

ONE-STEP SYNTHESIS OF AN ANTHRAQUINONE DERIVATIVE  
FROM AN ALIPHATIC POLYKETONE<sup>1</sup>

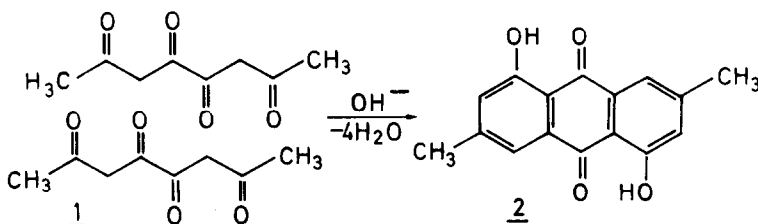
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The use of  $\beta$ -polycarbonyl compounds in biogenetic-type syntheses<sup>2</sup> was developed especially by Collie<sup>3</sup>, Robinson<sup>4</sup>, and Birch<sup>5</sup>. Robinson<sup>6</sup> suggested the possibility of heptaketopalmitic acid being the precursor of a naturally occurring anthraquinone pigment endocrocine. Notwithstanding many successful examples of biogenetic-type synthesis, no anthraquinone derivative has been obtained from  $\beta$ -polycarbonyl compounds.

We have now found that the 1,3,4,6-tetraketone oxalyldiacetone (1) undergoes an intermolecular condensation giving 3,7-dimethylanthrurufin (2).



The finely powdered oxalyldiacetone (1, 1.70 g, 0.01 M) prepared according to Claisen and Stylos<sup>7</sup> was dissolved in 30% potassium hydroxide (15 ml) and refluxed for 1 hr. The deep-red solution was acidified with 10% hydrochloric acid, the orange-red precipitate (0.44 g) filtered off and resuspended in a saturated solution of barium hydroxide octahydrate (25 ml) and refluxed for 3 hrs. The scarlet precipitate was collected and washed with hot water until the filtrate remained clear. The barium salt (0.24 g) was stirred with 1% hydrochloric acid and the resulting crude olive-green 3,7-dimethylanthrurufin (2, 0.108 g) sublimed at 140°/10<sup>-3</sup> mm giving orange needles (78 mg, 5.8%) with the m.p. 299-300°<sup>8</sup>. Mass m/e 268 (M<sup>+</sup>). Elemental analysis; found: C, 71.68;

H, 4.53%, calcd for  $C_{16}H_{12}O_4$ : C, 71.63; H, 4.51%. ir (KBr),  $\nu_{max}$  1619 s (C=O)  $cm^{-1}$ . uv (EtOH),  $\lambda_{max}$  (log  $\epsilon$ ) 229, 257, 417-437 (4.7, 4.2, and 4.0).

A similar condensation of 3,5,6,8-decanetetrone<sup>9</sup> and 2,11-dimethyl-4,6,7,9-dodecanetetrone<sup>10</sup> has been attempted, however without success.

3,7-Dimethylantrharufin (2, 67 mg) was refluxed for 5 hrs in acetic anhydride (10 ml) containing a few drops of pyridine. The excess acetic anhydride was evaporated and the lemon-yellow crystals collected. Recrystallization from aqueous ethanol gave yellow needles of 3,7-dimethylantrharufin diacetate (50 mg, 57%), m.p. 236°<sup>11</sup>. Mass m/e 352 ( $M^+$ ). Elemental analysis; found: C, 68.38, H, 4.92%, calcd for  $C_{20}H_{16}O_6$ : C, 68.18; H, 4.58%. ir (KBr),  $\nu_{max}$  1766 s (OAc), 1674 s (C=O)  $cm^{-1}$ . uv (EtOH)  $\lambda_{max}$  (log  $\epsilon$ ) 266 (4.6). <sup>1</sup>H-nmr ( $CD_2Cl_2$ ),  $\delta$  2.43 (6H s COCH<sub>3</sub>), 2.50 (6H s Ar-CH<sub>3</sub>), 7.19 (2H umc C<sub>2,6</sub>-H), 7.95 (2H umc C<sub>4,8</sub>-H).

Few examples of intermolecular self-condensation of either  $\beta$ - or  $\alpha$ -diketones are known. Diacetylacetone was condensed into the tetralone and/or naphthalene derivative<sup>12,13</sup>. Attempts to effect self-condensation of other  $\beta$ -diketones failed. On the other hand, the  $\alpha$ -diketones, diacetyl, and 2,3-pentanedione undergo intermolecular condensations into *p*-benzoquinone derivatives<sup>14,15</sup>.

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