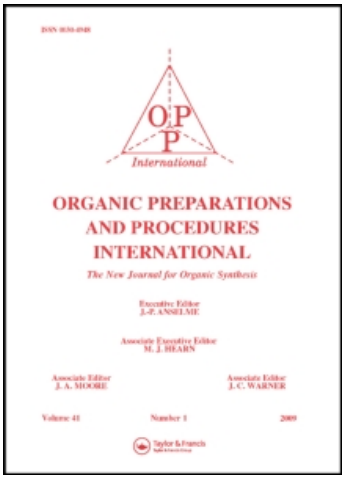

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A CONVENIENT SYNTHESIS OF 2, 3, 6, 7-TETRAMETHYLANTHRACENE

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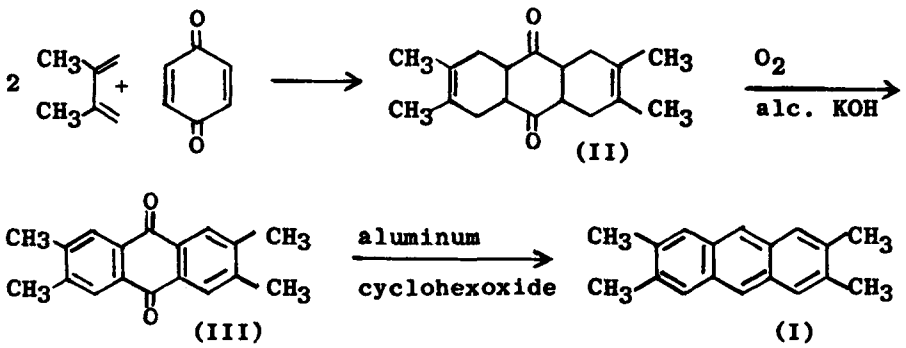

In connection with other work it was desirable to have available reasonable amounts (25-50 g) of isomerically pure 2,3,6,7-tetramethylanthracene (I).

Several disadvantages are apparent in the methods reported in the literature for the preparation of (I). For example, some routes result in mixtures of methylated anthracenes that are extremely difficult to separate and purify:[1] other methods[2] are not suited to securing the amounts of (I) needed.

The synthetic route chosen is patterned after one described by Morgan and Coulson[3] with certain important modifications.

Cycloaddition of p-benzoquinone with two equivalents of 2,3-dimethylbutadiene gave the adduct (II) in 50% yield after recrystallization from ethanol. Dehydrogenation of (II) in

boiling alcoholic potassium hydroxide in the presence of oxygen gave the tetramethylanthraquinone (III) in 96% yield. Finally, (III) was readily converted to 2,3,6,7-tetramethylanthracene in 85% yield by treatment with aluminum cyclohexoxide[4] in boiling cyclohexanol. This procedure gives large amounts of the highly pure anthracene easily from readily available starting materials.

EXPERIMENTAL

2,3,6,7-Tetramethyloctahydroanthraquinone (II).--A mixture of 123 g (1.5 mole) of 2,3-dimethylbutadiene[5] and 75 g (0.7 mole) of p-benzoquinone in 400 ml of 95% ethanol was stirred and refluxed for 20 hr in a flask equipped with an efficient condenser. The solution was then cooled and placed in a refrigerator overnight. The crystalline mass was collected and washed with cold ethanol. Recrystallization from 95% ethanol gave 95 g (50%) of adduct (II) as white needles, mp. 206-208° (lit.[3] mp 202-203°).

2,3,6,7-Tetramethylanthraquinone (III).--This compound was prepared essentially as given in reference 3 except that the mixture was refluxed for 24 hr to give a 96% yield of (III), mp 324° (lit.[3] mp 330°) pure enough for the next step.

2,3,6,7-Tetramethylanthracene (I).--To a solution of 1M aluminum cyclohexoxide in cyclohexanol[4] (200 ml) was added all at once 10 g (0.038 mole) of solid anthraquinone (III). The mixture was stirred and refluxed under nitrogen for 48 hr. After this time the reaction was cooled and then stirred well with 100 ml of water. The precipitate was collected and washed with ethanol. The solid was extracted with benzene

overnight in a Soxhlet apparatus. The benzene extract was concentrated and the solid collected and recrystallized from benzene to give 7.5 g (85%) of 2,3,6,7-tetramethylanthracene as white needles (faint yellow in mass), mp 298-302° (lit.[2] mp 299-300°). The uv spectrum was identical with that previously reported.[2]

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