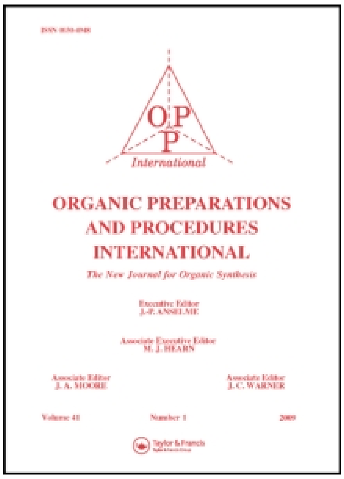

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AN EFFICIENT TECHNIQUE FOR THE CLEAVAGE OF HYDROCARBON PICRATES. THE PURIFICATION OF 1,8-, 2,6-, and 2,7-DIMETHYLNAPHTHALENE

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AN EFFICIENT TECHNIQUE FOR THE CLEAVAGE OF HYDROCARBON PICRATES.

THE PURIFICATION OF 1,8-, 2,6-, and 2,7-DIMETHYLNAPHTHALENE

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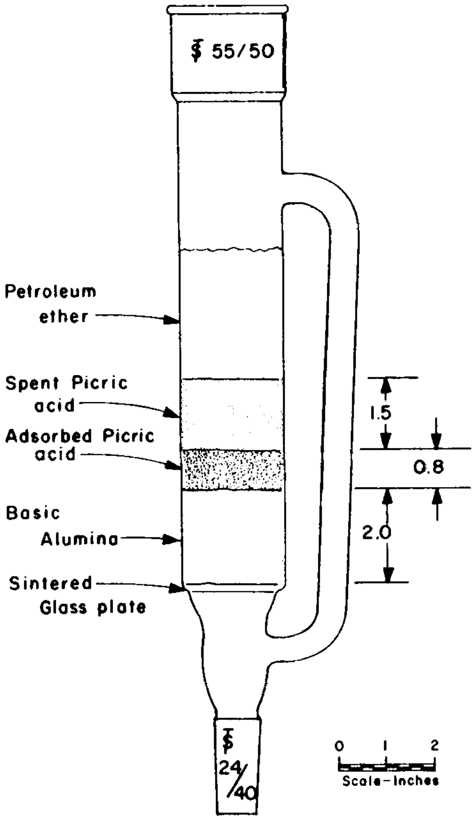
The cleavage of arene picrates to the hydrocarbons may be accomplished by extraction of picric acid from a benzene solution of the picrate with ammonium hydroxide[2a] or aqueous sodium carbonate.[2b] The separation of arenes from picric acid may also be done by adsorption of the latter on a column of alumina.[2c] The arenes are then recovered from the benzene eluate. These techniques are adequate for small-scale isolations, but they become cumbersome, tedious, and expensive when larger quantities are involved.

We now report a technique for dissociation of picrates of arenes that depends upon the leaching action of petroleum ether, which dissolves the arene but essentially no picric acid; this permits recovery of picric acid for reuse and considerably reduces the amount of hydrocarbon solvent and alumina needed for the separation. Most of the picric acid remains undissolved and out of contact with the alumina. The arene is then recovered by removing the solvent by rotary evaporation or distillation.

We describe in detail the application of this procedure to 2,7-dimethylnaphthalene because of the attention its isolation and purification have received.[4a-c] We have also applied purification via the picrate to 1,8- and 2,6-dimethylnaphthalene. Our glc data[3a] show that a 2% impurity of 2,6-dimethylnaphthalene[3b] was removed from 2,7-dimethylnaphthalene by this procedure.[3e] It is of interest that a 0.2% impurity (*m/e* 170) in zone-refined 2,6-dimethylnaphthalene was also removed.

We sought to extend the technique for cleavage of hydrocarbon picrates to those of more complex arenes. The picrates of phenanthrene, fluoranthene, and pyrene were prepared and tested. Of these, the picrate of phenanthrene was readily cleaved as described for that of 2,7-dimethylnaphthalene. However, the picrates of fluoranthene and pyrene are more stable and less soluble in petroleum ether and therefore require more time (double or triple) for cleavage. As expected, with prolonged reflux the liberated picric acid is dissolved and penetrates the alumina column. Consequently, there is no advantage in using the extraction apparatus of Fig. I. For this type of picrate, the previously described procedure[2c]



of using alumina to adsorb picric acid from a benzene solution of the picrate may be used; it is rapid and effective but more solvent and alumina are required, for example, the cleavage of 1 g. of fluoranthene picrate requires 500 ml. of benzene and at least 15 g. of basic alumina.

The choice between benzene and petroleum ether for cleavage of the hydrocarbon picrate may be made by testing the solubility in hot petroleum ether and observing a change in appearance[5] or a loss in weight due to extraction of hydrocarbon. The petroleum ether extraction of an equivalent weight of picric acid serves as a good comparison. It should be noted that the number of rings and molecular weight of the hydrocarbon are not always reliable criteria in judging whether a hydrocarbon picrate will readily decompose in petroleum ether; for example, the picrate of 1',2',3',4'-tetrahydro-1,2'-binaphthyl (4 rings, $C_{20}H_{18}$) is readily cleaved by petroleum ether in the extraction apparatus.[6a]

EXPERIMENTAL

Preparation and Recrystallization of Dimethylnaphthalene Picrates. To a 4-l., wide-mouth, Pyrex crystallizing bottle (Corning No. 1597) was added 78 g (0.5 mole) of 2,7-dimethylnaphthalene, mp. 92-95°, of approximately 98% purity,[3a,b] 126 g. (0.55 mole) of picric acid,[3d] and 2 l. of 95% ethanol. The suspension was boiled with a mantle (Glascol No.0-636) until solution was complete. The solution was allowed to cool to room temperature and the picrate of 2,7-dimethylnaphthalene crystallized spontaneously as bright yellow needles. After overnight refrigeration, the crystals were filtered and dried[3f] to give 165 g.(85%), mp. 136-138°. Successive recrystallizations from 1.8 to 2 l. of 95% ethanol gave 140 g. (72%); 130 g. (67%); 105 g. (54%) based on dried[3f] wt. The mp. after recrystallizations was 136-137° [lit.[3c] 135.5-136°].

The mp., dried[3f] wt. of picrate, and percent yield for the similarly prepared yellow-orange picrate of 1,8-dimethylnaphthalene at each step were: 153-156°, 132 g. (68%); 154.5-156°, 125 g. (65%); 155-156.5°, 115 g. (60%); and 155-157°, 100 g. (52%) [lit.[6b] 154.5-155.5]. Likewise, the picrate of 2,6-dimethylnaphthalene was prepared in 75% yield and recrystallized from 95% ethanol to give a 60% yield of yellow-orange crystals, mp. 141-143.5° [lit.[3c] 141-142°].

The Regeneration of Arenes from their Picrates. A dried[7a] 72-g. (0.182 mole) sample of the purified picrate was added to the glass filtration apparatus[7] (Fig. I) fitted with reflux condenser and containing 80 g. of basic alumina (2.2 in. x 2.7 in.). A 5-cm. Teflon-coated magnetic stirring bar was placed on the picrate crystals and a 1-l. recovery flask containing 500 ml. petroleum ether[7c] was attached to the apparatus. The contents of the flask were refluxed at a rate which kept a level of condensed solvent above the picrate as shown in the drawing. At intervals, the picrate crystals were agitated by manually manipulating the Teflon-covered magnetic stirring bar to reduce channeling. The extraction was continued for 5-6 hr. until the yellow-orange color of the picrate had changed to the pale yellow color of anhydrous picric acid. The height of the picrate layer in the apparatus shrank from 2.7 in. to 1.5 in. during the extraction. At the end of the extraction period, an orange-colored band (*ca.* 0.8 in.) had penetrated the alumina charge. The remainder of the alumina was colorless. The contents of the recovery flask were concentrated (rotary evaporation) to give 27 g. of 2,7-dimethylnaphthalene: mp. 96-97° [lit.[3c] 96-97°]. A second extraction for 2 hr. yielded an additional 1.5 g. of hydrocarbon (98% total yield for the regeneration).

The yields of 1,8-dimethylnaphthalene, mp. 63-64.5° [lit.[6b] 62.5-64°], and 2,6-dimethylnaphthalene, mp. 109.5-111° [lit.[3c] 110-111°], obtained by regeneration from their picrates were 95% and 97% respectively.

Phenanthrene, mp. 97-99°, fluoranthene, mp. 106-108.5°, and pyrene mp. 148.5-152.5°, were used to prepare the respective picrates. Recrystallization in each case from 95% ethanol gave yellow crystals, mp. 144-146.5° [lit.[8a] 145°]; orange needles, mp. 186-188° [lit.[8b] 186.8-188.1°]; and fine red needles, mp. 226-227.5° [lit.[8c] 219-220°] respectively. Decomposition of phenanthrene picrate as described for 2,7-dimethylnaphthalene gave 90% of colorless phenanthrene, mp. 98-99.5° [lit.[8a] 100°], while similar decomposition required 15-20 hr. for 19 g. of picrate using petroleum ether, bp. 60-68°, and 65 g. of basic alumina to give 80% of colorless fluoranthene, mp. 109.5-110.5° [lit.[8b] 110.6-111°]. A similar experiment with pyrene picrate gave pyrene, mp. 150-153° [lit.[8c] 149-150°].

In a separate regeneration, a 1-g. sample of fluoranthene picrate dissolved in 100 ml. benzene was added to a 2.5 x 15 cm. (50 g.) column of basic alumina. Four additional 100-ml. portions of benzene were passed through the column. Only a trace amount of fluoranthene was observed in the last portion of effluent. The benzene was removed by rotary evaporation to leave crystalline fluoranthene. The colored layer due to picric acid penetrated about 5 cm. into the alumina column.

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(c) API, GRA, 1969-.
(d) Continental Oil Company Graduate Research Fellowship, 1970-1971.

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(3) (a) A Hewlett-Packard Model 5750 instrument fitted with hydrogen flame and thermal conductivity detectors and containing a 0.25-in. x 10-ft. column of 80-100 mesh Chromosorb G (acid-washed and DMCS-treated) coated with a mixture of 15% Bentone-34 and 5% SE-52 was used for the glc analyses.
(b) The 2,6-dimethylnaphthalene used for glc comparison with pure and impure 2,7-dimethylnaphthalene studies showed a purity in excess of 99.9% by calorimetric mp. determination. We thank D. R. Douslin, H. Finke, and J. Messerly, API Research Project 62, Bureau of Mines, Bartlesville, Okla., for this information.
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(d) The picric acid was previously covered with anhydrous ethanol and isolated by filtration to remove the water (15%) present in commercial material.
(e) Usually 4-5 recrystallizations afforded the pure picrate as determined by glc[3a,b] of regenerated hydrocarbon.
(f) The dried wt. was obtained by drying a portion to free flowing crystals at 1 mm. at room temperature.

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(7) (a) The picrate was dried overnight at 1 mm. at room temperature. This is recommended since picric acid is soluble in water and ethanol, and the presence of the latter two reduces the effectiveness of the petroleum ether extraction.
(b) Picrate dust should be excluded from the sidearm of the extraction apparatus; otherwise it may become necessary to filter the soluion through a small amount of basic alumina to remove yellow color. We thank Mr. M. W. Adkins for discussions of the design and the construction of this apparatus.
(c) The petroleum ether, bp. range 30-40°, was dried and redistilled before use.

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