A New Route to Stilbene α-Ketol Derivatives

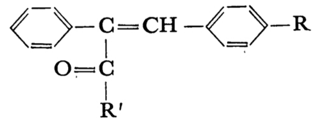
Sigeru Torii

Department of Industrial Chemistry, School of Engineering, Okayama University, Tsushima, Okayama

(Received June 25, 1966)

The need for a simple method of synthesizing α-acetoxymethylenecarbonylstilbenes (II), which are distinguished by a corticosterone-, deoxycorticosterone-, or cortisonelike chemotherapeutical activity,¹⁾ has led to direct preparation from α-acetyl-*cis*-stilbenes (I). II and stilbene α-ketols (IV) have been synthesized by Lettré *et al.*¹⁾ from stilbene α-carbonyl chlorides by the action of diazomethane, followed by treatment with acetic acid. The present paper will deal with the acetoxydation of I with lead tetraacetate in dry benzene or acetic acid.

I (R=H), mp 55°C (lit.²⁾ mp 55—56°C), was treated with an equivalent amount of lead tetraacetate in a solution of dry benzene or acetic acid at 80°C for 8 hr. The distillation of the products gave a fraction, 174—204°C/3 mmHg which crystallized upon trituration with ethanol to give II (R=H) in a 19% yield, needles, mp 94—94.5°C (*n*-hexane); IR: 1737 (acetoxy $\nu_{C=O}$), 1685 (conjugated $\nu_{C=O}$), and 1620 cm^{-1} ($\nu_{C=C}$). Found: C, 77.12; H, 5.75%. Calcd for $C_{18}H_{16}O_3$: C, 77.30; H, 5.93%. On the other hand, II (R=OCH_3), prepared similarly from I (R=OCH_3),³⁾,⁴⁾ was easily separated from an ethereal solution of the reaction products as a white leaflet in a 22% yield; it melted at 127.5—128°C (lit.¹⁾mp 128°C) (IR: 1740 (acetoxy $\nu_{C=O}$) and 1683 cm^{-1} (conjugated $\nu_{C=O}$)). (Found: C, 73.53; H, 5.85%. Calcd for $C_{19}H_{18}O_4$: C, 73.31; H, 5.94%).



I: R'=CH_3
II: R'=CH_2OCOCH_3
III: R'=OH
IV: R'=CH_2OH

The structure of II was proved by its conversion to α-phenyl-*trans*-cinnamic acid derivatives (III). Thus, the hydrolysis of II (R=H) was carried out by using 0.1 N potassium hydroxide in an aqueous methanol solution at room temperature; it gave III (R=H), mp 172.5°C (lit.⁵⁾ mp 173—174°C). Similarly, the hydrolysis of II (R=OCH_3) gave III (R=OCH_3), mp 187°C (lit. mp 188°C¹⁾ and 191—192°C⁴⁾).

The acetoxy compounds (II), when treated with 0.5—1 N hydrogen chloride in an aqueous methanol solution at room temperature, yielded IV in good yields. IR: 1680—1690 (ketol $\nu_{C=O}$) and 3500—3300 cm^{-1} (ν_{OH}).

The ketol (IV, R=H) was oxidized with potassium periodate⁶⁾ and a few drops of dilute sulfuric acid in an aqueous methanol solution at 20°C overnight, thus affording III (R=H), mp 173°C; mixed melting point, 172—173°C.

---

1) H. Lettré and O. Linsert, German Pat. 840091 (1952); *Chem. Abstr.*, **50**, 2676c (1956); O. Linsert and H. Lettré, U. S. Pat. 2691039 (1954); *Chem. Abstr.*, **49**, 15971 (1955).

2) H. E. Zimmerman, L. Singer and B. S. Thyagarajan, *J. Am. Chem. Soc.*, **81**, 108 (1959).

3) T. N. Ghosh, A. Bose and A. Raychaudhuri, *J. Indian Chem. Soc.*, **37**, 93 (1960).

4) E. Pavlovska, J. Lukac and M. Borovicka, Czech. Pat. 110222 (1964); *Chem. Abstr.*, **61**, 9439f (1964).

5) S. Goszczynski, *Roczniki Chem.*, **38**, 893 (1964); *Chem. Abstr.*, **62**, 16187h (1965).

6) K. Meyer and T. Reichstein, *Helv. Chim. Acta*, **30**, 1508 (1947).