p*-hydroxyphenyltropylium ions, an intense absorption maximum appeared in the region from 452 to 462 mμ (log ε=4.12 to 4.14),[7] whereas the corresponding absorption appears as an inflection at wavelengths above 382 to 392 mμ (log ε=3.91 to 3.99) for furano-*p*-hydroxyphenyltropylium ions. *p*-Hydroxyphenyltropylium ions involve C_{2v} axis of symmetry, and this should result in the appearance of the absorption band at 452 to 462 mμ due to an electron transfer along this molecular axis. However, as can be seen from Fig. 2, the corresponding absorption maximum could not be observed, making it possible to support the idea of a structure with a furan ring.

The electronic spectra of 25, 30, 35, and 40 in an aqueous solution are shown in Fig. 3. All the compounds show a broad absorption maximum in the longest wavelength region which may be comparable to that observed for *p*-benzoquinonetropide in an aqueous solution.

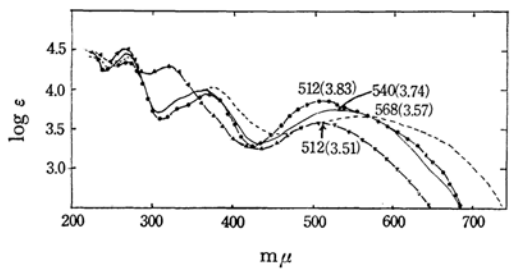

Fig. 3. Electronic spectra of 25, 30, 35 and 40 in water.
—— 25 ---- 30 -●- 35 -◀- 40

The spectra of the above four compounds were also measured in chloroform; the results are shown in Fig. 4. Compared with the spectra in water, the corresponding absorption maxima were shifted to wavelengths longer by about 100 mμ in chloroform and the solution was bright blue.

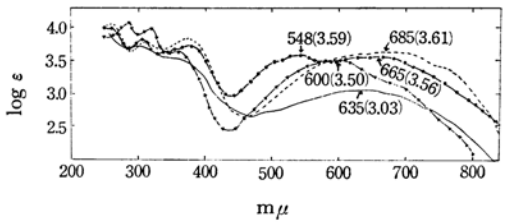

Fig. 4. Electronic spectra of 25, 30, 35 and 40 in chloroform.
—— 25 ---- 30 -●- 35 -◀- 40

This interesting solvent effect, noticed for the above four compounds, was considered to be characteristic of furano-*p*-benzoquinonetropide and related compounds. These spectroscopic results may be interpreted on the ground that, in these compounds, a polar structure makes a greater contribution in the ground state than in the excited state.[12] Namely, an ionic form, 25b, may be stabilized in the ground state to a greater extent than in the case of *p*-benzoquinonetropide. This seems to be quite likely, since the formation of a furan ring augments molecular coplanality and a larger electronegative substituent, such as an oxygen function attached directly to the seven-membered ring, may favor the ionic structure. Furthermore, the aromaticity of a furan ring may be increased in the ionic structure. The above-mentioned considerations explain the higher solubility in water and the higher melting points for these compounds than those for *p*-benzoquinonetropides.

These compounds were also quite stable in an aqueous or chloroform solution, they could be kept unchanged for several months when these solutions were stored in a cool place.

An application of the ring-closure reaction of tropylresorcinols to tropylphroroglucinol may provide a synthesis of a noble tropide system containing two furan rings such as 49. Following up the thermal isomerization of the tropyl group[9,10], in purified tropylphroroglucinol triacetate[5] at 185°C for 1 hr, the product was subjected to dehydrogenation with phosphorus pentachloride, thus forming compound 43 ($X=\frac{1}{2}PtCl_6$) in a yield of 37%. In general, the yields of the dehydrogenation products with phosphorus pentachloride decreased with the number of acetoxy groups on

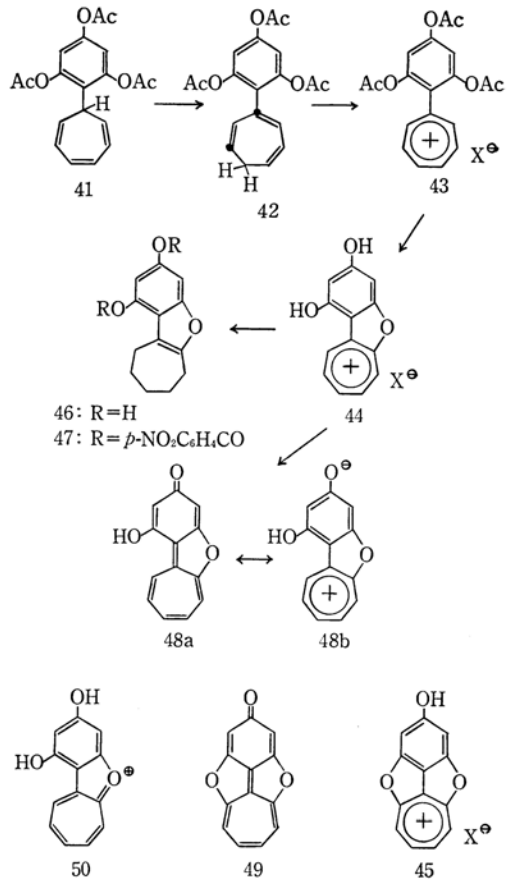

Chart 3

the phenolic nucleus. 43 also underwent acid hydrolysis when heated in hydrochloric acid, thus producing chloroplatinate salt. From the following data, the structure of this product may be represented by 44 rather than 45, the infrared spectrum being closely similar to that of 18 apart from the wavelength region where the hydroxy-group and out-of-plane absorptions appear. 44 was hydrogenated over platinum oxide to 46 after the consumption of 3 mol of hydrogen, and treated with *p*-nitrobenzoyl chloride, thus giving diacyl derivative, 47. These chemical data support the structure of 44 for the hydrolysis product of 43.

The measurement of the NMR spectrum led to the same conclusion. The NMR spectrum of 44 (X=Cl) in trifluoroacetic acid is reproduced in Fig. 5d. To facilitate signal assignments, the spectra of the other, related compounds are included in Figs. 5a to 5c. In Fig. 5a, phenol ring protons appear as a pair of doublets at 2.71_τ, 2.03_τ, while seven-membered-ring protons are also in the lower field, at 0.79_τ and 1.10_τ, with an intensity ratio of 1 : 2. Two protons at the position ortho to the phenol substituent are influenced by the ring-current effect, and the signal is shifted to a lower

12) N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1945); E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3261 (1958).

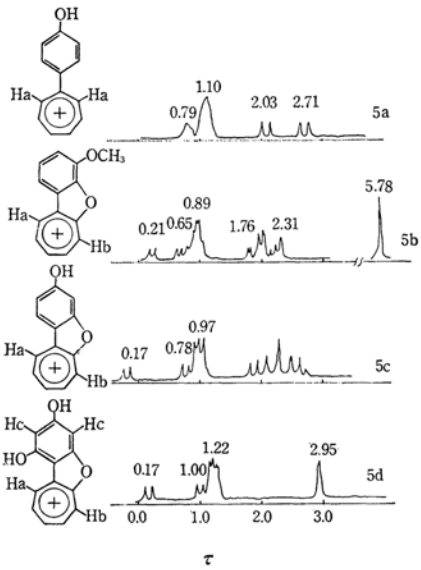

Fig. 5. NMR spectra of benzofuranotropylium ions.

field, appearing at 0.79_τ. As is clear from Fig. 5b, the NMR spectrum of 5 shows a methyl signal at 5.78_τ, ring proton signal between 1.76 and 2.31_τ, and peaks due to the tropylium-ion part at 0.21, 0.65, and 0.89_τ, with a ratio of 1 : 1 : 3. A low-field peak at 0.21_τ assignable to Hb may result from an anisotropic effect due to the oxygen atom of the furan ring. In a similar manner, signals at -0.17_τ and 0.78_τ of the NMR spectrum for 18 shown in Fig. 5c may be assigned to Hb and Ha respectively. A comparison of the spectrum shown in 5d with those discussed above makes it possible to assign the signal at 0.17_τ to Hb, and that at 1.00_τ to Ha. The fact that the ratio between the area intensities of the signal at 2.95_τ (Hc) and the absorption peak at $1.22—1.00_\tau$ and that at 0.17_τ is found to be 2 : 4 : 1 indicates the presence of five hydrogen atoms on the seven-membered ring. Although the signal peak at 2.95_τ is indicative of the structure of 45 rather than 44, it seems more likely to assume that two different protons appear formally in the same frequency field.

The contribution of the resonance form 50 increases the electron density at the carbon atoms of the seven-membered ring, this must be responsible for the reluctance of the seven-membered ring to form the compound 45 when attached by the second hydroxy group.

The treatment of 44 with a sodium bicarbonate solution made the aqueous solution in deep red. The coloring of the solution strongly indicates the formation of the compound 48, which, however, could not be isolated as crystals because of its higher solubility in water and its poor solubility in chloroform. The electronic spectra in 1 N sulfuric acid, in water, and in methanol are shown in Fig. 6. However, the electronic spectrum in chloroform could not be measured because of the poor solubility. The compound 48 may be present as a polar structure, 48b.

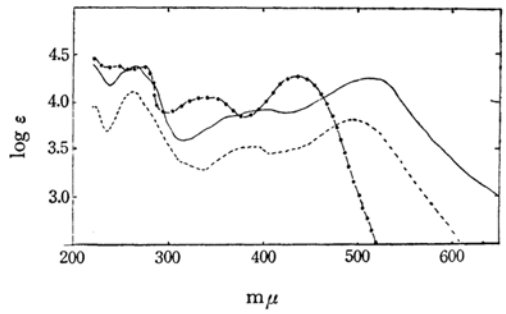

Fig. 6. Electronic spectra of 48.
—— in methanol ---- in water
-●- in 1 N sulfuric acid

Experimental

2-Hydroxy-5-methylphenyltropylium Ion (8). To a suspension of triphenylmethyl perchlorate (3.43 g) in methylene chloride (80 m*l*), a solution of 4-methyl-2-tropylphenol (7) (1.982 g) in methylene chloride (8.5 m*l*) was added with stirring. After the mixture had stood in an ice bath overnight, crystals were filtered out and washed with carbon tetrachloride to give orange plates, 8 (X=ClO_4) (2.38 g; 70.5%; mp 175°C with decomp.)

Found: C, 56.00; H, 4.22%. Calcd for $C_{14}H_{13}O_5Cl$: C, 56.67; H, 4.41%.

IR in the KBr disk: 3333, 3021, 1608, 1531, 1508, 1488, 1414, 1370, 1295, 1267, 1242, 1138, 1106, 1063, 825, 763, and 720 cm^{-1}.

The Disproportionation Reaction of the 2-Hydroxy-5-methylphenyltropylium Ion (8). Into hot 2 N hydrochloric acid (30 m*l*), 2-hydroxy-5methylphenyltropylium perchlorate (1 g) was gradually added, after which heating on a water bath was continued for an additional 10 min. The solution turned yellow, and a brown oily residue was separated out. The hot reaction mixture was washed with chloroform, hot-filtered, and cooled in an ice bath to afford yellow needles. On washing with chloroform, these afforded 9 (0.232 g; mp 193—194°C).

Found: C, 56.47; H, 3.97%. Calcd for $C_{14}H_{11}O_5Cl$: C, 57.06; H, 3.76%.

IR in the KBr disk: 3058, 2994, 1623, 1511, 1441, 1318, 1296, 1267, 1183, 1083, 884, 860, 814, 775, and 751 cm^{-1}.

The chloroform washing was shaken with aqueous sodium bicarbonate and then with water, dried, and evaporated up to an oil which was chromatographed in benzene on alumina. The infrared spectrum of the oil was identical with that of 7, except in the 700—800 cm^{-1} region.

IR in neat: 3534, 3021, 1605, 1495, 1471, 1431, 1328, 1277, 1192, 872, 808, 773, 755, and 708 cm^{-1}.

The Attempted Synthesis of Methyl-*o*-benzoquinonetropide. 2 - Hydroxy - 5 - methylphenyltropylium perchlorate (0.5 g) was shaken vigorously with

an aqueous sodium bicarbonate solution (30 m*l*), but the reaction mixture turned brown. The mixture was extracted with chloroform, and the extract was dried and evaporated up to an brown oil, which was then distilled *in vacuo* to give a pale yellow oil (12) (0.23 g; 69%; bp 125—135°C/0.1 mmHg).

IR in neat: 3030, 2915, 2857, 1600, 1565, 1470, 1429, 1385, 1330, 1279, 1242, 1227, 1200, 1190, 1157, 1121, 1100, 866, 797, 779, 754, 739, 704, and 675 cm^{-1}.

The Tropylation of 3-Acetylaminophenol. To a mixture of 3-acetylaminophenol (3 g) and ethyl tropyl ether (2.71 g), tropylium bromide (a trace) was added. The resulting mixture was heated for 20—30 min on a water bath. On cooling, crystals were filtered out, washed with water, and recrystallized from methanol to give pale yellow prisms, 13 (4.01 g; 90%; mp 186—188°C).

Found: C, 74.65; H, 5.99; N, 5.55%. Calcd for $C_{15}H_{15}O_2N$: C, 74.66; H, 6.27; N, 5.81%.

IR in the KBr disk: 3401, 3175, 3003, 1639, 1608, 1543, 1418, 1389, 1299, 1269, 1233, 1185, 1110, 1021, 973, 964, 880, 870, 812, 803, 756, and 709 cm^{-1}.

The Methylation of 13. To a solution of potassium hydroxide (1.87 g) in water (10 m*l*), 13 (500 mg) and dimethyl sulfate (1.68 g) were added with stirring. Stirring was continued for 2 hr, and then the separated crystals were recrystallized from methanol to give colorless prisms, 3-acetylamino-4-tropylphenol methyl ether (470 mg; 83%; mp 154—156°C).

Found: C, 75.51; H, 6.55; N, 5.18%. Calcd for $C_{16}H_{17}O_2N$: C, 75.27; H, 6.71; N, 5.49%.

IR in the KBr disk: 3226, 1967, 1637, 1597, 1538, 1506, 1445, 1404, 1387, 1304, 1266, 1179, 1033, 826, 753, 745, and 701 cm^{-1}.

The Oxidation of 13. To a mixture of 3-acetoamido-4-tropylphenol methyl ether (700 mg) and hot water (40 m*l*), magnesium sulfate (2.66 g) and then a solution of potassium permanganate (3.47 g) in water (20 m*l*) were added. After stirring for 5 hr, an insoluble material was filtered off and the filtrate was washed with chloroform, acidified with 2 N hydrochloric acid, and extracted with ethyl acetate to give yellow crystals (436 mg; 76%). A mixture of the crystals, 48% hydrobromic acid (0.5 m*l*), and acetic acid (2 m*l*) was refluxed for 10 min. After the removal of the acetic acid by evaporation, water (20 m*l*) was added and the resulting mixture was cooled in an ice-water bath to give crystals (286 mg; 82%). Recrystallization from water afforded pale yellow needles (mp 164—166°C), whose infrared spectrum was identical with that of 4-methoxy-2-aminobenzoic acid.

The Acetylation of 4-Tropylresorcinol. A mixture of 4-tropylresorcinol (1.8 g) and acetic anhydride (5 m*l*) was refluxed for 1 hr, thus affording crystals (2.5 g; 97%); recrystallization from methanol afforded colorless prisms, 15 (mp 80—81°C).

Found: C, 71.96; H, 5.78%. Calcd for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67%.

IR in Nujol: 1767, 1610, 1580, 1198, 1026, 974, 907, 877, 821, 752, 734, and 711 cm^{-1}.

The Acetylation of 4-Ethyl-6-tropylresorcinol (26). 26 (3 g) was treated with acetyl chloride (4 m*l*) in pyridine (5 m*l*). The oily product (4.29 g) was chromatographed in cyclohexane on alumina, and the crystalline product was recrystallized from methanol to give colorless prisms, 27 (mp 77°C).

Found: C, 73.49; H, 6.32%. Calcd for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45%.

IR in neat: 2967, 1779, 1493, 1458, 1439, 1376, 1196, 1087, 1033, 976, 904, 877, 866, 824, 752, and 711 cm^{-1}.

The Acetylation of Tropylresacetophenone (36). A mixture of 36 (7.16 g) and acetic anhydride (15.1 g) was refluxed for 1 hr, the crystals afforded on cooling (7.03 g; 83%) were recrystallized from methanol to give colorless prisms, 37 (mp 137—138°C).

Found: C, 71.72; H, 5.24%. Calcd for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67%.

IR in Nujol: 1754, 1626, 1595, 1486, 1412, 1359, 1316, 1247, 1198, 1176, 1126, 1047, 962, 928, 893, 855, 816, 752, and 711 cm^{-1}.

The Thermal Isomerization of 15. When 4-tropylresorcinol diacetate (15) (547 mg) was heated for 1 hr at 180—185°C, a viscous oil 16 was obtained.

IR in neat: 3058, 2907, 2857, 1776, 1613, 1575, 1460, 1370, 1205, 1160, 1026, 903, 880, 735, and 714 cm^{-1}.

The Thermal Isomerization of 41. 41 (600 mg) was kept at 185°C for 1 hr to give a viscous oil, 42 (598 mg).

IR in neat: 3049, 2890, 2841, 1792, 1779, 1623, 1580, 1488, 1429, 1372, 1311, 1225, 1176, 1124, 1050, 1026, 901, 838, 769, 741, 717, and 675 cm^{-1}.

1, 16, 27, 32, 37, and 42 were all dehydrogenated in a similar manner. The preparation of 2 is typical and will be described in detail.

2-Acetoxy-3-methoxyphenyltropylium Ion (2). To a suspension of phosphorus pentachloride (5.06 g) in carbon tetrachloride (90 m*l*), a solution of 2-acetoxy-3-methoxyphenyltropilidene (2.5 g) in carbon tetrachloride (10 m*l*) was added with stirring. The mixture was stirred for 4 hr and then allowed to stand overnight, after which the precipitates were filtered out, dried, and poured into ice water (15 m*l*). The water solution was filtered, the filtrate was washed with chloroform, and then 60% perchloric acid (1.5 m*l*) was added to the water layer, which thus afforded crystals (2.15 g; 62%). On recrystallization from water, these crystals afforded orange needles, 2 (X=ClO_4; mp 110—115°C).

Found: C, 53.95; H, 4.33%. Calcd for $C_{16}H_{15}O_7Cl$: C, 54.16; H, 4.26%.

IR in Nujol: 1761, 1435, 1319, 1282, 1189, 1090, 1010, 786, 762, 747, and 736 cm^{-1}.

Chloroplatinate of 17: 55%, yellow needles, mp 180°C with decomp.

Found: C, 42.06; H, 3.11; Pt, 19.55%. Calcd for $C_{17}H_{15}O_4 \cdot \frac{1}{2}PtCl_6$: C, 41.90; H, 3.10; Pt, 20.02%.

IR in Nujol: 1770, 1610, 1490, 1445, 1190, 1149, 1042, 1028, 901, 823, 770, 760, and 730 cm^{-1}.

Chloroplatinate of 28: 31.8%, yellow needles, mp 195°C with decomp.

Found: C, 44.41; H, 3.44; Pt, 19.19%. Calcd for $C_{19}H_{19}O_4 \cdot \frac{1}{2}PtCl_6$: C, 44.30; H, 3.72; Pt, 18.93%.

IR in Nujol: 1754, 1176, 1152, 1038, 1016, 871, and 731 cm^{-1}.

Chloroplatinate of 33: 15.8%, yellow needles, mp 217°C.

Found: C, 39.05; H, 2.56; Pt, 18.96%. Calcd for $C_{17}H_{14}O_4Cl \cdot \frac{1}{2}PtCl_6$: C, 39.15; H, 2.70; Pt, 18.70%.

IR in Nujol: 1779, 1600, 1176, 1045, 1017, 868, and

730 cm^{-1}.

Chloroplatinate of 38: 7.8%, yellow needles, mp 200°C.

Found: C, 40.20; H, 3.22; Pt, 20.59%. Calcd for $C_{17}H_{15}O_4 \cdot \frac{1}{2}PtCl_6$: C, 41.90; H, 3.10; Pt, 20.02%.

IR in Nujol: 1767, 1262, 1597, 1259, 1181, 1134, 1063, and 1013 cm^{-1}.

Chloroplatinate of 43: 36.5%, yellow needles, mp 197°C with decomp.

Found: C, 41.64; H, 3.16; Pt, 17.61%. Calcd for $C_{19}H_{17}O_6 \cdot \frac{1}{2}PtCl_6$: C, 41.84; H, 3.14; Pt, 17.90%.

IR in Nujol: 1776, 1764, 1608, 1441, 1196, 1186, 1164, 1125, 1050, 1031, 1020, 916, and 745 cm^{-1}.

The Hydrolysis of the 2-Acetoxy-3-methoxyphenyltropylium Ion (2). *a) With 2 N Hydrochloric Acid.* To 2 N hydrochloric acid (7 m*l*), heated on a water bath, 2 (X=ClO_4; 200 mg) was added, and the mixture was heated for 15 min on a water bath. When the mixture was cooled to room temperature, yellow needles and a brown oil were afforded. The crystals were filtered off, washed with chloroform, and recrystallized from water to give 5 (X=ClO_4; 48 mg; 27.1%; mp 200°C).

Found: C, 54.36; H, 3.72%. Calcd for $C_{14}H_{11}O_6Cl$: C, 54.11; H, 3.57%.

IR in Nujol: C, 1631, 1605, 1517, 1445, 1427, 1307, 1285, 1090, 1052, 988, 883, 838, 799, 763, and 745 cm^{-1}.

The mother liquor was extracted with chloroform. The chloroform extract and washing were washed with aqueous sodium bicarbonate and next with water, dried, and evaporated to give an oil, which was then chromatographed in cyclohexane on alumina to give a yellow oil (6).

IR in neat: 3040, 2950, 1770, 1608, 1582, 1471, 1443, 1370, 1318, 1280, 1215, 1193, 1176, 1105, 1087, 1026, 1009, 909, 848, 823, 781, 736, and 707 cm^{-1}.

b) With 2 N Hydrochloric Acid Containing Tropylium Bromide. To a hot solution of tropylium bromide (30 mg) in 2 N hydrochloric acid (4 m*l*), 2 (200 mg) was gradually added. After being heated for an additional 7 min, the reaction mixture was hot-filtered. The filtrate was cooled in an ice-water bath to afford crystals; on washing with chloroform, these afforded yellow needles, 5 (81 mg; 45.7%).

17, 28, 33, and 38 were all hydrolyzed in a similar manner. The preparation of 18 is typical and will be described in detail.

The Hydrolysis of the 2, 4-Diacetoxyphenyltropylium Ion (17). A mixture of 4 N hydrochloric acid (7 m*l*) and a 20% aqueous solution of chloroplatinic acid (3 drops) was heated on a water bath. To the mixture, 17 (X=$\frac{1}{2}PtCl_6$; 80 mg) was gradually added, after which heating was continued for an additional 10 min. The hot reaction mixture was then filtered, 20% aqueous chloroplatinic acid (4 drops) was added, and the mixture was cooled to room temperature, thus affording orange needles; these needles were filtered and washed with acetone to give 18 (14.85 mg; 23.0%; mp 280°C). 18 was dried *in vacuo* (1.0 mmHg) at 110°C for 5 hr to get an analytical sample.

Found: C, 39.08; H, 2.41; Pt, 24.03%. Calcd for $C_{13}H_9O_2 \cdot \frac{1}{2}PtCl_6$; C, 38.92: H, 2.26; Pt, 24.33%.

IR in Nujol: 3472, 1629, 1495, 1429, 1355, 1299, 1253, 1190, 1046, 789, 748, and 709 cm^{-1}.

18 (X=Cl) could be prepared in the following manner: a mixture of phosphorus pentachloride (5.43 g), 16 (2.47 g), and carbon tetrachloride (100 m*l*) was treated as above to afford the double salt of 17 (*ca.* 3.34 g). This was gradually added to hot 2 N hydrochloric acid (7.5 m*l*), a separated black tar was removed by decantation, and the water layer was washed with chloroform while warm and then cooled in an ice-water bath to afford red needles, 18 (X=Cl; 238 mg; 20.15%). The chloroform washing was shaken with water, dried, and chromatographed in benzene on alumina to give an oil, 19, which closely resembled 16 in infrared spectrum.

IR in neat: 3024, 2872, 2837, 1770, 1595, 1563, 1449, 1425, 1364, 1190, 1022, 901, 877, 787, 735, and 712 cm^{-1}.

Chloroplatinate of 29: 30%, orange needles, mp > 280°C.

Found: C, 41.92; H, 3.13; Pt, 22.55%. Calcd for $C_{15}H_{13}O_2 \cdot \frac{1}{2}PtCl_6$: C, 41.98, H, 3.05; Pt, 22.74%.

IR in Nujol: 1623, 1603, 1431, 1267, 1321, 1269, 1252, 1190, 1041, 762, and 752 cm^{-1}.

Chloride of 29: 25%, orange needles.

Chloroplatinate of 34: 45%, red needles, mp>290°C.

Found: C, 36.00; H, 2.12; Pt, 22.51%. Calcd for $C_{13}H_8O_2Cl \cdot \frac{1}{2}PtCl_6$: C, 35.86; H, 1.85; Pt, 22.40%.

IR in Nujol: 1626, 1506, 1490, 1429, 1339, 1305, 1282, 1188, 1050, 1000, 831, 818, 773, and 754 cm^{-1}.

Chloroplatinate of 39; orange needles, mp>290°C.

Found: C, 39.98; H, 2.98; Pt, 21.38%. Calcd for $C_{15}H_{13}O_3 \cdot \frac{1}{2}PtCl_6$: C, 40.47; H, 2.92; Pt, 21.92%.

IR in Nujol: 1658, 1618, 1435, 1364, 1312, 1277, 1182, 1060, and 752 cm^{-1}.

The Hydrolysis of the 2, 4, 6-Triacetoxyphenyltropylium Ion (43). To a hot mixture of 4 N hydrochloric acid (25 m*l*) and 20% chloroplatinic acid (0.9 m*l*), 43 (282 mg) was gradually added. The mixture was boiled for a few minutes and then hot-filtered through a glass filter to remove brown precipitates. The filtrate was cooled in an ice bath to give orange needles, which were collected by filtration. The filtrate was placed back with the above brown precipitates, and the whole was boiled again to extract additional soluble materials. This process was repeated three times, and the orange needles (44) thus obtained were recrystallized from 2 N hydrochloric acid-20% chloroplatinic acid (5 : 1), (111 mg; mp>315°C).

Found: C, 37.96; H, 2.58; Pt, 22.88%. Calcd for $C_{13}H_9O_3 \cdot \frac{1}{2}PtCl_6$: C, 37.44; H, 2.18; Pt, 23.38%.

The double salt of 43 with phosphorus pentachloride was hydrolyzed as above, using 2 N hydrochloric acid, to 44 (X=Cl) in only a 16.8% yield, but the use of 2 N hydrochloric acid containing tropylium bromide gave 44 (X=Cl) in a 43.5% yield.

Furano-*p*-benzoquinonetropide (25). 18 (X=Cl; 130 mg) was dissolved in hot water (4 m*l*), after which an insoluble matter was hot-filtered. The filtrate was cooled to *ca.* 35—37°C and added, drop by drop, into 5% aqueous sodium bicarbonate solution (1 m*l*) with stirring, whereon the reaction mixture immediately turned deep purple. This was extracted with chloroform, and the extract was washed with water, dried, and evaporated up at room temperature to afford black-purple needles, 25 (mp 165°C).

Found: C, 78.01; H, 4.60%. Calcd for $C_{13}H_8O_2$: C, 79.58; H, 4.11%.

IR in Nujol: 1626, 1466, 1299, 1242, 1205, 1042,

781, and 740 cm^{-1}.

29 (X=Cl), 34 ($X=\frac{1}{2}PtCl_6$), 39 ($X=\frac{1}{2}PtCl_6$) and 44 (X=Cl) were all treated as above with a 5% aqueous sodium bicarbonate solution; they gave deep violet or red solutions of 30, 35, 40, and 48 respectively.

The Catalytic Hydrogenation of the 3-Hydroxybenzofuranotropylium Ion (18). When a solution of 18 (X=Cl; 194 mg) in acetic acid was hydrogenated over a platinum oxide catalyst (8 mg) at room temperature, 3 equiv. of hydrogen (50.8 m*l*) were taken up. The catalyst was filtered, and the acetic acid was removed by evaporation to give colorless needles, 21 (155 mg; 92.1%; mp 136°C) after recrystallization from benzene.

Found: C, 77.49; H, 6.78%. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98%.

IR in Nujol: 3390, 1587, 1361, 1294, 1266, 1230, 1178, 1093, 1041, 1028, 777, and 735 cm^{-1}.

UV: λ_{max}^{MeOH} mμ: 255, 260, 282, 291.

The Catalytic Hydrogenation of 4-Tropylresorcinol (14). A mixture of 14 (196 mg), acetic acid (10 m*l*) and platinum oxide (66 mg) was hydrogenated. Three equivalents of hydrogen (6 m*l*) were taken up to give a colorless oil, 23 (196 mg; 97.4%).

IR in neat: 3448, 2907, 1608, 1587, 1473, 1460, 1351, 1284, 1250, 1166, 1016, 980, 782, 726, and 678 cm^{-1}.

The Catalytic Hydrogenation of the 3, 5-Dihydroxybenzofuranotropylium Ion (44). When a solution of 44 (X=Cl; 201.7 mg) in acetic acid (130 m*l*) was hydrogenated over platinum oxide (8 mg) at room temperature, 3 equiv. of hydrogen (66 m*l*) were taken up to afford a colorless oil, 46 (157 mg).

IR in neat: 3390, 2924, 1712, 1692, 1639, 1515, 1449, 1370, 1290, 1235, 1176, 1124, 1064, 1036, 995, 962, 929, 820, and 756 cm^{-1}.

The Acylation of 21. To a solution of 21 (132 mg) in pyridine (1.7 m*l*), *p*-nitrobenzoyl chloride (266 mg) was added, after which the mixture was kept at 120°C for 20 min. The pyridine was then evaporated, and water was added to the residue. After the solution had stood overnight, colorless needles, 22 were filtered out and recrystallized from methanol (183 mg; 80%; mp 128—131°C).

Found: C, 68.87; H, 4.40; N, 3.93%. Calcd for $C_{20}H_{17}O_5N$: C, 68.37; H, 4.88; N, 3.99%.

IR in Nujol: 1739, 1520, 1439, 1346, 1264, 1233, 1166, 1086, 1012, 848, 783, 742, and 722 cm^{-1}.

The Acylation of 4-Cycloheptylresorcinol (23). A solution of 23 (196 mg) in pyridine (1.5 m*l*) was treated with *p*-nitrobenzoyl chloride (370 mg) to give colorless prisms, 24 and then recrystallized from acetone (392 mg; 82% mp 228°C).

Found: C, 64.51; H, 4.70; N, 5.33%. Calcd for $C_{27}H_{24}O_8N_2$: C, 64.28; H, 4.80; N, 5.55%.

IR in Nujol: 1739, 1587, 1531, 1350, 1259, 1220, 1163, 1098, 1087, 1009, 870, 848, 779, and 715 cm^{-1}.

The Acylation of 46. A solution of 46 (157 mg) in pyridine (2.5 m*l*) was treated with *p*-nitrobenzoyl chloride (431 mg) as above, and the crystals thus obtained were recrystallized from methanol to give pale yellow needles, 47 (462 mg; mp 110°C).

Found: C, 63.01; H, 3.68; N, 5.29%. Calcd for $C_{27}H_{20}O_9N_2$: C, 62.79; H, 3.90; N, 5.42%.

IR in Nujol: 1739, 1600, 1524, 1346, 1258, 1121, 1087, 1062, 1008, 869, 851, and 714 cm^{-1}.

The Oxidation of 4-Tropylresorcinol (14) with Silver Oxide. A suspension of thermally-isomerized 4-tropylresorcinol (14) (at 190°C for 1 hr), anhydrous silver oxide (3.41 g), and anhydrous magnesium sulfate (1 g) in ether was stirred for 7 hr. The reaction mixture was then filtered, the filtrate was evaporated, and the oily residue (2.69 g) was heated with 20% chloroplatinic acid. The water layer was cooled in an ice bath to give orange needles (10 mg). Their infrared spectrum was identical with that of 18.

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