[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, HOLY CROSS COLLEGE]

Identification of Phenolic Ethers as Picrates

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The derivatives most frequently employed in the identification of phenolic ethers are those obtained by bromination, nitration and oxidation. The instructions for the preparation of these derivatives are variable, and the original article must be consulted for each individual ether. The products obtained vary from a mono- to a trinitro derivative, and from a mono- to a pentabromo derivative. In many cases, mixtures are obtained. The oxidation of ethers is limited to those containing a side-chain, and the length of the side-chain cannot be determined by this method.

The picrates of phenolic ethers have never been fully studied as a means of identification. In our study of the picrates of phenolic ethers, we arrived at a uniform method of procedure, whereby any phenolic ether can be identified from its picrate. These picrates can be precipitated conveniently, their forms are quite diverse and characteristic and were found to be constant after repeating the crystallization.

Experimental

All phenolic ethers used were Eastman pure, excepting the *p*-nitrophenyl benzyl ether which was prepared in our laboratory. Chemically pure

PICRATES OF CERTAIN PHENOLIC ETHERS

Ether	Color	Crystalline structure	M. p., °C.	Nitrogen, % Calcd.	Found
Anethole[a,b]	Orange-red	Long needles	69–70	11.14	11.60
Anisole[a]	Bright yellow	Tabular crystals	79–81	12.46	12.62
Benzyl	Orange-yellow	Prism clusters	77–78	9.83	9.91
Benzyl methyl	Cream	Square plates	115–116	11.96	11.99
n-Butyl phenyl[a]	Light yellow	Hexagonal plates	110–112	11.08	11.79
Catechol diethyl[a]	Red-brown	Rhombic crystals	69–71	10.63	10.76
o-Tolyl methyl	Light yellow	Short prisms	118–119.5	11.96	11.82
m-Tolyl methyl	Orange-yellow	Medium prisms	113–114	11.96	11.44
p-Tolyl methyl	Yellow-orange	Long prisms	88–89	11.96	12.32
o-Tolyl ethyl	Light yellow	Short prisms	117.5–118.5	11.57	11.23
m-Tolyl ethyl	Orange-yellow	Medium prisms	114–115	11.57	11.44
p-Tolyl ethyl	Yellow-orange	Long prisms	110–111	11.57	11.90
Eugenol	Brown-red	Long blades	62–63	10.68	10.45
Eugenol methyl	Red-brown	Rhombic crystals	114–115	10.32	10.97
Iso-eugenol[a]	Dark red	Silky needle clusters	46–47.5	10.68	10.71
Iso-eugenol methyl[c]	Very dark red	Slender rods	42–45	10.32	10.82
Guaiacol[a,d]	Orange-red	Short stout needles	88–89	11.89	11.42
Hydroquinone monomethyl	Orange-yellow	Long flat needles	43–44	11.89	11.96
Hydroquinone dimethyl[a]	Orange-red	Long blades	47–48	11.44	11.50
α-Naphthyl methyl	Yellow-orange	Silky needle clusters	127–127.5	10.85	10.25
β-Naphthyl methyl	Yellow	Fine needle clusters	113–113.5	10.85	10.48
α-Naphthyl ethyl	Yellow-orange	Fine needle clusters	107–108	10.47	10.63
β-Naphthyl ethyl	Orange-yellow	Fine needle clusters	99–100.5	10.47	10.58
p-Nitrophenyl benzyl	Very light yellow	Thin rectangular plates	84–84.5	12.23	12.16
Phenetole[a]	Very light yellow	Square plates	91–92	11.96	12.01
Phenyl	Yellow	Prisms	108–110	10.52	10.70
Pyrogallol trimethyl	Yellow	Thin rhombic plates	78.5–80	10.57	10.34
Resorcinol monomethyl[a]	Orange	Long blades	68–69.5	11.89	12.28
Resorcinol dimethyl[a]	Yellow-orange	Tetragonal needles	56–58	11.44	11.86
Resorcinol monoethyl	Red	Rhombic needles	105–106	11.44	10.98
Resorcinol diethyl	Brown-yellow	Long slender rods	108–109	10.63	10.94
Safrole	Orange-red	Long blades	104–105.5	10.74	10.62
Iso-safrole	Dark red	Thick needle clusters	74–75	10.74	10.89
Triphenylcarbinol methyl	Light yellow	Cubes	90–91	8.35	8.70
Veratrole[e]	Red-orange	Six-sided prisms	56–57.5	11.44	11.13

[a] Unstable on exposure to air. [b] Beilstein, Vol. VI, 4th ed., 1923, p. 568. [c] *Ibid.*, p. 956. [d] *Ibid.*, p. 770. [e] *Ibid.*, p. 771.

picric acid was dried in an oven at 100° for six hours. One millimole of the phenolic ether was dissolved in 10 cc. of warm chloroform. One millimole of picric acid plus 5% in excess (0.241 g.) was dissolved in 10 cc. of warm chloroform. The chloroform solution of the phenolic ether was then poured into the picric acid solution while stirring the mixture. This mixture was then set aside and allowed to crystallize in a 100-cc. beaker. The picrate was recrystallized from the smallest amount of warm chloroform. The form or habit of the crystals was then determined by means of a binocular microscope using a magnification of about seven.

The picrates of the four phenolic ethers found in the literature were reported by the investigators as being equimolecular addition products. Melting points were determined by the method of Mulliken[1] in which a thermometer calibrated by the Bureau of Standards was employed. All temperatures given are uncorrected. In the determination of nitrogen, Campbell and Gray's[2] modification of the Dumas method was used.

Discussion of Results

The molecular composition of all the picrates was found to be of the general type 1:1. All the stable picrates of the phenolic ethers can be prepared and recrystallized from 95% ethyl alcohol. The melting points of the picrates thus prepared correspond exactly to the melting points of the picrates prepared from chloroform. The instability of the unstable picrates is manifested by a loss of color upon exposure to air, a rise in melting point, and the amorphous form of the residual picric acid. The melting points of all the unstable picrates must be taken as soon after crystallization as possible, unless kept in a sealed container.

Anethole picrate is decomposed by ethyl alcohol, and the anethole polymerizes to di-anethole in the hot alcohol. The picrates of eugenol, iso-eugenol, eugenol methyl ether and iso-eugenol methyl ether form astatic liquid crystals from ethyl alcohol. The use of methyl alcohol as a solvent prevents this, but several days are required for crystallization. The picrates of anisole, phenetole and *n*-butyl phenyl ether are all decomposed by ethyl alcohol. Methyl alcohol prevents this to a certain extent. The picrates of the isomeric ethers are all darker, and possess lower melting points than the picrates of the normal ethers. The picrates of the α-naphthyl ethers are darker and possess higher melting points than the picrates of the β-naphthyl ethers.

The preparation and recrystallization of all the unstable picrates of phenolic ethers is possible through the use of chloroform as a solvent, thereby affording a general and uniform method of procedure in the preparation of all the picrates of the phenolic ethers. As optical crystallographic data are very important in the final identification of an organic compound, it is hoped to be able to report on the refractive indices of these picrates in a future communication.

Summary

1. The picrates of thirty-five phenolic ethers have been prepared and were found to be suitable derivatives for identification purposes.

2. The procedure is uniform and requires no special degree of skill.

3. The picrates are highly crystalline solids, easily purified and possessing sharp melting points.

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(1) Mulliken, "Identification of Pure Organic Compounds," Vol. I, John Wiley & Sons, Inc., New York City, 1904, p. 218.

(2) Campbell and Gray, *J. Soc. Chem. Ind.*, **49**, 447 (1930).