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The Synthesis of Hydroxy- and Methoxy-derivatives of *p*-Benzoquinonetropides¹⁾

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2-Methoxy- (10), 2-hydroxy- (15), and 2,6-dimethoxy- (20) *p*-benzoquinonetropide were synthesized by the dehydrogenation of tropyliated guaiacol, catechol, and pyrogallol dimethyl ether respectively. The electronic spectra of 10, 15, and 20 in water showed their long wavelength absorption maxima at 550—570 m μ . However, the spectra of these compounds in chloroform showed that the peaks had shifted to wavelengths shorter by 38—60 m μ than those in water. A solvent effect of this type can be understood as resulting from a transition to an excited state that is more polar than the ground state.

In 1962, Nozoe and Kitahara found a purple pigment, 5 to be formed on the neutralization with sodium bicarbonate of the *p*-hydroxy-phenyl tropylium ion (4) prepared by the dehydrogenation of 4-tropylphenol (1),²⁾ they named this pigment *p*-benzoquinonetropide.³⁾ At the same time, the 2,6-dimethyl derivative of 5 was synthesized by a Dutch group,⁴⁾ who reported that the product was so labile that no elemental analysis could be successfully made. A British group⁵⁾ recently reported failure in attempts to perform an elemental analysis of the compound 5 and to obtain the

hydroxy or methoxy derivatives (15 or 10) as more stable forms than 5. Jutz⁶⁾ observed a violet-red color by dissolving 4 in a buffer solution of pH 6—7. However, these previous papers did not report on analytically pure samples. Y. Kitahara and M. Funamizu synthesized anthraquinonetropide.⁷⁾

In our laboratory it was found that the compound 5 contained a half molecule of the water of crystallization and that its absorption spectrum varied with the solvent used.⁸⁾

In this paper we will report some information concerning the lability of 5 and the absorption spectra of the related compounds, 10, 15 and 20 which were obtained by the dehydrogenation of tropyliated guaiacol, catechol, and pyrogallol dimethyl ether respectively.⁸⁾

As was reported in the preceding paper⁸⁾ the dehydrogenation of unsubstituted tropyliphenol (1) with phosphorus pentachloride gave the *p*-hydroxyphenyltropylium ion (4) in a poor yield, together with much black slurry. However, the

1) The Ph. D. Thesis by 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), pp. 77, 78.

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

3) T. Nozoe, *J. Chinese Chem. Soc.*, **1962**, 156; T. Nozoe and K. Kitahara, 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), pp. 77, 78, 13, 14; Ph. D. Thesis of Kazuo Kitahara, Tohoku University (1963).

4) R. Van Helden, A. P. ter Borg and A. F. Bickel, *Rec. Trav. Chim.*, **81**, 599 (1962).

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

6) C. Jutz and F. Voithenleitner, *Chem. Ber.*, **97**, 31 (1964).

7) Y. Kitahara and M. Funamizu, presented at the 15th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1962.

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

dehydrogenation of compound 1 with triphenylmethyl salt⁹⁾ in dichloromethane afforded the compound 4 in a better yield; also, when the hydroxy group of 1 was blocked with a methyl or acetyl group, the corresponding methoxy- and acetoxy-phenyltropylium ions were obtained as the reaction products of the dehydrogenation with phosphorus pentachloride. The methoxyphenyltropylium ion (3) (R=Me) was quite stable against hydrolysis reaction, remaining almost intact after being heated in a 48% hydrobromic acid solution for more than 48 hr, since it has an electron-withdrawing group (tropylium ion) at the position para to the methoxy group. On the other hand, the acetoxy derivative 3 (R=Ac) was easily hydrolyzed on heating in 2N hydrochloric acid to form 4. For economic reasons and because of the greater availability of the starting materials in a pure form, we used dehydrogenation with acetylated tropyphenols throughout the present study.

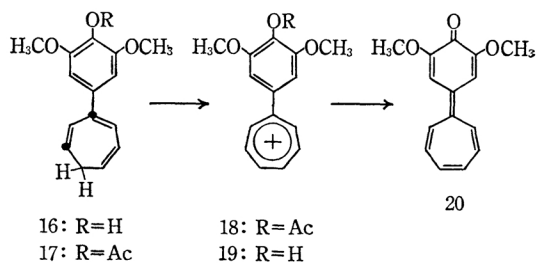
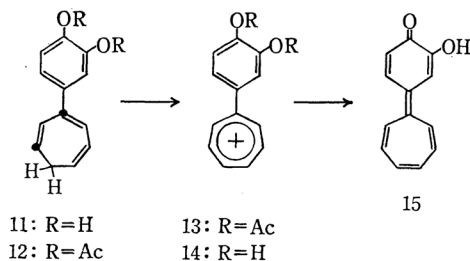
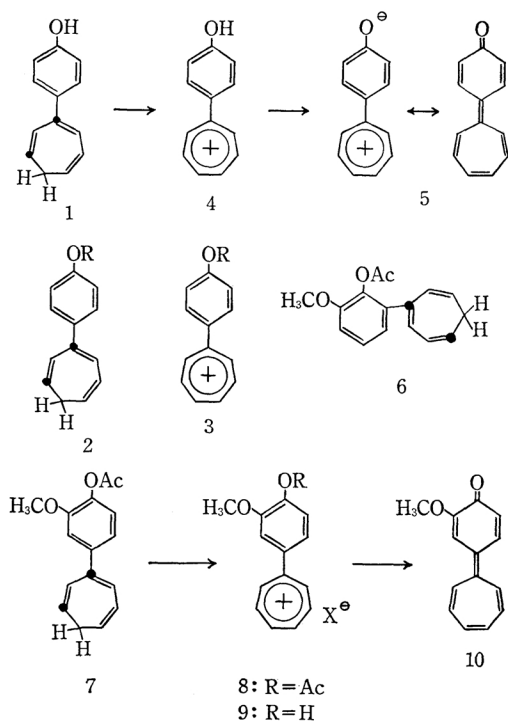
A mixture of 4- and 6-tropylguaiacol,⁸⁾ a tropylation product of guaiacol, was acetylated with acetic anhydride to give 7 and 6 separately. 7 showed a carbonyl band at 1733 cm⁻¹ an out-of-plane band of the adjacent 2 H at 826 cm⁻¹, and broad bands of the troyl group at 762 and 734 cm⁻¹. On the other hand, 6 showed an adjacent 3 H band at 782 cm⁻¹, so it is clear that 7 and 6 were 5- and 3-tropylguaiacol acetate respectively.

Since the isomerization of the troyl group of

these compounds does not proceed rapidly during the acetylation, the troylphenol acetates in this paper are mixtures with almost the same troyl-isomer ratio as the corresponding troylphenols or methyl ethers mentioned in the preceding paper.⁸⁾

7 was treated with two mole equiv. of phosphorus pentachloride and then dehydrogenated to 8 in a good yield. 8 was also obtained in a 44% yield by the dehydrogenation of 7 with bromine. 8 showed an acetyl carbonyl band at 1770 cm⁻¹ and, in-phase, a CH out-of-plane bending band at 760 cm⁻¹ the latter band being the typical one for aryltropylium ions. The dehydrogenation of 6 will be reported in the next paper.¹⁰⁾ To get the 4-hydroxyphenyltropylium ion (9), 8 was added to hot 2N hydrochloric acid and quantitatively hydrolyzed to the perchlorate of 9. While the perchlorate of 9 was sparingly soluble in water, the chloride was more easily soluble in water. Methoxy derivative 10 was obtained in a pure form by the treatment of the chloride with 4% aqueous sodium bicarbonate.

Catechol was troylated to give 4-troylcatechol⁸⁾ (11), which was then acetylated to diacetate (12). Hydride abstraction from 12 occurred in a 66% yield when it was allowed to react with phosphorus pentachloride. The stable salt (13) was heated in 2N hydrochloric acid to give red needles (14) (X=ClO₄), which showed a band at 3333 cm⁻¹ due to the hydroxy group and one at 758 cm⁻¹ due to an in-phase CH out-of-plane bending band and had no acetyl C=O peak. The elemental analysis also supports the idea that two acetyl groups were completely hydrolyzed to afford the 3,4-dihydroxyphenyltropylium ion.



9) H. J. Dauben, F. A. Godecki, K. M. Harmon and D. L. Pearson, *J. Am. Chem. Soc.*, **79**, 4557 (1957).

10) T. Nozoe and K. Takahashi, *This Bulletin*, **40**, 1480 (1967).

When the chloride of 14 was treated with aqueous bicarbonate, a deep purple solution was afforded, and then 15 was precipitated out in the form of black needles.

In order to get 2, 6-dimethoxy-*p*-benzoquinonetropide (20), 4-tropyl-2, 6-dimethoxyphenol (16)⁸⁾ obtained by the tropylation of pyrogallol dimethyl ether was acetylated and dehydrogenated to give 18, which was then treated with hot 2 N hydrochloric acid to give 19 (X=ClO₄). The chloride of 19 was treated with sodium bicarbonate to give a purple solution; there separated brilliant green plates, 20a, which were stable in the water layer but which turned into porous black precipitates, 20b, when they were filtered out. From the elemental analysis, 5, 10, and 15 were seen to contain a half molecule of water, but 20b was anhydrous. The compounds substituted with a large group at the 2, 6-position of *p*-benzoquinonetropide, such as 2, 6-di-*t*-butyl¹¹⁾ and 2, 6-dihalo¹²⁾ derivatives, also have been confirmed to be anhydrous. From these facts, it may be said that a half molecule of the water of the hydrate would be hydrogen-bonded with an oxygen atom of the carbonyl group, but the hydration would be made unstable by the steric hindrance of large substituents at both the 2 and 6 positions. Although 20a was unstable in the atmosphere and could not give any results in elemental analysis, it must be the hemihydrate of 20b.

10, 15, and 20 were scarcely soluble in all a nonpolar solvent (carbon tetrachloride, ether, or benzene), slightly soluble in water or chloroform, and easily soluble in acetone or acetonitrile.

The electronic spectra of 10, 15, and 20 in an aqueous sulfuric acid or hydrochloric acid solution were identical with those of 9, 14, and 19, indicating that *p*-benzoquinonetropide was present as the hydroxyphenyltropylium ion C in acidic media. In order to compare them with compound 4,

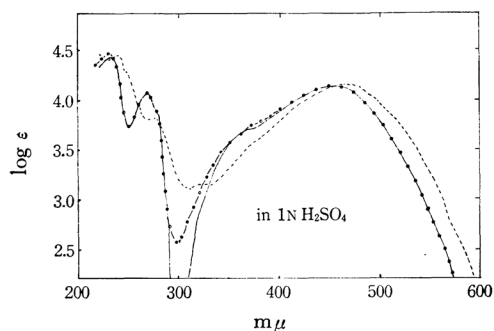


Fig. 1. Electronic spectra of 10, 15 and 20. — 10, -●- 15, ---- 20

11) T. Nozoe, K. Kitahara and H. Susumago, to be published; presented at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.

12) T. Nozoe, K. Takahashi and T. Morita, to be published; presented at the 19th Annual Meeting of the Chemical Society of Japan, Yokohama, April, 1966.

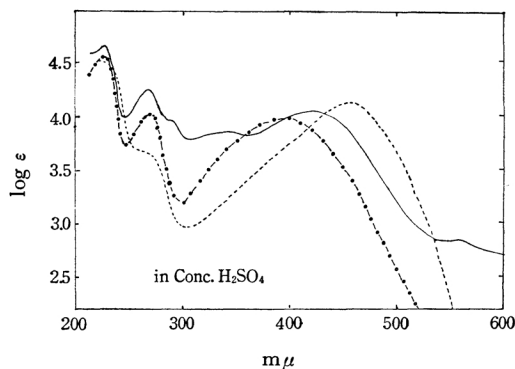


Fig. 2. Electronic spectra of 10, 15 and 20. — 10, -●- 15, ---- 20

the electronic spectra of 10, 15, and 20 in 1 N sulfuric acid are shown in Fig. 1. The bands at the longest wavelength region of these compounds appear at $m\mu$ ($\log \epsilon$); 452 (4.12), 452 (4.14), and 461 (4.12), respectively. It should be noted that the corresponding absorption bands of the above compounds shift to longer wavelengths relative to the corresponding methoxyphenyltropylium ions,⁸⁾ although the spectral patterns of the two series of compounds were quite similar. It has been pointed out that the protonation of methoxyphenyltropylium ions in the concentrated sulfuric acid forms a cation such as is shown by A. The spectra of 10, 15, and 20 in concentrated sulfuric acid are shown in Fig. 2. The absorption maxima in concentrated sulfuric acid in the longest wavelength region are located at $m\mu$ ($\log \epsilon$); 388 (4.14), 424 (4.05), 396 (3.99), and 453 (4.14) for 4, 9, 14, and 19 respectively. The absorption peaks observed for 4 and 14 are shifted closely to the maximum, at 385 $m\mu$, for the phenyltropylium ion in sulfuric acid, suggesting that 14 also exists as such a structure as B in a strong acidic solution. However, 9 and 19 do not behave in a similar manner, and the presence of the methoxy group caused difficulty in the protonation of these compounds.

The electronic spectra of 10, 15, and 20 in water (NaHCO₃ sol.) are shown in Fig. 3, together with

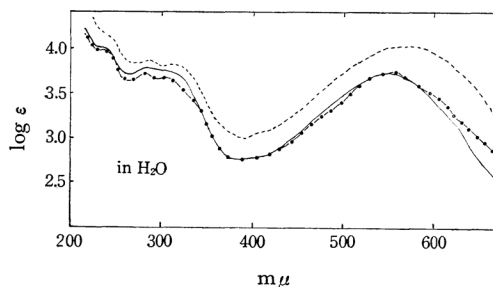
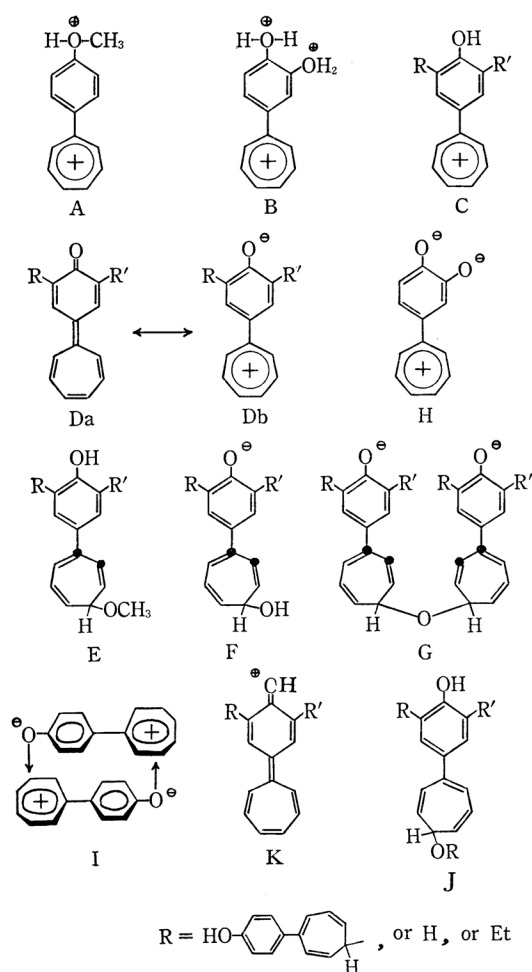


Fig. 3. Electronic spectra of 10, 15 and 20. — 10, -●- 15, ---- 20

that of 5. The D structure is probably responsible for these spectra. The absorption spectra of 10, 15, and 20 all of which contain a methoxy or hydroxy group at the 2 or 6 position, are quite similar to that of the parent compound, 5, except that the absorption maxima appear in a longer wavelength region, and the colors of these compounds seemed to be more stably maintained than that of 5, 15, and 20 were particularly stable; their color remained unchanged even on standing for a long time, either as a solid or in solutions. This stability may come from the formation of intramolecular hydrogen-bonding in compound 15 or from the symmetric substitution of the methoxy group in 20.



p-Benzoquinonotropides were soluble enough in chloroform for the electronic spectra to be measured; the results are shown in Fig. 4 for 10, 15, and 20. The dilution of the chloroform solution of 5 to 0.03 mmol/l resulted in a rapid fading of the color. The color of 10 was also liable to disappear on dilution, but 15 and 20 were found to be stable under these conditions. For 10 only the transient

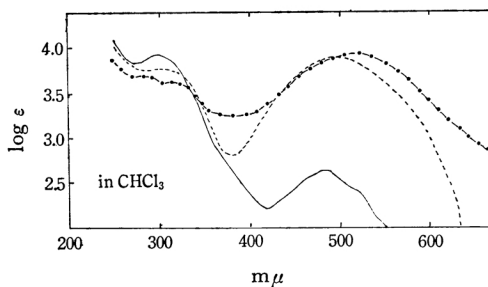


Fig. 4. Electronic spectra of 10, 15 and 20. — 10, -●- 15, ---- 20

absorption spectrum was observed, but the spectra of 15 and 20 in chloroform showed peaks shifted to wavelengths shorter by 38—60 $m\mu$ relative to those in water. These observations may be ascribed to the fact that a quinoid form, Da rather than a polar structure, Db is stabilized more in the ground state than in the excited state of *p*-benzoquinonotropide.¹³⁾

p-Benzoquinonotropides are stable in an aqueous sodium bicarbonate solution, and they undergo nucleophilic reaction with a base at the seven-membered ring in a strongly basic medium. In fact, 10, 15, and 20 did not show any absorption in the visible region, as is shown by the spectra of these compounds measured in 0.1 N sodium hydroxide solutions (Fig. 5).

When a 0.1 N sodium hydroxide solution was added to the aqueous solution of 15, the original purple color changed briefly to blue and then immediately became colorless. In the buffer solution at pH=11.5, an absorption peak at 552 $m\mu$ observed for 15 in sodium bicarbonate was shifted to 610 $m\mu$ with a subsequent change in color to blue. This phenomenon might be due to the formation of a structure such as H on deprotonation from the hydroxy group at the 2 position in 15.

On the other hand, as is shown in Fig. 6, the absorption of 10, 15, and 20 in the visible region

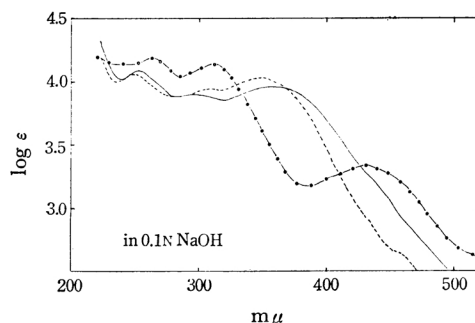


Fig. 5. Electronic spectra of 10, 15 and 20. — 20, ---- 10, -●- 15

13) N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954); E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3261 (1958).

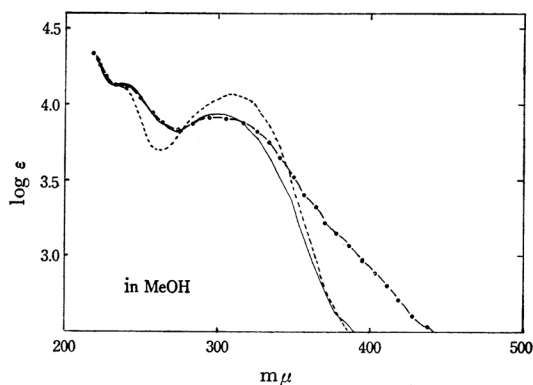


Fig. 6. Electronic spectra of 10, 15 and 20.
— 10, - - - 15, ···· 20

disappear in methanol. These absorption curves in methanol are typical for tropilidene derivatives, and these compounds seemed to be present in methanol as methyl troyl ethers, such as the E form. The fact that absorptions in a 0.1 *N* sodium hydroxide solution were observed at longer wavelengths than those in methanol may be ascribed to the greater contribution of the phenolate ion, $G^{14)}$ to 0.1 *N* sodium hydroxide.

Feldman and Winstein¹⁵⁾ reported the formation of a charge transfer complex between the troylium ion and mesitylene. In view of the fact that the dilution of the chloroform solution of 5 caused its visible absorption to disappear and the absorption to reappear when the dilute solution was evaporated on a filter paper, it was first believed that the absorption peak at 520 $m\mu$ should be assigned to that of a charge-transfer complex between phenolate anion and troylium ion moieties, as is shown by I. However, this interpretation had to be abandoned on the basis of the following experimental results. A comparison of the absorption maxima in 1 *N* sulfuric acid with those in water (in NaHCO_3 sol.) showed that the peaks observed in the visible region from 550 to 570 $m\mu$ in Fig. 3 may correspond to those observed in the 452–461 $m\mu$ region in Fig. 1. Thus, no new peak which was not observed in 1 *N* sulfuric acid was observed in a water solution. Furthermore, the large value of the extinction coefficient of the peaks at longer wavelengths ought to be interpreted as due to electron transfer along the molecular axis in the C_{2v} axis of symmetry in 5. If a band at 550 $m\mu$ of 10 is derived from a charge-transfer complex, the molecular extinction coefficient may be expected to be dependent upon the concentration. However, the molecular extinction coefficients found at different concentrations of the solution of 10 were constant. The phenomenon

14) It was not exactly known whether the phenolate ion exists as G or F.

15) M. Feldman and S. Winstein, *J. Am. Chem. Soc.*, **83**, 3338 (1961).

observed for 5 (the disappearance of the visible absorption in a dilute chloroform solution) was not seen in the stable derivatives, 15 and 20, indicating that 5 may be unstable in a chloroform solution and that it might be converted to a troylidene derivative such as J. On heating, or even on coming in contact with a trace of acid present in the atmosphere, J might change partly into the purple-colored type D *via* the hydroxyphenyltroylium ion. In the *p*-hydroxyphenyltroylium ion (4), the phenol part was in conjugation with the troylium part; this was the reason why the ortho position of the phenol ring was not susceptible to bromination.⁸⁾ Heating 4 in acetic anhydride did not give rise to an acetylation product, suggesting the probable contribution of K to this compound. The deprotonated form of 4, *p*-benzoquinonetropide (5), would be expected to effect a neutralization of the charge within a molecule more easily than in the case of K. The seven-membered ring in *p*-benzoquinonetropide has a higher electron density than the troylium ion; consequently, it has less affinity with the electron donor.

For the reasons mentioned above, the absorption peaks at 520–570 $m\mu$ should be assigned to those of a unimolecular *p*-benzoquinonetropide which exists as a resonance hybri

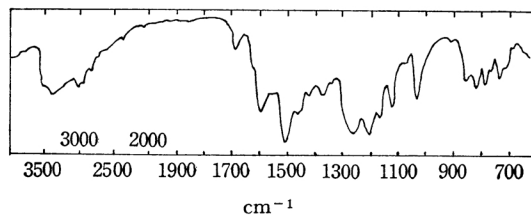


Fig. 7. IR spectrum of 10 in KBr disk.

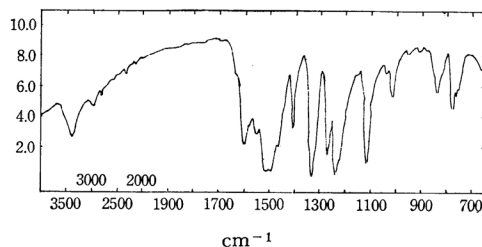


Fig. 7. IR spectrum of 20 in KBr disk.

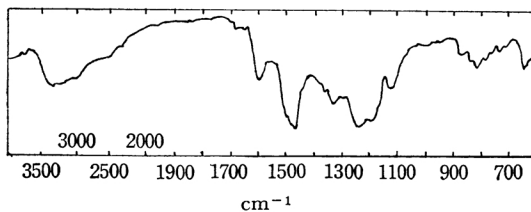


Fig. 7. IR spectrum of 15 in KBr disk.

and Db. It may be reasonably understood that *p*-benzoquinonetroptide and its derivatives have a purple color due to their long conjugation system and their ionic contributing structures.

The infrared spectra of 10, 15, and 20 are shown in Fig. 7. The carbonyl-stretching vibrations of these compounds, like those of other *p*-benzoquinonetroptides, may lie at lower frequencies than those of ordinary conjugated carbonyl compounds. *p*-Benzoquinonetroptides showed generally strong bands at 1480—1520 cm^{-1} , and, in view of the dipole moment of 2, 6-di-*t*-butyl-*p*-benzoquinonetroptide (5.81 D),¹¹ the strong band at 1492—1515 cm^{-1} in Fig. 7 may be assigned to the carbonyl-stretching vibration. Further studies will, however, be necessary before we can present a detailed discussion.

Experimental

The Acetylation of Tropyguaiacol To a mixture of 6- and 4-tropyguaiacol (13.946 g) which was afforded from the reaction of guaiacol (30 g) and ethyl troyl ether (21.25 g), acetic anhydride (16.6 g) was added. After the solution had been refluxed for 1 hr, the excess acetic anhydride was removed by suction and water was added to the residue. The mixture was then extracted with benzene, and the extract was dried and evaporated up to an oil which crystallized on standing. Recrystallization from methanol gave colorless needles, 7 (7.2 g; 43.5%; mp 121—123°C).

Found: C, 74.70; H, 6.07%. Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_3$: C, 74.98; H, 6.29%.

IR in Nujol: 1733, 1587, 1499, 1418, 1294, 1220, 1195, 1161, 1122, 1029, 863, 826, 762, and 734 cm^{-1} .

The uncrystallized portion was chromatographed in cyclohexane on an alumina column to give an oil, 6 (2.8 g; 16.85%).

Found: C, 74.68; H, 6.20%. Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_3$: C, 74.98; H, 6.29%.

IR in neat: 3030, 1764, 1608, 1577, 1437, 1316, 1279, 1209, 1190, 1172, 1103, 1087, 1002, 893, 782, 741, and 708 cm^{-1} .

The Acetylation of Tropolcatechol (11). A solution of 11 (1.5 g) in acetic anhydride (4 g) was refluxed for 1 hr, and the crystalline product thus obtained (2.11 g; 99.4%) was recrystallized from methanol to 12 (mp 38—39°C).

Found: C, 71.93; H, 5.60%. Calcd for $\text{C}_{17}\text{H}_{16}\text{O}_4$: C, 71.82; H, 5.67%.

IR in neat: 3012, 1761, 1504, 1429, 1370, 1269, 1202, 1156, 1116, 1101, 905, 848, 767, 735, and 714 cm^{-1} .

The Acetylation of 2, 6-Dimethoxy-4-trotylphenol (16). 16 (3.14 g) was treated with acetic anhydride (6 ml) as above, and the crude product was chromatographed in cyclohexane on an alumina column to give an oil, 17 (3.643 g; 99.4%).

IR in neat: 3030, 2933, 2849, 1764, 1592, 1504, 1449, 1416, 1393, 1368, 1340, 1241, 1211, 1182, 1160, 1126, 1008, 907, 833, 798, 766, and 735 cm^{-1} .

The Dehydrogenation of 4-Tropyguaiacol Acetate (7) a) *With Phosphorus Pentachloride.* A solution of 7 (2.0 g) in carbon tetrachloride (30 ml) was added to a well-stirred suspension of phosphorus

pentachloride (3.25 g) in carbon tetrachloride (90 ml). The mixture was then stirred for 6 hr and allowed to stand overnight. A precipitate was filtered out, dried, and poured into ice water (12 ml). The aqueous solution was then washed with chloroform and, filtered, and to the filtrate there was added 60% perchloric acid, affording yellow needles 8 ($\text{X}=\text{ClO}_4$; 2.38 g; mp 157—158°C).

Found: C, 54.06; H, 4.50%. Calcd for $\text{C}_{16}\text{H}_{15}\text{O}_7\text{Cl}$: C, 54.16; H, 4.26%.

IR in Nujol: 1770, 1603, 1529, 1515, 1486, 1311, 1282, 1215, 1094, 1010, 761, and 759 cm^{-1} .

Picric acid, instead of perchloric acid, afforded the picrate of 8 ($\text{X}=\text{Pic.}$; mp 142—144°C).

Found: C, 54.59; H, 3.66; N, 8.94%. Calcd for $\text{C}_{22}\text{H}_{17}\text{O}_{10}\text{N}_3$: C, 54.66; H, 3.55; N, 8.69%.

b) *With Bromine.* To a solution of 7 (200 mg) in carbon tetrachloride (2 ml), a solution of bromine (137 mg) in carbon tetrachloride (1 ml) was added gradually. The mixture was stirred for 10 hr and then allowed to stand for 24 hr. The yellow precipitate which formed was filtered and recrystallized from water to give red needles, 8 ($\text{X}=\text{Br}$; 115 mg; 44%; mp 171°C (decomp.)).

Found: C, 51.51; H, 5.64%. Calcd for $\text{C}_{16}\text{H}_{15}\text{O}_3\text{Br}\cdot 2\text{H}_2\text{O}$: C, 51.76; H, 5.16%.

The Dehydrogenation of 2, 6-Dimethoxy-4-trotylphenol Acetate (17). A solution of 17 (540 mg) in carbon tetrachloride (2 ml) was treated with a suspension of phosphorus pentachloride (786 mg) in carbon tetrachloride (23 ml) as has been described above. To the resulting water solution, 60% perchloric acid was added, and the crude product was recrystallized from water to give orange plates, 18 ($\text{X}=\text{ClO}_4$; 378 mg; 52%; mp 206°C).

Found: C, 53.00; H, 4.44%. Calcd for $\text{C}_{17}\text{H}_{17}\text{O}_8\text{Cl}$: C, 53.06; H, 4.45%.

IR in Nujol: 1767, 1592, 1522, 1479, 1466, 1408, 1342, 1266, 1195, 1172, 1125, 1089, and 761 cm^{-1} .

Picric acid, instead of perchloric acid, afforded the picrate of 18 ($\text{X}=\text{Pic.}$), which was recrystallized from ethanol to give red needles (mp 134—136°C).

Found: C, 53.62; H, 3.81; N, 8.06%. Calcd for $\text{C}_{23}\text{H}_{19}\text{O}_{11}\text{N}_3$: C, 53.80; H, 3.73; N, 8.18%.

The Dehydrogenation of 4-Tropolcatechol Diacetate (12). A solution of 12 (630 mg) in carbon tetrachloride (2 ml) was treated with a suspension of phosphorus pentachloride (938 mg) in carbon tetrachloride (30 ml) as has been described above.

Perchlorate of 13: yellow needles; 536 mg; 65.5%; mp 149—152°C.

Found: C, 53.22; H, 4.49%. Calcd for $\text{C}_{17}\text{H}_{15}\text{O}_8\text{Cl}$: C, 53.34; H, 3.95%.

IR in Nujol: 1795, 1779, 1605, 1534, 1490, 1274, 1198, 1122, 1087, 1029, 887, 826, and 762 cm^{-1} .

Picrate of 13: orange needles; mp 152—154°C.

Found: C, 53.19; H, 3.71; N, 8.33%. Calcd for $\text{C}_{23}\text{H}_{17}\text{O}_{11}\text{N}_3\cdot\text{H}_2\text{O}$: C, 53.07; H, 3.49; N, 8.08%.

The Hydrolysis of 8 ($\text{X}=\text{ClO}_4$). 8 ($\text{X}=\text{ClO}_4$; 100 mg) dissolved in warm 2 N hydrochloric acid (5 ml) was heated for 5 min and then cooled to room temperature to give crystals. Recrystallization from water afforded orange needles, 9 ($\text{X}=\text{ClO}_4$; 88 mg 98.6% mp 188—192°C).

Found: C, 53.72; H, 4.37%. Calcd for $\text{C}_{14}\text{H}_{13}\text{O}_6\text{Cl}$: C, 53.76; H, 4.19%.

IR in Nujol: 3333, 1605, 1587, 1515, 1477, 1304, 1279, 1236, 1215, 1098, 859, 826, 794, and 764 cm^{-1} .

9 ($\text{X}=\text{Cl}$) could be prepared in the following manner: The well-dried double salt of 8 afforded by 7 (2.274 g), phosphorus pentachloride (3.699 g), and carbon tetrachloride (100 ml) were gradually added to hot 2 N hydrochloric acid (15 ml). After being heated for an additional 5 min, the mixture was cooled to give red needles which, on recrystallization from water, afforded other red needles, 9 ($\text{X}=\text{Cl}$; 1.89 g; 85.8%; mp 158°C decomp.).

Found: C, 59.38; H, 6.49%. Calcd for $\text{C}_{14}\text{H}_{13}\text{O}_2\text{Cl}\cdot 2\text{H}_2\text{O}$: C, 59.06; 6.02%.

The Hydrolysis of 13 ($\text{X}=\text{ClO}_4$). 13 ($\text{X}=\text{ClO}_4$; 127 mg) was treated with hot 2 N hydrochloric acid (4 ml) as has been described above to give 14 ($\text{X}=\text{ClO}_4$; 86 mg; 86.7%), which was recrystallized from water-perchloric acid (30 : 1) to red needles (mp 212—214°C decomp.).

Found: C, 52.41; H, 3.92%. Calcd for $\text{C}_{13}\text{H}_{11}\text{O}_6\text{Cl}$: C, 52.27; H, 3.71%.

IR in Nujol: 3333, 1575, 1513, 1481, 1312, 1279, 1248, 1202, 1127, 1099, 1058, 961, 876, and 758 cm^{-1} .

14 ($\text{X}=\text{Cl}$) could be prepared in a similar manner in a 62% yield.

The Hydrolysis of 18. The well-dried double salt of 18 which was afforded from the reaction of phosphorus pentachloride (3.605 g) with 17 (2.48 g) was heated with 2 N hydrochloric acid (10 ml) for a few minutes, the solution was hot-filtered, and 60% perchloric acid was added to the filtrate. The crystals which formed were recrystallized from water to give red needles, 19 ($\text{X}=\text{ClO}_4$; 773 mg; 71%; mp 251°C decomp.).

Found: C, 52.05; H, 4.23%. Calcd for $\text{C}_{15}\text{H}_{15}\text{O}_7\text{Cl}$: C, 52.57; H, 4.41%.

IR in Nujol: 3378, 1608, 1520, 1490, 1475, 1425, 1340, 1292, 1222, 1205, 1188, 1090, 964, 845, 835, 776, and 766 cm^{-1} .

When the filtrate was cooled in an ice bath, without the addition of perchloric acid, it gave red needles, 19 ($\text{X}=\text{Cl}$), which were recrystallized from water. The infrared spectrum of the chloride was identical

with that of the perchlorate except for the band of ClO_4 .

The Synthesis of 2-Methoxy-*p*-benzoquinonetropide. A solution of 9 ($\text{X}=\text{Cl}$; 95 mg) in 5 ml of water was hot-filtered. The filtrate was cooled to *ca.* 30—35°C and, before the separation of the crystals, stirred into a 4% aqueous sodium bicarbonate solution (1 ml). A deep purple solution resulted, and black needles, 10 separated; the needles were filtered, washed with cold water, and dried (63.2 mg; 81%; mp 67—70°C).

Found: C, 76.02; H, 6.18%. Calcd for $\text{C}_{14}\text{H}_{12}\text{O}_2\cdot \frac{1}{2}\text{H}_2\text{O}$: C, 76.00; H, 5.92%.

IR in chloroform sol: 1627, 1595, 1568, 1510, 1490, and 1463 cm^{-1} .

The Synthesis of 2-Hydroxy-*p*-benzoquinonetropide. A solution of 14 ($\text{X}=\text{Cl}$; 46 mg) in water (3.0 ml) was treated with a 4% aqueous sodium bicarbonate solution (0.5 ml) as above to give black needles, 15 (33.8 mg; 84%; mp 143—144°C).

Found: C, 75.02; H, 5.02%. Calcd for $\text{C}_{13}\text{H}_{10}\text{O}_2$: C, 75.35; H, 5.35%.

IR in KBr disk: 3200, 1625, 1595, 1500, 1492, 1480, 1465, 1360, 1327, 1235, 1200, 1125, and 830 cm^{-1} .

The Synthesis of 2,6-Demethoxy-*p*-benzoquinonetropide. A hot solution of 19 ($\text{X}=\text{Cl}$; 50 mg) in water (2.5 ml) was added as above into a 4% aqueous sodium bicarbonate solution (0.67 ml). A deep purple solution resulted. On cooling in an ice bath, brilliant green plates, 20a separated out; these immediately turned into a black, porous, amorphous material, 20b (25.7 mg; 59%; mp 96—98°C) on exposure to air.

Found: C, 73.82; H, 5.62%. Calcd for $\text{C}_{15}\text{H}_{14}\text{O}_3\cdot \frac{1}{10}\text{H}_2\text{O}$: C, 73.82; H, 5.86%. Calcd for $\text{C}_{15}\text{H}_{14}\text{O}_3$: C, 74.36; H, 5.83%.

IR in the KBr disk: 1630, 1598, 1577, 1550, 1515, 1494, 1462, 1408, 1330, 1270, 1240, 1114, 1012, 836, and 777 cm^{-1} .

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