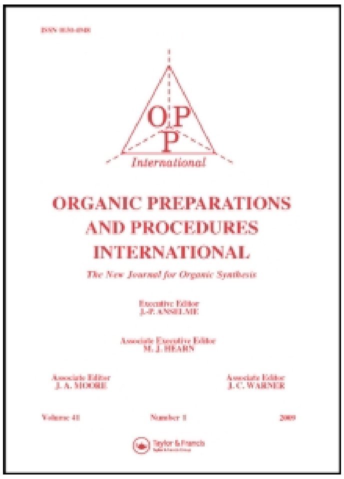

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PREPARATION AND REACTIONS OF 10-SPIROCYCLOPROPYLANTHRONE‡

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We have recently found need for large quantities of 10-spirocyclopropylanthrone (I) as a starting material in a series of synthetic preparations. Though spiroketone I has previously received attention,[1,2] its potential as a synthetic intermediate remains unexplored. This compound is a useful starting material for a number of syntheses[3] including the preparation of unsymmetrically 9,10-disubstituted anthracenes illustrated in Figure 2.

There are no existing routes to this spiroketone which are both efficient and convenient on a large (100 g) scale. Previous syntheses are limited to the examples shown in Figure 1. The preparation of this compound by Mustafa and Hilmy[4] requires a ten-fold excess of diazomethane and, in our hands, it gives no detectable yield of I when only one equivalent of diazomethane is used.[5] Prudence dictates use of the Mustafa procedure on a ten millimole scale.

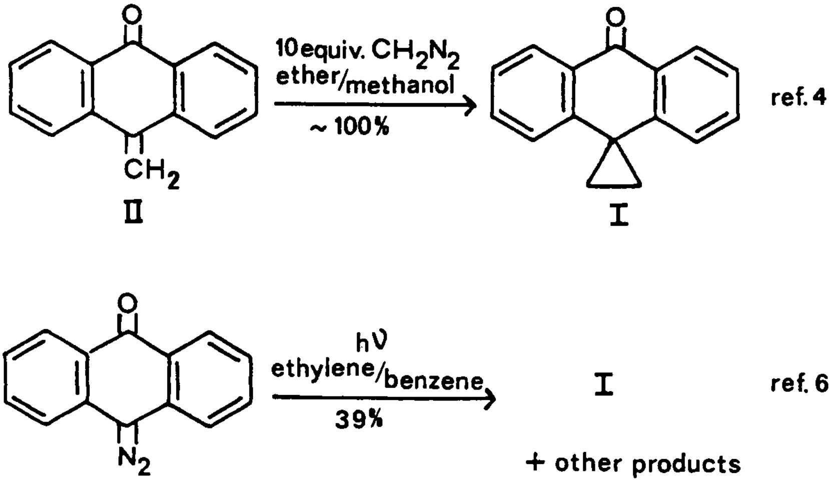

FIG. 1

We now report that reaction of one equivalent of dimethyloxosulfonium methylide[7] with 10-methyleneanthrone (II)[8] leads to spiroketone I in 86% crude yield. This procedure has been used to prepare up to 70 g of I in a single batch. Prepared in this fashion, I is of reasonable purity and is usable for our purposes without further purification.

Anthracenes substituted in the 10 position have been, for many years, conveniently synthesized by the addition of Grignard reagents to anthrone followed by acid mediated aromatization.[9] Extension of this procedure through use of I instead of anthrone leads to unsymmetrically disubstituted anthracenes with one alkyl substituent functionalized in the β-position, as shown in Figure 2. This affords, for example, potentially easy entry to the 10-substituted vinylanthracene series.

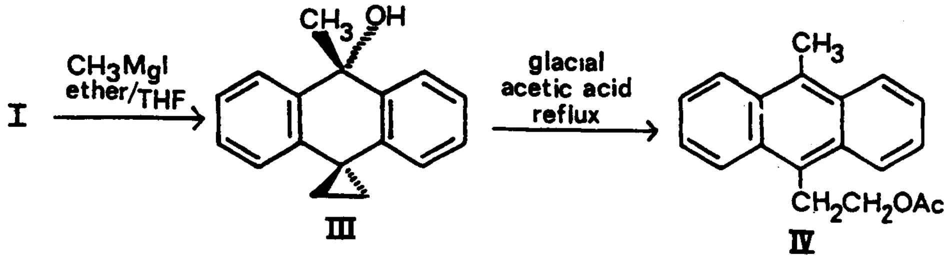

FIG. 2

Though reaction of I with one equivalent of either methyllithium or methylmagnesium iodide led to low yields (largely recovered starting material) of carbinol III, reaction with a five-fold excess of methylmagnesium iodide for long reaction times provided a 93% yield of III. Acetolysis gave the thermodynamically favored[10] anthracene derivative IV with no other products evident.

EXPERIMENTAL

All mps are uncorrected. IR spectra (thin film) were recorded on a Perkin-Elmer 567 spectrophotometer and ^{1}H-nmr spectra ($CDCl_3$, TMS ref.) were recorded on Varian Associates A-60 and Perkin-Elmer R-32 spectrometers. Mass spectra were taken on an AEI MS12 spectrometer.

10-Spirocyclopropylanthrone (I). -- Sodium hydride (1 g of 50% dispersion in mineral oil, 0.02 mole) was placed in a 100 ml three-necked round bottomed flask and washed three times with small portions of light petroleum ether. The flask was evacuated to remove the last traces of ether and fitted immediately with reflux condenser, pressure equalizing addition funnel, nitrogen inlet and magnetic stirring bar. Solid dimethyloxosulfonium iodide (4.6 g, 0.02 mole) was added and the system was flushed thoroughly with nitrogen and kept under nitrogen atmosphere until work-up. Careful dropwise addition of 25 ml dry DMSO (vacuum distilled from calcium hydride) led to rapid evolution of hydrogen gas and heat. If addition is too rapid and traces of oxygen remain in the vessel, there is danger of explosion and fire. When hydrogen evolution ceased, methylene anthrone (4.1 g, 0.02 mole) in 5 ml dry DMSO was added dropwise producing a deep red solution which was stirred overnight at room temperature and then quenched in 100 ml cold saturated aqueous sodium chloride. The mixture was stirred 10 minutes, vacuum filtered and washed with water on the filter, yielding 3.8 g (86%) of a buff colored product, mp. 146-149° (lit.[4] 152°). A small sample was recrystallized from aqueous ethanol (50% recovery), mp. 151-151.5°. IR: 1660 cm^{-1}, ^1H-nmr: δ 1.9 (s, 4H), δ 6.9-8.6 (m, 8H). The crude spiroketone was used in the following procedure.

Addition of Methylmagnesium Iodide to I. -- Magnesium turnings (6.25 g, 0.26 mole) were placed in a 500 ml three necked round bottomed flask fitted with a pressure equalizing addition funnel, reflux condenser and calcium chloride drying tube and the apparatus was flamed. Methyl iodide (35.4 g, 0.25 mole) in 60 ml anhydrous ether was added dropwise at a rate which maintained reflux. After reaction subsided, **I** (11.0 g, 0.05 mole), dissolved in 150 ml anhydrous tetrahydrofuran, was added dropwise and the solution was then refluxed for three days. The reaction mixture was poured into 200 ml saturated aqueous ammonium chloride and the organic layer was washed with saturated aqueous sodium chloride and dried over anhydrous calcium sulfate. Evaporation of solvents left 11.0 g (93%) buff colored solid. Recrystallization from Skelly B and benzene (50% recovery) gave off-white material, mp 138-140°. IR: 3300 cm^{-1} (broad, strong); ^{1}H-nmr: δ 1.1 (t, 2H), 1.6 (s, 3H), 1.9 (t, 2H), 2.3 (s, 1H), 6.9-7.9 (m, 8H); M.S.: m/e 237 (M^{+} + 1), 236 (M^{+}). The crude carbinol was spectroscopically similar and was used in the following procedure without purification.

Acetolysis of III -- Methylcarbinol III (0.29 g, 1.2 mmole) was dissolved in 10 ml glacial acetic acid and refluxed briefly. The solution was cooled, added to 40 ml water and extracted twice with 15 ml portions of ether. The combined ether extracts were washed three times with water, twice with 10% aqueous sodium bicarbonate, and dried over anhydrous magnesium sulfate. Evaporation of ether yielded 0.24 g (70%) yellow solid. Recrystallization from petroleum ether (60-80°) gave yellow needles, mp 117-119°. IR: 1730 cm^{-1}; ^{1}H-nmr: δ 2.05 (s, 3H), 3.05 (s, 3H), 3.79 (t, 2H), 4.45 (t, 2H), 7.4-7.65 (m, 4H), 8.2-8.5 (m, 4H); M.S.: m/e 278 (M^+). Crude and recrystallized samples had nearly identical IR and ^{1}H-nmr spectra.

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