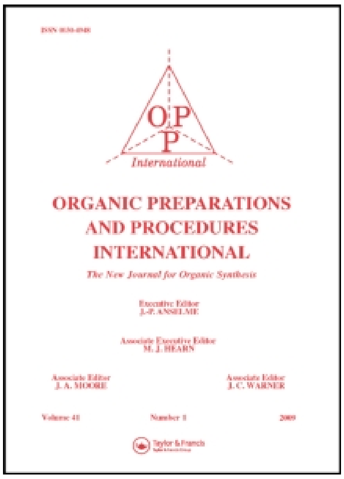

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RECOMMENDED SYNTHESES FOR 7-METHYLBENZ[a]ANTHRACENE, 12-METHYLBENZ[a]ANTHRACENE AND 7,12-DIMETHYLBENZ[a]ANTHRACENE

Melvin S. Newman[a]; J. M. Khanna[a]; Kenneth C. Lilje[a]
[a] Department of Chemistry, Ohio State University, Columbus, Ohio

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RECOMMENDED SYNTHESES FOR 7-METHYLBENZ[a]ANTHRACENE, 12-METHYLBENZ[a]ANTHRACENE AND 7,12-DIMETHYLBENZ[a]ANTHRACENE[†]

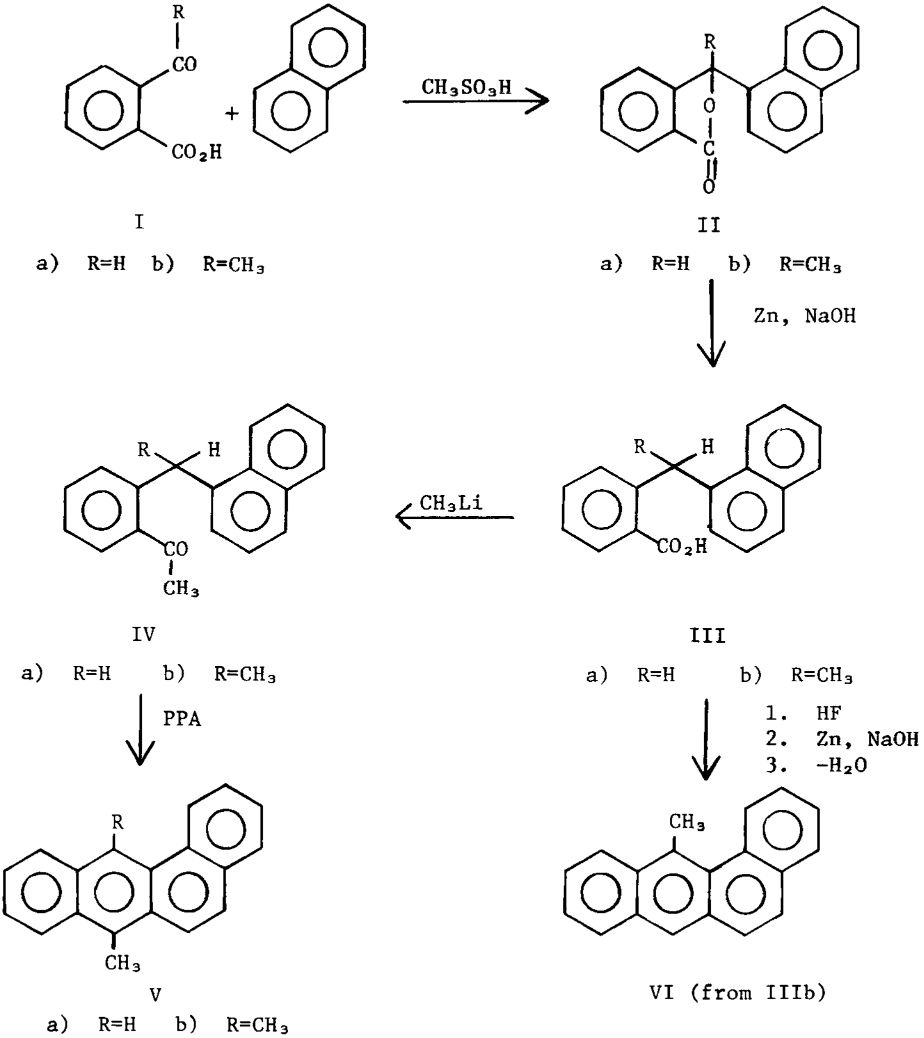
Melvin S. Newman*, J. M. Khanna[††], and Kenneth C. Lilje[††]

Department of Chemistry, Ohio State University, Columbus, Ohio 43210

Although syntheses of 7-methyl- and 12-methylbenz[a]anthracene and of 7,12-dimethylbenz[a]anthracene have been published, the recent renewed interest in these compounds and variously substituted analogs thereof, prompts us to outline the methods we prefer because of the ease of obtaining the starting materials and the reliability of the steps involved together with quite high yields of easily purified end products.

The syntheses of IIa and IIb have been described.[1] Reduction with zinc and alkali to IIIa and IIIb has in general been more reliable than reduction with zinc and acid.[2] The reactions of IIIa and IIIb with methyllithium proceed in 72 and 75% yields to IVa and IVb but the remaining material is the starting acids (IIIa and IIIb) so that the material balance is excellent. Ring closure of IVa and IVb by heating with PPA yields Va and Vb in 91 and 87% yields (pure).

The syntheses of VI *via* IIIb can be carried out readily by two routes. In one, IIIb is cyclized to 12-methyl-7(12H)-benz[a]anthracenone by HF and the crude anthrone immediately reduced to a secondary alcohol which can readily be dehydrated to VI (see Experimental Section for important details of this method) in 75% overall yield from IIIb. As some prefer not to use liquid HF, IIIb may be cyclized to 7-acetoxy-12-methylbenz[a]anthracene by heating with acetic anhydride and zinc chloride,[3] followed by reduction to VI in 69% yield (from IIIb).



EXPERIMENTAL

2-(1-Naphthylethyl)benzoic Acid, IIIb.- After keeping a mixture of 20.13 g (73.5 mmol) of IIb,[1] 160 ml of methanol, 60 ml of water, 24 g (430 mmol) of KOH, and 40 g (614 mmol) of Zn dust at reflux for 70 h the hot mixture was filtered through a bed of Hyflow Super Cell and the residue washed with 200 ml of hot water. After removal of methanol the residue was added to 200 ml of 18% HCl. The resulting precipitate was collected, washed, and dried to yield 20.14 g (72.8 mmol) of IIIb, mp 163.5-165.5°. Recrystallization from 200 ml ethanol afforded 17.54 g (63.6 mmol) (87%) of IIIb,[6] mp 166-163°. Reduction of IIb to IIIb may also be accomplished by Zn and formic acid as described.[7]

2-(1-Naphthylmethyl)acetophenone, IVa.– To a stirred solution of 25.0 g (0.095 mol) of IIIa in 500 ml of dry ether was slowly added 150 ml of 1.6 M methyllithium (0.24 mol) in ether. After stirring overnight at room temperature the mixture was acidified with dil HCl and the ether layer extracted with alkali to return 6.0 g, (0.023 mol, 24%) of IIIa. The remaining liquid 18.0 g (0.069 mol, 72%) was essentially pure IVa[8] and was used directly in the next step.

7-Methylbenz[a]anthracene, Va.– A stirred mixture of 17.0 g (65.5 mmol) of IVa and 450 g of PPA was heated on a steam bath for 90 min. This mixture was poured on ice and the solid produced was crsytallized from acetic acid to yield 14.5 g (60 mmol, 91%) of Va, mp 136.5-138°.[9]

12-Methylbenz[a]anthracene, VI.– To 125 ml of anhydrous HF in a plastic container was added with stirring 10.0 g (36.3 mmol) of powdered IIIb. After 20 min. the red solution was poured on ice. The resulting solid was collected and immediately added to 400 ml of 2N NaOH, 100 ml of toluene and 50 g (750 mmol) of Zn dust (activated with $CuSO_4$). After being held at reflux for 3 days the temperature was lowered and 100 ml of benzene added. The solid was filtered and extracted with 200 ml of hot benzene. The filtrate and washings were worked up as usual to yield 8.7 g of a yellow oil. This oil was heated with 50 ml of ethanol and 60 ml of benzene with 1 g of acid resin. After the usual work up a solid was obtained which on crystallization from 100 ml 5% benzene in ethanol afforded 6.58 g, (27.2 mmol, 75%) of VI as yellow plates, mp 135-137°. Chromatography of 1 g on 40 g of silica gel using benzene-hexane afforded 0.87 g of colorless VI,[9] mp 137-138.3°.

Alternately, a solution of 10.0 g (36.3 mmol) of IIIb in 75 ml of acetic acid, 75 ml of acetic anhydride, and 450 mg of $ZnCl_2$ was refluxed for 2 h then poured on ice. The resulting yellow solid was reduced over Zn and NaOH as described above to yield 0.8 g of yellow oil which was treated with acidic ethanol-benzene as described above to yield 6.1 g (25.2 mmol, 70%) of yellow VI, mp 135-136° which could be purified to yield colorless VI as above.

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†† Postdoctoral Research Associate.

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