

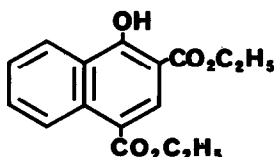
THE CONDENSATION OF ETHYL ARYL- AND HETARYLACETATES WITH DIETHYL ETHOXYMETHYLENEMALONATE

C. W. BIRD AND C. K. WONG

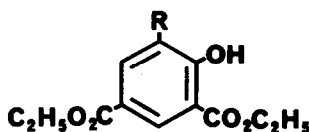
Department of Chemistry, Queen Elizabeth College, Campden Hill, London W8 7AH

(Received in UK 26 March 1975; accepted for publication 23 April 1975)

Some years ago a potentially useful method of ring annelation was reported^{1,2}, exemplified by the synthesis of the naphthol(I) from the sodium ethoxide promoted condensation of ethyl phenylacetate with diethyl ethoxymethylenemalonate. Our attempts to apply this process to the annelation of heterocyclic compounds have led to a reappraisal of this reaction.



I



II a R = C₆H₅
b R = α-C₄H₃S
c R = β-C₅H₄N

In our hands the reaction of diethyl ethoxymethylenemalonate with ethyl phenylacetate gives a product (24%) m.p. 90-91°³, whose composition is established by elemental analysis and mass spectroscopy as C₁₈H₁₈O₅. The infrared spectrum exhibits bands at 1710 (C=O), and 1665 cm⁻¹ (hydrogen-bonded C=O). The p.m.r. spectrum shows the presence of two ethyl groups (δ 1.39t and 1.46t, 4.42q and 4.50q), a phenyl group (δ 7.40-7.90m), a hydroxyl group (12.0 δ) and two meta protons (8.33 and 8.73 δ, J=3Hz). Hydrolysis of this compound to the dicarboxylic acid, and subsequent distillation from soda lime provided o-phenylphenol. These observations establish the structure of this compound as (IIa). Analogous compounds (IIb) and (IIc) have been obtained from the condensation of diethyl ethoxymethylenemalonate with ethyl 2-thienylacetate (12%, m.p. 99-100°) and ethyl 3-pyridylacetate (61%, m.p. 237-9°) respectively.

An attractive mechanistic sequence leading to the formation of (IIa) is outlined in the accompanying scheme. Additional aspects of this reaction are under investigation.

ACKNOWLEDGEMENT: We wish to thank the University of London for the award of a Postgraduate Scholarship to C.K.W.

REFERENCES

1. B. K. Menon, J. Chem. Soc., 1935, 1061
2. B. K. Menon, J. Chem. Soc., 1936, 1775
3. Compound (I) was reported¹ as having a melting point of 98°.

S C H E M E

