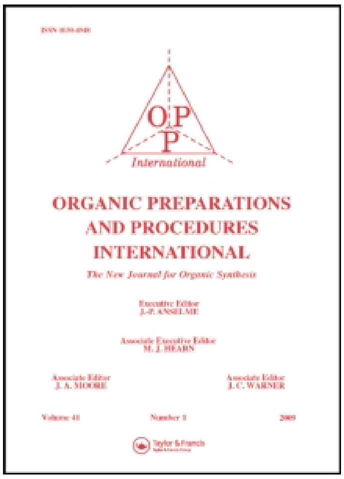

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PREPARATION OF 3-(9,10-DIHYDRO-1-ANTHRYL)PENTANE-2,4-DIONE

Y. Nakano[a]; H. Hiura[a]
[a] Facility of Science, Ibaraki University, Bunkyo, Mito, JAPAN

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broad).

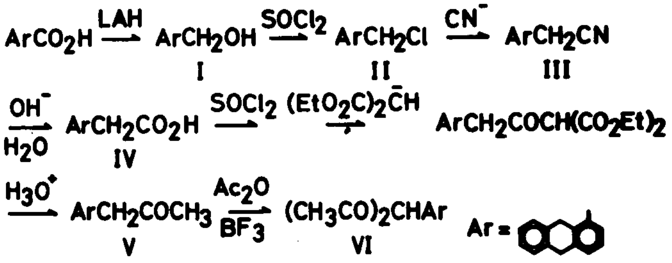
Anal. Calcd for $C_{64}H_{52}N_4 \cdot 3/2\ H_2O$: C, 84.98; H, 6.12; N, 6.24.

Found: C, 85.03; H, 5.91; N, 5.79.

PREPARATION OF 3-(9,10-DIHYDRO-1-ANTHRYL)PENTANE-2,4-DIONE

Submitted by Y. Nakano* and H. Hiura
(9/15/78)
Faculty of Science
Ibaraki University
Bunkyo, Mito 310
JAPAN

3-(9,10-Dihydro-1-anthryl)pentane-2,4-dione(VI) was obtained by the sequence shown below.



EXPERIMENTAL

Elemental analyses were performed with a Yanagimoto Model MT-1 CHN-corder. Infrared and ^1H NMR spectra were obtained with Hitachi Model EPI-S_2 and Hitachi Model R-20 spectrometers, respectively. Melting points are uncorrected.

1-Hydroxymethyl-9,10-dihydroanthracene(I).- Forty grams (0.19 mole) of 9,10-dihydro-1-anthroic acid[1] was added in small portions to a suspension of 12 g of $LiAlH_4$ in 1.2 l of ether under vigorous stirring. The reaction mixture was stirred and refluxed for 0.5 hr. After addition of water followed by 700 ml. of 10% H_2SO_4, a crystalline solid was obtained from the ether layer. Recrystallization from aqueous ethanol gave 34.4 g. (84%) of colorless crystals, mp. 74-75°. ^{1}H NMR ($CDCl_3$): τ 5.29 (2H s, Ar$\underline{CH_2}$OH), 7.57 (1H s, O$\underline{H}$).

Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.43, H, 6.41.

1-Chloromethyl-9,10-dihydroanthracene(II).- A mixture of the preceding alcohol (30 g, 0.143 mole), 500 ml of benzene and 20 ml of $SOCl_2$ was refluxed for 5 hrs. The cooled solution was washed with 10% $NaHCO_3$ solution and then with water. The benzene solution was dried and evaporated. The residue was recrystallized from a mixture of hexane and benzene to yield 24.7 g (80%) of II, mp. 63-65°. ^{1}H NMR ($CDCl_3$): τ 5.30 (2H s, Ar$\underline{CH_2}$Cl).

1-Cyanomethyl-9,10-dihydroanthracene(III).- To a mixture of NaCN (14.7 g, 0.3 mole) tetra-n-butylammonium chloride (0.8 g), and H_2O (6 ml) was added 22.8 g (0.11 mole) of II dissolved in 150 ml of ether.[2] The colorless crystals which formed were filtered and washed with ether. The filtrate was treated with the same amount of fresh NaCN solution under the same conditions. The combined crystals were recrystallized from benzene-hexane to afford 15.9 g (66%) of colorless neddles, mp. 109-110°. IR(KBr): 2230 cm^{-1}. ^{1}H NMR: τ 6.28 (2H s, Ar$\underline{CH_2}$CN).

Anal. Calcd for $C_{16}H_{13}N$: C, 87.64; H, 5.98; N, 6.39. Found: C, 87.73; H, 6.05; N, 6.56.

9,10-Dihydro-1-anthrylacetic acid(IV).- A mixture of III (17.7 g, 0.81 mole), ethanol (53 ml), and 10% NaOH solution (1240 ml) was refluxed for 6 hrs. After treatment with charcoal, the clear solution was acidified with acetic acid. The white precipitate was collected and recrystallized from benzene-hexane to afford 9.1 g (48%) of IV as colorless needles, mp. 155-157°. IR: 1710 cm^{-1}. ^{1}H NMR($CDCl_3$): τ -1.25 (1H broad, $CO_2\underline{H}$), 6.23 (2H s, Ar$\underline{CH_2}CO_2$H).

Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.56; H, 6.03.

1-(9,10-Dihydro-1-anthryl)propan-2-one(V).- A mixture of acid, IV (12 g, 0.051 mole), absolute benzene (300 ml) and 16.6 ml of thionyl chloride was refluxed for 3 hrs. with stirring. Benzene and excess $SOCl_2$ was removed at 30 mmHg below 100°. The residual oil (22.3 g) was used in the next step without further purification.

A mixture of absolute ethanol (2.5 ml) and CCl_4 (0.3 ml) was added to 2.54 g of magnesium turnings. After five minutes a solution of diethyl malonate (15.9 ml) in absolute ethanol (9.5 ml) and absolute ether (20 ml) was added dropwise to maintain gentle reflux. Reflux was continued for an additional 3 hrs. with stirring. To the mixture was added the solution of the acyl chloride (22.3 g) in ether (24 ml) with vigorous stirring. The mixture was stirred until a viscous layer appeared. After acidification with dil. H_2SO_4, the aqueous layer was separated and extracted ether. The combined ethereal solution was evaporated and the residue was heated with acetic acid (56.6 ml), conc. H_2SO_4 (7.8 ml), and H_2O (38 ml) for 4 hrs. The cooled reaction mixture was made alkaline with 20% NaOH solution and extracted with ether. The ethereal layer was dried (Na_2SO_4) and evaporated. Crude ketone V (obtained as an oil) was passed through a column of florisil with benzene as eluent and used in the next step without further purification. IR: 1720 cm^{-1}. ^1H NMR: τ 8.06(3H s, -$\underline{CH_3}$), 6.40 (2H s, Ar$\underline{CH_2}$C=O).

3-(9,10-Dihydro-1-anthryl)-pentane-2,4-dione(VI).- A mixture of V (22.3 g), acetic anhydride (23.3 ml), BF_3-acetic acid complex (39 g)[3] and anhydrous *p*-toluenesulfonic acid (1.63 g) was warmed to 50° with stirring for 24 hrs. Sodium acetate (38.1 g) dissolved in 370 ml of H_2O was added, and the mixture was refluxed for 2 hrs. The resulting black oil was extracted with ether, and washed with water twice. The β-diketone was extracted with 1N NaOH solution and was separated as an oily material on acidification with acetic acid. It was extracted with ether, and chromatographed on a column of silica gel with benzene. The crude β-diketone was obtained as a pale yellow solid. It was recrystallized from ethanol to give 3.6 g. of colorless crystals, mp. 93-95°; IR: 1600 cm^{-1}. ^{1}H NMR: τ 8.13 (6H s, -CH_3), -6.65 (broad, enolic OH), 2.4-3.1 (multiplet, aromatic protons), 4.3 and 6.0 (broad, methylene).

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52 . Found: C, 81.65; H, 6.32 .

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