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The Tropylation of Polyhydric Phenols and the Dehydrogenation of Their Products[1)]

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The tropylation reaction of polyhydric phenols, such as guaiacol, catechol, resorcinol, hydroquinone, 2, 6-dimethoxyphenol, pyrogallol and phloroglucinol, has been carried out. These polyhydric phenols were quite reactive with ethyl tropyl ether or with tropylium ion, and gave mono-, di-, or sometimes tri-tropyl derivatives. The dehydrogenation of tropylpolyhydric phenol methyl ethers gave stable aryltropilium ions. The methoxyphenyltropones and the methoxyphenyl tropolones were also synthesized in good yields starting from the 4-methoxyphenyltropylium ion.

In 1957, Vol'pin *et al.*[2)] reported the tropylation of phenols with the tropylium ion. However, no mention has been made of the structure of the tropylated products. In our laboratory, the investigation of the tropylation reaction of phenols has been going on for five years, and a part of the results obtained (4- and 2-tropylphenol (2), (3)

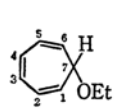
1) The Ph. D. Thesis by Kazuko Takahashi, Tohoku University (1963); presented in part at the 15th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1962.

2) M. E. Vol'pin, I. S. Akrem and D. N. Kursanov, *Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk,* **1957**, 1501.

were mainly afforded by the reaction of phenol with ethyl tropyl ether) have already been reported.[3] At the same time, a Dutch group[4] reported the formation of 2, 6-dimethyl-4-tropylphenol by the tropylation of 2, 6-dimethylphenol. Recently, a British group[5] has also studied the tropylation of guaiacol and catechol, but they have reported no detailed results. In our alboratory, the tropylation of polyhydric-, alkyl-,[6] halo,[7] and nitro-[7] phenols has been investigated for the last several years. In connection with this work, the author would like to report some of her results concerning the tropylation of polyhydric phenols, the dehydrogenation reaction of its products, and the synthesis of *p*-methoxyphenyltropones from the *p*-methoxyphenyltropylium ion.

In the following tropyl compounds derivated from polyhydric phenols, the polyhydric phenol group must be first at the 7-position of tropyl group. During the further heating or purification process, however, these compounds rearrange[8] to give a mixture of 3- and 1-tropyl compounds. In compounds 11, 16, 18, 19, and 21 the ratio of all the isomers of the mixture was not examined in detail.

Guaiacol was tropylated with ethyl tropyl ether (1) to 4 (42%), which was then reduced to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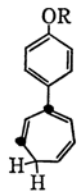
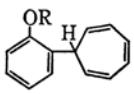
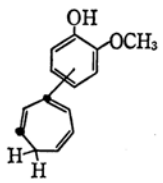

2: R=H
28: R=CH$_3$


3: R=H
31: R=CH$_3$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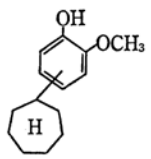
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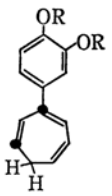
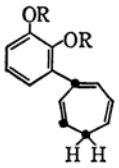
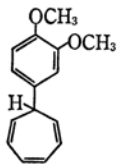

6: R=CH$_3$
8: R=H


7: R=CH$_3$
9: R=H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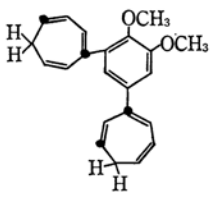
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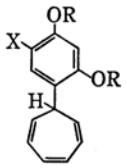
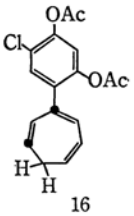

12: X=H, R=H
13: X=Et, R=H
14: X=COCH$_3$, R=H
15: X=Cl, R=H
32: X=H, R=CH$_3$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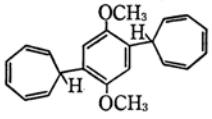
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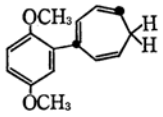
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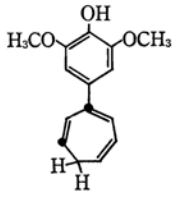
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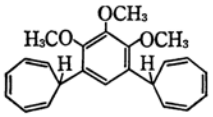
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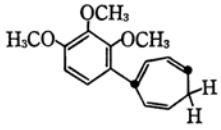
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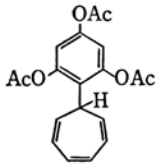
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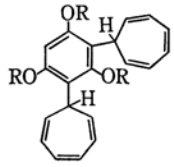
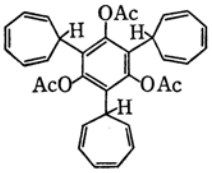

23: R=Ac
24: R=H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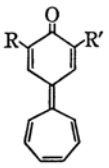
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3) T. Nozoe and K. Kitahara, *Chem. & Ind.*, **1962**, 1192; The Ph. D. Thesis of Kazuo Kitahara, Tohoku University (1963).

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) 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.

7) T. Nozoe, K. Takashashi and T. Morita, to be published; presented at the 18th Annual Meeting of the Chemical Society of Japan, Yokohama, April, 1966.

8) A. P. ter Borg, H. Kloosterziel and N. van Meurs, *Rec. Trav. Chim.*, **82**, 717 (1963); A. P. ter Bogr and H. Kloosteriziel, *ibid.*, **82**, 741 (1963).

cycloheptyl derivatives, 5. The methylation of 4 with dimethyl sulfate gave 6 and 7 in the ratio of 1 : 1. 6 and 7 showed absorptions at 821 cm^{-1} (adjacent 2H) and 787 cm^{-1} (adjacent 3H) respectively. 6 and 7 were oxidized with potassium permanganate to give 3, 4- and 2, 3-dimethoxybenzoic acid respectively. Therefore, it is clear that guaiacol was tropylated at the 5- and 3-positions. 4 was also obtained (50%) by the reaction of guaiacol with ditropyl ether.

When catechol was allowed to react with ditropyl ether, tropylation did not proceed smoothly because the reaction mixture was too viscous, but when catechol (1.5 mol) was treated with ethyl tropyl ether (1.0 mol), a transient blue color appeared and tropylation proceeded smoothly. The crude oily product was then distilled to give a mixture of 4'-(3'-tropyl)- and 4-(1'-tropyl)catechol (in the ratio of 4.6 : 1) (8) and a mixture of 3-(3'-tropyl)-, 3-(1'-tropyl)- and 3-(7'-tropyl)catechol (in the ratio of 15 : 2 : 1) (9). The crude oily product, on the other hand, when treated with dimethyl sulfate, gave 4-(7'-tropyl)catechol dimethyl ether (10) (29%), 3-tropylcatechol dimethyl ether (7) (5.6%), and ditropyl compounds (11) (25.3%). 10 and 11 were oxidized with potassium permanganate to give 3, 4-dimethoxybenzoic acid and 4, 5-dimethoxyisophthalic acid respectively. Since 8 and 9 were methylated to 6 and 7, these products proved to be 4- and 3-tropylcatechol respectively. Therefore, it is clear that catechol was tropylated at the 3 and 5 positions to give a 3, 5-ditropyl derivative rather than a monotropyl derivative.

Resorcinol (1.0 mol), 4-ethylresorcinol, and resacetophenone reacted similarly with ethyl tropyl ether (1.5 mol), giving the corresponding 4-(7'-tropyl) compounds, (12), (13) and (14) in good yields. The reaction of 4-chlororesorcinol with ethyl tropyl ether gave only a dark reddish resin. However, when the tropylation was carried out in methanol and the crude product was acetylated before purification, diacetate (16) was obtained in a 50% yield. It is not clear why free tropyl compound (15) failed to be obtained in a stable form. It should also be noted that resorcinols afforded no ditropyl compounds.

Hydroquinone did not react with ethyl tropyl ether at room temperature, but when the reaction was carried out at 170°C for 1.5 hr, and when the reaction mixture was then methylated, ditropyl compounds (17) (a trace) and monotropyl compounds (18) (22.6%) were separated. 18 was proved to be 2-tropylhydroquinone dimethyl ether, by its oxidation to 2, 5-dimethoxybenzoic acid. The methyl groups in 17 appear as a singlet at 3.73 ppm in the NMR spectrum ($CDCl_3$) and as a two-proton triplet at 3.1 ppm (J=5.5 cps, tertiary-protons in tropyl group) and a two-proton singlet at 6.89 ppm (aromatic). Its infrared absorption (867 cm^{-1}, isolated H) also showed it to be 2, 5-di(7'-tropyl)hydroquinone dimethyl ether.

2, 6-Dimethoxyphenol was tropylated to a 4-tropyl compound (19). Pyrogallol (1.5 mol) was treated with ethyl tropyl ether (1.0 mol), and the crude product was methylated before purification to 20 (44%) and 21 (15%). On oxidation, the methyl ethers gave 4, 5, 6-trimethoxyisophthalic acid and 1, 2, 3-trimethoxybenzoic acid respectively. On hydrogenation 20 gave 4, 6-dicycloheptylpyrogallol trimethyl ether. From these results, it was known that pyrogallol is tropylated at the 4 and 6 positions rather than at 5. Even when pyrogallol was used in excess in comparison with ethyl tropyl ether, the 4, 6-ditropyl compound, 20, was formed in a good yield.

Phloroglucinol reacted with ethyl tropyl ether to give only a dark reddish resin. The tropylation was carried out in methanol, and the crude reaction product was acetylated before purification to give a monotropyl compound (22) (53%) and a ditropyl compound (23) (a trace). On attempted purification, the above crude product gave a trace of ditropyl compound (24), together with much tar. The tropylation with excess ethyl tropyl ether in methanol gave a tritropyl compound (25) after acetylation.

As has been mentioned above, polyhydric phenols, such as catechol and pyrogallol, tended to give ditropyl rather than monotropyl compounds, whereas monohydric phenols, such as *p*-cresol and 4-ethylphenol, were tropylated to give monotropyl compounds. Ethyl tropyl ether (or methyl tropyl ether) is a good tropylation reagent for polyhydric phenols. Tropylium ion is also used for a tropylation reagent. The ion did not react smoothly with phenols in an acidic medium, but it reacted effectively with phenols in acetonitrile in the presence of trimethylamine, giving di- or tritropyl compounds. However, this method was not useful in preparing monotropyl derivatives of polyhydric phenols. Hydroquinone did not react with ethyl tropyl ether at room temperature, but it did react with the tropylium ion in the presence of trimethylamine, affording 2, 5-ditropylhydroquinone.*1

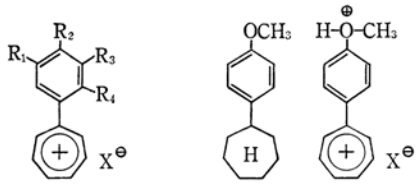
During the tropylation of catechol, guaiacol and pyrogallol, a transient deep blue color was observed. This was considered to be due to the formation of such compounds as 26,*2 which may be formed by the oxidation of tropylphenols with tropylium ions. The formation of 26 was not desired in getting the tropyl compounds; it was avoided by using methanol as a solvent.

The dehydrogenation of the tropylphenols obtained above was then investigated. 23) was treated with bromine (3 mol equiv.) in carbon tetrachloride to give a dehydrogenation product,

*1 This experiment was carried out by E. Kirii, whom the author wishes to thank.

*2 This will be discussed in the next paper.

27[9] (21.7%), along with a black tar. It is of interest that bromo-substitution did not take place at the phenol ring. This was perhaps due to the strong electron-drawing effect of the tropylium cation group. A mixture of *p*-(3-tropyl)- and *p*-(1-tropyl)anisol (in the ratio of 3.6 : 1) (28)[3] was



30 38

27: $R_1=R_3=R_4=H$, $R_2=OH$
29: $R_1=R_3=R_4=H$, $R_2=OCH_3$
33: $R_1=R_2=R_3=H$, $R_4=OCH_3$
34: $R_1=R_3=H$, $R_2=R_4=OCH_3$
35: $R_1=R_4=H$, $R_2=R_3=OCH_3$
36: $R_1=R_2=H$, $R_3=R_4=OCH_3$
37: $R_2=R_3=H$, $R_1=R_4=OCH_3$

similarly reacted with bromine to afford 29[9] in a 64% yield. When allowed to react with phosphorus pentachloride, 28 gave 29 in a good yield. 29 was then reduced to 30 and showed its absorption maximum at 422—428 mμ ($\log \varepsilon = 4.14$).

31 and 32 (obtained by the methylation of 2-(7'-tropyl)anisol (3)[3] and 12 respectively), 6, 7, and 18 were dehydrogenated to stable methoxyphenyltropylium ions, 33, 34, 35, 36, and 37 respectively. The ultraviolet spectra of 33, 34, 35, 36, and 37 in 6 N sulfuric acid and in concentrated sulfuric acid are shown in Figs. 1 and 2. The bands at the longest wavelength region in Fig. 2 appear at wavelengths shorter by 20 to 40 mμ than those in Fig. 1; the wavelengths are comparable with that of the phenyltropylium ion

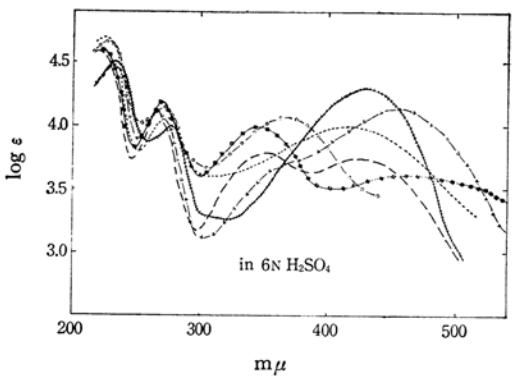


Fig. 1. UV spectra of 29, 33, 34, 35, 36 and 37.

29 -▽- 35
33 -○- 36
34 -■- 37

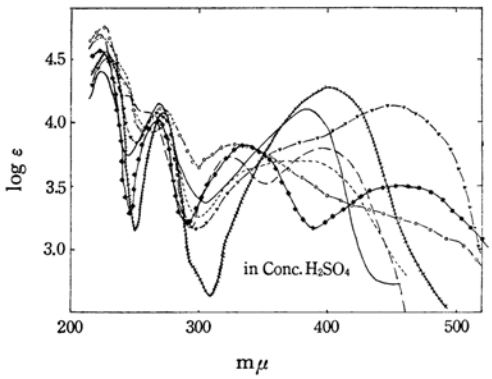
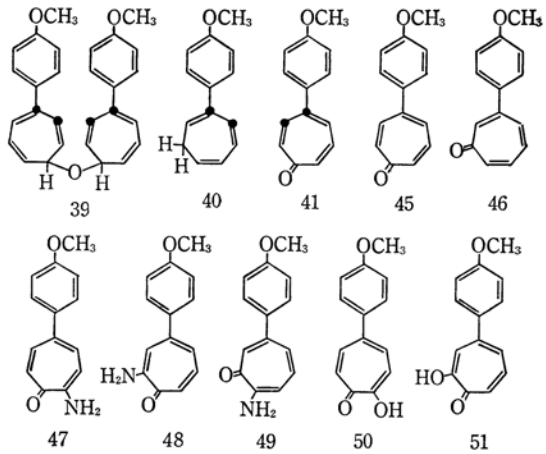


Fig. 2. UV spectra of phenyltropylium ion, 29, 33, 34, 35, 36 and 37.

Phenyltropylium ion -△- 35
29 -○- 36
33 -■- 37
34

(385 mμ), indicating methoxyphenyltropylium ions to be present in a protonated form, 38, in concentrated sulfuric acid. Methoxyphenyltropylium ions showed expected absorptions at 1329—1271 cm^{-1} (antisym. C–O stretching) and 994—1110 cm^{-1} (sym. C–O stretching), and a strong, sharp band of in-phase CH out-of-plane bending of the seven-membered cation in the 753—788 cm^{-1} region. These results are shown in Table 1, where they are compared with those[10] of the tropylium cation and tropone.

It is well known that the neutralization of an aqueous solution of a tropylium or phenyltropylium salt with sodium hydroxide results in the formation of ditropyl ether, while the treatment of the ditropyl ether with a trace of acid brings about a disproportionation reaction, giving tropone or



39 40 41 45 46

47 48 49 50 51

9) C. Jutz and F. Voithenleitner, *Chem. Ber.*, **97**, 29 (1964).

10) W von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **76**, 3203 (1954); Y. Ikegami, "Sekigaisen Kyushu Supekutoru," Kagaku no Ryoiki Zokan, No. 8, Nankodo, Tokyo, (1959), p. 33.

Table 1. Infrared spectra of aryltropylium ions

	2	3	4	5	C-O Stretching (cm^{-1}) Antisym.	Sym.	In phase CH out-of-plane bending of seven membered ring (cm^{-1})
29			OH		1261		762
31			OCH_3		1249	1005	767
35	OCH_3				1252	1012	759
36	OCH_3		OCH_3		1259	1110(996)	787
37		OCH_3	OCH_3		1269	1008	763
38	OCH_3	OCH_3			1271	1012(994)	757
39	OCH_3			OCH_3	1239	1009	770
	Tropylium ion						651
	Tropone						778

phenyltropone.[11] This reaction is useful for the preparation of tropone and tropolone derivatives not obtainable from a direct substitution reaction. In order to investigate the reaction conditions, the disproportionation reaction of the methoxyphenyltropylium ion was examined. An aqueous solution of 29 was neutralized with sodium bicarbonate to a viscous oil, 39. The disproportionation of 39 was effected in a modified manner; a benzene solution of 39 was refluxed for 3 hr with a trace of concentrated hydrochloric acid to give 40 and tropone mixture (41) in 80% of the theoretical yield. When 39 was allowed to react with acid in a usual manner, disproportionation failed to take place; only 29 was afforded, with much recovery, while when 39 was treated with picric acid, it gave the picrates of 29 and 41 in poor yields. 42, the picrate of 41, was fractionally recrystallized to give 43 and 44, which were then chromatographed in alcohol on an alumina column to give 45 and 46 respectively. From the ultraviolet spectra (Fig. 3) and from the infrared spectra, 45 (1632 cm^{-1}; C=O, 833 cm^{-1} adjacent 2H of the phenyl and tropone rings, 794 cm^{-1} adjacent 3 H of the tropone ring) proved to be 4-(*p*-methoxyphenyl)tropone, while 46 (1636 cm^{-1}; C=O, 825 cm^{-1}; adjacent 2 H of the phenyl ring, 755 cm^{-1} and 902 cm^{-1}; adjacent 4 H and isolated H, respectively) proved to be 3-(*p*-methoxyphenyl)tropone. 28 was oxidized with selenium oxide to the methoxyphenyltropone (41) in a poor yield.

To confirm the strctures of 45 and 46, they were converted into the corresponding tropolones using Nozoe's method.[12] 45 was treated with 80% hydrazine hydrate to give 47 (828 cm^{-1} and 823 cm^{-1}; adjacent 2 H of the phenyl and tropone rings) and 48. In a similar manner, 46 gave 49. The ultraviolet spectra of 47, 48 and 49 are shown in Fig. 4.

47 was hydrolyzed with alcoholic potassium hydroxide to 50 (3205 cm^{-1}; OH, 1608 cm^{-1}; C=O, 829 cm^{-1}; adjacent 2H). 48 and 49 were similarly hydrolysed to 51 (3205 cm^{-1}; OH,

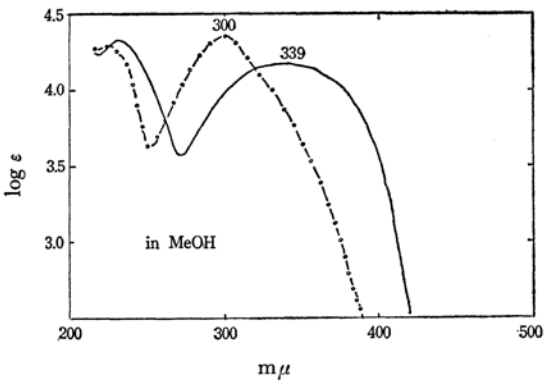


Fig. 3. UV spectra of 45 and 46.
-●- 46 —— 45

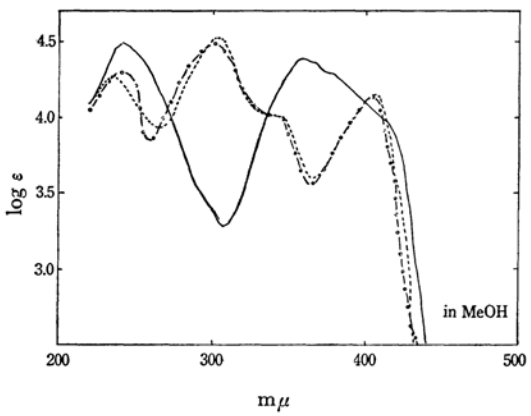


Fig. 4. UV spectra of 47, 48 and 49.
-○- 49 ---- 48 —— 47

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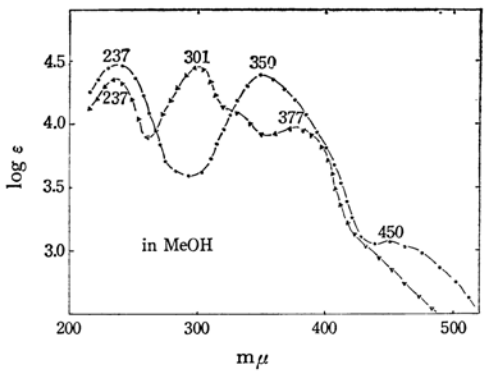

Fig. 5. UV spectra of 50 and 51.
-●- 50 -▲- 51

1603 cm^{-1}; C=O, 828 cm^{-1}; adjacent 2 H, 786 cm^{-1}; adjacent 3 H).

41 was converted to a mixture of 50 and 51 *via* aminotropones, and then the mixture was separated on the basis at the difference in solubility of the sodium salts. The chemical behavior of 50 and 51 has also been examined and will be reported on before long.

Experimental

The Tropylation of Guaiacol. a) To a well-stirred guaiacol (30 g), there were added a little ethyl tropyl ether (about 1—2 g) and a trace of tropylium bromide. After the reaction had been initiated, the remaining ethyl tropyl ether (total; 21.25 g) was gradually added. The mixture turned deep violet. After it had been stirred for 5 hr, the mixture was allowed to stand overnight at room temperature and then distilled to give 14.1 g (42%) of a yellow oil, 4; bp 167.5°C/5 mmHg.

Found: C, 78.17; H, 6.42%. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59%.

IR in neat: 3559, 1600, 1504, 1460, 1431, 1269, 1242, 1211, 1202, 1093, 1073, 990, 778, 758, 732, and 705 cm^{-1}.

b) Guaiacol (9.76 g) was treated with ditropyl ether (5.0 g) as above to give 5.37 g (50%) of 4.

The Reduction of Tropylguaiacol (4). A methanol solution of 4(1 g) was hydrogenated over palladium-carbon (10 mg), and then 366.5 m*l* of hydrogen was absorbed to give a colorless oil, 5; bp 150°C/5 mmHg.

IR in neat: 3584, 2941, 2865, 1613, 1590, 1517, 1479, 1468, 1447, 1279, 1217, 1079, 775, and 733, cm^{-1}.

The Methylation of 4. To a solution of 4(2 g) in 10 m*l* of 10% aqueous potassium hydroxide, dimethyl sulfate (1.77 g) was added. After it had been stirred for 5 hr, the mixture was allowed to stand overnight and then extracted with *n*-hexane (30 m*l*). The extract was washed with 1 N potassium hydroxide, dried over sodium sulfate and evaporated up to 10 m*l*. After the evaporated extract had been allowed to stand at room temperature, colorless needles (491 mg) were filtered and recrystallized from methanol to afford a mixture of 5-(3′-tropyl)- and 5-(1′-tropyl)guaiacol methyl ether (4.6 : 1) (6); mp 83—84°C.

Found: C, 79.05; H, 6.82%. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06%.

IR in Nujol: 1597, 1582, 1515, 1266, 1250, 1206, 1163, 1140, 1022, 860, 821, 762, and 742 cm^{-1}.

The filtrate was evaporated to give a crude oil (1.82 g), which was chromatographed in *n*-hexane on an alumina column to give 583 mg of a colorless oil, a mixture of 3-(3′-tropyl)-, 3-(1′-tropyl)- and 3-(7′-tropyl)guaiacol methyl ether (15 : 2 : 1) (7).

IR in neat: 3030, 2950, 1577, 1471, 1266, 1103, 1087, 1009, 787, 745, 734, 707, and 676 cm^{-1}.

Subsequent elution with benzene gave 68 mg of 6.

The Tropylation of Catechol. Ethyl tropyl ether (6.6 g) was stirred into powdered catechol (8 g), during which process a deep transient color appeared. The mixture was then stirred for 5 hr and allowed to stand for 48 hr at room temperature. After a small amount of benzene had been added, the unchanged catechol was filtered out and the filtrate was distilled under a vacuum to give a yellow oil (2.65 g; 27.4%; bp 160—180°C/0.5 mmHg). On standing, colorless needles were formed; these were filtered out and recrystallized from benzene to give 8 (1.19 g; 12.3%; mp 94°C).

Found: C, 78.10; H, 5.75%. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04%.

IR in Nujol: 3330, 1959, 1515, 1445, 1299, 1271, 1111, 899, 859, 812, 780, 762, 735, and 707 cm^{-1}.

NMR ppm^{CDCl_3}: 2.24 ($2H_7$; triplet; J_{7-1}=6.2 cps), 2.59 ($2H_7$; doublet; J_{1-7}=7.0 cps) and 6.80 ($3H_{aromatic}$).

The uncrystallized residue was chromatographed on a silica column in benzene - ethyl acetate (1 : 1). The first elute was recrystallized from petroleum ether to give a mixture of 3-(3′-tropyl); 3-(1′-tropyl)- and 3-(7′-tropyl)catechol (15 : 2 : 1) (9) (367 mg; 3.8%; colorless prisms, mp 63—65°C). 9 showed a depression in melting point on admixture with 8.

Found: C, 78.02; H, 5.98%. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04%.

IR in KBr disk: 3413, 3049, 2857, 1618, 1587, 1471, 1364, 1318, 1282, 1215, 1185, 1160, 1067, 1040, 862, 813, 786, 735 and 702 cm^{-1}.

NMR ppm^{CDCl_3}: 2.37 ($2H_7$; triplet; J_{7-1}=6.4 cps), 2.67 ($2H_7$; doublet; J_{1-7}=7.0 cps), 3.03 (H_7; triplet; J_{1-7}=5.6 cps), 5.52 ($H_{1,2}$; multiplet), 6.25 ($H_{2,3}$; quartet) and 6.78 ($3H_{aromatic}$).

The Methylation and the Oxidation of Tropylcatechol. Catechol (10 mg) was tropylated under conditions identical to those used in the preceding experiment. After the unchanged starting material had been removed by filtration, ethanol (44 m*l*), dimethyl sulfate (82.4 g), and solution of potassium hydroxide (26.2 g) in water (65.2 m*l*) were added with stirring. The mixture was stirred for 4 or 5 hr and then extracted with benzene. The benzene extract was dried with sodium sulfate and evaporated up to separate crystals (4.02 g; 29%; mp 70—77°C) which, on recrystallization from methanol, gave colorless prisms of 4-(7′-tropyl)catechol dimethyl ether (10); mp 78—79°C. 10 showed a depression in melting point on admixture with 6.

Found: C, 79.41; H, 6.95%. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06%.

IR in Nujol: 1587, 1515, 1344, 1263, 1224, 1155, 1138, 1025, 854, 830, 814, 758, 753 and 712 cm^{-1}.

NMR ppm^{CDCl_3}: 2.66 (H_7; triplet; J_{7-1}=5.6 cps), 3.84 (2Me; singlet), 5.39 ($2H_1$; quartet; J_{1-2}=9.9

cps), 6.21 ($2H_2$; broad doublet), 6.71 ($2H_3$; triplet; $J_{2-3}=3.0$ cps) and 6.86 ($3H_{aromatic}$).

An uncrystallized oily part was distilled *in vacuo* to give an oil (780 mg; 5.63%; bp 140—160°C/11 mmHg) and an undistilled residue (11) (2.37 g; 25.3%). The infrared spectrum of the former is identical with that of 7. 10 and 11 were oxidized under the same conditions as have been described for 6 and 7 to give 3, 4-dimethoxybenzoic acid (63%; mp 179°C) and 4, 5-dimethoxyisophthalic acid (65%; mp 245°C) respectively.

IR of 11 in neat: 2950, 2841, 1572, 1515, 1453, 1397, 1252, 1233, 1116, 1009, 843, 781, 734, and 709 cm^{-1}.

The Tropylation of Resorcinol. To well-crushed resorcinol (9.46 g), ethyl tropyl ether (7.805 g) was added. The mixture was heated on a water bath for a few minutes, thereby initiating the reaction. After it had been stirred for 4 hr, the mixture was allowed to stand overnight at room temperature, water was added, and the crystals (10.523 g) which separated were recrystallized from benzene, affording colorless prisms of the hemihydrate of 4-(7'-tropyl)resorcinol (12) (mp 124—128°C).

Found: C, 75.01; H, 6.49%. Calcd for $C_{13}H_{12}O_2 \cdot \frac{1}{2}H_2O$: C, 74.62; H, 6.26%.

IR in Nujol: 3472, 3311, 1613, 1593, 1355, 1300, 1239, 1198, 1020, 1011, 978, 787, 735, and 698 cm^{-1}.

The hemihydrate was kept at 100°C *in vacuo* (0.3 mmHg) for 2 hr and then recrystallized from anhydrous benzene to give an anhydrous product (colorless needles; mp 132—134°C).

Found: C, 78.17; H, 6.09%. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04%.

NMR ppm^{CDCl_3}: 3.40 (H_7; triplet; $J_{1-7}=5.1$ cps), 4.90 (OH; singlet), 5.42 ($2H_1$; quartet; $J_{1-2}=9.1$ cps), 6.22 ($2H_2$; broad doublet), and 6.63 ($2H_3$; triplet; $J_{3-2}=3.1$ cps).

The Tropylation of 4-Ethylresorcinol. In a manner similar to that used in the above experiment, but starting with 4-ethylresorcinol (5.08 g), ethyl tropyl ether (5.00 g), and a trace of tropylium bromide, there could be obtained 6.00 g (71%, after recrystallization from chloroform) of colorless prisms (13) (mp 101—104°C).

Found: C, 79.12; H, 6.81%. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06%.

IR in Nujol: 3403, 3268, 1597, 1497, 1351, 1302, 1235, 1179, 1164, 1080, 1020, 813, 775, 753, and 709 cm^{-1}.

The Tropylation of Resacetophenone. A mixture of resacetophenone (5.02 g), methanol (25 m*l*), and ethyl tropyl ether (3.0 g) was heated at 100—120°C for 10 min and then stirred at room temperature for 5 hr. The separated crystals were filtered out and recrystallized from alcohol to give 14 (3.75 g; 70.3%; mp 193—194°C).

Found: C, 74.54; H, 5.29%. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.83%.

IR in Nujol: 3226, 1634, 1608, 1582, 1497, 1337, 1316, 1285, 1186, 1049, 866, 747, and 708 cm^{-1}.

The Tropylation of 4-Chlororesorcinol. To a solution of 4-chlororesorcinol (4.82 g) in methanol (15 m*l*), ethyl tropyl ether (4.55 g) was added. After a 4-hr stirring of the mixture, the methanol was evaporated under a nitrogen atmosphere. To the residue pyridine (17 m*l*) was added. The mixture was then ice-cooled, and acetyl chloride (12 m*l*) was added to separate a colorless precipitate. After standing overnight, the reaction mixture was diluted with ice water and extracted with benzene. The benzene extract was washed first with 0.5 N hydrochloric acid and next with water, dried over sodium sulfate, and evaporated up to an oil, which was then distilled under a vacuum to give 16 (5.40 g; 50.7%; bp 160—180°C/2 mmHg).

IR in Neat: 3067, 3012, 2907, 2865, 1795, 1786, 1439, 1471, 1441, 1376, 1205, 1190, 1145, 1040, 1005, 903, 877, 822, 774, and 738 cm^{-1}.

The Tropylation of Hydroquinone. a) A mixture of hydroquinone (5.06 g) and ethyl tropyl ether (6.29 g) was refluxed on an oil bath for 1.5 hr and then allowed to stand overnight. A small amount of chloroform was added, and an unchanged part of hydroquinone was filtered off. The filtrate was then evaporated off to give a viscous oil. A mixture of this viscous oil, dimethyl sulfate (6.94 m*l*), and 38% aqueous potassium hydroxide (21.3 m*l*) was stirred for 5 hr, allowed to stand overnight, and then extracted with benzene. The extract was dried over sodium sulfate and chromatographed on an alumina column. To the first benzene elute a small amount of methanol was added to separate colorless prisms which, on filtration and then recrystallization from acetone, gave 17 (54 mg; mp 166—167°C).

Found: C, 83.33; H, 6.66%. Calcd for $C_{22}H_{22}O_2$: C, 82.98; H, 6.96%.

IR in Nujol: 1511, 1335, 1256, 1211, 1203, 1043, 867, 753, 734, and 709 cm^{-1}.

NMR ppm^{CDCl_3}: 3.10 ($2H_7$; triplet; $J_{7-1}=5.5$ cps), 3.73 (2Me; singlet), 5.39 ($4H_1$; quartet; $J_{1-2}=9.1$ cps), 6.21 ($4H_2$; broad doublet), 6.68 ($4H_3$; triplet; $J_{2-3}=3.5$ cps), and 6.89 ($2H_{aromatic}$; singlet).

The filtrate and the subsequent elute with benzene gave an oil which, on distillation under a vacuum, gave 18 (2.3 g; 22.6%; bp 130—150°C/1 mmHg).

Found: C, 79.62; H, 6.60%. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06%.

IR in neat: 2933, 1605, 1582, 1497, 1437, 1285, 1220, 1046, 1026, 870, 803, 727, and 703 cm^{-1}.

b) Tropylium perchlorate (92 g) was stirred in to an ice-cooled suspension of hydroquinone (17.73 g) in acetonitrile (80 m*l*) and triethylamine (54.8 g), after which the mixture was stirred for 5 hr. The precipitate was collected and washed with chloroform. The chloroform washing and the filtrate were added to 1 N hydrochloric acid (300 m*l*) and extracted with ether, and the extract was evaporated. The combined precipitate and the residue (25 g; 53.5%) were recrystallized from chloroform to give 2, 5-ditropylhydroquinone (mp 190—192°C).

Found: C, 82.66; H, 6.24%. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.26%.

IR in KBr disk: 3534, 3013, 1531, 1427, 1389, 1200, 1176, 1131, 761, and 705 cm^{-1}.

The Tropylation of 2, 6-Dimethoxyphenol. A mixture of 2, 6-dimethoxyphenol (3.97 g), ethyl tropyl ether (5.26 g), and tropylium bromide (trace) was heated on a water bath for 10 min, stirred for 4 hr at room temperature, and then allowed to stand overnight. The mixture was dissolved in chloroform, washed with water, dried over sodium sulfate, and evaporated up to an oil, which was then distilled under a vacuum to give 19 (3.14 g; 50%; bp 180—190°C/1 mmHg).

Found: C, 74.00; H, 6.42%. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60%.

IR in Neat: 3610, 3012, 1603, 1517, 1342, 1255, 1220, 1117, 917, 837, 784, and 734 cm^{-1}.

The Tropylation of Pyrogallol. Into to well-crushed pyrogallol (10 g), ethyl tropyl ether (7.2 g) was added with stirring. The stirring was continued for 4 hr. Ethanol (23.8 m*l*), dimethyl sulfate (45 g), and a solution of potassium hydroxide (14.3 g) in water (35.8 m*l*) were then successively added, and, after being stirring for 5 hr, the resulting mixture was extracted with benzene (100 m*l*). The benzene extract was evaporated, and the residual oil was then allowed to stand for 3 days at room temperature in order to separate crystals, which were filtered and recrystallized from methanol to give colorless prisms, 4, 6-di(7'-tropyl)-pyrogallol trimethyl ether (20) (4.10 g; 44%; mp 94°C).

Found: C, 79.38; H, 6.63%. Calcd for $C_{23}H_{24}O_3$: C, 79.28; H, 6.94%.

IR in Nujol: 1484, 1410, 1340, 1304, 1232, 1109, 1067, 1020, 1000, 789, 751, and 712 cm^{-1}.

NMR ppm^{CDCl_3}: 3.10 ($2H_7$; triplet; J_{7-1}=5.1 cps), 3.77 (2Me; singlet), 3.88 (Me; singlet), 5.34 ($4H_1$; quartet; J_{1-2}=9.1 cps), 6.20 ($4H_2$; broad doublet), 6.68 ($4H_3$; triplet; J_{2-3}=3.1 cps), and 7.05 ($H_{aromatic}$).

The filtrate was distilled under a vacuum to give an oil (2.0 g; 14.55%; bp 155—158°C/2 mmHg) which was chromatographed on alumina column and eluted with petroleum ether to give 630 mg of an oil, 21.

Found: C, 74.08; H, 6.85%. Calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02%.

IR in neat: 2941, 1597, 1497, 1466, 1414, 1295, 1263, 1099, 1050, 1013, 797, 745, and 709 cm^{-1}.

The Catalytic Reduction of 20. A solution of 20 (300 mg) in acetic acid (15 m*l*) was hydrogenated over platinum oxide (5 mg) to absorb 150 m*l* (calcd=160.7 m*l*) of hydrogen. The acetic acid was then evaporated, and the residual crystals (270 mg) were recrystallized from methanol to give 4, 6-dicycloheptylpyrogallol trimethyl ether as colorless prisms (mp 115°C).

Found: C, 76.35; H, 9.70%. Calcd for $C_{23}H_{36}O_3$: C, 76.62; H, 10.07%.

IR in Nujol: 2857, 1449, 1403, 1316, 1088, 1064, and 1009 cm^{-1}.

The Tropylation of Phloroglucinol. To phloroglucinol (5 g) in 6 m*l* of methanol, ethyl tropyl ether (2.82 g) was added and the mixture was stirred for 4 hr. Ethyl acetate-benzene (1 : 4) was added, and unchanged phloroglucinol was recovered. The solvent was evaporated, the reddish residue was dissolved in chloroform, and the solution was allowed to stand for 2 days, thus depositing an additional phloroglucinol (1.02 g), which was removed by filtration. The filtrate was evaporated to give an oil which crystallized on standing. Recrystallization from benzene gave colorless prisms 2, 4-di(7'-tropyl)phloroglucinol (24) (50 mg; mp 155°C).

Found: C, 78.35; H, 5.90%. Calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92%.

IR in Nujol: 3597, 1610, 1468, 1364, 1222, 1111, 1093, 756, 718, and 686 cm^{-1}.

The Acetylation of Tropylphloroglucinol. a) To phloroglucinol (8.8 g) in methanol (30 m*l*), ethyl tropyl ether (6.15 g) was added. The mixture was stirred for 5 hr and then allowed to stand overnight. The solvent was removed by evaporation under nitrogen. The residue and sodium acetate (8.8 g) in acetic anhydride (44 m*l*) was refluxed for 1 hr and then allowed to stand at room temperature to yield colorless needles, which were collected by filtration from the mother liquor, dried, and poured into water. After the solution had been allowed to stand overnight, the crystals (7.66 g; 53%) were filtered off and recrystallized from methanol to give colorless needles, 2-(7'-tropyl)phloroglucinol triacetate (22) (mp 131°C).

Found: C, 66.77; H, 4.98%. Calcd for $C_{19}H_{18}O_6$: C, 66.66; H, 5.30%.

IR in Nujol: 1764, 1610, 1590, 1196, 1172, 1124, 1040, 1022, and 717 cm^{-1}.

Excess acetic anhydride was evaporated *in vacuo* from the mother liquor to give a viscous oil, to which water was added. After 2 days, the aqueous layer was decanted and the residue was extracted with benzene. The extract was washed with water, dried, and evaporated, leaving an oil (10.27 g) which was fractionally crystallized from methanol. From the sparing and easily-soluble portions, 22 (1.95 g) and colorless prisms, 2, 4-di(7'-tropyl)phloroglucinol triacetate (23) (279 mg; mp 173—174°C), were afforded respectively.

Found: C, 72.15; H, 5.75%. Calcd for $C_{26}H_{24}O_6$: C, 72.21; H, 5.59%.

IR in Nujol: 1776, 1613, 1200, 1181, 1107, 1042, 907, 751, and 707 cm^{-1}.

b) Phloroglucinol (2.06 g) and ethyl tropyl ether (1.99 g) were treated as has been described above, and the resulting mixture was acetylated by refluxing it with acetic anhydride (10 m*l*) and sodium acetate (2.0 g) for 1 hr. After the solution had cooled, a crystalline precipitate was separated by filtration from the mother liquor. Recrystallization from methanol afforded colorless prisms, 2, 4, 6-tri(7'-tropyl)phloroglucinol triacetate (25) (446 mg; mp 197°C).

Found: C, 75.82; H, 5.89%. Calcd for $C_{33}H_{30}O_6$: C, 75.84; H, 5.79%.

IR in Nujol: 1770, 1182, 1101, 1022, 871, 750, 731, and 709 cm^{-1}.

From the mother liquor, excess acetic anhydride was removed, water was added and, after the solution had stood overnight, the water layer was decanted off. The residue was triturated with benzene, and the undissolved crystals (437 mg) were separated by filtration. The recrystallization of the crystals from methanol gave colorless prisms (mp 204°C), which showed an infrared spectrum (in an acetonitrile solution) identical with that of 25 and showed no depression on a mixed-melting-point test with 25.

Found: C, 75.96; H, 5.85%.

From these results this compound may be said to be a polymorphism of 25. The benzene-soluble portion was washed with water, dried, and evaporated to give an oil, which, on recrystallization from methanol, gave an additional crop of 25 (112 mg). From the second fraction and from the easily-soluble one, 22 (110 mg) and phloroglucinol triacetate were afforded respectively.

The Tropylation of 4-Ethylphenol. A mixture of 4-ethylphenol (5 g), ethyl tropyl ether (5.57 g), and a trace of tropylium bromide was stirred for 5 hr. After standing overnight, the reaction mixture was distilled to afford a yellow oil, 4-ethyl-2-tropylphenol (6.36 g; 73%; bp 130—140°C/0.8 mmHg).

Found: C, 84.69; H, 7.25%. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.6%.

IR in neat: 3597, 3003, 1613, 1508, 1453, 1433, 1266, 1190, 820, 746, and 704 cm^{-1}.

The Tropylation of *p*-Cresol. *p*-Cresol (11.01 g), ethyl tropyl ether (14.05 g) and a trace of tropylium bromide were treated as has been described above to give a yellow oil, 4-methyl-2-tropylphenol (16.92 g; 83%; bp 132—134°C/0.4 mmHg).

Found: C, 84.92; H, 7.04; O, 7.84%. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.13; O, 8.07%.

IR in neat: 3521, 3003, 1610, 1498, 1280, 1190, 814, 741, and 707 cm^{-1}.

An English group reported the melting point of 4-methyl-2-tropylphenol to be 65°C. In our case, however the tropyl group was thermally isomerized during distillation to a mixture of 7-, 3- and 1-tropyl compounds.

The Oxidation of Tropylphenol Methyl Ethers 6, 7, 20, 22, 23 and 33. A sample (500 mg) of tropylphenol methyl ether dissolved in acetone (50 m*l*) was treated with potassium permanganate (3—5 g). After the solution had been refluxed for 2 to 3 hr with stirring, the manganese dioxide was filtered off and dissolved in aqueous sodium bisulfite. The resulting, feebly-basic solution was washed by shaking it with ether, after which the aqueous layer was acidified with 2 N hydrochloric acid and thoroughly extracted with ether. The ether extract obtained from the acidified solution was dried and evaporated up to colorless needles. Recrystallization from water gave the corresponding methoxybenzoic acids as follows:

6	3, 4-Dimethoxybenzoic acid	(50%)
7	2, 3-Dimethoxybenzoic acid	(29%)
18	2, 5-Dimethoxybenzoic acid	(75%)
20	4, 5, 6-Trimethoxybenzoic acid	(84%)
21	1, 2, 3-Trimethoxybenzoic acid	(75%)
31	2-Methoxybenzoic acid	(78%)

4-Hydroxyphenyltropylium Ion. To a cold solution of *p*-tropylphenol (1 g) in carbon tetrachloride (5 m*l*), a solution of bromine (900 mg) in carbon tetrachloride (1 m*l*) was added, drop by drop. The black tar which formed was removed by decantation, and the solution was stirred to give orange needles. After one night, the needles were filtered off, dried, and recrystallized from a little water to give orange needles, 27 (X=Br; mp 215°C; 182 mg).

IR in Nujol: 3344, 1597, 1513, 1456, 1307, 1261, 1238, 1174, 850, 762, and 719 cm^{-1}.

60% Perchloric acid was added to the water layer (recrystallization filtration) to give red needles, 27 ($X=ClO_4$; 32 mg; mp 197°C).

Found: C, 55.33; H, 4.05%. Calcd for $C_{13}H_{11}O_5Cl$: C, 55.22; H, 3.92%.

The filtered carbon tetrachloride solution was evaporated at 40—50°C; and the residue was allowed to stand one week under a vacuum and then recrystallized from water to give 27 (X=Br; 80 mg) and ($X=ClO_4$; 13 mg), the total yield was 21.7%.

4-Methoxyphenyltropylium Bromide. To a solution of 4-tropylanisol (28) (1 g)-NMR ppm of 28; 2.30 ($2H_7$; triplet; J_{1-7}=6.5 cps), 2.71 ($2H_7$; doublet; J_{1-7}=7.4 cps), 3.76 (Me; singlet), 5.25—6.41 ($H_{1,2,3}$), 6.84 ($H_{aromatic\ 2,6}$), and 7.36 ($H_{aromatic\ 3,5}$) in carbon tetrachloride (4 m*l*), a solution of bromine (900 mg) in carbon tetrachloride (1 m*l*) was stirred in, drop by drop, over a period of 20 min. After it had then been stirred for an additional 2 hr in a cold water bath, the mixture separated orange crystals which were filtered off (550 mg) and recrystallized from water to give orange needles, 29 (X=Br; mp 122°C, 130—140°C (decomp.)).

Found: C, 54.01; H, 5.41%. Calcd for $C_{14}H_{13}OBr \cdot 2H_2O$: C, 53.68; H, 5.47%.

IR in Nujol: 1592, 1513, 1475, 1307, 1256, 1181, 1014, 839, 767, and 718 cm^{-1}.

The mother liquor was evaporated at 40—50°C. The residue was allowed to stand at 40—50°C under a vacuum and recrystallized from water to give additional 29 (X=Br; 460 mg). 60% Perchloric acid was added to the aqueous mother liquor to precipitate 29 ($X=ClO_4$; mp 174°C; total yield, 64%).

The Catalytic Reduction of 29. A solution of 29 (280 mg) in acetic acid (10 m*l*) was hydrogenated over 5 mg of a platinum oxide catalyst at room temperature. Four equiv. of hydrogen were taken up. The catalyst was filtered, and 40 m*l* of water were added. This mixture was then extracted with *n*-hexane. The extract was washed with aqueous sodium bicarbonate, dried, and evaporated to a clorless oil, 30.

IR in neat: 1942, 1605, 1511, 1453, 1242, 1175, 1036, and 817 cm^{-1}.

The Catalytic Reduction of 28. A solution of 28 (1 g) in acetic acid (20 m*l*) was treated as above to give a colorless oil, the infrared spectrum of which was identical with that of 30.

The Hydrolysis of 30. A solution of 30 (300 mg) in acetic acid (4 m*l*) and 48% hydrobromic acid (0.7 m*l*) was refluxed for 4 hr. The reaction mixture was then poured into water (20 m*l*), and the separating colorless crystals (223 mg) thus separated were recrystallized from petroleum ether (mp 105°C). The melting point was undepressed on admixture with authentic *p*-cycloheptylphenol.

The Hydrolysis of 29. A solution of 29 (X=Br; 100 mg) in acetic acid (3 m*l*) and 48% hydrobromic acid (1 m*l*) was kept at 100°C for 48 hr. After the solution had then been cooled by room temperature, 29 (70 mg) was recovered by filtration. The filtrate was evaporated by evacuation, and perchloric acid was added to the residue. The resultant crystals (mp 190°C) were found to be identical with 27 ($X=ClO_4$) on the basis of the infrared spectra. The filtrate was made basic by aqueous sodium bicarbonate to afford a violet color, suggesting the presence of 27.

2-Tropylanisole. To a mixture of 2-tropylphenol (4.4 g) and dimethyl sulfate (6.03 g), potassium hydroxide (2.77 g) in water (26 m*l*) was added. After it had then been stirred overnight, the mixture was extracted with ether. The ether extract was evaporated to give an oil which crystallized on cooling. Recrystallization from methanol gave colorless needles, 2-(7′-tropyl)anisole (31) (4.46 g; mp 84—91°C).

Found: C, 85.22; H, 7.03%. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12%.

IR in Nujol: 1597, 1587, 1496, 1245, 1193, 1160, 1107, 1053, 1028, 764, 752, and 710 cm^{-1}.

4-Tropylresorcinol Dimethyl Ether (32). To a mixture of 4-tropylresorcinol (4.25 g) and dimethyl sulfate (10.36 g), 10% aqueous potassium hydroxide (47.6 m*l*) was added with stirring. After it had then been stirred for an additional 4 hr, the mixture was extracted with benzene. The benzene extract was evaporated to give crystals. On recrystallization from methanol, these afforded colorless needles, 33 (3.77 g;

76%; mp 89°C).

Found: C, 78.87; H, 6.91%. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06%.

The Dehydrogenation of Six Tropylphenol Methyl Ethers, 28, 31, 32, 6, 7, and 18, with Phosphorus Pentachloride. To a suspension of phosphorus pentachloride (5.6 g) in carbon tetrachloride (110 m*l*), a solution of tropylphenol methyl ether (2.13—2.45 g) in carbon tetrachloride (10 m*l*) was added with stirring. The mixture was stirred for 5 more hr and then allowed to stand overnight. The precipitate was filtered, dried by evacuation, and dissolved in to water. To the filtered solution, 60% perchloric acid, 20% hexachloroplatinic acid, and a saturated alcohol solution of picric acid were added, and the solution was recrystallized from water containing traces of the corresponding acid, thus producing the corresponding methoxyphenyltropylium ions as follows:

29 (83.5%):

Perchlorate: yellow needles, mp 174°C (decomp.).

Chloroplatinate: yellow needles, mp 203°C.

Found: C, 41.13; H, 3.22; Ash., 23.72%. Calcd for $C_{28}H_{26}O_2PtCl_6 \cdot H_2O$: C, 40.99; H, 3.44; Ash., 23.78%.

Picrate; yellow needles, mp 162°C.

Found: C, 57.06; H, 3.54; N, 9.70%. Calcd for $C_{20}H_{15}O_8N_3$: C, 56.47; H, 3.55; N, 9.88%.

The double salt of 29 with phosphorus pentachloride was recrystallized from a little water to give yellow needles, 29 (X=Cl).

33 (71%);

Perchlorate: yellow needles, mp 186°C (decomp.).

Found: C, 56.65; H, 4.26%. Calcd for $C_{14}H_{13}O_5Cl$: C, 56.68; H, 4.42%.

IR in Nujol: 1592, 1522, 1429, 1289, 1252, 1087, 1013, 759, and 725 cm^{-1}.

Chloroplatinate: yellow needles, mp 166°C.

Found: C, 41.87; H, 3.01; Ash., 24.59%. Calcd for $C_{28}H_{26}O_2PtCl_6$: C, 41.91; H, 3.27; Ash., 24.31%.

Picrate: yellow needles, mp 137—138°C.

Found: C, 56.83; H, 3.31; N, 9.62%. Calcd for $C_{20}H_{15}O_8N_3$: C, 56.47; H, 3.55; N, 9.88%.

34 (71%):

Viscous oil obtained by heating 32 at 190°C for 1 hr was treated with phosphorus pentachloride.

Perchlorate: yellow-orange needles, mp 208—209°C.

Found: C, 55.22; H, 4.49%. Calcd for $C_{15}H_{15}O_6Cl$: C, 55.14; H, 4.63%.

Chloroplatinate: yellow-orange needles, mp 270°C.

Found: C, 41.82; H, 3.60; Ash., 22.43%. Calcd for $C_{15}H_{15}O_2 \cdot \frac{1}{2}PtCl_6$: C, 41.78; H, 3.51; Ash., 22.62%.

IR in Nujol: 1587, 1259, 1110, 996, 787, 755, and 727 cm^{-1}.

Picrate: yellow needles, mp 158°C.

Found: C, 54.84; H, 3.46; N, 9.68%. Calcd for $C_{21}H_{17}O_9N_3$: C, 55.39; H, 3.76; N, 9.23%.

35 (77.1%):

Perchlorate: red needles, mp 227°C.

IR in Nujol: 1587, 1511, 1269, 1157, 1008, and 763 cm^{-1}.

Chloroplatinate: red needles, mp 213°C (decomp.).

Found: C, 41.93; H, 3.36; Ash., 22.68%. Calcd for $C_{30}H_{30}O_4PtCl_6$: C, 41.79; H, 3.51; Ash., 22.62%.

Picrate: red needles (recrystallized from methanol), mp 148°C.

Found: C, 55.01; H, 3.39; N, 9.12%. Calcd for $C_{21}H_{17}O_9N_3$: C, 55.39; H, 3.76; N, 9.23%.

Chloride: red needles, mp 165—166°C.

Found: C, 60.24; H, 6.24%. Calcd for $C_{15}H_{15}O_2Cl \cdot 2H_2O$: C, 60.03; H, 6.41%.

36 (60%):

Perchlorate: orange needles, mp 162°C.

Found: C, 55.00; H, 4.87%. Calcd for $C_{15}H_{15}O_6Cl$: C, 55.14; H, 4.63%.

IR in Nujol: 1580, 1527, 1481, 1429, 1321, 1280, 1093, 992, and 757 $cm.^{-1}$

Chloroplatinate: yellow needles, mp 180°C (decomp.).

Found: C, 41.39; H, 3.44; Ash., 22.48%. Calcd for $C_{30}H_{30}O_4PtCl_6$: C, 41.79; H, 3.51; Ash., 22.62%.

Picrate: red needles, mp 117°C (from methanol).

Found: C, 55.63; H, 3.69; N, 9.09%. Calcd for $C_{21}H_{17}O_9N_3$: C, 55.39; H, 3.76; N, 9.23%.

37 (60%):

Perchlorate: orange needles.

Found: C, 55.43; H, 4.17%. Calcd for $C_{15}H_{15}O_6Cl$: C, 55.14; 4.63%.

Chloroplatinate: red needles, mp 167°C.

Found: C, 42.65; H, 3.54; Ash., 21.50%. Calcd for $C_{30}H_{30}O_4PtCl_6$: C, 41.79; H, 3.51; Ash., 22.62%.

Picrate: red needles, mp 131—132°C (from alcohol).

Found: C, 55.19; H, 3.61; N, 8.66%. Calcd for $C_{21}H_{17}O_9N_3$: C, 55.39; H, 3.76; N, 9.32%.

IR (X=ClO_4) in Nujol: 1528, 1498, 1480, 1439, 1325, 1300, 1235, 1090, 1010, 879, 826, 807, 770, 741, and 715 cm^{-1}.

The Reaction of the 4-Methoxyphenyltropylium Ion with Sodium Bicarbonate. The double salt of 29 (22 g), obtained by the reaction of 4-tropylanisole (12 g) with phosphorus pentachloride (27 g) in carbon tetrachloride (500 m*l*), was suspended in water (250 m*l*); the suspension was then warmed on a water bath for a few minutes. Into the cooled solution sodium bicarbonate (26 g) was then stirred to afford a viscous oily, product. This was extracted with chloroform, and the extract was dried and evaporated to give an oil, 39 (14.5 g).

IR in neat: 2976, 2924, 1626, 1600, 1575, 1511, 1294, 1250, 1181, 1033, and 831 cm^{-1}.

39 was also afforded by the reaction of 4-methoxyphenyltropylium bromide or perchlorate with sodium bicarbonate.

The Reaction of 39 with Concentrated Hydrochloric Acid. Concentrated hydrochloric acid (0.5 m*l*) was stirred into 39 (100 mg) to afford yellow needles. To this well-stirred reaction mixture, water (1 m*l*) was then added. The separated crystals (100 mg) were filtered and dissolved into a small amount of water. To this solution perchloric acid was added to afford yellow needles (mp 174°C), which showed the same infrared spectrum as that of 29 (X=ClO_4).

The Reaction of 41 with Picric Acid. A mixture of 39 (100 mg) and a saturated aqueous solution of picric acid (1 m*l*) was heated on a water bath. After cooling, the crystals were filtered and fractionally recrystallized from methanol to give yellow needles, mp 162°C (30 mg) and mp 128—131°C (40 mg). The former showed the same infrared spectrum as that of the 4-methoxyphenyltropylium ion. The latter was chromatographed in alcohol on alumina to afford a trace of pale yellow crystals which showed an infrared spectrum identical to that of 41.

***p*-Methoxyphenyltropone (41).** A solution of 39 (14.5 g) in benzene (50 m*l*) was refluxed on an oil bath. To this concentrated hydrochloric acid was added as follows: 2 m*l* at the beginning of refluxing, 1 m*l* after 10 min, 2 m*l* after 50 min more, and finally 2 m*l* after an hour more. Refluxing was continued for 3.5 hr. After the mixture had been cocled to room temperature, crystals were filtered off and washed with benzene. Water (300 m*l*) was added to these crystals, and the water layer were extracted with benzene (8 m*l*). The extract was washed with water, dried over sodium sulfate, and evaporated up to pale yellow crystals, 41 (4.4 g imp 68—78°). The yield of 41 was 80%, based on the *p*-methoxyphenyltropylium ion (29) and 68% based on 4-tropylanisole (28).

IR in the KBr disk: 2985, 2899, 1623, 1567, 1504, 1460, 1294, 1250, 1179, 1030, 868, 830, and 794 cm^{-1}.

The above filtrate and benzene washing were mixed up, washed with water, and dried. Dry hydrogen chloride gas was introduced to the benzene solution in order to precipitate the hydrochloride of 41. The precipitate was removed by decantation and treated as has been described above to afford 41 (300 mg). The benzene solution was washed with water, dried, and evaporated to an oily residue, which was then distilled *in vacuo* to give colorless needles (1.905 g; mp 60—65°C).

Found: C, 84.35; H, 7.09%. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12%.

This compound, 40 is considered to be an isomer of 28 on the tropyl group.

IR of 28 (mp 38—39°C) in the KBr disk: 2976, 2849, 1600, 1519, 1464, 1445, 1298, 1256, 1185, 1120, 1036, 833, 823, 800, 768, and 740 cm^{-1}.

IR of 40 in the KBr disk: 2976, 2849, 1603, 1517, 1464, 1443, 1295, 1256, 1181, 1120, 1036, 833, 806, 789, 768, 741, 725, and 708 cm^{-1}.

The Oxidation of 4-Tropylanisole with Selenium Oxide. To a solution of 28 (1 g) in 10 m*l* of dioxane containing 10% of water, selenium oxide (561 mg) was added. The mixture was refluxed for 3 hr in a nitrogen atmosphere, and then the separated selenium (115 mg) was filtered off. The filtrate was concentrated under nitrogen to give an oily residue. This was extracted with ether, and the extract was dried and evaporated. An oily resiude (509 mg) was dissolved in dry benzene, and to this dry hydrogen chloride gas was introduced to precipitate the hydrochloride of 41. The precipitate was separated by decantation, and then 150 mg of an oil was afforded by the decomposition of the salt with water. The infrared spectrum of the oil was identical with that of 41.

IR in neat: 3030, 2941, 1631, 1575, 1511, 1488, 1299, 1258, 1183, 1032, 870, 831, and 795 cm^{-1}.

After the dry benzene solution had been washed with water, dried, and then chromatographed in benzene on alumina, 28 (289 mg) was recovered.

Picrate of 41. A mixture of 41 (4.4 g) and picric acid (6.17 g) in alcohol was warmed for 5 min. The product 42 (8.4 g; 92%; mp 131—134°C) was fractionally recrystallized from ethanol to give 43 (4.54 g; mp 140°C) and 44 (2.07 g; mp 159°C).

Found (for 43): C, 54.38; H, 3.41; N, 9.16%.

Found (for 44): C, 54.55; H, 3.36; N, 9.68%.

Calcd for $C_{20}H_{15}O_9N_3$: C, 54.43; H, 3.43; N, 9.52%.

4-(*p*-Methoxyphenyl)tropone (45). A solution of 43 (4.542 g) in alcohol was chromatographed on alumina to give crystals (2.02 g; 92%). Recrystallization from cyclohexane afforded pale yellow needles (mp 85—86°C).

Found: C, 79.07; H, 5.54%. Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70%.

IR in Nujol: 1632, 1598, 1575, 1512, 1465, 1444, 1293, 1263, 1245, 1218, 1178, 1114, 1023, 863, 833, and 794 cm^{-1}.

2, 4-Dinitrophenylhydrazone of 45. Red needles, mp 204°C,

Found: C, 61.43; H, 3.90; N, 14.16%. Calcd for $C_{20}H_{16}O_5N_4$: C, 61.22; H, 4.11; N, 14.28%.

3-(*p*-Methoxyphenyl)tropone (46). 44 (2.07 g) was treated such as has been described above to afford pale yellow needles, 46 (797 mg; 80%; mp 83°C), which were then recrystallized from cyclohexane.

Found: C, 79.68; H, 5.60%. Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70%.

IR in Nujol: 1636, 1606, 1590, 1573, 1520, 1505, 1468, 1460, 1450, 1440, 1337, 1292, 1250, 1235, 1172, 1114, 1032, 977, 902, 825, 786, and 755 cm^{-1}.

2, 4-Dinitrophenylhydrazone of 46. Red needles, mp 166°C.

Found: C, 61.42; H, 4.08; N, 14.23%. Calcd for $C_{20}H_{16}O_5N_4$: C, 61.22; H, 4.11; N, 14.28%.

The Reaction of 45 with Hydrazine Hydrate. 45 (507 mg) in ethanol (5.8 m*l*) and hydrazine hydrate (0.5 m*l*) were refluxed for 1 hr. After cooling to room temperature, the separated crystals (470 mg; mp 150—184°C) were filtered off and the filtrate was evaporated to give additional crystals (60 mg). The combined crystals (530 mg; 99.5%) were fractionally recrystallized from benzene, giving sparingly-soluble gold plates, 47 (188 mg; mp 201—202°C) and easily-soluble yellow needles, 48 (5.81 mg; mp 180—181°C)

Found (for 47): C, 73.79; H, 5.64; N, 6.47%.

Found (for 48): C, 74.02; H, 5.53; N, 6.02%. Calcd for $C_{14}H_{13}O_2N$: C, 73.99; H, 5.77; N, 6.16%.

IR of 47 in Nujol: 3300, 1634, 1605, 1541, 1504, 1339, 1292, 1266, 1241, 1188, 1032, 828, 823, 725, and 719 cm^{-1}.

IR of 48 in the KBr disk: 3413, 3195, 1592, 1515, 1437, 1422, 1397, 1235, 1178, 1031, 810, and 756 cm^{-1}.

The Reaction of 46 with Hydrazine Hydrate. 46 (442 mg) in ethanol (5 m*l*) and 80% hydrazine hydrate (0.43 m*l*) were treated as has been described above to afford yellow needles, 49 (460 mg; 97.3%; mp 206°C) after recrystallization from benzene.

Found: C, 74.49; H, 5.58; N, 5.98%. Calcd for $C_{14}H_{13}O_2N$: C, 73.99; H, 5.77; N, 6.16%.

IR in Nujol: 3425, 3300, 1626, 1587, 1511, 1429, 1247, 1181, 1027, 903, 842, 810, 790, 758, and 711 cm^{-1}.

5-(*p*-Methoxyphenyl)tropolone (50). To a mixture of potassium hydroxide (986 mg), water (2.94 m*l*), and ethanol (14 m*l*), 47 (166 mg) was added. The mixture was then refluxed for 10 hr. Hot water (50 m*l*) and 2 N sulfuric acid were added to adjust the pH to ca. 2. The colorless crystals obtained were filtered, sublimed under a vacuum, and recrystallized from ethanol to give pale yellow needles, 50 (160 mg; 95.8%; mp 161°C).

Found: C, 73.93; H, 5.13%. Calcd for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30%.

IR in Nujol: 3205, 1608, 1548, 1513, 1425, 1364, 1295, 1259, 1206, 1176, 1029, 864, 829, 798, and 757 cm^{-1}.

4-(*p*-Methoxyphenyl)tropolone (51). *a) From 48.* A mixture of potassium hydroxide (231 mg), water (0.69 m*l*), ethanol (3.29 m*l*) and 48 (39 mg) was treated as above to give pale yellow needles, 51 (38 mg; 97%; mp 140—141°C, recrystallized from ethanol), which showed depression on a mixed-melting-point test with 50.

Found: C, 73.94; H, 5.09%. Calcd for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30%.

IR in Nujol: 3205, 1603, 1543, 1416, 1282, 1233, 1218, 1186, 1176, 1036, 992, 849, 828, 814, 786, and 765 cm^{-1}.

b) From 49. 49 was treated as above to give pale yellow needles, 51 (88%; mp 139—140°C), which was identified by a mixed-melting-point test and by a comparison of the infrared spectrum with that of 51.

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