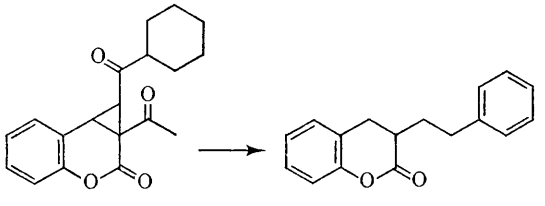
A Novel Reductive Retro-Claisen Reaction

By G. E. RISINGER* and H. H. HSIEH

(*Coates Chemical Laboratories, Department of Biochemistry, Louisiana State University Baton Rouge, Louisiana* 70803)

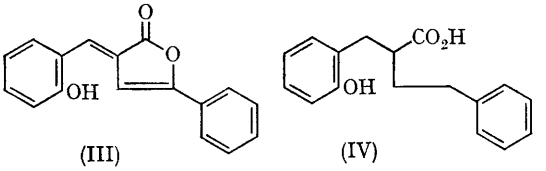
IN the course of investigating 3-acetyl-3,4-phenacylidenecoumarin (I),[1] it was discovered that catalytic hydrogenation of (I) affords anomalous products. Under atmospheric hydrogenation conditions, (I) readily absorbs two moles of hydrogen; on extending the reaction time to 72 hr., a third mole is absorbed. The product of this reaction is not a C_{19} compound but analyses for $C_{17}H_{16}O_2$ (II). This compound was shown to be



(I) + AcOH (II)

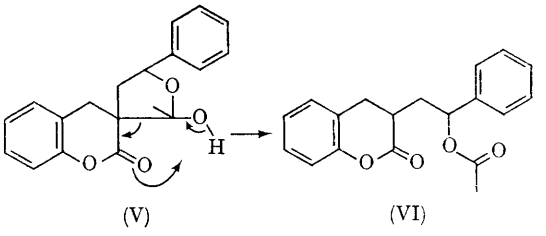
3-2′-phenethyldihydrocoumarin by means of the following synthetic scheme: by modifying the azlactone synthesis,[2] the butenolide (III) was synthesized by treating salicylaldehyde and β-benzoylpropionic acid with acetic anhydride and sodium acetate; hydrogenation of (III), followed by hydrolysis, affords a mixture of (II) and (IV); (IV) was converted into (II) by heating the mixture in the presence of acetic anhydride.

The best explanation for this novel reaction is that the initial rapid absorption of two moles of hydrogen affords the tetrahydro-compound (V).



(III) (IV)

The spiro-structure of this compound does not allow adequate adsorption to the catalyst. Thus, instead of undergoing the expected hydrogenolysis, compound (V), *via* a retro-Claisen, affords 3-2′-acetoxy-2′-phenethyldihydrocoumarin (VI) which yields (II) on hydrogenolysis.



(V) (VI)

(*Received, July 17th,* 1967; *Com.* 737.)

[1] O. Widman, *Ber.*, 1902, **35**, 1153; 1918, **51**, 533, 907, 1210; 1919, **52**, 1652; S. Wawzonek and C. E. Morreal, *J. Amer. Chem. Soc.*, 1960, **82**, 439.

[2] F. W. Schueler and C. Hanna, *J. Amer. Chem. Soc.*, 1951, **73**, 3528; F. R. Filler and L. M. Hebron, *ibid.*, 1959, **81**, 391.